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List of Abbreviations

AIBN: azobisisobutyronitrile.
BR: butadiene rubber.
DMF: dimethylformamide.
DMSO: dimethylsulfoxide.
DSC: differential scanning calorimetry.
DVB: divinylbenzene.
E.A: elemental analysis.
EDMA: ethylene dimethacrylate.
EPR: (ethylene-co-propylene) rubber.
FTIR: Fourier transform infrared.
GPC: gel permeation chromatography.
 ^1H -NMR: proton nuclear magnetic resonance.
HS: 4-hydroxystyrene
(HS-S) (X mol% HS) copolymer: copolymer of 4-hydroxystyrene and styrene containing X mol % of 4-hydroxystyrene units
meg: miliequivalent
2-Me-5-VP: 2 methyl-5-vinylpyridine.
Mn: number average molecular weight.
Ms: mass spectrum.
Mw: weight average molecular weight.
PCHMA: poly(cyclohexyl methacrylate).
PCL: polycaprolactone.
PE: polyethylene.
PHS: poly(4-hydroxystyrene).
PMA: poly(methyl acrylate).
PMMA: poly(methyl methacrylate).

poly(2-Me-5-VP): poly (2-methyl-5-vinylpyridine).

poly(2-VP): poly(2-vinylpyridine).

poly(4-VP): poly(4-vinylpyridine).

PS: polystyrene.

PVBA: poly(4-vinylbenzoic acid)

PVC: poly(vinylchloride)

PVP: poly(4-vinylpyridine).

PVPHP: poly(vinyl pyridinium hydrobromide perbromide)

(PVPHP-St) copolymer: copolymer of vinyl pyridinium hydrobromide perbromide and styrene.

rpm: revolutions per minute.

S: styrene

SBR: (styrene-butadiene) rubber

t-BOC: t-butyloxycarbonyl group.

THF: tetrahydrofuran

Tg: glass-transition temperature

TGA: thermogravimetric analysis

Tm: crystalline melting temperature.

VBA: 4-vinylbenzoic acid.

(VBA-S) (X mol % VBA) copolymer: copolymer of 4-vinylbenzoic acid and styrene containing X mol % of 4-vinylbenzoic acid units.

VP: 4-vinylpyridine.

2-VP: 2-vinylpyridine.

4-VP: 4-vinylpyridine.

(4-VP-EDMA) copolymer: copolymer of 4-vinylpyridine and ethylene dimethacrylate..

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Chronology of the Research Project

The original aim of this research project was to study ways in which the properties of polyvinylpyridines could be modified to improve their usefulness through enhanced reactivity or compatibility with other polymers. All of our initial efforts were directed towards the chemical modification of polyvinylpyridines, both soluble and crosslinked materials, through a series of reactions adapted from model compounds. These approaches met only with very limited success and were eventually abandoned as work in the area of compatibilization of vinylpyridine containing polymers reached fruition. As a result this thesis will focus mainly on the compatibilization study (part 1) while our initial effort to functionalize polyvinylpyridines is reported in part 2.

Abstract

Hydrogen-bonding interactions have been used to compatibilize polystyrene with poly (4-hydroxystyrene) by introducing 4-vinylpyridine units into polystyrene. Similarly, polystyrene has been compatibilized with poly (4-vinylpyridine) by introducing first 4-hydroxystyrene and second 4-vinylbenzoic acid units into polystyrene. Differential scanning calorimetry and FTIR spectroscopy were used to study the compatibility of the different systems. The lowest degree of polystyrene modification which is necessary in order to achieve compatibilization with poly (4-hydroxystyrene) and poly (4-vinylpyridine) has been estimated. Hence, it has been found that at least a 50 mol % of 4-vinylpyridine or 4-hydroxystyrene units has to be introduced into polystyrene in order to achieve its compatibility over the entire range of composition with poly (4-hydroxystyrene) or poly (4-vinylpyridine) respectively. Lower polystyrene modifications lead to only partially compatible systems.

It has been found also that at least 40 mol % of 4-vinylbenzoic acid units have to be introduced into polystyrene in order to achieve its compatibility with poly (4-vinylpyridine). Introduction of 4-vinylbenzoic acid units instead of 4-hydroxystyrene units into polystyrene did not improve significantly its compatibility with poly (4-vinylpyridine). This is surprising in view of the higher strength of the hydrogen-bonding between 4-vinylbenzoic acid and 4-vinylpyridine units when compared to the strength of the hydrogen-bonded complex of 4-hydroxystyrene and 4-vinylpyridine units. This has been attributed to the strong self-complexation of the 4-vinylbenzoic acid units.

It has been shown that the Kwei equation is the most appropriate to describe the dependence between glass-transition temperature and composition for our systems.

FTIR spectroscopy has been shown to be useful to monitor the specific interactions in a polymer blend complexation between 4-hydroxystyrene units and 4-vinylpyridine units was indicated by a new band at ca. 1327 cm^{-1} . Complexation between 4-vinylbenzoic acid units and 4-vinylpyridine units was indicated by new bands at ca. 2488 and 1937 cm^{-1} (OH groups complexed to pyridyl groups) and at 1703 cm^{-1} (COOH groups complexed to pyridyl groups).

Reversible covalent crosslinks have been used to compatibilize polystyrene with poly (methyl acrylate). Hence, 4-vinylphenyl boronic acid units have been introduced into both polymers. Melt mixing of the modified polymers yield blends for which compatibility is attributed to co-crosslinking through the dehydration of the boronic acid units and formation of boronic anhydride linkages.

The second part of the thesis deals with several attempts at the chemical modification of the soluble poly (4-vinylpyridine) and poly (2-methyl-5-vinylpyridine). It has been found that significant amounts of new functionalities could be introduced but the chemical modifications were generally accompanied by side reactions, which diminished considerably the usefulness of the final products. During our studies on chemical modifications of poly (4-vinylpyridine), it was found that quaternized 4-vinylpyridine-ethylene dimethacrylate copolymers, unlike their free amine precursors, were extremely sensitive to dilute alkali and dissolved to afford low molecular weight by-products. A detailed study of the mechanism of this unusual self-catalyzed reaction allowed us to propose that an intramolecularly catalyzed process involving attack of pyridinium methide pseudo-bases onto neighboring ester groups

is responsible for the cleavage of the ethylene dimethacrylate crosslinks.

1.1. INTRODUCTION

1.1.1. Generalities

Extensive research has been done in the area of polymer blends. The incentive for such an extensive research is the obtention of materials with useful properties through the mere mixing of two polymers. In particular, the final properties of the blend will greatly depend on its physical state, that is, whether it is a single-phase or a two-phase system. A single-phase system will result if the two polymers are miscible and it will have uniform properties often reflecting on the influence of each of its components. On the other hand, if two polymers are immiscible there will be a segregation of one of the components either as a dispersed or continuous phase. The properties of such a two-phase system will largely depend on the size and the shape of the dispersed phase, as well as on the extent of adhesion or interaction between the dispersed phase and the continuous matrix.

Both two-phase and single-phase systems find important applications. For instance, "impact polystyrene" is among important commercial two-phase blends. The initial commercial impact polystyrenes were melt blends of polystyrene and rubber, but these had a poor rubber efficiency. However, when styrene is polymerized in situ

from a solution of styrene and rubber, a high impact blend is obtained. It absorbs a large amount of energy before failure can occur [1].

Poly(vinylchloride) - impact poly(methylmethacrylate) blend: in this two-phase blend, impact poly(methylmethacrylate) offers improved heat distortion temperatures, while poly(vinylchloride) allows flame retardant temperatures. This blend is used in extruded paneling, seat backs for mass transit, machine housing, aircraft interior components, fume ducting and industrial wall paneling [2, 3].

Bisphenol A polycarbonate blended with ABS (acrylonitrile-butadiene-styrene copolymer) exhibits a high notched impact strength due to the bisphenol A polycarbonate component and also shows improvement of resistance to environmental stress cracking due to the ABS copolymer of the blend. [2,3,4]

Although a number of two-phase blends have found commercial applications, it is advantageous to use single-phase polymer blends rather than their two-phase counterparts as the former offer numerous advantages. Perhaps the most significant such advantage is that of mechanical compatibility. In addition, it has been observed that some miscible blends exhibit higher tensile strengths than their constituents, as shown for the

blends of a copolymer of α -methylstyrene-methacrylonitrile with poly(vinylchloride) [5] and for the blends of poly(2,6-dimethyl-1,4-phenylene oxide) and polystyrene [6].

Miscible blends also offer advantages over immiscible blends in fabrication as they possess improved surface characteristics and weld-line strengths. In practical applications, it is often necessary to mix additives such as crosslinking agents, antioxidants, and plasticizers to polymers. In general a uniform distribution of these additives through the polymeric matrix is needed for obtaining high performance, however, if the polymeric matrix is an immiscible blend the additives often show a tendency to segregate preferentially in one of the two phases of the system, this, in turn, may lower significantly the performance of the blend [7]. However, if the blend is miscible such additive segregation will not occur.

Although miscible blends are usually superior to others, they are also generally much more difficult to obtain as most polymers do not mix well. Thus, a review of polymer compatibility covering the literature to 1971 found that only 40 of 292 systems studied showed compatibility [8]. Paul and Barlow in their review "Polymer-Polymer Miscibility" [9] gave a list of polymers which are miscible with poly(vinylchloride), polystyrene, poly(phenylene

oxide), nitrocellulose, polycaprolactone, poly(methylacrylate), polyhydroxyether of bisphenol A, and polycarbonate of bisphenol A. Overall, only a total of about 60 miscible systems were presented.

1.1.2 Polymer-Polymer Compatibility:

Thermodynamic Considerations

Consideration of the thermodynamics of polymer-polymer mixing provides a better understanding of the reason for the incompatibility which is observed for most polymers mixtures. According to the second law of thermodynamics, the polymers will mix if the Gibbs free energy of mixing, ΔG_{mix} is negative. The calculation of ΔG_{mix} includes an evaluation of the enthalpy of mixing, ΔH_{mix} , and the entropy of mixing, ΔS_{mix} .

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \text{ (eq.1)}$$

The entropy of mixing differs for mixing two high molecular weight polymers compared to two low molecular weight species, e.g., solvents. Physically, the difference is in the number of ways the two types of molecules can be arranged in the mixture which can be easily visualized by a simple pictorial representation. Figure 1 shows two-dimensional lattices with 100 sites in each that will contain molecules or segments with volume V_r . The left side of Figure 1 shows 50 molecules of solvent 1 (black

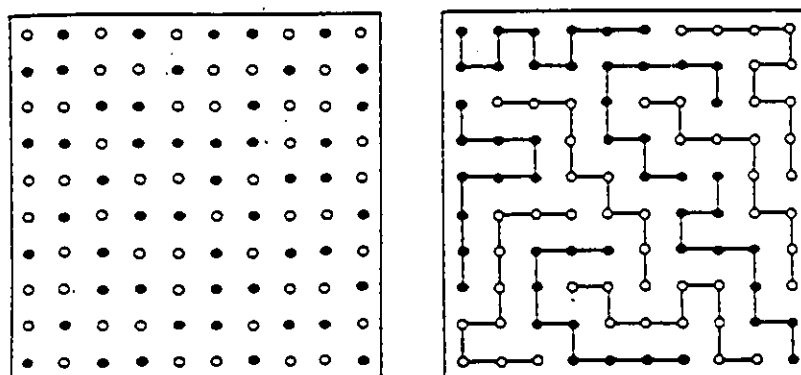


Figure 1. Schematic illustration of the mixing of small molecules (left) and larger polymer molecules (right) (ref. 9).

dots) and 50 molecules of solvent 2 (open dots), each having volume V_r . Only one of the many possible arrangements is shown, however, there are approximately 10^{30} other possible arrangements. In the example of the right, the 50 dots of each kind are connected into five chains of 10 dots. There are only 10^3 different arrangements for this second system. Thus the combinatorial entropy of mixing for polymers is dramatically less than that for the two low molecular weight compounds. At the limit, for very high molecular weights, the combinatorial entropy of mixing is essentially zero. The fact that for high molecular weight polymers the contribution of ΔS_{mix} to the free energy of mixing process is negligible explain why most polymers will yield immiscible systems unless $\Delta H_{mix} < 0$. ΔH_{mix} will be negative if exothermic interactions are present between the mixed polymers.

Several theories have been developed to predict the phase behaviour of polymer-polymer systems. Certainly, the simplest model for polymer-polymer mixtures is the Flory-Huggins theory [10] which was first applied to polymer blends by Scott [11]. The Flory-Huggins theory assumes that the polymer molecule is composed of segments linked to each other by covalent bonds and that these segments are placed on a space-filling lattice in a random manner. The number of combinations of the positions of the two types of

segments in the mixture gives rise to combinatorial entropy of mixing, ΔS_{mix} . Scott obtained the following expression for the entropy of mixing of two polymers:

$$\Delta S_{\text{mix}} = - \frac{RV}{V_r} \left[\frac{V_A}{X_A} \ln \frac{V_A}{X_A} + \frac{V_B}{X_B} \ln \frac{V_B}{X_B} \right] \quad (\text{eq. 2})$$

where V is the total volume of the mixture, V_r is a reference volume which is taken as close to the molar volume of the smallest polymer repeat unit as possible, V_A and V_B are the volume fractions of polymer A and polymer B in the mixture, respectively, X_A and X_B are the degree of polymerization of polymer A and polymer B in terms of the reference volume V_r , respectively. For high molecular weight polymers X_A and X_B are very large and therefore the ΔS_{mix} term has a negligible contribution to the Gibbs free energy of mixing.

The enthalpy of mixing, ΔH_{mix} , follows a quadratic dependence on composition:

$$\Delta H_{\text{mix}} = \frac{RTV}{V_r} X_{AB} V_A V_B \quad (\text{eq. 3})$$

where X_{AB} is the interaction parameter between the two polymers and is related to the enthalpy of interaction of the polymer repeat units, each of molar volume V_r . For nonpolar systems X_{AB} can be estimated from Hildebrand [12] solubility parameters.

$$\chi_{AB} = \frac{V_r}{RT} (\delta_A - \delta_B)^2 \quad (\text{eq. 4})$$

Where δ_A and δ_B are the Hildebrand solubility parameters for polymers A and B, respectively.

Combining equations 2 and 3 gives the free energy of mixing, ΔG_{mix} :

$$\Delta G_{\text{mix}} = \frac{RTV}{V_r} \left[\frac{V_A}{X_A} \ln V_A + \frac{V_B}{X_B} \ln V_B + \chi_{AB} V_A V_B \right] \quad (\text{eq. 5.})$$

Since the contribution from first two terms is very small for high molecular weight polymers, the sign of ΔG_{mix} depends largely on the sign of the χ_{AB} interaction parameter.

1.1.3 Glass Transition Temperature and Polymer-Polymer Miscibility.

A miscible blend of two polymers is characterized by the presence of a single glass-transition temperature while an immiscible one is characterized by the presence of two glass-transition temperatures: one corresponding to each of the two phases.

There are several classical equations that can correlate and predict the dependence between the glass-transition temperature of a miscible system and its

composition. The following are the most frequently employed equations listed here in chronological order.

1) Gordon-Taylor equation:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2}$$

where T_g , T_{g1} , and T_{g2} are respectively the glass-transition temperatures of the blend, of homopolymer 1, and of homopolymer 2. w_1 and w_2 are the corresponding weight fractions, and k is the ratio between the volume expansion coefficients of the homopolymers.

$$k = \frac{\beta_{R,2} - \beta_{G,2}}{\beta_{R,1} - \beta_{G,1}} = \frac{\Delta\beta_2}{\Delta\beta_1}$$

$$\beta_{R,1} = \frac{d(V_{R,1})}{dT}, \quad \beta_{G,1} = \frac{d(V_{G,1})}{dT}$$

where $V_{R,1}$ and $V_{G,1}$ are specific volumes for homopolymer 1 in the rubbery and glassy states respectively. Likewise $V_{R,2}$ and $V_{G,2}$ are the specific volumes for homopolymer 2.

The Gordon and Taylor equation was originally derived to predict T_g of binary copolymers from the glass-transition temperatures of the pure polymers and their coefficients of expansion [13]. Then, it was applied to predict the T_g of a compatible mixture of two polymers.

Gordon and Taylor derived their equation on the basis of theoretical and practical considerations which show that in the interpretation of packing phenomena, copolymers can be treated like solutions of small molecules, and that ideal volume-additivity of the repeating units in copolymers is frequently realized.

2) Jenckel-Heusch equation [14]

$$T_g = w_1 T_{g1} + w_2 T_{g2} + w_1 w_2 b (T_{g2} - T_{g1})$$

Where T_g , T_{g1} , T_{g2} , w_1 and w_2 have the same meaning as in the previous case, and b is an empirical parameter that varies from system to system.

3) Fox equation

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

Where T_g , T_{g1} , T_{g2} , w_1 and w_2 have the same meaning as before. The Fox equation is empirical and it may be expected to apply to systems which are compatible and not too strongly polar [15]. Data on copolymers and on polymer-diluent systems illustrate that this is substantially true [16].

4) Couchman equation [17, 18]

$$\ln T_g = \frac{w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}}$$

Where T_g, T_{g1}, T_{g2}, w_1 and w_2 have the same meaning as previously, while ΔC_{p1} and ΔC_{p2} are the changes in the heat capacity of the polymers 1 and 2 at their glass-transition temperatures.

The Couchman equation is based on the entropy continuity condition at T_g . The respective mole fractions of the two components in the system are denoted as x_1 and x_2 and the molar entropies of these pure components are denoted in turn as S_1 and S_2 . The molar entropy, S_{tot} , of the mixed system may be written generally as

$$S_{tot} = x_1 S_1 + x_2 S_2 + S_{mix}$$

where S_{mix} includes any and all excess entropy changes associated with mixing of the two components. For the simplest case, where the excess entropy of mixing is solely conformational, then, the character and extent of specific interactions may be largely unchanged at T_g and $\Delta S_{mix} = 0$. Let S_1^o and S_2^o denote pure component molar entropies at respectively T_g , T_{g1} and T_{g2} and let C_{p1} and C_{p2} denote the molar heat capacities of these components, then the total molar entropy excluding ΔS_{mix} may be written as

$$S_{tot} = x_1 \left[S_1^o + \int_{T_{g1}}^{T_g} (C_{p1}/T) dT \right] + x_2 \left[S_2^o + \int_{T_{g2}}^{T_g} (C_{p2}/T) dT \right]$$

A relation of this form is obtained for both the glassy and rubbery state. Since S_1^o and S_2^o are continuous at

respectively T_{g1} and T_{g2} , the continuity of S_{tot} at T_g and the approximation that the transition isobaric heat capacity increments ΔC_{p1} and ΔC_{p2} are temperature independent provides the expression:

$$\ln T_g = \frac{x_1 \Delta C_{p1} \ln T_{g1} + x_2 \Delta C_{p2} \ln T_{g2}}{x_1 \Delta C_{p1} + x_2 \Delta C_{p2}}$$

For convenience the x_i are exchanged for mass fractions w_i (recalling that the ΔC_{p_i} are then per unit mass).

5) Kwei equation [19]

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2$$

Where T_g , T_{g1} , T_{g2} , w_1 , w_2 and k have the same meaning as before, while the quadratic term $q w_1 w_2$ is assumed to be proportional to the number of specific interactions between the two polymers.

The applicability of all these five different equations that correlate the glass-transition temperatures of a miscible system to its composition has been proven. The characteristics of the miscible system will determine which of these equations will best fit the experimental data. Gordon-Taylor, Fox and Couchman equations apply to those systems for which, compatibility is not due to strong interactions between the components. The Jenckel-Heusch and Kwei equations contain terms that take into account strong

interactions which may exist between the polymers. The T_g values for mixtures of poly(styrene-co-acrylonitrile) and poly(methylmethacrylate) followed the Gordon-Taylor equation [20], while the T_g values for blends of poly(2,6-dimethyl-1,4-phenylene oxide) with polystyrene followed the Couchman equation [18]. Percec et al. [21] modified the structures of nonmiscible poly(2,6-dimethyl-1,4-phenylene oxide) and poly(epichlorohydrin) by introducing either donor (carbazolyl) or acceptor (3,5-dinitrobenzoyl) pendant units. Blends of the modified polymers were found to be miscible and their glass-transition temperatures followed the Kwei equation.

1.1.4 Hydrogen-bonding and its role in the Miscibility of Polymer Blends.

Knowing that exothermic interactions between two polymers leads to a $\Delta G_{mix} < 0$ and consequently to miscibility, it is useful to incorporate functional groups which are able to interact in exothermic fashion when designing possible miscible polymeric systems. Among these specific interactions that range from covalent bonding to weak dispersive forces are hydrogen-bonding interactions. Hydrogen-bonding has been recognized as an important promotor of miscibility in many polymeric systems.

Poly(vinyl chloride) - based polymer blends.

Due to its widespread use and interesting properties, poly(vinyl chloride) is one of the most studied components of polymer blends. It is capable of weak interactions. The α -hydrogen of PVC is capable of hydrogen-bonding with polymers which have "basic properties".

Blends of PVC and butadiene-acrylonitrile copolymer were first examples of miscible blends [22]. Butadiene-acrylonitrile copolymers have therefore been utilized as permanent plasticizers for PVC since the 1940's.

Torsion pendulum studies of blends of PVC and (ethylene-vinyl acetate) copolymers showed a single-phase blend when the vinyl acetate level in the copolymer was 65-75%, while a two-phase blend was obtained for (ethylene-vinyl acetate) copolymers containing less than 50% of vinylacetate. The glass-transition temperatures for these miscible blends obeyed approximately the Fox equation [23].

PVC is compatible with an (ethylene-vinyl acetate sulfur dioxide) terpolymer that has a molar composition of 72.7 / 18.5 / 8.8 [24]. Compatibility was demonstrated by phase-contrast microscopy, torsion pendulum studies and differential scanning calorimetry; the latter study showed that the glass-transition temperatures of the compatible blends followed the Fox equation. The incorporation of sulfur dioxide allowed the utilization of much higher

concentration of ethylene in the terpolymer than is possible with simpler ethylene-vinyl acetate copolymers.

Koleske and Lundberg [25] showed by torsion pendulum measurements that blends of PVC and polycaprolactone are compatible and the T_g values of the blends showed a good fit with both the Fox and the Gordon-Taylor expressions. Crystallinity can effect the glass-Transition temperature measured for polymers. Thus, Koleske and Lundberg obtained a T_g of polycaprolactone of 202°K by using their data on the compatible blends of PVC and polycaprolactone. They assumed that this T_g value corresponded to a 100% amorphous polycaprolactone. This T_g is 16°K lower than the T_g of the annealed polycaprolactone which showed some degree of crystallinity in spite of its annealing.

Polymer stereochemistry also has an effect on miscibility. PVC and isotactic poly(methyl methacrylate) are immiscible over the entire range of composition, while with syndiotactic PMMA miscible blends result up to a blend corresponding to a monomer ratio of 1:1, PVC: PMMA. At higher syndiotactic PMMA contents, two-phase behaviour is observed with one phase of pure s-PMMA and the other phase corresponding to the 1:1, PVC/s-PMMA composition [26].

Parmer, Dickson, and Porter studied the degree of miscibility and interactions in blends of poly(vinylchloride) /poly(methylmethacrylate) and

poly(vinylchloride)/ poly(cyclohexylmethacrylate) using FTIR, DSC, and solid state magic angle NMR methods [27]. Changes in relaxation times in the PMMA carbonyl with increasing PVC content in the blend were consistent with a miscible system. While the relaxation time values for the PCHMA carbonyl did not change significantly on blending with PVC, indicative of a phase-separated system. Immiscibility was due to the different alkyl groups, possibly because of steric or packing effects.

Blends of chlorinated PVC and a polyurethane [containing a poly(tetramethylene adipate) segment capped with 2-hydroxyethyl acrylate] were shown to be partially miscible over the entire compositional range. They exhibited a single, broad, and composition-dependent glass-transition temperature by DSC. The miscibility of the system was most likely the result of strong molecular interaction between the α -hydrogen in the chlorinated PVC and the carbonyl on the poly(tetramethylene adipate) segment of the urethane [28].

Blends of PVC and an ethylene / N,N-dimethyl acrylamide copolymer yield a single T_g when the copolymer contains between 17-25% wt. of N,N-dimethyl acrylamide. Interaction between the "basic" disubstituted amide and the α -hydrogen of PVC was proposed to account for the observed miscibility [29].

In summary, all polymers that show compatibility with PVC are characterized by the presence of carbonyl groups or other "basic" groups which are able to interact with the α -hydrogen of the PVC.

Novolac-based polymer blends.

Novolac resins of moderate molecular weight, 800 to 1600g, are compatible with polyacrylates, polymethacrylates, poly(vinylacetate), poly(styrene-co-acrylonitrile), polycarbonate, and poly(vinyl methyl ether). However, poly(4-vinylphenol) was found to be incompatible with poly(methylacrylate). In the compatible blends, the carbonyl frequency shifted ca. 20 cm^{-1} indicating chemical interaction between the novolac resin and the carbonyl containing polymer. Large positive deviations of the experimentally observed T_g from the calculated weight-average values were noted [30].

Kwei investigated the effect of the stereoconfiguration of the polymer on hydrogen-bonding interaction or compatibility. He studied compatibility between novolac resins and isotactic or syndiotactic poly(methylmethacrylate). When i-PMMA was used the T_g of the mixtures obeyed the Kwei equation

$$T_g = w_1T_{g1} + w_2T_{g2} + Qw_1w_2$$

with $q = 81$. However, in the case of s-PMMA the T_g of the mixtures obeyed instead the equation:

$$T_g = [(w_1 T_{g1} + k w_2 T_{g2}) / (w_1 + k w_2)] + q w_1 w_2$$

with $k=12$ and $q=123$. The value q was assumed to be a measure of the efficacy of hydrogen bond formation, then the author concluded that the higher value of q in the case of s-PMMA suggested that more facile contacts exist between the syndiotactic chains and the novolac resins [19]. These results seem to agree with those obtained by Shurer et al. [26] who found that poly(vinyl chloride) is incompatible with i-PMMA but is compatible with s-PMMA.

Para-substituted novolac resins, viz., the H, Cl, NO₂, and the t-butyl derivatives, were synthesized and blended with poly(methyl methacrylate) [31]. These studies were conducted to gain insight into the effect of the strength of hydrogen bonding on miscibility. In order to determine the thermodynamic parameters of hydrogen bond dissociation, the ratio of the relative peak intensities of free carbonyl to hydrogen-bonded carbonyl was followed with temperature. Calculated hydrogen bond dissociation energies ranged from 4 to 7 kcal/mol. The order NO₂ > Cl > H > t-butyl was in agreement with the acidic strength and the electron-withdrawing effect of the substituent. DSC results showed that all blends were compatible. Blends T_g 's of the p-Cl,

p-NO₂, and p-tBu, substituted novolacs with PMMA obeyed the Kwei equation:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + q w_1 w_2$$

with $q=44.82$, -41.92 , and -39.42 respectively. While blends T_g 's of p-H novolac resin / PMMA system obeyed the Kwei equation:

$$T_g = [(w_1 T_{g1} + k w_2 T_{g2}) / (w_1 + k w_2)] + q w_1 w_2$$

with $k=0.992$ and $q=40.12$. The values of q which are proportional to the strength of the hydrogen-bonding were, similar in all cases, despite the fact that the hydrogen-bonding interaction between the different substituted novolacs and PMMA were of very different strength, however, the q value obtained was the net sum of all types of interactions, self-association between the novolac resins, and intermolecular association between the novolac resin and PMMA.

1.1.5 Infrared Studies of Polymer Blends.

Fourier-transform infrared (FTIR) spectroscopy, with its inherent sensitivity, offers considerable potential for studying the compatibility of polymer blends. Specific interactions between two polymers bring about new bands, or shifting and broadening of already existent bands.

Coleman et al. reported FTIR studies of polycaprolactone (PCL) - poly(vinyl chloride) (PVC) blends both in the melt (75°C) and in the solid state at room temperature. The authors found that in the molten amorphous state, the C=O group of the PCL (1737 cm^{-1}) shifted progressively to lower frequencies as a function of PVC concentration. Moreover, the width at half-height of the carbonyl band varied with PVC composition, as well, this curve indicated that interactions of the carbonyl band with PVC approached saturation at concentrations which correspond to an approximately 4:1 molar ratio of PVC/PCL. This was explained on the basis of the relative sizes of the structural repeating units of the two polymers: the length of the $-(\text{CH}_2)_5\text{COO}-$ units of PCL is approximately 3.4 times that of the $-\text{CH}_2\text{CHCl}-$ unit of PVC. Thus on average, a molar excess of about 4:1, PVC:PCL is necessary to ensure a saturation effect [32].

In contrast with PVC-PCL system, FTIR studies on the poly(propiolactone) - poly(vinyl chloride) blend system showed its incompatibility. Frequency shifts and band broadening of the carbonyl band of poly(propiolactone) were not observed as a function of poly(vinylchloride) concentration. DSC studies confirmed these results. It was concluded that the negative contribution to the heat of mixing from specific interaction between both polymers was

not sufficient to override the differences in solubility parameters of the two polymers.[33].

Varnell and Coleman [34] performed FTIR studies of two more polyesters with PVC, poly(α -methyl - α -n-propyl- β -propiolactone) and poly(δ -valerolactone). They found that those polyesters were compatible with PVC. Shifting and broadening of the carbonyl bands upon blending with PVC was observed.

FTIR studies of blends of poly(vinyl phenol) with poly(vinyl acetate) and (ethylene-vinyl acetate) copolymers revealed infrared bands attributed to intermolecular hydrogen-bonding interactions involving the phenolic hydroxyl group with the acetate carbonyl group. The carbonyl stretching vibration of poly(vinyl acetate) occurs at 1739 cm^{-1} . Upon blending with poly(vinyl phenol), an additional band attributed to hydrogen-bonded carbonyl groups was observed at 1714 cm^{-1} . Furthermore, as the concentration of poly(vinyl acetate) in the blends was increased the free hydroxyl band of poly(vinyl phenol) (3525 cm^{-1}) was reduced, and the frequency maximum of its hydrogen-bonded hydroxyl band (3360 cm^{-1}) was concurrently increased to 3450 cm^{-1} . Similar results were observed for blends of poly(vinyl phenol) and the (ethylene-vinyl acetate) copolymer containing 70 wt% vinyl acetate. Finally, DSC studies revealed a single glass-transition temperature for the systems [35].

Kim and Tonami [36] showed that hydrogen-bonding existed in the atactic poly(methacrylic acid)-poly(ethylene oxide) polymer complex. Infrared studies proved the existence of hydrogen bonds between the carboxylic groups and the ether oxygens.

Naito et al. [20] performed an infrared analysis of blends of poly(methyl acrylate) and (styrene-acrylonitrile) copolymer. Hydrogen bonding was detected in this blend by a downward shift ($10\text{--}15\text{ cm}^{-1}$) in the infrared stretching frequency of the methacrylate carbonyl group.

1.1.6. Miscibility of polymers blends through their covalent crosslinking.

It has been pointed out that specific interactions between two polymers bring about their compatibility. Then, it seems obvious that covalent crosslinking between two polymers should afford compatible systems. Indeed, there are several examples in the literature where compatibility between two polymers has been achieved by crosslinking them through covalent bonds.

Polyimides are well established among the most successful polymers for high temperature applications. However, a shortcoming of these polymers is their relatively high cost. Adduci and Dandge [37] investigated the possibilities of combining polyimides with other polymers with the objective of modifying their properties. In this connection, it was highly desired to obtain compatible blends. The authors found that polyamic acids, precursors for polyimides, prepared from various aromatic diamines containing methylene ether and/or sulfone linkages and pyromellitic dianhydride or benzophenone tetracarboxylic acid dianhydride were fully compatible with resol prepolymers at <70% resol. No phase separation of the blend components occurred upon curing and hard, thermally stable resins showing superior adhesion to glass were obtained. It was proposed that the cured films could

be a homogeneous physical mixture of the three-dimensional resol network and a linear polyimide possibly with an interpenetrating structure and/or a resin in which resol has chemically reacted with polyamic acid.

Yoshihiko et al. [38] investigated the properties of poly (vinyl alcohol) crosslinked with polyisocyanate compounds. The temperature of the dynamic mechanical-absorption peak [$T(E'' \text{ max.})$] shifted toward the higher temperature side as the amount of crosslinking agent increased. Moreover, films cured in DMSO showed a larger shift of the [$T(E'' \text{ max.})$] than those cured in water for the same concentration of crosslinking agent. Thus, the crosslinking density of the former was higher than that of the latter.

Polyblends of poly (butylene terephthalate) and poly (ethylene-co-propylene) rubber have been prepared by two techniques. First, by bulk polymerization of 1,4-butanediol with dimethyl terephthalate in the presence of suspended EPR rubber particles. Second, by blending in an extruder, which afforded polyblends which had much improved impact strength properties. However, they did not possess good mechanical properties and were also prone to delamination. Crosslinking of the blends by ^{60}Co γ -rays radiation improved the properties of the blends as the delaminating phenomenon was eliminated but it did not improve significantly their mechanical properties [39].

Temperature dependence of the dynamic modulus (G') and the loss tangent ($\tan \delta$) was measured for unvulcanized and vulcanized blends of (styrene-butadiene) rubber (SBR) with butadiene rubber (BR) [40]. It was found that transitions of unvulcanized blends were separated at about -40°C and -5°C corresponding to SBR and BR respectively. The transition at -40°C corresponding to the T_g of SBR and that one at -5°C corresponding to T_m of BR. This separation of transitions temperatures is typical of heterogeneous structures. In contrast, only one transition temperature was observed for vulcanized blends. It shifted linearly according to the ratio of polymers in the blend. It was then concluded that homogeneity of the vulcanized blends could be attributed to the existence of co-crosslinks between the two polymers.

Polypropylene and (ethylene-propylene) rubber were shown to be incompatible. Two glass-transition temperatures were observed at about 16°C (PP) and -34°C (EPR). When blends were irradiated with ^{60}Co γ -rays, a third phase appeared as a secondary transition region at -18°C . This new phase was assumed to be the result of crosslinking between PP and EPR. The irradiated blends possessed higher impact strength [41].

Crosslinked polymer blends with excellent mechanical properties and resistance to surface layer separation have been claimed in the patent literature [42]. The

crosslinked polymer blends were prepared by melt mixing of 5-95% of propylene polymers (with 0-20% α -olefin comonomers) and 95-5% styrene polymers (with organic peroxides).

Poly (phenylene oxide) was modified by crosslinking it with polystyrene and/or butadiene-styrene copolymer. Crosslinking was performed through irradiation of the blend in the presence of a monomeric crosslinking agent (triallyl isocyanurate) and/or a polymeric crosslinking agent (1,2-polybutadiene) and, optionally a polymerization initiator (dicumyl peroxide). The irradiated film showed a tensile strength of 780 kg/cm² and had a glass-transition temperature of 198°C [43].

Nakamura et al. [44] report that the compatibility of polyethylene and poly (vinyl chloride) with each other is remarkably improved by blending them in the presence of a peroxide and a polyfunctional monomer, e.g. triallyl isocyanurate. The good mechanical properties of the crosslinked blends are caused by the formation of crosslinked product while blending, which acts as a good compatibilizing agent for polyethylene with poly (vinyl chloride). The formation of the crosslinked product at the PE-PVC interface is confirmed by a high peeling strength in PE/PVC adherends and by the Kraus plots of the co-crosslinked blends. Nakamura also showed that 6-diallylamino-1,3,5-triazine-2,4-dithiol is effective as a

co-crosslinking agent for polyethylene and poly (vinyl chloride). The co-crosslinked PE/PVC system showed improvement of adhesion properties and compatibility [45]. Figure 2 shows the structures of the co-crosslinked PE/PVC blends, first by triallyl isocyanurate and second by 6-diallylamino-1,3,5-triazine-2,4-dithiol.

Finally, the same research group obtained even better compatibility between PE and PVC by using 4,6-bis(allylamino)-1,3,5-triazine-2-thiol. The co-crosslinked system had a finely dispersed phase structure and its mechanical properties were described as excellent [46]. Figure 3. shows the structure of the co-crosslinked PE/PVC blends using 4,6-bis(allylamino)-1,3,5-triazine-2-thiol.

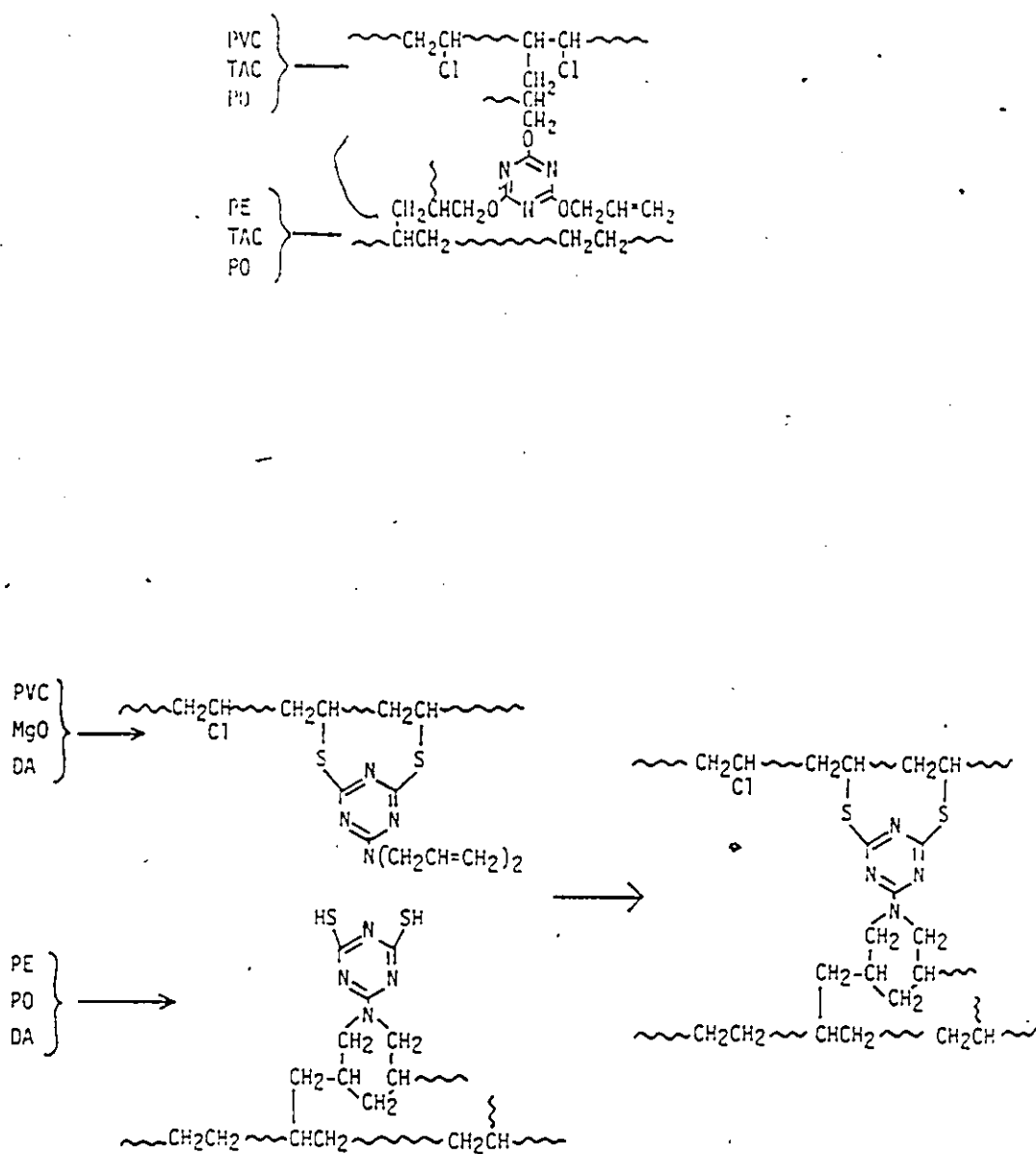


Figure 2. Structures of the co-crosslinked PE/PVC blends:
 A: Crosslinking agent: triallyl isocyanurate.
 B: Crosslinking agent: 6-diallylamino-1,3,5-triazine-2,4-dithiol.

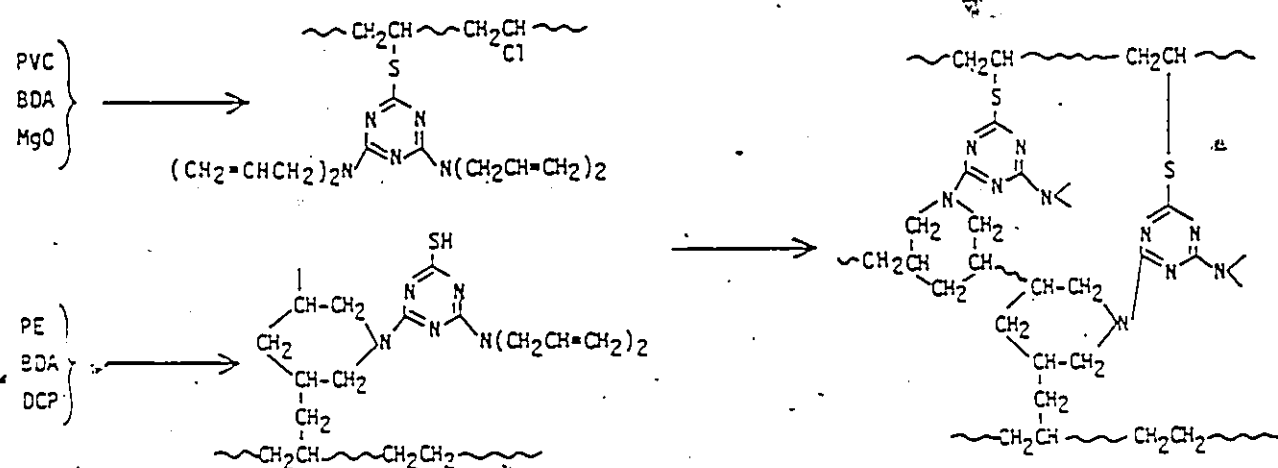


Figure 3. Structure of the co-crosslinked PE/PVC blends using 4,6-bis(allylamino)-1,3,5-triazine-2-thiol as crosslinking agent.

1.2 RESULTS AND DISCUSSION

1.2.1 Compatibilization of polystyrene (PS) with poly (4-vinylpyridine) (PVP) by introducing into PS acidic 4-hydroxystyrene units.

PS is incompatible with PVP over the entire range of composition. We have found that the introduction of acidic 4-hydroxystyrene units into PS brings about compatibility with PVP. Hydrogen-bonding between the basic pyridine units and the acidic 4-hydroxystyrene units is responsible for this compatibility. In general, it is desired to induce compatibility between two polymers by modifying them as little as possible. Our aim was to estimate the lowest mol % of 4-hydroxystyrene units which it would be necessary to introduce into PS in order to achieve its compatibility with PVP. In the literature, there are numerous examples of compatibility studies between homopolymers whose compatibility was attributed to hydrogen-bonding interactions. However, there are fewer studies like ours. In the case of two homopolymers even weak hydrogen-bonding interactions may cause compatibility; this is because the probability of interaction is high. However, in our case, where one of the components of the blend is a copolymer (4-hydroxystyrene/styrene copolymer), the probability of interaction of the acidic units in the copolymer and the basic units in PVP is lower than that which is obtained

with two homopolymers. Therefore, it was thought that a systematic study of this type might provide some insight into the utility of hydrogen-bonding in causing compatibility. In practical terms, hydrogen-bonding interactions would be useful as a means to achieve compatibility if only a few mol % of 4-hydroxystyrene units, were required to achieve the goal of compatibilization.

We prepared several (4-hydroxystyrene-styrene) copolymers and tested their compatibility with PVP. Figure 4 shows the structure of the various polymers and copolymers used in this study. While their molecular weight data as well as their glass-transition temperatures (T_g) are shown in Table 1.

We studied the compatibility of the various blends by differential scanning calorimetry (DSC) and FTIR techniques. DSC studies allow the measurement of T_g of a polymer. A compatible blend is characterized by a single phase with a single T_g. In contrast, an incompatible blend is characterized by the presence of two T_g's, due to the fact that the components of the blend separate into two different phases. The DSC instrument operates with one sample vial and one reference vial. Those vials, usually called pans, are made of metal (aluminium, stainless steel or gold). The two pans are then heated at a programmed rate so that the temperatures of the two pans are

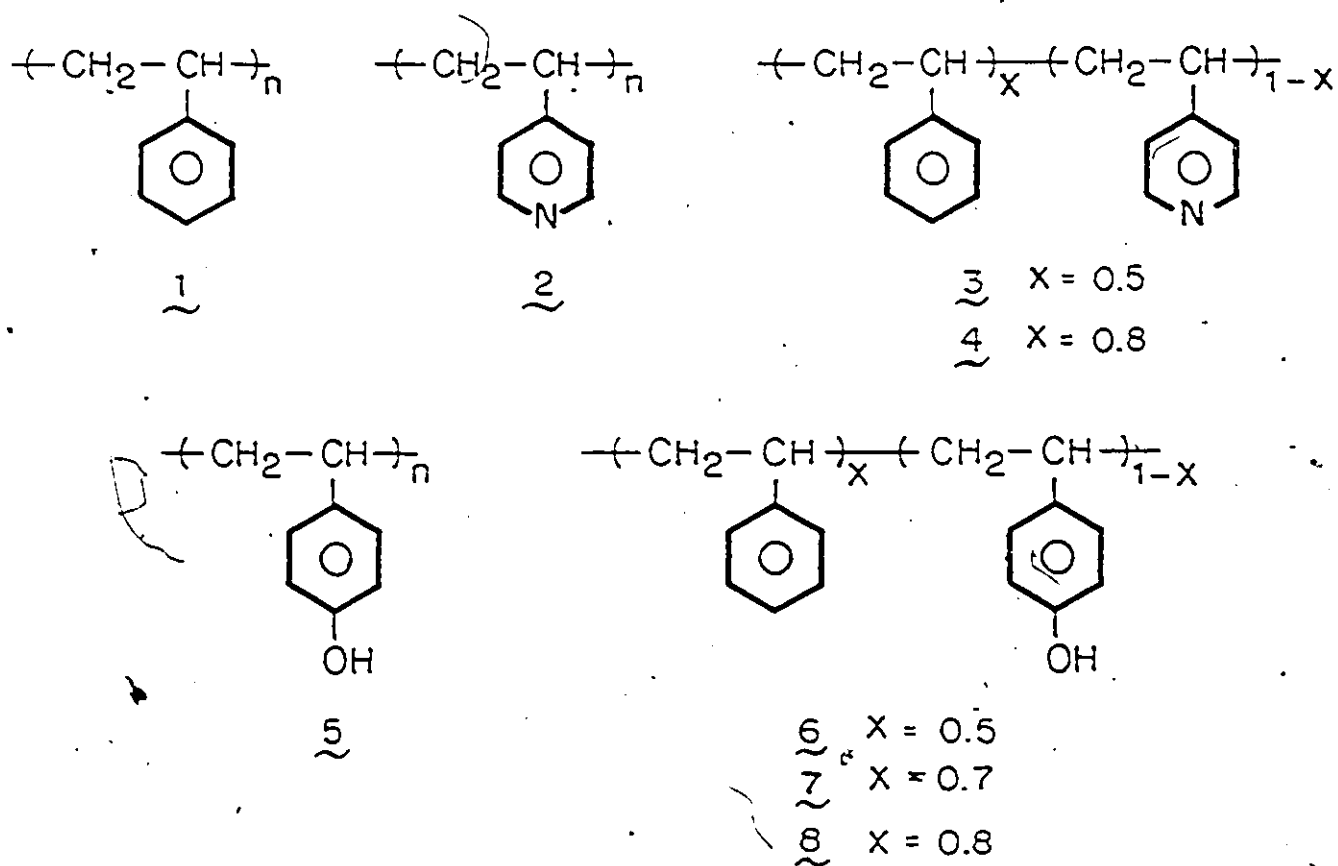


Figure 4. Structure of the various polymers and copolymers used in this study.

Table 1. Composition and characteristics of the various polymers.

Polymer #	Composition (mole %)		GPC Molecular Weight		Tg (°C) ^a
	styrene	4-vinyl-4-hydroxypyridine	Mn (10 ⁻³)	Mw (10 ⁻³)	
1	100	--	4.0	31.4	7.9
2	--	100	--	46.7 ^b	88
3	50	50	23.6	45.2	1.9
4	80	20	21.7	42.9	2.0
5	--	--	4.4	9.5	2.2
6	50	--	16.2	31.5	1.9
7	70	--	14.6	34.9	2.4
8	80	--	26.7	46.0	1.7

a) Measured by DSC

b) Polymer 2 was insoluble in THF, molecular weight was obtained by viscosity measurement using parameters given in ref. 47

identical. When an endothermic transition takes place in the sample pan, the reference pan is heated to compensate for the heat absorption upon transition of the sample. The extra energy added to the reference is then registered. The second technique, FTIR spectroscopy, as we have already mentioned in our introduction, allows the detection of specific interactions taking place between both polymers in the blend. These specific interactions bring about new bands or shifting and broadening of already existant bands.

1.2.1.1 Differential scanning calorimetry (DSC) studies.

DSC compatibility studies of poly (4-vinylpyridine) (PVP) with poly(4-hydroxystyrene) (PHS).

In view of the strong interactions between these two polymers which can form stable complexes, the method used in sample preparation is of particular importance. Both polymers, PVP and PHS are soluble in methanol. When methanol solutions of these polymers are mixed, a 1:1 molar ratio insoluble complex is formed regardless of the relative amounts of the individual polymers used. Any excess of either polymer remains in solution. Analytical data on the precipitated complexes after thorough washing with methanol always confirmed that a 1:1 molar ratio

complex was formed. DSC showed a single Tg at 210°C for the precipitated polymer complex. This value, which is significantly higher than that observed for each individual component of the mixture (155 and 138°C respectively for PVP and for PHS), indicated that strong interactions were resulting from significant hydrogen-bonding between the two polymers, amounting essentially to a form of thermally reversible crosslinking that significantly reduces the mobilities of individual chains in the compatible polymer blend. While the mixing of methanol solutions of the two polymers can lead only to 1:1 molar ratio mixtures, the use of pyridine as solvent allowed the preparation of compatible blends containing PVP and PHS in any proportion. Sample preparation consisted in the dissolution of both polymers in pyridine followed by mixing of solutions containing the desired proportions of each polymer; no precipitation is observed upon mixing and solvent evaporation leads to the desired blend. Pyridine was chosen as solvent as it can interact with PHS thereby limiting polymer-polymer complex formation and preventing precipitation when PVP is added. As the solvent is evaporated slowly, complexation of the polymers can occur by interaction of the reactive groups on both polymers leading to homogeneous films of the polymer blend.

Figure 5 shows the DSC thermograms obtained for PVP/PHS blends. DSC studies on the dry films of the

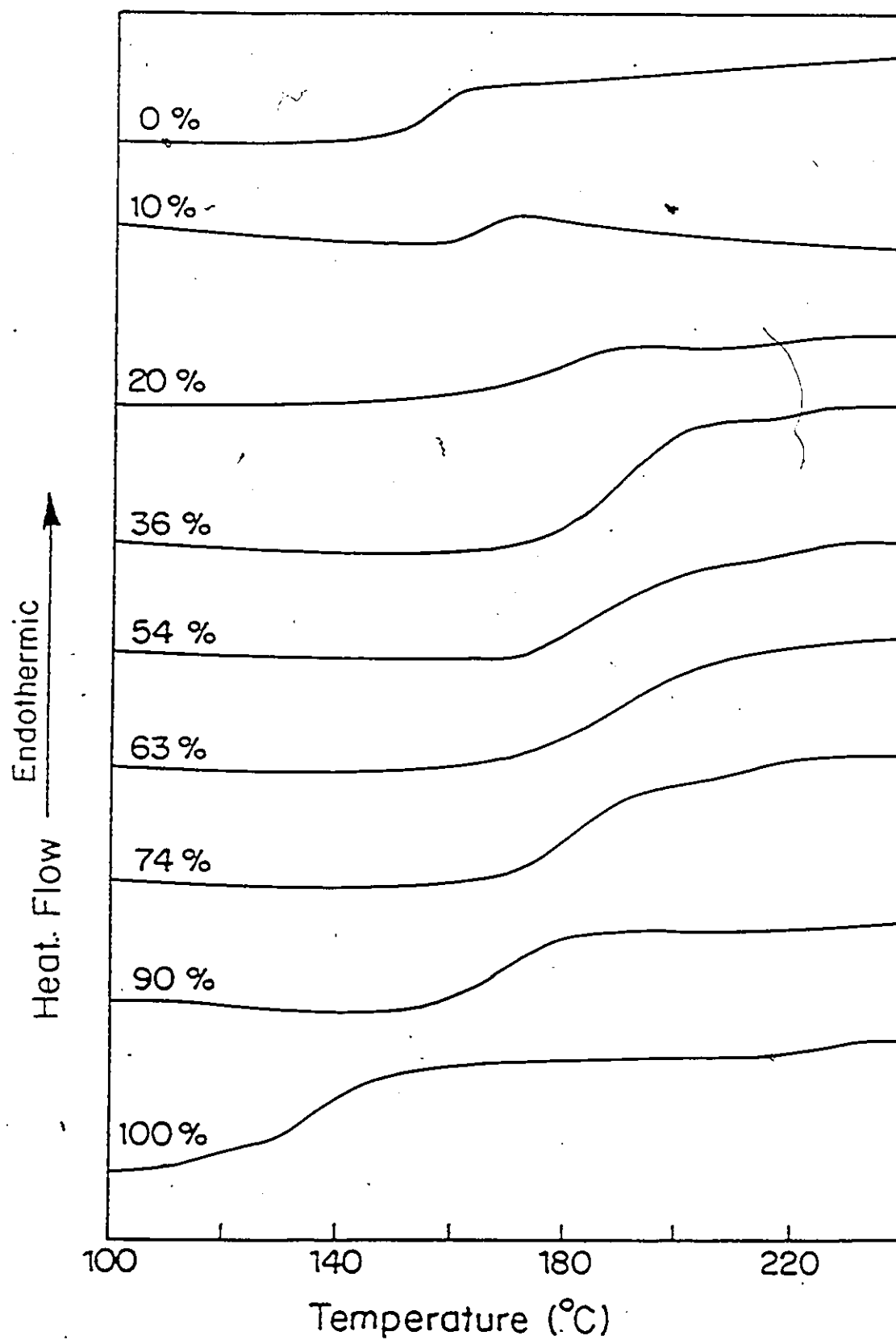


Figure 5. DSC thermograms of blends of PVP and PHS, at different compositions. The weight per cent of PHS is shown above the DSC thermograms.

polymer blends were carried out with preheating until 220°C at 10°C/min followed by slow cooling to room temperature prior to Tg determination at 20°C/min. In all cases a single Tg higher than that of either individual polymer was observed. Tg for all blends exhibited large positive deviations from the calculated weight-average values of Tg. This positive deviation appears to be proportional to the extent of mutual interactions between both polymers. Maximum deviation, and therefore highest Tg, was obtained when blends with compositions approaching a 1:1 molar ratio were used.

We observed that the Tg for the 1:1 molar ratio blend was 188°C, while we obtained a Tg at 210°C for the same 1:1 molar ratio blend but this blend was prepared by mixing methanol solutions of the individual polymers, PVP and PHS. As described earlier when methanol solutions of PVP and PHS were mixed, a 1:1 molar ratio insoluble complex was formed regardless of the relative amounts of the individual polymers used. On the other hand, when pyridine solutions were mixed no precipitation was observed and interaction between both polymers takes place very slowly as the solvent evaporates. It appears that the two different methods of blend preparation bring about different blend structures. To explain the higher Tg (210°C) obtained for the 1:1 molar ratio blend prepared by using methanol as solvent, we propose a compact structure where most probably

one single polymeric chain is interacting with another polymeric chain, and hydrogen-bonding achieves its maximum efficacy (Figure 6). This kind of structure also could explain the formation of the 1:1 molar ratio blend regardless the amount of individual polymers used. Another empirical observation that supports this proposed structure is the physical appearance of the precipitate obtained. The precipitate was a nice free-flowing powder while it would be expected that if one polymeric chain were interacting with several other chains, the precipitate would have had a gel type appearance. For the blends using pyridine as solvent we propose an entangled type structure (Figure 6) where one polymeric chain is interacting with several others, that is, blends with a tri-dimensional network structure. Efficacy of hydrogen-bonding interaction is lower and this can explain the lower T_g observed (188°C). Moreover, we would like to remark that the different T_g 's are due without doubt to different structures of the blends. The different T_g 's can not be attributed to the possibility of residual pyridine in the blends. First, thermogravimetric analyses showed that all residual pyridine (sometimes as high as 9 wt.%) was eliminated after the first heating scan and prior to T_g measurements. Second, the 1:1 molar ratio blend obtained using pyridine as solvent was scanned several times and a T_g significantly lower than 210°C was always obtained. Finally, the fact that structure of a blend depends on its

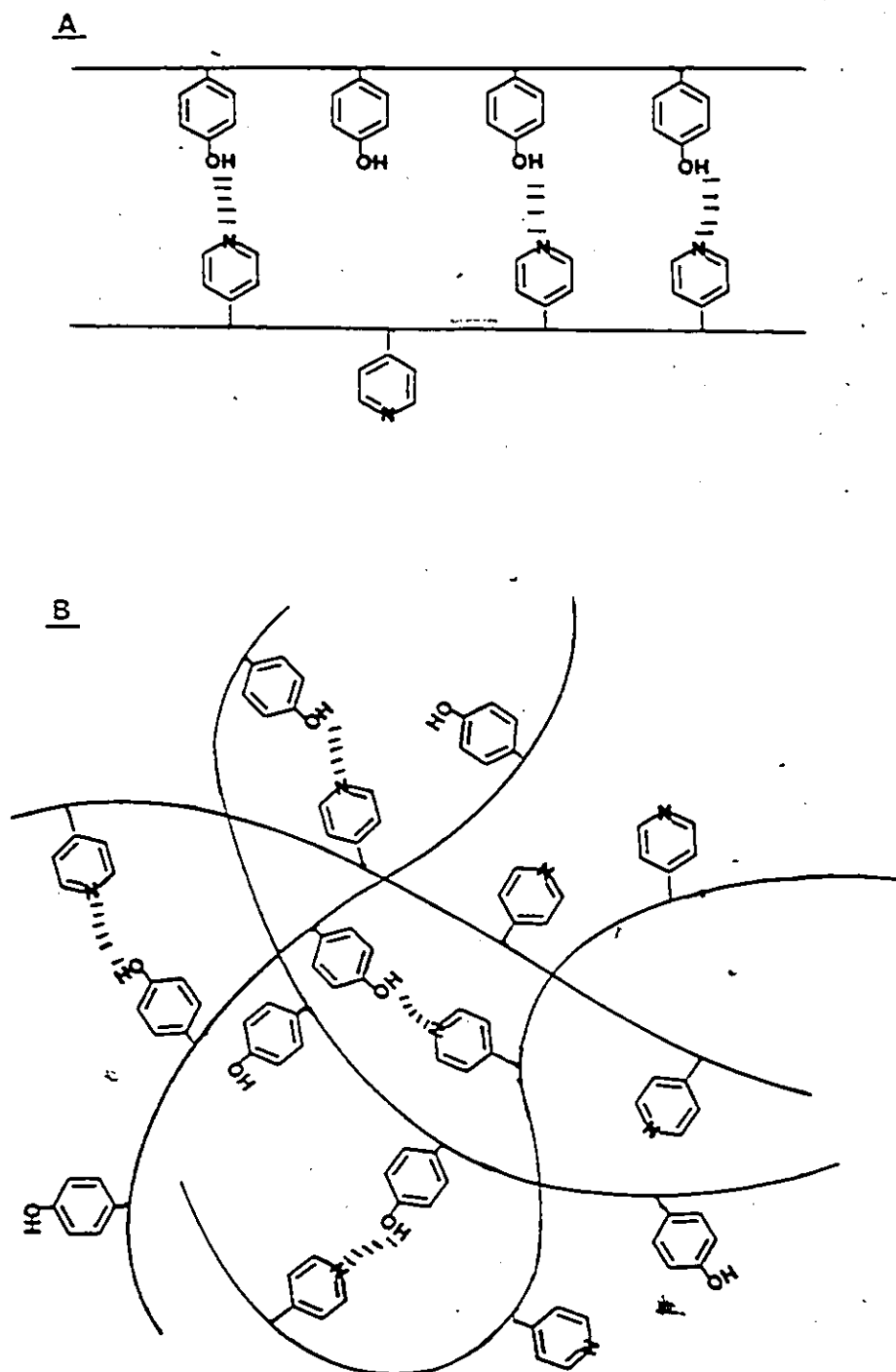


Figure 6. Structure of PVP/PHS blends; A: methanol as solvent, B: pyridine as solvent.

preparation method has been recognized before. For instance, our results are somewhat analogous to those obtained by Tsutsui et al.[48]. Their studies of poly(acrylic acid)/poly(vinyl pyrrolidone) blends indicated that the extent of hydrogen-bonding interaction depended on the blend preparation. Films cast from homogeneous solutions in dimethyl sulfoxide showed less extensive hydrogen-bonding than did those prepared by evaporation of solvents from emulsions of the preformed complexes in water/ethanol.

DSC compatibility studies of polystyrene (PS) with poly (4-vinylpyridine) (PVP) and various (4-vinylpyridine-styrene) (VP-S) copolymers, and of PVP with the various (VP-S) copolymers.

These blends were also prepared by mixing the appropriate amounts of pyridine solutions followed by solvent evaporation and drying. The results obtained in DSC measurements on these polymer blends are reported in Table 2. All samples underwent a first heating scan to 220°C at 10°C/min. followed by a slow cooling to room temperature prior to T_g determination in a second heating scan at 20°C/min. Two distinct T_g were observed for blends of PS with PVP, indicating incompatibility, over the entire range of composition. PS is not only incompatible

Table 2. Glass transition temperatures of mixtures of polystyrene with poly(4-vinylpyridine) and various copoly(styrene-4-vinylpyridine), and of poly(4-vinylpyridine) with various copoly(styrene-4-vinylpyridine)

Composition of Blend		Tg ₁ (°C)	Tg ₂ (°C)
Polymer mix	% weight ratio		
1 + 2	26:74	92	149
1 + 2	50:50	90	147
1 + 2	77:23	88	148
1 + 3	50:50	70	104
1 + 4	50:50	84 ^a	--
2 + 3	50:50	128	148
2 + 4	50:50	115	140

^a A single Tg was observed for this blend.

with PVP but also incompatible with a modified PS containing 50 mol % of 4-vinylpyridine units. However, in a 50:50 weight % mixture, PS appears to be compatible with a modified PS containing only 20 mol % of 4-vinylpyridine units. Finally we observed two Tg for blends of PVP and various (VP-S) copolymers. PVP does not form compatible blends with (VP-S) copolymers even in the case of the (VP-S) copolymer containing 50 mol % of 4-vinylpyridine units. It was interesting to see that the introduction of 4-vinylpyridine units into PS caused incompatibility with the PS homopolymer. Similarly, the introduction of styrene units into PVP caused incompatibility with PVP homopolymer.

DSC compatibility studies of poly (4-vinylpyridine) (PVP) with the various (4-hydroxystyrene-styrene) (HS-S) copolymers.

These blends were also prepared using pyridine as solvent. Blends of PVP and (HS-S) (50 mol % HS) copolymer were compatible over the entire range of composition. Figure 11 shows experimental Tg's of these blends vs. weight % of PVP in the blend. Again Tg showed large positive deviations with respect to weight-average Tg. Maximum Tg deviations did not occur for a stoichiometric blend of interacting units but were observed for blends containing ratios of basic (pyridyl) units to acidic

(phenolic) units between 2 and 1.4. It appears that the excess of basic units is needed to attain the maximum interaction between both polymers; this is likely to be due to the fact that not all pyridine units are able to complex with phenolic units probably because of the presence of the intercalated styrene units.

PVP was also found to be miscible with the (HS-S) (30 mol % HS) copolymer, but only for those mixtures which were rich in PVP: a minimum of 60 wt. % of PVP was required to observe a single T_g for the blend, while samples with lower amounts of PVP showed two T_g values (Figure 7). Similar results were obtained for mixtures of PVP and the (HS-S), (20 mol % HS) copolymer. In this case however the compatibility range was even narrower: compatibility being only observed for those mixtures which contained at least 68 wt. % of PVP (Figure 8).

1.2.1.2 Gordon-Taylor, Jenckel-Hausch, Fox, Couchman, and Kwei equations. Their applicability to the systems: PVP/PHS, PVP/copoly (HS-S) (50 mol % HS).

As described earlier in the introduction, the above equations correlate and predict the dependence between the

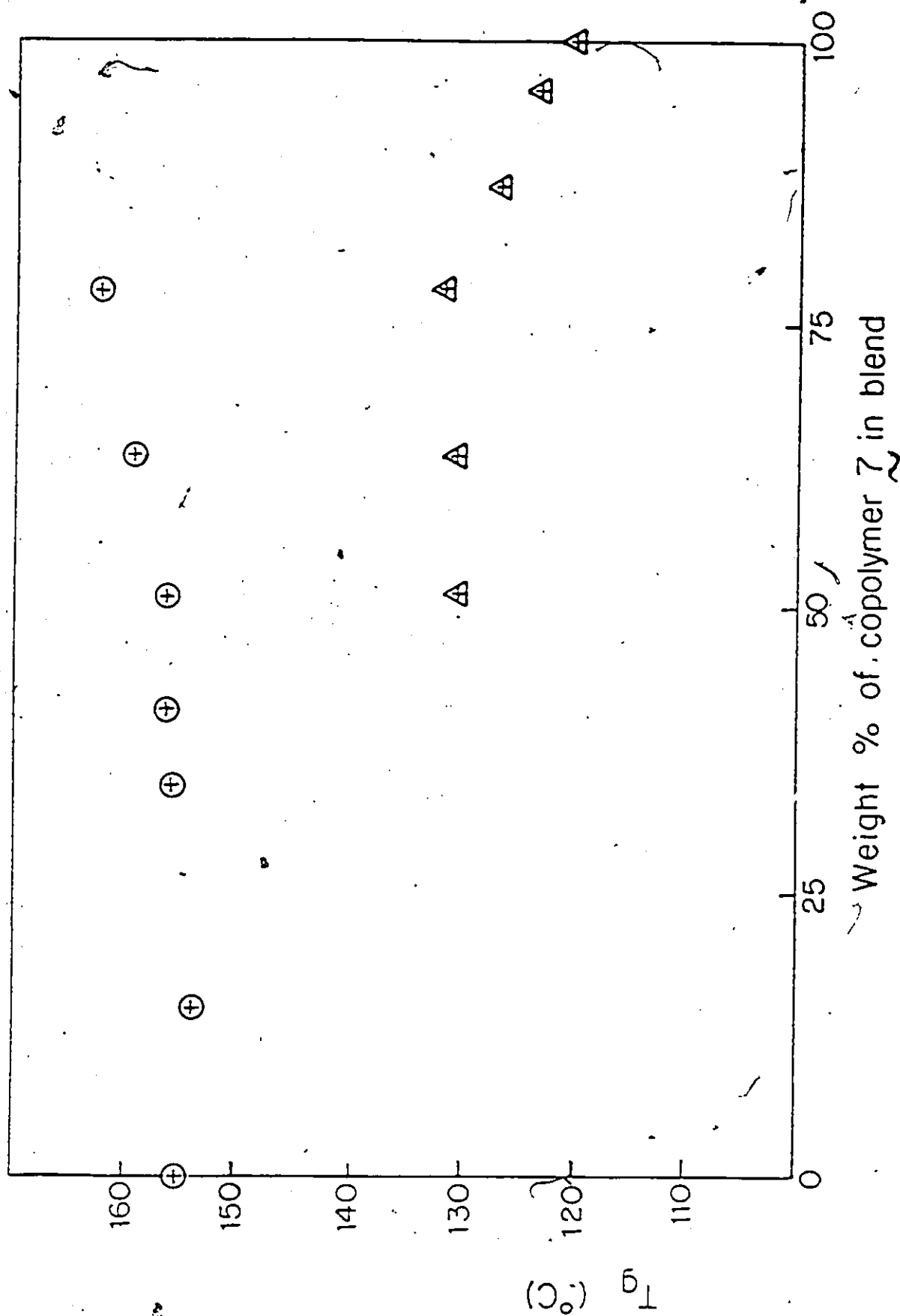
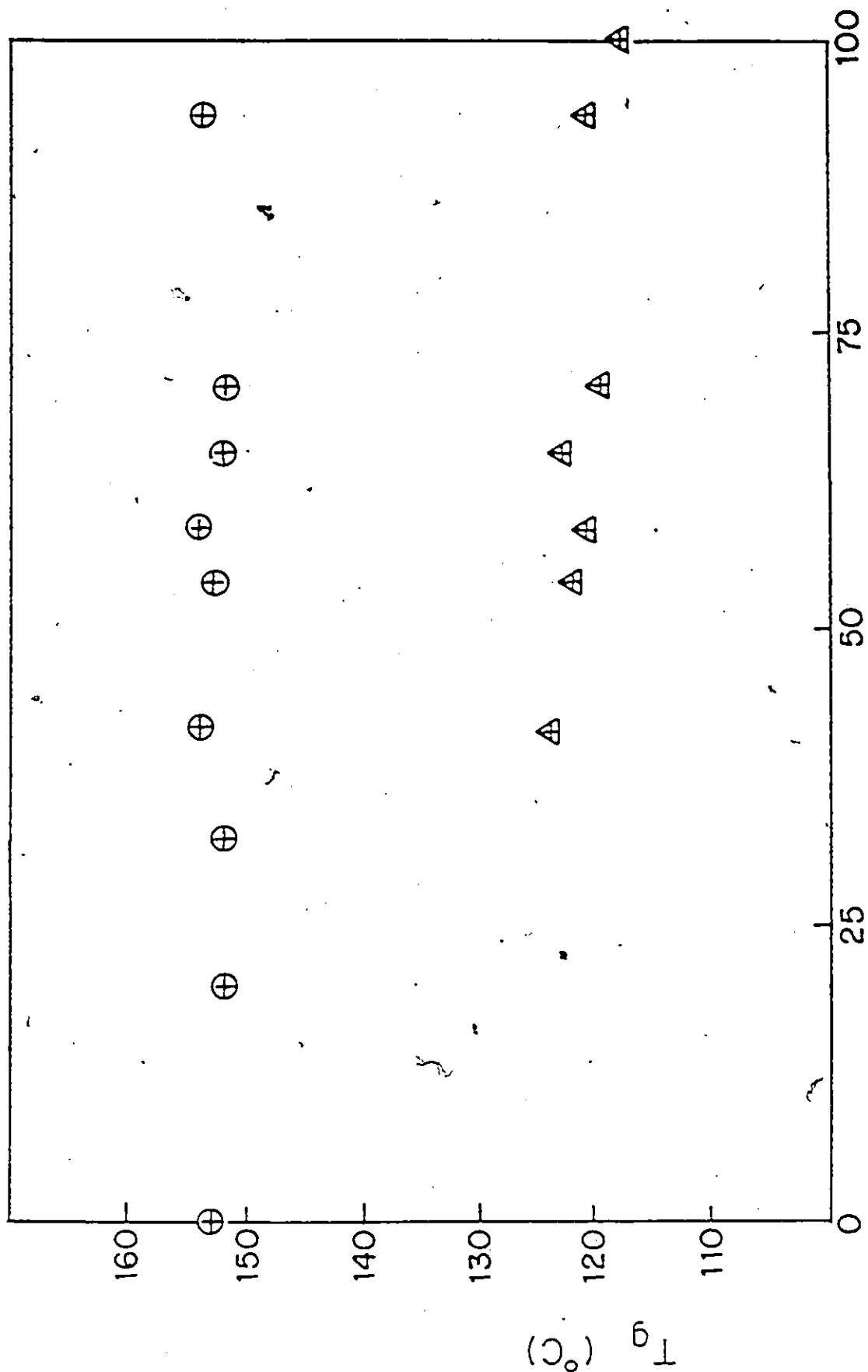


Figure 7. Glass-transition temperature of blends of PVP and copoly (HS-S) (30 mol % HS) versus weight per cent of the copolymer in the blend.



Weight % of copolymer 8 in blend

Figure 8. Glass-transition temperatures of blends of PVP and copoly (HS-S) (20 mol % HS) versus weight per cent of the copolymer in the blend.

glass-transition temperature of a miscible system and its composition.

* Gordon-Taylor equation:

$$T_g = (w_1 T_{g1} + k w_2 T_{g2}) / (w_1 + k w_2)$$

* Jenckel-Heusch equation:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + w_1 w_2 b (T_{g1} - T_{g2})$$

* Fox equation:

$$1/T_g = (w_1/T_{g1}) + (w_2/T_{g2})$$

* Couchman equation:

$$\ln T_g = (w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2}) / (w_1 \Delta C_{p1} + w_2 \Delta C_{p2})$$

* Kwei equation:

$$T_g = [(w_1 T_{g1} + k w_2 T_{g2}) / (w_1 + k w_2)] + q w_1 w_2$$

The experimental values for the glass-transition temperatures of the miscible systems PVP/PHS and PVP/copoly(HS-S) (50 mol % HS) were analyzed by standard non-linear least square procedures to test which of the above equations affords the best fit for the experimental data.

PVP/PHS system.

Figure 9 shows the experimental T_g of this system vs. weight % of PVP and theoretical curves predicted by the Gordon-Taylor and the Jenckel-Heusch equations. We obtained $k = 10$ for the Gordon-Taylor equation as the value giving the best fit of the experimental data. We see in Figure 9, that the Gordon-Taylor equation failed to fit the experimental data at all. This equation even failed to imitate the shape of the experimental graph. We have plotted also the Gordon-Taylor equation with $k = 0.055$ which was the value we obtained when fitting the Kwei equation, again the experimental data did not fit at all. The fact that the Gordon-Taylor equation did not fit our experimental data was not surprising since this equation does not take into account the strong interactions that exist in our system. In contrast, the Jenckel-Heusch equation with $b = -12.59$ gave a rather good fit of the experimental data. This is because the parameter b takes interpolymetric interactions into account. Figure 10 shows the theoretical curves predicted by the Fox, Couchman, and Kwei equations. The Couchman equation was plotted by using the following heat capacity changes: $\Delta C_{p1}(\text{PHS}) = 0.37 \text{ J/g.}^\circ\text{K}$ and $\Delta C_{p2}(\text{PVP}) = 0.30 \text{ J/g.}^\circ\text{K}$ which are experimental values. The Fox and Couchman equations did not fit the experimental data. It should be noted that the T_g values that were obtained applying both equations were

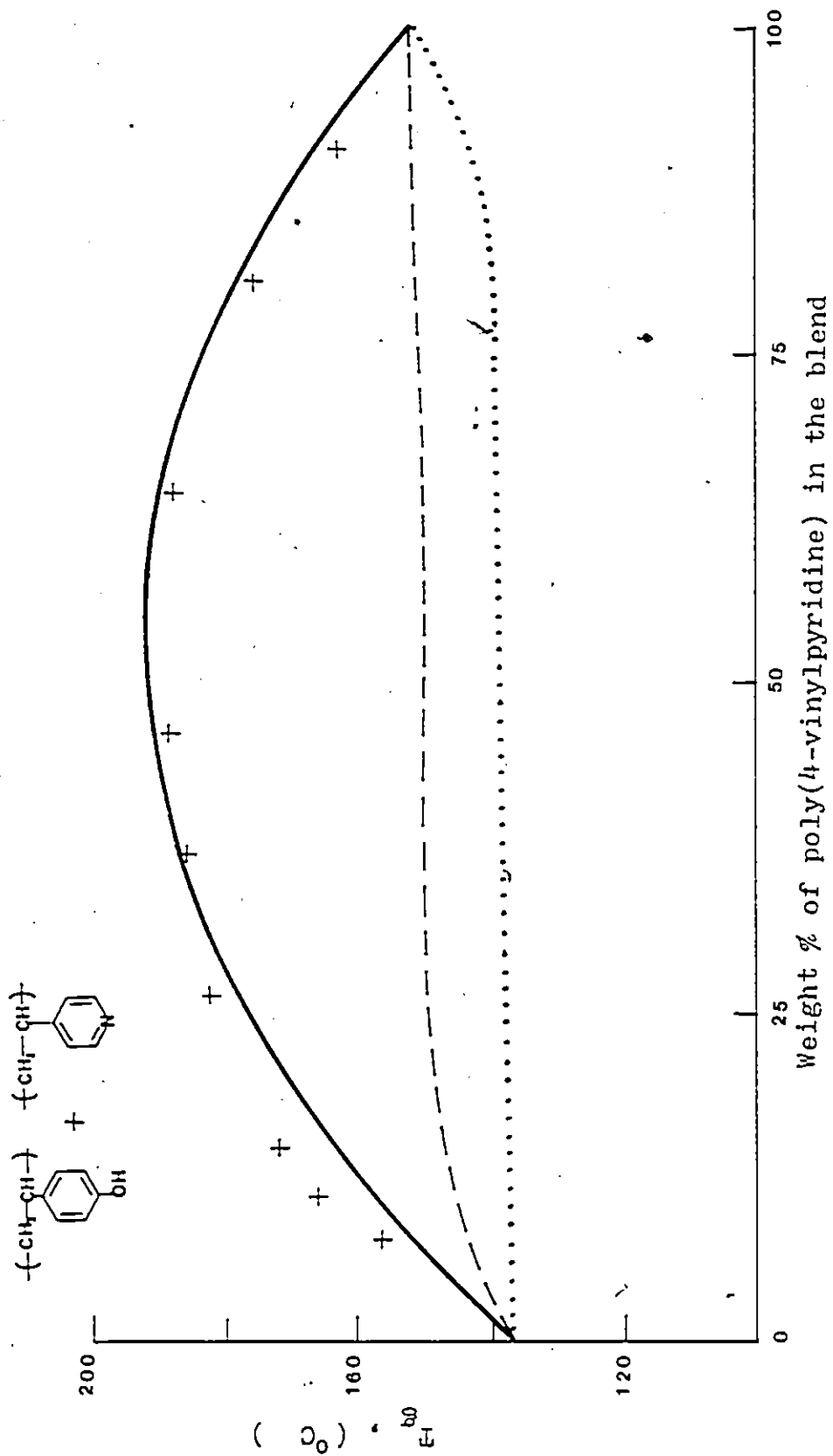


Figure 9. Glass-transition temperatures of PVP/PHS blends vs. weight % of PVP in the blend, and theoretical curves predicted by Gordon-Taylor (...), ($k = 0.055$), ($k = 10$), and Jenckel-Heusch (—) equations.

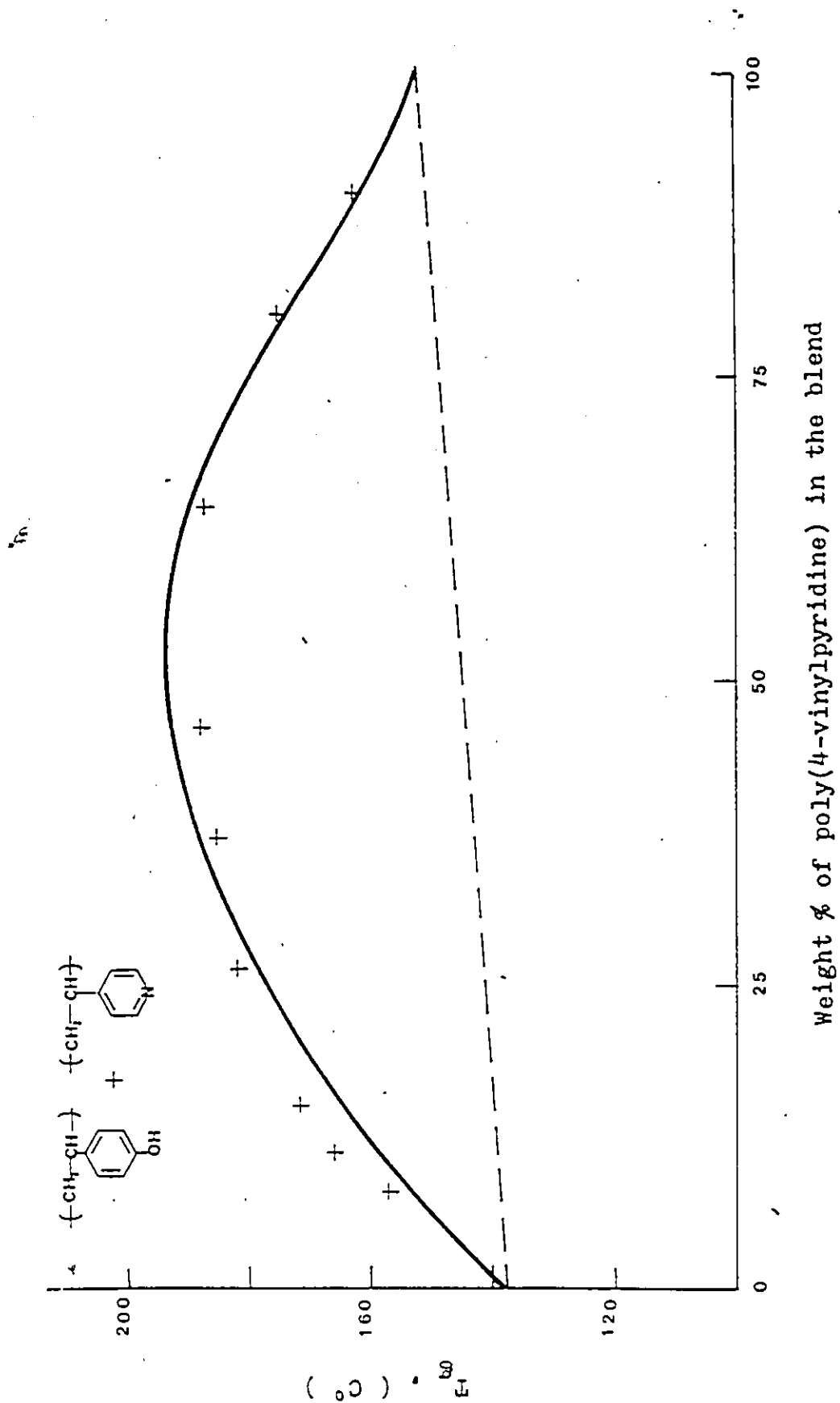


Figure 10. Glass-transition temperatures of PVP/PHS blends vs. weight % of PVP in the blend, and theoretical curves predicted by Kwei (—), Fox (-----), and Couchman (-----) equations.

approximately the same within 1.5°C. This is because the Couchman equation reduces to the Fox equation if $Tg_2/Tg_1 = 1$ and $\Delta Cp_1 Tg_1 = \Delta Cp_2 Tg_2$ which is the case for PVP/PHS system.

The Kwei equation with $k = 0.055$ and $q = 218.7$ fitted well the experimental data. This equation afforded by far the best fit and is most appropriate to describe this system. The value q which is assumed to be proportional to the strength of the interchain interaction correlated well with the value q given for other systems. For instance, Percec et al. [21] found q values that ranged from 50 to 70 for their systems in which interpolymeric interactions were based on electron donor-acceptor complexes. Kwei [19] reported $q = 81$ for the hydrogen-bonding interaction taking place between the carbonyl group of isotactic poly(methylmethacrylate) and the hydroxyl group of a novolac resin. We observe that for other systems where the specific interaction was weaker than that of the PVP/PHS system, the values of q were indeed lower than ours.

PVP/copoly(HS-S) (50 mol % HS) system

Figure 11 shows the experimental values of Tg for this miscible system vs. the weight % of PVP as well as the theoretical curves predicted by Jenckel-Heusch, Fox, Couchman and Kwei equations. When using the Gordon-Taylor

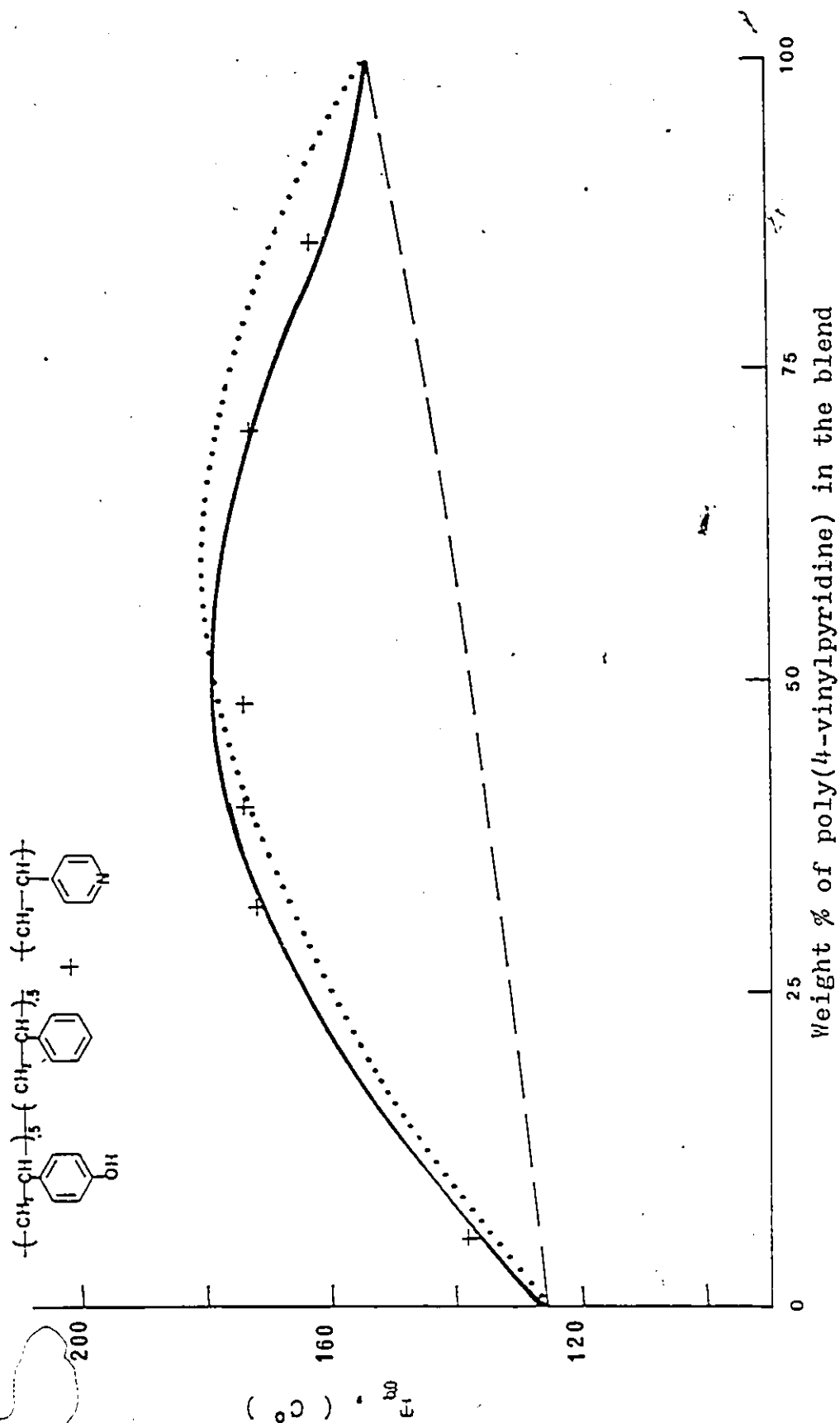


Figure 11. Glass-transition temperatures of blends of PVP and copoly (HS-S) (50 mol % HS) vs. weight % of PVP in the blend, and theoretical curves predicted by Kwei (—), Jenckel-Hensch (...), Fox (-----), and Couchman (----) equations.

equation the non-linear least square procedures gave an almost constant T_g ($150 \pm 2^\circ\text{C}$) value for all blends over the whole range of composition. This indicated the complete inability of this equation to represent our experimental data. Similarly, the Fox and Couchman equations did not fit the experimental data. The Couchman equation was plotted by using $\Delta C_{p1} = 0.294 \text{ J/g.}^\circ\text{K}$ and $\Delta C_{p2} = 0.30 \text{ J/g.}^\circ\text{K}$ which are experimental heat capacity changes for copoly(HS-S) (50 mol % HS) and PVP respectively. Again we observe that the T_g values which are obtained by applying the Fox or Couchman equations were very close. Their difference being within 1°C .

The Jenckel-Heusch equation with $b = -5.45$ and the Kwei equation with $k = 0.077$ and $q = 208.9$ gave good fits of our experimental data. Again this is because these equations take into account interactions between the polymers in the blend. It is very interesting and important to note that the values of q for both systems, PVP/PHS and PVP/copoly(HS-S) (50 mol % HS), are very similar: 218.7 and 208.9 respectively. This suggests that parameter q indeed represents the strength of the hydrogen-bonding interactions within the systems studied. Since the hydrogen-bonding interactions are the same in both systems, the same value q is obtained.

1.2.1.3 Thermogravimetric Analyses (TGA)

Thermogravimetric analyses are desirable, when studying compatibility of a blend by DSC, mainly because of two reasons: First, blends are usually prepared by a solvent method, and it is necessary to avoid the presence of traces of solvent in the blend, since the solvent behaves as a plasticizer lowering the T_g of the blend; this would lead to irreproducible T_g values. Thermogravimetric analyses may help determine whether all traces of solvent (usually from 3 to 6 wt. %) are eliminated or not during the first heating scan and annealing period that the samples usually undergo prior to T_g measurements. A thermogravimetric analysis also allows the measurement of the decomposition temperature of the polymer which helps to determine the appropriate temperature at which annealing can be carried out. Table 3 shows the decomposition temperatures of the polymers and copolymers used in this study. We see that PS 1, $M_n=4000$, $M_w=31,400$, $M_w/M_n=7.9$, starts to decompose at 250 °C, and has a peak decomposition temperature at 370 °C. Probably, its rather low starting decomposition temperature (250 °C) is due to its broad molecular weight distribution. In contrast, PVP 2 shows a higher thermal stability, it starts to decompose at 280 °C, however its peak decomposition temperature is at 356 °C. Finally, PHS 5 and the (HS-S) copolymers 6, 7 start to decompose by 290 °C, with peak

Table 3. Thermogravimetric analyses of PS, PVP, PHS, and various (HS-S) copolymers^a. (See Figure 4).

Step decomposition temperatures, °C.				
Polymer #	Start	Peak	End	Loss weight %
1	250	368	408	99
2	280	356	383	97
5	290	369	445	78
6	300	380	425	95
7	300	375	425	98

Table 4. Thermogravimetric analyses of some representative polymeric blends used in this study^a. (See Figure 4).

Step decomposition temperatures, °C.					
Blend	%wt. ratio	Start	Peak	End	Loss weight %
2+5	37:63	295	361	441	81
1+2	50:50	280	380	437	100
2+6	48:52	320	375	439	96
2+7	45:55	320	379	435	97
2+8	46:54	310	379	433	96

a) Reported decomposition temperatures were obtained in a second heating scan at 20°C/min. Samples underwent a first heating scan until 220°C at 10°C/min. During this first heating scan, it was observed a loss of weight from 3 to 6 wt.%, between 120-160°C, corresponding to evaporation of residual solvent (pyridine). These conditions under which thermogravimetric analyses were performed are the same as those used for DSC measurements.

decomposition temperatures at ca. 370 °C. It should be noted, that while all other polymers and copolymers decompose almost completely at ca. 400 °C, PHS 5 shows only a loss of 78 wt. % at 445 °C. Figure 12 shows the TGA curves (loss of weight vs. temperature) of PS and PVP. A perfectly straight baseline is observed from room temperature until the start of the decomposition step. This indicates the absence of solvent in the samples after the first heating scan. Similarly, Figure 13 shows the TGA curves obtained for PHS and the (HS-S) (50 mol % HS) copolymer, once again the absence of solvent in the samples is confirmed.

Thermogravimetric analyses have also been performed for some representative polymeric blends. Table 4 shows these results. All blends decompose almost completely by 430 °C except PVP/PHS, 2+5, blend for which we observe a loss of weight of only 81% at 441 °C, this reflects the presence of PHS in the blend. We have mentioned that PHS only decomposes up to 78% at 445 °C. Also, all blends show a peak decomposition temperature between 361 and 380 °C. Finally, the start of the decomposition step for all blends is higher or equal to 280 °C. Figure 14 shows the TGA curves for PVP/PHS (2+5) and PS/PVP (1+2) blends. Also, the TGA curves for blends of PVP 2 with the (HS-S) copolymers 6, 7 are shown in Figure 15.

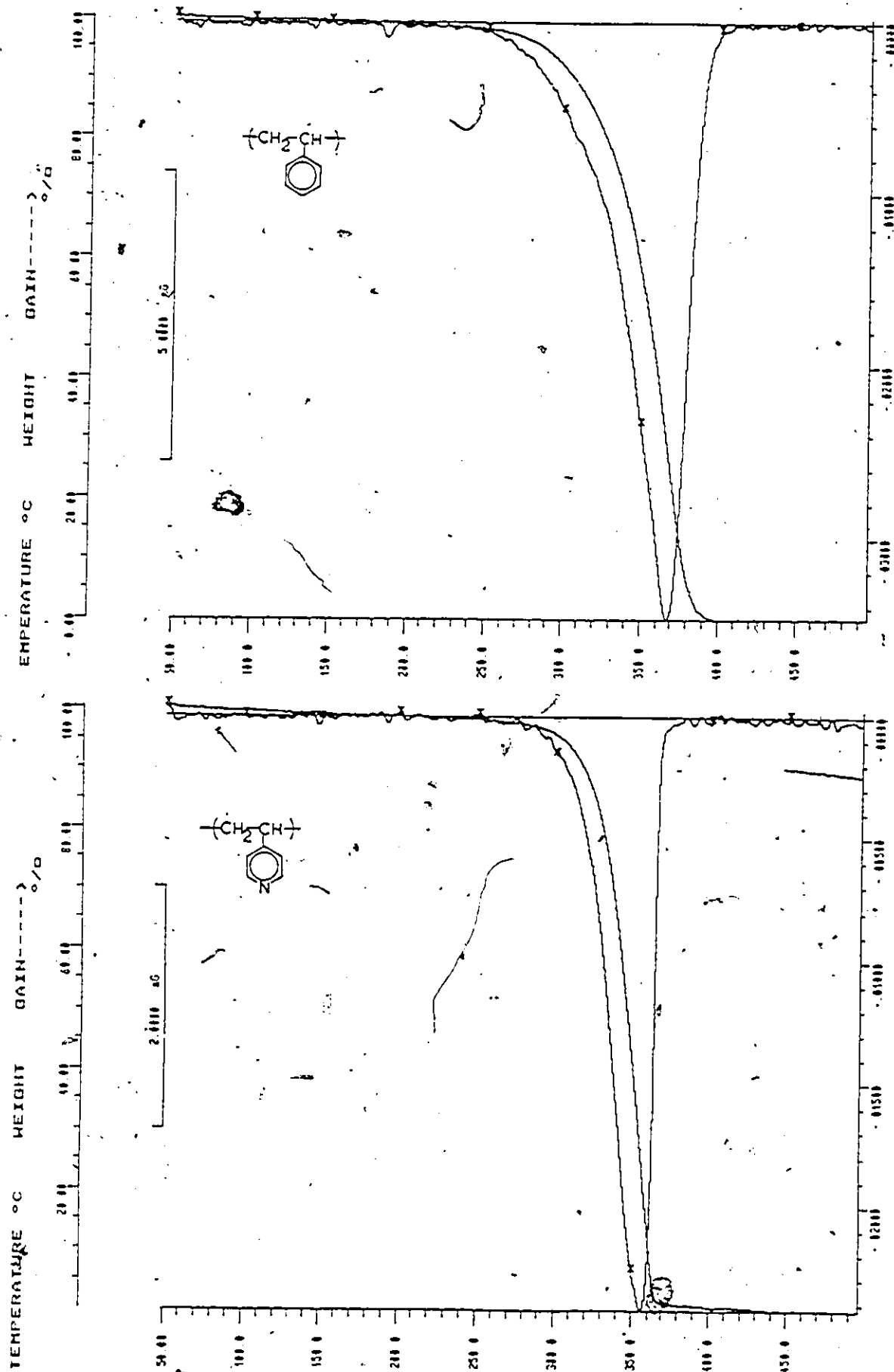


Figure 12. TGA curves (loss of weight vs. temperature) of polystyrene and poly (4-vinylpyridine). The derivative of the TGA curves is also shown.

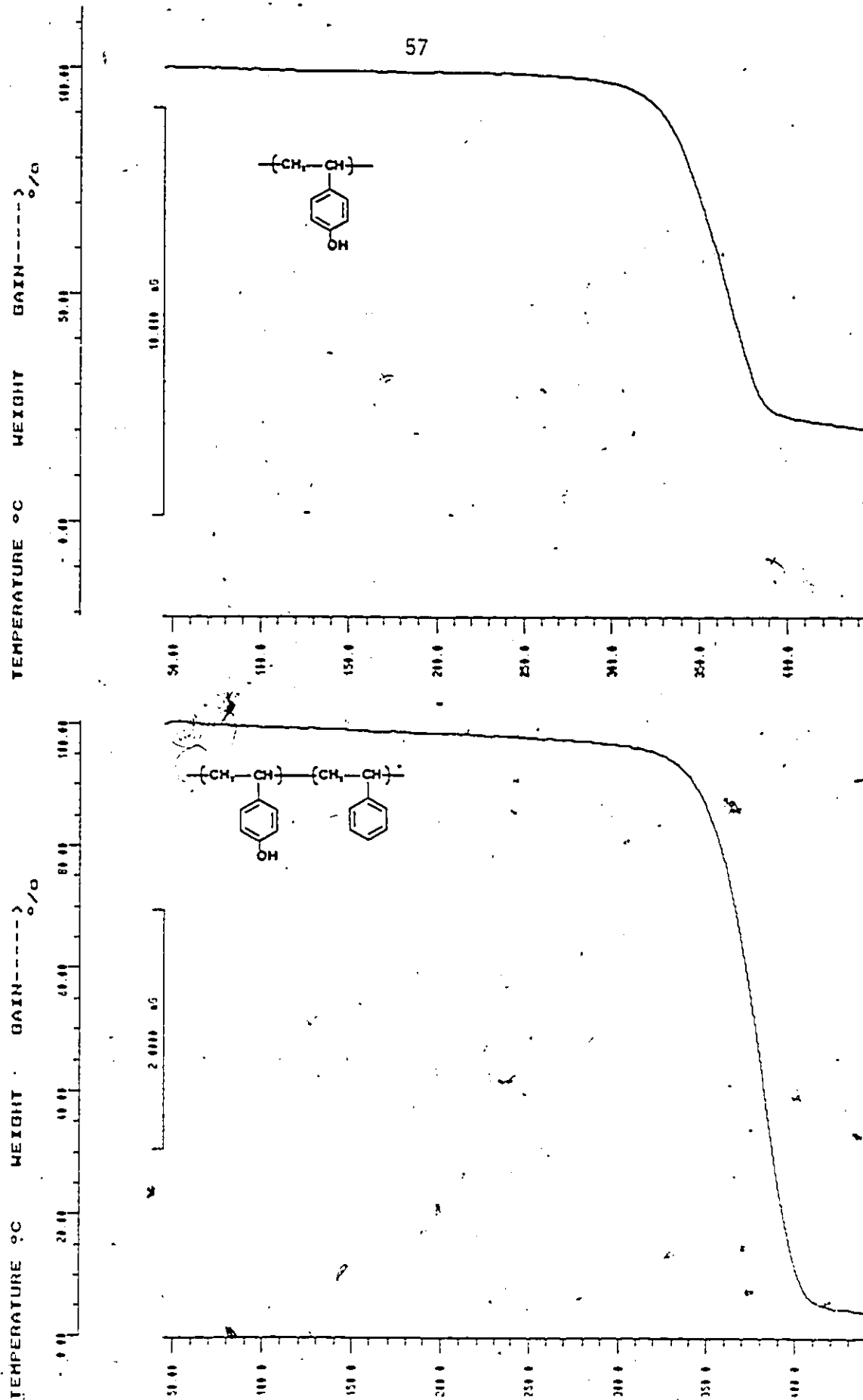


Figure 13. TGA curves (loss of weight vs. temperature) of poly (4-hydroxystyrene) and copoly (HS-S) (50 mol % HS).

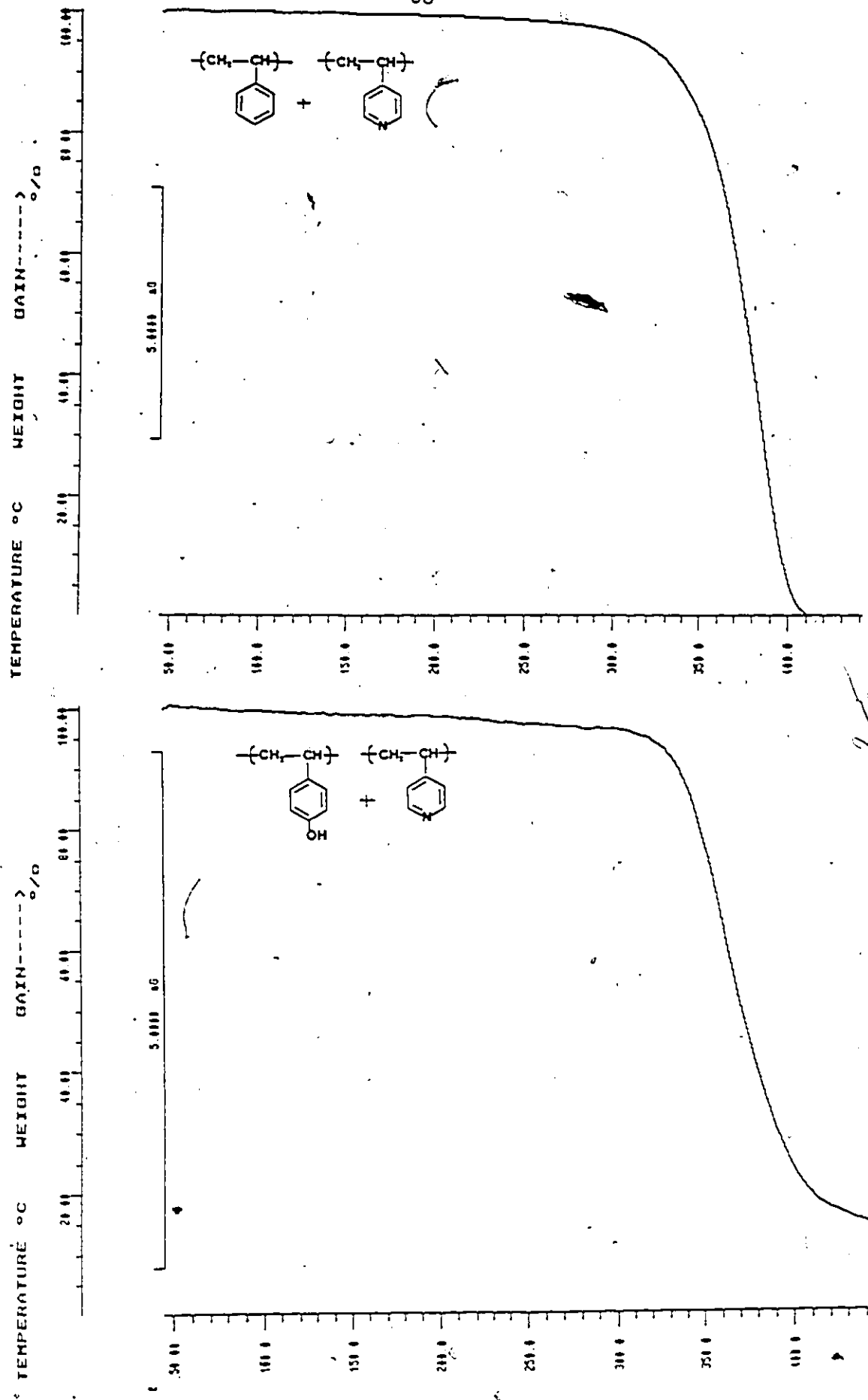


Figure 14. TGA curves (loss of weight vs. temperature) of PVP/PS blend (containing 50 wt. % of each component), and of PHS/PVP blend (containing 37 wt. % of PVP).

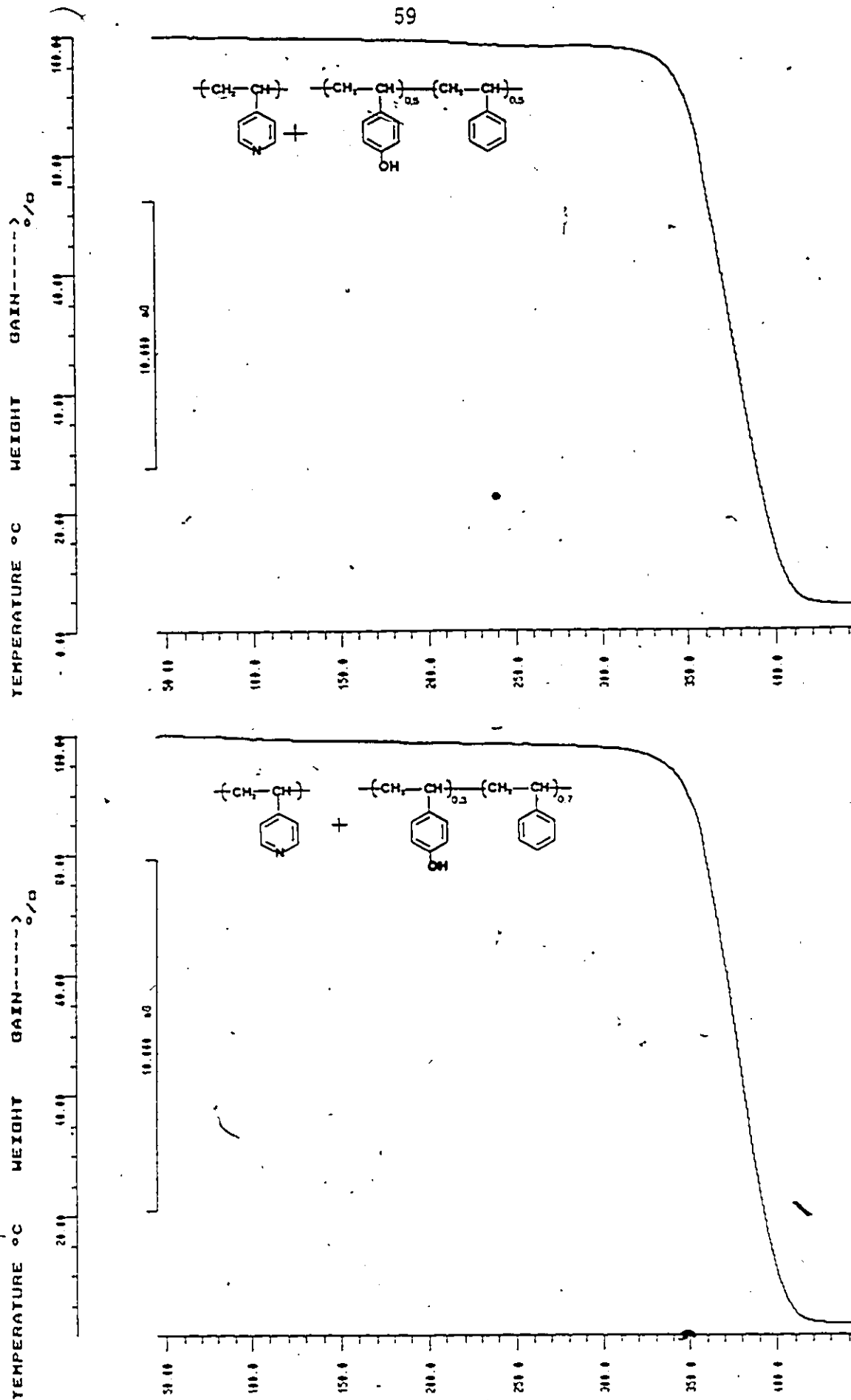


Figure 15. TGA curves of PVP/copoly (HS-S) (50 mol % HS) blend (containing 48 wt. % of PVP) and of PVP/copoly (HS-S) (30 mol % HS) blend (containing 45 wt. % of PVP).

1.2.1.4 FTIR studies of PVP/PHS blends.

FTIR spectrum of PHS

Cummings and Wood [49] give a detailed table listing the observed frequencies and the approximate descriptions of the various modes of vibration for p-methyl phenol Table 5. Using the data given in this table and comparing it to the spectrum of PHS, one may reasonably assign the bands occurring at 825, 1100, 1170, 1445, and 1595-1610 cm^{-1} , to the aromatic ring. The relatively broad bands in the 1200-1400 cm^{-1} region of the spectrum are attributed to O-H deformation and C-O stretching vibrations which are mixed to some degree. Of particular significance to the current study is the high-frequency region from 3800 to 3000 cm^{-1} , where the hydroxyl stretching vibration is observed. In this region, the PHS spectrum is characterized by a very broad band centered at 3360 cm^{-1} , attributed to a wide distribution of hydrogen-bonded hydroxyl groups, and a much narrower band observed at 3525 cm^{-1} which is associated with free (non hydrogen-bonded) hydroxyl groups. The difference in frequency between the free hydroxyl stretching vibration and the maximum in the band of the hydrogen-bonded hydroxyls which is ca. 176 cm^{-1} is assumed to be proportional to the strength of intermolecular hydrogen bonds (self-association). Several papers deal with the relationship between $\Delta\nu_{\text{OH}}$ and the strength of a given hydrogen-bonded complex. It is found in many cases a

Table 5. Observed frequencies and the approximate descriptions of modes of vibration for p-methyl phenol (ref.49)

Approximate description	<i>p</i> -Methyl	
	Obs.	Calc.
$\nu(\text{C-H})$	3062	3091
$\nu(\text{C-H})$	3030	3037
$\nu(\text{C-X})$	1213	1215
$\nu(\text{C-C})$	1615	1608
$\nu(\text{C-C})$	1515	1519
$\nu(\text{C-OH})$	1252	1262
$\beta(\text{C-H})$	1170	1167
$\beta(\text{C-H})$	1018	1019
$\tau(\text{CCC})$	843	863
$\nu(\text{C-OH}) + \nu(\text{C-X})$	738	721
$\nu(\text{C-OH}) + \nu(\text{C-X})$	462	451
$\nu(\text{C-H})$	3062	3085
$\nu(\text{C-H})$	3030	3042
$\nu(\text{C-C})$	1598	1615
$\nu(\text{C-C})$	1428	1427
$\nu(\text{C-C}) + \delta(\text{OH})$	1328	1320
$\beta(\text{C-H})$	1291	1278
$\beta(\text{C-H})$	1102	1098
$\beta(\text{C-X})$	320	332
$\tau(\text{CCC})$	643	641
$\beta(\text{C-OH})$	426	466
$\delta(\text{OH}) + \nu(\text{C-O-H})$	1170	1178
$\nu(\text{O-H})$	3611	3611

Table 6. Observed frequencies and the approximate descriptions of modes of vibration for 4-methyl pyridine. (ref.49)

Approximate description	4Me-pyridine	
	Obs.	Calc.
$\nu(\text{CH})$	3050	3075
$\nu(\text{CH})$	3040	3074
$\nu(\text{CY})$	1212	1239
$\nu(\text{CC})$	1604	1605
$\nu(\text{CC}), \nu(\text{CN})$	1495	1498
$\beta(\text{CH})$	1220	1215
$\beta(\text{CH})$	1070	1050
breathing	994	1009
$\nu(\text{CY})$	801	815
$\nu(\text{CY})$	514	533
$\nu(\text{CH})$	3040	3072
$\nu(\text{CH})$	3010	3071
$\nu(\text{CC}), \nu(\text{CN})$	1566	1561
$\beta(\text{CH})$	1417	1406
$\beta(\text{CH})$	1365	1339
$\nu(\text{CC})$	1289	1270
$\beta(\text{CH})$	1090	1088
$\tau(\text{CCC})$	669	639
$\beta(\text{CY})$	341	352
$\gamma(\text{CH})$	872	952
$\gamma(\text{CH})$	799	809
$\delta(\text{CC})$	728	757
$\delta(\text{CC})$	490	518
$\gamma(\text{CY})$	211	242

linear relationship between $\Delta\nu_{OH}$ and the strength of the hydrogen-bond involved.

FTIR of PVP

Table 6 shows a detailed list of the frequencies of 4-methyl-pyridine as given by Cummings and Wood [49]. In the spectrum of PVP, one may assign the bands occurring at 1595 cm^{-1} to C=C stretching vibration of the aromatic ring, and those occurring at 1556 and 1494 cm^{-1} to C=C + C=N stretching vibrations of the aromatic ring.

FTIR of PHS/PVP Blends

Figure 16 shows the FTIR spectra from 3800 to 650 cm^{-1} which were obtained for films of PHS/PVP over the entire range of composition. A detailed study of the spectra in the frequency region from 1650 to 650 cm^{-1} revealed that the bands situated in this region did not change their vibrational frequencies significantly as a result of blending. The spectra in this region are just the weighted sum of the spectra of PHS and PVP. In contrast, drastic changes are observed in the O-H stretching vibration region (Figure 17). We have previously mentioned that the pure PHS exhibits two bands in the hydroxyl stretching region: one at ca. 3525 cm^{-1} (free hydroxyls), and the second, a

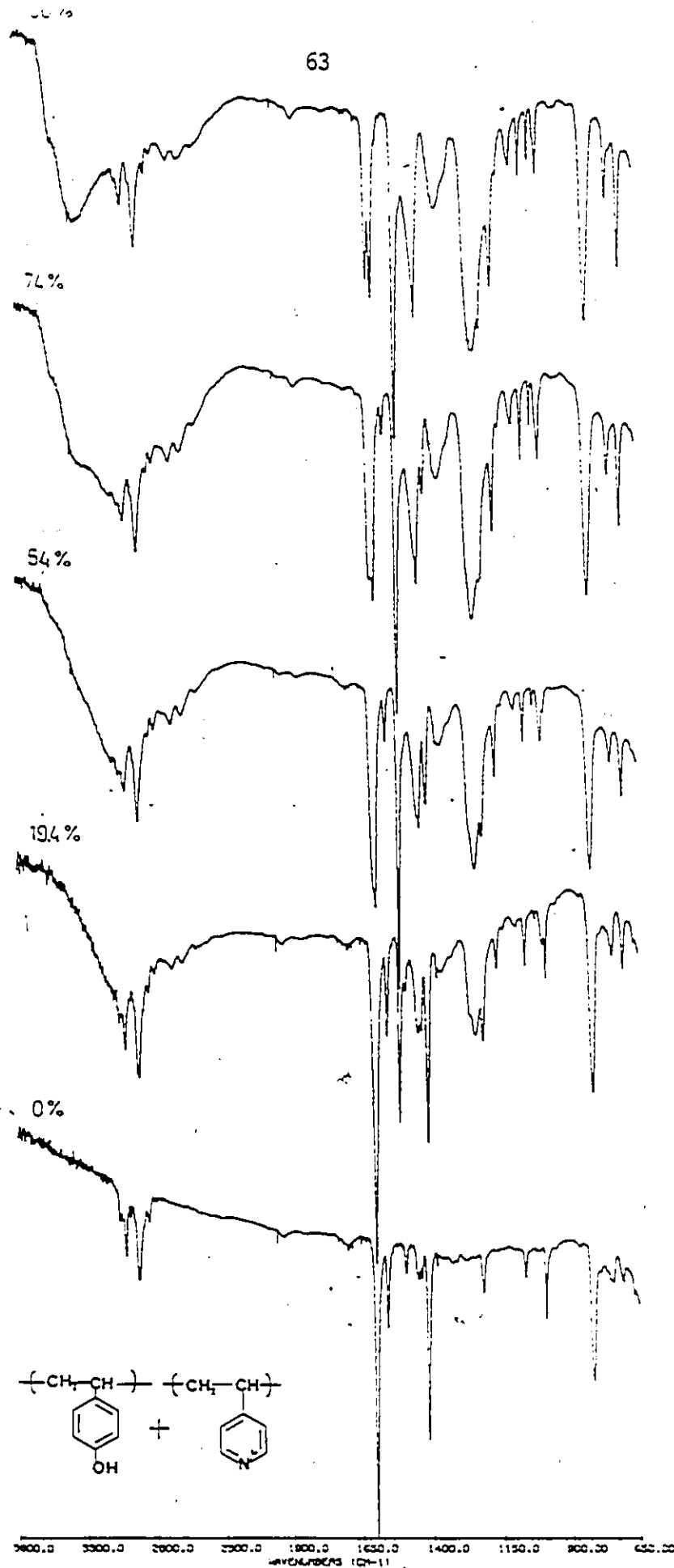


Figure 16. FTIR spectra in the range 3800-650 cm⁻¹ for PHS/PVP blends. Weight % of PHS in the blend is shown above each spectrum.

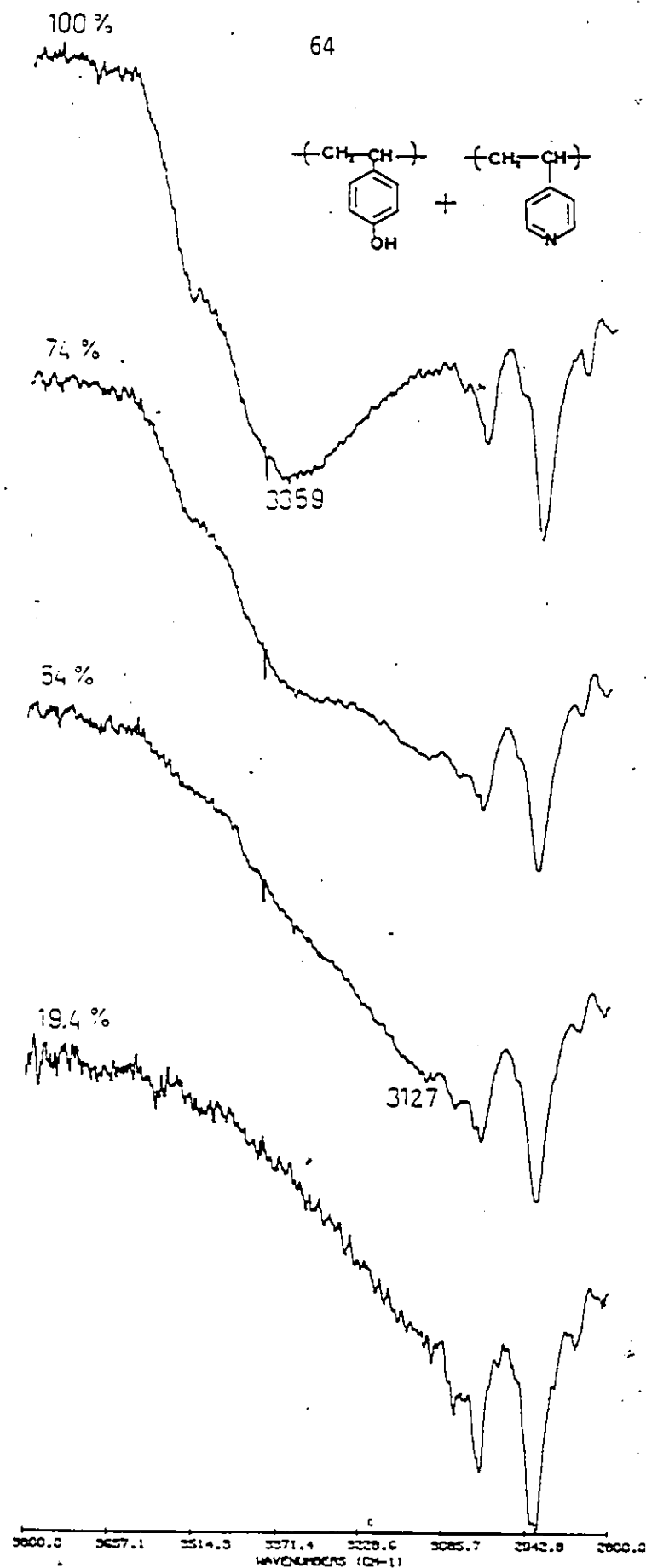


Figure 17. FTIR spectra in the range 3800-2800 cm⁻¹ for PHS/PVP blends. Weight % of PHS in the blend is shown above each spectrum.

very broad band centered at ca. 3360 cm^{-1} (hydrogen-bonded hydroxyls, self-association). As seen in Figure 17, as the concentration of PVP is increased in the blends the free hydroxyl band is reduced and is no longer visible in the spectrum of the 20:80 PHS/PVP blend. Concurrently, the hydrogen-bonded hydroxyl band (3360 cm^{-1}) is also reduced, and is replaced progressively by a new very broad band centered at ca. 3127 cm^{-1} , this new O-H stretching band is attributed to hydroxyls which are hydrogen-bonded to pyridine groups. In the 74:26wt% PHS/PVP blend, it is evident that the O-H band is made up of three components: the first is due to free hydroxyls, the second to hydrogen-bonded hydroxyls (self-association of PHS), and the third to hydroxyl groups associated with the pyridine groups of PVP. Meanwhile, in the 54:46wt% PHS/PVP, the bands corresponding to free and self-associated hydroxyl groups are less evident, and the band corresponding to hydroxyl groups complexed with pyridine groups is easily seen. Similarly, in the blend 19.4:79.6wt% PHS/PVP, we observe that the OH band is mainly made up of one component only : hydroxyl groups complexed to pyridine groups this band being centered at 3127 cm^{-1} . Cummings and Wood [49] have reported a O-H stretching band at 3125 cm^{-1} for the phenol:pyridine complex.

In conclusion, it can be said that the FTIR studies reveal that hydrogen-bonding between the hydroxyl groups of

PHS and the pyridine groups of PVP is indeed taking place and that it is likely that it is this interaction which is responsible for the compatibility of the system.



1.2.2 Compatibilization of polystyrene (PS) with poly (4-hydroxystyrene) (PHS) by introducing into PS the basic 4-vinylpyridine units.

PS is immiscible with PHS. Compatibility between these two polymers can be achieved if basic units are introduced into PS. We have introduced 4-vinylpyridine units into PS. Then, compatibility studies between the various modified PS and PHS were performed. These studies allowed the estimation of the lowest level of modification which was needed to achieve compatibility. Figure 4 shows the structure of the various polymers and copolymers used in this study and Table 1 shows their molecular weight data and glass-transition temperatures.

1.2.2.1 Differential scanning calorimetry (DSC) studies.

DSC compatibility studies of polystyrene (PS) with poly (4-hydroxystyrene) (PHS) and various (4-hydroxystyrene-styrene) (HS-S) copolymers, and of PHS with the various (HS-S) copolymers.

These blends were also prepared by mixing the appropriate pyridine solutions followed by solvent evaporation and drying. All samples underwent a first heating scan until 220°C at 10°C/min. followed by slow

cooling to room temperature prior to T_g determination in a second heating scan at $20^\circ\text{C}/\text{min}$. The results which were obtained are shown in Table 7. It is seen that PS 1 is incompatible with PHS 5. Two T_g values were obtained for their blends over the entire range of composition. Moreover, PS 1 is incompatible with (HS-S) copolymers containing 50 and 30 mol % of 4-hydroxystyrene. Likewise, PHS 5 did not show compatibility with (HS-S) copolymers containing 30 or even as much as 50 mol % of 4-hydroxystyrene units.

DSC Compatibility studies of PHS with the various (4-vinylpyridine-styrene) (VP-S) copolymers.

PHS is miscible with the (VP-S) (50 mol % VP) copolymer. Their blends exhibited a single T_g over the whole range of composition. Table 8 shows the T_g values which were obtained. T_g showed large positive deviations with respect to weight-average T_g . For this system, maximum T_g deviation was observed for blends containing a ratio of acidic to basic units of about 2. Therefore, it is seen that an excess of acidic units is required to achieve maximum interaction. This being probably due to the inability of all phenolic units to complex with the pyridyl units in the (VP-S) copolymer because of the intercalated styrene units.

The content of 4-vinylpyridine units in the (VP-S) copolymer was decreased to 20 mol %, and DSC studies showed

Table 7. Glass-transition temperatures of mixtures of polystyrene with poly (4-hydroxystyrene) and various copoly (styrene-4-hydroxystyrene), and of mixtures of poly (4-hydroxystyrene) with various copoly (styrene-4-hydroxystyrene). (See Figure 4)

Composition of Blend			
Polymer mix	% weight ratio	(Tg1 °C)	(Tg2 °C)
1 + 5	64:36	86	138
1 + 5	57:43	83	127
1 + 5	23:77	85	119
1 + 5	15:85	83	130
1 + 6	50:50	73	122
1 + 7	50:50	78	106
5 + 6	50:50	126	146
5 + 7	50:50	118	145

Conditions for DSC measurements: First scan from 35 to 220°C at 10°C/min., followed by slow cooling to room temperature (20-30 min.) and a second scan from 35 to 250 °C at 20°C/min. All experiments are done under nitrogen atmosphere.

Table 8. Glass-transition temperatures of blends of poly (4-hydroxystyrene) (PHS) with copoly (4-vinylpyridine-styrene) (50 mol % 4-vinylpyridine).

Wt. % PHS	Tg (°C)
0	118
11	141
17	151
22	159
37	168
46	170
59	169
74	158
86	155
100	138

Conditions for DSC measurements: First scan from 35 to 220°C at 10°C/min. followed by slow cooling to room temperature. Tg were obtained in a second heating scan at 20°C/min. All experiments are done under nitrogen atmosphere.

that blends of PHS with the (VP-S) (20 mol % VP) copolymer were not compatible over the entire range of composition. Figure 18 shows the DSC traces for this system. We see that compatibility is observed only for the blend 69.5:30.5 wt. % PHS/ copoly (VP-S) (20 mol % VP). This indicated that only those mixtures rich in PHS are compatible: a minimum of 70 wt % of PHS being required to achieve compatibility. For blends containing a lower wt % of PHS, incompatibility is indicated by the presence of two glass transition temperatures.

1.2.2.2 Gordon-Taylor, Jenckel-Heusch, Fox, Couchman, and Kwei equations. Their applicability to the system: PHS/copoly (VP-S) (50 mol % VP).

Experimental Tg of PHS/ copoly (VP-S) (50 mol % VP) blends vs. weight % of PHS and the theoretical curves predicted by the Jenckel-Heusch, Fox, Couchman, and Kwei equations are shown in Figure 19. We could not apply the non-linear least square procedures to the Gordon-Taylor equation. This equation could not fit our experimental data at all. It is seen in Figure 19 that the Fox and Couchman equations did not fit our experimental data either. The Couchman equation was plotted by using $\Delta C_{p1} = 0.28 \text{ J/g.}^\circ\text{K}$ and $\Delta C_{p2} = 0.37 \text{ J/g.}^\circ\text{K}$ which are experimental heat capacity changes for copoly (VP-S) (50 mol % VP) and PHS respectively. On the other hand, the Jenckel-Heusch equation with $b = -8.71$ and the Kwei's equation with $k =$

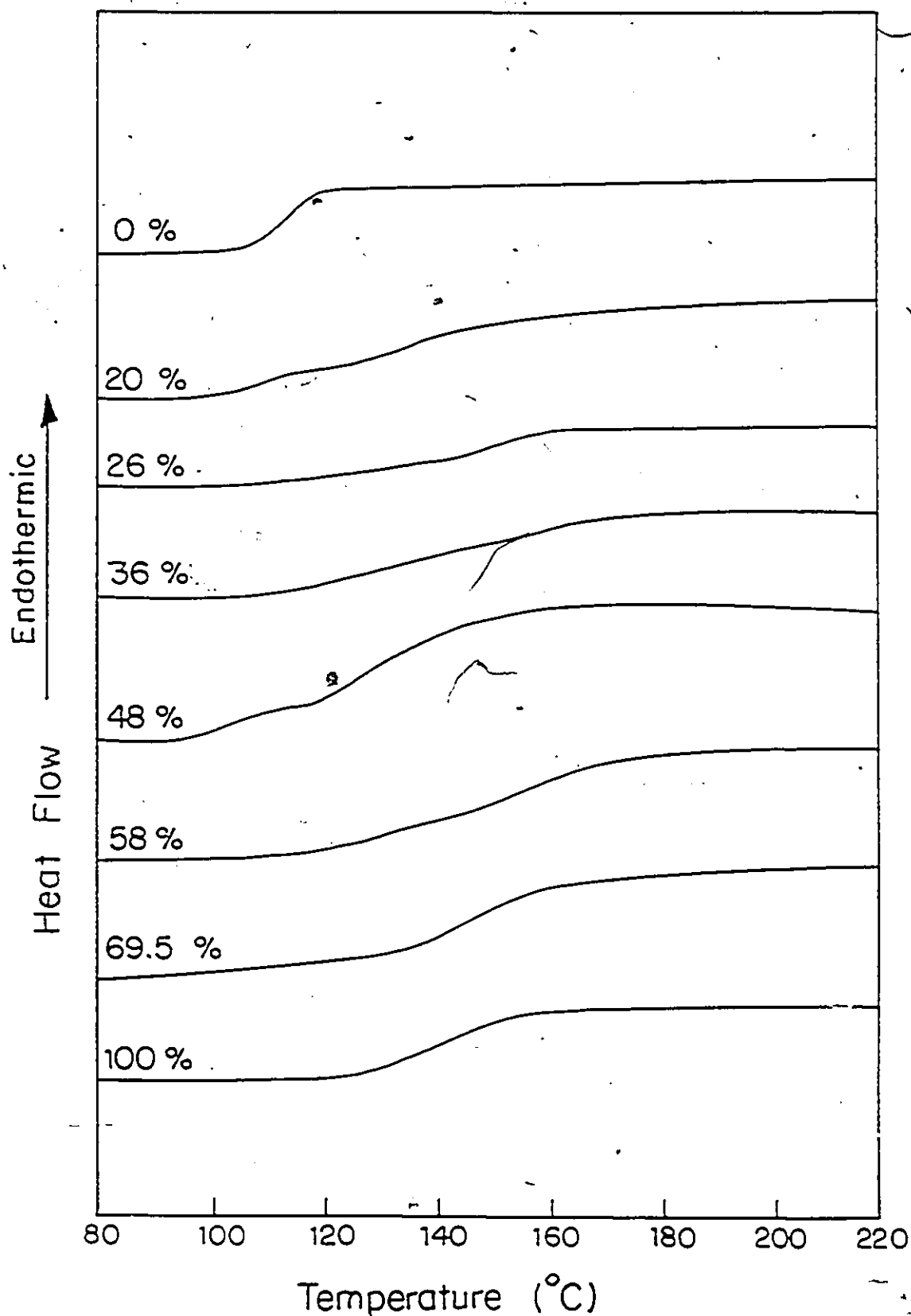


Figure 18. DSC traces of blends of poly (4-hydroxystyrene) and copoly (4-vinylpyridine-styrene) (20 mol % VP) at different compositions. The weight per cent of poly (4-hydroxystyrene) is shown above each DSC trace.

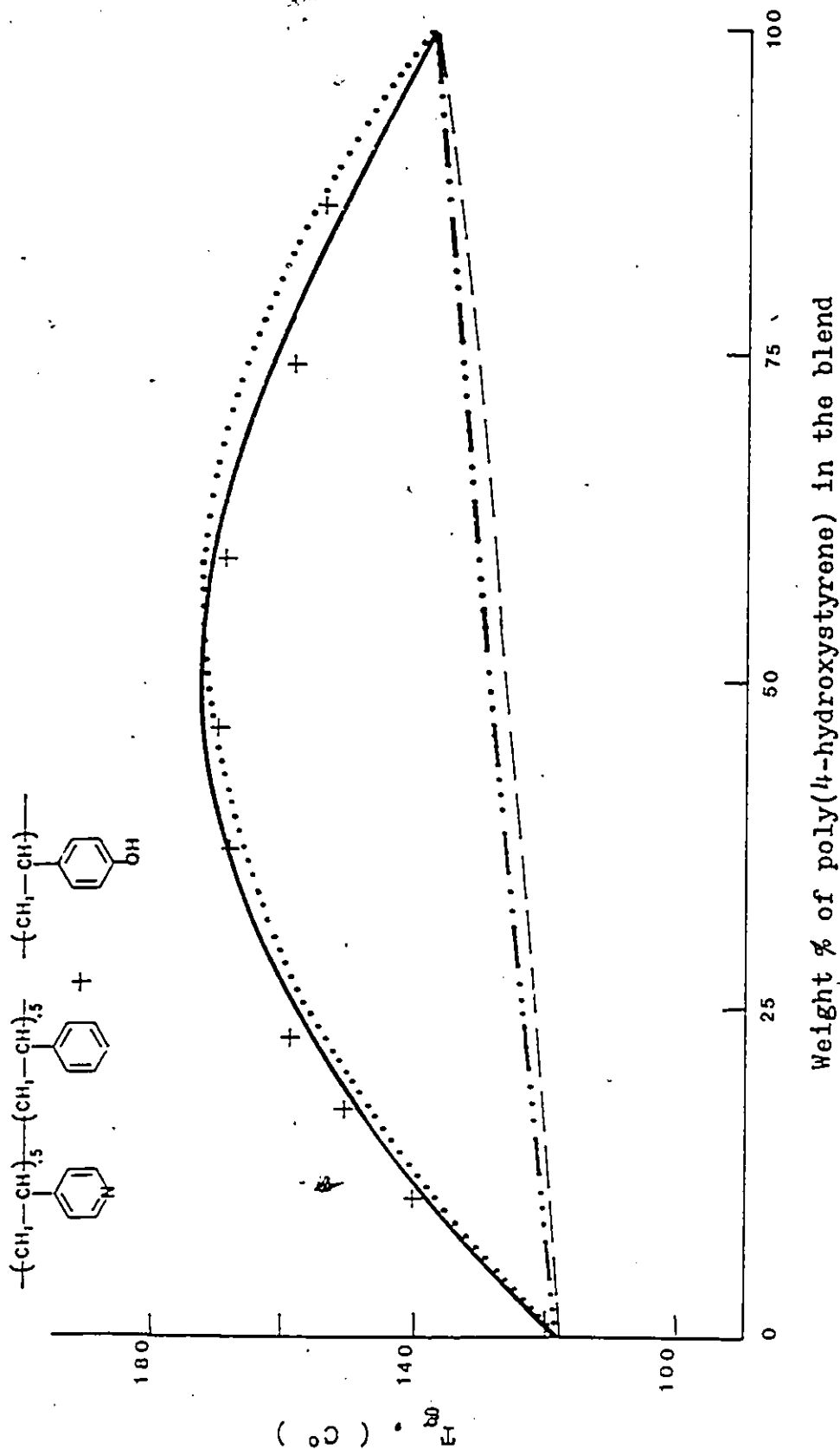


Figure 19. Glass-transition temperatures of blends of PHS and copoly (VP-S) (50 mol % VP) vs. weight % of PHS, and theoretical curves predicted by Kwei (—), Jenckel-Heusch (....), Couchman (— · — · —), and Fox (---) equations.

0.095 and $q = 209.9$ did represent well the experimental data. It is significant to note that the value q for this system is very similar to the value q for the previous miscible systems: PVP/PHS, ($q = 218.9$), and PVP/ copoly (HS-S) (50 mol % HS), ($q = 208.9$). In all our miscible systems the hydrogen-bonding interactions taking place between the components of the blend are the same. As a result, the values q which are proportional to the strength of the interaction, are quite similar. In the Jenckel-Heusch equation, the b values are assumed to be proportional to the interaction strength too, however, we did obtain different b values for our miscible systems. The b values were -12.6, -5.5, -8.7 for the PVP/PHS, PVP/ copoly (HS-S) (50 mol % HS), and PHS/copoly(VP-S) (50 mol % VP) systems respectively. The Jenckel-Heusch equation always gave fits less perfect than those obtained using the Kwei equation. Probably, this fact was reflected in the b values, to the point that comparison between them is not possible.

1.2.2.3 Thermogravimetric analyses

Thermogravimetric analyses of the various (4-vinylpyridine-styrene) (VP-S) copolymers, and of some representative blends used in this study.

Thermogravimetric analyses for PS, PHS, and (HS-S) copolymers were already given in section 1.2.1.3. It is seen in Table 9 that the (VP-S) copolymers 3, 4 start to decompose

Table 9. Thermogravimetric analyses of the various (1-vinylpyridine-styrene) (VP-S) copolymers, and some representative blends used in this study. (See Figure 4).

Polymer #	% Weight ratio	Step decomposition temperatures, °C.			
		Start	Peak	End	loss wt. %
3	--	280	362	400	98
4	--	279	358	400	99
1+5	50:50	300	389	441	91
5+3	46:54	300	367	443	90
5+4	48:52	300	379	441	90

All samples underwent a first heating scan to 220 °C prior to decomposition temperature measurements. All experiments are done under nitrogen atmosphere.

by 280°C and are half decomposed by 362°C (peak step decomposition). Blends of PHS 5 and (VP-S) 3, 4 copolymers show similar patterns of decomposition with decomposition starting at 300°C. All samples underwent a first heating scan to 220°C prior to decomposition temperature measurements. In almost all cases a weight loss from 3 to 6% is observed during the first heating scan. This weight loss corresponds to the evaporation of residual pyridine in the samples. In the second heating scan a straight baseline is observed until the decomposition temperatures. For example, the TGA curves of copoly (VP-S) (50 mol % VP) 3 and the PHS/ copoly (VP-S) (50 mol % VP), 5 + 3, blend containing 46 wt % of PHS are shown in Figure 20.

1.2.3 Compatibilization of polystyrene (PS) with poly (4-vinylpyridine) (PVP) by introducing into PS the 4-vinylbenzoic acid units.

In our previous work, we studied the compatibilization of PS with PVP by introducing acidic 4-hydroxystyrene units into PS. Our results showed that a modified PS containing 50 mol % of 4-hydroxystyrene units is compatible with PVP over the entire range of composition. However, the modified PS containing 30 mol % of 4-hydroxystyrene units is only compatible with PVP over a narrow range of composition, that is, compatibility is observed only for those mixtures containing a minimum of 60 wt. % of PVP. In view of these results, we decided to introduce into PS 4-vinylbenzoic acid

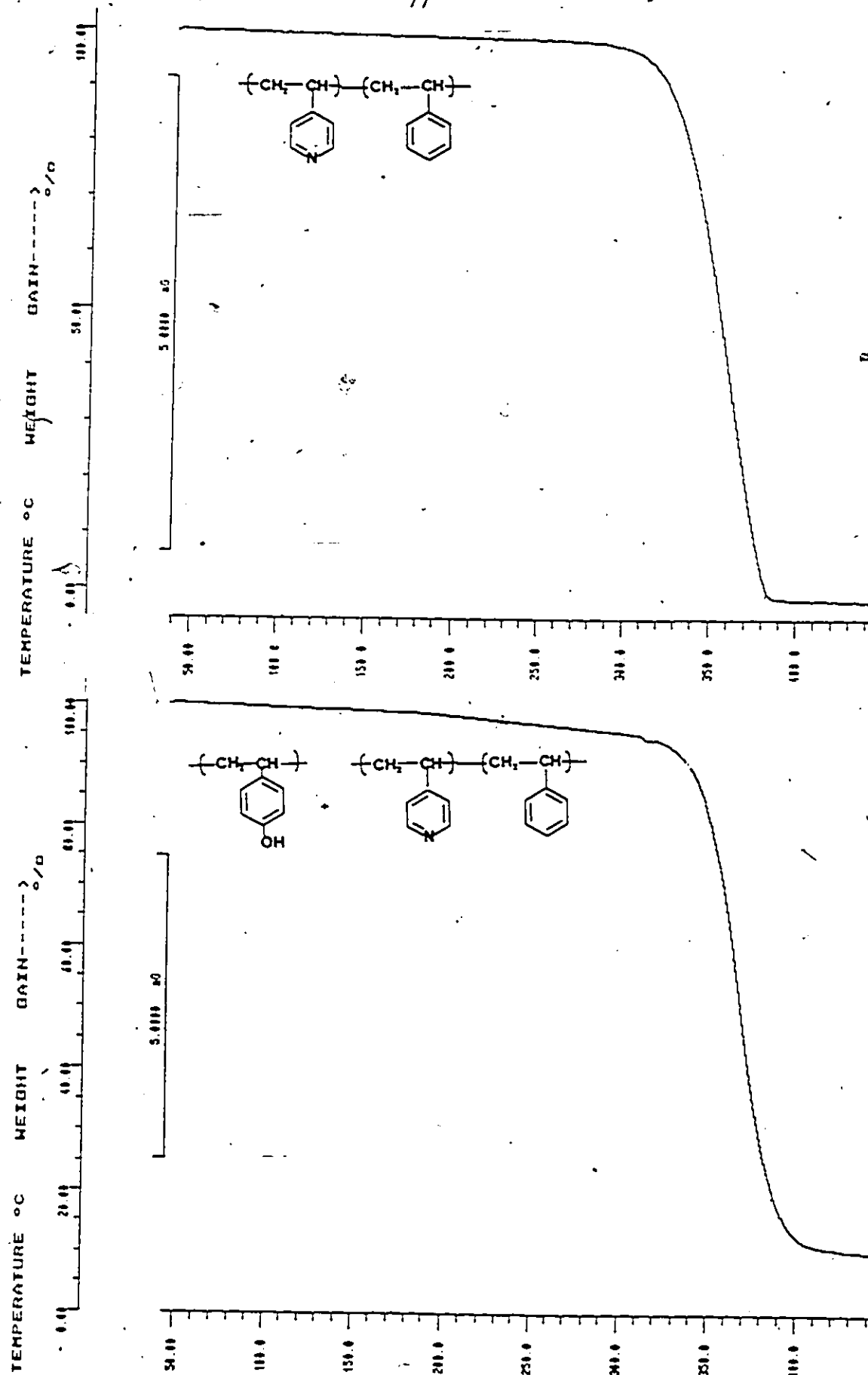


Figure 20. TGA curves of copoly (VP-S) (50 mol % VP) and the 46:54 wt.% blend of PHS and copoly (VP-S) (50 mol % VP).

units, which are much more acidic than the 4-hydroxystyrene units. We expected in this way to obtain compatible systems using lower degrees of modification of PS since the hydrogen-bonding between the 4-vinylbenzoic acid units and the pyridine units of PVP was expected to be stronger.

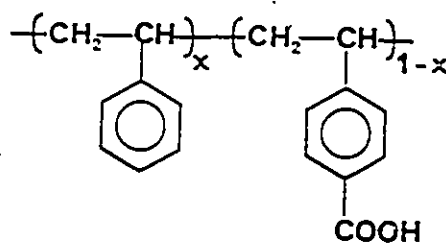
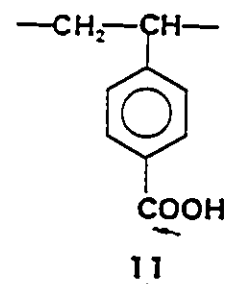
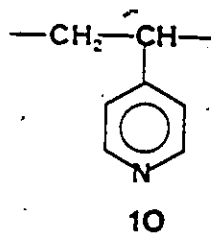
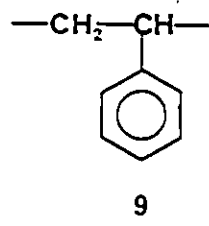
Figure 21 shows the structure of the various polymers and copolymers used in this study and Table 10 gives their molecular weights and glass-transition temperatures.

All blends were prepared using pyridine as solvent and following the same procedure that has been described previously.

1.2.3.1 Differential scanning calorimetry studies.

DSC compatibility studies of polystyrene (PS) with poly (4-vinylbenzoic acid) (PVBA) and the various (4-vinylbenzoic acid-styrene) (VBA-S) copolymers.

DSC studies of PS/PVBA blends show clearly that PS is incompatible over the entire range of composition with PVBA. Table 11 shows the glass transition temperatures which were obtained for blends of different compositions. Two T_g were observed for all blends. The T_g of PVBA, 260°C, was decreased upon blending with PS, for instance, a T_g of 222°C was observed for PVBA in the blend containing 75 wt % of PS. Most probably the presence of PS in the blends interfered



	1-x
<u>12</u>	0.56
<u>13</u>	0.40
<u>14</u>	0.26
<u>15</u>	0.15
<u>16</u>	0.11

Figure 21. Structure of the various polymers and copolymers used, in the study of the compatibilization of PVP with PS by introducing 4-VBA units into PS.

Table 10. Composition and characteristics of the various polymers and copolymers used in the study of the compatibilization of PS with PVP by introducing 4-VBA units into PS. (See Figure 21).

Polymer #	Composition (mol %)			GPC molecular weights (10^{-3})			
	Styrene	4-vinyl pyridine	4-vinyl benzoic acid	Mn	Mw	Mw/Mn	Tg (°C)
9	100	--	--	32.9	17.7	1.86	101
10	--	100	--	--	35.7*	--	149
11	--	--	100	98.9	98.5	1.00	260
12	44	--	56	77.6	39.5	1.96	221
13	60	--	40	69.7	31.3	2.23	195
14	74	--	26	52.5	25.9	2.03	170
15	85	--	15	44.2	23.3	1.90	140
16	89	--	11	35.0	19.6	1.80	--

* Polymer 10 was insoluble in THF. The Mw was obtained by viscosity measurement using parameters giving in ref. 47.

Table 11. Glass-transition temperatures of blends of PS and PVBA.

Wt. % PVBA in blend	Tg1 (°C)	Tg2 (°C)
0	101	
25	102	222
50	104	224
75	108	228
100		260

Conditions for DSC measurements: First heating scan from 35 to 220°C at 10°C/min., after annealing at 220°C for 5 min., and then quenching with liquid nitrogen. The reported Tg were obtained in a second heating scan at 20°C/min. All measurements were done under nitrogen atmosphere.

Table 12. Glass-transition temperatures of blends of PS and (VBA-S) (40 mol % VBA) copolymer.

Wt. % copoly (VBA-S) (40 mol % VBA)	Tg1 (°C)	Tg2 (°C)
0	101	
25	101	---
50	104	180
75	104	180
100		195

Conditions for DSC measurements: First heating scan from 35 to 220°C at 10°C/min., then annealing at 220°C for 8 min. Finally, the samples were allowed to cool slowly to room temperature and the reported Tg were obtained in a second heating scan at 20°C/min. All measurements were done under nitrogen atmosphere.

with the self-hydrogen bonding complexation of PVBA, therefore, it exhibited a lower Tg.

Polystyrene is also incompatible with modified polystyrenes containing 40, 26, and 15 mol % of 4-vinylbenzoic units. Tables 12, 13, and 14 show these results. DSC measurements indicated that two Tg were obtained in all cases. Again the Tg values of the (4-vinylbenzoic acid-styrene) copolymers were decreased upon blending with polystyrene, for instance, the Tg of the (VBA-S) (40 mol % VBA) copolymer, 195°C, was decreased to 180°C upon blending with PS, similarly the Tg of the (VBA-S) (26 mol % VBA) and (VBA-S) (15 mol % VBA) copolymers, 167 and 140°C, were decreased to 157, and 131°C respectively upon blending with PS. While the Tg of PS (101°C) upon blending with the copolymers remained almost invariable. It is observed that the modified polystyrenes are incompatible with polystyrene, even in the case of the lowest modification: 15 mol % of 4-vinylbenzoic acid.

DSC compatibility studies of poly (4-vinylbenzoic acid) (PVBA) with the various (4-vinylbenzoic acid-styrene) (VBA-S) copolymers.

Poly(4-vinylbenzoic acid) (PVBA) is incompatible with all the (4-vinylbenzoic acid-styrene) copolymers which can be considered as "modified poly (4-vinylbenzoic acid)s". Table

Table 13. Glass-transition temperatures blends of PS and (VBA-S) (26 mol % VBA) copolymer.

Wt. % copoly (VBA-S) (26 mol % VBA)	Tg1 (°C)	Tg2 (°C)
0	101	
25	100	167
50	98	158
75	102	157
100		168

Conditions for DSC measurements: First heating scan from 35 to 220°C at 10°C/min., and after annealing the samples at 220°C for 8 min. and allowing them to cool slowly to room temperature, the Tg were obtained in a second heating scan at 20°C/min. All measurements were done under nitrogen atmosphere.

Table 14. Glass-transition temperatures of blends of PS and (VBA-S) (15 mol % VBA) copolymer.

Wt. % copoly (VBA-S) (15 mol % VBA)	Tg1 (°C)	Tg2 (°C)
0	101	
25	102	133
50	101	131
75	104	138
100		140

Conditions for DSC measurements: First heating scan from 35 to 220°C at 10°C/min., and after annealing the samples at 220°C for 8 min. and allowing them to cool slowly to room temperature, the Tg were obtained in a second heating scan at 20°C/min. All measurements were done under nitrogen atmosphere.

15 shows the T_g values that were obtained for blends of PVBA with copoly (VBA-S) (40 mol % VBA), we observed two T_g transitions for all blends, these two T_g did not change significantly as function of concentration. Likewise, Tables 16 and 17 show the glass transition temperatures for blends of PVBA and the copolymers containing 26 and 15 mol % of VBA with styrene. It was interesting to see that poly (4-vinylbenzoic acid) became incompatible with the "modified poly (4-vinylbenzoic acid)s" and, similarly, that polystyrene became incompatible with the "modified polystyrenes", and that this incompatibility could be seen even in the cases of low degrees of modification. Comparable results have been obtained in the case of other systems. For example, Fujioka et al. [50] reported that polystyrene becomes incompatible with a modified polystyrene containing 11.4 mol % of n-butyl methacrylate, and poly (n-butyl methacrylate) becomes incompatible with a modified poly (n-butyl methacrylate) containing a mol % of styrene units higher than 25.

DSC compatibility studies of blends of poly (4-vinylbenzoic acid) (PVBA) and poly (4-vinylpyridine) (PVP).

Blends of PVBA with PVP exhibited a single sharp glass-transition temperature over the entire range of composition. The T_g values showed large positive deviation with respect to calculated weight-average glass transition temperatures (max, deviation: 30°C), which indicated that strong interactions result from significant hydrogen bonding between the two

Table 15. Glass-transition temperatures of blends of PVBA and copoly (VBA-S) (40 mol % VBA)^a.

Wt. % PVBA	Tg ₁ (°C)	Tg ₂ (°C)
0	195	--
25	199	255
50	200	255
75	198	262
100	--	260

Table 16. Glass-transition temperatures of blends of PVBA and copoly (VBA-S) (26 mol % VBA)^a.

Wt. % PVBA	Tg ₁ (°C)	Tg ₂ (°C)
0	170	--
25	174	260
50	173	254
75	180	260
100	--	260

- a. Conditions for DSC measurements: First heating scan from 35 to 265 °C at 10 °C/min., after annealing samples at 265 °C for 5 min., and allowing them to cool slowly to room temperature, the Tg were obtained in a second heating scan at 20°C/min. All heating scans were done under nitrogen atmosphere.

Table 17. Glass-transition temperatures of blends of PVBA and copoly (VBA-S) (15 mol % VBA).

Wt. % PVBA	Tg ₁ (°C)	Tg ₂ (°C)
0	141	--
25	144	253
50	143	257
75	144	258
100	--	260

Conditions for DSC measurements were the same as for previous system.

Table 18. Glass-transition temperatures of blends of PVBA and PVP.

Wt. % PVBA	Tg (°C)
0	149
25	205
37.5	223
50	233
62.5	244
75	250
100	260

Conditions for DSC measurements: First heating scan from 35 to 260°C at 10 °C/min, after annealing samples at 260 °C for 2 min. and quenching them with liquid nitrogen, the Tg were obtained in a second heating scan at 20 °C/min.

polymers. Such hydrogen-bonding interactions amount to thermally reversible crosslinking that reduce significantly the mobilities of individual chains in the compatible polymer blend. Figure 22 shows the DSC traces of blends of PVBA and PVP at different compositions. Table 18 shows the glass transition temperatures obtained.

DSC compatibility studies of poly (4-vinylpyridine) (PVP) and the various (4-vinylbenzoic acid-styrene) (VBA-S) copolymers.

We showed that PVP was incompatible with PS but compatible with PVBA over the entire range of composition due to hydrogen-bonding interactions between the basic units of PVP and the acidic units of PVBA. Then we have modified PS by introducing 4-vinylbenzoic acid units, to induce its compatibility with poly (4-vinylpyridine). Figure 23 shows the DSC traces of blends of PVP and (VBA-S) copolymer containing 40 mol % of 4-vinylbenzoic acid units. The system was compatible over the entire range of composition, a sharp single glass transition temperature was observed in all cases, and Tg's showed positive deviation with respect to calculated weight-average glass transition temperatures.

When the degree of polystyrene modification was decreased, that is, only 26 mol % of 4-vinyl-benzoic acid units were introduced, it was observed that blends of PVP and the modified polystyrene were incompatible. Figure 24 shows

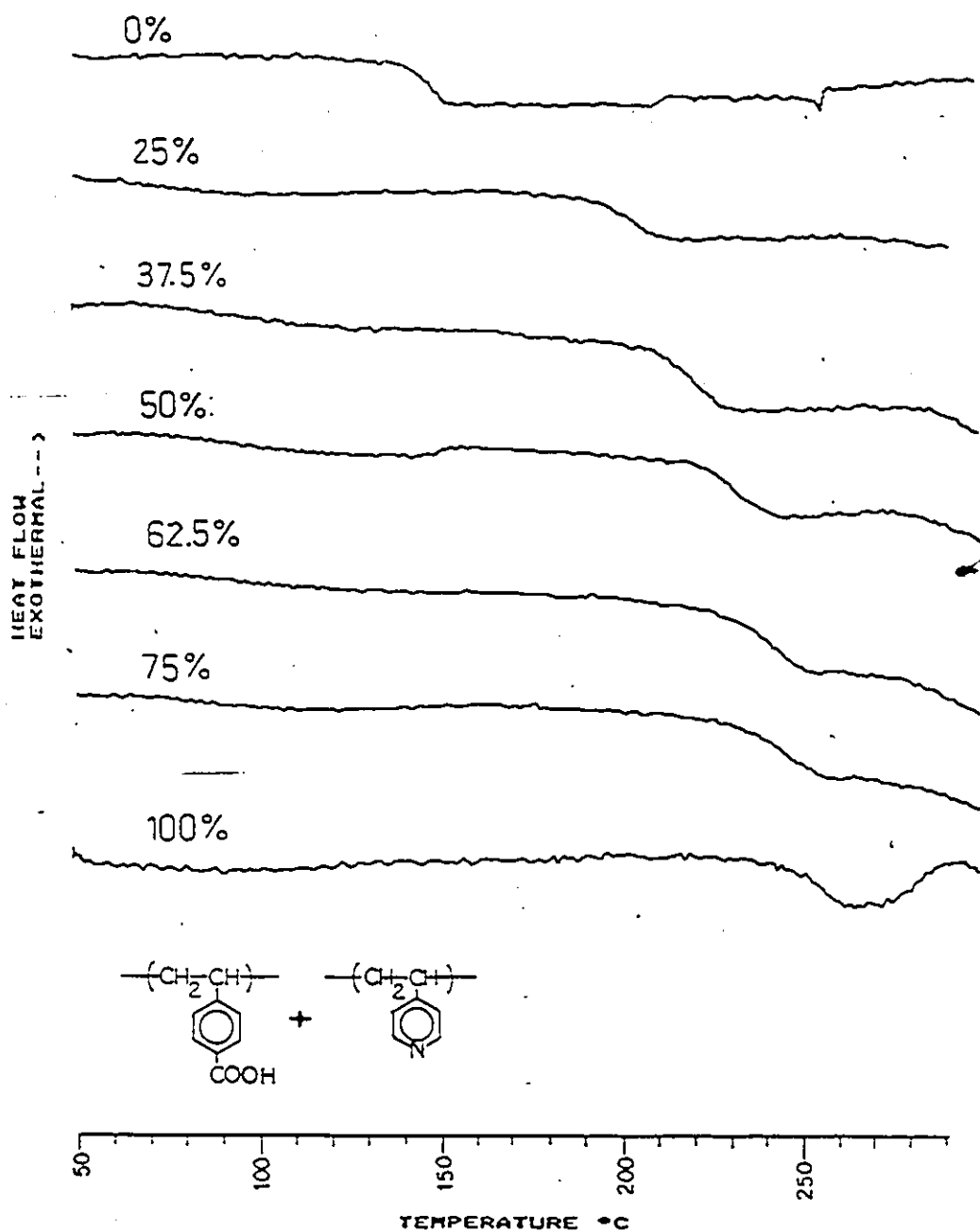


Figure 22. DSC traces of blends of poly (4-vinylbenzoic acid) and poly (4-vinylpyridine) at different compositions. The weight per cent of PVBA is shown above each DSC trace.

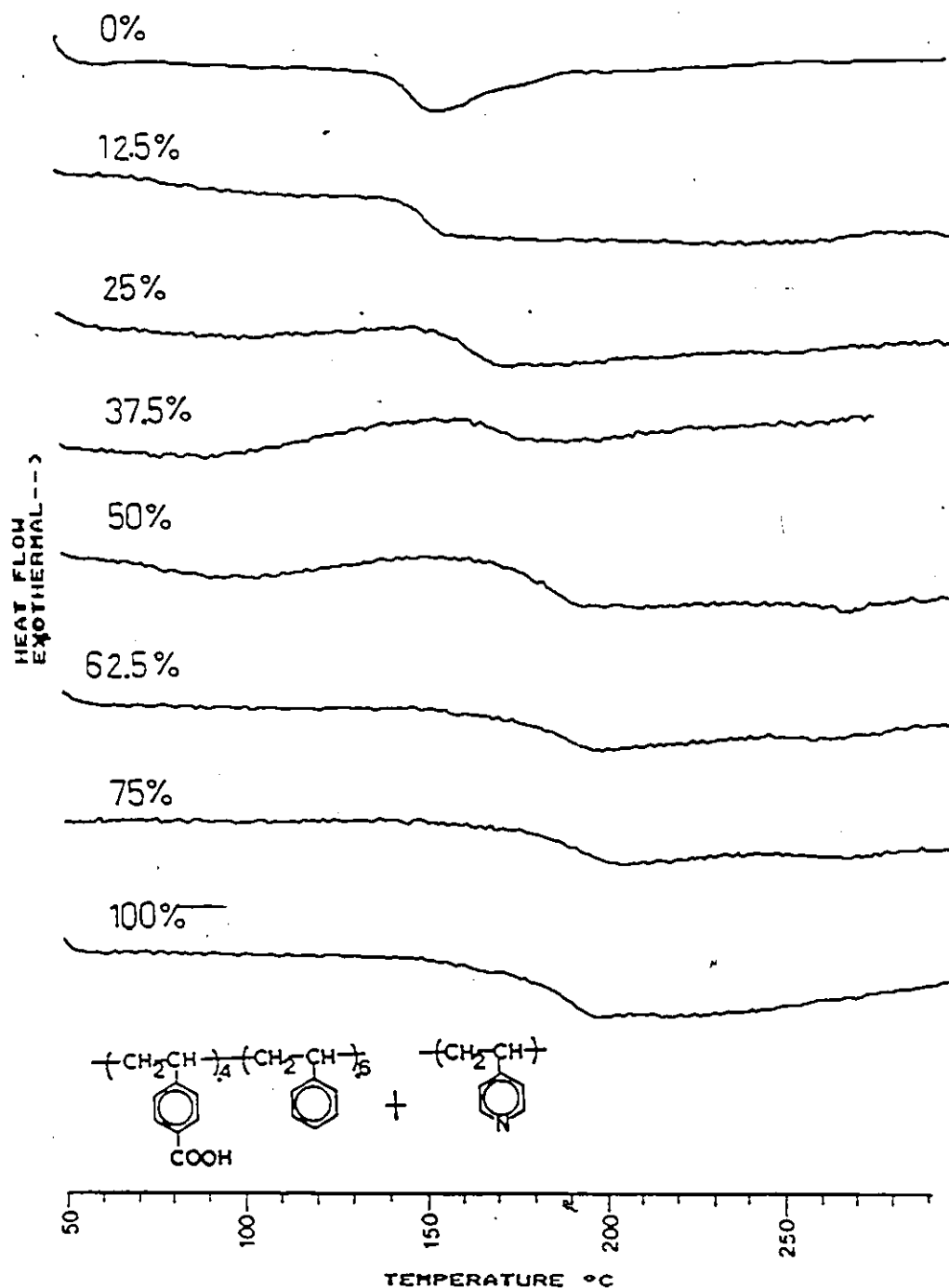


Figure 23. DSC traces of blends of poly (4-vinylpyridine) and copoly (4-vinylbenzoic acid-styrene) (40 mol % VBA) at different compositions. The weight per cent of copoly (VBA-S) (40 mol % VBA) is shown above each DSC trace.

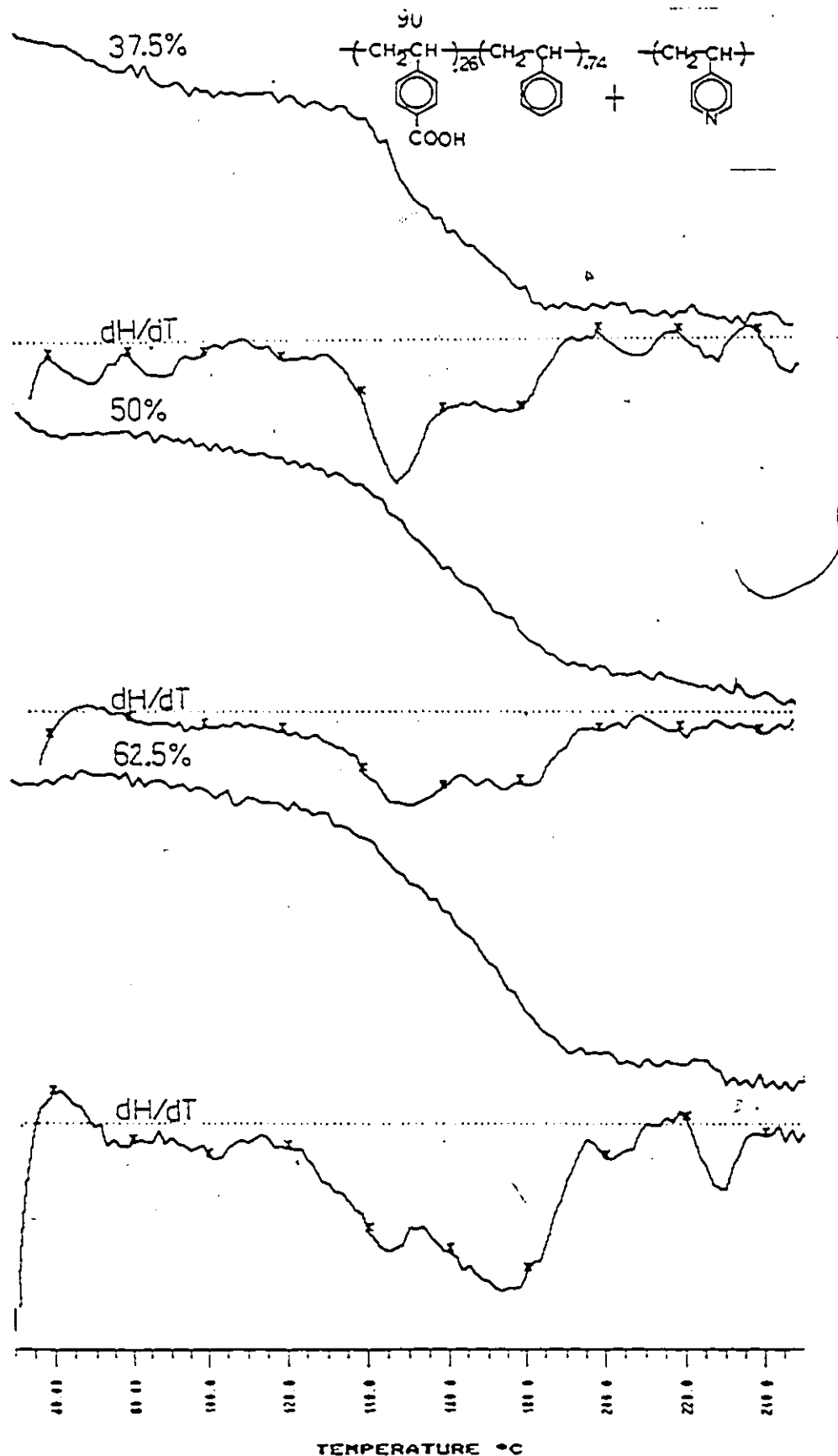


Figure 24. DSC traces of blends of PVP and copoly (VBA-S) (26 mol % VBA) at different compositions. DSC traces (Heat flow vs. Temperature) are given with their respective derivatives. The weight per cent of the copolymer in the blend is shown above each DSC trace.

the DSC thermograms for blends of PVP with (VBA-S) (26 mol % VBA) copolymer. Due to the fact that the T_g values of PVP (149°C) and of the copolymer (168°C) were only 20°C apart, analysis of the thermograms giving the heat flow in the sample vs. temperature gave what appeared to be a single broad glass transition temperature. However, analysis of the thermograms giving the derivative of heat flow vs. temperature, showed the presence of two maxima which corresponded to the glass transition temperature of each of the two polymers in the blend. Therefore, it can be concluded that the system formed incompatible blends.

In the case of blends of PVP and copoly (VBA-S) (15 mol % VBA), the T_g difference between both polymers is too small (10°C), therefore the blends exhibited what it appeared to be single glass transition temperatures (Figure 25). For this system the derivative of heat flow vs. temperature also showed a broad single maximum. While, the results of the DSC experiments were inconclusive due to the closeness of the T_g values of the individual components the FTIR studies of this system showed clearly its incompatibility.

Therefore this study shows that in order to compatibilize polystyrene with poly (4-vinylpyridine) by introducing 4-vinylbenzoic units into polystyrene, it is necessary to introduce at least 40 mol % of VBA units into

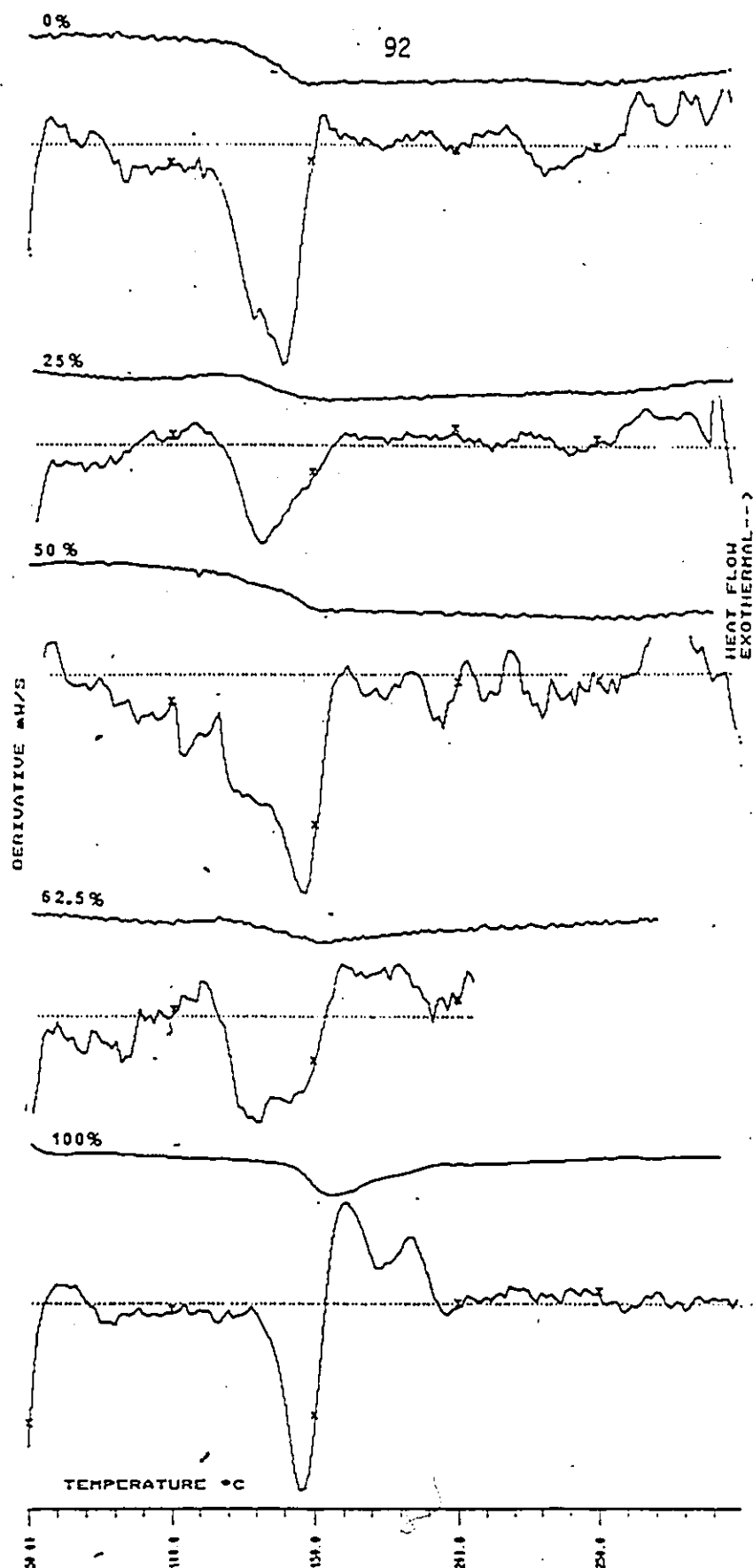


Figure 25. DSC traces of blends of PVP and copoly (VBA-S) (15 mol % VBA) at different compositions. DSC traces (Heat flow vs. Temperature) are given with their respective derivatives. The weight per cent of PVP is shown above each DSC trace.

the polystyrene. Incompatibility is always observed if lower amounts are used.

1.2.3.2 Gordon-Taylor, Jenckel-Heusch, Fox, Couchman, and Kwei equations. Their applicability to the systems: PVP/PVBA and PVP/copoly (VBA-S) (40 mol % VBA).

Experimental glass-transition temperatures, obtained for the PVP/PVBA and PVP/ copoly (VBA-S) (40 mol % VBA) miscible systems, were analyzed by standard non-linear least-square procedures to know which of the above equations represented the best the experimental data.

PVP-PVBA system

Figure 26 shows the experimental glass-transition temperatures of this system vs. weight fraction of PVBA (w_2), and the theoretical curves predicted by the Gordon-Taylor and Jenckel-Heusch equations. We obtained $k = 3.208$ (Gordon-Taylor eq.) and $b = -7.09$ (Jenckel-Heusch eq.) as the values giving the best fit of the experimental data. As we can see in Figure 26, the Gordon-Taylor equation fits the experimental data within ca. $\pm 1.5^\circ\text{C}$, while the Jenckel-Heusch equation fit the experimental data within ca. $\pm 5^\circ\text{C}$. However, the fact that the Gordon-Taylor equation fits the experimental glass-transition temperatures of this miscible

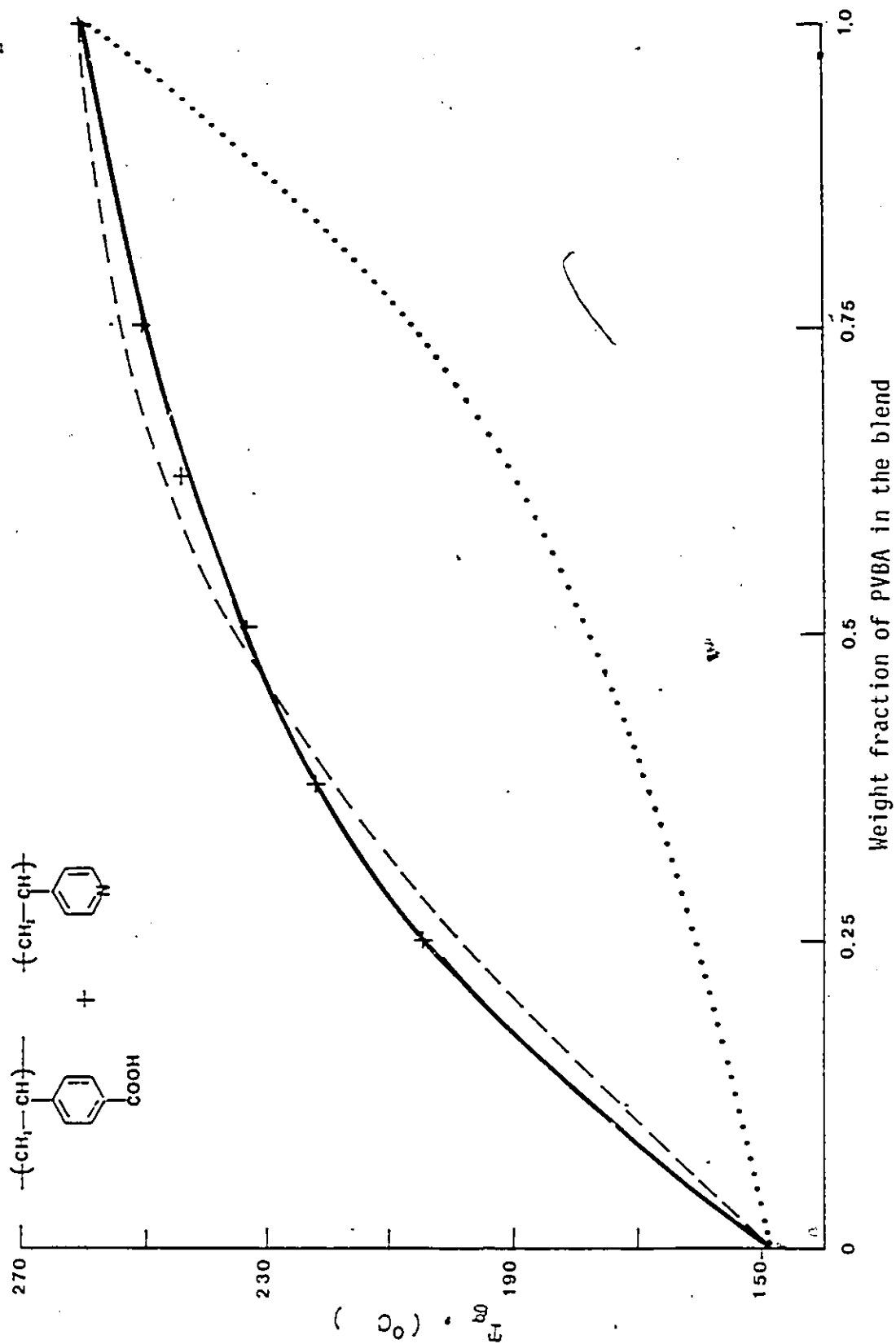


Figure 26. Glass-transition temperatures of blends of PVP and PVBA vs. weight fraction of PVBA, and theoretical curves predicted by Gordon-Taylor (—) ($k = 3.208$), (...) ($k = 0.353$), and Jenckel-Heusch (---) equations.

system so well was surprising. This is in view of the previous failure of the Gordon-Taylor equation to fit experimental T_g values for miscible systems where strong interactions between the components of the blend exist. Indeed, the Gordon-Taylor equation could not fit the experimental data for all other miscible systems. Percec et al. [21] have studied miscible systems based on electron donor-acceptor interpolymeric interactions, and the Gordon-Taylor equation could not fit their data. Kwei [31] also studied systems containing novolac resins and isotactic or syndiotactic poly (methylmethacrylate) and the experimental T_g values of these systems did not follow the Gordon-Taylor equation.

Theoretical curves predicted by the Fox, Couchman, and Kwei equations are shown in Figure 27. The Couchman equation was plotted by using the following heat capacity changes: ΔC_{p1} (PVP) = 0.30 J/g. $^{\circ}$ K, ΔC_{p2} (PVBA) = 0.51 J/g. $^{\circ}$ K which were experimental values. The Fox and Couchman equations could not fit the experimental data, while the Kwei equation with $k = 0.353$ and $q = 229.6$ gave a very good fit. The Kwei equation takes into account the existence of specific interactions between two polymers by means of the quadratic term qw_1w_2 . The value q is assumed to be proportional to the strength of the interchain interaction and w_1w_2 is proportional to the number of bonds. Hence, the Kwei equation has been shown appropriate for fitting experimental

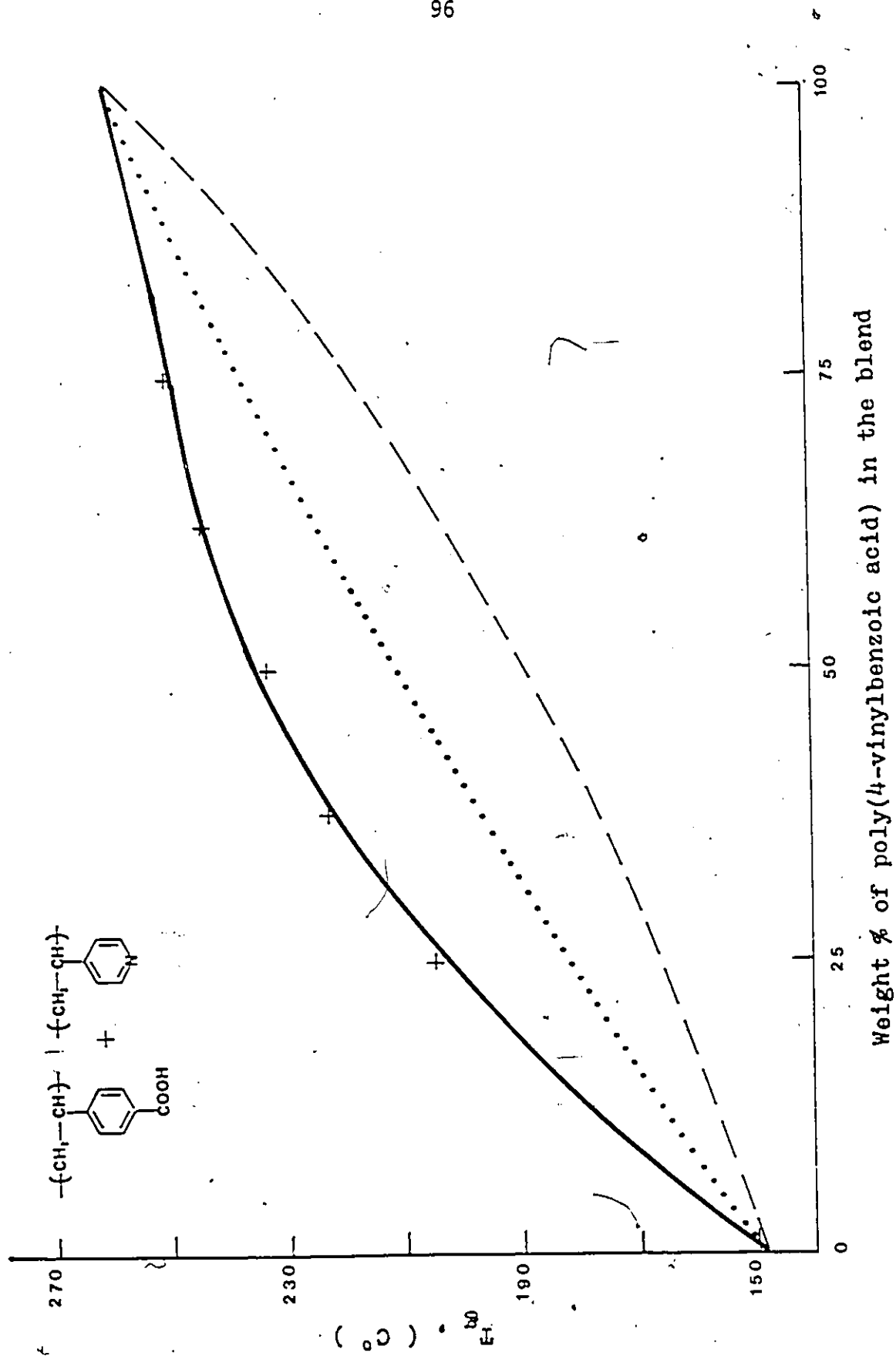


Figure 27. Glass-transition temperatures of blends of PVP and PVBA vs. weight % of PVBA, and theoretical curves predicted by Kwei (—), Couchman (...), and Fox (---) equations.

data for systems where strong interchain interactions were present in the system. For instance, the systems studied by Percec [21] and Kwei [31] that have been already mentioned.

PVP/copoly (VBA-S) (40 mol % VBA) system

Figure 28 shows the experimental T_g values for this system vs. the weight fraction of (VBA-S) (40 mol % VBA) copolymer (w_2), and the theoretical curves predicted by the Gordon-Taylor and the Jenckel-Heusch equations. Standard non-linear least-square procedures gave $k = 3.193$ for the Gordon-Taylor equation, and $b = -1.373$ for the Jenckel-Heusch equation. When comparing the experimental data to the theoretical curves obtained, we saw that the Jenckel-Heusch equation was able to fit the data better than the Gordon-Taylor equation, this is probably due to the constant parameter b which incorporates the strength of the interchain interactions as is done by parameter q in the Kwei equation. The Kwei equation:

$$T_g = (w_1 T_{g1} + k w_2 T_{g2} / w_1 + k w_2) + q w_1 w_2$$

for $k = 1$ becomes:

$$T_g = w_1 T_{g1} + w_1 T_{g2} + q w_1 w_2.$$

We see the above equation is equivalent to the Jenckel-Heusch equation:

$$T_g = w_1 T_{g1} + w_1 T_{g2} + b (T_{g1} - T_{g2}) w_1 w_2$$

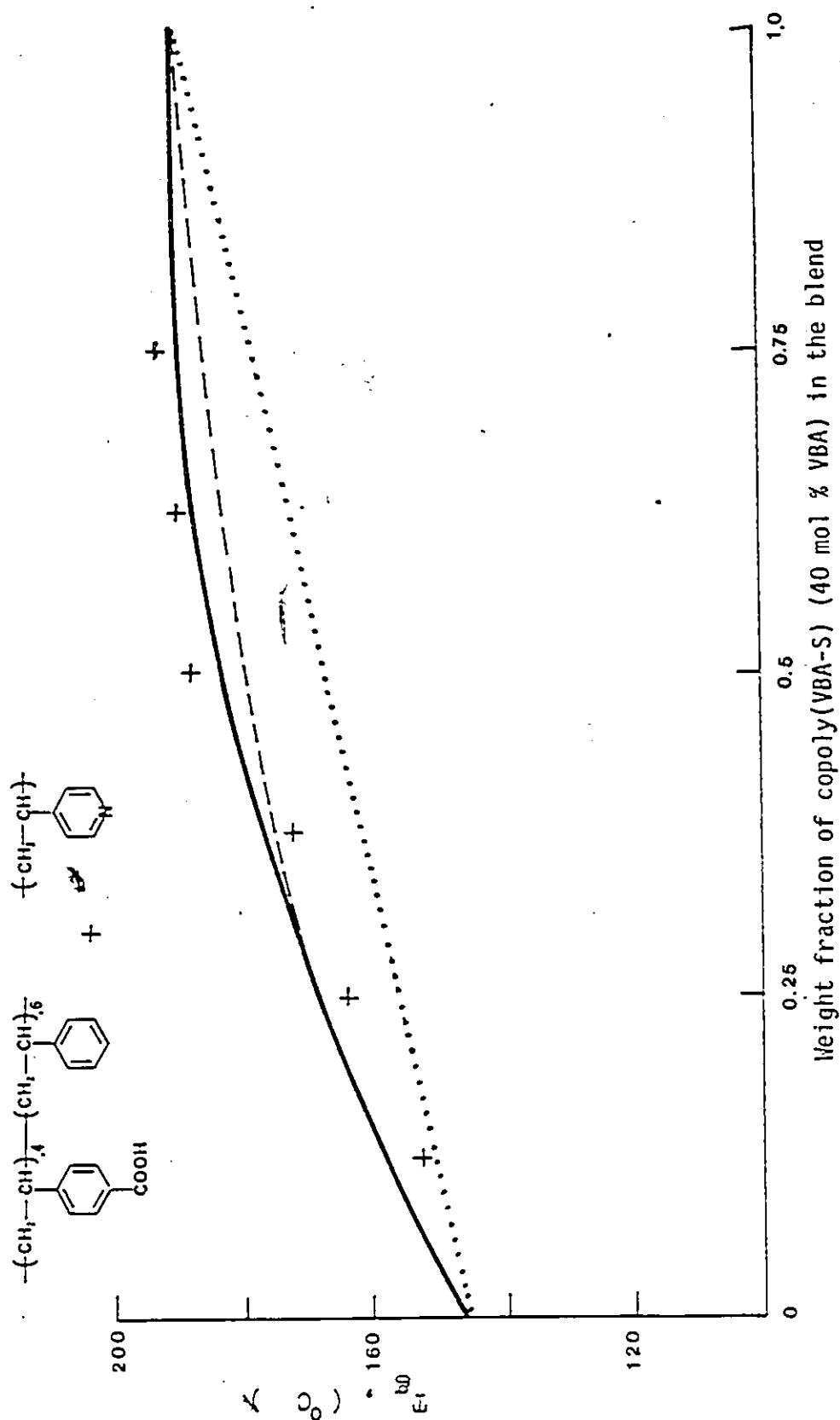


Figure 28. Glass-transition temperatures of blends of PVP and copoly (VBA-S) (40 mol % VBA) vs. weight fraction of the copolymer, and theoretical curves predicted by Gordon-Taylor (---) ($k = 3.193$), (....) ($k = 0.47$), and Jenckel-Heusch (—) equations.

with $q = b (Tg_1 - Tg_2)$ therefore, b is also proportional to the strength of the interchain interaction.

Theoretical curves predicted by the Fox, Couchman, and Kwei equations are shown in Figure 29. The Couchman equation was plotted by using $\Delta C_{p1}(\text{PVP}) = 0.30 \text{ J/g.}^\circ\text{K}$, $\Delta C_{p2} = \text{copoly (VBA-S) (40 mol \% VBA)} = 0.46 \text{ J/g.}^\circ\text{K}$ which are experimental values obtained from evaluation of the heat capacity change at glass-transition temperature. The Couchman, and Fox equations failed to fit the experimental data. The Kwei equation gave a relatively modest fit with $k = 0.47$ and $q = 111.35$. It should be noted however that the experimental data for this system was rather peculiar. It can be seen clearly that glass-transition temperatures for blends with a concentration lower than 50 weight % of PVP follow a different trend from glass-transition temperatures for blends with a concentration higher than 50 weight % of PVP. Such a phenomenon has been observed before; for instance, Fahrenholtz and Kwei [30] studied the systems containing a novolac resin and poly (vinyl methyl ether) or poly (ethyl acrylate) and for both systems, those blends containing less than 50 weight % of the novolac resin did not show a significant deviation from calculated average glass-transition temperatures (Figure 30). Prud'homme et al. [51] also obtained experimental T_g values that followed different trends depending on the composition of the blends for the

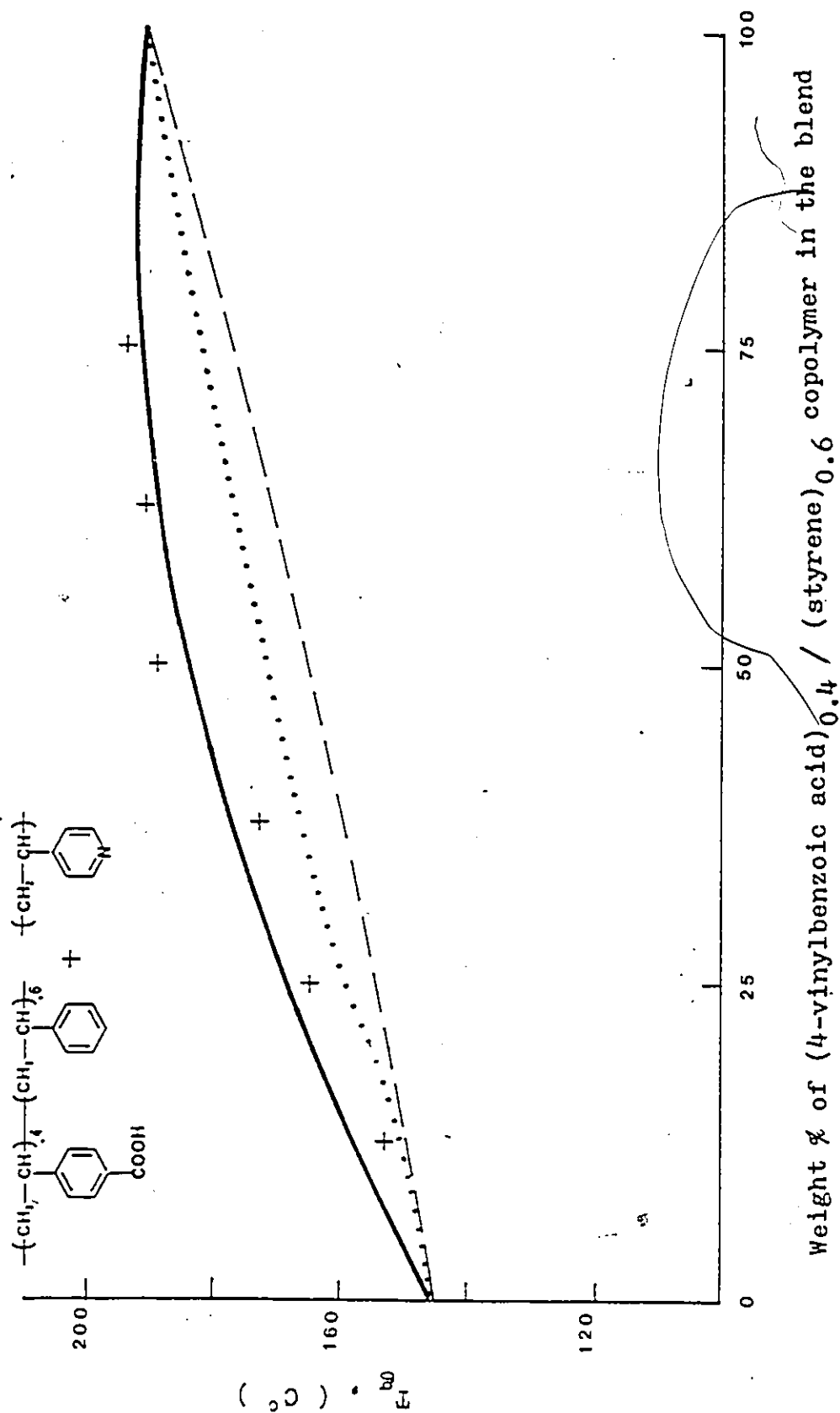


Figure 29. Glass-transition temperatures of blends of PVP and copoly (VBA-S) (40 mol % VBA) vs. weight % of the copolymer, and theoretical curves predicted by Kwei (---), Couchman (...), and Fox (—) equations.

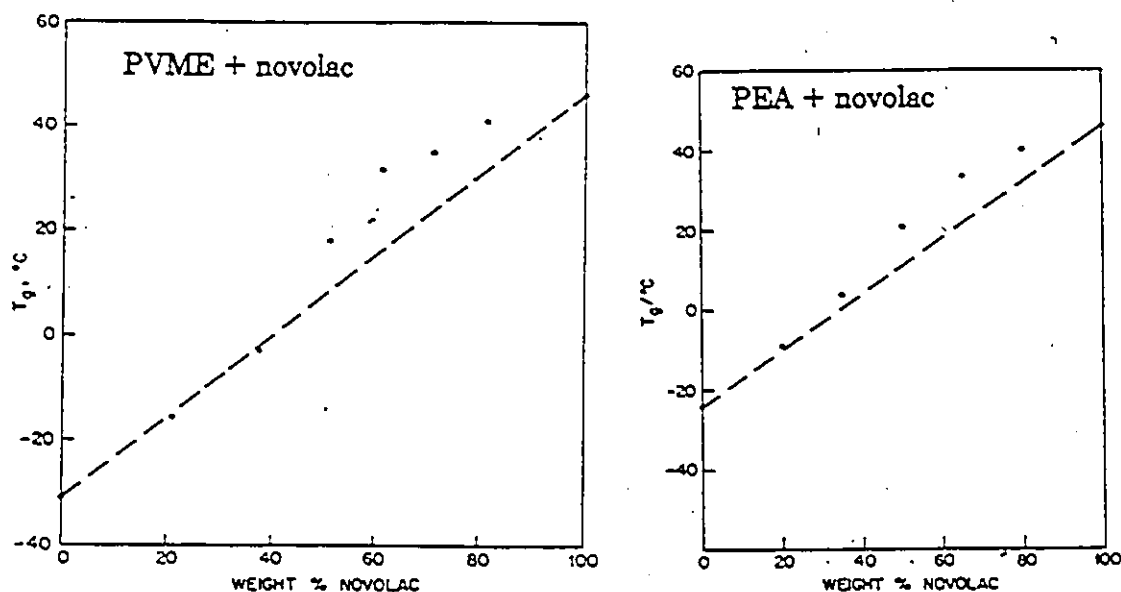


Figure 30. Glass-transition temperatures vs. wt % of novolac for blends of poly (vinylmethyl ether)/novolac and poly (ethyl acrylate)/novolac. (Ref. 30)

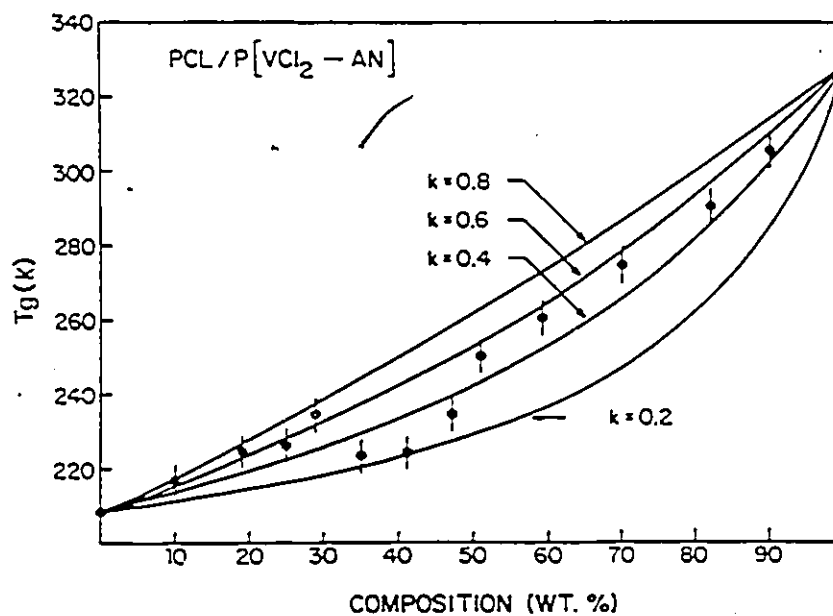


Figure 31. Glass-transition temperatures vs. wt % of polycaprolactone for blends of polycaprolactone a copoly (vinylidene chloride-acrylonitrile) (20 mol % acrylonitrile). (Ref. 51)

system containing polycaprolactone and poly (vinylidene chloride-acrylonitrile) (Figure 31).

1.2.3.3 Thermogravimetric Analyses.

Thermogravimetric analyses of poly (4-vinylbenzoic acid) (PVBA), various (4-vinylbenzoic acid-styrene) (VBA-S) copolymers, and various representative blends used in this study.

Table 19 shows the TGA results for polymers, copolymers and some blends used in this study. Their structures are shown in Figure 21. The results were obtained in a second heating scan from 35 to 550°C at a rate of 10°C/min. All samples underwent a first heating scan from 35 to 220°C and annealing periods of 2 or 5 min at 220°C. These were the same thermal treatments as were used when measuring glass-transition temperatures. In the first heating scan, it was usually observed that a loss of weight (3-6%) corresponding to the evaporation of residual solvent (pyridine) in the samples took place. In the second heating scan a clean baseline was observed until the decomposition temperature was reached, this confirmed the no solvent remained in the samples after annealing.

The TGA of PVBA revealed an interesting feature (Figure 32) between 300 and 349°C PVBA losses 5.93 wt. %, this loss

Table 19. Thermogravimetric analyses of the various polymers, copolymers, and some representative blends used in the study of compatibilization of PS with PVP by introducing 4-VBA into PS. (See Figure 21).

Polymer #	% Weight ratio	Step decomposition temperatures, °C.			
		Start	Peak	End	loss wt. %
<u>11</u>	--	300.8	320	349.2	5.9
	--	368.3	419.2	497.5	61.6
<u>12</u>	--	250	387.5	474.2	85.3
<u>13</u>	--	250	351.7	445.8	90.3
<u>14</u>	--	260	372.5	451.7	94.8
<u>15</u>	--	260	368.3	430	98.3
<u>11+9</u>	50:50	250	400	455	89.2
<u>11+10</u>	50:50	270	336.7	458.3	75.6
<u>13+9</u>	50:50	280	358.8	446.7	95.7
<u>13+10</u>	50:50	280	362.5	448.3	92.7
<u>13+11</u>	50:50	270	395.8	460	83.9
<u>14+9</u>	50:50	290	387.5	446.7	97.7
<u>14+10</u>	50:50	280	355	437.5	94.7
<u>14+11</u>	50:50	280	395.8	491.7	74.1

All blends have undergone a first heating scan before decomposition temperature measurements. Conditions for this first heating scan are the same as those used for DSC measurements.

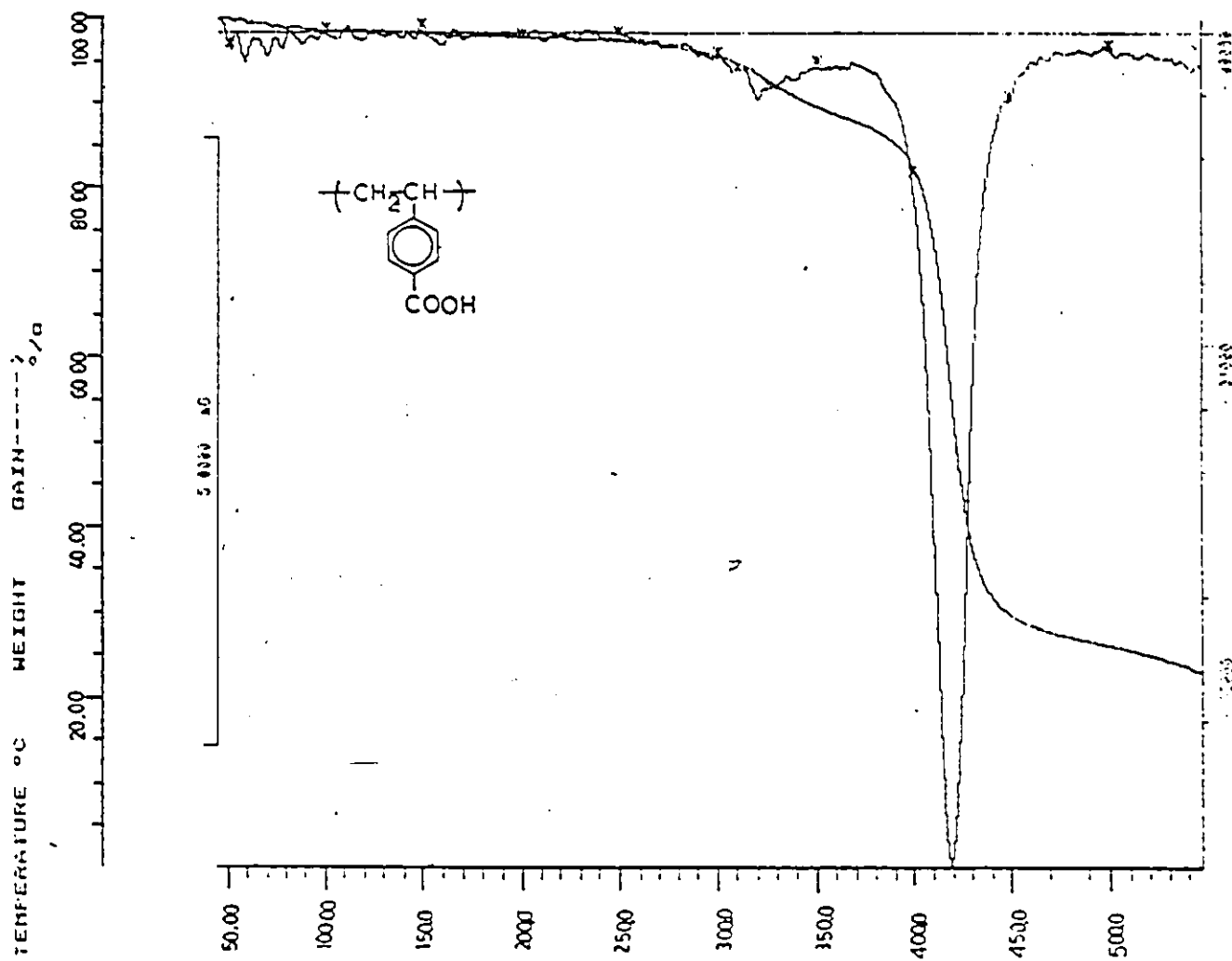


Figure 32. TGA of poly (4-vinylbenzoic acid)

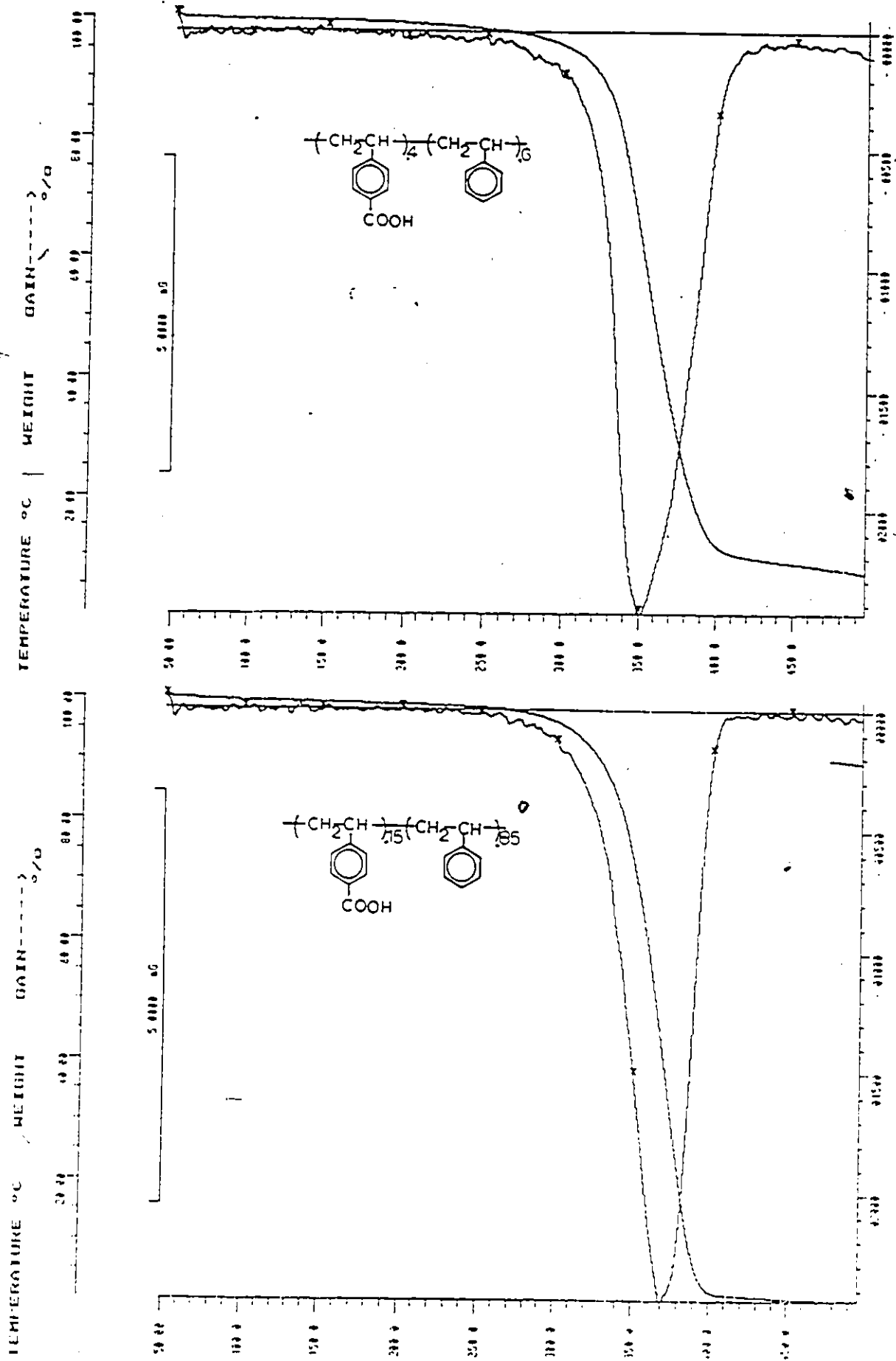


Figure 33. TGA curves of copoly (4-vinylbenzoic acid-styrene)s containing 40 and 15 mol % of VBA units.

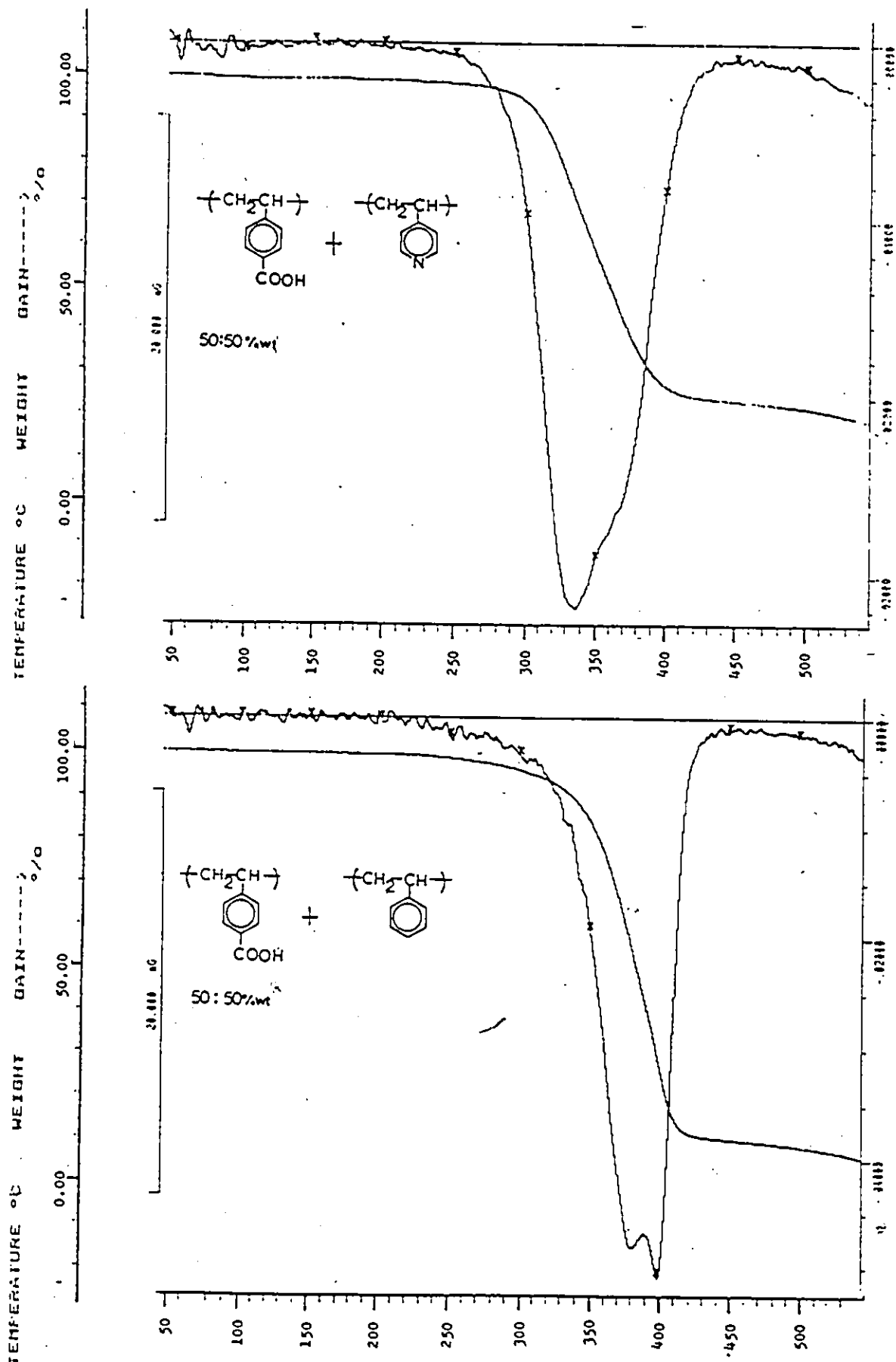


Figure 34. TGA curves of PVBA/PVP and PVBA/PS blends.

of weight corresponds presumably to the dehydration of the carboxylic groups and formation of anhydride groups. The theoretical loss of weight for the anhydride formation is 6.07 wt. %. Moreover, it should be noted that the resultant polymeric anhydride is thermally very stable. Its decomposition started at 368°C, with a peak decomposition at 419°C and only a 61.6% loss of weight by 500°C. The TGA curves for two of the (VBA-S) copolymers are shown in Figure 33. The TGA curves reveal that the presence of styrene in the copolymers lowers their thermal stability with respect to the PVBA homopolymer. The copolymers had decomposition temperatures similar to polystyrene. Figure 34 shows the TGA curves for PVBA/PVP and PVBA/PS blends. The presence of PVP and PS in these blends determine the start of the decomposition peak, 270 and 250°C respectively, while the presence of PVBA in the blends is revealed in the total loss of weight. We have mentioned that PVBA is characterized by a 61.6 % loss of weight by 500°C. Then, blends of PVBA/PVP and PVBA/PS loose 75.6 and 89.2 wt % respectively. While, all other blends that do not contain PVBA decompose almost completely.

1.2.3.4 Fourier-transform infrared studies of poly (4-vinylbenzoic acid)/poly (4-vinylpyridine) system and various 4-vinylbenzoic acid-styrene copolymers/poly (4-vinylpyridine) systems.

Poly (4-vinylbenzoic acid)

O-H stretching: 3550-2500 cm^{-1} broad band.

C=O stretching: a 1694 cm^{-1} band corresponding to hydrogen-bonded carboxyl groups ($-\text{COOH} \cdots \text{O}=\text{C}-$) due to the self-complexation of the carboxylic acid groups. Most of the carboxylic acid groups are self-complexed as it is deduced by the size and broadness of the 1694 cm^{-1} band. However, a shoulder at 1721 cm^{-1} also reveals the presence of free carboxylic acid groups (Figure 35). This 1721 cm^{-1} band is absent in the spectra of low molecular weight analogues, for instance, the spectrum of benzoic acid shows only a single broad band at 1692 cm^{-1} , benzoic acid exists as a dimer in solid state. The presence of free C=O groups in the spectrum of poly (4-vinyl-benzoic acid) can be explained by the inability of some carboxylic acid groups to reach other carboxylic acid groups due to the presence of the polymeric chain.

Poly (4-vinylpyridine)

The infrared spectrum of PVP has been discussed in section 1.2.1.4. We must recall that there are no bands near 1700 and 1300 cm^{-1} areas; therefore, there is no interference with the C=O and C-O stretching areas of poly (4-vinylbenzoic acid).

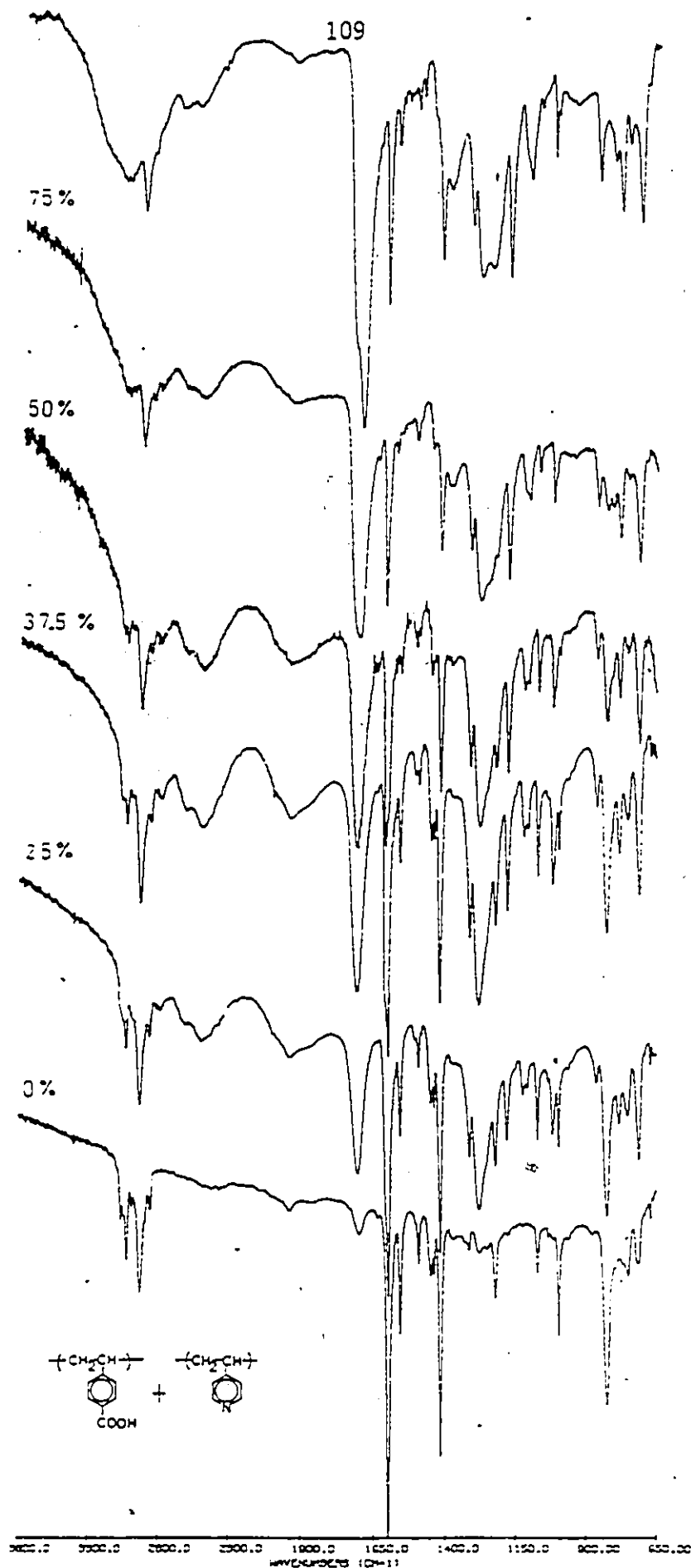


Figure 35. FTIR spectra in the region 3800-650 cm⁻¹ of PVBA/PVP blends. The wt % of PVBA is shown above each spectrum.

**Poly (4-vinylbenzoic acid)/poly (4-vinylpyridine)
blends**

OH stretching: Upon mixing with poly (4-vinylpyridine) the broad band at 3500-2500 cm^{-1} corresponding to the OH stretching in poly (4-vinylbenzoic acid) is replaced by two equally intense broad bands at ca. 2488 and 1937 cm^{-1} (Figure 36). For the low molecular weight adduct, benzoic acid: pyridine, these bands are located near 2450 and 1930 cm^{-1} [52]. Hadzi, [53] has interpreted these two bands in the case of the benzoic acid-pyridine adduct as arising from a double-minimum potential function for the OH stretching motion with a low central barrier, on the basis that deuteration of the OH group moves the 2450 cm^{-1} band to 1900 cm^{-1} , indicating that at least the 2450 cm^{-1} band arises from an OH motion. Also, it is observed that the spectrum of the cooled sample does not show much variation in the 1900-2450 cm^{-1} region, as would be the case if an equilibrium were present between $\text{BH}^+ \dots \text{A}^- = \text{B} \dots \text{HA}$ (B: pyridine, HA: benzoic acid) or if the lower band were a difference or "hot" band. In the poly (4-vinylbenzoic acid)/poly (4-vinylpyridine) blends these bands at 2488 and 1937 cm^{-1} show little dependence on composition of the blend. It has been accepted that the exact spectral location of these bands has little correlation with the actual dimensions and presumed strength of the hydrogen bond in the case of short, strong bonds [52]. On the other hand, in the case of longer hydrogen bonds, the

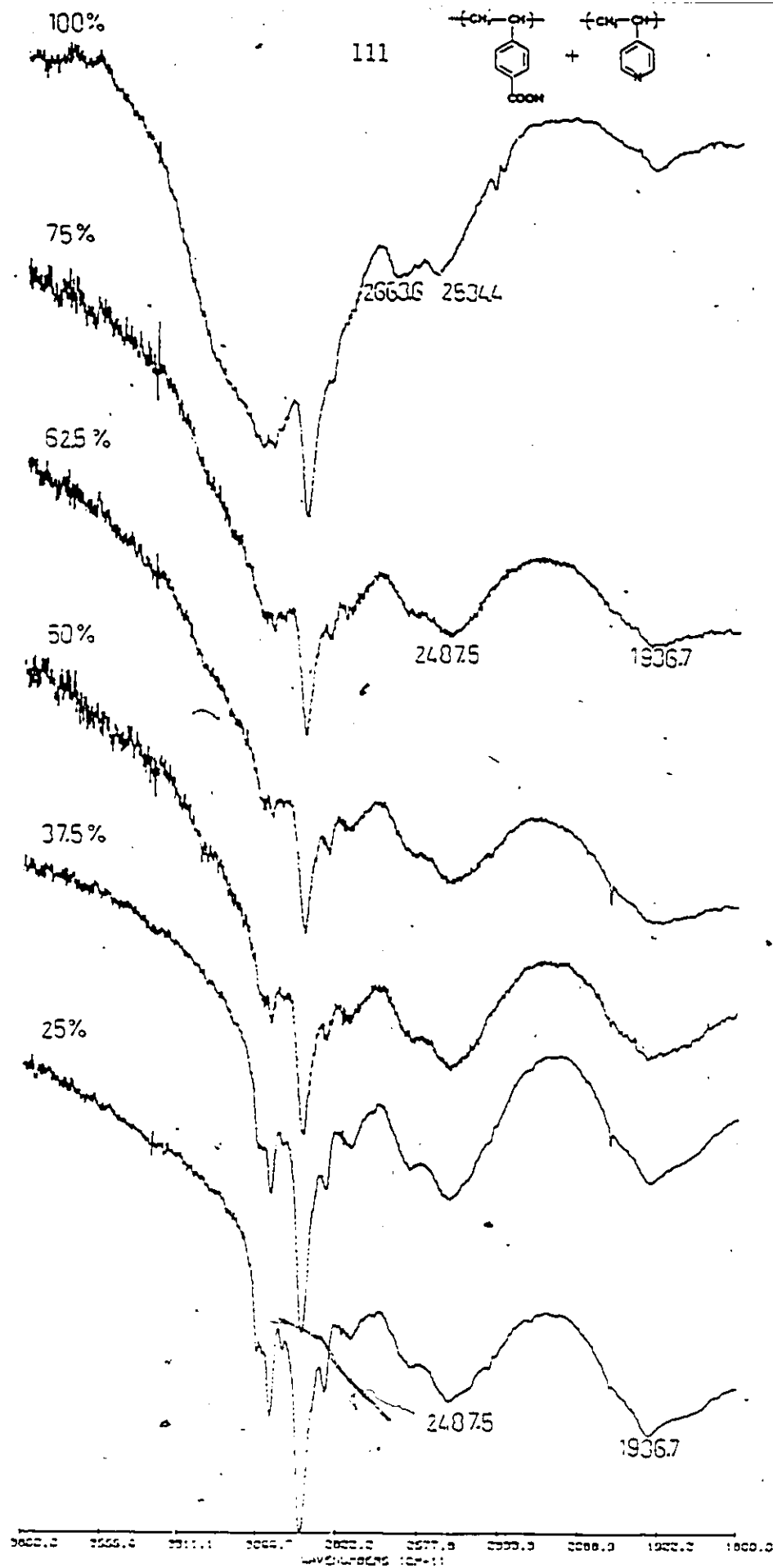


Figure 36. FTIR spectra in the region 3800-1800 cm^{-1} of PVBA/PVP blends. The wt % of PVBA is shown above each spectrum.

frequency of the stretching mode of OH is an index to the hydrogen-bond strength and dimensions [54].

C=O stretching: (Figure 37) the carbonyl stretching band for poly (4-vinylbenzoic acid) is made up of two components, a band at ca. 1721 cm^{-1} corresponding to free C=O groups and a band at 1694 cm^{-1} corresponding to self-hydrogen bonded C=O groups. Therefore, the carbonyl stretching band is very broad. The blend poly (4-vinylbenzoic acid) 75 wt %/poly (4-vinylpyridine) 25 wt % shows a broad C=O band centered at 1704 cm^{-1} . It is probably made up of three components: free C=O groups, C=O groups that are hydrogen-bonded with pyridine and self hydrogen-bonded C=O groups. Upon increasing the weight percent of poly (4-vinylpyridine) in the blend, the components corresponding to free C=O groups and self hydrogen bonded C=O decrease. The blend containing 25 wt % of poly (4-vinylbenzoic acid) and 75 wt % of poly (4-vinyl-pyridine) shows a C=O band at 1703 cm^{-1} . Due to the large excess of poly (4-vinylpyridine) in the blend, it can be considered that this C=O band is made up of one component mainly: C=O groups hydrogen-bonded to poly (4-vinylpyridine).

A plot of the half width of the C=O band vs. composition of the blend (Figure 38) shows the changes which affect the C=O band upon complexation. For this system it is observed that the half-width of the C=O band decreases significantly upon complexation with poly (4-vinylpyridine). This can be explained by the fact that the C=O band for poly (4-

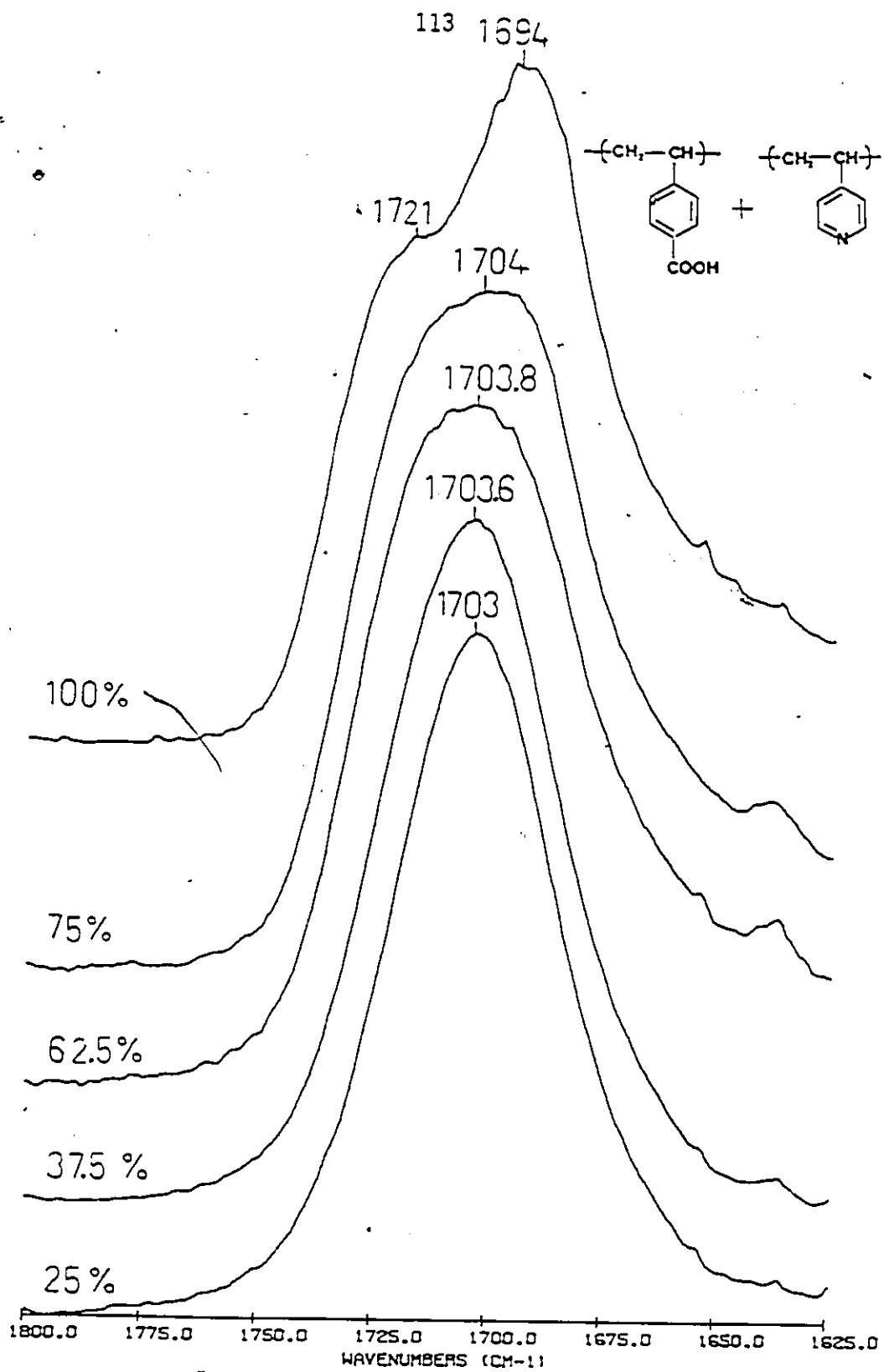


Figure 37. FTIR spectra in the region 1800-1625 cm⁻¹ of PVBA/PVP blends. The wt % of PVBA is shown above each spectrum.

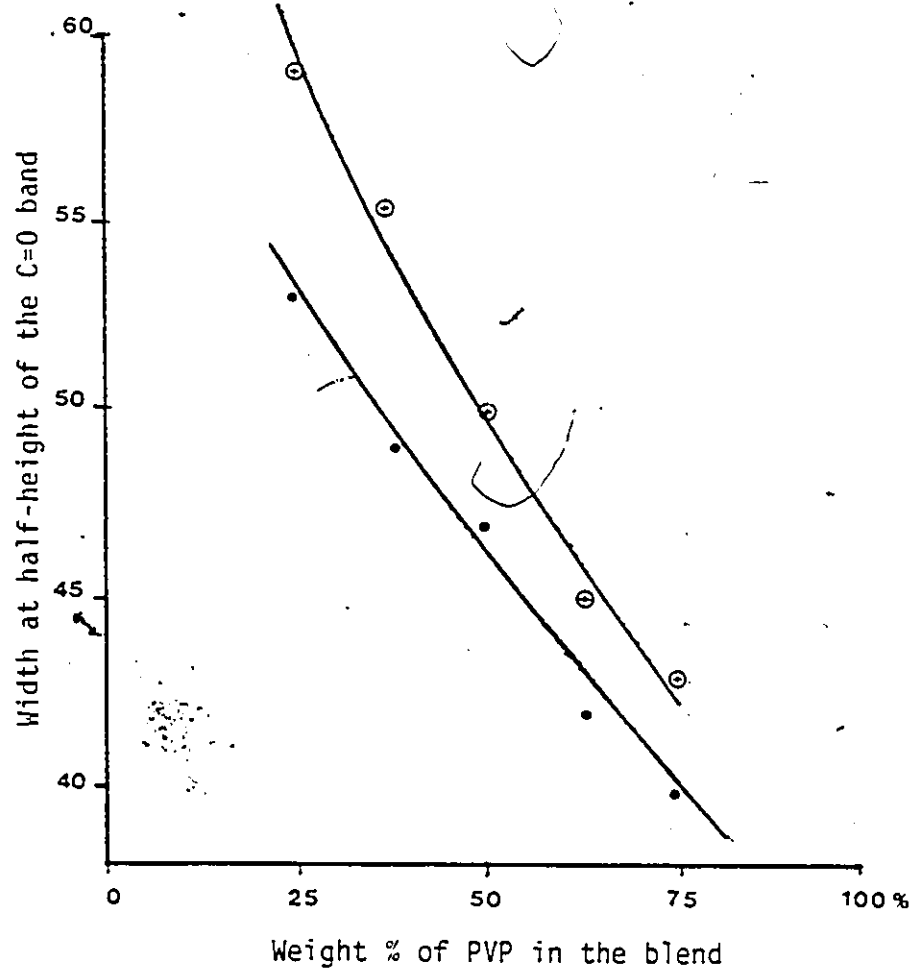


Figure 38. Plot of the width at half-height of the carbonyl stretching frequency as a function of PVP concentration for $\ominus$ PVBA/PVP and, $\bullet$ copoly (VBA-S) (40 mol % VBA)/PVP blends.

vinylbenzoic acid) is very broad since it is made up of two components, free and self-complexed C=O groups, and upon complexation with poly (4-vinylpyridine) the C=O band is made up of only one component: C=O groups complexed with poly (4-vinylpyridine), this explains why the C=O band is narrower upon complexation with the basic units.

The infrared spectrum of benzoic acid in its dimeric state shows a C=O band at 1692 cm^{-1} , complexation with pyridine does not appear to perturb the structure of the CO_2H group much from its dimer state since the adduct benzoic acid: pyridine also shows its C=O band at 1692 cm^{-1} . For the adduct of p-methylbenzoic acid and pyridine, a slightly different situation it is observed since the C=O band of this adduct is at 1708 cm^{-1} while the self-complexed C=O band of p-methylbenzoic acid is at 1678 cm^{-1} [52]. This system is similar to the poly (4-vinylbenzoic acid)/poly (4-vinylpyridine) system for which the hydrogen-bonded C=O group to pyridine is at 1703 cm^{-1} while the self-complexed C=O groups for poly (4-vinylbenzoic acid) exhibit a band at 1694 cm^{-1} .

C-O stretching:

Hadzi and Sheppard ascribed characteristic bands at $1300 \pm 15\text{ cm}^{-1}$ and at 1420 cm^{-1} to C-O stretching modes [55]. For PVBA/PVP system, two bands are observed at 1282 and 1241 cm^{-1} , they are attributed to C-O stretching modes. When the % of

PVP increases in the blend, the band at 1241 cm^{-1} disappears progressively. For the blend containing 75% of PVP a single band at 1278 cm^{-1} is observed instead of the 1282 and 1241 cm^{-1} bands (Figure 35)

Bands in the $1200\text{--}1750\text{ cm}^{-1}$ region characteristic of RCO_2 or RCO_2^- are of importance in establishing the state of ionization of the RCO_2H moiety of the complex. In the $1200\text{--}1350\text{ cm}^{-1}$ region are found bands characteristic of RCO_2H which are completely absent from the spectrum of the sodium salt of the acid. A carbonyl band near 1700 cm^{-1} is characteristic of non-ionized $-\text{CO}_2\text{H}$ group, a band near 1600 cm^{-1} is characteristic of the $-\text{CO}_2^-$ group. The 1400 cm^{-1} symmetrical carboxylate stretching frequency is sometimes weak and easily confused with other vibrations. The sodium salt of p-methylbenzoic acid exhibits bands at 1552 and 1421 cm^{-1} that are attributed to $-\text{CO}_2^-$ group [52]. Bands for $-\text{CO}_2^-$ groups are absent in all poly (4-vinylbenzoic acid)/poly (4-vinylpyridine) blends. Therefore, there are only hydrogen-bonding interactions between both polymers. The acidity of the benzoic acid units is not high enough for proton transfer to take place. Johnson and Rumon [52] studied the spectroscopic properties of 18 strongly hydrogen-bonded pyridine-benzoic acid adducts and their correlation with ΔpK value of the complex (ΔpK referring to the difference in pK_a of the pyridinium ion and the benzoic acid in water), they determined that proton transfer takes place.

when ΔpK values are of ca. 3.7. For example, for adduct of 2,4-dinitro benzoic acid: pyridine whose $\Delta pK = 3.81$, bands at 1670 and 1635 cm^{-1} are attributed to RCO_2^- groups.. For benzoic acid the pK_a is 4.20 and for the pyridinium ion is 5.23, the $\Delta pK = 1.03$, thus the interaction is only of hydrogen-bonding type.

Blends of copoly (VBA-S) (40 mol % VBA) and poly (4-vinylpyridine).

These blends are compatible over the entire range of composition as shown by DSC studies. Likewise, FTIR studies show that hydrogen-bonding interactions are present in all blends, this indicates compatibility.

O-H stretching: the new bands at 2488 and 1937 cm^{-1} , that are characteristic of OH groups complexed to pyridine groups, were present in all blends (Figure 39).

C=O stretching: the carbonyl band of the vinylbenzoic acid-styrene copolymer was made up of two components: a free C=O groups at 1728 cm^{-1} and a self complexed C=O groups at 1691 cm^{-1} . It should be noted that in the case of this copolymer these two bands were more easily distinguished than was the case for the poly (4-vinylbenzoic acid) homopolymer. This is probably due to the fact that less carboxylic acid groups were self-complexed in the case of the copolymer due

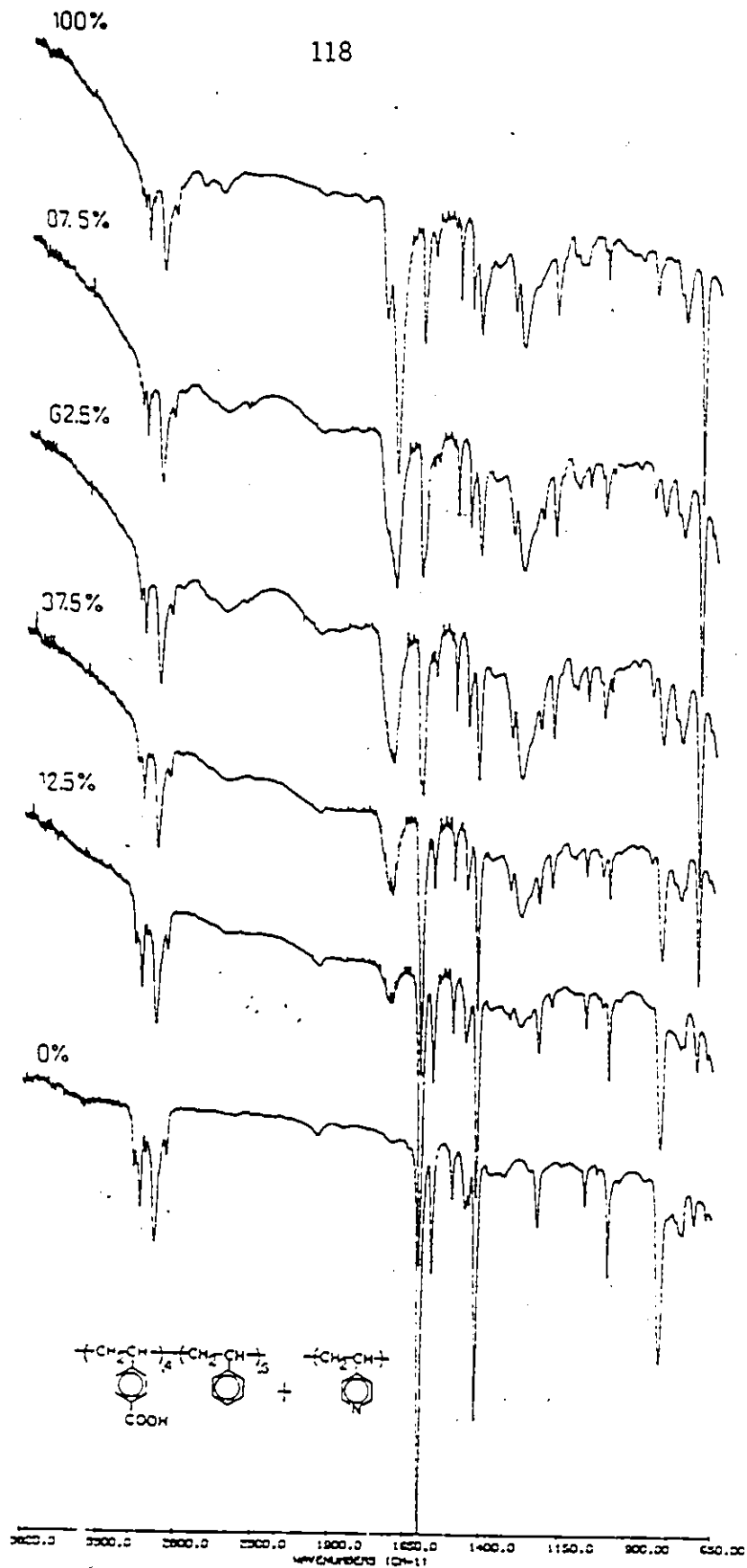


Figure 39. FTIR spectra in the region 3800-650 cm^{-1} of copoly (VBA-S) (40 mol % VBA)/PVP blends. The wt % of copoly (VBA-S) (40 mol % VBA) is shown above each spectrum.

to the intercalated styrene units. Upon increasing the concentration of poly (4-vinylpyridine) in the blends, the bands corresponding to free C=O groups (1728 cm^{-1}) and self-complexed C=O groups (1691 cm^{-1}) decreased and the new C=O band corresponding to C=O groups complexed with poly (4-vinylpyridine) increased (Figure 40). For instance, for the blend containing only 25 wt % of poly (4-vinylpyridine), a clear shoulder at 1720 cm^{-1} corresponding to free C=O groups was still observed as well as self-complexed groups shown by the 1692 cm^{-1} band. In contrast, the blend containing 37.5 wt % of poly (4-vinylpyridine) did not show clearly the band corresponding to free C=O groups as more C=O groups appeared to be complexed with poly (4-vinylpyridine), as is shown by the increase in the band at 1696 cm^{-1} . For blends having higher concentrations of poly (4-vinylpyridine) we observed a broad single band shifting progressively from 1692 to 1703 cm^{-1} . The latter frequency being observed for the blend having 75 the wt % of PVP. Therefore, it may be said that in this case where the wt % of PVP was very high, this C=O band was made up mainly of C=O groups complexed with pyridine groups. It should be noted that for the system poly (4-vinylbenzoic acid) - poly (4-vinylpyridine) we also obtained a characteristic C=O band at 1703 cm^{-1} for the C=O groups hydrogen-bonded with poly (4-vinylpyridine).

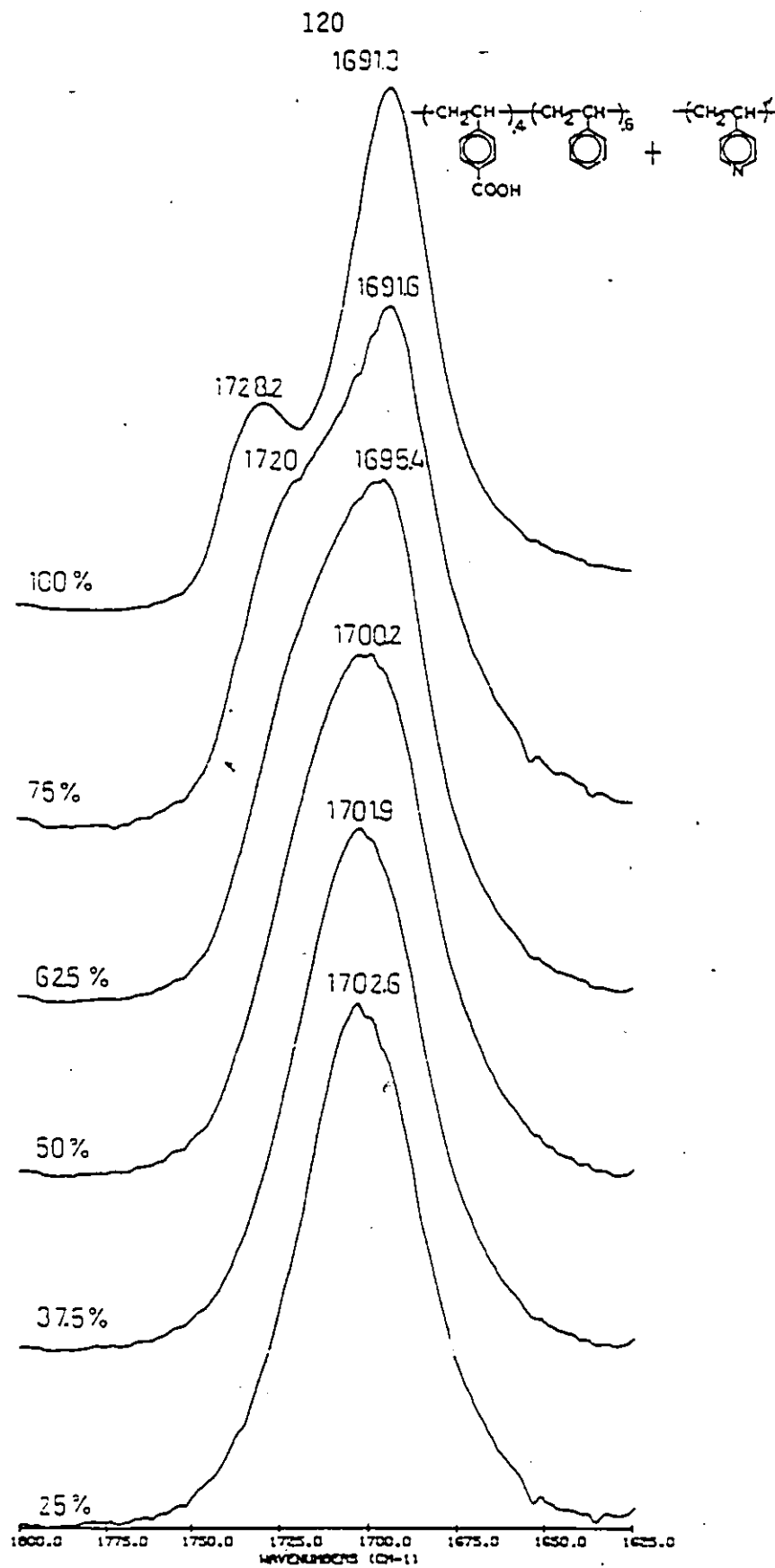


Figure 40. FTIR spectra in the region 1800-1625 cm^{-1} of copoly (VBA-S) (40 mol % VBA)/PVP blends. The wt % of copoly (VBA-S) (40 mol % VBA) is shown above each spectrum.

Blends of copoly (VBA-S) (26 mol % VBA) and poly (4-vinylpyridine)

These blends were incompatible as shown both by the DSC results and by the FTIR studies. The latter indicated that hydrogen-bonding was happening at least to a small extent. This was revealed by the presence of bands at 2488 cm^{-1} and 1937 cm^{-1} which were characteristic of OH group hydrogen-bonded with pyridine groups (Figure 41). However, the study of the C=O band showed that hydrogen-bonding was not happening to an extent large enough to cause variation in shape and frequency of the carbonyl band (Figure 42). The C=O band for the copolymer, which was made up of two well distinguished components: 1730 and 1691 cm^{-1} bands corresponding respectively to free and hydrogen-bonded C=O groups, remained invariable upon increasing the concentration of poly (4-vinylpyridine) in the blend.

Blends of copoly (VBA-S) (15 mol % VBA) and poly (4-vinylpyridine).

For these incompatible blends, there were no bands at 2488 and 1937 cm^{-1} (Figure 43). Furthermore, the C=O band did not change upon increasing the concentration of poly (4-vinylpyridine) in the blends. Only two components were always observed, free C=O band at 1733 cm^{-1} at self hydrogen-bonded C=O band at 1690 cm^{-1} . (Figure 44)

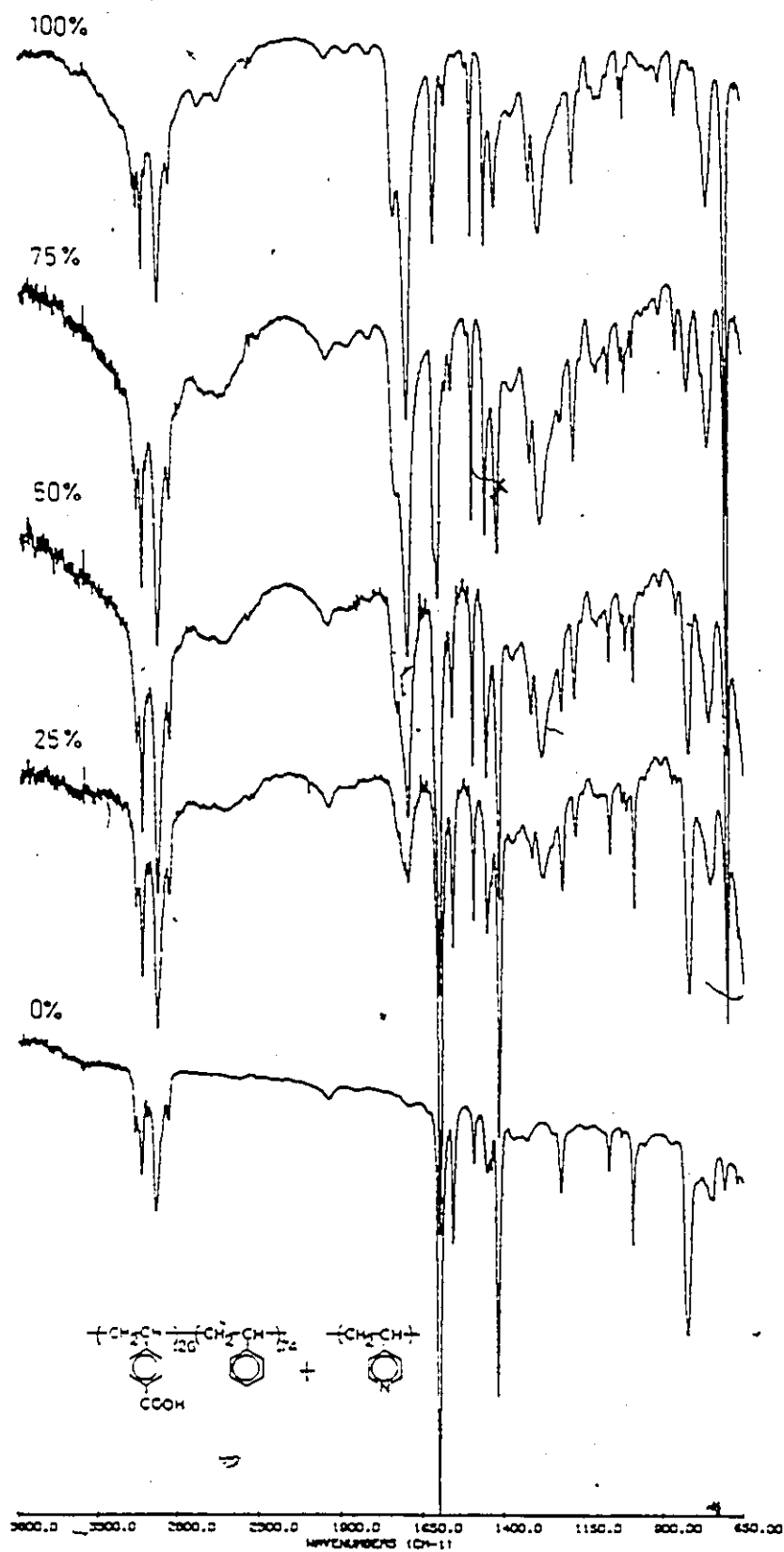


Figure 41. FTIR spectra in the region 3800-650 cm^{-1} of copoly (VBA-S) (26 mol % VBA)/PVP blends. The wt. % of copoly (VBA-S) (26 mol % VBA) is shown above each spectrum.

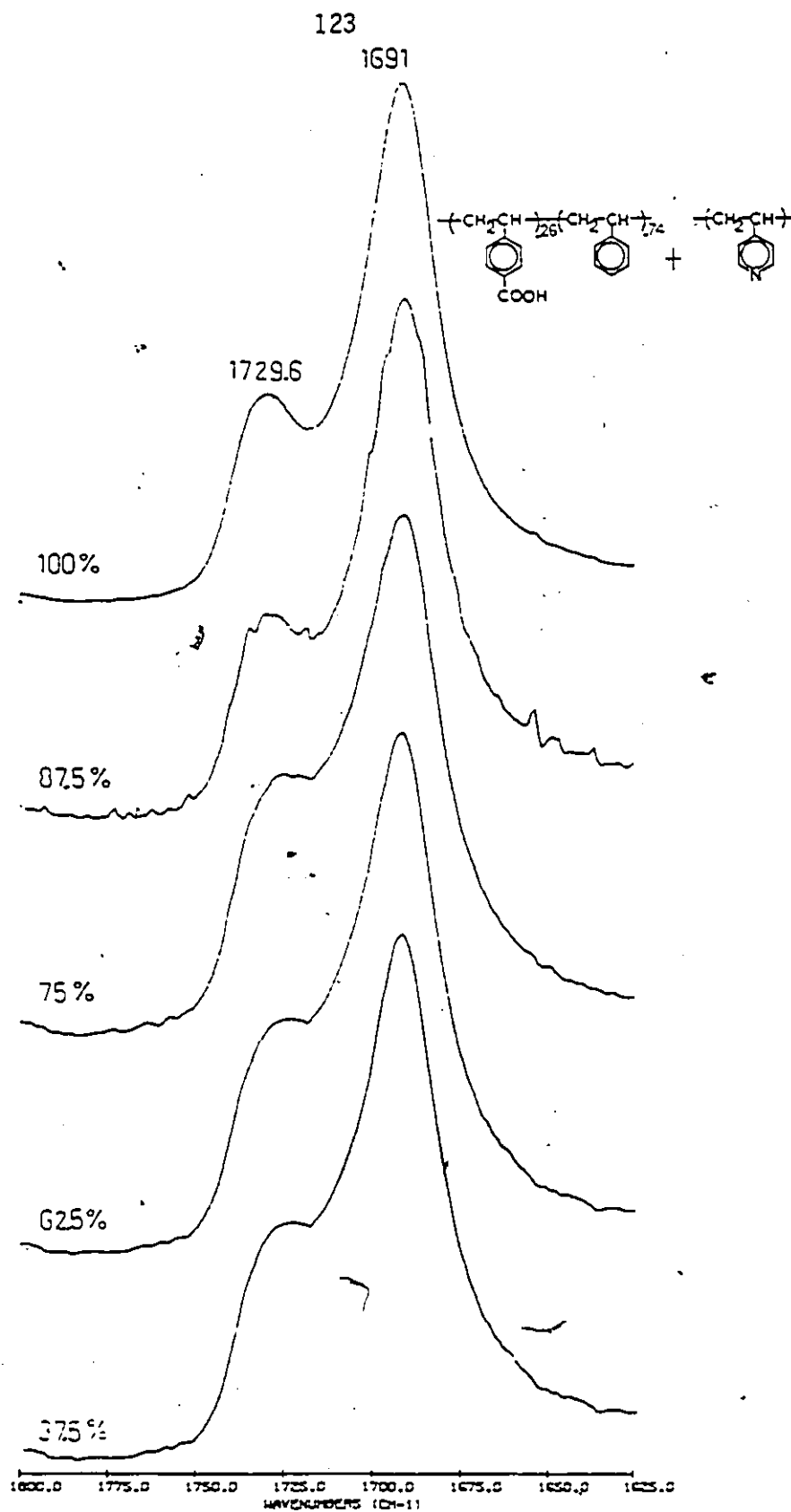


Figure 42. FTIR spectra in the region 1800-1625 cm^{-1} of copoly(VBA-S) (26 mol % VBA)/PVP blends. The wt. % of copoly (VBA-S) (26 mol % VBA) is shown above each spectrum.

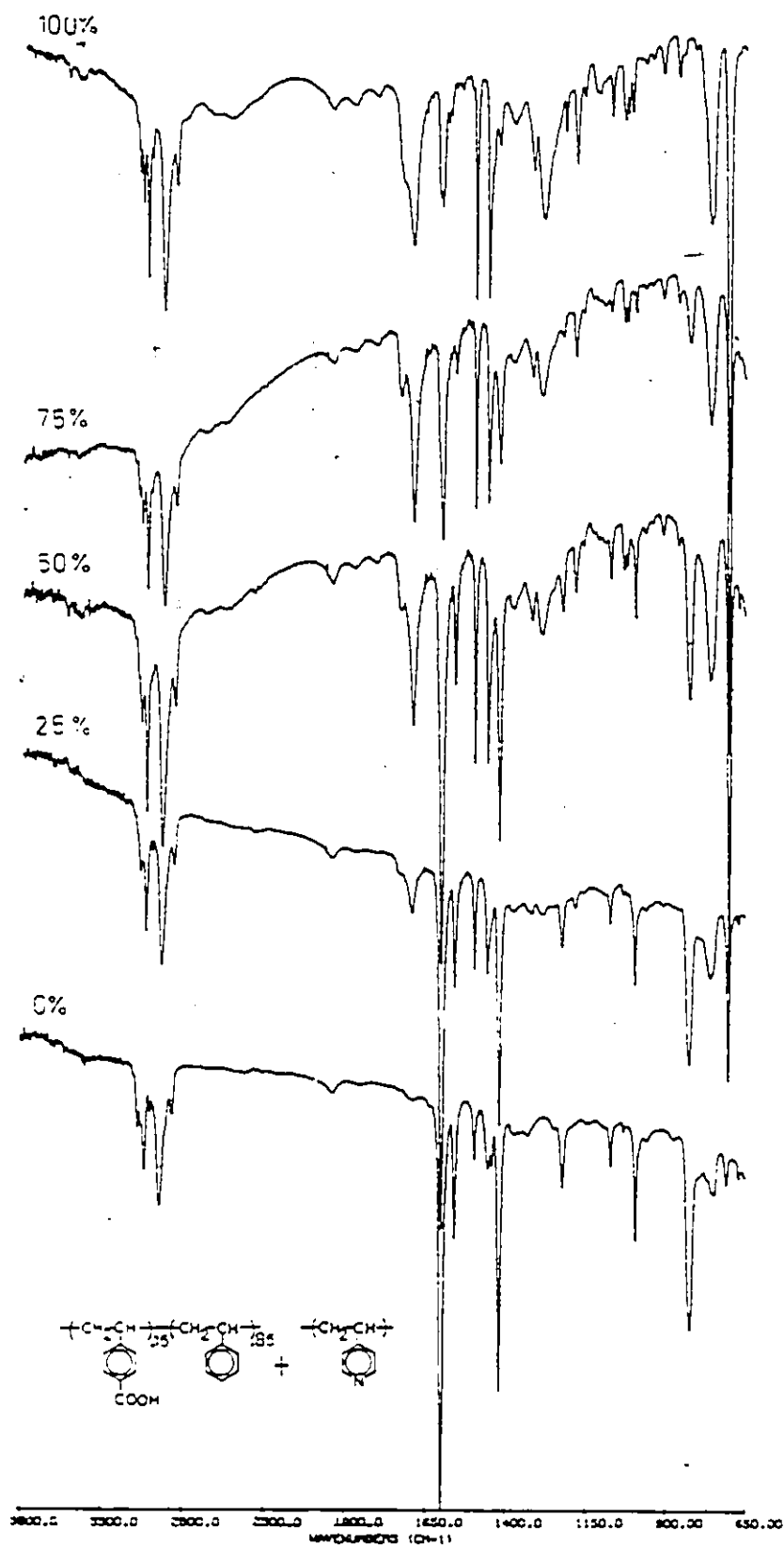


Figure 43. FTIR spectra in the region 3800-650 cm⁻¹ of copoly (VBA-S) (15 mol% VBA)/PVP blends. The wt. % of copoly (VBA-S) (15 mol % VBA) is shown above each spectrum.

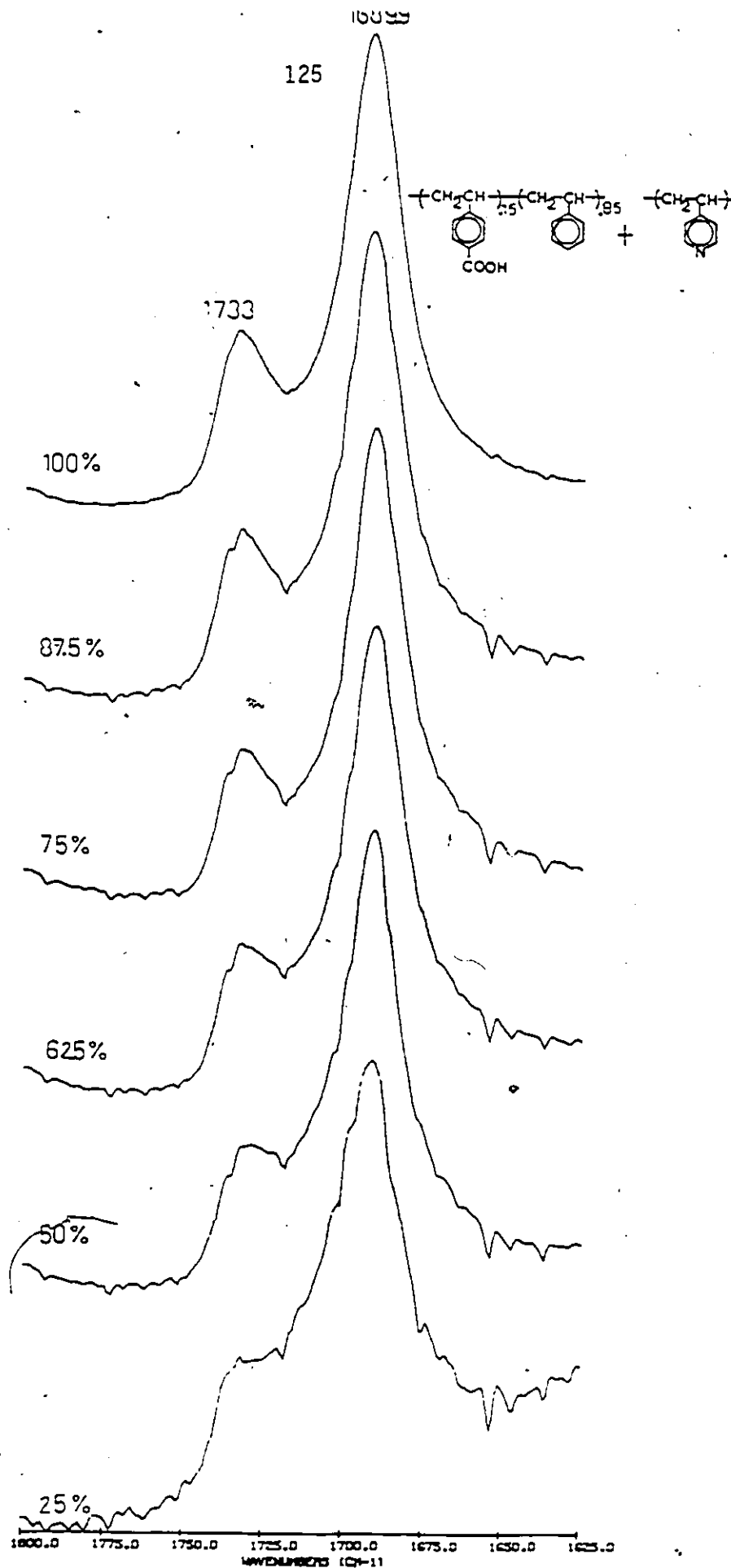


Figure 44. FTIR spectra in the region 1800-1625 cm⁻¹ of copoly (VBA-S) (15 mol % VBA)/PVP blends. The wt. % of copoly (VBA-S) (15 mol % VBA) is shown above each spectrum.

FTIR studies have shown that in the system poly (4-vinylbenzoic acid)/poly (4-vinylpyridine) hydrogen-bonding between the acidic and basic units happens to a large extent as is shown by the presence in the IR spectra of the blends of the 2488 and 1937 cm^{-1} bands which are characteristic of OH groups complexed with pyridine and the C=O band at 1703 cm^{-1} characteristic of the C=O groups complexed with pyridine groups. Similar results have been obtained for the system copoly (VBA-S) (40 mol % VBA)/poly (4-vinylpyridine). This hydrogen-bonding interaction is responsible for the compatibilization of the systems. On the other hand for systems where the mol % of acidic units in the styrene copolymer is decreased to 26 and 15 mol % and for which incompatibility was shown, the C=O band did not change upon blending with poly (4-vinylpyridine).

Therefore the infrared study suggests that it is necessary to introduce into PS at least 40 mol % of VBA units in order to achieve its compatibility with PVP.

1.2.4 Compatibilization of Polystyrene (PS) with Poly(methyl acrylate) (PMA) by introducing 4-vinylphenyl boronic acid units into both polymers.

It was our initial aim to explore the possibilities of compatibilizing two polymers by introducing a boron containing unit into one of them. Then, if the other polymer contains electron-donor units, complexation between the electron accepting boron containing polymer and the electron donating polymer would take place resulting in the formation of a compatible blend. The idea was attractive since coordination between electron-deficient boron compounds and electron-donor compounds is known to be a highly exothermic process. For instance Table 20 gives the enthalpies of formation for a series of amines: BF_3 complexes [56]. We see in this table that the enthalpies of formation for this kind of complexes are much higher than those for hydrogen-bonding complexations (2-10 kcal/mol). It should be pointed out that the use of complexation between boron containing polymers and electron-donor polymers in the field of compatible mixtures has not been attempted or reported previously.

At first glance, one may think of preparing a polystyrene containing pendant alkyl borane units such as:

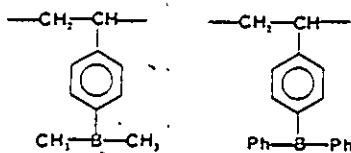
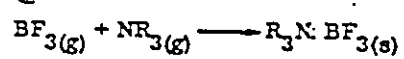


Table 20. Enthalpy of formation of BF_3 :amine complexes (ref. 56).

<i>Amine</i>	ΔH° , Kcal./Mole
NH_3	-22.0
ND_3	—
NH_2Me	-26.0
NHMe_2	-28.2
NMe_3	-26.6
$\text{C}_3\text{H}_5\text{N}$	-(27-30)
$n\text{-C}_4\text{H}_9\text{-NH}_2$	—
$\text{tert-C}_4\text{H}_9\text{NH}_2$	—
PMe_3	-18.9

However, the synthesis and manipulation of polymers of this kind would be very difficult. It is known that alkyl boranes are flammable and very sensitive to hydrolysis. Although, we also know that stability of alkyl boranes or boranes is increased drastically when they are complexed with electron-donor compounds; for instance, trimethylamine borane, $(\text{CH}_3)_3\text{N}^+\text{BH}_3^-$ has a melting point of 94°C and is stable for hours at 125°C . Therefore, the handling of the mixtures of the polymers would be easier than the handling of the alkylboron containing polymer by itself.

However, in order to facilitate handling we decided to prepare polymers functionalized with more stable boron containing units.

Therefore, we chose to prepare a polystyrene containing 4-vinylphenyl boronic acid units. Modified polystyrenes containing various amounts of 4-vinylphenyl boronic acid units were synthesized by a three-step process: first, reaction of polystyrene with bromine in presence of thallic triacetate to obtain a partly brominated polystyrene. Second, lithiation of this brominated polystyrene with n-butyllithium followed by reaction with trimethyl borate. Third, hydrolysis leads to the desired polystyrene containing 4-vinylphenyl boronic acid units. These modified polystyrenes were blended with polymers containing electron-donor groups and compatibility studies were carried out.

Blends of copoly (4-vinylphenyl boronic acid-styrene) (17.8 mol % 4-vinylphenyl boronic acid) and poly(4-vinylpyridine) were prepared using pyridine as common solvent. Pyridine solutions (ca. 1%) of both polymers are made and mixed in appropriate ratio, then the solvent is evaporated at atmospheric pressure until a dry film is obtained. Final solvent removal is then effected under vacuum first at room temperature for 48 h and then at 50°C for 3 h. Wet pyridine (ca. 2% water) was used to prepare the solution of copoly (4-vinylphenyl boronic acid-styrene) (17.8 mol % 4-vinylphenylboronic acid) since the copolymer is insoluble in dry pyridine due to the fact that when they are dried these copolymers crosslink because some of the 4-vinylphenyl boronic acid units convert to 4-vinylphenylboronic anhydride units. This phenomenon is explained in detail in section 1.2.5.

Figure 45 shows DSC thermograms obtained for these blends. The copoly (4-vinylphenylboronic acid-styrene) (17.8 mol % 4-vinylphenyl boronic acid) exhibits a T_g at 140°C and poly (4-vinylpyridine) at 148°C. T_g for both polymers are very close to each other. This is a non-ideal case for studying compatibility using the DSC technique since overlapping of both T_g 's may lead to erroneous conclusions. Indeed, for this system a single T_g is observed for blends over the entire range of composition, however, if compatibility is to be attributed to the system, it is necessary to observe a composition dependent

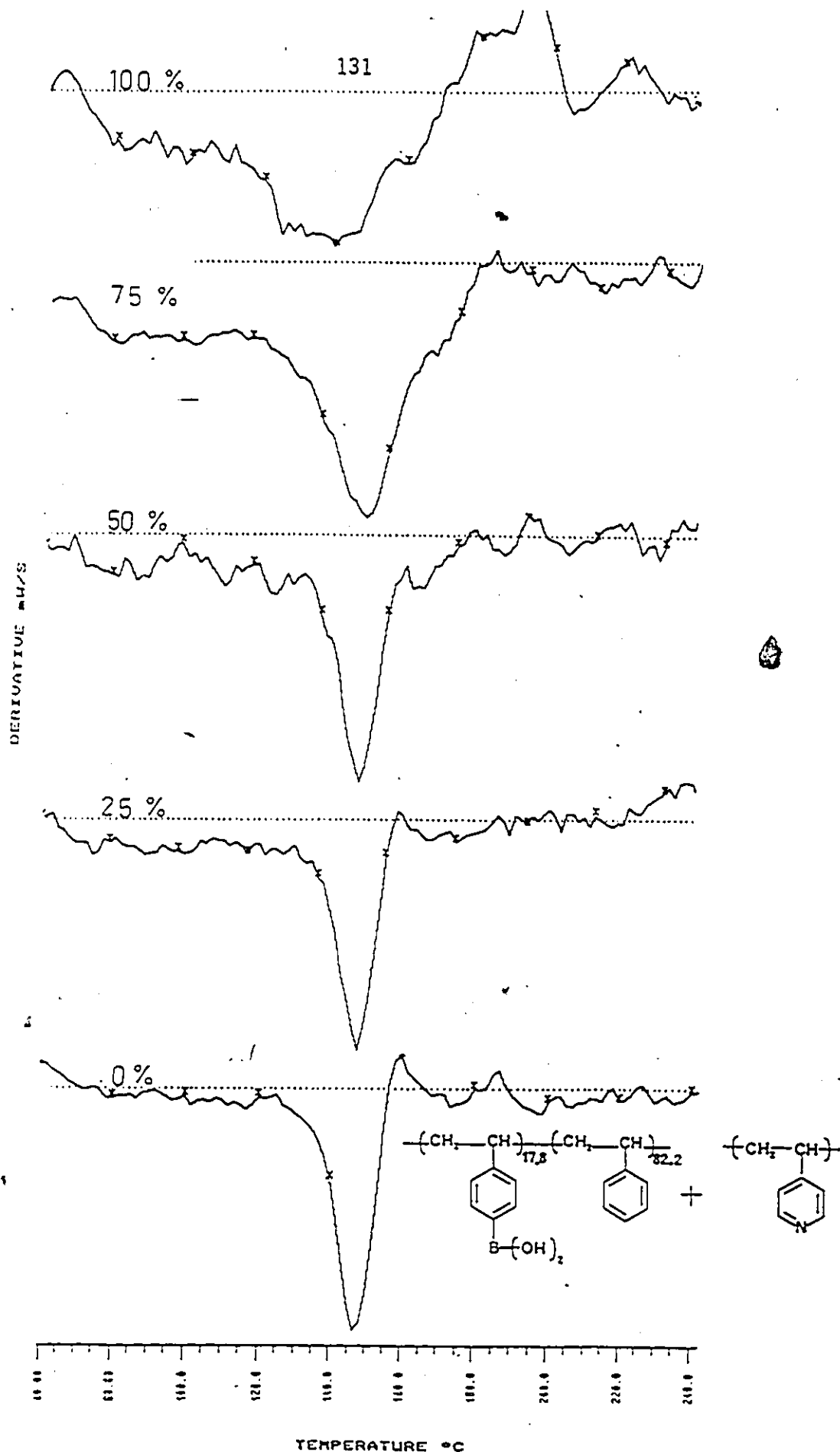


Figure 45. DSC thermograms of blends of PVP and copoly(4-vinylphenyl boronic acid-styrene) (17.8 mol % 4-vinylphenyl boronic acid). The weight % of the copolymer in the blend is given above each thermogram.

T_g. It is observed that T_g is at 148°C for all blends. Therefore, it may be concluded that the system is incompatible. Moreover, FTIR studies of films of these blends show that the spectra are just the weighted sum of the spectra of both polymers in the blend (Figure 46). There are no new bands or shifting and broadening of already existent bands. This means that the specific interactions between both polymers through complexation of the electron-deficient boron-containing polymer and the electron-donor pyridyl units of poly(4-vinylpyridine) did not in fact occur. If complexation had occurred, new characteristic bands corresponding to the N:B stretching vibration would have been observed. It must be concluded therefore that the coordination capability of the boronic acid units is negligible in this system. It is very important to note that the infrared spectra of copoly(4-vinylphenyl boronic acid-styrene) and its blends with poly(4-vinylpyridine) do not exhibit any significant hydroxyl band suggesting that the boronic acid units in the copolymer had been converted to boronic anhydride units. This means that the copolymer has a great tendency to self-crosslink regardless of the presence of poly(4-vinylpyridine). In view of this occurrence incompatibility is observed as the two components of the blend fail to interact in the way which would bring about compatibility. Indeed the characteristic band at 1340 cm⁻¹ for the B-O stretch corresponding to the boronic anhydride units is

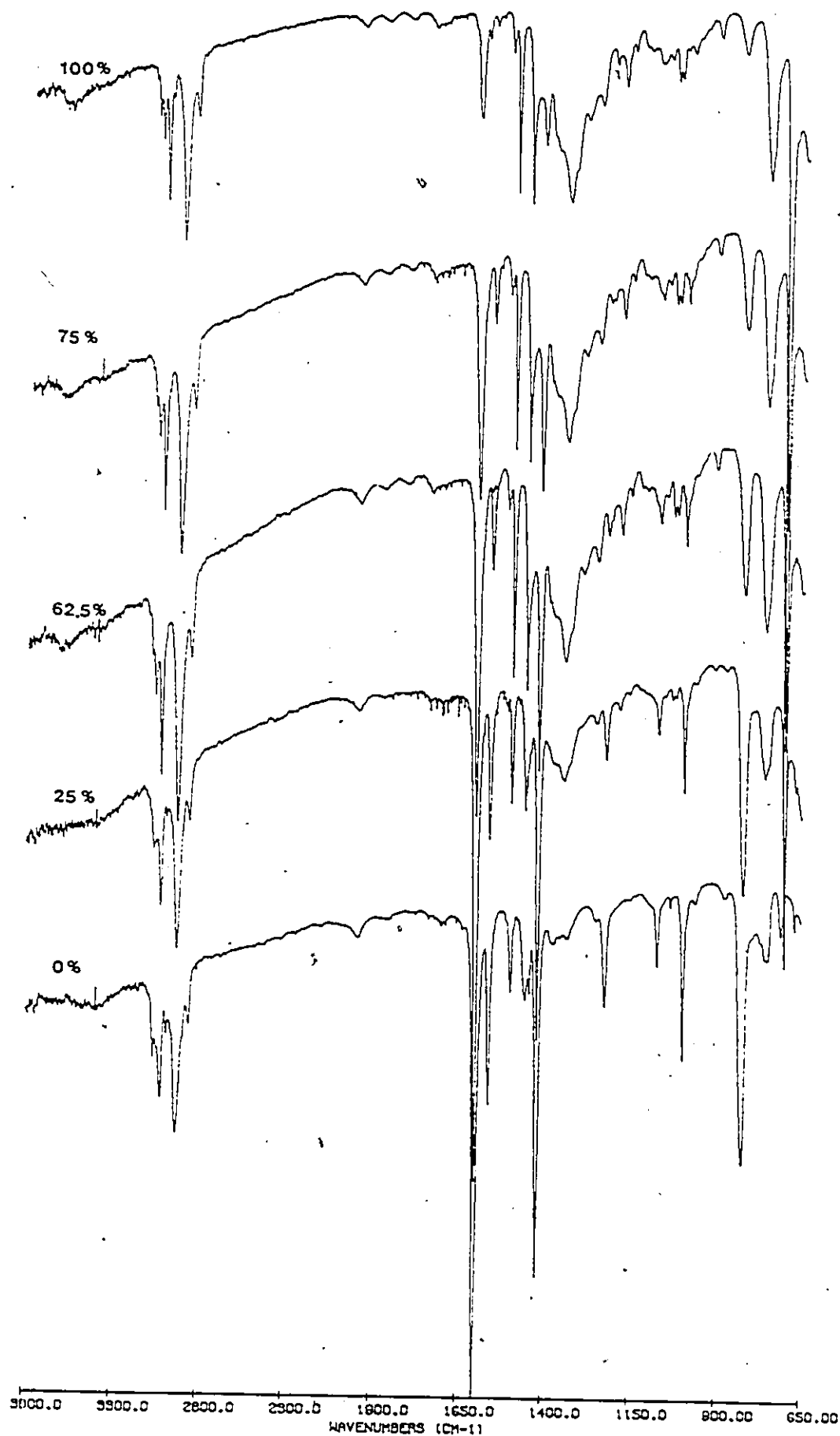


Figure 46. FTIR spectra in the region $3800\text{--}650\text{ cm}^{-1}$ of blends of PVP and copoly(4-vinylphenyl boronic acid-styrene) (17.8 mol % 4-vinylphenyl boronic acid). The weight % of the copolymer in the blend is given above each spectrum.

present in all blends. Figure 47 shows the biphasic structure that we attribute to these blends.

It was thought that these modified polystyrenes containing 4-vinylphenyl boronic acid units might be compatible with polymers containing hydroxyl groups. In this case compatibility might result from chemical reactions taking place between the boronic acid units of the modified polystyrene and the hydroxyl groups of the other polymer to form boronate units. Indeed, we observed partial compatibility for blends of copoly (4-vinylphenyl boronic acid-styrene) (13.4 mol % 4-vinylphenyl boronic acid) and poly (4-hydroxystyrene). Figure 48 shows the DSC thermograms of these blends which were prepared using wet THF as the common solvent. It is observed that the copoly (4-vinylphenyl boronic acid-styrene) exhibits a T_g at 120°C while poly (4-hydroxystyrene) ($M_w = 31600$ $M_w/M_n = 1.9$) exhibits a T_g at 157°C . Blends containing 75 and 62.5 wt. % of copoly (4-vinylphenyl boronic acid-styrene) (13.4 mol % 4-vinylphenyl boronic acid) exhibit only one glass-transition temperature. Blends containing up to 50 wt. % of the copolymer exhibit two glass-transition temperatures, this indicates the presence of two phases, thus, incompatibility is attributed to those blends.

In general, it may be concluded that the capability of our copoly (4-vinylphenyl boronic acid-styrene)s for complexing with electron-donor containing polymers is too weak to cause compatibility. Also, their capability to

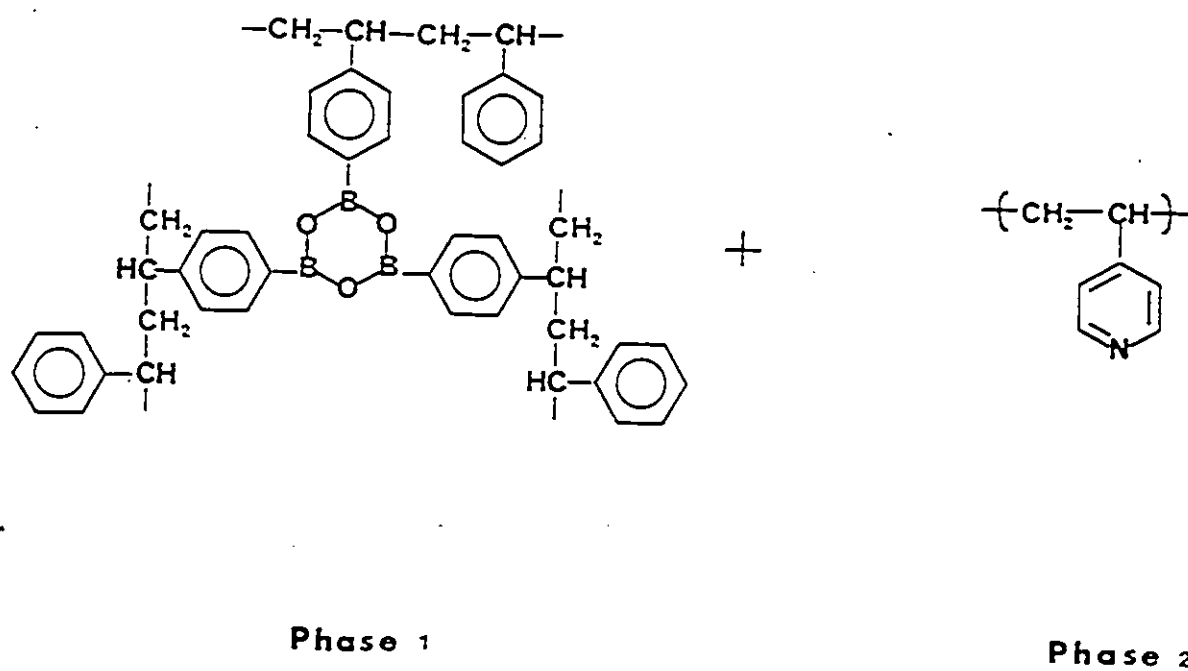


Figure 47. Structure of incompatible blends of PVP and copoly(4-vinylphenyl boronic acid-styrene) (17.8 mol % 4-vinylphenyl boronic acid).

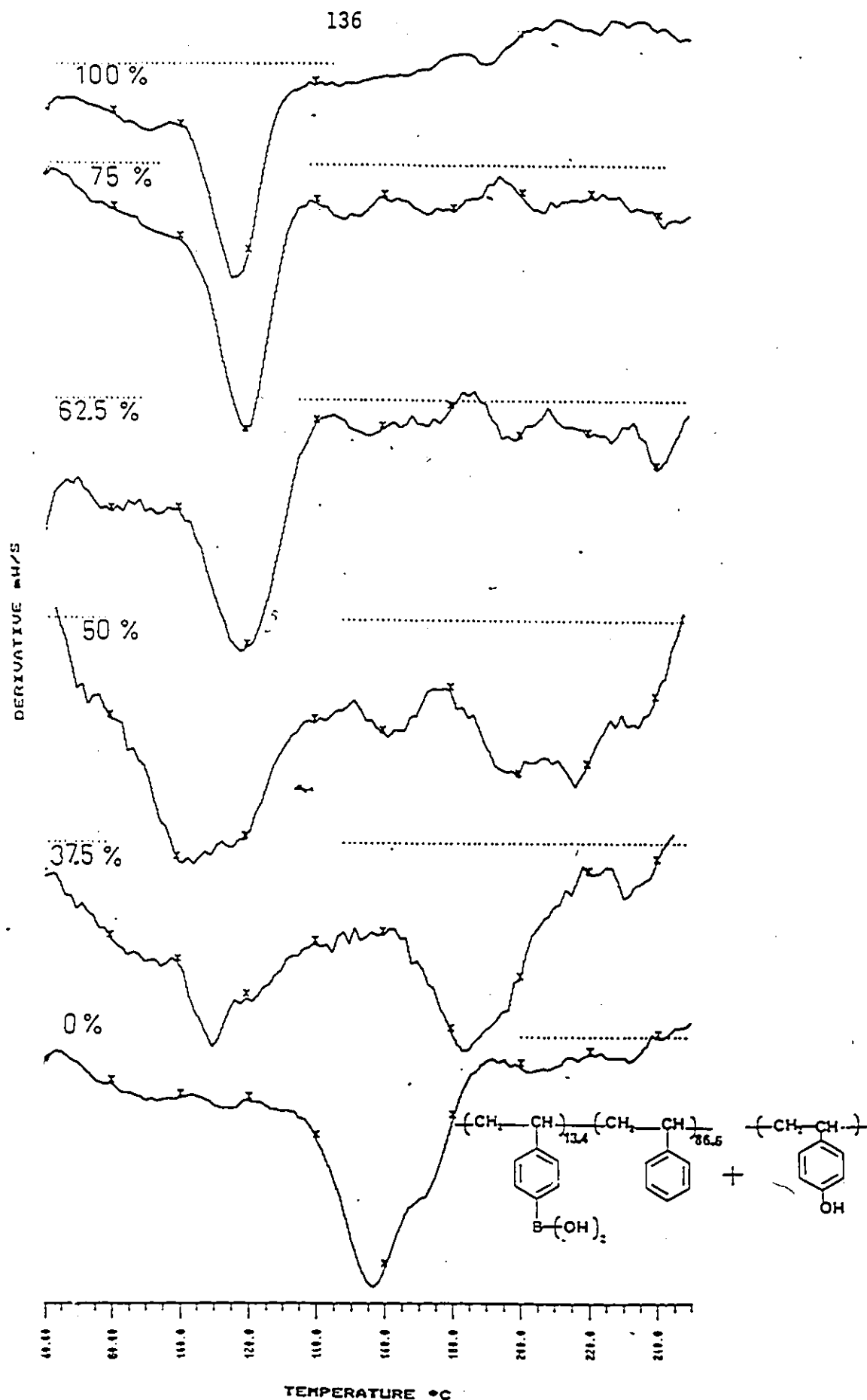


Figure 48. DSC thermograms of blends of PHS and copoly(4-vinylphenyl boronic acid-styrene) (13.4 mol % 4-vinylphenyl boronic acid). The weight % of the copolymer in the blend is given above each thermogram.

form boronate linkages with phenols containing polymers was not efficient enough to cause compatibility over the entire range of composition. Probably, higher amounts of 4-vinylphenyl boronic acid units would need to be introduced into polystyrene in order to observe compatibility over the entire range of composition.

During the course of these studies, we observed repeatedly the capability of the (4-vinylphenyl boronic acid-styrene) copolymers to self-crosslink due to the ease with which 4-vinylphenyl boronic acid units convert to 4-vinylphenyl boronic anhydride units. In view of these observations, we thought that in order to compatibilize two different polymers, it might be sufficient to introduce some 4-vinylphenyl boronic acid units into both polymers; thus, formation of boronic anhydride units between the two modified polymers could bring about their compatibility. Figure 49 illustrates this hypothesis. This idea was very attractive mainly because two polymers could be compatibilized through covalent, yet reversible crosslinks. We have shown previously that the boronic anhydride linkages are easily broken in wet tetrahydrofuran.

We chose polystyrene and poly(methyl acrylate) as the polymers to be compatibilized through the formation of covalent reversible crosslinks. Copolymers of 4-vinylphenyl boronic acid and styrene, and of 4-vinylphenyl boronic acid and methyl acrylate were prepared by radical copolymerization of the respective monomers;

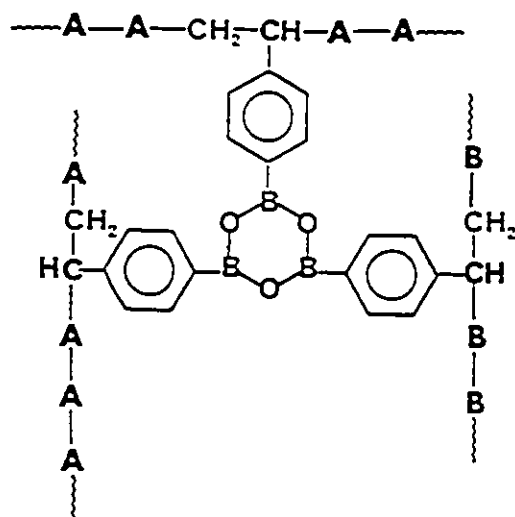
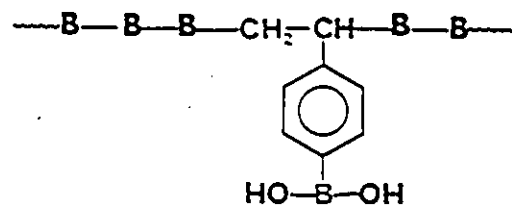
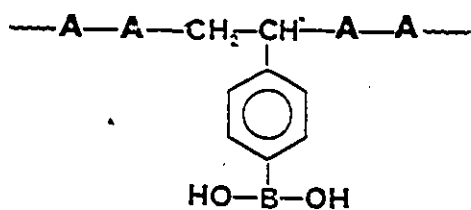


Figure 49. Structure of blends of polymers A and B for which compatibility may be achieved by introducing into both of them 4-vinylphenyl boronic acid units.

subsequently, the compatibility of blends of the "modified polymers" was tested by DSC and FTIR techniques. Table 21 shows the molecular weights and glass-transition temperatures of the various copolymers used in this study.

Our studies revealed once again that the method of sample preparation is of particular importance to obtain a compatible system from mixtures of copoly (4-vinylphenyl boronic acid-styrene) and copoly (4-vinylphenyl boronic acid-methyl acrylate). Indeed, several methods of sample preparation failed to yield compatible systems, while as will be seen later compatible blends can in fact be obtained.

In the first technique used in the preparation of the samples, solutions of the individual copolymers (ca. 1%, wt/v) in wet THF (2% water) are mixed in appropriate ratio (it should be noted once again that these 4-vinylphenyl boronic acid containing copolymers have a crosslinked structure under dry conditions). The solvent is then evaporated at atmospheric pressure until dry films are obtained. Final solvent removal is effected under vacuo. Figure 50 shows the DSC thermograms of blends of copoly (4-vinylphenyl boronic acid-styrene) (16.7 mol % boronic acid units) 1, with copoly (4-vinylphenyl boronic acid-methyl acrylate) (8.6 mol % boronic acid units) 3. Similarly, Figure 51 shows the DSC thermograms of blends of copolymers 2 and 4 prepared using the same method. The DSC thermograms that are given were obtained in a second

Table 21. Characteristics of the copolymers used in the study of the compatibilization of a polymer blend through covalent-crosslinks.

Copolymer #	Copolymer composition (mol %)		GPC molecular weight			
	Styrene	Methylacrylate 4-vinylphenyl boronic acid	Mn	Mw	Mw/Mn	Tg(°C)
1	83.3	16.7	25.1	73.7	2.9	138
2	91.4	8.6	19.9	49.6	2.5	120
3	91.4	8.6	9.0	40.5	4.5	25
4	94.7	5.3	10.1	40.9	4.1	25

* GPC Measurements (relative to polystyrene) were performed with wet THF (2% water) as solvent.

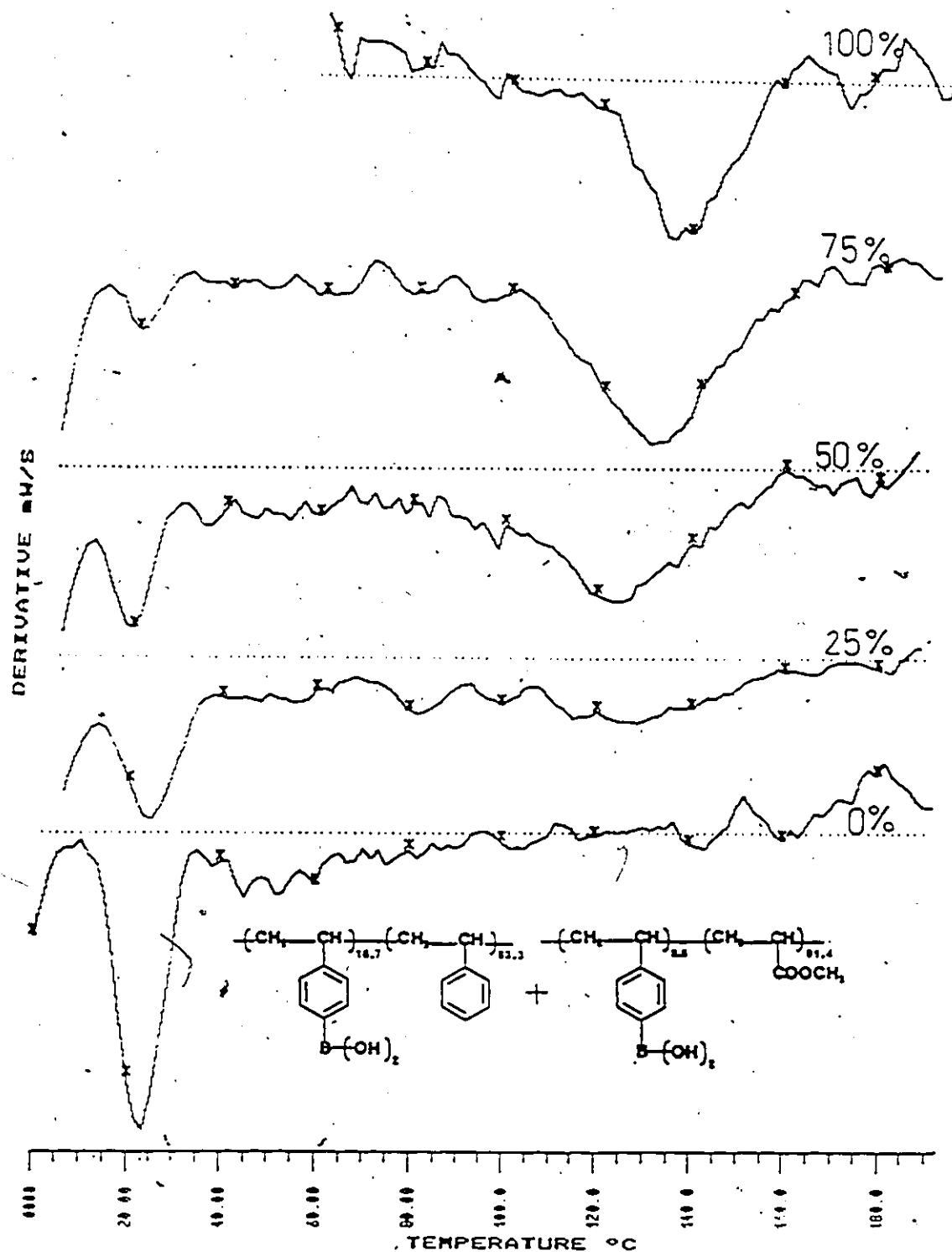


Figure 50. DSC thermograms of blends of copoly(4-vinylphenyl boronic acid-styrene) (16.7 mol % 4-vinylphenyl boronic acid) and copoly(4-vinylphenyl boronic acid-methylacrylate) (8.6 mol % 4-vinylphenyl boronic acid). The weight % of the styrene copolymer is given above each thermogram. Method of blend preparation: slow evaporation of THF.

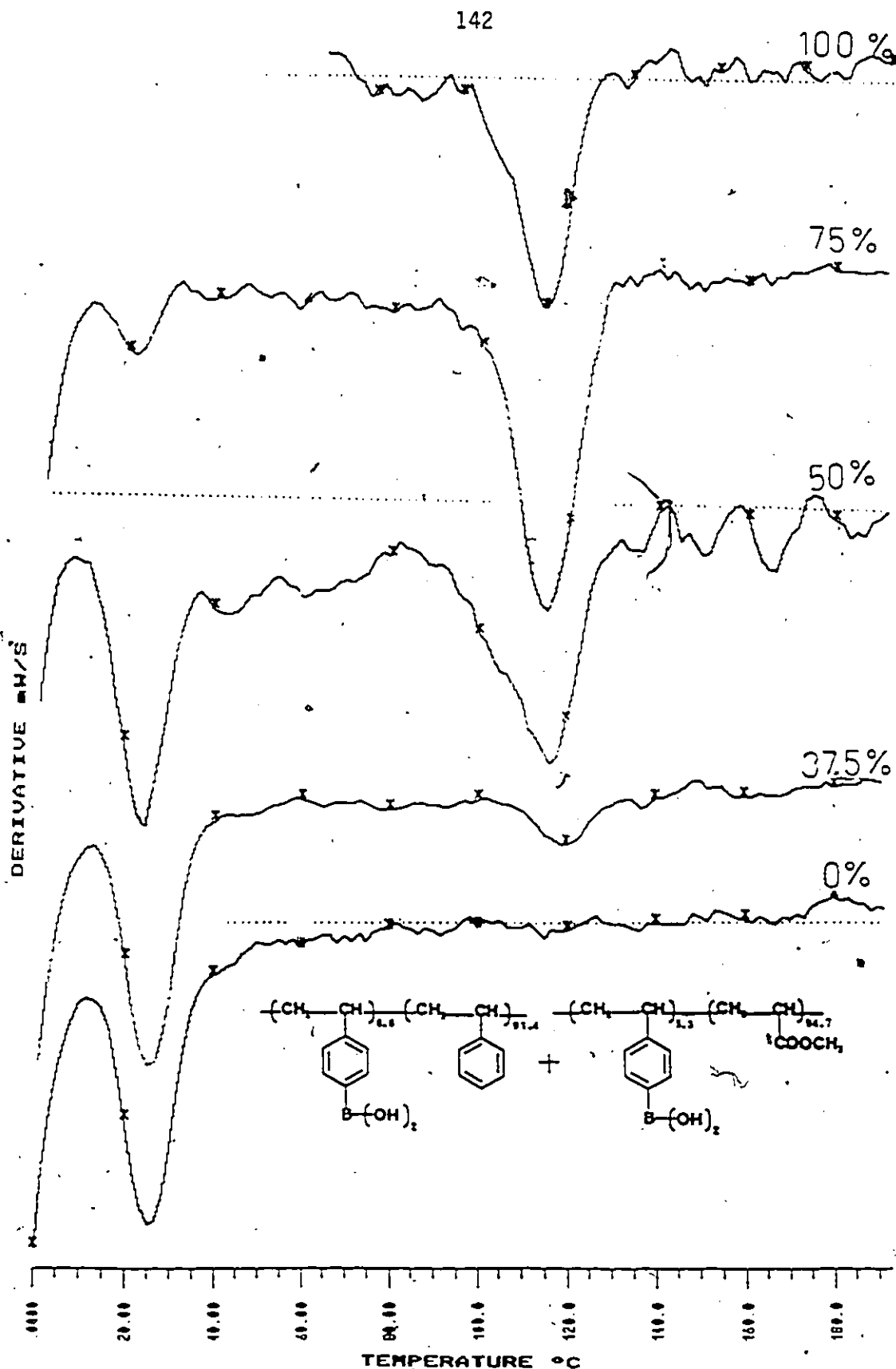


Figure 51. DSC thermograms of blends of copoly(4-vinylphenyl boronic acid-styrene) (8.6 mol % 4-vinylphenyl boronic acid) and copoly(4-vinylphenyl boronic acid-methylacrylate) (5.3 mol % 4-vinylphenyl boronic acid). The weight % of the styrene copolymer in the blend is given above each thermogram. Method of preparation of the blend: slow evaporation of THF.

heating scan at 20°C/min. Samples underwent a first heating scan to 200°C at 10°C/min and annealing for 10 min at 200°C. These DSC thermograms show that the blends are incompatible as two well distinguished glass-transition temperatures are obtained over the entire range of composition. At first these results were surprising, as interspecies crosslinking had not occurred but the polymers had self crosslinked. Each polymer in the blend exhibits the same T_g as that measured for the pure self-crosslinked polymer. FTIR spectra also indicate that the polymers in the blend are self-crosslinked. FTIR spectra show a very weak or almost null hydroxyl band for films of the blends cast onto sodium chloride discs. The lack of hydroxyl band indicates that most boronic acid units had converted to boronic anhydride units. Figure 52 shows the FTIR spectra of blends of copolymers 1 and 3 cast from THF solutions. The observed incompatibility may result from the fact that the boronic acid units dehydrate at the very end of the solvent evaporation stage when separation of the polymers in two different phases has already happened. Figure 53 illustrates the different steps of this process.

Thermogravimetric analyses of polymers and blends used in this study are reported in Table 22. The introduction of 4-vinylphenyl boronic acid units into polystyrene and poly (methyl acrylate) increases their thermal stability. Modified polystyrenes containing 16.7 and 8.6 mol % of 4-vinylphenyl boronic acid units, 1 and 2, start to decompose

Figure 52. FTIR spectra in the range 3800-650 cm^{-1} of blends of copoly(4-vinylphenyl boronic acid-styrene) (16.7 mol % 4-vinylphenyl boronic acid) and copoly(4-vinylphenyl boronic acid-methylacrylate) (8.6 mol % 4-vinylphenyl boronic acid). The weight % of the styrene copolymer is given above each spectrum. Films have been cast onto sodium chloride discs from THF solutions.

Homogeneous solution of copoly(4-vinylphenyl boronic acid-styrene)
and copoly(4-vinylphenyl boronic acid-methyl acrylate)

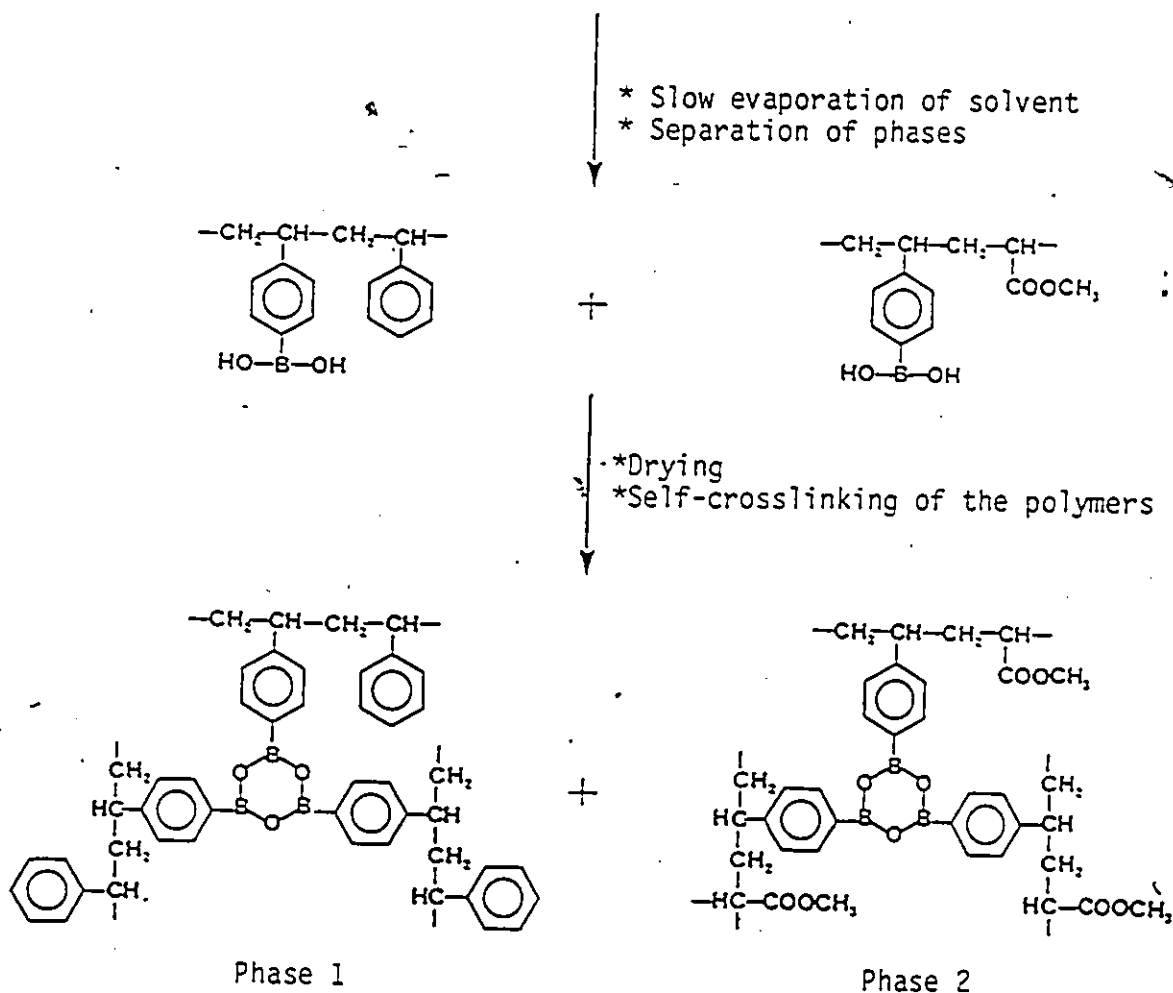


Figure 53. Process leading to the separation and incompatibility of blends of modified polystyrene and poly(methyl acrylate) containing 4-vinylphenyl boronic acid units. Method of blend preparation: slow evaporation of THF.

Table 22. Thermogravimetric analyses of polymers, copolymers and representative blends used in the study of polymer compatibilization through covalent-crosslinks ^a. (See Table 2)

Polymer #	Step decomposition temperatures (°C)			Loss weight %
	Start	Peak	End	
1	280	370	429	91.6
2	285	370	428	98.0
3	300	380	452	87
4	300	380	439	91
5 ^b	250	370	472	98
(1+3) ^c	300	379	442	91

a. All sample underwent a first heating scan to 200°C. In this first heating scan a loss of 2-3 wt % is observed corresponding to evaporation of residual solvent.

b. Poly(methylacrylate)

c. Blend 50:50 wt %

at ca. 285°C while pure polystyrene starts to decompose at ca. 260°C. Modified poly (methyl acrylate)s containing only 8.6 and 5.3 mol % of 4-vinylphenyl boronic acid units, 1 and 4, start to decompose at ca. 300°C which indicates a greater thermal stability compared to that of pure poly(methyl acrylate) which starts to decompose at ca. 250°C. The greater thermal stability of the 4-vinylphenyl boronic acid containing polymers can be attributed to the presence of the boronic anhydride linkages. Similarly, a blend of copolymers 1 and 3 starts to decompose at 300°C. Figure 54 shows the TGA curves for copolymers 1 and 3 and Figure 55 for poly(methyl acrylate) and a blend of copolymers 1 and 3.

It is known that phenyl boronic acid undergoes a rapid dehydration in non-polar solvents such as benzene and carbon tetrachloride while polar solvents tend to stabilize the boronic acid units. Therefore, the blends were next prepared using toluene as common solvent. It was expected that the boronic acid units would dehydrate promptly before complete evaporation of the solvent and therefore before separation of phases. Unfortunately, the self-crosslinked copolymers are insoluble in wet toluene, even after standing overnight, this probably due to the great stability of the boronic anhydride linkages in toluene. Consequently, solutions of the copolymers in toluene had to be prepared by an indirect procedure: first the copolymers were solubilized in wet THF, then toluene was added to

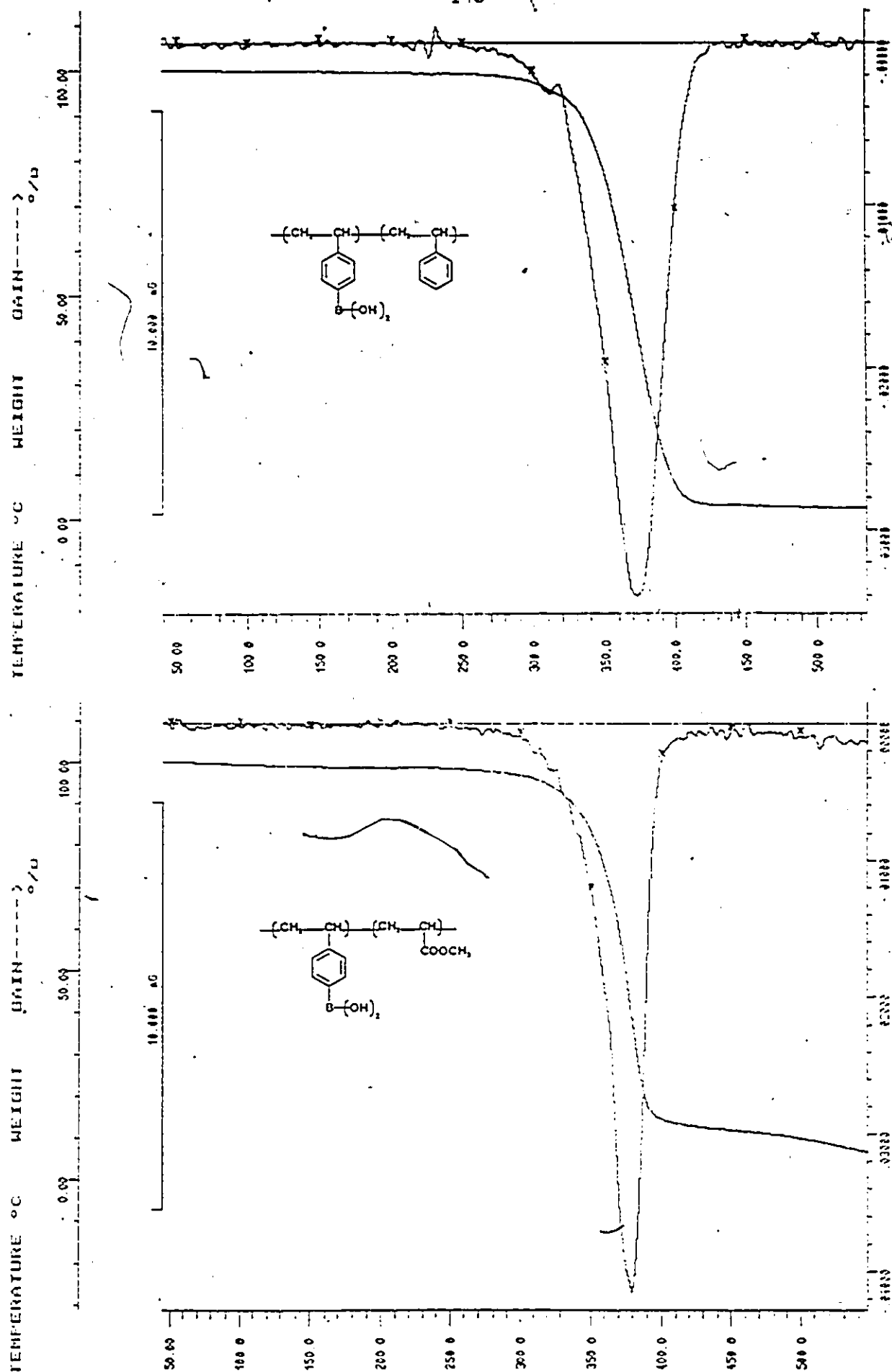
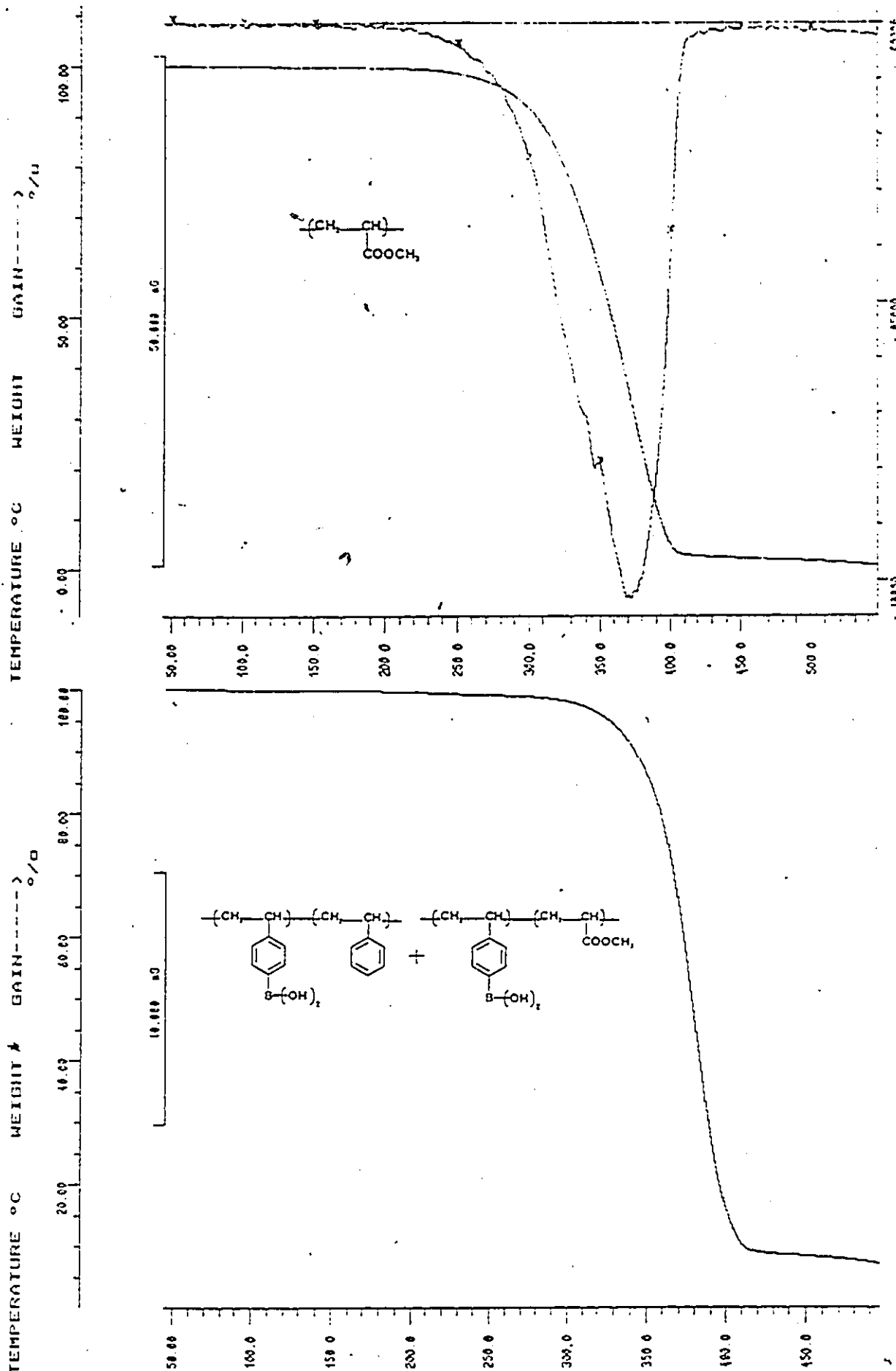


Figure 54. TGA curves of modified polystyrene and polymethylacrylate containing 16.7 and 8.6 mol % of 4-vinylphenyl boronic acid units respectively.



these solutions and finally, removal of the THF by distillation at atmospheric pressure afforded solutions of the copolymers in toluene. Toluene solutions of both copolymers 2 and 4 were then mixed in appropriate ratios and the solvent was allowed to evaporate slowly at atmospheric pressure until a dry film was obtained. Final solvent removal was then effected under vacuo. DSC studies of these blends unfortunately do reveal again a phase separated system. Figure 56 shows these DSC results and Figure 57 shows the FTIR spectra of films of blends of polymers 2 and 4 cast from toluene solutions onto sodium chloride discs. Other approaches to the preparation of compatible samples were also used in an effort to co-crosslink the polymers. For instance, the toluene solutions of the mixed polymers were refluxed through a soxhlet extractor charged with dry molecular sieves. In this way, it was hoped that thorough drying of the solvent could cause co-crosslinking of the polymers. However, boronic anhydride formation did not take place in solution since gelation was not observed. After refluxing the toluene solutions for 8 h and subsequent distillation, the obtained blends were dried under vacuum. DSC thermograms revealed again a phase separated system.

In one of our experiments, THF solutions of the mixed polymers were rotoevaporated at room temperature, and after complete evaporation of the THF solvent, the solid mixture was kept on the rotary evaporator for 2 h at 60°C. This

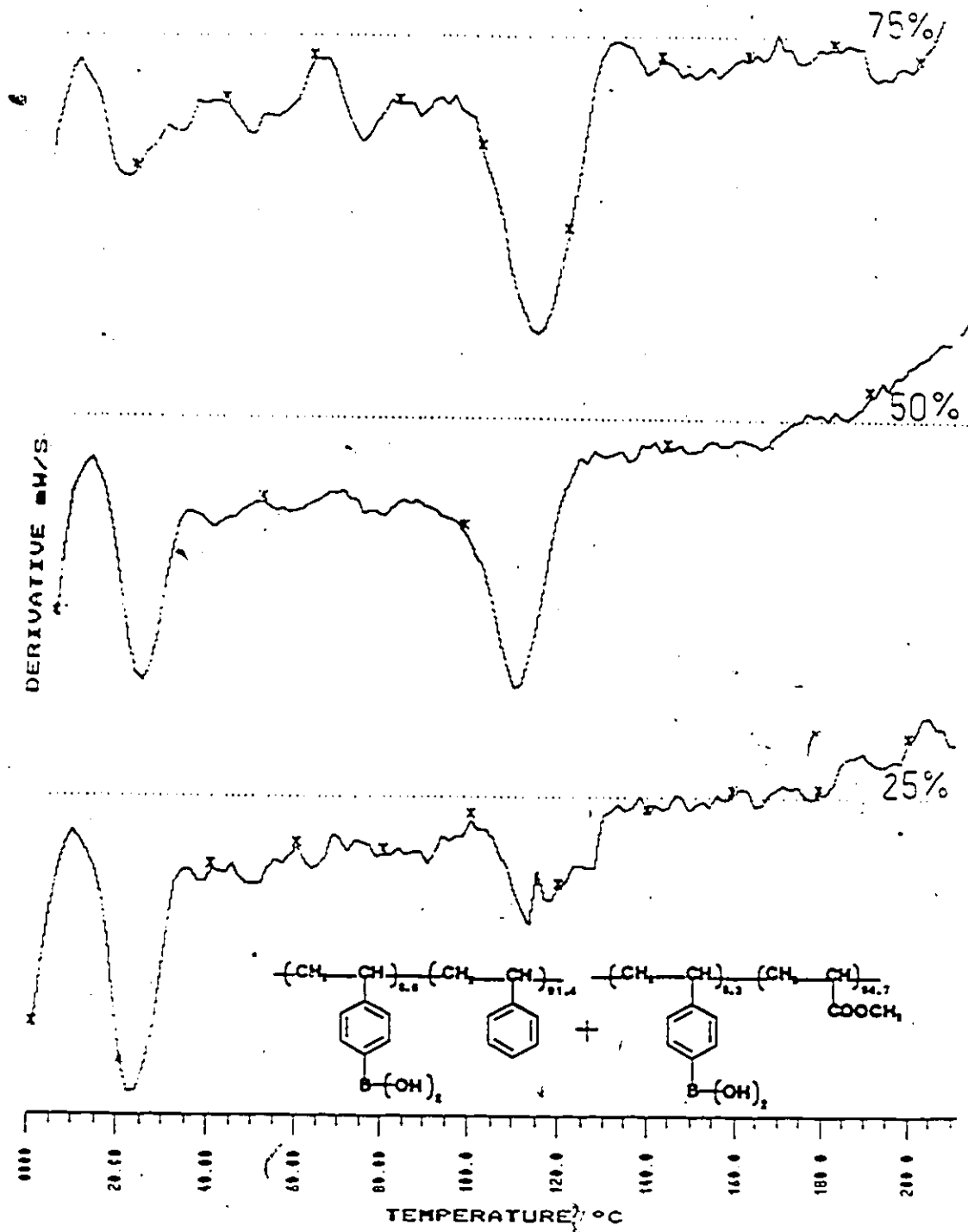


Figure 56. DSC thermograms of blends of copoly(4-vinylphenyl boronic acid-styrene) (8.6 mol % 4-vinylphenyl boronic acid) and copoly(4-vinylphenyl boronic acid-methylacrylate) (5.3 mol % 4-vinylphenyl boronic acid). The weight % of the styrene copolymer is given above each thermogram. Method of blend preparation: slow evaporation of toluene.

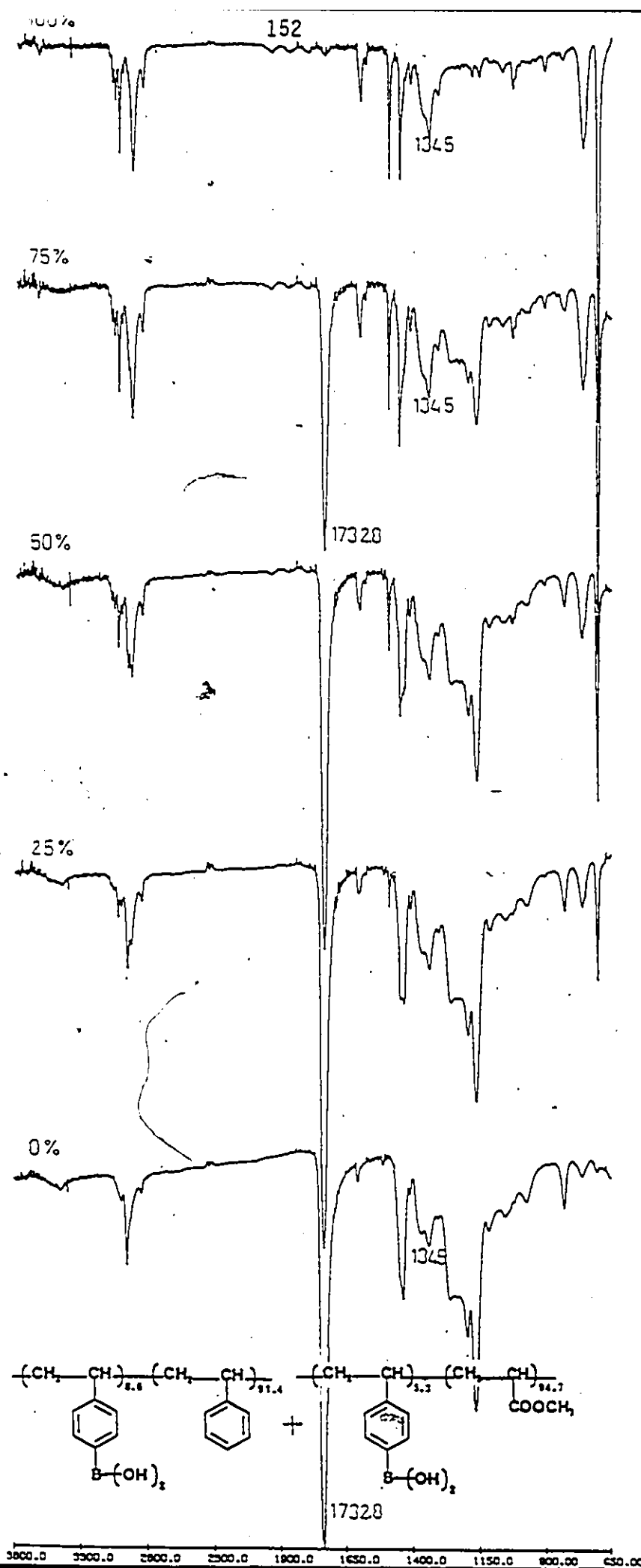


Figure 57. FTIR spectra of blends of modified polystyrene and polymethylacrylate containing 8.6 and 5.3 mol % of 4-vinylphenyl boronic acid units, respectively. The weight % of the styrene copolymer in the blend is given above each spectrum. Films have been cast onto sodium chloride discs from toluene solutions.

specific experiment turned out to be of particular importance as the DSC thermogram indicated the presence of three phases: a phase of self-crosslinked copoly (4-vinylphenyl boronic acid-styrene) (8.6 mol % boronic acid units) exhibiting a glass-transition temperature at 118°C, a second phase of self-crosslinked copoly (4-vinylphenyl boronic acid-methyl acrylate) (8.6 mol% boronic acid units) exhibiting a glass-transition temperature at 15°C, and a third phase exhibiting a glass-transition temperature at 40°C, this third phase is the result of the co-crosslinking of the two copolymers. Figure 58 shows the DSC thermogram of this blend. As has been said previously these results are very important because they indicate that the expected co-crosslinking mechanism can take place under certain conditions with formation of a third compatible phase of the two polymers. Analysis of the possible reasons that explain why through this particular method of sample preparation the polymers are able to co-crosslink and not through the other methods led us to withdraw the following conclusions: Slow evaporation of THF from the samples as was used in our very first approach did not lead to co-crosslinking because the polymers are given the possibility of separating into two phases due to the slowness of the solvent evaporation. Similar conclusions can be withdrawn with respect to the incompatibility of blends prepared by slow evaporation of toluene. On the other hand, we think that low concentration of the reactive boronic acid units.

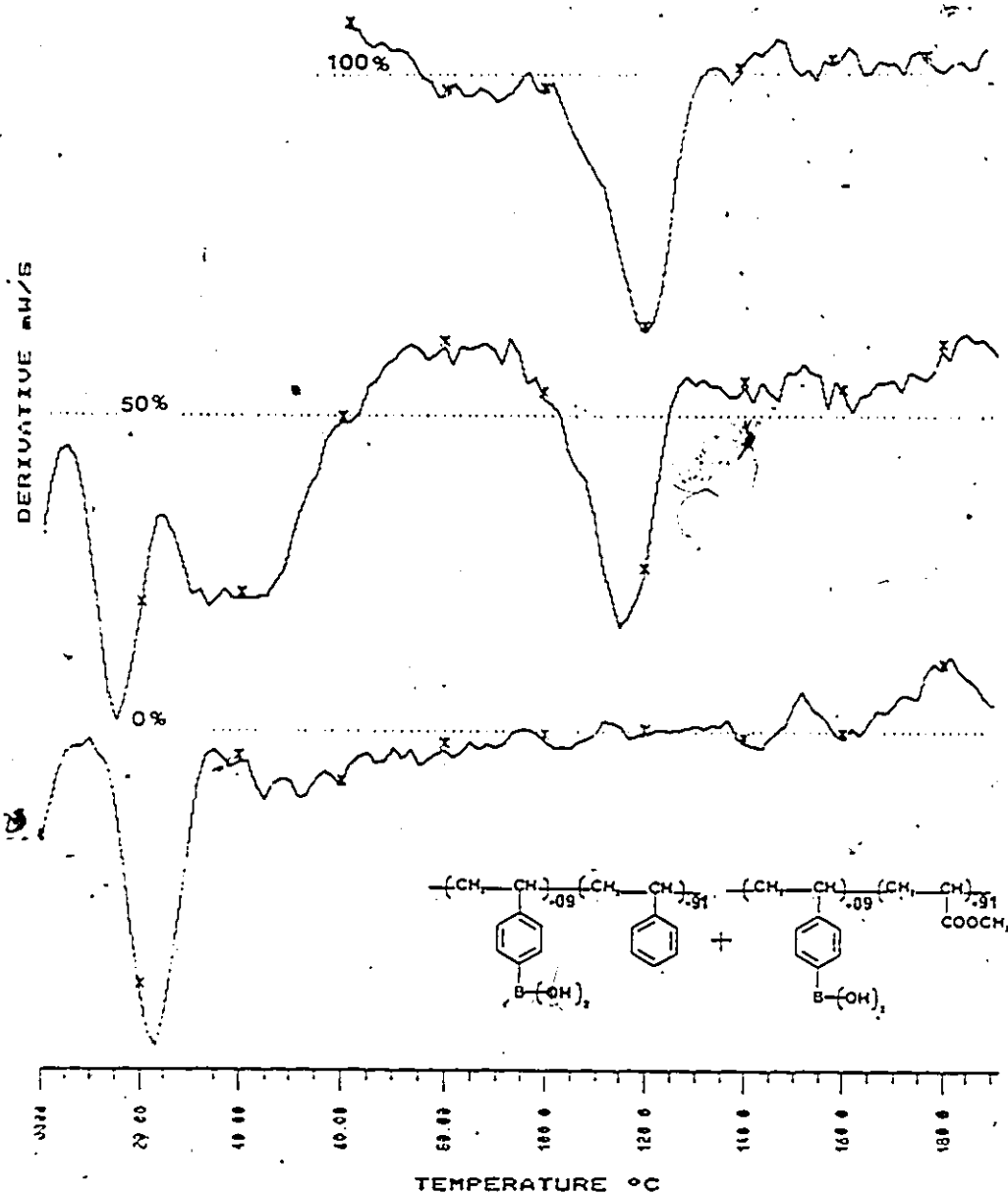


Figure 58. DSC thermograms of blends of modified polystyrene and polymethylacrylate containing both 8.6 mol % of 4-vinylphenyl boronic acid units. Method of blend preparation: rapid evaporation of THF and heating of the blend at 60 °C.

and their consequent inability of reaching each other was the reason for the failure of the approach where it was tried to dehydrate the boronic acid units in solution by refluxing the toluene solvent through a soxhlet charged with molecular sieves (it should be noted again that the boronic anhydride reaction is trimolecular). Finally, in that approach where a third compatible phase was observed, the polymers could not separate completely into two phases due to the rapid evaporation of the solvent, also heating a 60°C favored the boronic anhydride formation.

In view of these results we thought that complete compatibilization of this system, resulting in a blend consisting of only one homogeneous phase, might be achieved if the samples were prepared by melt mixing. Solutions of the mixed polymers in THF were therefore rotoevaporated and the resultant solid blends were then heated in the oven at 80°C for 2 h and then vacuum was applied and the heating was continued for another hour. DSC thermogram of a 50:50 wt % blend of copolymers 1 and 3 obtained by the melt mixing technique indicates that complete compatibilization was obtained, only one broad single glass-transition temperature is observed at 80°C and T_g for the individual polymers, 138 and 25°C are absent (Figure 59). FTIR for this blend (KBr pellet) (Figure 60) indicates that not all 4-vinylphenyl boronic acid units have converted to 4-vinylphenyl boronic anhydride units as there is a hydroxyl band at ca. 3500 cm^{-1} . This is in contrast with the

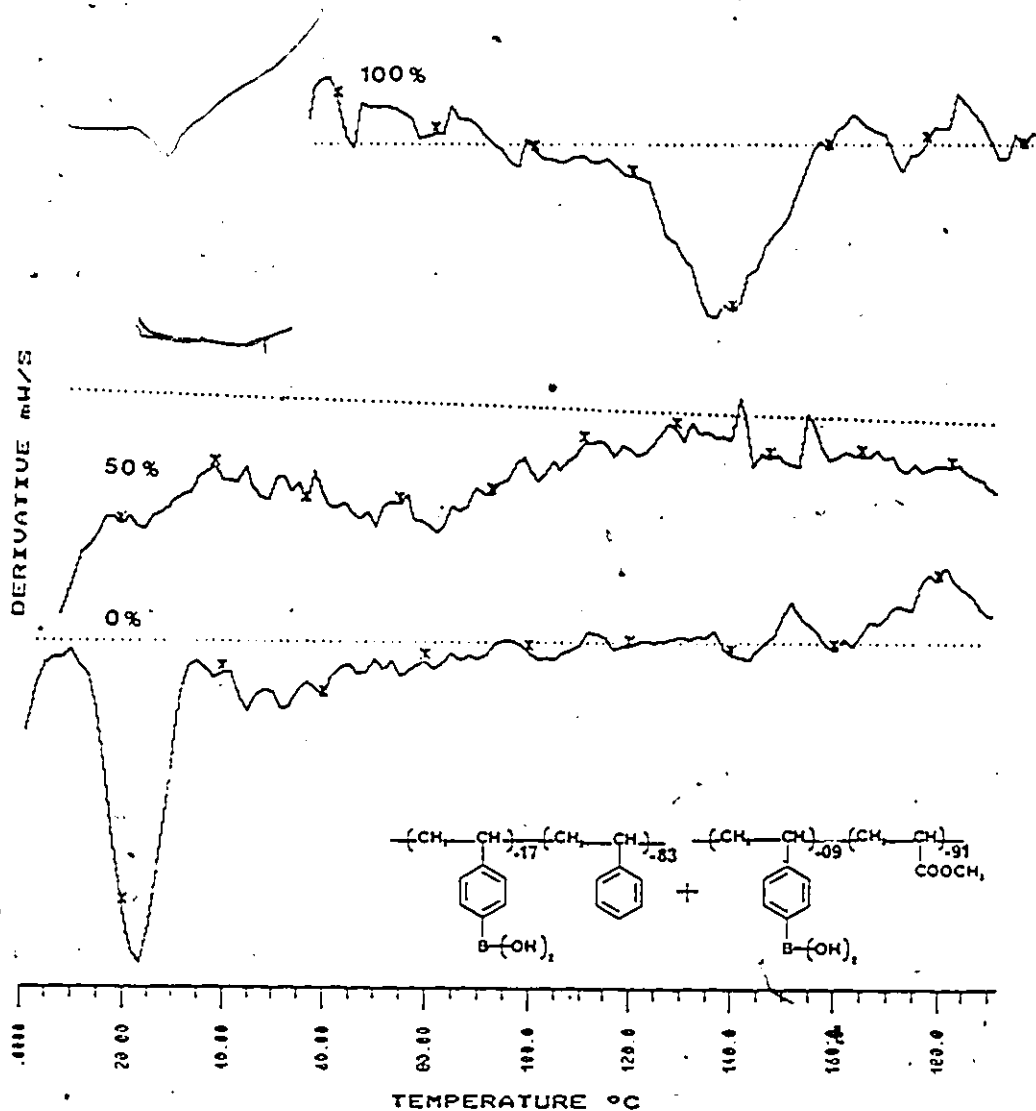


Figure 59. DSC thermogram of a 50:50 wt. % blend of modified polystyrene and polymethylacrylate containing 16.7 and 8.6 mol % of 4-vinylphenyl boronic acid units, respectively. Method of blend preparation: melt mixing at 80 °C.

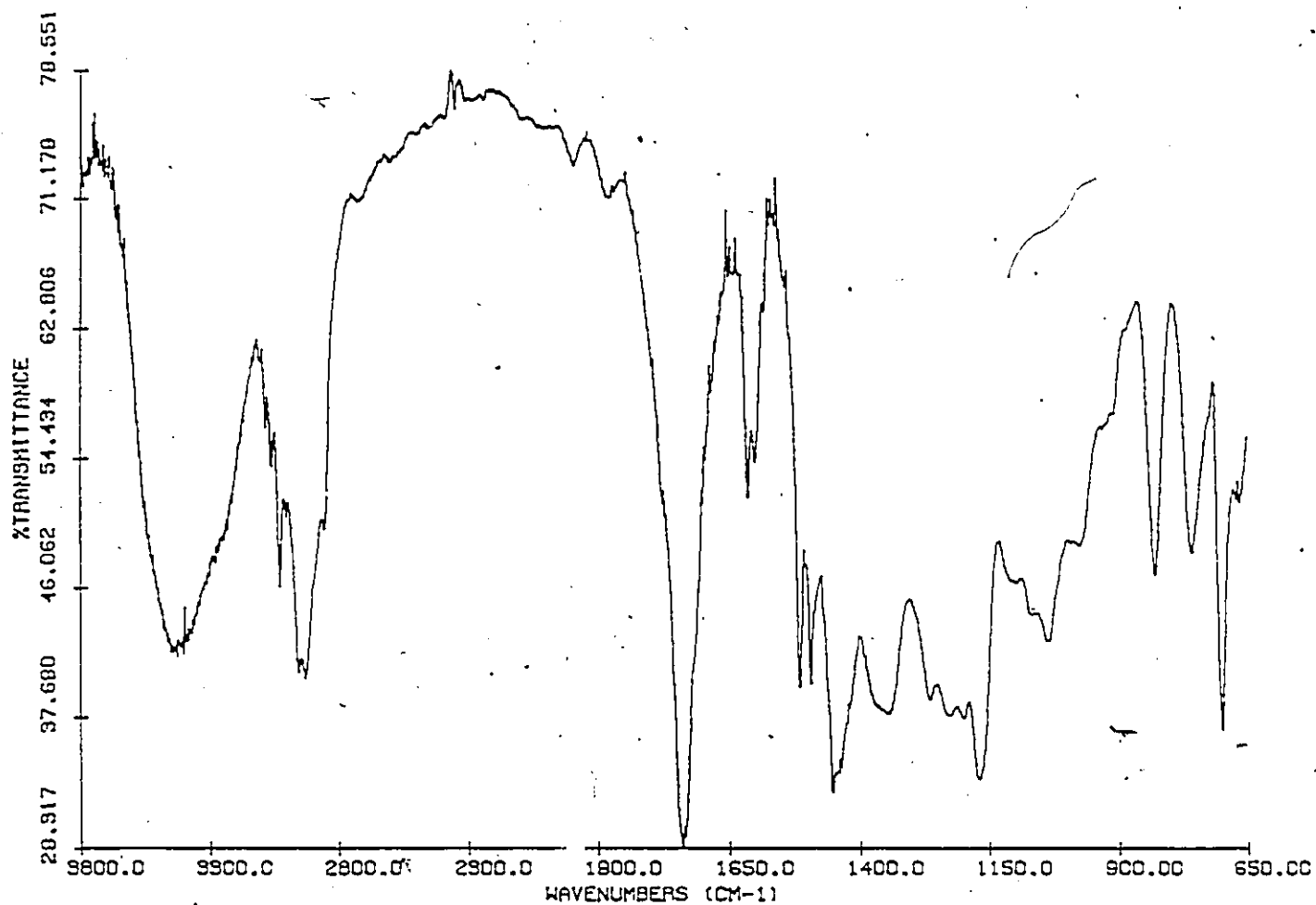


Figure 60. FTIR spectrum of a 50:50 wt. % blend prepared by melt mixing of modified polystyrene and polymethylacrylate containing 16.7 and 8.6 mol % of 4-vinylphenyl boronic acid units respectively.

infrared spectra of our incompatible systems for which it was observed that most 4-vinylphenyl boronic acid units had converted to boronic anhydride units during the self-crosslinking of individual polymers as indicated by the absence of hydroxyl band in the spectra. It seems obvious that self-crosslinking is more efficient than co-crosslinking a fact which is understandable if one considers that co-crosslinking involves the reaction of two incompatible polymers. Despite the fact that probably no more than 50% of the boronic acid units are co-crosslinking the system, the goal of full compatibilization was accomplished. It is seen that the compatibilization of polystyrene with poly(methyl acrylate) which are very dissimilar polymers and consequently very difficult to compatibilize has been achieved very efficiently as no large degrees of modification had to be introduced into the polymers: only 16.7 and 8.6 mol % of 4-vinylphenyl boronic acid units were introduced into polystyrene and poly(methyl acrylate) respectively.

1.2.5 Syntheses of polymers and copolymers used in the studies of compatibility of polymers through H-bonding and reversible covalent crosslinks.

Syntheses of polymers and copolymers containing styrene, 4-hydroxystyrene, 4-vinylpyridine, and 4-vinylbenzoic acid.

We used in our studies two poly (4-hydroxystyrene)s: poly (4-hydroxystyrene) obtained from Maruzen Oil Co. (resin PHM), and poly (4-hydroxystyrene) synthesized by a two-step procedure involving first the polymerization of 4-tert-butyloxycarbonyloxystyrene followed by removal of the t-butyloxycarbonyl groups by acidolysis. The polymer from Maruzen Oil Co. had a low molecular weight, $M_w=9500$, and $M_w/M_n=2.2$ and exhibited a glass-transition temperature at 138°C . The poly(4-hydroxystyrene) that we synthesized had a $M_w=31600$, and $M_w/M_n=1.9$ and exhibited a glass-transition temperature at 157°C .

The procedure employed for synthesizing poly(4-hydroxystyrene) was developed by Fréchet et al. [57] and it is the most efficient synthetic route to pure, unoxidized high molecular weight poly(4-hydroxystyrene). Direct radical polymerization of 4-hydroxystyrene is not a convenient route since it affords a low molecular weight polymer which contains a significant excess of oxygen with respect to the calculated amount. Moreover, Still and

Whitehead [58] have reported an anomalous behavior of 4-hydroxystyrene in its polymerization with AIBN as initiator. Thus, the viscosity of the polymer and the rate of polymerization remained constant, regardless of initiator concentration; in fact, a polymer of similar viscosity can be obtained in the absence of AIBN or even in the presence of 5% tert-butylcatechol. Still and Whitehead concluded that 4-hydroxystyrene polymerizes through a non-radical mechanism and suggested an ionic mechanism involving self-initiation to produce a low molecular weight polymer.

Copolymers of 4-hydroxystyrene and styrene were also obtained through the copolymerization of styrene and 4-tert-butyloxycarbonyloxystyrene and subsequent removal of the t-butyloxycarbonyl groups by acidolysis. These copolymers containing 50, 30, and 20 mol % of 4-hydroxystyrene had M_w of 31500, 34900 and 46000 and M_w/M_n of 1.9, 2.4 and 1.7 respectively, also exhibited glass-transition temperatures at 125, 120 and 118°C respectively.

Poly(4-vinylpyridine) and copolymers of 4-vinylpyridine and styrene were synthesized by radical polymerizations of the respective monomers. We used two poly(4-vinylpyridine)s in our studies. One was obtained by radical polymerization in toluene with AIBN as initiator, this polymer had a $M_w=46700$ and a glass-transition temperature of 155°C. The other was obtained by the same procedure but by using ethyl acetate as solvent.

This polymer had a $M_w=35700$ and a glass-transition temperature of 148°C . Copolymers containing 50 and 20 mol % of 4-vinylpyridine had M_w of 45200 and 42900 and M_w/M_n of 1.9 and 2.0 also they exhibited glass-transition temperatures at 118 and 114°C . Their composition corresponded to those of the copolymerization feed and could be verified by the $^1\text{H-NMR}$ integration data (Figure 61).

Poly(4-vinylbenzoic acid) and various copoly (4-vinylbenzoic acid-styrene) were obtained by radical polymerization in dimethylformamide using AIBN as initiator. Table 23 shows the copolymerization feed composition, polymer composition and yields that were obtained. The composition of the polymers was determined using $^1\text{H-NMR}$ integration data. Figures 62 and 63 show the $^1\text{H-NMR}$ spectra in the range 8-6 ppm for poly(4-vinylbenzoic acid) and its copolymers with styrene. Figure 64 show their FTIR spectra. These spectra are characterized by the presence of two carbonyl bands at 1730 and 1692 cm^{-1} corresponding to free and self-hydrogen bonded carbonyl groups. It is observed that in poly(4-vinylbenzoic acid) most carbonyl groups are self-hydrogen bonded while for the copolymers with styrene there is a decrease of self-hydrogen bonded carbonyl groups, this due to the presence of the intercalated styrene units.

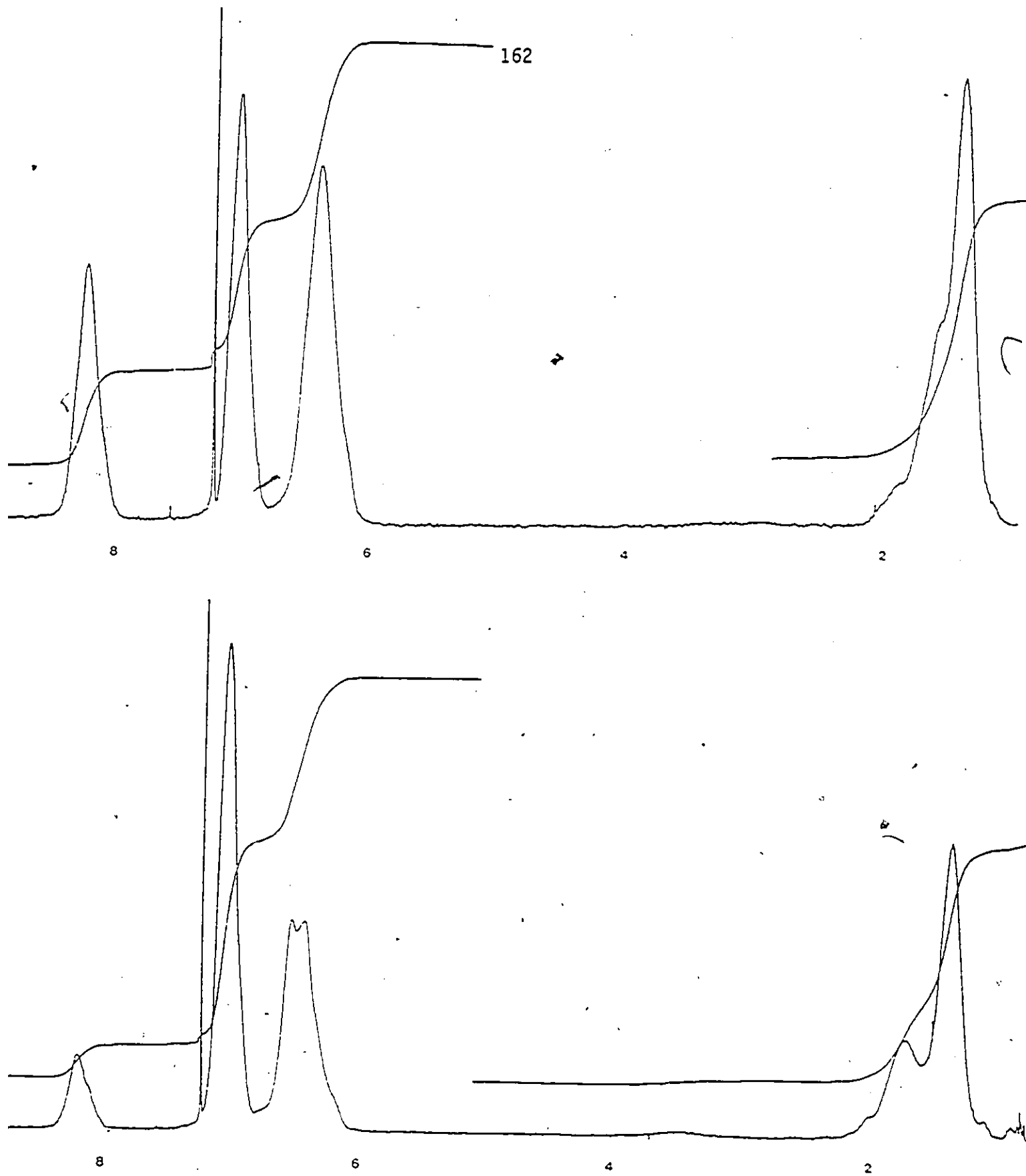


Figure 61. ^1H -NMR spectra of various copoly(4-vinylpyridine-styrene)s.

Table 23. Characteristics of the copolymerizations of 4-vinylbenzoic acid and styrene.

Feed composition (mol %)		Copolymer composition (mol %) ^a		Yield %
4-VBA	S	4-VBA	S	
100		100		85
50	50	56	44	79
30	70	40	60	77.5
20	80	26	74	71.6
10	90	15	85	58.4
5	95	11	89	47

a. Copolymer composition was determined using ¹H-NMR integration data.

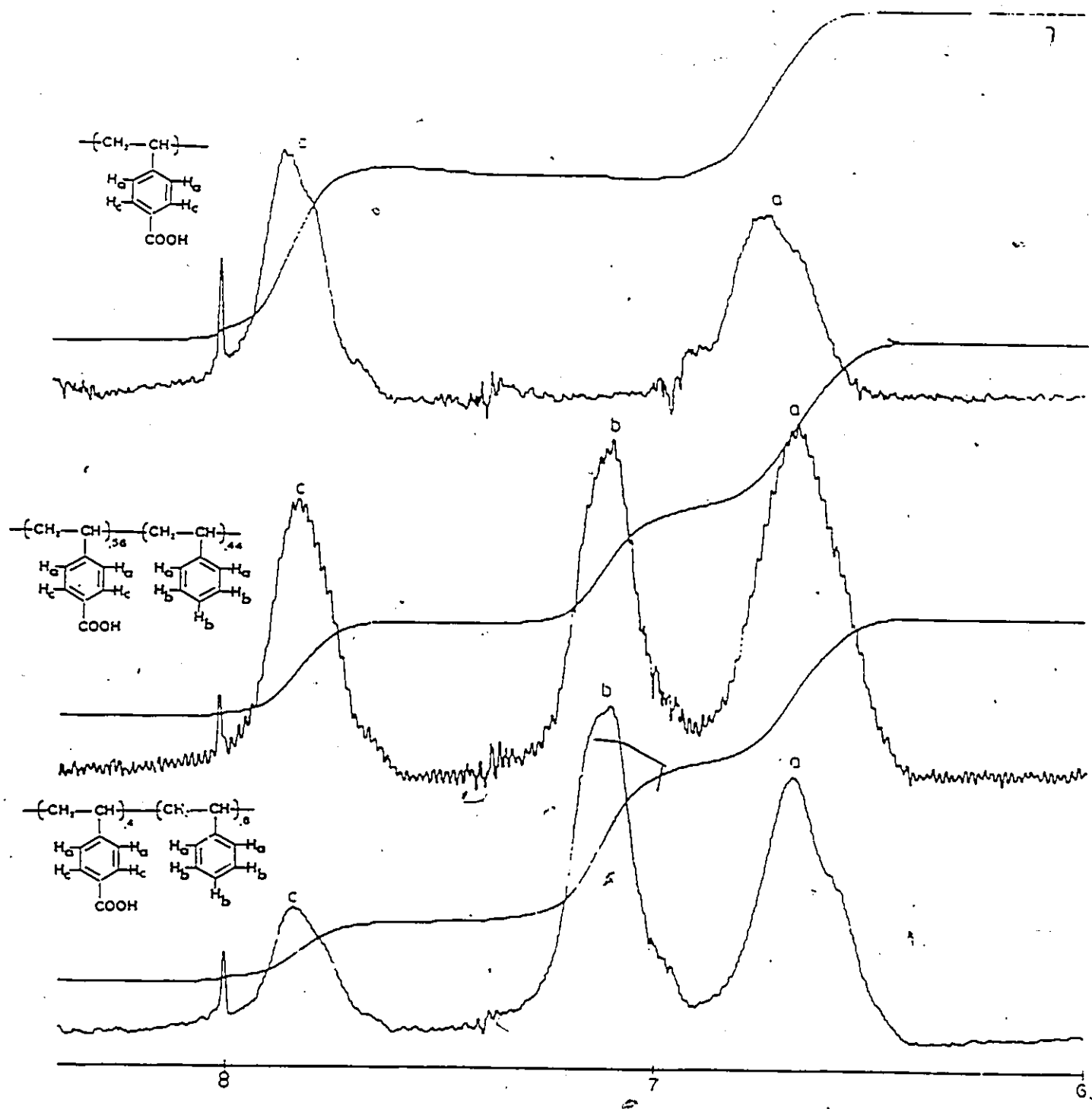


Figure 62. ^1H -NMR spectra of PVBA and copoly(VBA-S)s containing 56 and 40 mol % of VBA.

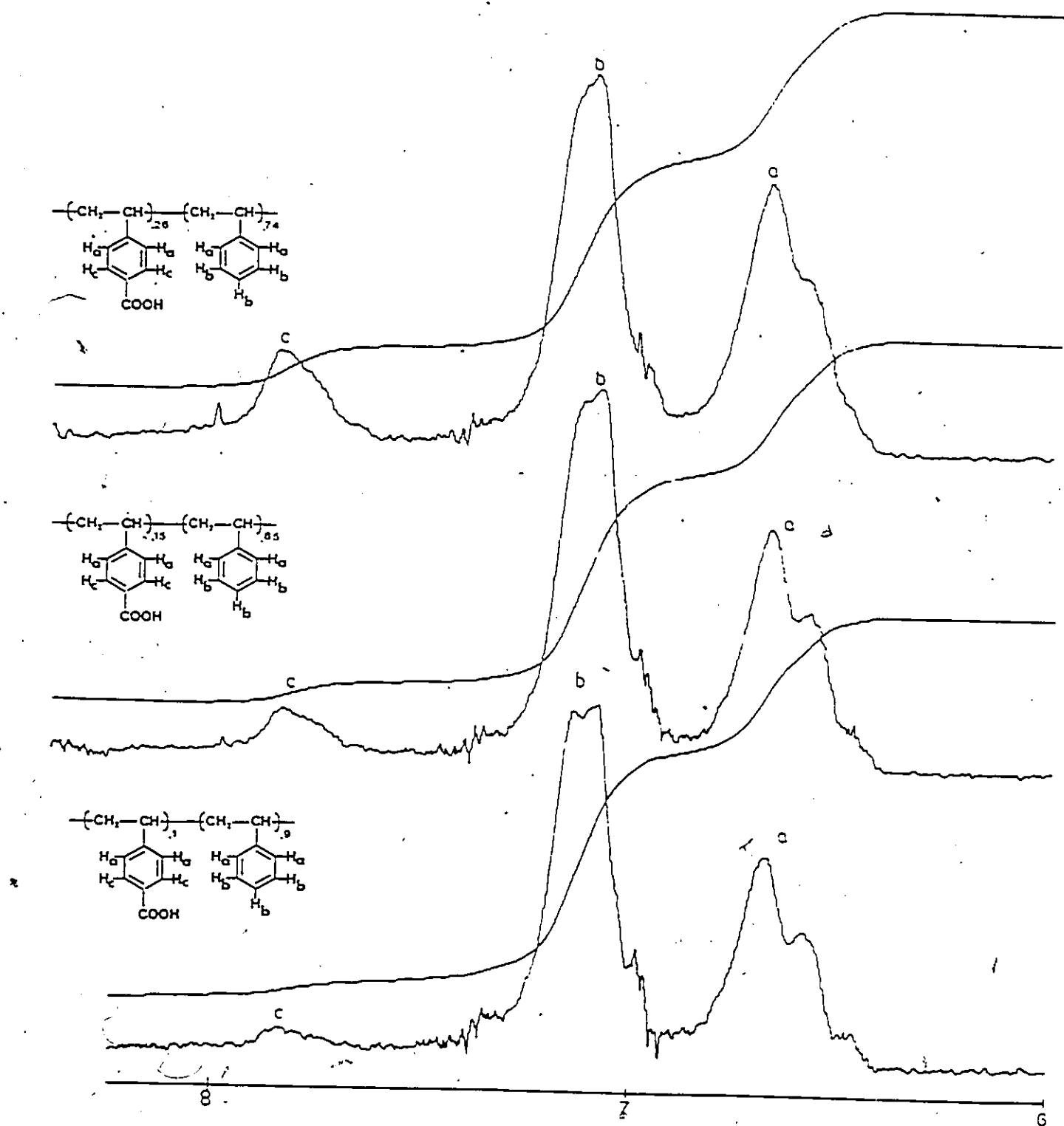


Figure 63. ^1H -NMR spectra of copoly(VBA-S)s containing 26, 15, and 10 mol % of VBA units.

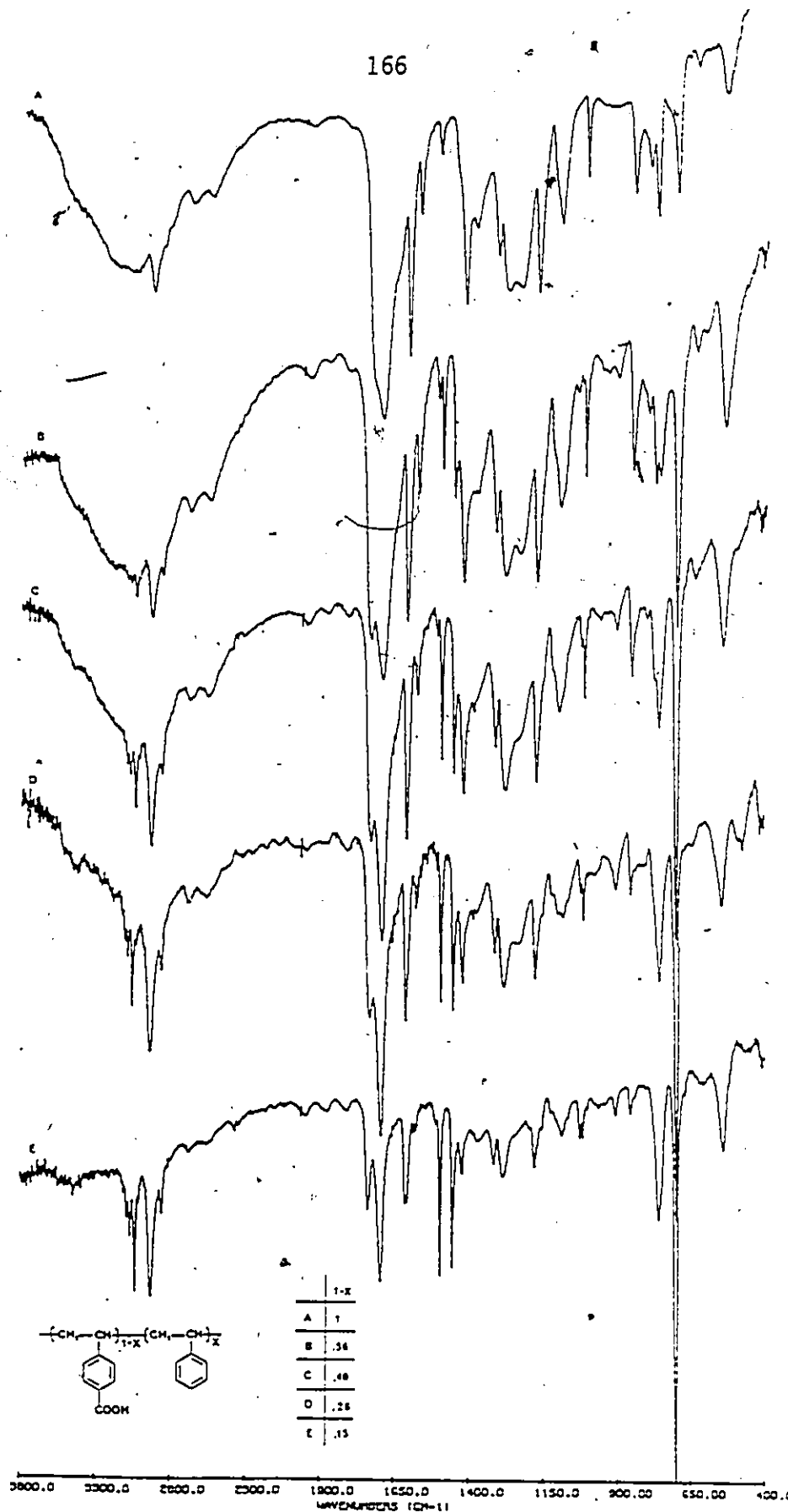


Figure 64. FTIR spectra in the region $3800-650 \text{ cm}^{-1}$ of PVBA and the various, copoly(VBA-S)s.

Synthesis of (4-vinylphenyl boronic acid-styrene) copolymers by chemical modification of polystyrene

This synthesis consists of the following steps: First, reaction of polystyrene with bromine in presence of thallic triacetate to obtain a partly brominated polystyrene. Second, lithiation of this brominated polystyrene with n-butyllithium followed by reaction with trimethyl borate, and hydrolysis lead to the desired (4-vinylphenyl boronic acid-styrene) copolymers. Figure 65 shows these different steps.

Electrophilic aromatic bromination of polystyrene in presence of thallic triacetate proceeded in high yields. Thus, the desired degree of modification is easily obtained by adjusting the amount of added bromine. Copolymers of 4-bromostyrene and styrene containing 3, 7, 14, 26 and 48 mol % of 4-bromostyrene were prepared using this method.

Lithiation of (4-bromostyrene-styrene) copolymer was performed in benzene at 60°C by addition of n-butyllithium to the polymer dissolved in benzene. Large excess of n-butyllithium is needed (ca. 10x) when a lower excess of n-butyllithium is used (ca. 5x), copolymers containing large amount of unreacted 4-bromostyrene units are obtained. However, we found that lithiation of soluble (4-bromostyrene-styrene) copolymers in benzene can be done only for copolymers containing a maximum of ca. 14 mol % of 4-bromostyrene units. If this lithiation is tried on

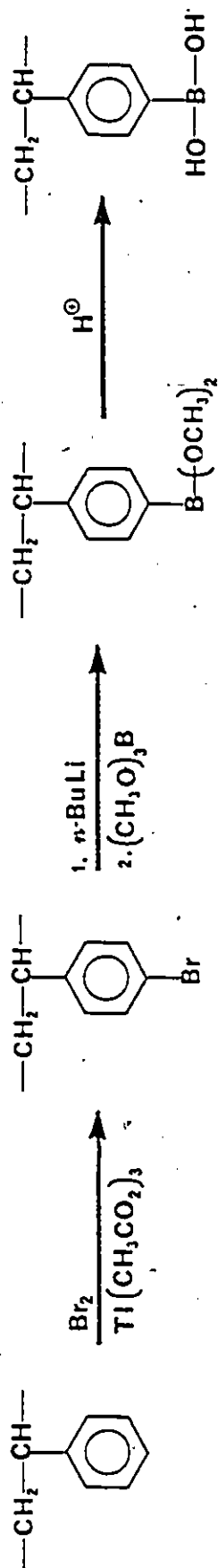


Figure 65. Steps in the preparation of copoly(4-vinylphenyl boronic acid-styrene)s by chemical modification of polystyrene.

copolymers containing a higher mol % of 4-bromostyrene units, the soluble copolymer crosslinks easily in the reaction medium. For instance, we could not lithiate a copolymer containing 26 mol % of 4-bromostyrene units using benzene as solvent. Crosslinking of the polymer takes place likely through reaction of lithiated units with unreacted 4-bromostyrene units (Wurtz reaction). We tried to avoid crosslinking of the polymer changing several reaction parameters, for instance, we tried to perform the lithiation at room temperature, however, lithiation of the copolymer with *n*-butyllithium in benzene does not take place even after 8 h of reaction unless the temperature is raised to 60°C. Also, we tried to perform the lithiation adding the solution of the polymer in benzene to the solution of *n*-butyllithium in benzene at 60°C, but crosslinking of the polymer still happened. This because lithiation of the polymer in benzene is slow even at 60°C; therefore, there are always lithiated units in presence of unreacted 4-bromostyrene units and the Wurtz reaction takes place. In conclusion, it was shown that lithiation of (4-bromostyrene-styrene) copolymers could be performed in benzene with *n*-butyllithium only if the mol % of 4-bromostyrene units in the copolymer is lower or equal to ca. 14 mol %.

Lithiations of (4-bromostyrene-styrene) copolymers containing high concentration of 4-bromostyrene units were performed in tetrahydrofuran at -40°C. Lithiation of the

polymer proceeds smoothly and no crosslinking is observed. It should be noted that it is always necessary to use a large excess of n-butyllithium.

Reaction of the lithiated polymer with trimethyl borate proceeds quantitatively. The lithiated polymer has to be added to the trimethyl borate instead of adding the trimethyl borate to the polymer. This prevents possible crosslinking of the polymer through reaction of two aromatic lithiated units with one mol of trimethyl borate where two of the methoxy groups of trimethyl borate are replaced.

These copolymers of 4-vinylphenyl boronic acid and styrene show a very interesting and important behavior. They crosslink upon drying, but a unique feature is that this covalent crosslinking is reversible. The crosslinking is due to the dehydration of the 4-vinylphenyl boronic acid units of the polymers to give 4-vinylphenyl boronic anhydride units (Figure 66). At the beginning, it was surprising and difficult to believe that this reaction was taking place, since as is shown in Figure 66, this is a trimolecular reaction, and therefore the probability of a three molecule encounter in the solid state cannot be very high especially if one considers that those reactive units are attached to a polymeric matrix. However, we believe that the reactive units may always remain in close proximity due to self-hydrogen bonding, this can explain

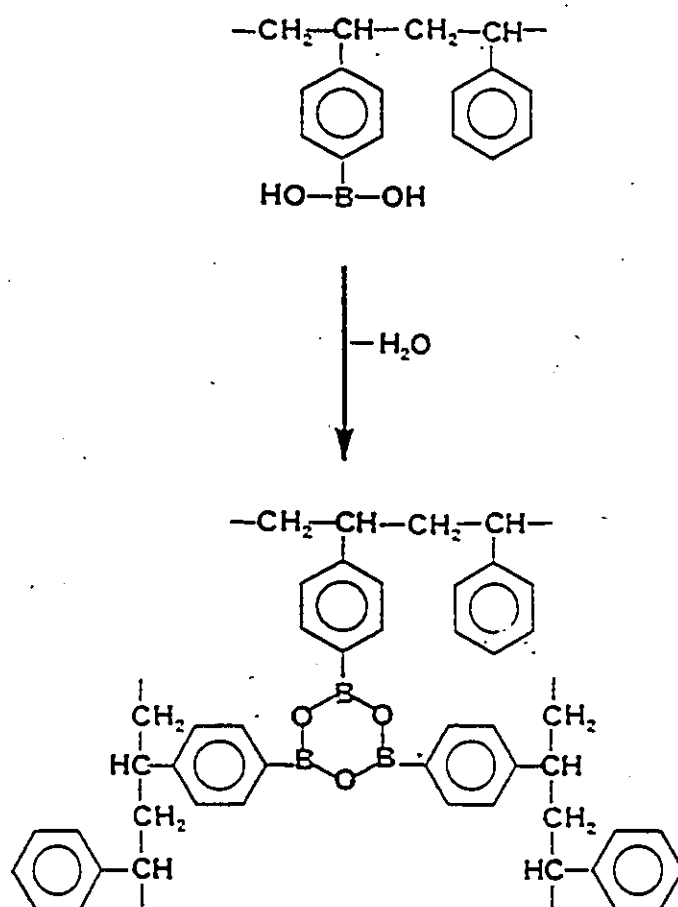


Figure 66. Structure of self-crosslinked copoly(4-vinylphenyl boronic acid-styrene)s

their prompt subsequent dehydration with formation of the boronic anhydride units.

The crosslinked polymers are easily solubilized in THF by adding a few drops of water. The anhydride bonds are broken and the polymer becomes soluble in THF, a polar solvent in which the boronic acid units are highly stabilized. On the other hand, the polymers are insoluble in wet benzene, solubilization is not observed even after overnight standing of the polymer in wet benzene. This due to the high stabilization of the boronic anhydride units in benzene.

Lennarz and Snyder [59] recognized this ability of 4-vinylphenyl boronic acid containing polymers to crosslink due to their ability to undergo dehydration to the boronic anhydride. They prepared poly(4-vinylphenyl boronic acid) by free radical initiated polymerization of 4-vinylphenyl boronic acid). Elemental analyses showed that ca. 50-75% of the boronic acid units converted to their anhydride units. These authors dried their sample of poly (4-vinylphenyl boronic acid) under very harsh conditions; e.g, at 100°C in vacuo over three days.

We found that anhydride formation takes place under very mild conditions; for example at room temperature in vacuo over a period of 48 h.

Elemental analyses of our copolymers of 4-vinylphenyl boronic acid and styrene prepared by chemical modification of polystyrene show that only few anhydride linkages are

crosslinking the polymers, since elemental analyses can be satisfied if it is assumed that the copolymer contains mainly boronic acid units. On the other hand, copolymers with similar compositions but obtained by radical copolymerization showed larger degrees of anhydride linkages, since elemental analyses could only be satisfied if it was assumed that the copolymer contained mainly boronic anhydride units.

B-O vibrational frequencies for both 4-vinylphenyl boronic acid and 4-vinylphenyl boronic anhydride are found in the same region near 1345 cm^{-1} . The presence of anhydride units can be recognized by the near disappearance of the hydroxyl bands at ca. 3575 cm^{-1} corresponding to $\text{B}(\text{OH})_2$ groups.

Synthesis of (4-vinylphenyl boronic acid-styrene) and (4-vinylphenyl boronic acid-methyl acrylate) copolymers by radical copolymerization of the respective monomers.

The synthesis of 4-vinylphenyl boronic acid was performed following the procedure of Cazes [60]. This author reported the preparation of 4-vinylphenyl boronic acid via the Grignard reaction. Methyl borate was added to a cooled solution (-78°C) of the Grignard reagent of p-bromostyrene in tetrahydrofuran. Subsequent hydrolysis lead to the desired 4-vinylphenyl boronic acid in 66%

yield. We employed p-chlorostyrene in our synthesis. Normant and Braun [61] have also reported on the preparation of 4-vinylphenyl boronic acid from p-chlorostyrene and have obtained a yield of 80%. However, Letsinger and Hamilton [62] obtained only 60% yield for the preparation of 4-vinylphenyl boronic acid from p-chlorostyrene. They also obtained a 38% yield of polymeric material. Thus, it appears that the extent of polymerization during the preparation of 4-vinylphenyl boronic acid via the Grignard reaction is governed by rather subtle variations in the reaction conditions and/or in the purity of the reagents. In our hands, the preparation of 4-vinylphenyl boronic acid from p-chlorostyrene only gave 50% yield. Also, $^1\text{H-NMR}$ of the air-dried crystals which are obtained after recrystallization in toluene show that the compound that is obtained consisted in a mixture of 60 mol % of 4-vinylphenyl boronic anhydride and 40 mol % of 4-vinylphenyl boronic acid. The crystals were then dried under vacuum for 48 h to obtain 100 mol % of 4-vinylphenyl boronic anhydride. Figure 67 shows the $^1\text{H-NMR}$ spectra for the mixture 4-vinylphenyl boronic anhydride/4-vinylphenyl boronic acid and for pure 4-vinylphenyl boronic anhydride.

Figure 68 shows MS spectrum of 4-vinylphenyl boronic anhydride. The molecular ion is clearly observed at $m/e = 390$. Assignment for several fragments are given in figure 68.

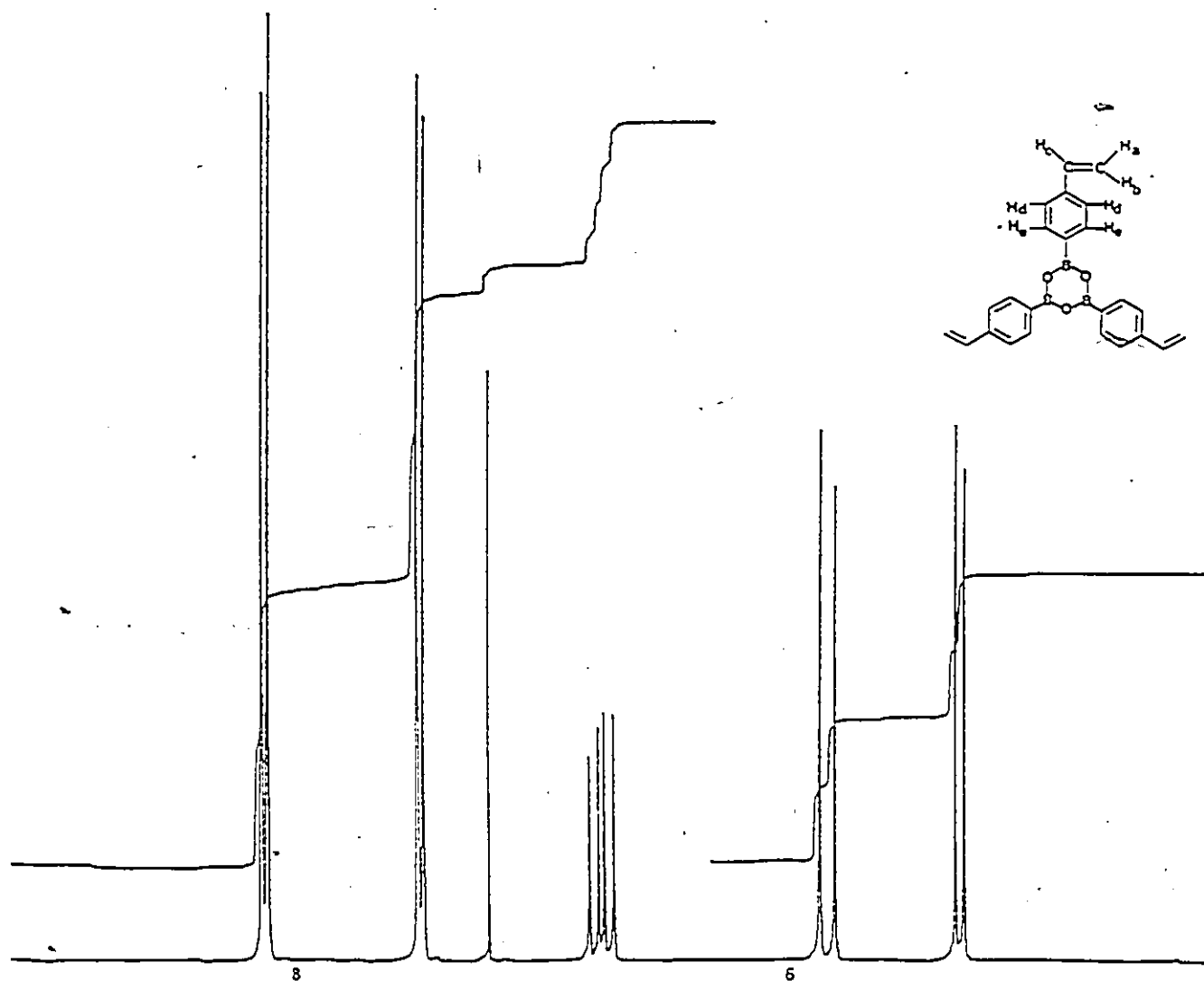
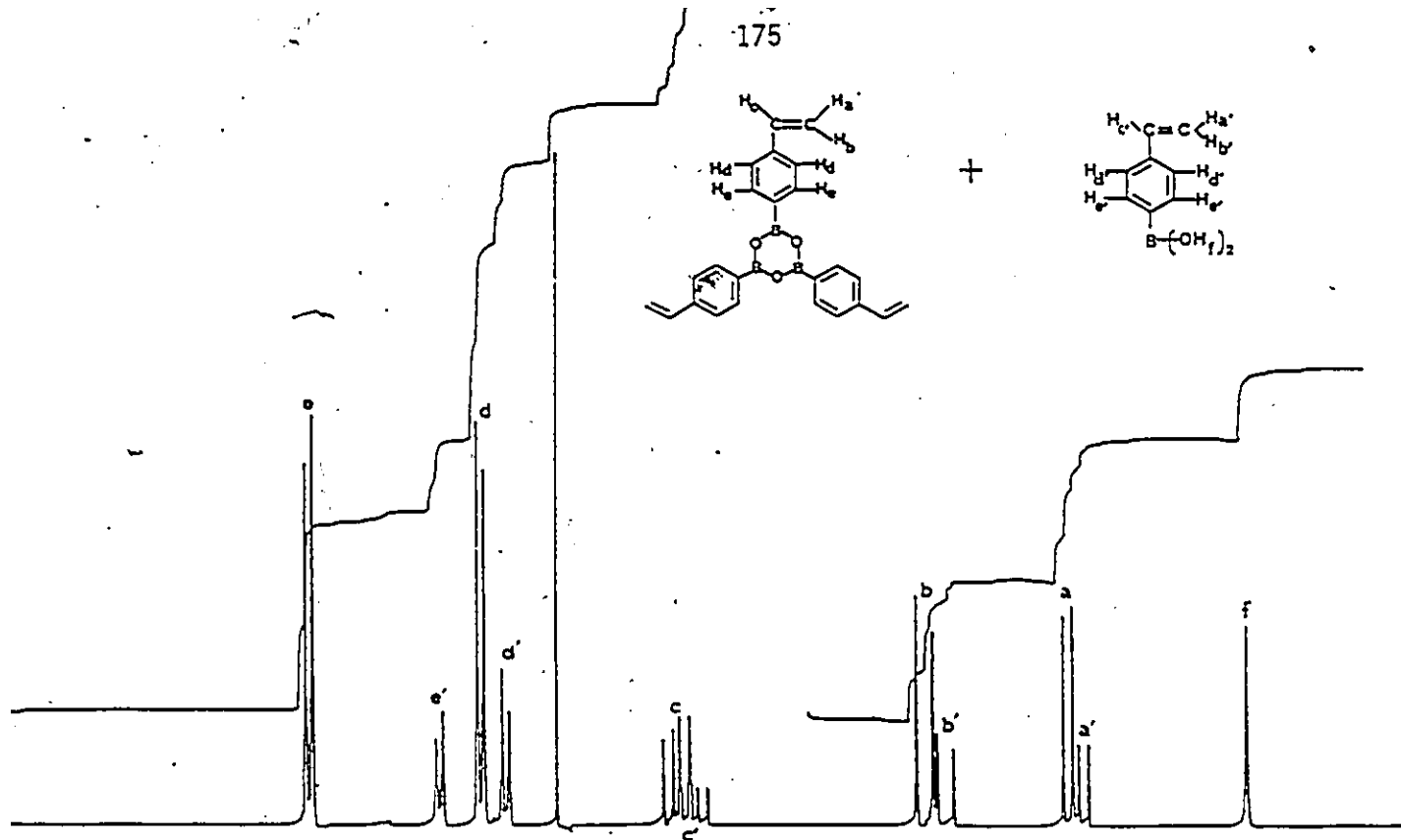


Figure 67. 1H -NMR of a 4-vinylphenyl boronic anhydride/4-vinylphenyl boronic acid mixture and of pure 4-vinylphenyl boronic anhydride.

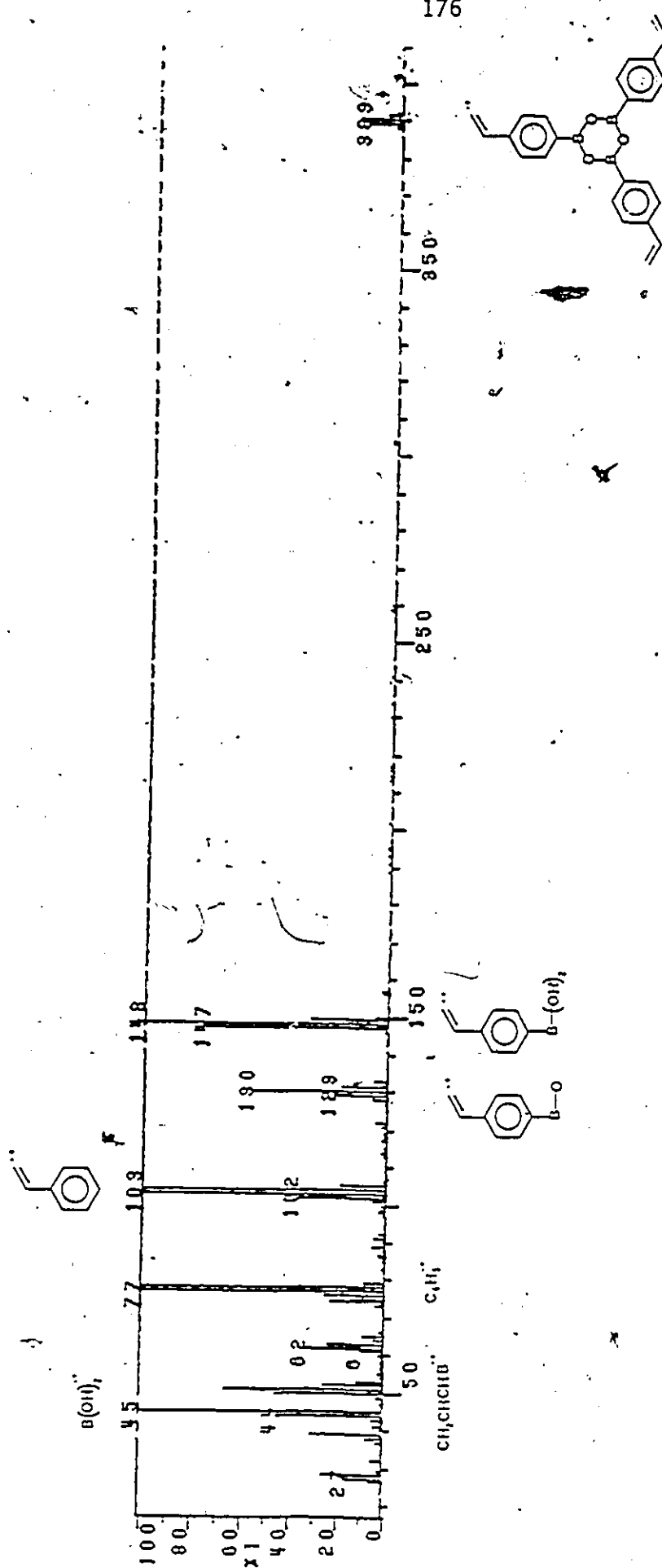


Figure 68. Mass spectrum of 4-vinylphenyl boronic anhydride.

Various copolymers of 4-vinylphenyl boronic acid and styrene and of 4-vinylphenyl boronic acid and methyl acrylate were prepared by radical copolymerization of the respective monomers. The copolymerizations were run in wet dimethylformamide in order to break the anhydride linkages of 4-vinylphenyl boronic anhydride which was a starting monomer for our copolymerizations. Copolymerizations were run to 100% conversion. However, the composition of our copolymers with styrene possessed a composition which was very different from that of the monomer feed. For instance, a feed copolymerization of 10 mol % of 4-vinylphenyl boronic acid and 90 mol % of styrene, afforded a copolymer containing 16.7% mol % of 4-vinylphenyl boronic acid and 83.3 mol % of styrene and the yield of the copolymerization with respect to the feed composition was 56%. On the other hand, the compositions of the 4-vinylphenyl boronic acid and methyl acrylate copolymers were very similar to the feed copolymerization composition.

Elemental analyses of all these copolymers showed that most of the boronic acid groups had converted to boronic anhydride groups, as well infrared spectra of the copolymers showed only very weak hydroxyl bands. Molecular weight measurements were taken after dissolving the copolymers in wet THF. GPC with polystyrene calibration showed the following results: (4-vinylphenyl boronic acid-styrene) copolymers had Mw between 50000 and 74000 with Mw/Mn between 2.5 and 3 and (4-vinylphenyl boronic acid-

methacrylate) copolymers had M_w between 40000 and 41000 with M_w/M_n between 4.0 and 4.5. Radical polymerizations are characterized in many instances by a molecular weight distribution of 2. It is seen that our copolymers possess rather a broad molecular distribution and this probably reflects the very different polymerization reactivity ratios that the monomers may possess. For instance, M. Hartmann et al [63] reported 0.28 and 0.83 as copolymerization reactivity ratios of 4-vinylphenyl boronic acid and styrene respectively. The radical copolymerization of the monomers was performed in a dioxane: water, 95:5 v/v, mixture as solvent and AIBN as initiator.

The glass-transition temperatures of the copolymers of 4-vinylphenyl boronic acid and styrene containing 16.7 and 8.6 mol % of 4-vinylphenyl boronic acid units were 138 and 120°C respectively; these high glass-transition temperatures are due to the presence of the crosslinking anhydride linkages which reduce the mobility of the polymer. The glass-transition temperature of polystyrene is ca. 100°C. It is seen that incorporation of 16.7 mol % of 4-vinylphenyl boronic acid units increases the glass-transition temperature to 138°C. Similarly, incorporation of 8.6 mol % of 4-vinylphenyl boronic acid into poly(methyl acrylate) increases the glass-transition temperatures from 0°C, [the glass-transition of poly(methyl acrylate)], to 25°C. A copolymer containing 5.3 mol % of 4-vinylphenyl

boronic acid units also exhibits a Tg of 25°C. This was unexpected since the Tg should be proportional to the amount of incorporated boronic acid units, as was seen for the styrene copolymers. We think that the very close composition of the methyl acrylate copolymers and probably different degrees of anhydride formation are responsible for the identical glass-transition temperatures which were observed.

1.3 CONCLUSIONS

Poly(4-vinylpyridine) is shown to be miscible over the entire range of composition with poly(4-hydroxystyrene) and modified polystyrene containing 50 mol % of 4-hydroxystyrene. On the other hand, when it is blended with modified polystyrenes containing 30 and 20 mol % of 4-hydroxystyrene, miscibility is observed only for those mixtures rich in poly (4-vinylpyridine). For blends of poly(4-vinylpyridine) and poly(4hydroxystyrene) the maximum Tg deviation from calculated weight-average Tg values occurs for that blend which contains a stoichiometric ratio of interacting units. In contrast, for blends of poly(4-vinylpyridine) and copoly (4-hydroxystyrene-styrene) (50 mol % 4-hydroxystyrene), maximum Tg deviation does not occur for a stoichiometric blend of interacting units. Instead a broad maximum in the curve Tg versus composition is seen for blends which contain ratios of basic (pyridine) units to acidic (phenol) units between 2 and 1.4. It appears that an excess of basic units is needed to attain the maximum interaction between both polymers; this is likely to be due to the fact that not all pyridine groups are able to complex with the phenolic units probably because of the presence of the intercalated styrene units.

Similarly, poly(4-hydroxystyrene) is shown to be miscible with a modified polystyrene containing 50 mol % of 4-vinylpyridine units. For this system, maximum Tg

deviation is observed for blends containing a ratio of acidic to basic units of about 2. It is found that an excess of acidic units is required to achieve maximum interaction. Once again this is probably due to the inability of all phenolic units to complex. For blends of poly (4-hydroxystyrene) and copoly (4-vinylpyridine-styrene) (20 mol % 4-vinylpyridine), miscibility is observed only for those mixtures rich in poly(4-hydroxystyrene).

Poly(4-vinylpyridine) is shown to be miscible over the entire range of composition with poly(4-vinylbenzoic acid) and modified polystyrene containing 40 mol% of 4-vinylbenzoic acid units. On the other hand, when it is blended with modified polystyrene containing 26 mol% of 4-vinylbenzoic acid units, immiscibility is observed over the entire range of composition. For blends of poly(4-vinylpyridine) and poly(4-vinylbenzoic acid) the maximum Tg deviation occurs for that blend which contains stoichiometric ratio of interacting units while for the blends of poly(4-vinylpyridine) and copoly(4-vinylbenzoic acid-styrene) (40 mol % 4-vinylbenzoic acid) maximum Tg deviation occurs for blends containing a ratio of basic to acid units of about 2.5, that is, an excess of basic units is required to achieve maximum interaction.

In order to compatibilize poly(4-vinylpyridine) or poly (4-hydroxystyrene) with polystyrene, a rather high percentage of complementary units (acidic or basic) must be

incorporated into the polystyrene. Similar percentages of acidic units regardless their acidic strength have to be introduced into polystyrene in order to cause compatibility with poly(4-vinylpyridine). The enthalpy of formation for the phenol-pyridine complex determined by spectroscopic methods as reported in several papers [54,64, 65, 66] ranges from -5 to -6.5 kcal. mol⁻¹ while that of the benzoic acid-pyridine complex is significantly higher: -10.6 kcal mol⁻¹ [67,68]. In spite of this large difference in enthalpy of formation, similar percentages of 4-hydroxystyrene or 4-vinylbenzoic acid have to be introduced into polystyrene in order to obtain compatibility with poly(4-vinylpyridine). It is shown that the increase in the strength of the H-bonding interaction does not necessarily improve the compatibility of the system, this is due to the fact that functional units capable of interacting through H-bondings are also capable of self-complexation. Indeed, when introducing 4-vinylbenzoic acid units instead of 4-hydroxystyrene units into polystyrene, the strengths of the acid self-complexation and the acid-base complexation are increased concurrently.

The Kwei equation is shown to be most appropriate empirical equations to describe the dependence between the glass-transition temperature of the miscible blends and their composition. The values of the k and q parameters in the Kwei equation are as follows:

PVP/PHS blends: $k = 0.005$, $q = 219$

PVP/copoly (HS-S) (50 mol % HS) blends: $k = 0.077$, $q = 209$

PHS/copoly (VP-S) (50 mol % VP) blends: $k = 0.095$, $q = 210$

It is shown that for systems with the same H-bonding interactions, q values of the same magnitude are obtained.

For blends containing 4-vinylbenzoic acid units:

PVP/PVBA blends : $k = 0.353$ $q = 229.6$

PVP/copoly (VBA-S) (40 mol % VBA) blends: $k = 0.47$ $q = 211$

It is shown that for the system PVP/PVBA where the H-bonding interactions are stronger, a higher value of q is obtained, however, this value is not very different from those obtained before. This is due to the fact that the q values obtained are the sum of all types of interactions, self-association and intermolecular association. The q value obtained for PVP/PVBA system which is not very different from the q value obtained for PVP/PHS system indicates the incorporation of the PVBA/PVBA self-association which is stronger than PHS/PHS self-association. It is shown that total strength of H-bonding interactions within the systems is about the same. This explains why similar percentages of 4-hydroxystyrene or 4-vinylbenzoic acid have to be introduced into polystyrene in order to obtain compatibility with poly(4-vinylpyridine). The q value obtained for PVP/copoly (VBA-S) (40 mol % VBA) which is significantly lower than expected indicates the incorporation of large number of acid-acid self-complexations.

It is also shown that FTIR spectroscopy is a powerful tool to detect specific interactions within a polymer blend as is shown for PVP/PHS system which exhibits a new O-H band at 3127 cm^{-1} characteristic of the 4-vinylpyridine-4-hydroxystyrene complex. Also, miscible systems of PVP with PVBA and copoly. (VBA-S) (40 mol % VBA) exhibit new O-H bands at ca. 2488 and 1937 cm^{-1} and a new C=O band at 1703 cm^{-1} characteristic of 4-vinylpyridine-4-vinylbenzoic acid complex, while these bands are absent in immiscible blends of PVP with copolymers of 4-vinylbenzoic acid and styrene containing 26 and 15 mol % of 4-vinylbenzoic acid units.

Finally, it is shown that compatibility between two polymers can be achieved by introducing 4-vinylphenyl boronic acid units into both. The compatibility is due to the formation of boronic anhydride linkages. The reversibility of these covalent boronic anhydride linkages makes this system very attractive.

1.4 EXPERIMENTAL

1.4.1 Synthesis of polymers and copolymers used in the study of polymer compatibilization through H-bonding interactions.

1.4.1.1 Synthesis of poly(4-hydroxystyrene).

Two poly(4-hydroxystyrene)s were used in our studies: For our studies on compatibilization of poly(4-vinylpyridine) with polystyrene, we used poly(4-hydroxystyrene) obtained from Maruzen Oil Co. (resin PHM), this was purified by reprecipitation into water from a methanol solution. The polymer was dried under vacuum for 48 h at room temperature and then for 5 h at 50°C.

IR: 3532 cm^{-1} (free hydroxyl stretch), 3400 cm^{-1} (hydrogen-bonded hydroxyl stretch), 1170.9 and 1225 cm^{-1} (C-O stretch)

$^1\text{H-NMR}$ (in DMSO/TMS 1%), 1.4 and 1.8 (broad bands, 3H, aliphatic backbone), 6.5 (broad band, 4H, aromatic ring), 9.0 (broadband, 1H, OH group)

For our studies on the compatibilization of poly(4-hydroxystyrene) with a modified polystyrene containing 4-vinylphenyl boronic acid units, we used poly(4-hydroxystyrene) synthesized by a two-step procedure involving first the polymerization of 4-tert-butyloxycarbonyloxystyrene followed by removal of the t-butyloxycarbonyl (t-BOC) groups by acidolysis.

a. Synthesis of poly (4-tert-butyloxycarbonyloxystyrene)

20.0 g (91 mmoles) of 4-tert-butyloxy carbonyloxystyrene are dissolved in 20 ml of toluene and 0.75 g of AIBN are added. The polymerization is carried out for 7 h at 75°C under a nitrogen atmosphere. After polymerization the polymer is recovered by precipitation into methanol from toluene solution. The polymer is dried under vacuum at room temperature overnight. 16 g (80% yield) of white polymer are obtained.

IR: 1758cm^{-1} (carbonate stretch vibration), 1146.8 and 1277cm^{-1} (C-O stretch vibrations)

$^1\text{H-NMR}$: (in $\text{CDCl}_3/\text{TMS } 1\%$) 1.55 (sharp singlet corresponding to t-butyl group, there is overlapping of the broad band corresponding to aliphatic backbone, 12 H), 6.55 (broad band, 2H, aromatic ring), 6.85 (broad band, 2H, aromatic ring)

b. Removal of t-BOC protecting groups from poly(4-tert-butyloxycarbonyloxystyrene).

14 g (63.6 mmoles) of poly (4-tert-butyloxycarbonyloxystyrene) are dissolved in ca. 80 ml of dichloromethane, then 70 ml of trifluoroacetic acid are added dropwise at room temperature. The reaction mixture is stirred for 8 h. The polymer is recovered by solvent evaporation and precipitation into petroleum ether from THF solution. After filtration the polymer is dried under vacuum, first overnight at room temperature and then for 5h

at 60°C. 7.20 g (94% yield) of poly(4-hydroxystyrene) is obtained.

IR: 3532cm⁻¹ (free hydroxyl stretch), 3400cm⁻¹ (hydrogen-bonded hydroxyl stretch), 1170.9 and 1225cm⁻¹ (C-O stretch)

¹H-NMR: (in DMSO/TMS 1%), 1.4 and 1.8 (broad bands, 3H, aliphatic backbone), 6.5 (broad band, 4H, aromatic ring), 9.0 (broad band, 1H OH group)

1.4.1.2. Synthesis of (4-hydroxystyrene: styrene) copolymers.

Copolymers containing 80, 70, and 50 mol % styrene were prepared in a two-step procedure involving first the copolymerization of styrene and 4-tert-butyloxycarbonyloxystyrene followed by removal of the t-butyloxycarbonyl (t-BOC) groups by acidolysis.

a. Synthesis of (4-tert-butyloxycarbonyloxystyrene-styrene) copolymer.

Copolymers containing 80, 70, and 50 mol % of styrene were prepared. In a typical copolymerization, 4.43 g (20 mmoles) of 4-tert-butyloxycarbonyloxystyrene and 2.10 g (20 mmoles) of styrene are dissolved in 6.5 g of toluene. Then, 65 mg of AIBN are added to the solution of the monomers and the polymerization is carried out for 7 h at 75°C under nitrogen atmosphere. After polymerization the copolymers are precipitated into methanol from a toluene

solution. The white copolymer is dried under vacuum, first overnight at room temperature, and then for 5 h at 60°C to yield 5.70 g (87 % yield)

IR: 1758 cm^{-1} (carbonate stretch vibration), 1146.8 and 1277 cm^{-1} (C-O stretch vibrations).

$^1\text{H-NMR}$: (in CDCl_3/TMS 1%), 1.48 (sharp singlet, t-butyl) 1.6 (broad band, aliphatic backbone), 6.4 (broad band, aromatic ring), 6.9 (broad band, aromatic ring). The $^1\text{H-NMR}$ integration data are in agreement with the composition of the copolymers.

b. Removal of t-BOC protecting groups from (4-tert-butyloxycarbonyloxystyrene:styrene) copolymers.

In a typical reaction, about 4.0 g of the copolymers are dissolved in 20 ml of dichloromethane and 15 ml of trifluoroacetic acid are added. An evolution of gas is observed and the reaction mixture is stirred for 4 h. The copolymers are recovered by solvent evaporation and precipitation into petroleum ether from THF solution. The filtered copolymers are dried under vacuum for 5-6 h at 65°C. Yields from 90 to 100% are obtained.

IR: 3532 cm^{-1} (free hydroxyl stretch), 3400 cm^{-1} (hydrogen-bonded hydroxyl stretch), 1170.9 and 1225 cm^{-1} (C-O stretch). The infrared spectra showed no remaining carbonate band at 1758 cm^{-1} .

$^1\text{H-NMR}$: 1.5 (broad band, aliphatic backbone), 1.8 (broad band, aliphatic backbone), 6.54 (broad band, aromatic

ring), 7.08 (broad band, aromatic ring), 9.02 (broad band, OH groups). The ^1H -NMR integration data are in agreement with the expected compositions.

1.4.1.3 Synthesis of (4-vinylpyridine-styrene) copolymers

Copolymers containing 20 and 50 mol % of 4-vinylpyridine units were prepared by radical copolymerization of both monomers. In a typical copolymerization, 5.26 g (50 mmoles) of 4-vinylpyridine and 5.21 g (50 mmoles) of styrene are dissolved in 10.5 g of toluene. Then, 0.1047 g of AIBN are added to the solution of monomers in toluene. Polymerization is carried out stirring the reaction mixture for 7 h at 75°C under nitrogen atmosphere. After polymerization, the polymer is recovered by precipitation into petroleum ether from THF solution. The copolymer containing 20 mol % of 4-vinylpyridine was recovered by precipitation into methanol from a toluene solution. The filtered copolymers are dried in vacuo first overnight at room temperature and then for 5 h at 50°C. Yields from 90-100% are obtained.

IR: 1601 cm^{-1} (C=C stretch, phenyl groups), 1556, 1494 cm^{-1}

(mixed C=C and C=N stretch of pyridyl groups)

^1H -NMR: (in CDCl_3/TMS 1%), 1.44 (broad band, aliphatic backbone), 6.30 (broad band, aromatic ring), 6.94 (broad band, aromatic ring), and 8.44 (broad band, aromatic ring).

The ^1H -NMR integration data are in agreement with the expected compositions of the polymers

1.4.1.4 Synthesis of poly(4-vinylbenzoic acid).

5.21 g (35.2 mmol) of 4-vinylbenzoic acid are dissolved in 5 g of DMF and 50 mg of AIBN are added to this solution. Polymerization is carried out stirring, for 7 h at 75°C under nitrogen atmosphere. After polymerization, more DMF is added to the solid polymerization mixture, and after complete dissolution of the polymer (polymer does not dissolve immediately) the thick solution is precipitated into ethylacetate. The filtered polymer is washed with ethylacetate and dried under vacuum for 48 h at room temperature and finally at 50°C for 7 h. The obtained polymer is soluble in DMF, THF, and methanol, and insoluble in dichloromethane, acetone and petroleum ether. 4.5 g (77% yield) of poly(4-vinylbenzoic acid) are obtained.

IR: 3550-2500 cm^{-1} (O-H stretch, broad band), 1694 cm^{-1}

(C=O stretch, hydrogen-bonded C=O groups), 1721 cm^{-1}

(C=O stretch, free C=O groups), 1282 and 1241 cm^{-1}

(C=O stretch.)

^1H -NMR: (in $\text{DMSO}-d_6/\text{TMS}$ 1%), 1.7 (broad band, 3H, aliphatic backbone), 6.6 (broad band, 2H, aromatic ring), 7.7 (broad band, 2H, aromatic ring), 12.8 (broad band, 1H, carboxylic group).

1.4.1.5 Synthesis of (4-vinylbenzoic acid-styrene) copolymers.

(4-vinylbenzoic acid-styrene) copolymers of different compositions were obtained by radical copolymerization using AIBN as initiator. In a typical, copolymerization 3.06 g (20 mmol) of 4-vinylbenzoic acid and 2.06 g (20 mmol) of styrene are dissolved in 5 g of DMF (the ratio weight of monomers/weight of solvent is kept constant and equal to one for all copolymerizations). Then, 50 mg of AIBN are added (weight of initiator with respect to weight of monomers is kept constant and equal to 1% for all copolymerizations). The mixture is polymerized under nitrogen for 7 h at 75°C. After polymerization, the reaction mixture is rotoevaporated, and the polymer dissolved in THF (ca. 25 ml) and precipitated into large excess of ethyl acetate. The polymer is dried under vacuum at 50°C overnight. Yields between 50 and 80% are obtained. IR: 3000-2500 cm^{-1} (O-H stretching), 1730 cm^{-1} (C=O stretching for free C=O groups) 1691 cm^{-1} (C=O stretching for hydrogen-bonded C=O groups), 1240 cm^{-1} (C-O stretching). $^1\text{H-NMR}$: (in CDCl_3/TMS 1%), 1.56 (broad band, aliphatic backbone), 6.56 (broad band, aromatic ring), 7.04 (broad band, aromatic ring), 7.66 (broad band, aromatic ring), 12.8 (broad band, carboxylic proton, -COOH) The $^1\text{H-NMR}$ integration data allowed to calculate the composition of the copolymers. Then, copolymers containing 56, 40, 26, 15 and 11 mol % of 4-vinylbenzoic acid units were obtained.

1.4.2 Synthesis of polymers and copolymers used in the study of polymer compatibilization through covalent crosslinking:

1.4.2.1 Synthesis of (4-vinylphenyl boronic acid-styrene) copolymers through the chemical modification of polystyrene.

The synthesis of (4-vinylphenyl boronic acid-styrene) copolymers by chemical modification of polystyrene consisted was carried out in several steps as described below. First, preparation of (4-bromostyrene-styrene) copolymers by direct bromination of polystyrene with bromine in the presence of thallic triacetate. Second, lithiation of the (4-bromostyrene-styrene) copolymers with n-butyllithium followed by reaction of the lithiated copolymer with trimethyl borate. Finally, hydrolysis of this last intermediate leads to the obtention of the desired (4-vinyl phenyl boronic acid-styrene) copolymers.

a. Synthesis of (4-bromostyrene-styrene) copolymers.

Several (4-bromostyrene-styrene) copolymers were prepared. The desired mol % of 4-bromostyrene in the copolymers is easily adjusted by modifying the amount of added bromine. To a solution of 15.63 (0.15 mol) of polystyrene in 125 ml of CCl_4 is added 0.4 g $[\text{Tl}(\text{CH}_3\text{CO}_2)_3 \cdot 1.5 \text{ H}_2\text{O}]$, mol. wt. 408.53, 0.98 mmol of thallic triacetate. Then, 0.4 ml (7.8 mmol) of bromine in 5 ml

of CCl_4 are added dropwise while the polymer is stirred in the dark at reflux temperature. After 4 h of reaction, the reaction mixture is cooled, and filtered out to remove any solid impurity. The polymer is precipitated by pouring the CCl_4 solution into large excess of methanol. Finally the precipitated polymer is filtered out and purified by redissolving it in methylene chloride and subsequent precipitation by pouring into excess of methanol. The polymer is dried under vacuum at room temperature for 24 h to yield 20.00 g (85% yield) of a light-yellow polymer.

$^1\text{H-NMR}$: (in CDCl_3/TMS 1%): 1.4 (broad band, aliphatic backbone), 1.5 (sharper band, aliphatic backbone), 1.8 (broad band, aliphatic backbone), 6.5 (broad band, aromatic ring), 7.1 (broad band, aromatic ring).

IR: 1010 cm^{-1} (C-Br stretch, strong new band), 822 cm^{-1} (C-H out-of-plane bending vibration characteristic of para-disubstituted aromatic ring)

E.A: Polymer halogen content was measured by Volhard titration of 200-300 mg samples ignited in a Parr peroxide bomb.

Polymer 1: (feed composition: 5 mol % Br_2), found (0.28 meq Br/g of polymer, 3 mol % of 4-bromostyrene in the copolymer).

Polymer 2: (feed composition: 10 mol % Br_2), found (0.64 meq Br/g of polymer, 7 mol % of 4-bromostyrene in the copolymer).

Polymer 3: (feed composition: 20 mol % Br_2), found (1.22 meq Br/g of polymer, 14 mol % of 4-bromostyrene in the copolymer)

Polymer 4: (feed composition: 30 mol % Br_2), found (2.09 meq Br/g polymer, 26 mol % of 4-bromostyrene in the copolymer)

Polymer 5: (feed composition: 50 mol % Br_2), found (3.38 meq Br/g of polymer, 48 mol % of 4-bromostyrene in the copolymer)

b. Synthesis of copoly (4-vinylphenyl boronic acid-styrene) (14 mol % 4-vinylphenyl boronic acid units in the copolymer)

To a solution of 1.92 g (2.33 mmoles Br) of copoly (4-bromostyrene-styrene) (14 mol % 4-bromostyrene) in 20 ml of dry benzene is added 1.0 ml (10 mmoles) of 10 M n-Buli. The reaction mixture is stirred under nitrogen and the temperature is raised to 60°C. After 2.5 h the red thick solution of lithiated polymer is allowed to cool to room temperature. Then, the polymer is taken up with a syringe and added to 6 ml (52.5 mmoles) of trimethyl borate under nitrogen atmosphere at 0°C. The reaction mixture is stirred for 1 h. Finally, the reaction mixture is hydrolyzed by pouring it slowly into a mixture of 20 ml of dioxane, 5 ml of water, and 2 ml of concentrated HCl. The reaction mixture is stirred at room temperature for 2 h. The polymer is precipitated by

pouring the reaction mixture into a large excess of methanol. After drying the polymer under vacuum at room temperature 1.65 g of a white polymer are obtained.

IR: 1328 cm^{-1} (B-O stretch, strong band), 1410 cm^{-1} (stretch corresponding to those aromatic rings with boron attached directly), 3582 cm^{-1} (O-H stretch, weak band)

EA: found (B: 1.32%, 1.22 mmoles of B/g of polymer, 13.43 mol % of 4-vinylphenyl boronic acid units in the copolymer)

c. Synthesis of copoly (4-vinylphenyl boronic acid-styrene) (26 mol % 4-vinylphenyl boronic acid units in the copolymer)

To 11.0 ml (110 mmoles) of 10 M n-Buli in 50.0 ml of dry THF at -40°C is added a solution of 5.20 g (11 mmoles Br) of copoly (4-bromostyrene-styrene) (26 mol % of 4-bromostyrene units) in 50 ml of dry THF. The reaction mixture is stirred under nitrogen atmosphere at -40°C for 4.5 h. Once lithiation of the polymer takes place, the reaction mixture becomes red and thick. The red solution is then taken up with a syringe and added to 50 ml (440 mmoles) of trimethyl borate at 0°C . The reaction mixture is stirred under nitrogen for 5 h. Finally, the reaction mixture is rotoevaporated until ca. half of original volume and hydrolyzed by pouring it into a solution consisting of 100 ml of dioxane, 25 ml of water and 10 ml of concentrated HCl. The reaction mixture is stirred for 4 h at room temperature. After hydrolysis the solution is

rotoevaporated until ca half of original volume and the polymer is precipitated by pouring the dioxane solution of the polymer into large excess of methanol. Purification of the polymer is performed by redissolving the polymer in THF and reprecipitating the polymer into methanol. The filtered polymer is dried under vacuum at room temperature for 24 h to yield 3.36 g of a white polymer.

IR: 1343cm^{-1} (B-O stretch, strong band) 1411cm^{-1} (stretch corresponding to those aromatic rings with boron attached directly), 3528cm^{-1} (O-H stretch, weak band)

E.A: found [C: 85.49%, H: 7.54%, B: 1.71%, Br: 0.1%, O: 5.16% (obtained difference)]

Structure of polymer after elemental analysis: (4-vinylphenyl boronic acid-styrene) 17.8 mol % of 4-vinylphenyl boronic acid units, 82.2 mol % of styrene units) for which the calculated composition is (C: 85.82%, H: 7.38%, B: 1.72%, O: 5.09%)

1.4.2.2 Synthesis of (4-vinylphenyl boronic acid-styrene) and (4-vinylphenyl boronic acid - methyl acrylate) copolymers by radical copolymerization of the respective monomers.

a. Synthesis of 4-vinylphenyl boronic acid.

A 1 l 3-necked flask is set up with a condenser and addition funnel and the set up is kept under nitrogen atmosphere. 6.08 g of magnesium (0.25 mol) is suspended

in 100 ml of dry THF and the temperature is kept at 50°C. Magnesium is activated by addition of one crystal of iodine and one drop of methyl iodide. Once the yellow color of iodine disappears, a solution of 27.8 g (0.20 mol) of p-chlorostyrene in 100 ml of dry THF is added dropwise to the THF-Mg suspension. The temperature is kept at 50°C and the rate of addition of the p-chlorostyrene solution is adjusted so that a soft bubbling of the THF is observed. After addition of the p-chlorostyrene solution (3 h), the reaction mixture is kept refluxing softly for 1 h. Then, 100 ml of dry THF are added to the reaction mixture and the temperature is lowered to -78°C. The cooled organomagnesium solution is vigorously stirred and treated with a cold solution of trimethyl borate (34 ml, 0.3 moles) in dry THF from a jacketed-addition funnel which is kept at -15°C with acetone and dry ice. After fast addition of the cold trimethyl borate solution, the reaction mixture solidifies as a white mass. Finally, hydrolysis is performed by adding slowly ca. 150 ml of 10% HCl. Hydrolysis takes place immediately, the organic phase is separated and dried with magnesium sulfate. THF is rotoevaporated and the residue is recrystallized in toluene at 50-80°C. The toluene solution of 4-vinylphenyl boronic acid is kept at 0°C for 48 h to obtain complete precipitation. After filtration the white crystals are air-dried, ^1H -NMR indicates that a mixture of 4-vinylphenyl boronic acid: 4-vinylphenyl boronic anhydride

40:60 mol % is obtained. When the crystals are dried under vacuum at room temperature for 48 h, 4-vinylphenyl boronic anhydride is the only compound obtained. 12 g (50% yield).

$^1\text{H-NMR}$: (in CDCl_3/TMS 1%), 4-vinylphenyl boronic anhydride 8.12 (doublet, 2H, aromatic ring), 7.48 (doublet, 2H, aromatic ring), 6.74 (multiplet, 1H, vinyl group), 5.84 (multiplet, 1H, vinyl group), 5.32 (multiplet, 1H, vinyl group)

4-vinylphenyl boronic acid: 7.68 (doublet, 2H, aromatic ring), 7.42 (doublet, 2H, aromatic ring), 6.70 (multiplet, 1H, vinyl group), 5.82 (multiplet, 1H, vinyl group), 5.3 (multiplet, 1H, vinyl group), 4.7 (singlet, 2H, hydroxyl groups).

IR: 4-vinylphenyl boronic anhydride: 1634 cm^{-1} (C=C stretch, aromatic ring), 1343 cm^{-1} (B-O stretch), 1089 cm^{-1} (C-B stretch), 990 and 907 ($\text{CH}=\text{CH}_2$ stretch, vinyl group)

MS: 4-vinylphenyl boronic anhydride:

$(\text{CH}_2\text{CHC}_6\text{H}_4\text{BO})_3 \cdot^+$, 390; $\text{CH}_2\text{CHC}_6\text{H}_4\text{B}(\text{OH})_2 \cdot^+$, 148; $\text{CH}_2\text{CHC}_6\text{H}_4\text{BO} \cdot^+$, 130; $\text{CH}_2\text{CHC}_6\text{H}_4 \cdot^+$, 103; $\text{C}_6\text{H}_5 \cdot^+$, 77; $\text{CH}_2\text{CHCHB} \cdot^+$, 51; $\text{B}(\text{OH})_2 \cdot^+$, 45.

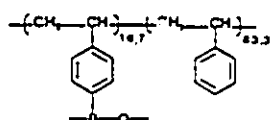
b. Synthesis of (4-vinylphenyl boronic acid-styrene) copolymers by radical copolymerization of 4-vinylphenyl boronic acid and styrene.

Several (4-vinylphenyl boronic acid-styrene) copolymers containing various amounts of 4-vinylphenyl

boronic acid units were made by radical copolymerization using AIBN as initiator. In a typical copolymerization, 2.81 g (27 mmols) of styrene and 0.39 g of 4-vinylphenyl boronic anhydride (mol wt.:389.88 g, 3 mmols of B) are dissolved in 3.2 g of wet dimethylformamide (2% water). Wet dimethylformamide is used in order to break the anhydride bonds of 4-vinylphenyl boronic anhydride. Then, 34.5 mg of AIBN are added to the solution of monomers in DMF (weight of initiator with respect to the weight of monomers is kept constant for all copolymerizations). The reaction mixture is polymerized under nitrogen at 75°C for 7 h. After polymerization, the almost solid reaction mixture is poured into a large excess of methanol and this is stirred until the polymer becomes a loose precipitate. After filtration, the polymer is purified by redissolving it in THF and reprecipitation in methanol. The polymer is filtered out and dried in vacuo for 48 h at room temperature to afford 1.8 g of the desired copolymer (56% yield).

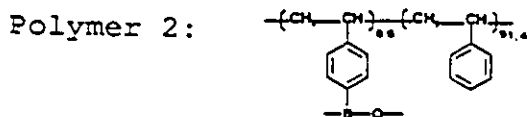
IR: 1345 cm^{-1} (B-O stretch, strong band), 1410 cm^{-1} (stretch corresponding to aromatic rings with boron attached directly).

EA: Polymer 1:



found: (C: 88.58%, H: 7.29%, B: 1.66%, O: 2.46%)

calculated: (C: 88.44%, H: 7.42%, B: 1.66%, O: 2.48%)



found: (C: 90.39%, H: 7.48, B: 0.87%, O: 1.26%)

calculated: (C: 90.33%, H: 7.51%, B: 0.87%, O: 1.29%)

b. Synthesis of (4-vinylphenyl boronic acid-methyl acrylate) copolymers by radical copolymerization of 4-vinylphenyl boronic acid and methyl acrylate.

Several (4-vinylphenyl boronic acid-methyl acrylate) copolymers containing various amounts of 4-vinylphenyl boronic acid units were made by radical copolymerization using AIBN as initiator. In a typical copolymerization, 2.33 g (27 mmoles) of methyl acrylate and 0.39 g of 4-vinylphenyl boronic anhydride (mol.wt. 389.88 g, 3 mmoles of B) are dissolved in 3.2 g of wet DMF (2% water). Then, 34.5 mg of AIBN are added to the solution of monomers in DMF and the polymerization is carried out for 7 h at 75°C under nitrogen atmosphere. After polymerization, a few mls of THF are added to the reaction mixture until a thick solution is obtained. Then, the polymer is precipitated from the THF:DMF solution into water as follows: a few drops of the THF:DMF solution of the polymer are added to a large excess of water, the polymer precipitates as a thin film on the surface of the water, the polymeric film is withdrawn from the water and then more polymer is precipitated. Stirring during the precipitation of the polymer is not convenient in this case since the polymer

IR: 1732.8 cm^{-1} (C=O stretch, very strong), 1604 cm^{-1} (C=C stretch, aromatic ring), 1345 cm^{-1} (B-O stretch, strong), 1161 cm^{-1} (C-O stretch, strong), 3474 cm^{-1} (O-H stretch, very weak)

$$\text{---}(\text{CH}_2\text{---}\text{C}(\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})\text{---})_n\text{---}(\text{CH}_2\text{---}\text{C}(\text{COOCH}_3)\text{---})_{n'}\text{---}$$
[illegible]

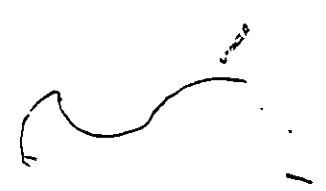
found: (C: 56.61%, H: 7.12%, B: 0.64%, O: 35.63%)
calculated: (C: 57.22%, H: 6.90%, B: 0.65%, O: 34.9%)

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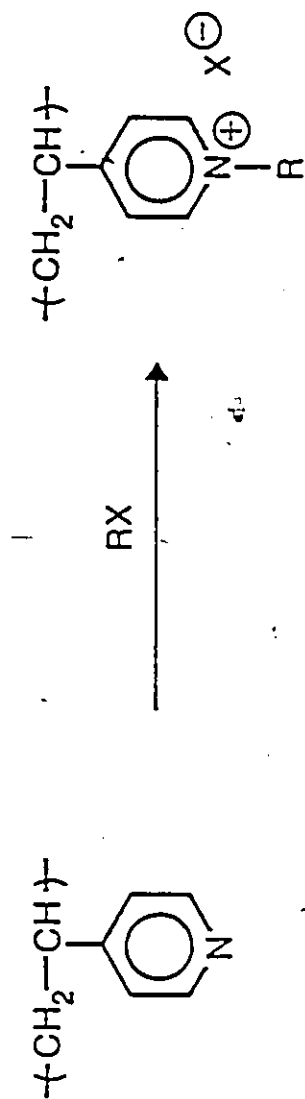
2.1. INTRODUCTION

2.1.1. Generalities

Unlike polystyrene which is truly an industrial polymer, poly(vinyl pyridine) is still a speciality polymer with a unit cost several times that of polystyrene. The differences in reactivity of the two polymers are even more noticeable. Polystyrene is very susceptible to modification by electrophilic aromatic substitution, reactions of this type being used for example in its chloromethylation or sulfonation; while poly(vinyl pyridine) is very resistant to electrophilic aromatic substitution but has a high chemical reactivity which is due to its nucleophilic and weakly basic ring nitrogens. Typical reactions of poly(vinyl pyridine) include its quaternization by nucleophilic attack on alkyl halides or by protonation (Scheme 1)

In addition, while polystyrene is non-polar, poly(vinyl pyridine) is quite polar and thus can be expected to interact strongly with other polar molecules, or to act as a good ligand for a variety of metal ions. It is this special reactivity of poly(vinyl pyridine) which makes it so attractive a material for a number of speciality applications.

This introduction will not attempt to be encyclopedic in its coverage of recent developments in the chemistry of the various poly(vinyl pyridines) but it will, rather, focus on a number of recent applications of the polymers or



SCHEME 1

derivatives thereof. In the following text 2-vinyl pyridine, 4-vinyl pyridine and 2-methyl-5-vinylpyridine will be abbreviated as 2-VP, 4-VP and 2-Me-5-VP respectively, while the corresponding polymers will be referred to as poly (2-VP), poly (4-VP) and poly (2-Me-5-VP). The notations VP and PVP will be used where no specific designations are required.

2.1.2. Polymerization of vinyl pyridines

This topic has been the object of numerous studies and is well documented, however a brief review is in order as it provides a valuable insight into the chemistry of PVP. As the presence of the pyridyl nitrogens is expected to have little influence on propagating free radicals, the radical polymerization of VP is very comparable to that of styrene [1]. Differences do exist as VP is generally more reactive than styrene, but these are not too significant. Emulsion copolymerization is used extensively in the preparation of VP-butadiene rubber.

In contrast, the interaction of cationic initiators with the basic pyridyl ring nitrogens results in their deactivation by complex formation, and thus, PVP cannot be prepared by classical cationic polymerization. However, the reaction of VP with acidic or electrophilic molecules does induce polymerization in a process which is often referred to as a 'spontaneous polymerization'; this may lead to polymers containing both vinyl and ionene-type

linkages [2].) As expected, VP polymerizations proceed extremely well under anionic conditions, partly due to the high electronegativity of the ring nitrogen [3]. Finally, highly isotactic poly(2-VP) has been prepared by coordinate polymerization with organo-metallic compounds as initiators. The stereospecificity of the polymerization is attributed [4] to the fact that the ring nitrogen of 2-VP, being close to the vinyl group, can participate effectively in the addition complex and can thus ensure that all incoming monomer molecules have the proper orientation: this is not the case with other VP monomers for which direct participation of the ring nitrogen is not possible.

2.1.3. Preparation of crosslinked PVP resins

Numerous procedures for the preparation of crosslinked resins containing VP units can be found in the literature. In most cases the resins are prepared by suspension polymerization with divinylbenzene [DVB] as the crosslinking agent. When a low ($\leq 5\%$) percentage of DVB is used, the resin beads which are obtained have good chemical reactivity but no permanent pore structure [5,6]; a resin of this type is commercially available from Reilly Tar and Chemical Co. and has been used in a number of applications [7]. Macroporous resins with appreciable dry-state surface areas can be prepared when the polymerization is carried out in suspension in the presence of a suitable porogen using larger percentages of DVB [8]. As will be

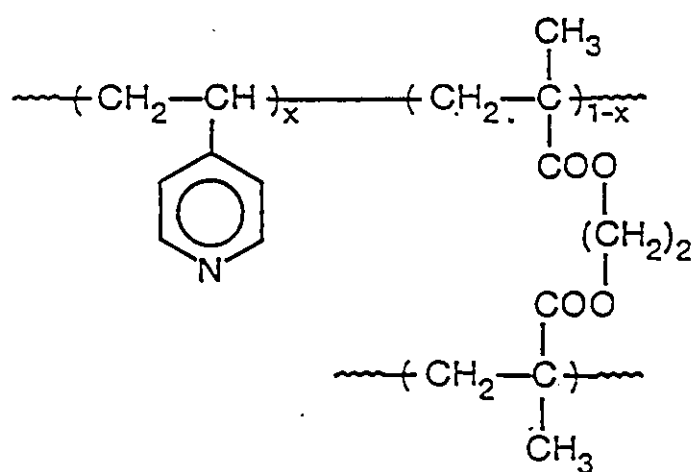
described in a section of this thesis, we have recently prepared [9] crosslinked VP resins with high surface areas using ethylene dimethacrylate [EDMA] as crosslinking agent (Scheme 2).

Although high porosities are often desirable for specific applications, the incorporation of a large amount of comonomers such as divinylbenzene or ethylene dimethacrylate which contain no amino groups into the final VP resin can adversely affect its properties: to overcome this problem macroporous VP resins can be prepared using crosslinking agents such as divinylpyridine.

Another interesting approach to the preparation of crosslinked polymers containing VP units used by Nishide et al. [10,11] involves the crosslinking of preformed poly(4-VP) with 1,4-dibromobutane to yield a partly quaternized crosslinked product.

2.1.4. Selected applications of PVP and derivatives

Numerous important applications of PVP or VP-containing polymers will not be reviewed here as they each constitute a field of their own too large to be covered adequately: these include the use of vinyl pyridine rubber in the tire and rubber industry, applications in the textile industry, applications in classical ion exchangers, etc.



Insoluble
 $x = 0.6 - 0.95$

SCHEME 2

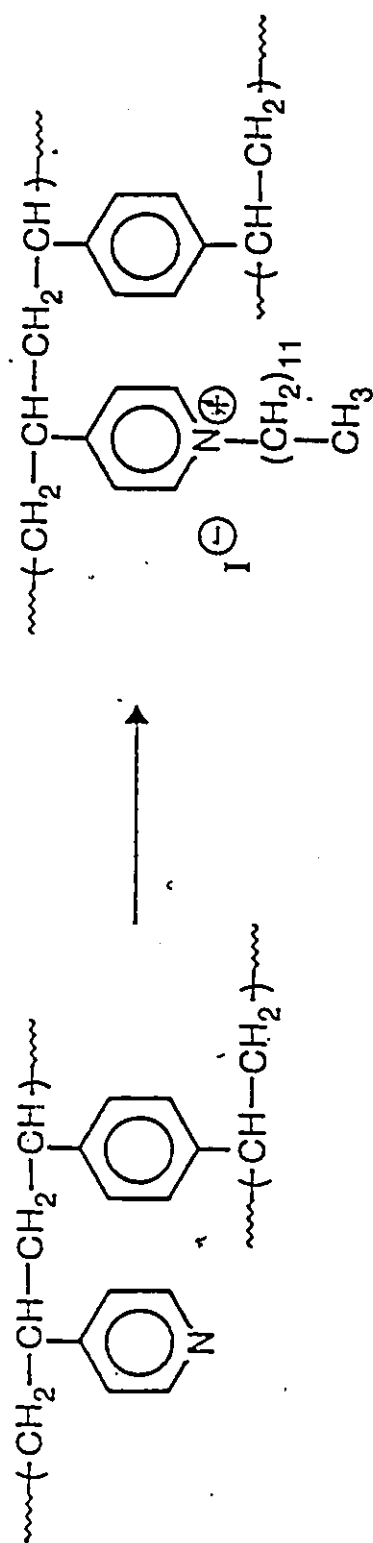
2.1.4.1 Quaternized resins in triphase reactions

Triphase reactions have received much attention since Regen first described [12] the use of a crosslinked polystyrene resin bearing quaternary ammonium groups as catalyst in a nucleophilic displacement reaction. Although most of the resins which have been tested to date were based on styrene copolymers [13], recent work by Serita et al. [14] has shown that quaternized poly(vinyl pyridine) resins could also be used efficiently. Thus, DVB crosslinked PVP was quaternized by C-2 to C-16 alkyl bromides to produce catalyst resins (Scheme 3) which were used in the Finkelstein reaction of various n-octyl halides.

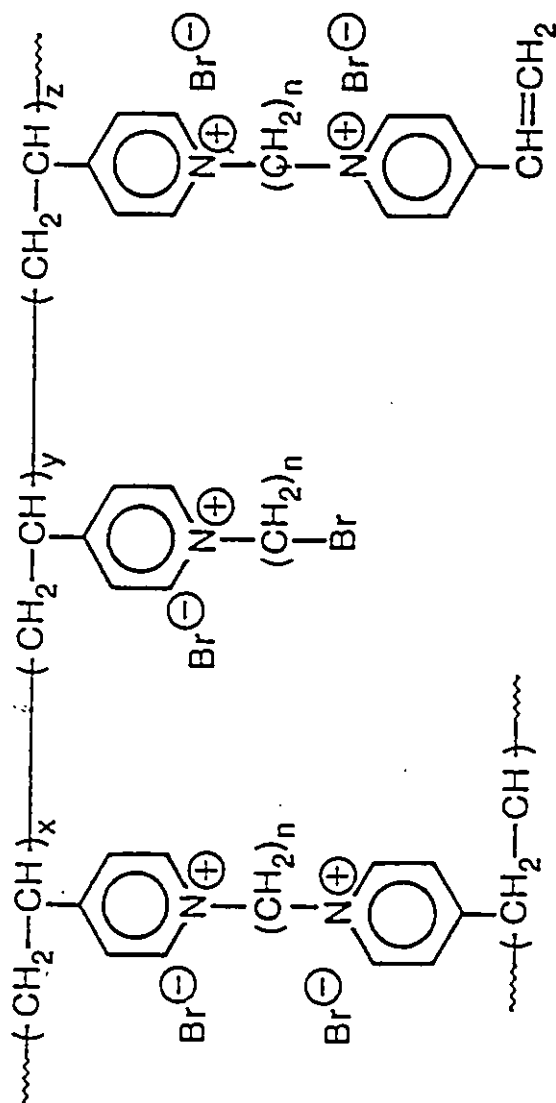
As expected, reaction rates were found to increase with catalyst concentration, while the catalysts possessing long-chain alkyl quaternized pyridine groups showed the highest activity. In a second report, Serita et al. [15] described the use of similar resins as catalysts for the reaction of aqueous cyanide ion with benzene solutions of 1-bromooctane.

The approach of Noguchi et al. [16] differed from that of Serita et al. in that the catalysts were prepared by spontaneous polymerization of 4-VP in the presence of α -w dihaloalkanes. The polymers which were obtained had complex structures as shown in Scheme 4.

The catalytic activity of these resins in the substitution of 1-octyl bromide with cyanide ion seemed to



SCHEME 3



SCHEME 4

vary with the length of the alkyl chain of the dihalide used in the preparation of the polymer, increasing from $n=3$ to $n=12$. However, the resins were found to decompose slowly under the conditions of the reaction.

2.1.4.2 Adsorption of metal ions

Interest in selective ion-exchange resins and chelate-forming resins has continued to grow with a number of publications and patents describing polymeric ligands based on partly or fully quaternized PVP. For example, porous crosslinked VP-DVB resins quaternized by reaction with sulphuric acid have been used for the removal of heavy metal ions such as Cr(VI) from waste water [17] or gold from aqueous solution [18]. A similar resin was also shown to be efficient in the recovery of uranium [19], while a copolymer of 2-Me-5-VP and DVB was used successfully in the demercuration of the waste water from mercury cells used in the electrolysis of brine [20].

Several attempts have also been made to adjust the tertiary structure of chelate-forming resins in order to achieve optimum sorption of a specific metal ion [21]. The approach of Nishide and Tsuchida [10,11,22] was to treat soluble PVP with a metal ion used as a template, then freeze the conformation of the polymer-ligand by a crosslinking reaction. After leaching out the metal ion used as template, the resins prepared by this procedure show enhanced selectivities for their respective template

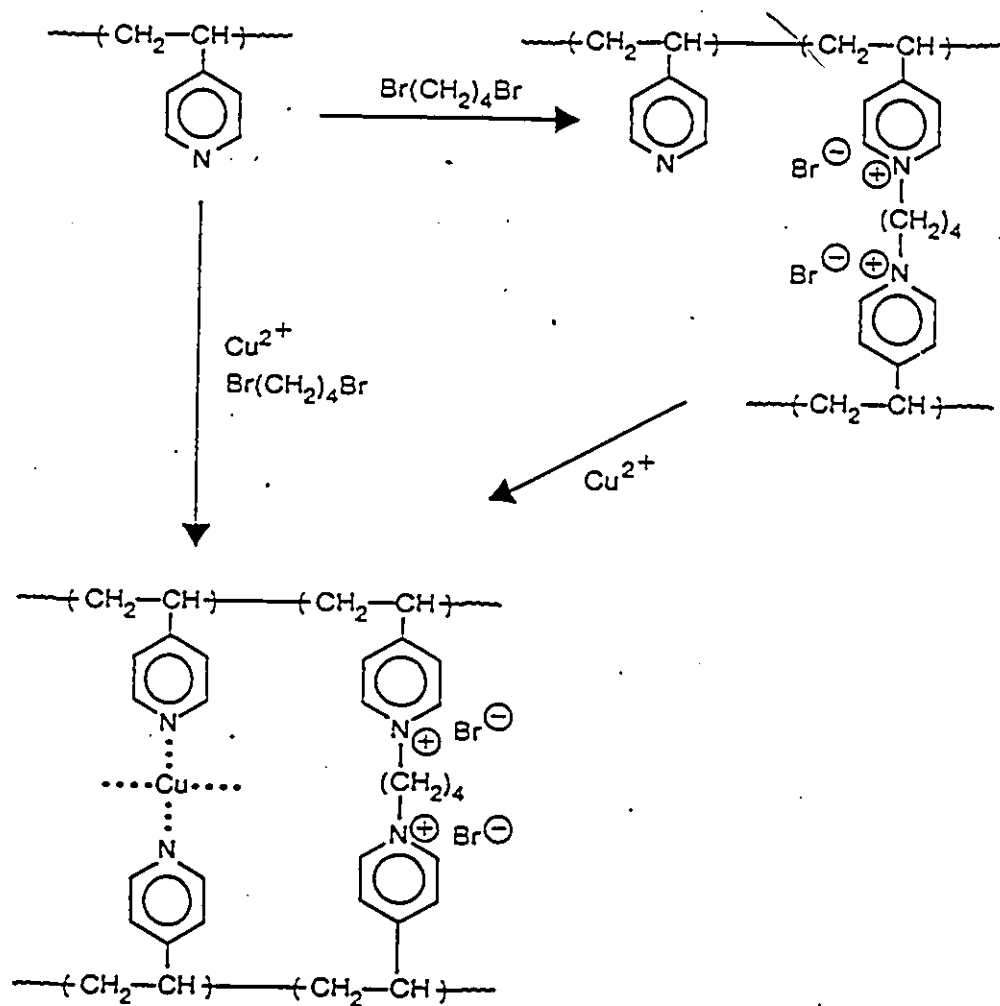
ions over polymers crosslinked in the absence of a metal ion template (Scheme 5).

Although it was expected that the polymer-ligand chain could be maintained at the optimal conformation for the coordination sphere of a specific metal ion, the crosslinked polymer still exhibits some flexibility and can adopt different conformations once the template ion is removed, and thus complete ion selectivity is not achieved.

Another interesting development in this area was reported by Effendiev et al. [23] who prepared a soluble PVP partly quaternized (10-60%) with a benzylic halide, cast a film of the polymer with a bis-acrylamide, then crosslinked the film by irradiation. The resulting resin is useful in the sorption of Cu (II) showing a maximum efficiency at approximately 30% quaternization, with a capacity of 3.55 mmole/g vs c. 0.9 mmole/g for Co (II) or Ni (II). Polymers with less than 20% or more than 40% quaternization are less effective.

2.1.4.3 Removal of organic contaminants from waste water

Vinyl pyridine-DVB copolymers have shown excellent potential for the removal of phenols from waste water. Due to the presence of the slightly basic pyridyl groups, these resins are much superior to the styrene-DVB copolymers which are also used in similar applications. In addition, the resins are less prone to fouling by inorganic salts



SCHEME 5

present in solution than the more classical anion exchange resins. High breakthrough capacities can be achieved with the porous crosslinked PVP resins, while elution of the absorbed phenols from the polymer can be achieved by simple solvent extraction using methanol or acetone, or by thermal treatment [24-26].

Similarly, PVP resins have been used for the removal of aromatic compounds [27], or carboxylic acids [28] from waste water, while quaternized PVP resins were useful in the adsorption of organic soaps and detergents [29]. In addition, recent work on crosslinked PVP or poly (VP-styrene) membranes showed that these were useful in the separation of aqueous amine solutions by pervaporation; good efficiency was obtained in the separation of dipropylamine from water [30].

2.1.4.4 Polymeric reagents based on PVP

The presence of the reactive pyridyl ring on the repeating unit of the polymer makes PVP attractive for use as reagents. The electron rich nitrogen can readily complex or add to numerous reagents to provide new modified PVP resins with reactive groups. These reagents generally have reactivities similar but not identical to those of comparable derivatives of low molecular weight pyridines; differences in reactivity are due to a number of factors such as neighbouring group effects, configurational

effects, local concentration of reactive species, ionic interactions, solubility, etc.

These differences in reactivity may be of critical importance in some cases while in others, the fact that the reactive polymers can be made insoluble and thus easily recyclable, may be sufficient to justify their use instead of the corresponding low molecular weight species.

2.1.4.4a Halogenating reagents

Our own laboratory's work with PVP-based reagents started with the study of crosslinked poly(vinyl pyridinium hydrobromide perbromide) [PVPHP]. The brominating agent prepared from a resin containing 98% VP and 2% DVB proved to be very effective in reactions with both alkenes and carbonyl compounds [31], while similar resins containing styrene as comonomer had lower reactivities. A somewhat similar polymer containing 60% styrene [PVPHP-St] was reported two years later by Zupan et al. [32] who noticed that their PVPHP-St reagent was best used in chloroform rather than in methanol as was the case for PVPHP derived from a 98% VP resin. In the latter solvent reactions with PVPHP-St were accompanied by side-product formation resulting from methanol additions. Although this undesirable side-reaction might have been due to the presence of free acid in the polymeric reagent, it seems more likely that this difference in reactivity between PVPHP and PVPHP-St is due to the presence of 60% styrene in

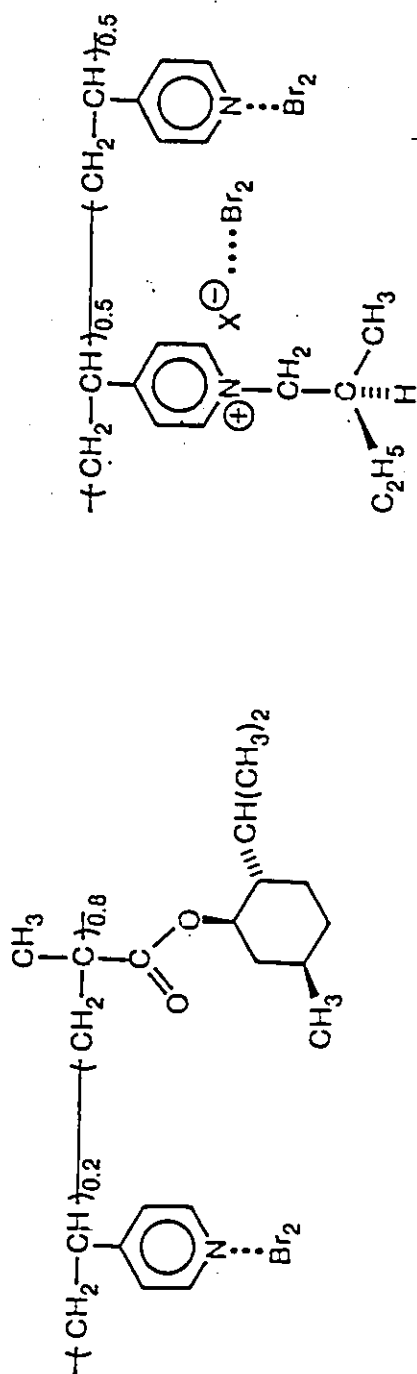
the second polymer. This has a profound influence on the polarity of the reactive sites and on the micro-environment within the reactive polymer, affecting in turn the outcome of the reaction. It should be noted, however, that PVPHP can also be used in non-polar solvents [7].

Chiellini and co-workers [33] have attempted to use chiral copolymers containing 4-VP-bromine adducts (Scheme 6) in the asymmetric bromination of olefins but their attempt was unsuccessful as the reaction proceeded with no measurable enantioselectivity. However, the authors noted some large difference in reactivities with structurally similar branched β -olefins, suggesting that the polymeric reagent is extremely selective due to its sensitivity to the steric environment of the reacting alkene molecule.

Another PVP-based halogenating agent, PVP-Cl₂, found in the patent literature, can be used to prepare N-chlorosuccinimide and N-chlorophthalimide in almost quantitative yields [34].

2.1.4.4b Oxidizing agents

As was seen above, PVP resins have excellent complexing properties which allow their use in the removal of heavy metal ions from waste water. This ability to complex ions such as Cr(VI) coupled to the excellent reactivity of pyridine-based chromium (VI) oxidizing agents makes the use of analogous PVP-based polymeric reagents particularly attractive as the polymeric reagents have



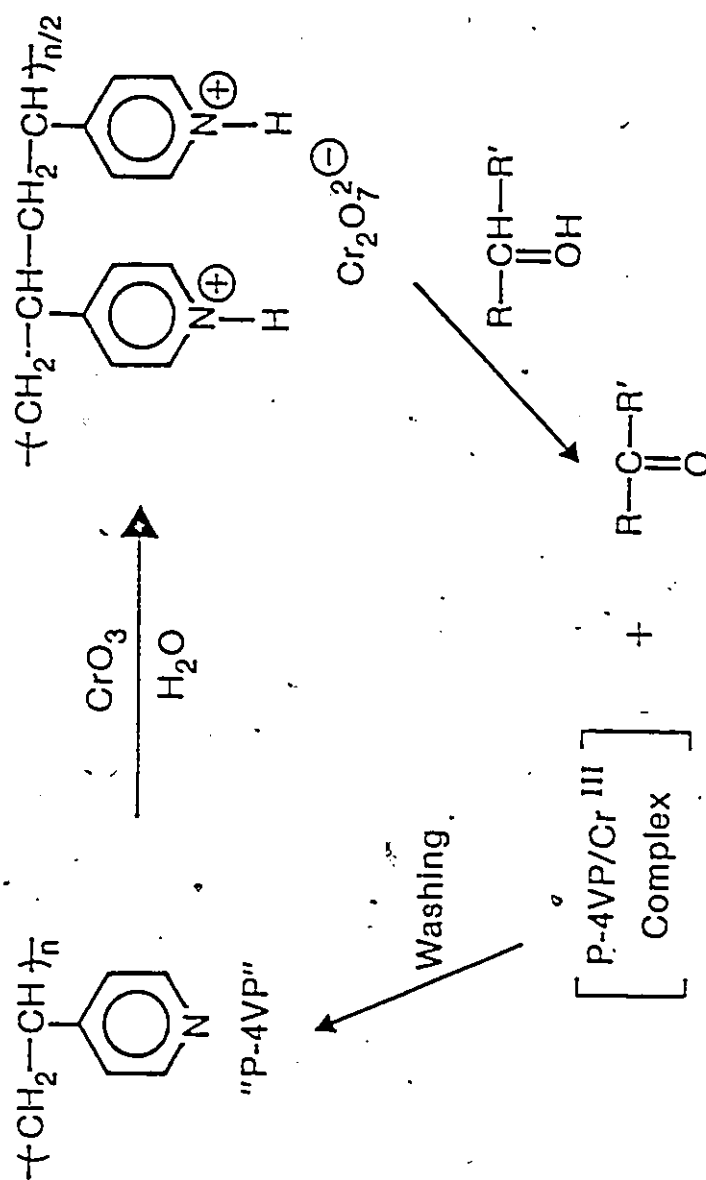
SCHEME 6

significant advantages over their low molecular weight counterparts.

- (1) Both the oxidized and reduced forms of Cr can be retained firmly by the polymer, thereby facilitating recovery of the soluble reaction products once the oxidation is complete.
- (2) The polymeric reagent is safer to handle in large amounts than the low molecular weight reagent.
- (3) Application in semi-continuous processes is possible, with regeneration of the polymeric reagent.

Several reports of the preparation of oxidizing agents based on complexes of PVP with various chromium (VI) salts have appeared recently. The contribution of our laboratory was the preparation of a PVP-chlorochromate reagent [5] and of a PVP-dichromate reagent [6]. Both reagents are easily prepared by reaction of 2-5% crosslinked PVP, with chromium trioxide-HCl for the former and chromium trioxide-water for the latter (Scheme 7). The reagents are very effective in the oxidation of alcohols to the corresponding carbonyl compounds without over-oxidation. Unlike the corresponding pyridine-based reagents which are often used in very large excess, the polymeric reagents can be used in essentially equimolar amounts and afford easier processing after reaction. Recovery and recycling of the polymer is easily accomplished.

Similar and complementary reagents have been described recently [35] in a very interesting study which also



SCHEME 7

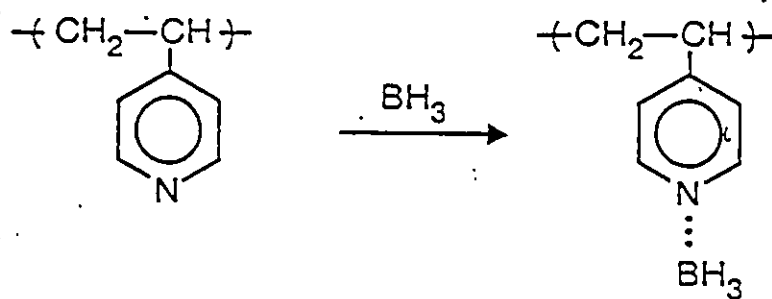
explores the influence of the structure of the resin on its performance in subsequent oxidation reactions.

Finally, a PVP-bromine complex can be used [36] for the conversion of thiols into disulphides. In addition to its ease of handling, the reagent is more selective and milder than alternate low molecular weight reagents.

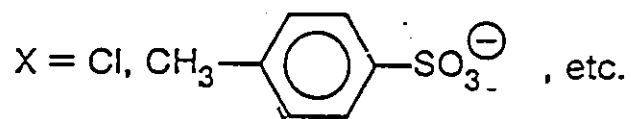
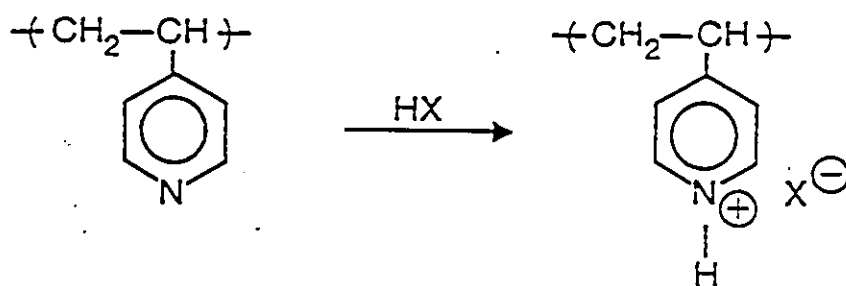
2.1.4.4c Reducing agents

The electron rich character of the pyridyl moieties of PVP makes it ideal for the formation of complexes with diborane (Scheme 8). Such complexes have been prepared and the resulting PVP-borane reagent has been used in the reduction of carbonyl compounds.

Hallensleben [37] prepared PVP-borane reagents by reaction of soluble or crosslinked PVP-HCl with sodium borohydride. Unfortunately the reagent has a low reactivity and affords low yields of alcohols in its reactions with various carbonyl compounds. Menger and co-workers have recently improved this reagent by changing both its preparation and the reduction procedure [38]. Thus, PVP-borane is prepared by a ligand-exchange process involving PVP and the borane-methyl sulfide complex in THF. The desired PVP-borane reagent, in which approximately 80% of the pyridyl rings are involved in borane complexation, precipitates from solution. The reduction of carbonyl compounds with this PVP-borane reagent requires that an equivalent amount of boron trifluoride etherate be added to the reaction



SCHEME 8



SCHEME 9

mixture. Under these conditions high yields are obtained in the reduction of both aldehydes and ketones, although only approximately two-thirds of the borane fixed on the polymer is available for reaction.

2.1.4.4d Miscellaneous applications as reagents or supports

One of the simplest yet very useful applications of PVP is as an insoluble acid acceptor (Scheme 9). Crosslinked PVP is particularly well-suited for this application, as the salt which is formed by reaction with acid can be separated quantitatively from the reaction medium by filtration.

Applications include the preparation of esters from acid chlorides and alcohols [7], the trimethylsilylation of alcohols and amines with trimethylsilyl chloride [39], the preparation of 2-chlorosulphonyl acetidinones from penicillin oxides [40], etc. An added advantage is that the PVP can be recovered quantitatively from its salt and reused.

In other applications, quaternized PVP resins proved well-suited to act as supports in the immobilisation of enzyme mixtures [41] or in microbial cell encapsulation [42].

2.1.4.4e PVP-based catalysts

The basic character and excellent ligand properties of the pyridyl moieties suggest that PVP resins and other polymers containing VP units can be used in the preparation of various catalysts. The following are but a few of the recent examples.

Menger and Chu have reported the use of a PVP-p-toluenesulfonate supported on celite as catalyst for the preparation of the tetrahydropyranyl ethers of various alcohols [34].

Kawabata et al. have found that a crosslinked PVP-hydrochloride was an effective and mild catalyst for the acetalisation of carbonyl compounds and for the esterification of carboxylic acids [44]. The PVP-based catalyst was superior to other resins containing strong acid cation exchange groups as it did not cause side reactions when placed in contact with substrate functionalities which are normally very sensitive to acid. Similar application of crosslinked PVP-HCl for the formation of enamines and ketals have also been described [7].

The ability of PVP to complex Cu salts has been used extensively in the preparation of various catalysts. Such polymeric catalysts have been used recently in ketazine syntheses [45], in the oxidative cleavage of 4-methyl catechol to the corresponding cis-cis monomethyl muconate [46], in the oxidative coupling of 2,6-disubstituted

phenols [47] or of dephenylmethanimine [48], and in the oxidative polymerization of phenols [49].

The complexes of other heavy metal ions such as Ir or Rh (III) with PVP have also been used by Carlock [50] as hydrogenation, hydroformylation, or isomerisation catalysts, while Co complexes are useful in hydroformylation [51].

2.1.4.4f Resist materials based on PVP

The photochemical reactivity of pyridine and other amine oxides has been studied extensively. As these photoreactions often result in the formation of intermolecular bonds following cleavage of the N-O bonds, they are potentially useful in the design of negative resists from polymers containing N-oxide moieties. Examples of such applications can be found in the work of Loucheux and co-workers [52-53] who crosslinked thick films of copolymers of styrene and 4-VP-oxide by irradiation at 280-320 nm. Similar behaviour [53] was observed with the N-oxides of the homopolymers of 2-Me-5-VP, 4-vinyl quinoline or 9-vinyl acridine.

A second approach to the preparation of photocrosslinkable resins on PVP matrices involves the binding of a photosensitive group to the PVP. This can be easily accomplished by partial or complete quaternization of PVP with an alkyl halide containing photoreactive groups such as C=C double bonds. Irradiation of a polymer film

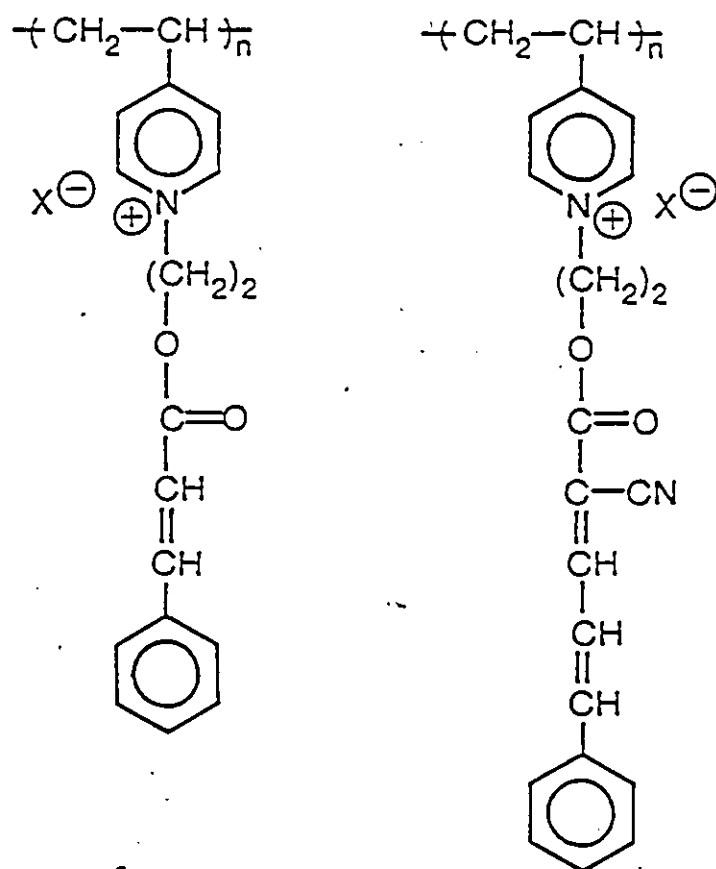
containing such modified PVP units results in photocrosslinking through the pendant groups with formation of a negative relief image.

Thus, modification of poly(4-VP) with allyl bromide gives a polymer containing 84% of quaternary groups [54]. Irradiation of a film of this polymer caused the exposed areas to become insoluble while the unexposed areas of the film could be dissolved with water-based developers. Similar photocrosslinkable derivatives of PVP (Scheme 10) have been prepared by reacting PVP with 2-bromoethyl esters of cinnamic acid or of cyano cinnamylidene acetic acid [55].

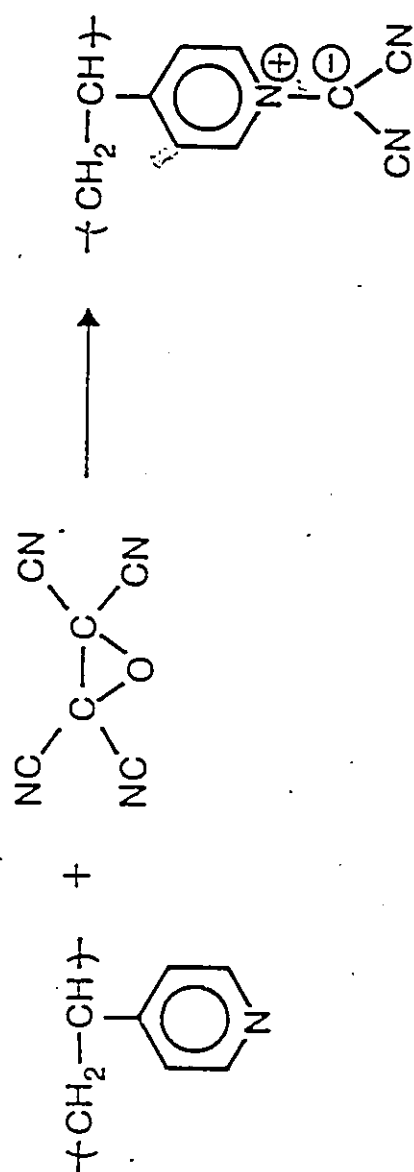
A third approach used by Loucheux and co-workers [56] is somewhat similar to the first as it involves the photocleavage of N-C ylid bonds instead of the N-O bonds of N-oxides. A polymer containing some pyridinium dicyanomethylide units can be prepared by reaction of PVP with tetracyano ethylene oxide (Scheme 11).

Irradiation of the ylided polymer at 410 nm causes it to crosslink in the exposed areas, likely through formation and subsequent reaction of an intermediate carbene. Although this photoreticulation reaction is enhanced by the addition of a triplet sensitizer, the polymer has a very low sensitivity.

Numerous other photopolymerizable compositions containing PVP or copolymers of VP can be found in the literature.



SCHEME 10



SCHEME 11

2.1.4.4g Miscellaneous other applications

Amongst numerous other applications of PVP, the following are noteworthy. PVP has been used as a ligand for a Co(II)-Schiff base complex in the preparation of a porous absorbent capable of retaining significant amounts of oxygen. Desorption was readily accomplished under reduced pressure [53]. Other applications as adsorbent resins include the adsorption of SO₂ [58] or I₂ [59] on PVP-DVB resins.

4-VP-DVB resins quaternized with C-8 to C-18 alkyl iodides show bactericidal activity but are prone to fouling [60], similar resins prepared in our laboratory had lower activities than other bactericidal resins derived from chloromethylated polystyrene [61].

Chiellini and co-workers [62] found that soluble 4-VP polymers partly quaternized with butyl bromide were effective phase transfer catalysts in the ethylation of phenyl acetonitrile with bromoethane in the presence of aqueous 50% sodium hydroxide. Other partly quaternized VP-containing copolymers have found applications in reverse osmosis membranes. These include copolymers of 4-VP and vinylidene chloride crosslinked with 1,4-diiodobutane [63]. Increasing the 4-VP content of these membranes results in increases in both the water permeability and the NaCl rejection. Other novel membranes for ion transport have also been prepared from 2-VP-grafted Penton films [64], partly sulphonated copolymers of 4VP-styrene-DVB on

asbestos paper [65], styrene-2-VP and styrene-4-VP copolymers [66], and 4-VP-styrene copolymers quaternized with α -w-diido alkanes [65].

Poly(4-VP) was found to enhance the rate of polycondensation of dimethyl tartrate with hexamethylene diamine [68], while highly porous copolymers of 4-VP and DVB are useful as column packings in the separation of amines by gas chromatography [69]. Finally, poly(2-VP) Complexes have continued to draw sustained interest for their application in lithium pace maker batteries [70].

2.2 RESULTS AND DISCUSSION

2.2.1 N-oxidation of poly(vinylpyridine)s. N-oxides of poly(vinylpyridine)s as intermediates in chemical modifications of poly(vinylpyridine)s.

The general usefulness of the poly(vinylpyridine)s has been illustrated in the introduction part. Our laboratory's interest in functional polymers which can be used as speciality materials in a variety of applications from reagents [71,72] to photoresists [73] and particularly the interest in potential novel uses for functionalized vinylpyridine resins has led us to investigate the chemical modifications of various poly(vinylpyridine)s.

Pyridine-N-oxides are important chemical intermediates in the functionalization of pyridine moieties because they undergo many chemical transformations that proceed only with difficulty or not at all in the parent pyridine system. After the desired transformations are completed, the N-oxide group (if still present) can be removed under mild conditions with a variety of reagents. The chemistry and properties of pyridine-N-oxide and its derivatives have been comprehensively reviewed [74,75,76,77]

We were interested in preparing, for instance, poly(2-chloromethyl-5-vinylpyridine), since it would be a useful intermediate in the preparation of other functional polymers. Concerns that the chloromethyl group would react rapidly with the pyridyl nitrogen were alleviated by the knowledge that 2-chloromethyl-5-vinylpyridine can be

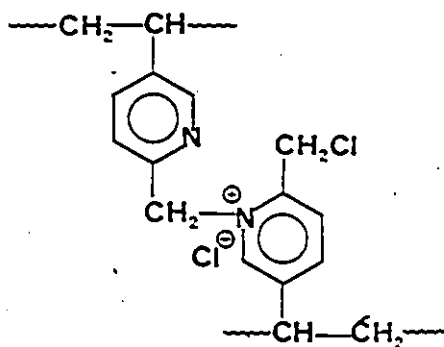
isolated [78]. Although reaction with the polymer would be susceptible to crosslinking by self-quaternization, it was felt that the reaction might still be useful especially for the preparations of polymers with multiple ligands of the type used in selective ion exchange or other chelation processes. For example, reaction of poly (2-chloromethyl-5-vinylpyridine) with a primary or secondary amine would lead to a modified poly (2-methyl-5-vinylpyridine) containing 2-methylamine derivatives. This type of polymers is interesting because the basicity and the ligand properties of poly(2-methyl-5-vinylpyridine) are modified. Other amines could also be introduced by similar processes.

In order to prepare poly(2-chloromethyl-5-vinylpyridine), we chose to treat poly (2-methyl-5-vinyl-N-oxide-pyridine) with trichloroacetyl chloride. The model reaction of 2-picoline-N-oxide with trichloroacetyl chloride in chloroform affords 2-chloromethylpyridine in good yield (70-80%) [78].

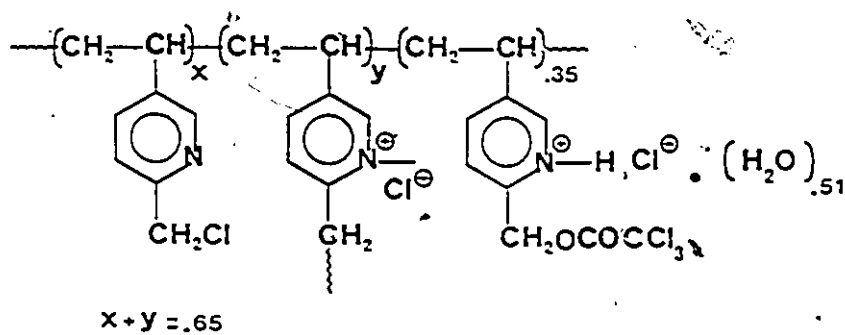
N-oxides of poly (2-methyl-5-vinylpyridine), poly(4-vinylpyridine), (2-methyl-5-vinylpyridine-styrene) copolymers, and crosslinked (4-vinylpyridine-divinylbenzene) polymer were prepared using two methods: N-oxidation with $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$, and N-oxidation with m-chloroperbenzoic acid in chloroform. Both methods gave excellent results with quantitative N-oxidation being obtained for all substrates. However, it should be noted that the work-up of the N-oxide polymer is long and tedious when using $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$, while

the work-up using m-chloroperbenzoic acid is rapid and simple.

Reaction of poly (2-methyl-5-vinyl-N-oxide pyridine) with trichloroacetyl chloride in chloroform, afforded a polymer containing 65% of 2-chloromethyl-5-vinylpyridine units, but the polymer crosslinked in the reaction mixture after 2 h of reaction. The crosslinked polymer had a pink color that became red later. As was anticipated, this crosslinking of the polymer is due to reaction of the 2-chloromethyl groups with the pyridine groups through a quaternization reaction (Scheme 12). The ability of 2-chloromethyl pyridine to undergo this reaction is well known. For instance, Koenig et al. [78] reported that after distillation of 2-chloromethyl pyridine which is a colorless oil, it turned pink after a few minutes and solidified to a red solid after few hours. The infrared spectrum and elemental analysis of the crosslinked polymer suggest that it has the structure given in Scheme 13. The infrared spectrum shows bands at 1760 and 2000-2500 cm^{-1} corresponding to the 2-pyridylmethyl trichloroacetate hydrochloride. These moieties are intermediates in the reaction of 2-chloromethyl-N-oxide pyridine with trichloroacetyl chloride. Their presence in the polymer even after long periods of reaction are due to the fact that the rapid crosslinking of the polymer prevents their further reaction to give the desired 2-chloromethyl-5-vinylpyridine product.



SCHEME 12



SCHEME 13

The fact that 2-chloromethyl pyridine is unstable and tends to quaternize is not unexpected, however, it is known that 2-chloromethyl pyridine is conveniently stored as the hydrochloride. It was our hope to be able to isolate the hydrochloride of the poly (2-chloromethyl-5-vinylpyridine) prior to the occurrence of extensive crosslinking. Unfortunately, the quaternization reaction occurs at very early stage in the reaction of the polymeric N-oxide and trichloroacetyl chloride.

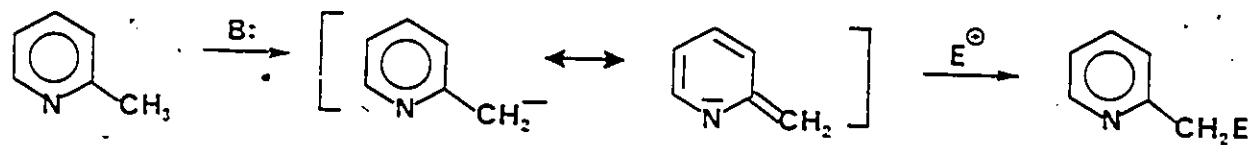
In an attempt to reduce the extent of the spontaneous crosslinking reaction the concentration of N-oxide units on the starting polymer was reduced through the use of copolymers of 2-methyl-5-vinylpyridine and styrene containing only 25 or 10% of 2-methyl-5-vinylpyridine units. In the reaction of these copolymers in N-oxide form with trichloroacetyl chloride in chloroform we observed that the reaction mixture did not turn pink as fast as was the case for the homopolymer of poly (2-methyl-5-vinyl-N-oxide pyridine), but crosslinking occurred nevertheless to a significant extent with the characteristic pink color.

2.2.2. Reaction of poly(2-lithiomethyl-5-vinylpyridine) with a Schiff base.

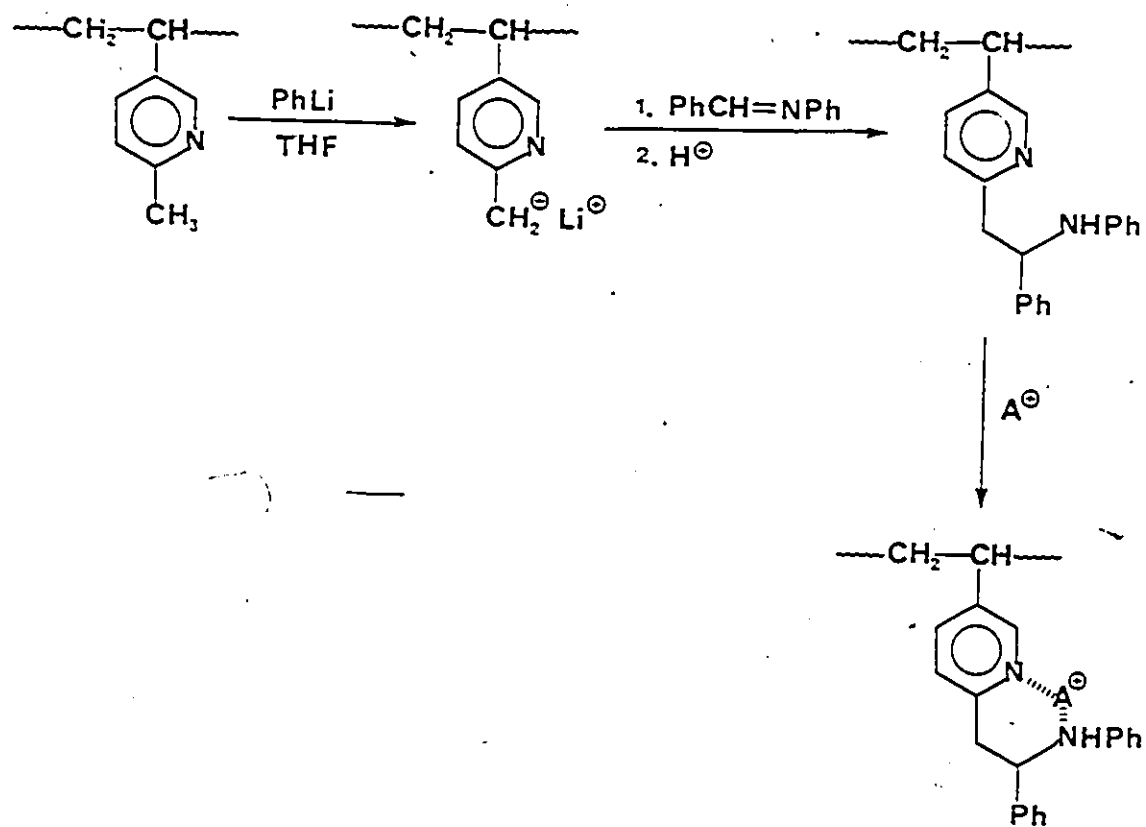
Alkyl groups in positions α and γ to the ring nitrogen in pyridines are significantly reactive, especially in processes which proceed via base-catalyzed deprotonation, as the resulting anions are resonance-stabilized (Scheme 14). These anions are then able to react with a wide range of electrophiles to give condensation products. It was thought that poly(2-methyl-5-vinylpyridine) could be modified by using the acidic properties of its methyl group. For instance, reaction of poly(2-lithiomethyl-5-vinylpyridine) with a Schiff base (Scheme 15) would lead to a polymer containing two different nitrogen ligands. As can be seen in Scheme 15, a polymer containing such ligands could exhibit very interesting complexing properties, for example, both nitrogens should readily complex cations with formation of stable 6-membered rings.

Shuman and Amstutz [79] have studied the reaction of 2-picolyllithium with Schiff bases.

Poly(2-lithiomethyl-5-vinylpyridine) is obtained by reacting phenyllithium with poly(2-methyl-5-vinylpyridine) in dry THF; in contrast, all attempts to obtain the anion using lithium were unsuccessful. Formation of the anion is easily detected by the appearance of its characteristic red color.



SCHEME 14



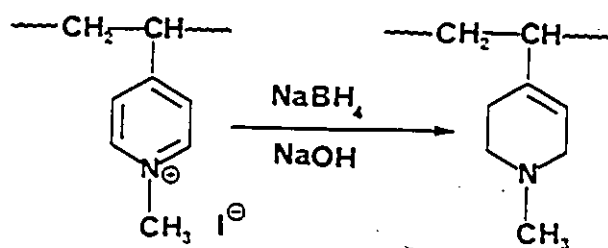
SCHEME 15

Reaction of the poly(2-lithiomethyl-5-vinylpyridine) with benzalaniline led to the desired modification. However, only 50% of the units were modified as indicated by ^1H -NMR spectrum and elemental analysis of the obtained polymer.

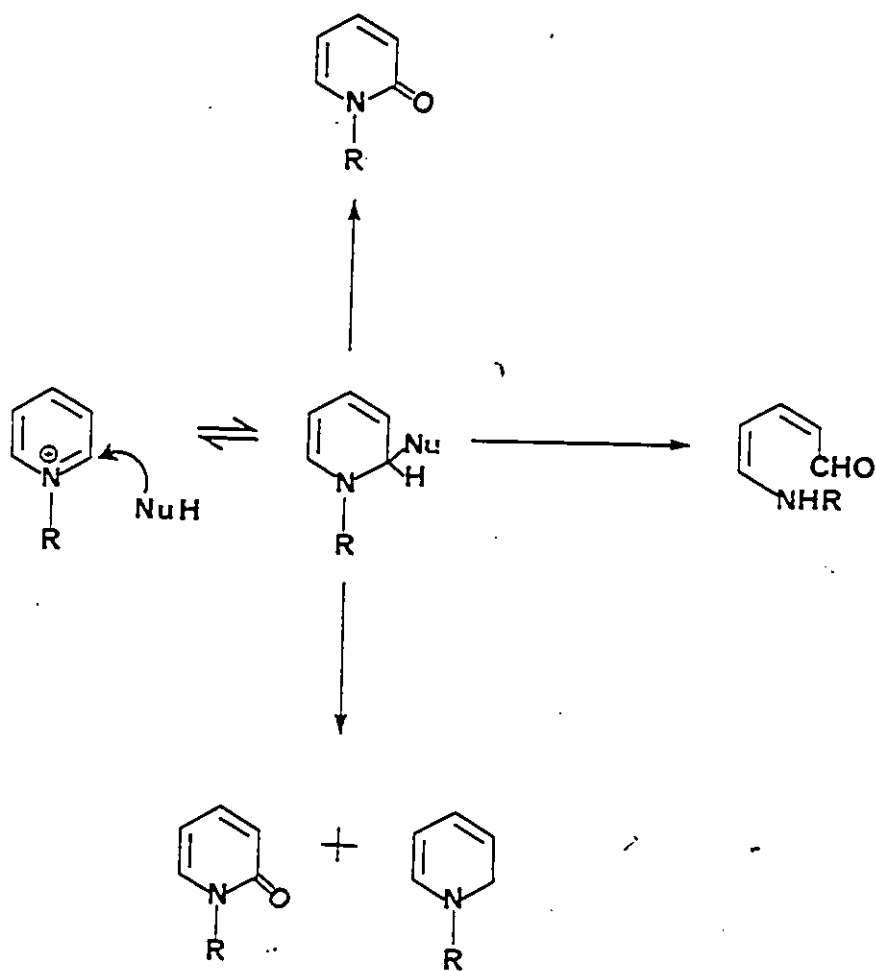
2.2.3. Reduction of quaternized poly(4-vinylpyridine) with sodium borohydride.

Pyridine is not reduced by sodium borohydride. On the other hand, borohydride reduction of alkyipyridinium salts proceeds readily to give tetrahydropyridine derivatives. Jackson and Bolto [80] have reported the borohydride reduction of poly(4-vinylpyridine) quaternized with methyl iodide to afford a poly (4-vinyltetrahydropyridine) derivative (Scheme 16). The reduced polymer was said to be soluble in chloroform, ethanol, methanol, and dilute hydrochloric acid. We prepared quaternized poly(4-vinylpyridine) with dimethyl sulfate and proceeded to its reduction with sodium borohydride. Since Jackson and Bolto did not describe the conditions under which they performed the reduction, we followed the experimental procedure used by Saito and May [81] for the reduction of monomeric quaternized pyridine derivatives.

In our hands, the reduction of the quaternized polymer always yielded a crosslinked material. However crosslinking



SCHEME 16



SCHEME 17

of the reduced polymer often occurred during work-up. Two different work-up procedures were used to isolate the reduced polymer. In all cases, the polymer precipitated out of solution during the reduction. In the first work-up we used, the precipitated reduced polymer was filtered and dissolved in methanol, then precipitated in large excess of ethyl acetate and dried under vacuum at room temperature. After drying, the polymer was no longer soluble in methanol or chloroform. In the second work up the precipitated reduced polymer was extracted from the reaction mixture with chloroform then the chloroform solution of the reduced polymer was dried with magnesium sulfate, and the solvent was evaporated. After drying the obtained polymer was no longer soluble in chloroform.

Analysis of the infrared spectra for the reduced polymers which were obtained using the two different work-up procedures show that both reduced polymers are identical. Figure 1 shows the FTIR spectrum of the starting polymer: poly(N-methyl-4-vinylpyridinium methyl sulfate) and of the reduced polymers. A comparison of the infrared spectra of the reduced polymers with that of 1-methyl-1,2,3,6-tetrahydropyridine shows that the reduced polymers indeed contain mainly tetrahydropyridine units. Most of the bands in the spectra of the reduced polymers in the range $1460-400\text{ cm}^{-1}$ are identical in shape, intensity and frequency to those found in the spectrum of 1-methyl-1,2,3,6 tetrahydropyridine. Figure 2A shows the infrared

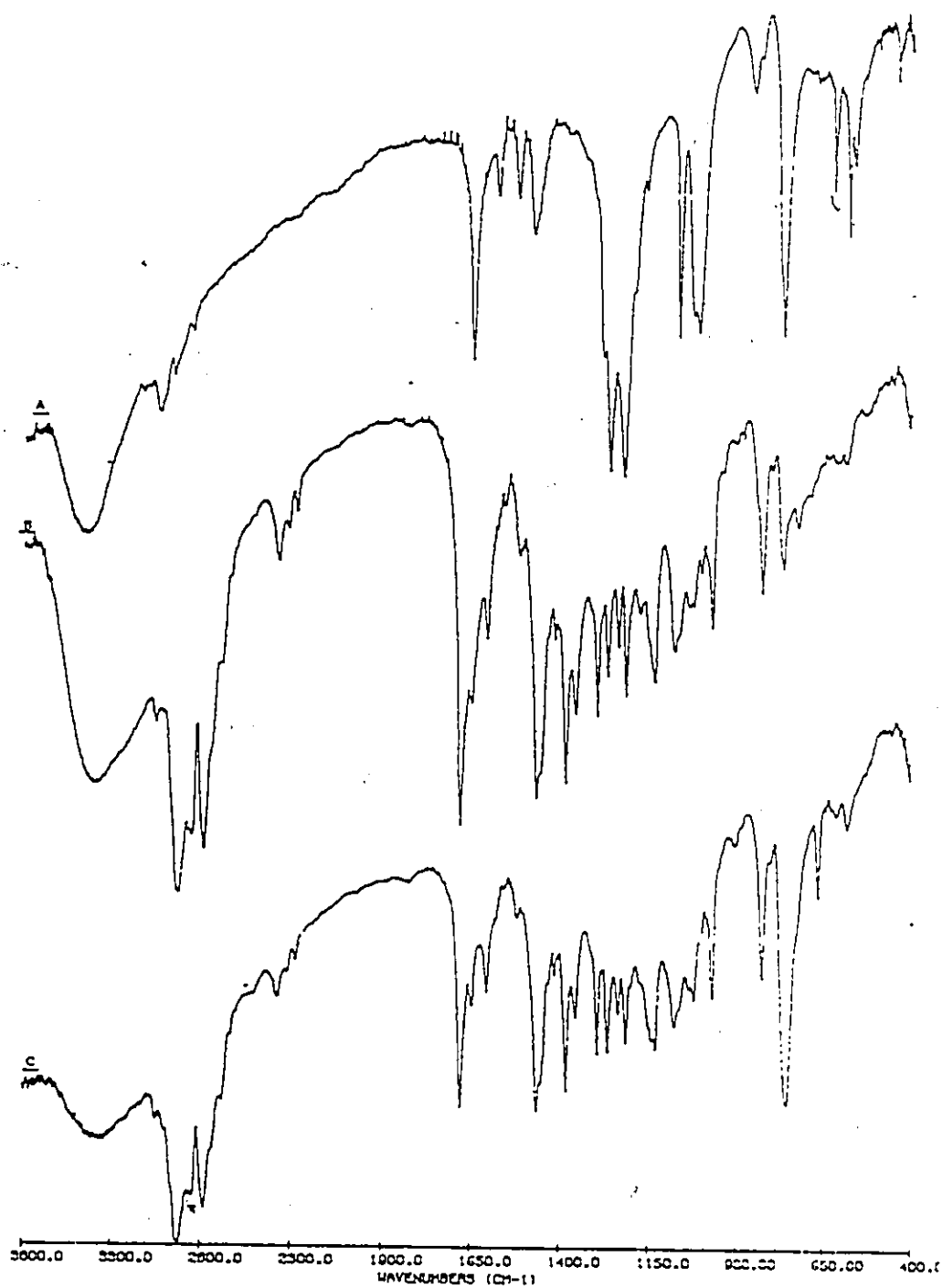
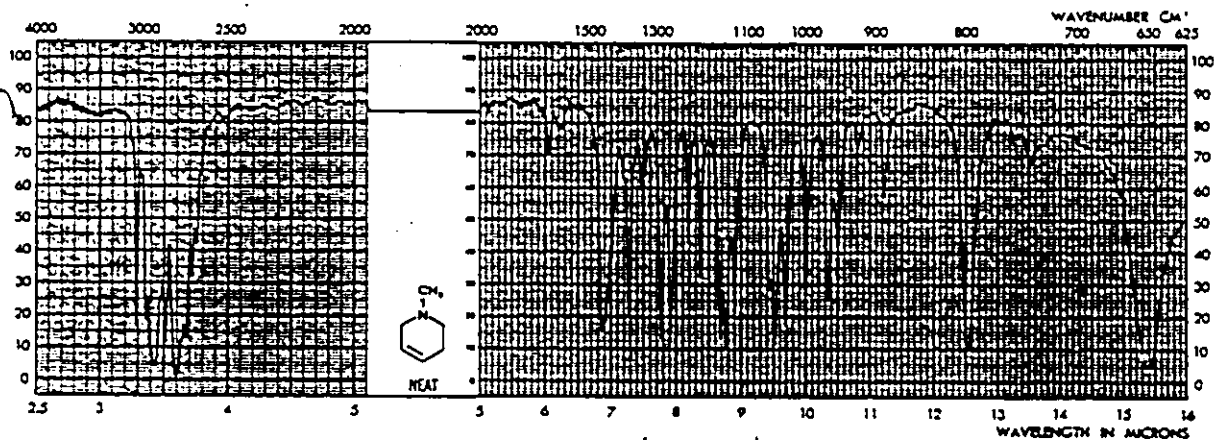


Figure 1. FTIR spectra of: A) poly(N-methyl-4-vinylpyridinium methyl sulfate), B) and C) reduced polymers obtained by reaction of the polyalkylpyridinium salt with sodium borohydride using methods 1 and 2 respectively.

17,690-7
 1-Methyl-1,2,3,6-tetrahydropyridine, 99%
 M.W. 97.16 b.p. 113-114° n_D^{20} 1.4570 d_4^{20} 0.837



Acrolein (acrylaldehyde)
 $H_2C=CHCHO$ M.W. 56.06 n_D^{20} 1.4065
 b.p. 53°

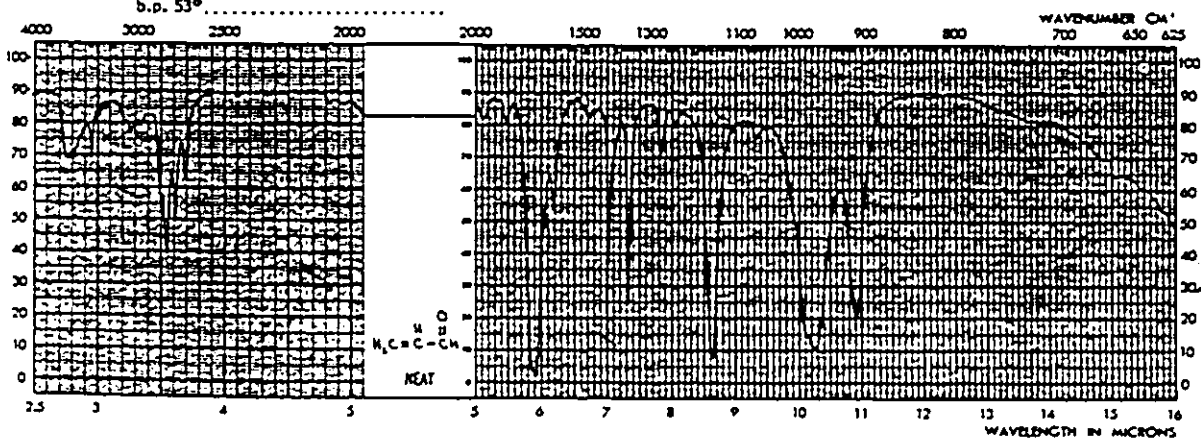


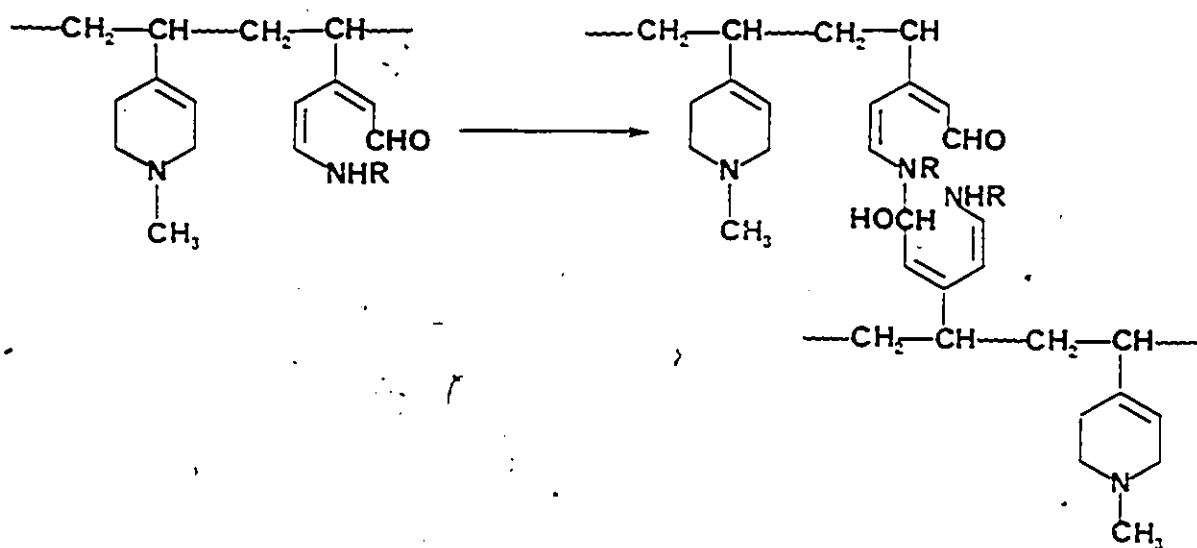
Figure 2. FTIR spectra of A) 1-methyl-1,2,3,6-tetrahydropyridine and B) acrolein. IR spectra have taken from Aldrich catalog.

spectrum of 1-methyl-1,2,3,6-tetrahydropyridine. For our reduced polymers some of the bands in the range 1460-650 cm^{-1} are: 1461, 1377, 1350, 1289, 1259, 1229, 1208, 1128, 1080, 966 cm^{-1} and for 1-methyl-1,2,3,6-tetrahydropyridine: 1460, 1370, 1334, 1282, 1266, 1235, 1212, 1136, 1030, 966 cm^{-1} . However, the spectra of the reduced polymers also show bands at 2368, 2315, and 2268 cm^{-1} as well as a strong band at 1675 cm^{-1} ; these are absent in the spectrum of 1-methyl-1,2,3,6-tetrahydropyridine. We believe that these bands correspond to the side-product that is causing the crosslinking of the reduced polymer. There is also a hydroxyl band that always can be attributed to water in the polymer due to the fact that it is very hygroscopic and difficult to dry completely. We could not attribute the extra bands to a specific by-product. However, it is known that the positive charge in pyridinium ions favours attack by nucleophiles at the α or γ - positions under mild conditions to give adducts that normally undergo further reaction very rapidly (Scheme 17). Our reductions were done in alkaline solution, therefore in the presence of nucleophilic hydroxide ion. Scheme 17 shows that the adduct resulting from reaction of hydroxide ion with the pyridinium units can give three kinds of derivatives: pyridinone, dihydropyridine and a 5-amino conjugated aldehyde. The pyridinone derivative does not possess bands at 2368, 2315, and 2268 cm^{-1} nor does the dihydropyridine

derivative. However, the 5-amino conjugated aldehyde could be responsible of the strong band at 1675 cm^{-1} ($-\text{CHO}$) and the set of bands at 2368 , 2315 and 2268 cm^{-1} . Figure 2B shows the infrared spectrum of acrylaldehyde. We observe that the set of bands corresponding to the aldehyde function of acrylaldehyde (2817 , 2778 , 2703 cm^{-1}) is remarkably similar in shape and intensity to the set of bands at 2368 , 2315 and 2268 cm^{-1} in the spectra of our reduced polymers. The lower frequencies of these bands in our polymers could be due to the extended conjugation and/or a hydrogen-bonded interaction between the amine and the aldehyde group. Similarly, the lower frequency of the carbonyl group (1675 cm^{-1}) in our reduced polymers with respect to the carbonyl frequency of acrylaldehyde (1695 cm^{-1}) may be explained by the presence of hydrogen-bonding interactions.

Moreover, the presence of these 5-amino conjugated aldehyde units in the reduced polymers could explain the post-crosslinking of the polymer through reaction of the amino groups with the carbonyl groups (Scheme 18). We must recall at this point that even only a few reactions will result in crosslinking and therefore insolubilization of the polymer.

Jackson and Bolto [80] have reduced poly(N-methyl 4-vinylpyridinium iodide) and we have tried to reduce poly(N-methyl-4-vinylpyridinium methyl sulfate) in similar fashion. However the polymer crosslinked. In view of our



SCHEME 18

results, we decided to prepare the same polyalkylpyridinium salt that Jackson and Bolto used. However, the sodium borohydride reduction of poly(N-methyl-4-vinylpyridinium iodide), yielded identical results to those obtained for the reduction of poly (N-methyl-4-vinylpyridinium methyl sulfate.) Again the reduced polymer crosslinked and its infrared spectrum showed the set of bands at 2368, 2315, and 2268 cm^{-1} and the strong band at 1675 cm^{-1} observed previously.

Finally, we were able to obtain an uncrosslinked and therefore, soluble reduced poly(4-vinylpyridine) by applying the following modifications to our original alkaline borohydride reduction: First, the concentration of sodium hydroxide was decreased from 1N to 0.4N; second, the reaction time was decreased from 5 h to 3 h and finally, instead of isolating the free amine, we isolated its pyridinium salt formed in situ by addition of hydrochloric acid. Figure 3 shows the FTIR spectra of starting poly(N-methyl-4-vinylpyridinium iodide), and that of the obtained reduced polymer. The reduced polymer does not possess the set of bands at 2368, 2315 and 2268 cm^{-1} neither the strong band at 1675 cm^{-1} . Among the bands corresponding to the tetrahydropyridine units in the reduced polymer are: 1423.6 cm^{-1} corresponding to the bending vibration of the methyl group (N-CH₃), 1125 and 1051.3 cm^{-1} corresponding to N-C vibrations.

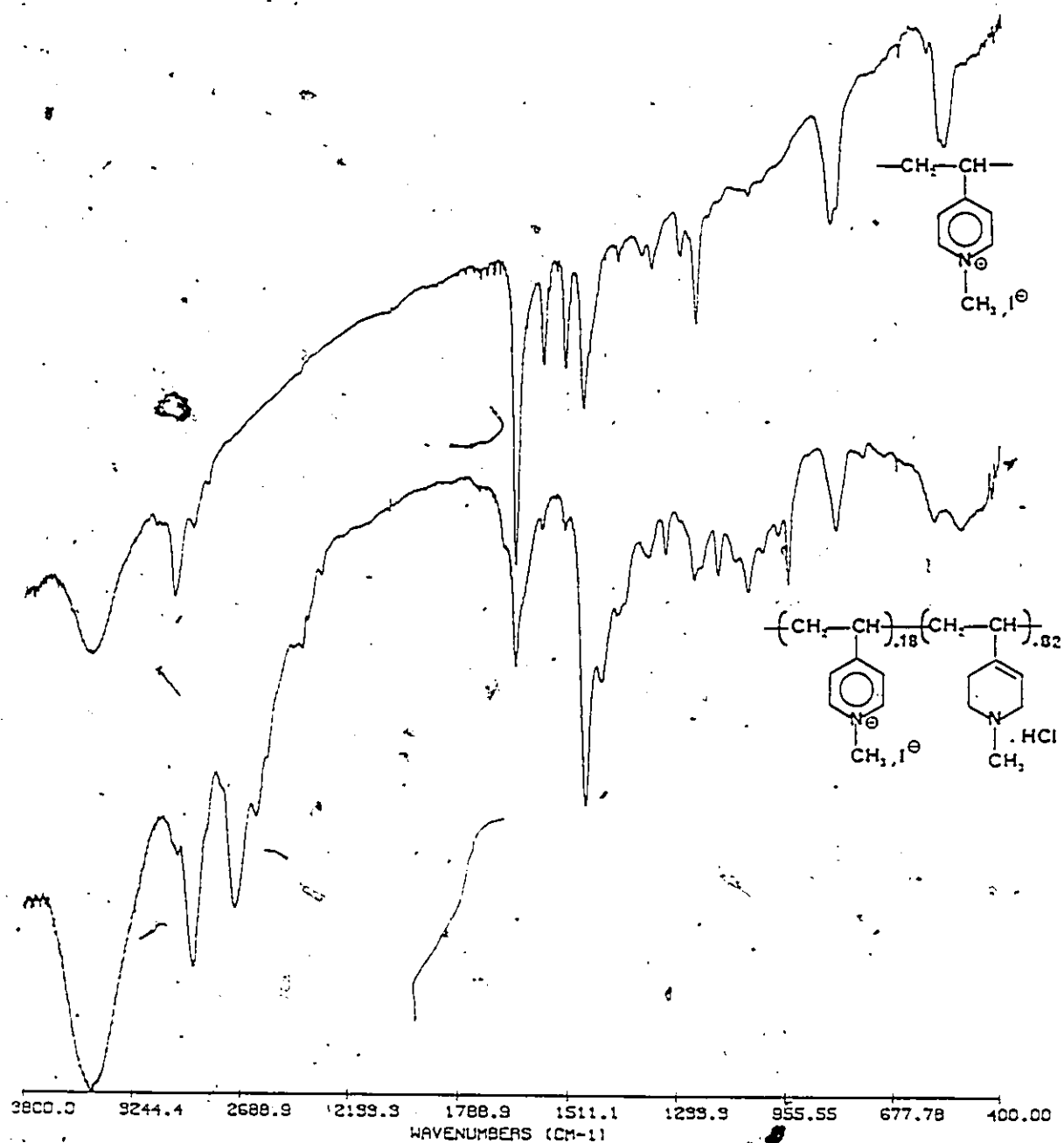
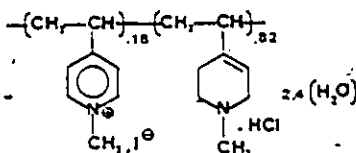


Figure 3. FTIR spectra of poly(N-methyl-4-vinylpyridinium iodide) and the reduced polymer obtained by reaction of the polyalkylpyridinium salt with sodium borohydride using method 3.

Elemental analysis of our reduced polymer shows that the reduction was accomplished up to an extent of approximately 82%. 18% of the N-methylpyridinium iodide units remain intact and therefore the final polymer has the following structure.



E.A:

Found: C: 44.44%, H: 6.85%, N: 6.38%, I: 10.62%, Cl: 14.36%, O: 17.39%

Calculated: C: 43.93%, H: 8.3%, N: 6.4%, I: 10.69%, Cl: 13.24%, O: 17.43%

The presence of un-reduced 1-methyl-4-vinylpyridinium units in the polymer is shown clearly in its ^{13}C spectrum. Figure 4 shows the ^{13}C spectra of poly(N-methyl-4-vinylpyridinium iodide) and of the reduced polymer. Resonances at 146.8 and 129.6 ppm correspond to the remaining alkylpyridinium units. All characteristic resonances of the tetrahydropyridine units are also clearly identified.

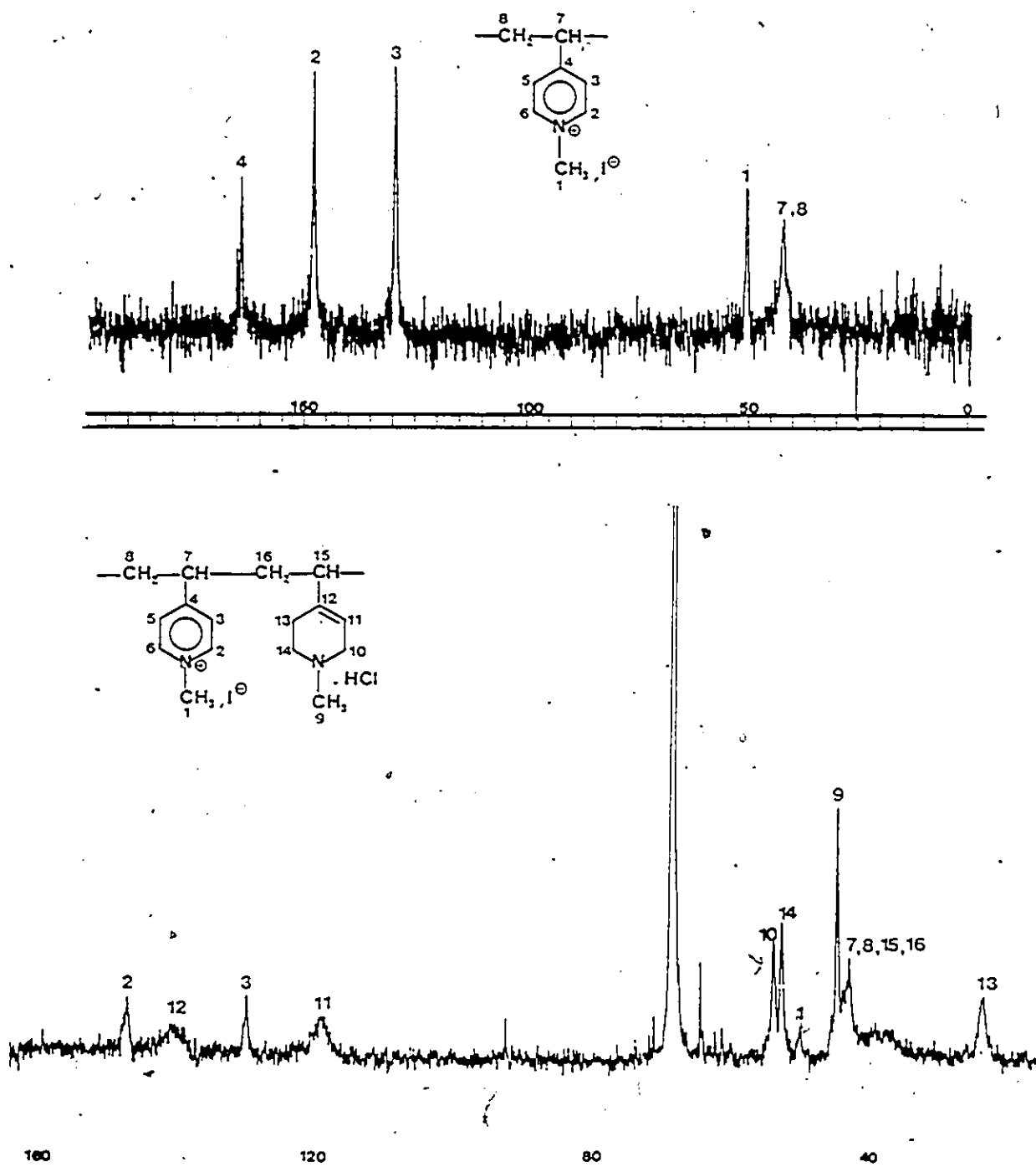


Figure 4. ^{13}C spectra of poly(N-methyl-4-vinylpyridinium iodide) and the reduced polymer obtained by reaction of the polyalkylpyridinium salt with sodium borohydride using method 3.

2.2.4 Study of the mechanism of the self-catalyzed solubilization of crosslinked and quaternized 4-vinylpyridine-ethylene dimethacrylate resins.

Most of the reactions included in our studies on the chemical modification of poly (vinylpyridine)s were performed on soluble polymers. This facilitates the monitoring of the reactions as possible problems, such as the formation of undesired side-products or of crosslinks can easily be seen. However, our ultimate aim was the modification of crosslinked polymers which are more widely used in practical applications. Therefore, we also performed several modifications on crosslinked poly(vinylpyridine)s. We prepared crosslinked poly(4-vinylpyridine) by suspension polymerization using different crosslinking agents such as divinylbenzene and ethylene dimethacrylate. Quaternization was among the chemical modifications performed on the insoluble polymers. One of our procedures called for the quaternization to be carried out in basic solution. During the quaternization of the 4-vinylpyridine-ethylene dimethacrylate resin in basic solution, we observed that the polymer had lost its initial macroporous structure and had become jelly-like. This suggested that a large number of crosslinks had been destroyed during the reaction, a most unusual finding in view of previous findings [82].

A series of crosslinked 4-VP-EDMA copolymer beads containing from 2 to 25 wt % of the crosslinking agent was

prepared by radical polymerization in suspension. The copolymers were quaternized in refluxing nitromethane with excess of n-butylbromide. Typically, the quaternization reaction with n-butylbromide was incomplete, reaching a maximum of approximately 50%, but no efforts were made to force the reaction to completion. Table 1. shows the characteristics of the 4-VP-EDMA copolymers.

The hydrolysis of the quaternized copolymers was followed visually by simple immersion of the sample in a vial containing 0.1 to 2 mol/l of NaOH at room temperature. It was observed that extensive swelling of the beads occurred with formation of a green-brown coloration, until complete dissolution was eventually observed with the formation of a homogeneous dark brown solution. This observation is surprising in view of the fact that very harsh conditions are normally required to hydrolyze other polymers containing EDMA-based crosslinks. For instance, Hradil and Svec [82] investigated the synthesis of a polymeric sorbent bearing carboxylic groups. They prepared a 2-3-dihydroxypropyl methacrylate-ethylene dimethacrylate copolymer that contained 40 wt % of EDMA. Hydrolysis of the ester groups of the 2-3-dihydroxypropyl methacrylate units would yield the desired polymeric sorbent bearing carboxylic groups. Their studies on the alkaline hydrolysis of the crosslinked polymer showed that crosslinked methacrylate copolymers are rather resistant to alkaline hydrolysis. Thus, heating the polymer at 80°C for

Table 1. Characteristics of 4-vinylpyridine-ethylene dimethacrylate copolymers.

Polymer feed		Copol- ymer	Quater- nization	Dissolution	
4-VP (wt. %)	EDMA (wt. %)			NaOH (mol/l)	Time (h)
		4-VP (wt. %) ^a	(%)		
98	2	95	24	0.1, 0.5	150 ^b
			31	0.1, 0.5	150 ^b
96	4	93	28	0.1, 0.5	140 ^b
			40	0.1, 0.5	100
				1.0	72
94	6	90	27	0.1, 0.5	150 ^b
			36	0.1, 0.5	130 ^b
				1.0	120
92	8	89	38	0.5, 0.5	120
				1.0	90
87	13	85	33	0.1	150 ^b
				1.0	120
			48	0.1	72
				0.5	48
				1.0	18

^a Determined by elemental analysis of nitrogen.

^b The time required for dissolution is only approximative as there is no sharp change between gel and solution.

16h with 12.3 wt% NaOH only afforded a product containing 0.11 mmol/g of -COONa groups, which corresponds to 2.7% conversion. Under more drastic conditions (26.5 wt. % NaOH, 102°C , 16 h) a conversion of 22.8% was obtained. Under these conditions hydrolysis of only the 2-3-dihydroxypropyl methacrylate units had happened. Hydrolysis of the EDMA units required both high temperature ($80\text{--}120^{\circ}\text{C}$), very long reaction times, and high concentrations of alkali (5-10M).

Similarly, the unquaternized copolymer of 4-VP and EDMA is totally unaffected by 0.1M NaOH even if placed in the presence of n-butylpyridinium bromide, which could potentially act as a phase-transfer catalyst in the reaction.

Clearly, the dissolution reaction is the result of some base-catalyzed hydrolysis process involving the ester bonds of EDMA, which constitute the crosslinks of the network polymer. Cleavage at any other point of the polymer chains can be excluded as copolymers of 4-VP and 2,5-divinylpyridine or 4-VP and divinylbenzene are found to be perfectly stable in basic medium even after similar quaternization with n-butylbromide. It is interesting to note that the rate of dissolution of the quaternized 4-VP-EDMA copolymers increases with increasing concentration of the alkali solution, reaching a maximum at 1 mol/l, then decreases with no dissolution observed when the concentration reaches 2 mol/l. This finding is in

agreement with previous data [83] which indicate that the rate of hydrolysis of esters decreases with increasing ionic strength. Similarly, while a 0.1M NaOH solution dissolves the quaternized resins, an increase in ionic strength to 2 mol/l by addition of potassium bromide to the dilute alkali solution prevents the dissolution of the polymer.

It might be argued that, as quaternization improves the hydrophilicity of the copolymers as well as its swelling in aqueous medium, transport of the hydroxide ions to the ester crosslinks is greatly facilitated, thereby enhancing their cleavage. This possibility can be excluded by a simple comparison with the behavior of the very hydrophilic copolymer of 2-hydroxyethyl methacrylate and EDMA. Although extensive swelling is observed when the latter polymer is treated with a 0.1-1 M solution of NaOH, no dissolution is observed even upon addition of n-butylpyridinium bromide.

Although it has been reported that poly(4-VP) is a catalyst for the hydrolysis of esters [84], it does not appear that the remaining unquaternized 4-VP units can be held responsible for the facile hydrolysis of the EDMA units of the chain in the quaternized copolymer. In fact, the catalytic activity of both free and quaternized 4-VP copolymers in the hydrolysis of an ester such as n-butylacetate appears to be negligible as shown in Figure 5; clearly, the rate of hydrolysis of the low molecular weight

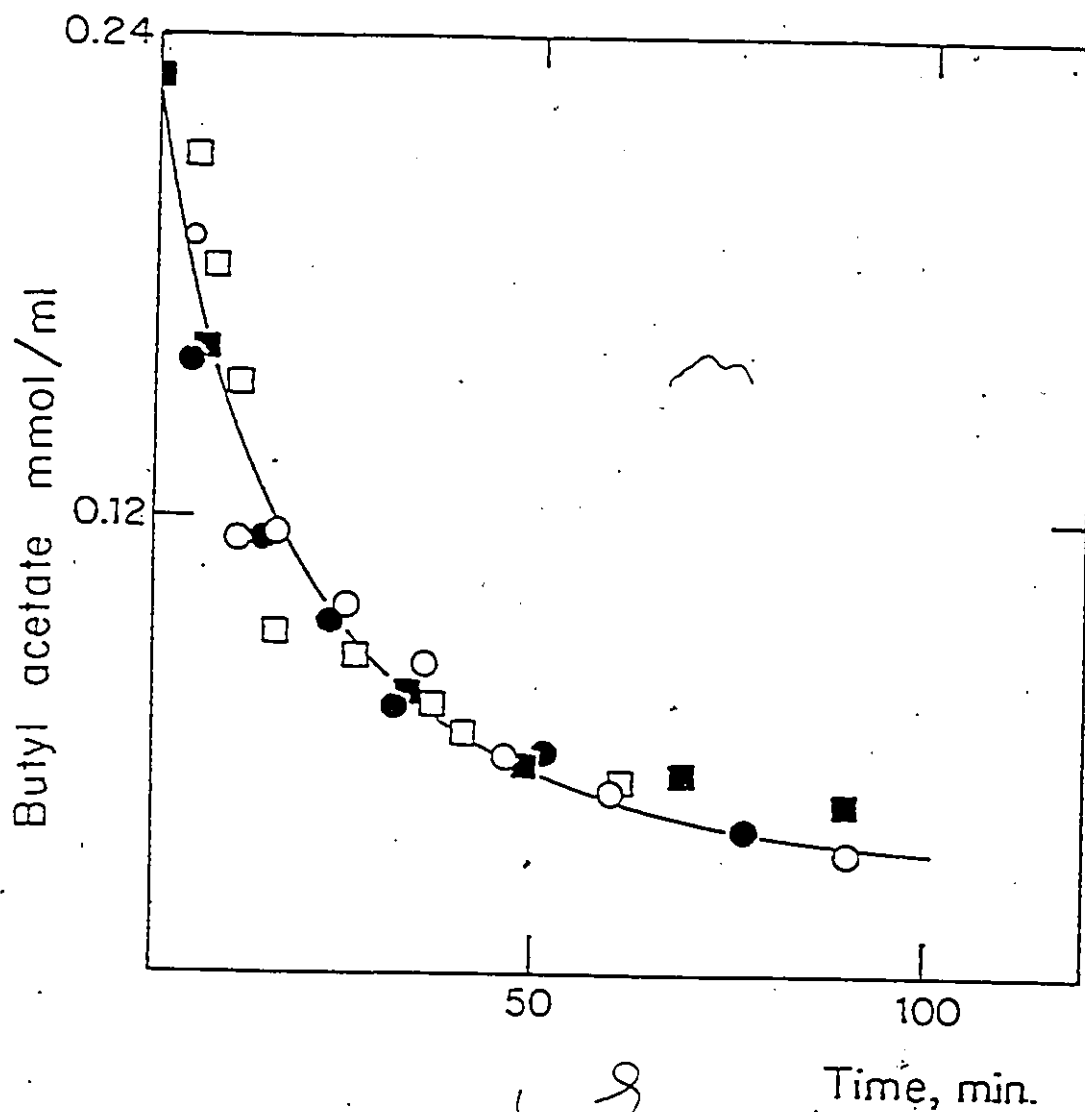


Figure 5. Hydrolysis of 2 ml of a solution (0.6 M) of n-butyl acetate in n-amyl alcohol at 30°C using; ○ 3 ml 0.5 M NaOH + 0.050 g quaternized 4-VP-DVB copolymer (30% substituted); □ 3 ml 0.5 M NaOH + 0.026 g n-butylpyridinium bromide; ● 3 ml 0.5 M NaOH; ■ 3 ml 0.5 M NaOH + 0.050 g 4-VP-DVB copolymer.

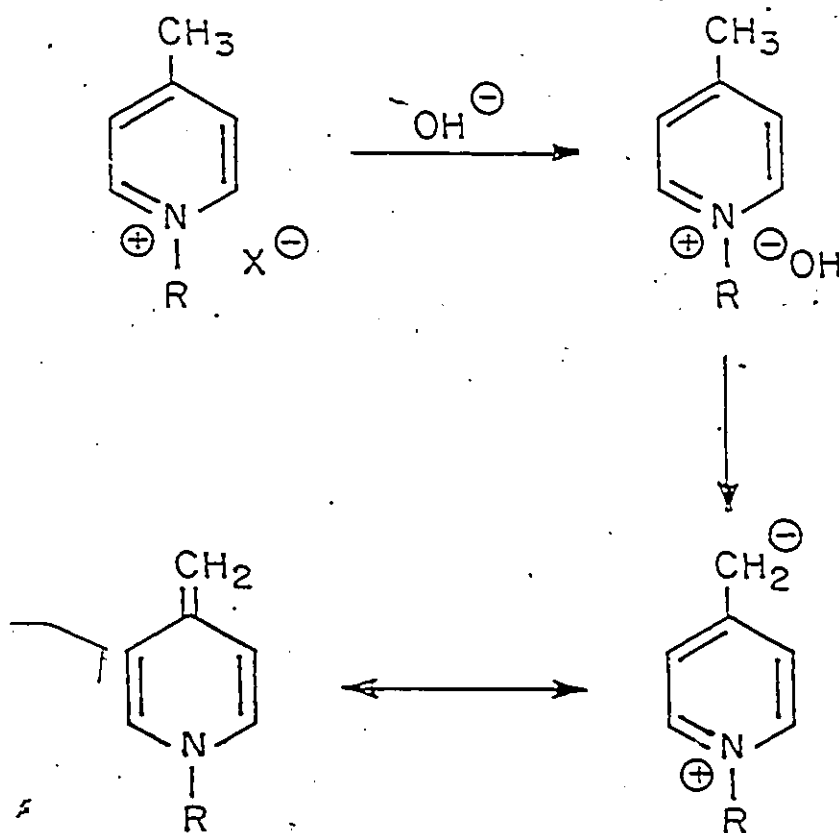
ester is unaffected by addition of the 4-VP or quaternized copolymers. Similarly, a solution of a sterically hindered ester such as n-butyl pivalate, which can be regarded as a model for the methacrylate units within the polymer, is perfectly stable when treated with 0.1 M NaOH, even in the presence of quaternized 4-VP copolymers.

These findings suggest strongly that a simple base hydrolysis mechanism involving the EDMA units is not responsible for the dissolution of the crosslinked polymer.

An alternate mechanism might involve an alkaline hydrolysis process catalyzed by the quaternized polymer itself acting as an internal phase-transfer catalyst. Quaternary pyridinium salts are generally considered to have a low activity as phase-transfer catalyst [85,86]. For instance, Herriot and Picker [85] reported a rate constant of $1.6 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$ for the reaction of thiophenoxide with 1-bromooctane in benzene-water using n-butylpyridinium bromide as phase-transfer catalyst. In contrast, a rate constant of $3.7 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ was obtained using a more effective phase-transfer catalyst such as tetra-butyl phosphonium chloride. However, despite of the low activity of the quaternary pyridinium salts, it is not inconceivable that their activity might be enhanced through their immobilization on the polymer near the reactive ester bond. If such were the case, then it would be expected that other polymeric phase-transfer catalysts, crosslinked in similar fashion with EDMA, should undergo

the same facile dissolution reaction. A simple probe for this mechanism was constructed by the copolymerization of vinylbenzylchloride with EDMA, followed by quaternization with tri-n-butylamine. The resulting polymer was found to have a very high stability in aqueous base and no dissolution was observed. Since benzyl tributyl ammonium salts are significantly better phase-transfer catalysts than n-butylpyridinium salts [85] this alternate mechanism is clearly not operative.

All the facts outlined above seem to point in the direction of an intramolecularly catalyzed process for this splitting reaction. Interactions from distant moieties within the polymer can be excluded as the reaction is not catalyzed by external additives and the polymer itself is not a catalyst for the hydrolysis of low molecular weight esters. It is therefore reasonable to assume that a close proximity of the ester bond and the reactive group is required for cleavage to occur. The formation of pyridinium methide pseudo-bases by reaction 2- or 4-pyridinium salts with alkali (Scheme 19) has been known for over 90 years [87]. The carbanion of the pseudo-base is itself a strong nucleophile [88] with good reactivity. In the case of copolymers containing quaternized pyridine groups, such methides can also form in alkaline medium, and we believe that the cleavage reaction is the result of attack of these anionic species on neighboring ester groups, likely through a six-membered ring intermediate. A

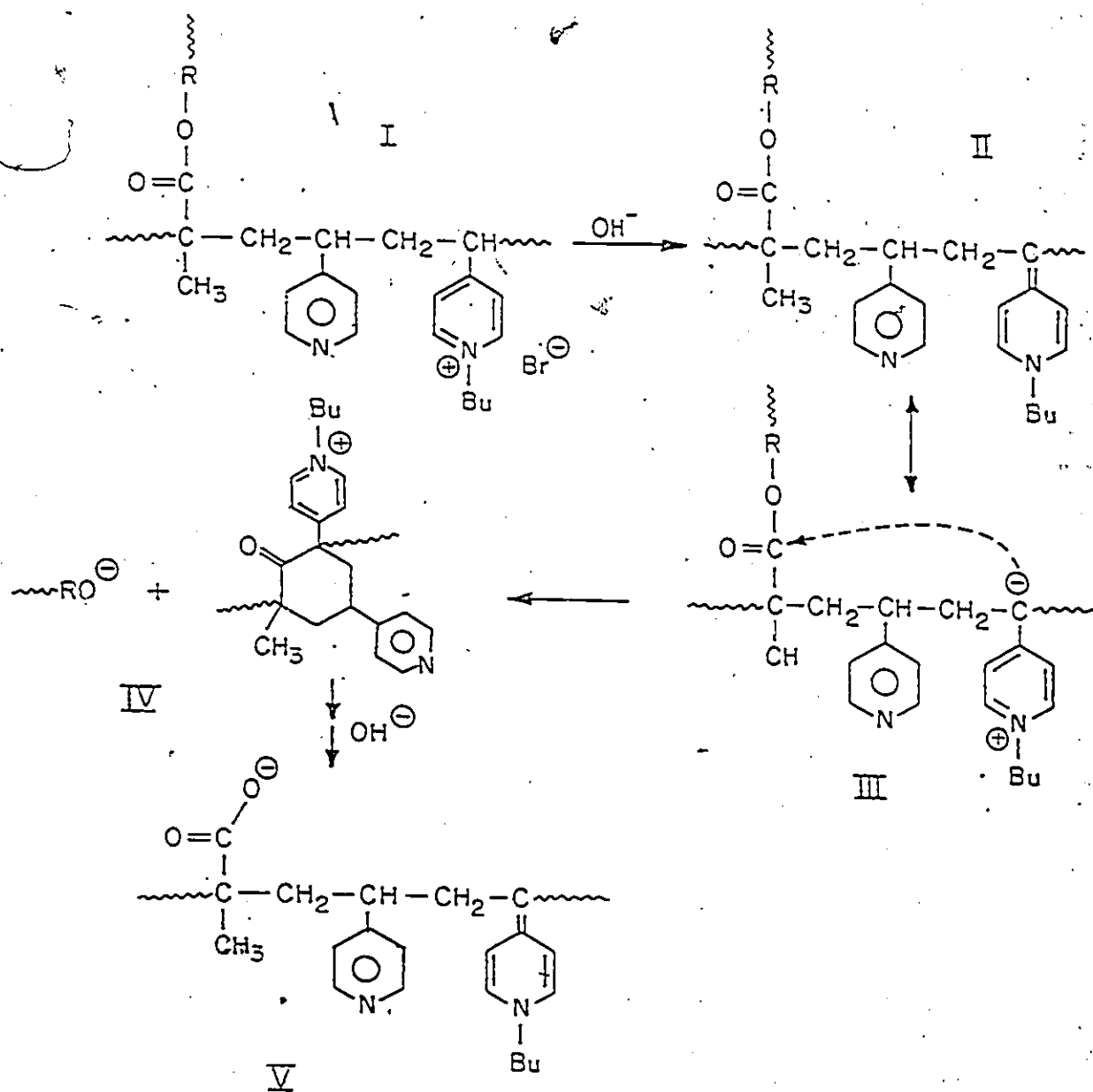


SCHEME 19

possible pathway for this reaction is outlined in Scheme 20.

The key step in this reaction is the formation of the six-membered ring intermediate IV by attack of the anionic end of methide III onto the carboxyl group. This step can be achieved only if the polymer chain possesses good mobility, a requirement which is fulfilled in the swollen polymer when the degree of crosslinking is not excessive (below 15%). A modelling study of the reaction using space-filling molecular models confirms that formation of the required six-membered ring intermediate from the 4-vinylpyridinium copolymer is achieved readily. In contrast, molecular model studies for an analogous 2-vinylpyridinium copolymer indicate that steric problems may prevent the formation of the six-membered ring intermediate, and indeed copolymers of 2-VP and EDMA quaternized with n-butylbromide do not dissolve in aqueous base, even though methide formation does occur.

The suggested mechanism involving the pseudo-base requires the presence of a vinylpyridine diad close to the ethylene dimethacrylate unit. The side from which the anion approaches the crosslinking unit is unimportant, as long as the six-membered ring intermediate is available. This means that in order to split one crosslink, it is sufficient that only one of the four properly placed vinylpyridine units in the vicinity of the EDMA unit be active. Therefore, according to this mechanism, a 4-VP



SCHEME 20

unit isolated between EDMA groups can never be active. Both units in 4-VP diads surrounded by EDMA can theoretically be active, but the vicinity of two crosslinks restricts chain mobility and ring formation is not probable. The same reasoning applies to 4-VP triads. With growing sequence length, the chain mobility increases, but at the same time the number of inactive units also increases because in all sequences only the second and the penultimate vinylpyridine units may be active.

The probability of sequences in a copolymer with known composition is calculated from the following equation [89]

$$(p_{M_1})_N = (p_{11})^{N-1} (1-p_{11})$$

where $(p_{M_1})_N$ is the probability of a sequence with length N made up of monomer 1, and p_{11} is defined by the equation:

$$p_{11} = \frac{r_1}{r_1 + M_2/M_1}$$

where M_1 and M_2 are the mole fractions of both monomers in the polymerization feed, and r_1 is a reactivity parameter for the monomer 1. Because the reactivity parameters for the couple 4-VP/EDMA have not been published, we used parameters calculated from the Q, e data [90]: $r_1=0.98$ and $r_2=0.78$.

The sum of probabilities of sequences with length $N=1$ to ∞ is unity. As has been mentioned above, the sequences

with $N = 1, 2$ and 3 are not considered to be active. From the sequences with $N \geq 4$ units, only 2 units are active (the second and the penultimate). Thus, the fraction of all active units in the copolymer, $(p_{M_1})_{act}$, is given by the equation :

$$(p_{M_1})_{act} = (1 - p_{11}) \cdot \sum_{N=4}^{\infty} 2/N (p_{11})^{N-1}$$

where we have chose $N = 50$ as the maximum length of calculated sequences of 4-VP units. Table 2 shows the obtained values for $(p_{M_1})_{act}$. This function reaches a maximum at an EDMA concentration in the polymerization feed of about 12 mol %, i.e., at 88 mol % of 4-VP. At a higher concentration of 4-VP the fraction of active units decreases because of the increasing length of sequences in which a major portion of the units remain inactive. At a lower concentration of 4-VP, there is an increase in the amount of short, 1-3- membered sequences, also considered to be inactive. At the same time, the fraction of crosslinking agent increases, and the EDMA monomer can itself be connected in sequences bearing two or more units which are more stable.

In principle, the number of catalytically active units should be higher, or equal to the number of units of the crosslinking monomer. This is fulfilled up to, about 15

Table 2. Statistical calculations of sequence distribution of 4-vinylpyridine units in its copolymers with ethylene dimethacrylate.

M_1^a	N^b	$(pm_1)N^c$	$(pm_1)_{act}^d$
98.0	50	0.642	0.08
95.7	50	0.894	0.13
91.2	50	0.991	0.16
88.9	50	0.998	0.17
85.3	40	0.998	0.17
75*	20	0.997	0.14
60*	13	0.998	0.08
40*	7	0.998	0.03

a Mol % of 4-VP in the copolymer, polymers shown with * have not been prepared.

b Maximum length of calculated sequences of 4-VP units.

c Sum of all probabilities of 4-VP sequences up to the length N.

d Sum of the theoretically active fractions of 4-VP units in the sequences up to the length N.

mol. % of EDMA in the feed. All copolymers below this limit can theoretically be fully hydrolyzed.

However, to make the cleavage reaction really possible, it is necessary that the active units be quaternized. A kinetic study of the quaternization of poly(4-VP) with n-butylobromide has been carried out by Fuoss [91, 92] who reported that alkylation of a given vinylpyridine unit in the polymer decreases the reactivity of the neighboring units. In a later study, the heterogeneity of such a system was described mathematically by Noa [93] who proved that the rate constants for the successive quaternizations of the triads $AAA \xrightarrow{k_0}$, $ABA \xrightarrow{k_1}$, $ABB \xrightarrow{k_2}$, BBB are in the ratio of 1: 0.3 : 0.3. In the above equation, A and ~~A~~ represent free and quaternized 4-VP units respectively. These data indicate that the triads ABA in which a quaternized 4-VP unit is flanked by two free 4-VP units are the most probable. For the suggested mechanism to operate, as shown in Scheme 20, triads such as ABA, ABB, BBB, or BBA must be located in at least one of the four positions which are adjacent to the crosslinking dimethacrylate unit. Therefore, it seems obvious that only a low degree of quaternization is necessary to ensure that the cleavage reaction will be observed. It should be emphasized, however, that high degrees of quaternization can only enhance the likelihood of complete cleavage of the dimethacrylate units.

The copolymerization statistics revealed that at about 12 mol % of EDMA the copolymer contains the greatest number of active units. About every fourth 4-VP unit in the copolymer is located at an active site. Also, there are about two active 4-VP units per crosslinking unit. Thus, it would be sufficient to quaternize only one half of the active units to make the copolymer soluble. A quaternization to 50% secures the presence of a sufficient number of reactive groups and ensures their proper sequential distribution for the splitting of crosslinks to be observed. The results summarized in Table 2 support this concept and suggest that the pseudo-base mechanism is likely to be responsible for the observed phenomenon.

2.3. CONCLUSIONS.

The chemical modification of polymers has drawn much attention in recent years as new reactive polymers can be prepared from commodity materials such as polystyrenes or acrylic resins. Such reactive polymers have led to interesting new developments in areas as varied as catalysis, separation media, or asymmetric processes. It was felt that new interesting structures could be obtained by the simple chemical modification of the soluble poly(vinylpyridine)s or of their crosslinked analogs. This part of the thesis has dealt with several attempts at the modification of poly (4-vinylpyridine) and poly (2-methyl-5-vinylpyridine). Attempts at chemical modification involving N-oxide or quaternized polymers as intermediates were made. Unfortunately these approaches were generally not successful. Significant amounts of new functionalities could be introduced but the processes were generally accompanied by side reactions. For instance, preparation of poly(2-chloromethyl-5-vinylpyridine) has been shown unfeasible due to the facile quaternization that the polymer undergoes spontaneously once it is modified. Similarly, attempts to increase the ligand ability of poly(2-methyl-5-vinylpyridine) by reacting poly (2-lithiomethyl-5-vinylpyridine) with a Schiff base led to the obtention of the desired polymer, but only 50% of modification was achieved which limits the usefulness of the polymer. It was also shown that the reduction of

quaternized poly(4-vinylpyridine) was accompanied by a ring-opening side-reaction reaction, which could only be avoided by careful tuning of the reaction conditions. However, under those conditions only 80% of modification was obtained.

In view of our inability to suppress these side-reactions which diminished considerably the usefulness of the final products the project was discontinued and all of our attention was devoted to the continuation of the study of chemical modification in the context of the compatibilization of polymers, expanding the scope of the research from the original poly(vinylpyridine) target to other systems.

During our studies on the chemical modification of poly(4-vinylpyridine), it was found that quaternized 4-vinylpyridine-ethylene dimethacrylate copolymers, unlike their free amine precursors, were extremely sensitive to dilute alkali and dissolved to afford low molecular weight-by-products. Our studies on the mechanism of this unusual self-catalyzed reaction allowed us to conclude that an intramolecularly catalyzed process involving attack of pyridinium methide pseudo-bases on neighboring ester groups, is responsible for the cleavage of the EDMA crosslinks. Although an unequivocal confirmation of the proposed mechanism will probably require the preparation of difficultly accessible model compounds containing hindered ester groups at well-defined locations near a pyridinium

methide group, this work provides an interesting probe for the intramolecular reactivity of groups located on both the main chain and the side chain of crosslinked polymers. It confirms that polymer segments, as well as pendant groups, have great mobilities resulting in extensive site-site interactions [71,94] despite the presence of crosslinks. This study also contributes to dispell some of the widely held notions that groups located at or near crosslinking points have greatly reduced or negligible reactivities.

2.4 EXPERIMENTAL

2.4.1 N-Oxidations of poly (vinylpyridine)'s

a) Synthesis of poly(4-vinylpyridine).

To a solution of 25.00 g (0.24 mol) of freshly distilled 4-vinylpyridine (bp. 68-69°C at 15 mm Hg) in 20 ml of ethyl acetate is added 0.1 g (6×10^{-4} mol) of azobisisobutyronitrile (AIBN). After bubbling nitrogen through the mixture for few minutes, it is stirred under nitrogen atmosphere at 75°C for 10 h. The polymer is dissolved in pyridine and precipitated by pouring into excess of toluene. After filtration the polymer is washed three times with toluene and three times with hexane, then dried under vacuum at 40°C to give 20.05 g (80% yield) of product. The polymer is soluble in methanol, methylene chloride, chloroform, dimethylformamide and dimethylsulfoxide. Insolubility is observed in acetone, ether, ethyl acetate, tetrahydrofuran, toluene and hexane.

$^1\text{H-NMR}$: (in CDCl_3 / TMS 1%): 1.46 (broad band, 3H, aliphatic chain), 6.30 (broad band, 2H, pyridine ring), 8.23 (broad band, 2H, pyridine ring).

IR: 1595 cm^{-1} (C=C stretching vibration of the aromatic ring), 1556 and 1494 cm^{-1} (C=C + C=N stretching vibrations of the aromatic ring).

b) Synthesis of poly(2-methyl-5-vinylpyridine)

To a solution of 53.00-g (0.45 mol) of freshly distilled 2-methyl-5-vinylpyridine (bp. 78-80°C at 20 mm Hg) in 29 ml of ethyl acetate is added 0.2 g (1.2×10^{-3} mol) of AIBN. After bubbling nitrogen through the mixture for few minutes, it is stirred under nitrogen atmosphere at 75°C for 10 h. The polymer is dissolved in tetrahydrofuran and precipitated by pouring into excess of petroleum ether. After filtration, the polymer is washed three times with petroleum ether, then dried under vacuum at 40°C to give 44.2 g (83% yield) of the white polymer.

$^1\text{H-NMR}$ (in CDCl_3 / TMS 1%): 1.47 (broad band, 3H, aliphatic backbone), 2.4 (sharper band, 3H, CH_3 group), 6.70 (broad band, 2H, aromatic ring), 7.60 (broad band, 1H, aromatic ring).

IR: 1600 cm^{-1} ($\text{C}=\text{C}$, stretching vibration of the aromatic ring) 1568 cm^{-1} ($\text{C}=\text{N}$, stretching vibration of the aromatic ring), 1485 cm^{-1} (bending vibration of $-\text{CH}_3$ group)

c) Synthesis of (2-methyl-5-vinylpyridine: styrene) copolymers.

A solution is prepared consisting of 2.23 g (18.7 mmoles) of 2-methyl-5-vinylpyridine, and 7.78 g (74.7 mmoles) of styrene in 10 ml of ethyl acetate. To this solution is added 0.04 g of AIBN. After bubbling nitrogen through the mixture for few minutes, it is stirred under nitrogen atmosphere at 75°C for 10 h. The polymer is then

dissolved in chloroform and precipitated by pouring into excess of petroleum ether. After filtration the white polymer is washed three times with petroleum ether, then dried under vacuum at 40°C to give 6.00 g (59.4% yield) of the white polymer. The same procedure is employed to copolymerize 1.13 g (9.5 mmoles) of 2-methyl-5-vinylpyridine and 8.87 g (85.2 mmoles) of styrene. In this case 8.32 g (83% yield) of the polymer are obtained.

$^1\text{H-NMR}$ (in CDCl_3/TMS 1%): 1.50 (broad band, aliphatic chain), 2.40 (sharper band, $-\text{CH}_3$ on the pyridine ring) 6.50 (broad band, aromatic H's), 6.93 (broad band, aromatic H's), 7.57 (broad band, aromatic H's). Both copolymers show the same characteristic bands. The composition of the copolymers is easily calculated by using the $^1\text{H-NMR}$ integration data. The first copolymer contains 25 mol% of 2-methyl-5-vinylpyridine units and the second contains 11 mol%.

IR: 1600 cm^{-1} ($\text{C}=\text{C}$, stretching vibration of aromatic rings) 1493 and 1451 cm^{-1} ($\text{C}=\text{C} + \text{C}=\text{N}$ stretching vibration of both aromatic rings)

E.A: First copolymer; found, N:3.01%; therefore, the copolymer contains 23 mol% of 2-methyl-5-vinylpyridine units. Second copolymer; found, N: 1.48%; therefore, the copolymer contains 11 mol% of 2-methyl-5-vinylpyridine units

d) Synthesis of macroporous polymer of 4-vinylpyridine and divinylbenzene.

The crosslinked polymer is obtained by a radical polymerization in suspension. To 150 ml of a 1 wt.% solution of polyvinylpyrrolidone in water is added a solution consisting of 15.0 g of 4-vinylpyridine, 9.0 g of divinylbenzene, 0.2 g of AIBN and 27.0 g of butylacetate. The polymerization mixture is degassed by bubbling nitrogen through for 10 min to remove oxygen. Then, the mixture is polymerized under stirring (300 rpm) at 80°C for 7 h. The product is washed thoroughly with water and then washed with methanol in a soxhlet for 48 h. Finally, the polymer is dried under vacuum at 60°C to give 16.0 g (67% yield) of white product.

IR: 1595 cm^{-1} (C=C stretching vibration of both aromatic rings: pyridine and phenyl), 1556 and 1494 cm^{-1} (C=C + C=N stretching vibrations of pyridine ring)

e) N-oxidation of poly (2-methyl-5-vinylpyridine) with hydrogen peroxide in acetic acid medium.

To a solution of 3.0 g (25 mmoles) of poly (2-methyl-5-vinylpyridine) in 13.0 ml of acetic acid is added 12.0 ml of hydrogen peroxide (30%) dropwise. The reaction mixture is stirred for 24 h. at 50°C. Then, water is added to the reaction mixture and this is concentrated using a vacuum rotatory evaporator. More water is added and again is evaporated. This procedure is repeated until the

distillat is free of acetic acid. Finally, the polymer dissolved in water (ca. 3%) is freeze-dried. 3.5 g of a light and white polymer are obtained. The polymer is soluble in methanol and insoluble in other common solvents (acetone, methylene chloride, tetrahydrofuran, ethyl acetate, hexane, benzene)

$^1\text{H-NMR}$ (in D_2O , ref:1,1,1,-3,3,3-hexamethyldisilazane) 1.67 (broad band, 3H, aliphatic chain), 2.20 (sharper band, 3H, $-\text{CH}_3$ group), 6.77 (broad band, 2H, aromatic ring), 7.40 (broad band, 1H, aromatic ring)

IR: 1256 and 1227 cm^{-1} (N-O stretch, strong bands).

E.A: Polymer structure ($\text{C}_8\text{H}_9\text{NO}$). 0.5 (H_2O), found (C: 66.54%, H: 6.88%, N: 9.81%, O: 16.79%) calculated (C:66.65%, H:7.01%, N: 9.71%, O:16.65%)

f) N-oxidation of poly (4-vinylpyridine) with hydrogen peroxide in acetic acid medium.

10.00 g (95 mmoles) of poly (4-vinylpyridine) are N-oxidized following the same procedure as for the N-oxidation of poly (2-methyl-5-vinylpyridine) with hydrogen peroxide in acetic acid medium. 11.67 g of the N-oxide of poly (4-vinylpyridine are obtained).

$^1\text{H-NMR}$ (in D_2O , ref:1,1,1,-3,3,3-hexamethyldisilazane), 1.60 (broad band, 3H, aliphatic chain), 6.77 (broad band, 2H, aromatic ring), 7.83 (broad band, 2H, aromatic ring)

IR: 1484 cm^{-1} (C=C + C=N stretch), 1236 and 1179 cm^{-1} (N-O stretch, very strong bands)

E.A: Polymer structure: $(C_7H_7NO) \cdot (H_2O)_{0.5}$ found (C: 64.71%, H: 6.18%, N: 10.73%), calculated (C: 64.65%, H: 6.20%, N: 10.78%, O: 18.38%)

g) N-oxidation of poly (2-methyl-5-vinylpyridine) with m-chloroperbenzoic acid.

5.00 g (42 mmoles) of poly (2-methyl-5-vinylpyridine) are dissolved in 25 ml of chloroform and 8.5 g (49 mmoles) of m-chloroperbenzoic acid are added. The temperature is kept at 20°C for 7 h. Then, the chloroform solution is poured into a large excess of ethyl acetate. The precipitated polymer is filtered and washed thoroughly with ethyl acetate. 6.2 g of a white polymer are obtained after drying under vacuum for 24 h.

1H -NMR (in $CDCl_3$ / TMS 1%): 1.60 (broad band, 3H, aliphatic chain), 2.33 (sharper band, 3H, CH_3 group), 6.37 (broad band, 1H, aromatic ring), 6.97 (broad band, 1H, aromatic ring), 7.60 (broad band, 1H, aromatic ring).

IR: 1256 and 1227 cm^{-1} (N-O stretch, very strong bands)

E.A: Polymer structure: $(C_8H_9NO) \cdot 0.8 (H_2O)$, found: (C: 64.78%, H: 6.39%, N: 9.41%, O: 19.42%) calculated: (C: 64.78%, H: 7.16%, N: 9.36%, O: 19.33%)

h) N-oxidation of (2-methyl-5-vinylpyridine: styrene) copolymers with m-chloroperbenzoic acid.

3.0 g (6.95 mmol of N) of (2-methyl-5-vinylpyridine: styrene) (25 mol % 2-methyl-5-vinylpyridine) are dissolved in 20 ml of chloroform and 1.42 g (85% pure, 7 mmol) of m-chloroperbenzoic acid are added. The temperature is kept at 20°C for 7 h. Then the polymer is precipitated from the chloroform solution in a large excess of methanol. The precipitated polymer is filtered and washed thoroughly with methanol. 3.3 g of a white polymer are obtained after drying under vacuum for 24 h. The same procedure is employed for the N-oxidation of the (2-methyl-5-vinylpyridine: styrene) (11 mol% 2-methyl-5-vinylpyridine).

¹H-NMR (in CDCl₃ /TMS 1%): 1.47 (broad band, aliphatic backbone chain), 2.33 (sharper band, -CH₃ group), 6.50 (broad band, aromatic ring), 6.97 (broad band, aromatic ring), 7.4 (broad band, aromatic ring). Both polymers show same characteristic bands)

IR: 1222 cm⁻¹ (N-O stretch, strong band)

i) N-oxidation of macroporous polymer of 4-vinylpyridine and divinylbenzene

4.71 g (28.6 mmol of N) of the macroporous polymer are suspended in chloroform and 7.30 g (85% pure, 36 mmol) of m-chloroperbenzoic acid are added. The reaction mixture is stirred for 48 h at 60°C. Mechanical stirring

is used so the macroporous beads are not broken. After the reaction time, the polymer is filtered and washed several times with methanol and ether alternatively. The polymer is dried under vacuum for 2 days at room temperature and then at 40°C for 5 h. 5.22 g of the N-oxide polymer are obtained.

IR: 1246 and 1172 cm^{-1} (N-O stretch, strong bands)

E.A: Structure of the polymer $(\text{C}_7\text{H}_7\text{NO})_{0.686}$
 $(\text{C}_{10}\text{H}_{10})_{0.314}(\text{H}_2\text{O})_{0.75}$ found: (C: 69.83%, H: 6.27%, N:
 7.07%, O: 16.83%) calculated: (C: 69.97%, H: 6.98%,
 N: 7.03%, O: 16.81%)

The polymer was dried for 20 h at 78°C under vacuum and in presence of P_2O_5 .

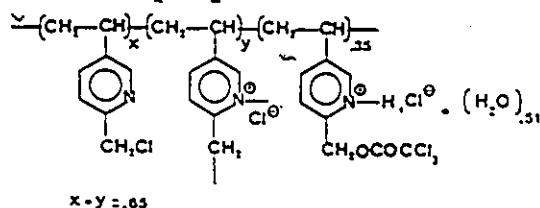
2.4.2.a. Attempts at the preparation of poly (2-chloromethyl-5-vinylpyridine) by reaction of the N-oxide of poly (2-methyl-5-vinylpyridine) with trichloroacetyl chloride.

0.6 g of poly (N-oxide-2-methyl-5-vinylpyridine) are dried by means of an azeotropic distillation with chloroform. Then 0.5 ml of trichloroacetyl chloride are added. The reaction mixture is stirred while the solvent (CHCl_3) is kept refluxing. After 2 h of reaction a pink coloration is observed and after 4 h there is formation of a red precipitate. The red solid is filtered out and washed with chloroform several times. It was insoluble in

many common solvents (methanol, ether, acetone, ethyl acetate, methylene chloride, dimethylformamide, hexane, tetrahydrofuran)

IR: 1760 cm^{-1} (carbonyl stretch, 2-pyridylmethyl trichloroacetate hydrochloride units), $2000\text{--}2500\text{ cm}^{-1}$ ($\text{N}^+\text{--H, Cl}^-$ stretch)

E.A: Structure of the polymer.



found: (C: 48.85%, H: 4.63%, N: 6.21, Cl: 31.88%, O: 8.43%),
calculated: (C: 47.54%, H: 4.30%, N: 6.36%, Cl: 33.0%, O: 8.8%)

2.4.2.b. Attempts at the preparation of (2-chloromethyl-5-vinylpyridine: styrene) copolymers by reaction of the N-oxide of (2-methyl-5-vinylpyridine: styrene) copolymers.

0.7 g of the N-oxide of the copolymer containing 25 mol% of 2-methyl-5-vinylpyridine units, which is dried under vacuum at 80°C for 5 h, are dissolved in 15 ml of dry chloroform and 0.5 ml of trichloroacetyl chloride are added. The reaction mixture is stirred and heated at reflux temperature. After few 3 h of reaction crosslinking of the polymer is observed with the characteristic red color.

IR: 1760 cm^{-1} (carbonyl stretch of 2-pyridylmethyl trichloro acetate hydrochloride units)

2.4.3. Reaction of poly (2-methyl-lithium-5-vinylpyridine) with a Schiff base

2.4.3.a Synthesis of benzaniline

To 10.6 g (0.1 mole) of freshly distilled benzaldehyde are added 9.3 g (0.1 mole) of freshly distilled aniline with rapid stirring. After a few seconds reaction occurs with evolution of heat and separation of water. The mixture is allowed to stand for 15 min and is poured with vigorous stirring into 20 ml of 95% ethanol. Then the mixture is allowed to stand, first 10 min. at room temperature, and then 30 min in ice water. The almost solid mass is next filtered by suction, pressed out and air-dried. 15 g (83% yield) of benzaniline are obtained.

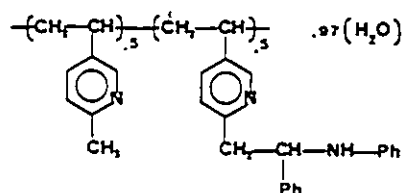
$^1\text{H-NMR}$ (in CDCl_3 / TMS 1%): 7.25 (multiplet, 8H, aromatic rings), 7.75 (multiplet, 2H, aromatic ring) 8.25 (singlet, 1H, olefinic proton)

2.4.3.b. Reaction of poly (2-lithiomethyl-5-vinylpyridine) with benzaniline.

To 5.3 ml (1.89 M, 10 mmoles) of phenyl lithium is added dropwise a solution of 1.2 g (10 mmoles) of poly(2-

methyl-5-vinylpyridine) in 20 ml of dry tetrahydrofuran. The reaction mixture is stirred under nitrogen at 50°C for 1.5 h. A thick red solution is formed. The red coloration being characteristic of the anion $-\text{CH}_2^-\text{Li}^+$. Then, a solution of 1.85 g (10 mmoles) of benzalaniline in 15 ml of dry THF is slowly added to the reaction mixture. Stirring is continued for 3 h. Hydrolysis is affected by adding ca. 20 ml of a 20% ammonium chloride solution with rapid stirring. The tetrahydrofuran phase is separated and dried with magnesium sulfate. The polymer is precipitated in large excess of a solution of ethyl acetate and hexane (1:2) from the THF solution. The polymer is filtered and dried under vacuum overnight. 1.06 g of a white polymer are obtained.

^1H -NMR: Structure of the polymer:



(in CDCl_3 /TMS 1%, the solution (polymer + CDCl_3) has been dried previously with CaCl_2): 1.5 (broad band, aliphatic backbone), 2.4 (sharper band, CH_3 group), 4.75 (broad band, $-\text{CH}_2$ group), 6.6 (broad band, aromatic rings) 7.5 (broad band, aromatic rings). The NMR integration indicates that 50% of modification has been accomplished.

IR: 1600 cm^{-1} ($\text{C}=\text{C}$ stretching, both rings: phenyl and pyridine), 1026 cm^{-1} ($\text{C}-\text{N}$ stretching).

E.A: found (C: 76.39%, H: 7.13%, N:9.48%), calculated (C: 76.63%, H: 7.31%, N: 9.24%, O: 6.82%)

2.4.4 Quaternizations of poly(vinylpyridine)s.

a) Quaternization of poly(4-vinylpyridine) with dimethylsulfate in basic aqueous solution.

To 3.0 g (29 mmoles) of poly(4-vinylpyridine) in 30 ml of water are added 9 ml (95 mmoles) of dimethylsulfate. The reaction mixture is stirred at room temperature and its pH is maintained at 8 by adding few drops of a 20% solution of sodium hydroxyde. After 6 h, the reaction mixture is poured in a dialysis bag and dialyzed against distilled water for 48h. After dialysis the aqueous solution is concentrated on a rotary vacuum evaporator until a ca. 3% solution of the polymer in water is obtained. This solution is freeze-dried affording a light white polymer, 5.1 g (72% yield).

$^1\text{H-NMR}$ (in D_2O , ref: 1,1,1-3,3,3- hexamethylsilazane), 1.76 (broad band, 3H, aliphatic backbone chain), 3.56 (sharp band, 3H, methyl group of the counterion), 4.06 (broad band, 3H, methyl group attached to pyridinium ring), 7.23 (broad band, 2H, aromatic pyridinium ring), 8.30 (broad band, 2H, aromatic pyridinium ring).

IR: 1646 cm^{-1} (quaternized pyridinium ring, C=N^+ - stretch, very strong band), 1251 and 1223 cm^{-1} (sulfate stretch vibrations, very strong bands)

E.A: Structure of the polymer: $(C_9H_{13}NSO_4) \cdot (H_2O)$ found: (C:43.52%, H: 5.38%, N: 5.66%, S: 12.85%, O: 32.59%), calculated: (C: 43.36%, H:6.08%, N: 5.62%, S: 12.86%, O: 32.09%)

b) Quaternization of poly (4-vinylpyridine) with dimethylsulfate in organic phase.

9.6 ml (100 mmoles) of dimethylsulfate are added to a solution of 8.0 g (76 mmoles) of poly (4-vinylpyridine) in 150 ml of nitromethane. The reaction mixture is stirred at 50°C for 24 h. A white precipitate is formed which is filtered. The polymer is dissolved in methanol and precipitated by pouring into excess of ethyl acetate. The polymer is dried under vacuum overnight at 40°C. 12.5 g of white polymer are obtained (63.6% yield). The polymer is soluble in water and methanol.

1H -NMR (in D_2O , ref: 1,1,1-3,3,3-hexamethylsilazane) 1.76 (broad band, 3H, aliphatic backbone chain), 3.56 (sharp band, 3H, methyl group of the counter-ion), 4.06 (broad band, 3H, methyl group attached to pyridinium ring), 7.23 (broad band, 2H, aromatic pyridinium ring), 8.30 (broad band, 2H, aromatic pyridinium ring)

IR: 1646 cm^{-1} (quaternized pyridinium ring, $C=N^+$ stretch, very strong band), 1251 and 1223 cm^{-1} (sulfate stretch vibration, very strong bands)

E.A: Structure of the polymer $(C_9H_{13}NSO_4) \cdot 1.5 (H_2O)$ found: (C:41.47%, H: 6.37, N:5.52%, S:12.58, O: 34.15%),

calculated: (C:41.84%, H: 6.26%, N: 5.42%, S: 12.42%, D: 34.07%)

c) Quaternization of poly(4-vinylpyridine) with methyl iodide in organic phase.

30 ml (0.5 mol) of methyl iodide are added to a solution of 5.0 g of poly (4-vinylpyridine) in 200ml of nitromethane. The reaction mixture is stirred at 35°C for 24 h. A white precipitate is formed which is filtered and washed with nitromethane and acetonitrile. The polymer is dried under vacuum at room temperature, overnight. A light-yellow, water soluble polymer is obtained (11.32 g, 93% yield)

$^1\text{H-NMR}$ (in D_2O , ref: 1,1,1-3,3,3 hexamethylsilazane) 2.10 (broad band, 3H, aliphatic backbone chain) 4.17 (broad band, 3H, methyl group of pyridinium ring), 7.70 (broad band, 2H, aromatic pyridinium ring), 8.50 (broad band, 2H, aromatic pyridinium ring).

IR: 1642 cm^{-1} (quaternized pyridine ring, $\text{C}=\text{N}^+$ - stretch vibration)

E.A: Structure of the polymer ($\text{C}_8\text{H}_{10}\text{NI}$) . 0.5 (H_2O) found (N: 4.97% I: 50.80%), calculated (N: 5.47%, I: 49.60%)

d) Quaternization of poly (4-vinylpyridine) with benzyl bromide in organic phase.

To a solution of 8.0 g (76 mmoles) of poly (4-vinylpyridine) in 150 ml of nitromethane are added 11.3 ml (95 mmoles) of benzyl bromide. The reaction mixture is stirred at room temperature for 3 days. A white precipitate is formed which is filtered and washed thoroughly with ether. The polymer is dried overnight under vacuum at room temperature. 19.8 g (88.5% yield) of a white polymer are obtained which is soluble in methanol, dimethylformamide and dimethylsulfoxide and is insoluble in water, ethyl acetate, tetrahydrofuran, chloroform, ether and acetone.

IR: 1638 cm^{-1} (stretching vibration, pyridinium ring)

E.A: Structure of the polymer: $(\text{C}_{14}\text{H}_{14}\text{N}^+\text{Br}) \cdot (\text{H}_2\text{O})$ found: (C: 56.97%, H: 5.42%, N: 4.73%, Br: 27.03% O: 5.86%), calculated (C: 57.15%, H: 5.49%, N: 4.76%, Br: 27.15%, O: 5.44%)

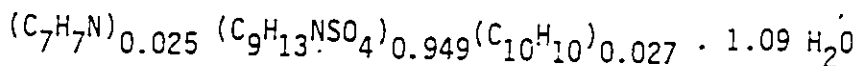
e) Quaternization of a crosslinked poly (4-vinylpyridine).

A crosslinked polymer of 4-vinylpyridine and divinylbenzene containing ca. 3 mol % of divinylbenzene is sold by Reilly Tar and Chemical Corp. under the trade name R-8050. To 11.57 g of the R-8050 polymer in enough water to cover the polymer are added 20 ml of dimethylsulfate. The reaction mixture is stirred mechanically for 3 days at room temperature. During the reaction time the pH of the

reaction mixture is kept at 8 by adding few drops of a 20% solution of sodium hydroxide. The polymer is filtered and washed thoroughly with water, methanol and finally with ether. The polymer is then dried under vacuum for 48 h to give 22.5 g of the quaternized product.

IR: 1642 cm^{-1} ($\text{C}=\text{N}^+$ - stretch, pyridinium ring), 1254 and 1220 cm^{-1} (sulfate stretch, very strong bands)

E.A: Structure of the polymer



found: (C: 44.64%, H: 5.58%, N: 5.55%, S: 12.39%),

calculated: (C: 44.01%, H: 6.16%, N: 5.56%, S: 12.41%)

f) Quaternization of a crosslinked (4-vinylpyridine-ethylene dimethacrylate) polymer with dimethylsulfate in basic solution.

(i) Synthesis of crosslinked (4-vinylpyridine-ethylene dimethacrylate) polymer.

The crosslinked polymer is obtained by a radical polymerization in suspension. To 150 ml of a 1 wt.% solution of polyvinylpyrrolidone in water is added a solution consisting of 15 g of 4-vinylpyridine, 5 g of ethylene dimethacrylate, 0.2 g of AIBN, and 27 g of butyl acetate. The polymerization mixture is degassed by bubbling nitrogen through for 10 min to remove oxygen. Then, the mixture is polymerized under stirring (300 rpm).

at 80°C for 7 h. The product is washed thoroughly with water and then washed with methanol in a soxhlet for 48 h. Finally, the polymer is dried under vacuum at 60°C to give 19 g (95% yield) of product.

IR: 1731 cm^{-1} (C=O stretch, ethylene dimethacrylate units) 1597 and 1558 cm^{-1} (C=C and C=N stretches, aromatic pyridine ring), 1177 cm^{-1} (C-O stretch, ethylene dimethacrylate units)

E.A.; found N: 9.64% which indicates that the crosslinked copolymer contains approximately 17 mol % of EDMA units and 83 mol % of 4-VP units.

(ii) Attempt to the quaternization of (4-vinylpyridine-ethylene dimethacrylate) polymer with dimethylsulfate in basic solution.

To 4.97 of the (4VP-EDMA) copolymer in enough water to cover the polymer are added 10 ml of dimethylsulfate. The reaction mixture is stirred mechanically for 48 h at room temperature. During the reaction time the pH of the reaction mixture is kept at 8 by adding few drops of a 20% solution of sodium hydroxide. The work-up of the polymer was extremely difficult since during the reaction the polymer lost its original bead structure acquiring a gel type structure. Filtration of the polymer was very slow, even in the case of filtration through a piece of cloth. This experiment was of particular importance because it led us to the realization that the polymer was uniquely

susceptible to alkaline cleavage, a totally unexpected finding for such type of polymers [82].

2.4.5 Reduction of quaternized poly(4-vinylpyridine) with sodium borohydride.

a) Reduction of poly(N-methyl-4-vinylpyridinium methyl sulfate) with sodium borohydride in alkaline solution.
Method 1.

To 2.0 g (8 mmoles) of quaternized poly (4-vinylpyridine) ($\text{CH}_2\text{-CH-C}_5\text{H}_4\text{N}^+\text{-CH}_3$, $\text{CH}_3\text{SO}_4\text{-}\cdot\text{H}_2\text{O}$, mol. wt. 294.24 g) in 15 ml of 1N sodium hydroxide are added 0.3 g (8 mmoles) of sodium borohydride in 6 ml of water. Almost immediately there is precipitation of a white polymer. The reaction mixture is stirred for 5 h at 50°C . Then the polymer is filtered and dissolved in methanol and precipitated by pouring in large excess of ethyl acetate. The polymer is dried under vacuum at room temperature for 24 h to yield 1.0 g of a white polymer.

IR: 2368, 2315 and 2268 cm^{-1} (bands corresponding to an conjugated aldehyde which is a by-product and whose structure is presented in the discussion), 1675 cm^{-1} (conjugated aldehyde), 1128 cm^{-1} (-N-CH_3 stretch, corresponding to 1-methyl-1,2,3,6-tetrahydropyridine units)

E.A: found (C: 61.16%, H: 7.69%, N: 8.31%, S: 0%, O: 22.84%). If we assume that the polymer is made up of 1-methyl-1,2,3,6-tetrahydropyridine units, the calculated

composition is: (C: 60.63%, H: 10.78%, N: 8.79%, S: 0%, O: 20.09%)

b) Reduction of poly(N-methyl-4-vinylpyridinium methyl sulfate) with sodium borohydride. Method 2.

1 g (4 mmoles) of the quaternized polymer are reduced with sodium borohydride in basic solution following previous procedure but the work up of the polymer is performed as follows: After the 4 h of reaction the whole reaction mixture is extracted three times with chloroform. The chloroform solution (ca. 50 ml) is dried with magnesium sulfate. Chloroform then is distilled in a vacuum rotatory evaporator to obtain 0.45 g a light-yellow polymer.

IR: The spectrum is identical to that one of the previous reduced polymer. 2.368, 2315 and 2268 cm^{-1} (conjugated aldehyde, by-product), 1675 cm^{-1} (conjugated aldehyde, by-product), 1128 cm^{-1} (N-CH₃ stretch, corresponding to 1-methyl-1,2,3,6-tetrahydropyridine)

c) Reduction of poly(N-methyl-4-vinylpyridinium iodide) with sodium borohydride. Method 2.

1 g (3.9 mmoles) of the quaternized poly(4-vinylpyridine) ($\text{CH}_2\text{-CH-C}_6\text{H}_5\text{N}^+\text{-CH}_3, \text{I}^- \cdot 0.5 \text{ H}_2\text{O}$, mol w. 256.09 g) are reduced following the previous procedure (Method 2) 0.56 g a light-yellow polymer are obtained. The polymer is insoluble in many common solvents. Its IR-

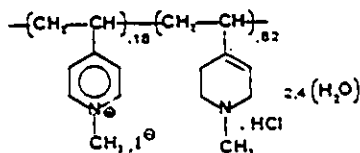
spectrum is identical to those of previous reduced polymers.

d) Reduction of poly (N-methyl-4-vinylpyridinium iodide) with sodium borohydride. Method 3

To 1.0 g (3.9 mmoles) of poly (N-methyl pyridinium iodide) in 10 ml of NaOH 0.4N are added 0.175 g (4.7 mmoles) of sodium borohydride in 2.5 ml of water. The mixture is stirred for 3 h at room temperature. After, to the reaction mixture is added HCl until pH 5. The acidified solution is dialyzed then the aqueous solution is concentrated to ca. 3% polymer and freeze-dried to afford 0.8 g of a light-white polymer.

IR: The polymer is made up of ca. 18 mol % of remaining quaternized units and 82 mol % of reduced units. Characteristic bands corresponding to these two units are seen in the spectrum. 1639 cm^{-1} (pyridinium units), 1462 cm^{-1} ($-\text{CH}_2-$ bending vibration, corresponding to 1-methyl-1,2,3,6, tetrahydropyridine rings), 1424 cm^{-1} ($-\text{CH}_3$ bending vibration)

E.A: Structure of the polymer



found (C: 44.44%, H: 6.85%, N: 6.38%, I: 10.62%, Cl: 14.36%, O: 17.39%), calculated (C: 43.93%, H: 8.3%, N: 6.4%, I: 10.69%, Cl: 13.24%, O: 17.43%)

2.4.6. Synthesis and quaternization of a series of crosslinked 4-vinylpyridine-ethylene dimethacrylate copolymer beads.

A series of crosslinked 4-VP-EDMA copolymer beads containing from 2 to 25 wt. % of the crosslinking agent is prepared. The copolymers are then quaternized. 4-vinylpyridine (Reilly Tar and Chem. Corp.) and ethylene dimethacrylate are distilled under reduced pressure before use. The radical polymerization proceeded in suspension in a 250 ml Buchi glass autoclave equipped with an anchor-type stirrer. To 150 ml of a 1 wt. % solution of polyvinylpyrrolidone (K-90, M.W. 360,000, Fluka A.G) in water is added a mixture of 20 g of monomers, 24.6 g of cyclohexanol, 2.4 g dodecanol and 0.2 g of azobisisobutyronitrile. The polymerization mixture is degassed by bubbling nitrogen through for 10 min to remove oxygen. The reactor is closed and the mixture is polymerized under stirring (400 rpm) at 80°C for 7 hours.

The product is washed thoroughly with water, extracted 24 hours each time with water and acetone, washed with methanol, then with ether, and dried.

The copolymers are then quaternized with excess of n-butylbromide in refluxing nitromethane while the reaction is monitored by following the disappearance of n-butylbromide by gas chromatography. The actual amount of quaternization is determined from the results of elemental analysis for bromide ions after thorough washing of the products with nitromethane and water.

E.A:

Copolymer 1, N: 12.65%, (95 wt. % 4-VP)

Copolymer 2, N: 12.38%, (93 wt. % 4-VP)

Copolymer 3, N: 11.98%, (90 wt. % 4-VP)

Copolymer 4, N: 11.85%, (89 wt. % 4-VP)

Copolymer 5, N: 11.32%, (85 wt. % 4-VP)

After quaternization elemental analysis of Br were:

Copolymer 1, Br: 13.38%, (24 mol % of quaternization),

Br: 16.20%, (31 mol % of quaternization).

Copolymer 2, Br: 14.78%, (28 mol % of quaternization),

Br: 19.00%, (40 mol % of quaternization).

Copolymer 3, Br: 14.05%, (27 mol % of quaternization),

Br: 17.35%, (36 mol % of quaternization).

Copolymer 4, Br: 17.88%, (38 mol % of quaternization)

Copolymer 5, Br: 15.64%, (33 mol % of quaternization),

Br: 20.29%, (48 mol % of quaternization).

Claims to original research

Compatibilization of polystyrene with poly (4-hydroxystyrene, has been achieved by introducing 4-vinylpyridine units into polystyrene. Compatibilization of polystyrene with poly (4-vinylpyridine) has been achieved by introducing first 4-hydroxystyrene and second 4-vinylbenzoic acid units into polystyrene. It has been fully demonstrated that very strong H-bonding interactions do not necessarily improve the compatibility of a polymer system if strong H-bonding self-complexation is involved.

Reversible covalent crosslinks have been used to compatibilize polystyrene and poly (methyl acrylate): a novel approach to the compatibilization of polymers.

A mechanism involving the pyridinium methide units located on the main chain of the polymer in the vicinity of the ethylene dimethacrylate crosslinks has been proposed to account for the unusual dissolution of partly quaternized 4-vinylpyridine-ethylene dimethacrylate copolymers in dilute alkali. This study confirmed the mobility of polymer segments and the reactivity of sites located at or near the crosslinks of highly reticulated resins.

PUBLICATIONS ARISING FROM THIS THESIS

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