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Polymeric Imaging Systems Based on Radiation-Induced Molecular Cleavage and Rearrangement.

by

Théodore (Ted) G. Tessier

A thesis submitted to the School of Graduate Studies of the University of Ottawa as a partial fullfilment for the requirements of the degree of Master of Science in Chemistry

University of Ottawa

February 1984

J. M. J. Fréchet	Théodore G. Tessier
Research Supervisor	M. Sc. Candidate

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TABLE OF ABBREVIATIONS

AIBN	-	azobisisobutyronitrile
b.p.	-	boiling point
deep UV radiation	-	light with a wavelength below 300 nm
DMF	-	Dimethyl formamide
DMSO	-	Dimethyl sulfoxide
FT-IR	-	Fourier-Transform Infrared
g-P	-	grams of polymer
Gs	-	scission efficiency
Gx	-	cross-linking efficiency
Hz	-	Hertz
J	-	coupling constant (NMR data)
	-	Joules (exposure doses)
M_n	-	number average molecular weight
mJ	-	millijoules
m. p.	-	melting point
M. S.	-	Mass spectrum
M_w	-	weight average molecular weight
o-NBA	-	o-Nitrobenzaldehyde
NMR	-	Nuclear magnetic resonance
PACOST	-	Poly-(p-acetoxystyrene)
PMMA	-	Poly-(methyl methacrylate)
P(MTFMA)	-	Poly-(methyl α-trifluoromethyl acrylate)

ppm	-	parts per million
PPMA	-	Poly-(phenyl methacrylate)
TEBAC	-	Triethylbenzyl ammonium chloride
TLC	-	thin layer chromatography
UV	-	ultraviolet
uC	-	microcoulomb
µm	-	micron
(P)	-	styrene polymer backbone

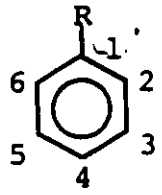
KEY TO SPECTRAL DATA

(a)

	NMR	IR
d	doublet	----
m	multiplet	medium
s	singlet	strong
t	triplet	----
vs	-----	very strong
w	-----	weak

(b)

For NMR spectra, numbering of aromatic carbons was based on the <u>initial</u> site of attachment to the polymer backbone (R) (ie. prior to irradiation), as shown,



-if mono or p-disubstituted, then C2=C6 and C3=C5

a - refers to the starting polymer units

b -refers to the photoproduct polymer units

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ABSTRACT

The general lithographic methods are reviewed in the context of classical one and two-component resist systems. Work reported in the literature on the photo-Fries rearrangement of esters and amides, the photorearrangement of o-nitrobenzaldehyde, and the e-beam sensitivity of poly-(methyl methacrylate) analogs is reviewed. The use of these radiation-induced molecular cleavages or rearrangements as the basis for polymeric imaging systems is proposed.

Preparation of a series of photo-Fries susceptible polymers containing pendant aryl ester or aryl amide groups is outlined. Solution and solid-state photochemistry studies of these polymers indicate their relative sensitivity to UV irradiation. When o- and p-rearrangement photoproducts are predominant, their photostabilizing effect prevents complete conversion; whereas when the photodegradation product is the major photoproduct, the reaction proceeds to near completion. Imaging experiments with these polymers as one-component photoresist systems are presented.

Efforts aimed at introducing o-nitrobenzaldehyde pendant groups into styrene and acrylate polymer backbones via the phenolate of 5-hydroxy-2-nitrobenzaldehyde are reported. A solid-state film photochemistry study of one of these "modified" polymers indicates the presence of the o-nitrosobenzoic acid photoproduct as well as some cross-linking as a result of subsequent diazo-coupling of adjacent nitroso groups. Imaging experiments presented confirm the occurrence of this secondary process.

The preparation of a methyl α-(trifluoromethyl acrylate)

homopolymer and a series of its styrene copolymers is outlined. Data showing the greater e-beam scission efficiencies (Gs values) of these polymers over PMMA is shown. Imaging experiments confirmed the enhanced sensitivities of these α-trifluoromethyl PMMA analog containing polymers relative to PMMA.

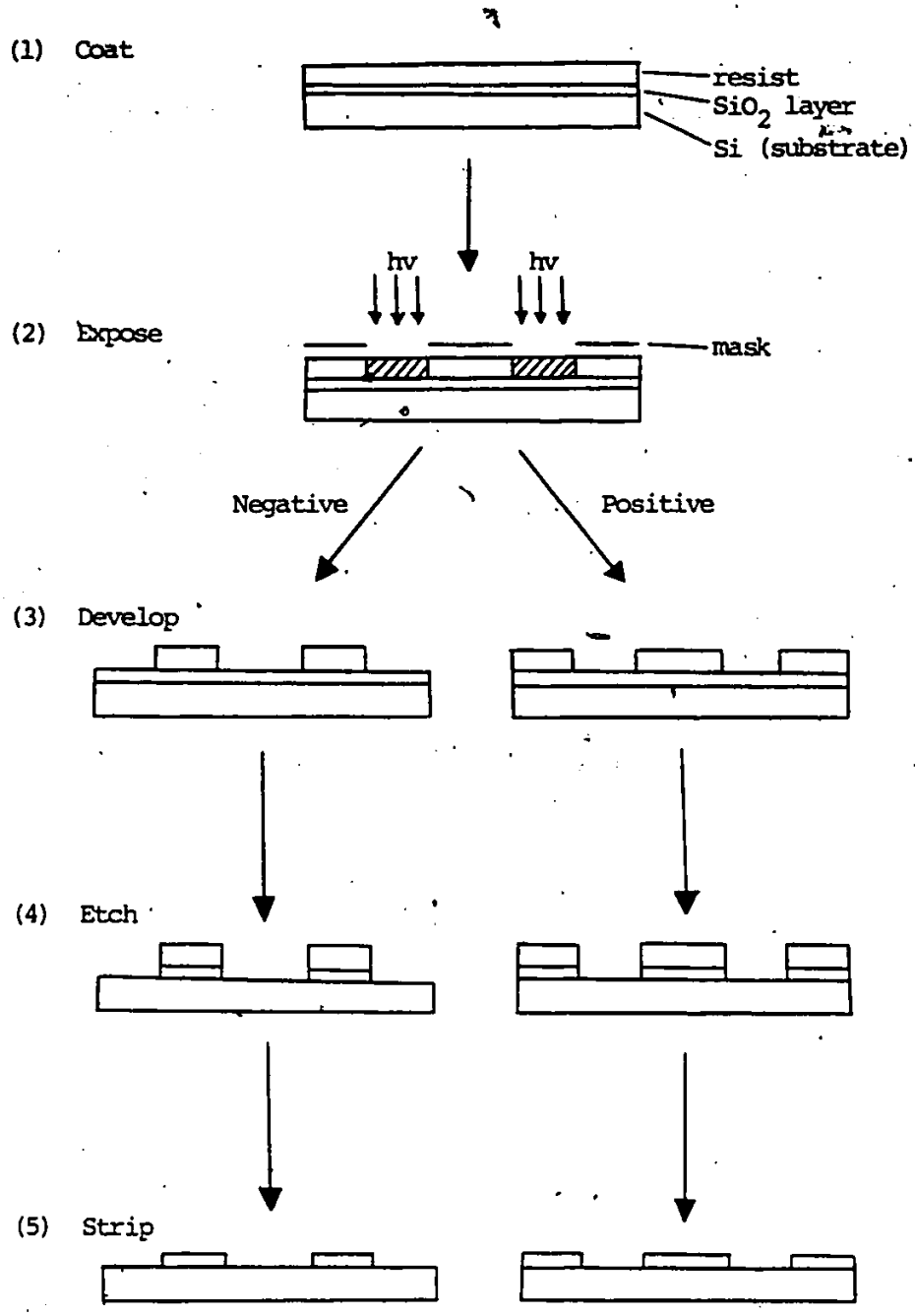
INTRODUCTION

General Lithographic Methods:

Radiation sensitive organic monomeric and polymeric compounds, called resists have found wide application as the imaging layer in the production of high-density electronic circuits. This microlithographic process arises as a result of radiation-induced chemical changes in the irradiated areas of a resist film which renders it either more or less soluble than the unexposed areas. A resist that increases in solubility after irradiation is termed a positive resist; whereas one that decreases in solubility is termed a negative resist. Either of these solubility differences between exposed and unexposed areas allows resolution of a 3-dimensional image upon development in an appropriate solvent.

The basic photolithographic process is summarized in Figure 1. A thin, even film of the photoresist is applied over the surface of a substrate, usually by spinning the film at high speeds. Subsequent exposure through a mask allows the light to strike only selected areas of the resist film. The exposed resist is then developed in a suitable solvent. In the case of a positive resist, the exposed areas of the film are selectively removed to give a positive image. Conversely, a negative resist is developed in a solvent which selectively removes the unexposed areas of the film giving a negative image. In both cases, the resulting 3-dimensional relief image is a replication of the transparent and opaque regions of the mask.

Figure 1 : General Sequence of the Photolithographic Process



The photoresist that remains after the development process serves to mask the underlying substrate for subsequent image transfer steps. For example, as shown in Figure 1, the SiO_2 layer of the non-resist protected areas of the silicon wafer substrate can be selectively removed by etching in a buffered hydrofluoric acid solution. Following the etching process, stripping away of the remaining photoresist results in a positive or negative tone relief image in the underlying substrate[1].

Numerous types of resist materials have found uses in the production of semiconductors. Of these various types, two different main groups are encountered most frequently. One-component resist systems contain a polymer capable of radiation-induced reactions which gives rise to an image. In two-component systems, the resist consists of an inert film-forming matrix resin and a low molecular weight photoactive compound called a sensitizer. This sensitizer undergoes the radiochemical transformation responsible for imaging. The following brief overview will focus on materials representative of both these groups.

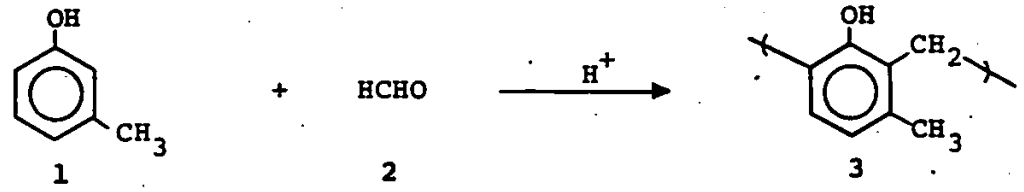
Novolac, a Common Two-Component Resist System:

Süs and Schaefer[2] discovered the first positive resist, which was based on the use of a two-component system made up of a novolac matrix resin and a diazoquinone photoactive compound. This same type of two-component system remains in wide use by semi-conductor manufacturers today.

The matrix resin used in novolac is a copolymer (3) of a phenol (1) and formaldehyde (2) obtained via cationic polymeriza-

tion in the presence of an acid.

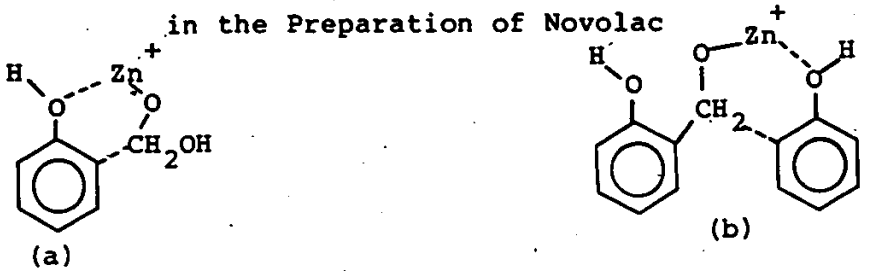
Scheme 1



In order to ensure good aqueous developing characteristics, novolac resins intended for lithographic purposes are generally of low molecular weight. Addition of an excess of the phenol ensures a low molecular weight due to the step-growth nature of this copolymerization. This excess also ensures that the polymer chain ends are capped with an unreactive phenol, rather than a reactive methylol which could be subject to undesired further polymerization at a later time.

If no further precautions are taken, then a highly complex low molecular weight polymer containing o-o, o-p and p-p methylene linkages is obtained. Drum and Leblanc[3] have indicated that a more ordered copolymer containing almost exclusively o-o methylene linkages can be obtained by adding a divalent catalyst such as zinc acetate in acetic acid to the polymerization mixture. They proposed that this catalyst has an o-directing effect on both the initial condensation of hydrated formaldehyde (Figure 2a) as well as on the subsequent formation of the methylene bridge (Figure 2b).

Figure 2 : Mechanism Justifying O-Directed Condensation in the Preparation of Novolac



Novolac resins were found to be good matrix resins due to their excellent film forming properties, adhesion to a large variety of substrates, and solubility in organic solvents. The high solubility of these resins in aqueous base is also crucial for complementing the effect of the sensitizer in the system.

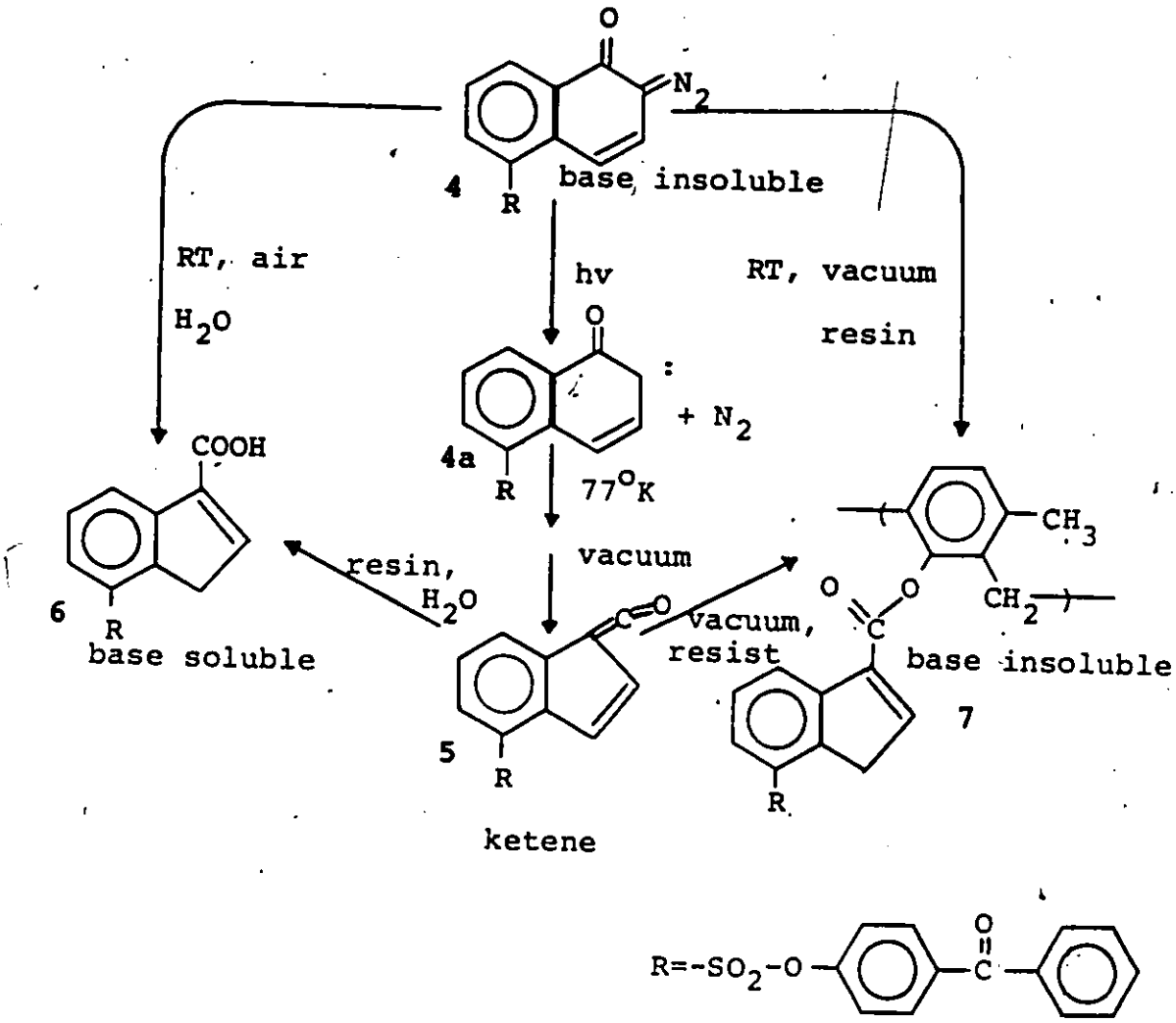
The commercial preparations basically consist of novolac resin and sensitizer dissolved in an organic solvent. Spin-coating a film of this solution on a substrate and removal of the solvent leaves a film of resin, with sensitizer randomly located throughout. The presence of the unexposed sensitizer drastically reduces the dissolution rate of the novolac resin in aqueous base.

The diazonaphthoquinone sulfonate sensitizers that are commonly used are soluble in organic solvents but are very insoluble in aqueous base. For this reason, their presence drastically decreases the solubility of the matrix resin. The most commonly used photoactive compounds of this class are thoroughly covered by Deforest[4].

The mechanism of the photomodification of these sensitizers was first proposed by Süs[5]. Recent low temperature studies by Pacansky and Lyerla[6] have served to confirm this mechanism.

Their work is summarized in Scheme 2.

Scheme 2



Absorption of a photon of energy by the naphthaquinone chromophore (4) generates a highly reactive carbene (4a) with evolution of nitrogen. This carbene subsequently rearranges to a somewhat less reactive ketene (5). The ketene reacts exclusively with the traces of water remaining in the resist mixture rather than with the phenolic groups of the resin due to the greater ease of movement of the water molecules in the film. As a result, a 3-indenecarboxylic acid (6) is obtained as a photoproduct under

normal processing conditions. If the irradiation is carried out under vacuum in the absence of water, then the phenolic ester (7) is obtained.

The generation of the base-soluble acid photoproduct in the exposed areas of the film drastically increases the aqueous base solubility of the matrix resin in these areas. As a result of this differential solubility between exposed and unexposed areas, a positive image (see Figure 1) is obtained upon development in aqueous base.

Poly-(Methyl Methacrylate):

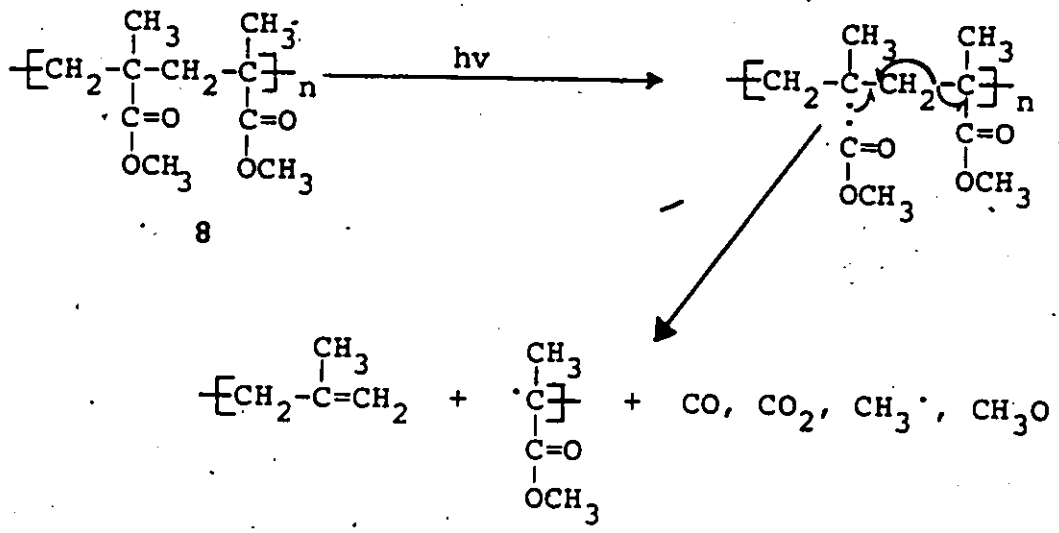
Poly-(methyl methacrylate) (PMMA) (8) is a classical example of a positive one-component electron beam resist. Haller et al.[7] have shown that high intensity electron beam radiation reduces the molecular weight of this polymer by initiating main chain degradation. The large difference in molecular weight between exposed and unexposed areas of a PMMA film results in a corresponding difference in solubility, which in turn gives rise to an image upon development in an appropriate organic solvent. Although PMMA has excellent film forming properties and extremely high resolution, it is a relatively insensitive resist, requiring a working dose of 50 - 100 $\mu C/cm^2$, and it has a low resistance to reactive ion etching[1].

Under normal circumstances, ionizing radiation can potentially induce either a random main chain scission, or a cross-linking of neighbouring polymer chains. Usually, one of these two effects predominate, as is the case with PMMA[1]. Quantitative

analysis of the effect of radiation dose on molecular weight allows the determination of a polymer's G-values[8]. Gs refers to the number of main chain scissions that occurs per 100 eV of energy, whereas Gx refers to the number of cross-links per 100 eV. Quantitative measurement of these G-values are used to effectively predict the resist potential of a polymer.

The mechanism of PMMA degradation remains somewhat unclear. Work reported by Hiraoka and others[9] has suggested that main chain cleavage may occur as illustrated in Scheme 3.

Scheme 3



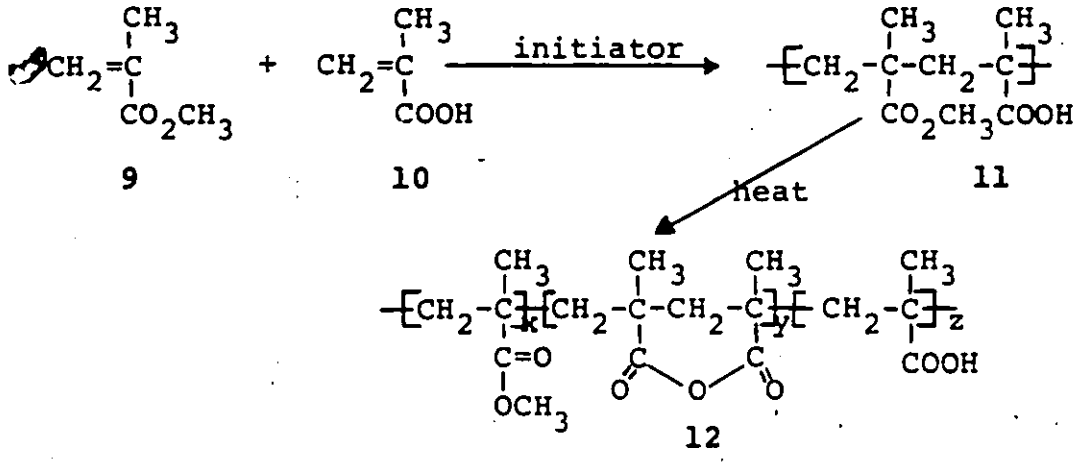
Hiraoka[9] suggests that homolysis of the main chain carbon to carbonyl bond occurs first, allowing the formation of a stable tertiary radical on the main chain. In the second step, rearrangement of the radical with β scission could result in chain cleavage and generation of a stable tertiary radical.

The successful studies of Haller et al.[7] on E-beam degradation of PMMA, have motivated several research groups in recent

years to study a large number of analogs of PMMA. The objective of these efforts has been to find analogs of PMMA which possess higher radiation sensitivities, as measured by greater Gs values while at the same time maintaining Gx equal to zero. It was also hoped that these analogs would have a greater reactive ion etch resistance than PMMA.

Moreau and coworkers[10] developed a terpolymer of methyl methacrylate (9), methacrylic acid (10), and methacrylic anhydride which was found to have a much greater E-beam sensitivity than PMMA. As outlined in Scheme 4, the synthesis of "Terpolymer" first involves the copolymerization of 9 and 10.

Scheme 4



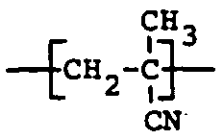
9 10 11 12

Heating the resulting copolymer (11) gives the terpolymer (12). Only traces of insoluble intermolecular anhydride were formed in this way, and were readily removed by filtration. This polymer is currently being used commercially. The sensitivity data for this polymer is given in Table 1.

Two basic approaches have been used for developing new PMMA analogs. The first involves introduction of halogen substituents

onto the ester side chain[11]. The other more commonly reported approach involves replacing the α-substituent with a polar group capable of destabilizing the polymer chain. Figure 2 illustrates some of the analogs that have been studied. Their degradation data and etch resistance are summarized in Table 1.

Figure 2 : Some Analogs of PMMA



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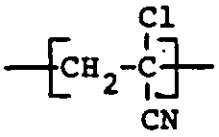

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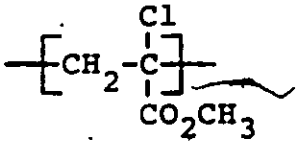

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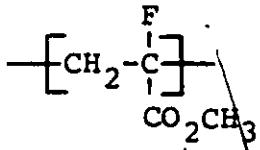

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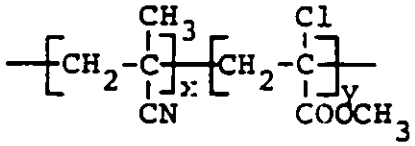

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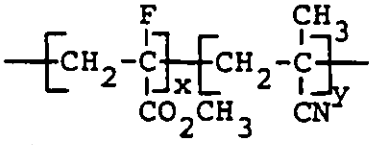

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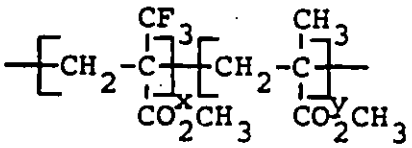

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Table 1: E-Beam Radiation Degradation Susceptibilities and Etch Rates for some PMMA Analogs.

Structure Number	Mole ratio (x:y:z)	Gs/Gx (Effect/100eV)	Etch Rate[a] (A^o/min.)	Reference
8	1.0:0	1.3/0.0	85[b]	1
13	1.0:0	3.3/0.0	30	12
14	1.0:0	4.6/3.2	--	13
15	1.0:0	6.0/0.9	158	14
16	1.0:0	0.5/1.0	40	15
17	0.5:0.5	3.9/0.0	50	16
18	0.16:0.84	2.3/0.0	38	15
19	0.11:0.89	2.4/0.0	79	15
12	0.70:0.15:0.15	4.5/0.0	20[b]	10

[a] CF_4 plasma, 4% O_2; [b] CF_4 plasma, 8% O_2

The terpolymer **12** and poly-(methacrylonitrile) (**13**) give the most favourable results of the series. In both cases, the Gs value is increased from 1.3 to 4.5[10] and 3.3[12] respectively while keeping Gx equal to zero. There is also a marked increase in their resistance to etching relative to PMMA.

Introduction of a halogen at the α-position as in the case of poly-(methyl α-chloroacrylate) (**15**) and poly-(methyl α-fluoroacrylate) (**16**) tends to result in an increase in both Gs and Gx values as shown by Helbert[14] and Pittman[15]. This is especially apparent in the case of **16** where Gx is greater than Gs. Pittman

et al.[15] report that a negative image is obtained upon developing **16**, as could be predicted from the G-values. Helbert et al.[14] found that copolymerization of α-chlorosubstituted acrylates with methyl methacrylate in molar ratios lower than 1:1 gave polymers with Gs values intermediate between PMMA and **15**, which still had a zero value of Gx. Lai et al.[16] reported that poly-(methacrylonitrile-methyl α-chloroacrylate) (**17**) having a 1:1 molar ratio has a Gx value of zero and an improved Gs value. Increasing the concentration of the α-halogen-substituted monomer beyond 50% gives rise to a copolymer with some cross-linking tendency (Gx greater than 0)[16].

Pittman et al.[15] also found that poly-(methyl-α-trifluoromethylacrylate-methyl methacrylate) copolymer (**19**) had a greater Gs value than PMMA, with no Gx value for all the molar ratios that were available for testing (up to 70:30). The E-beam resist sensitivity of **19** ranged from $2 - 3 \times 10^{-5}$ μC/cm^2 versus $5 - 10 \times 10^{-5}$ μC/cm^2 for PMMA. Pittman et al[15] reported difficulties in copolymerizing the α-trifluoromethyl substituted monomer with methyl methacrylate by free radical means and were unsuccessful at obtaining the homopolymer. Ito et al.[17], however were successful in their attempts to obtain poly-(methyl (α-trifluoromethyl) acrylate) (**20**) by anionic polymerization.

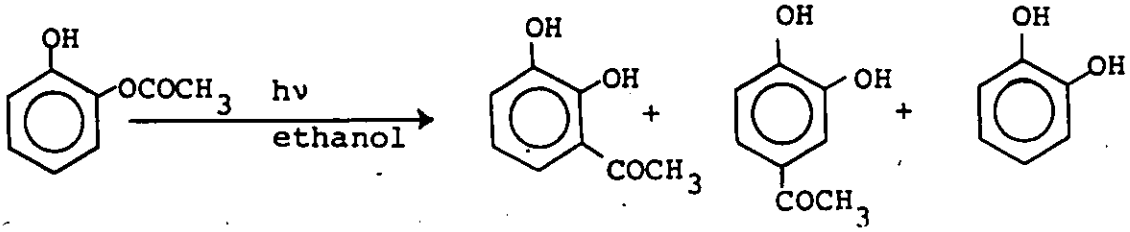
The encouraging results obtained with copolymer **19**[15] and the recent availability[17] of homopolymer **20** have led us to study its E-beam sensitivity. A section of this thesis outlines the lithographic testing of this homopolymer (**20**).

Photo-Fries Rearrangement of Esters and Amides:

The Fries reaction involves the conversion of a phenol ester to ortho and/or para hydroxyketones upon treatment with aluminum chloride. Adjustment of the reaction conditions allows one of the two products to predominate. Reviews discussing this rearrangement have been published by Blatt[18] and Shine[19].

Anderson and Reese[20] first reported the occurence of the photo-induced Fries rearrangement. UV irradiation of an alcoholic solution of catechol monoacetate (21) gave a mixture of 22% 2,3-dihydroxyacetophenone (22), 18% 3,4-dihydroxyacetophenone (23) and 46% catechol (24).

Scheme 5



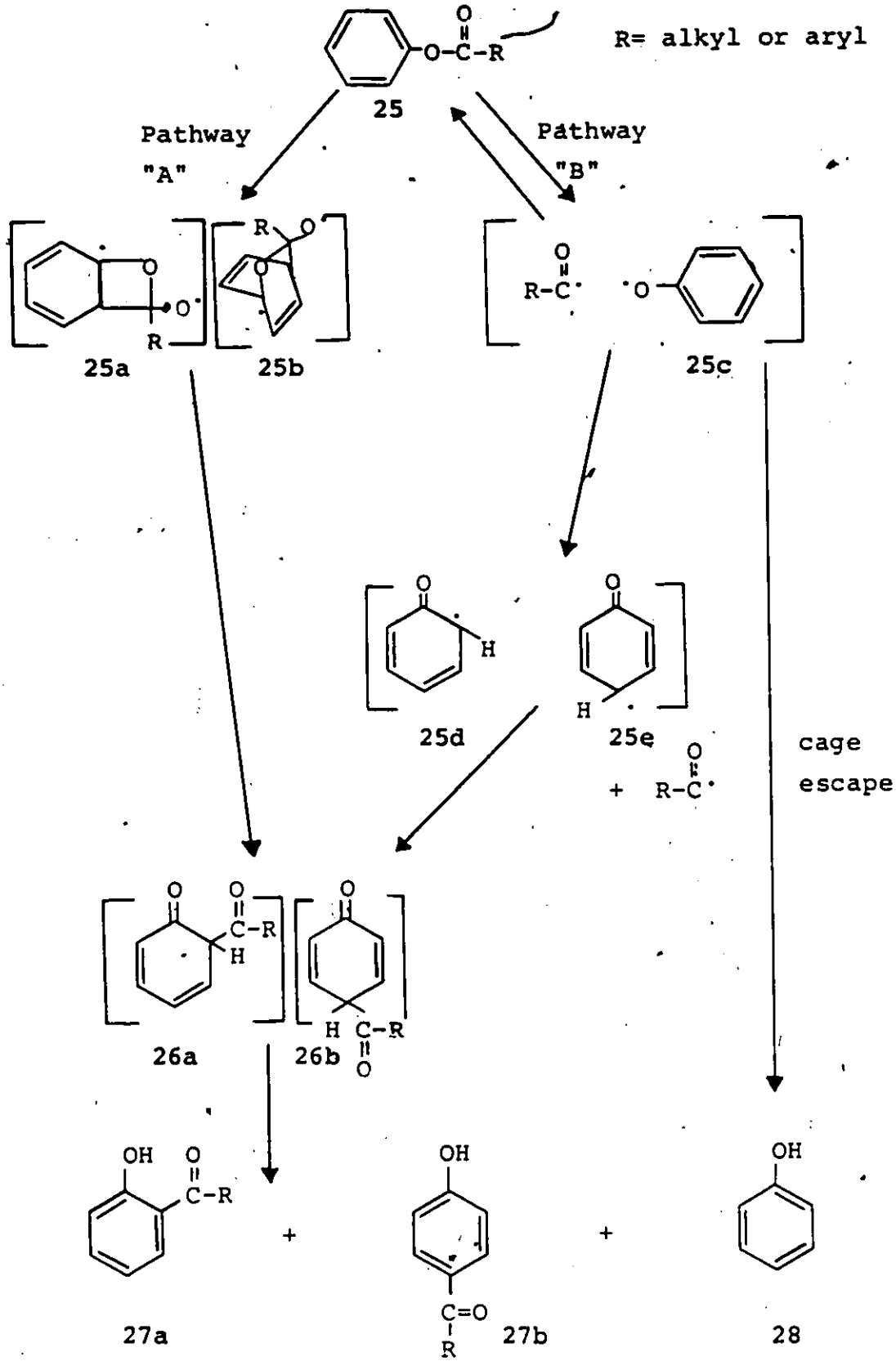
21 22 23 24

Shortly thereafter, Kobsa[21] reported that UV irradiation of p-t-butylphenyl benzoate gave good yields of 2-hydroxy-5-t-butylbenzophenone. Since these original discoveries, the photo-Fries reaction in both small organic molecules and polymers has been extensively studied and reviewed[22,23]. The scope of this reaction has been extended from phenyl esters to include other compounds containing phenoxyl groups including: phenyl carbonates[24], phenoxyacetic acids[25], and hydroxyphenyl cinnamates[26]. Elad et al.[27] found that the photo-Fries rearrangement also occurs with aryl amides. The following overview will deal exclusively with

the reported work on aryl esters and aryl amides.

Cross-over UV irradiation experiments with phenyl p-chlorobenzoate and p-chlorophenyl benzoate, reported by Finnegan and Mattice[28] gave only monochlorohydroxybenzophenones as products. The absence of any dichlorophotoproduct is proof of the intramolecular nature of the photo-Fries reaction. Two basic reaction mechanisms for the photo-Fries rearrangement have received significant support in the literature. Both of these mechanisms are summarized in Scheme 6. Pathway A, first proposed by Anderson and Reese[29], involves a concerted mechanism, where the photorearrangement of **25** proceeds through bicyclic diradical intermediate products **25a** and **25b**. Kobsa[21] suggested pathway B, which was later termed the cage recombination mechanism. This mechanism suggests that UV irradiation induces homolytic cleavage at the C-O bond of the ester linkage resulting in the generation of an acyl and a phenoxyl radical **25c** held within a solvent cage. Recombination of the acyl radical with **25c** regenerates the starting ester **25**. The phenoxyl radical **25c** also exists in resonance forms **25d** and **25e**. Recombination of the acyl radical with these resonance forms gives o- and p-acylcyclohexadienones (**26a** and **26b**), which were also proposed as key intermediates in pathway A. These intermediates can then tautomerize to give the o- and p-hydroxyketones **27a** and **27b**. Diffusion of **25c** from the solvent cage and hydrogen abstraction from the solvent gives rise to phenol **28**[21]. Although slightly modified versions of the concerted mechanism have been proposed by Bellus[23], and Sandner et al.[30], experimental evidence strongly supports the cage recombi-

Scheme 6: Proposed Mechanisms for the Photo-Fries Rearrangement



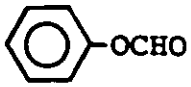
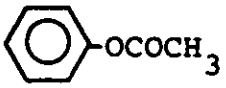
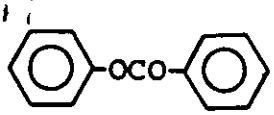
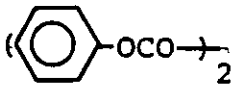
nation mechanism.

Meyer and Hammond[31] studied the photorearrangement of phenyl acetate in the vapor phase. Although they were unable to detect the presence of the phenoxyl radical, the products they obtained could be accounted for in terms of the free-radical mechanism. Later Kalmus and Hercules[32] reported observing both phenoxyl radicals **25c** and cyclohexadienone in the flash spectra of phenyl acetate in a number of solvents.

Since the o-hydroxyphenones of type **27a** absorb more strongly in the ultraviolet region of the spectrum than the initial ester, the rate of photorearrangement decreases markedly with time[22]. As a result, the photolysis mixture contains almost invariably some remaining starting material. **27a** is also very photochemically stable. The p-hydroxyphenones (**27b**) and phenol **28** absorb much less in the deep UV than **27a** and are also quite resistant to further irradiation effects[22].

Studies by a number of researchers have illustrated that the product distribution obtained in a photo-Fries reaction varies according to the structure of the starting ester. Data listed in Table 2 illustrates this observation. Since investigators used different reaction times and sources of ultraviolet light, the yields of hydroxyphenones and phenols listed below are only approximations. As seen in Table 2, the formate and oxalate esters give little or no hydroxyketone upon UV irradiation and large amounts of the phenol.

Table 2: Photorearrangement of Aryl Esters in Ethanol

Structure Number[a]	Structure	Hydroxyphenone* ortho	Hydroxyphenone* para	Phenol*
29[33]		0	0	49
30[29]		19	15	28
31[29]		20	28	14
32[33]		0	0	49

* % yield calculated as consumed ester; [a] reference number.

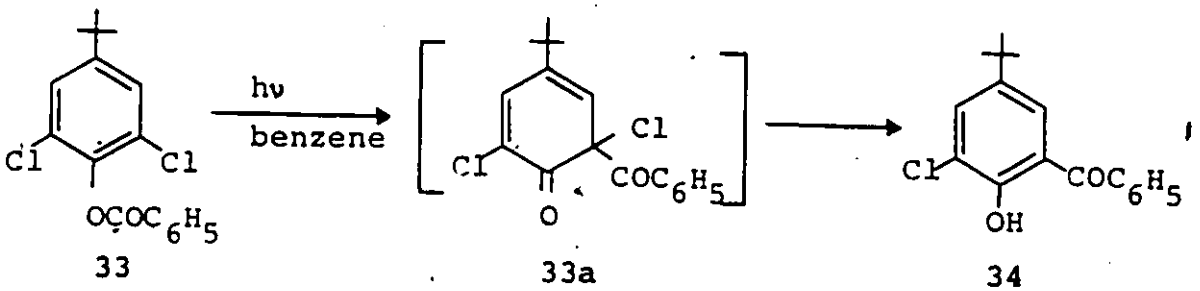
Work reported more recently, by Kuz'min et al.[34] has further illustrated the same efficient decarbonylation of aryl formates. UV irradiation of phenyl benzoate (**31**) on the other hand, gives primarily the o- and p-hydroxyketones.

The solvent used in a photolysis experiment has been shown to have considerable effect on the relative distribution of photolysis products obtained. Sandner et al.[30] studied the photolysis of p-tolyl acetate in a number of solvents and found that increasing solvent viscosity has no effect on the amount of o-hydroxyketone produced but reduces markedly the amount of cresol generated. Kalmus and Hercules[32] have reported that the quantum yield of p-hydroxyacetophenone from photolysis of **30** was about 5 times greater in ethanol than in hexane or Freon. These au-

thors[32] have proposed that the larger distance involved in p-recombination requires a strongly caging solvent. Since ethanol has a relatively high degree of molecular association, it provides the strongest solvent cage. Kalmus and Hercules[32] also found that phenol formation in ethanol was about 2.5 times less than in hexane, and explained this result by suggesting that the weaker solvent cage provided by hexane enhances escape of phenoxyl radicals. Due to the close proximity of the acyl radical to the o-position, recombination proceeds regardless of the solvent used[32]. The effect of solvent on the small amounts of decarboxylation, decarbonylation and solvolysis side-products obtained during photolysis of aryl esters has been studied by Finnegan and Knudson[35] and Hageman[36].

The photo-Fries rearrangement of aryl esters can result in displacement of certain o- and p-substituents of the aromatic ring. Kobsa[21] first observed this occurence with o- or p-chloro substituents. Irradiation of 2,6-dichloro-4-t-butylphenylbenzoate (33) in benzene (Scheme 7) gave 5-t-butyl-3-chloro-2-hydroxybenzophenone (34) by displacement of one of the chloro substituents.

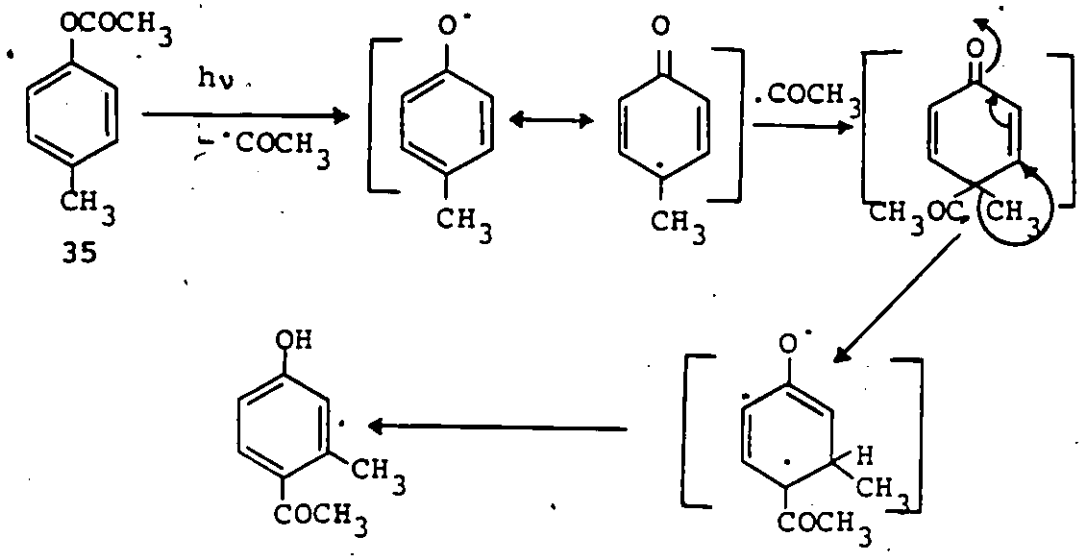
Scheme 7



33 33a 34

Kobsa[21] has proposed that radical addition of a benzoyl radical in the o-position takes place affording the intermediate **33a**. Subsequent chlorine displacement and tautomerization would give **34**. The methoxyl group[37] has also been eliminated from both ortho and para positions by the photo-Fries rearrangement. More recently, Pathak and Khanna[38] have reported 1,2-migration of a methyl group as a result of this photorearrangement. They found that photolysis of 4-methylphenyl acetate (**35**) gave 4-hydroxy-2-methylacetophenone (**36**) rather than the expected o-hydroxyketone. The mechanism proposed for this reaction[38] is shown in Scheme 8.

Scheme 8

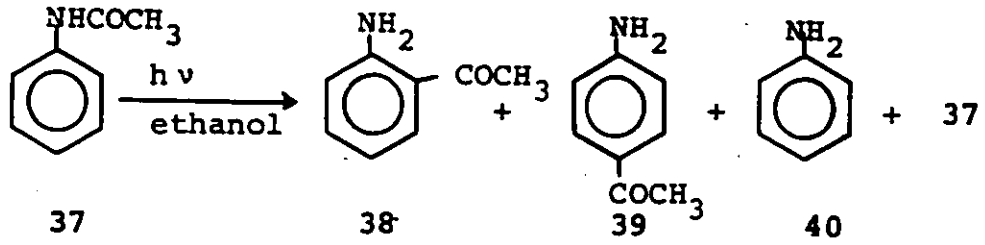


35 36

The photo-Fries rearrangement of aryl amides was first reported by Elad et al.[27] with acetanilide (**37**). Photolysis of **37**[27], (Scheme 9) was found to give a mixture of o- and p-amino benzophenones (**38** and **39**), as well as aniline (**40**) and some unreacted starting material. Detection of carbon monoxide and hydrogen in the products of the photorearrangement suggested that

it occured via the same cage recombination pathway suggested for aryl esters in Scheme 6.

Scheme 9

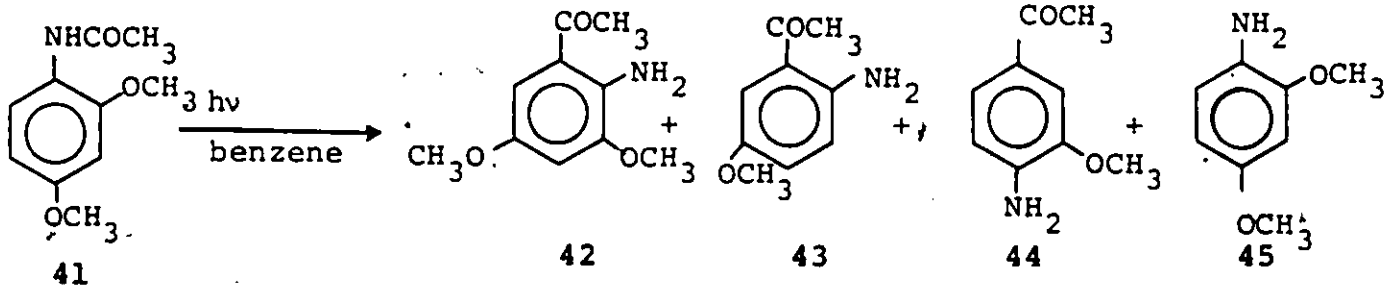


37 38 39 40

Kalmus and Hercules[39] substantiated this proposed mechanism by flash photolysis of **37**. Carlsson et al.[40] have shown the photo-Fries rearrangement of fully aromatic amides to give the expected products.

The displacement of o- and p-substituents by the photo-Fries rearrangement seen in aryl esters has also been reported for aryl amides. Bradshaw et al.[41] found that UV irradiation of 2,4-dimethoxyacetanilide (**41**) as shown in Scheme 10, gave a mixture of 63% 2-amino-3,5-dimethoxyacetophenone (**42**), 5% 2-amino-5-methoxyacetophenone (**43**), 11% 4-amino-3-methoxy-acetophenone (**44**) and 8% 2,4-dimethoxyaniline (**45**).

Scheme 10



41 **42** **43** **44** **45**

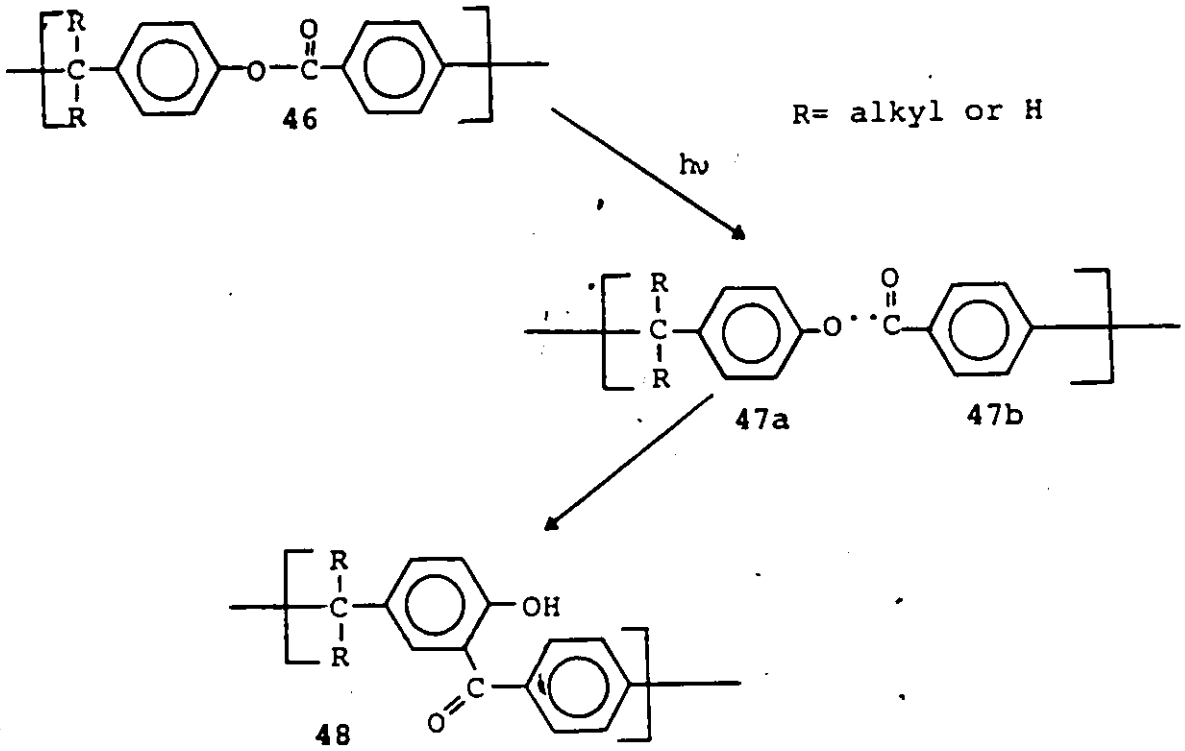
Products **42** and **43** were formed as a result of displacement of o- or p-methoxyl substituents by the acyl radical. Similarly, Shi-

zuka and Tanaka[42] studied the rearrangement of p-substituted acetanilides, and reported that the acyl radical did not displace methyl or chloro groups at the 4 position but did displace iodo and bromo substituents.

Shortly after the discovery of the photo-Fries reaction in small organic molecules[20,21], interest in studying this rearrangement in polymers developed. The introduction of rearrangement products into aromatic polyesters[43,44,45] and polyamides[46] has been studied by several authors as a means of introducing stabilizers into a polymer chain. The photostabilizing action of o-hydroxy aromatic compounds has recently been reviewed by Allen[47] and Ranby and Rabek[48].

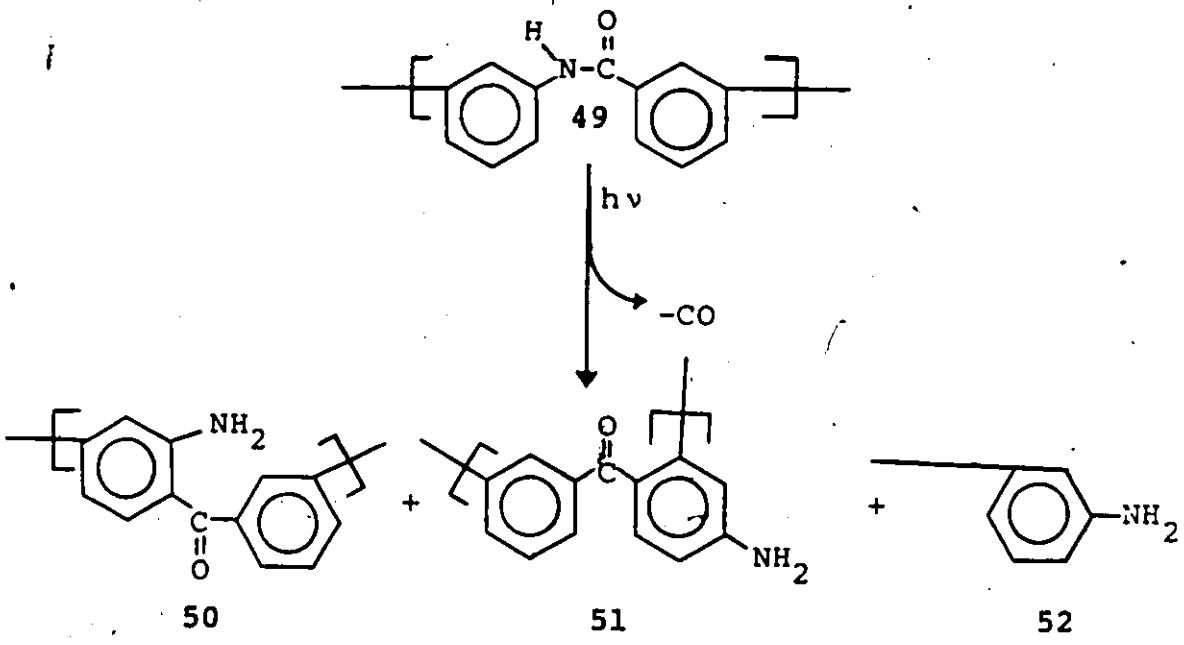
Cohen et al.[45] studied the photo-Fries rearrangement of a number of fully aromatic polyesters in the solid-state.

Scheme 11



UV irradiation of polyester films of type **46** (Scheme 11) results in some cleavage of the main chain at the C-O ester bond giving the intermediate **47**. Subsequent rearrangement of **47b** to the corresponding o-substituted product results in the incorporation of a UV stabilizing unit **48** into the polymer chain. Thin coatings of these clear rearranged polymers could be used to protect substrates which are ordinarily sensitive to UV light[45]. Similarly, Carlsson et al.[40,46] have studied the photodegradation of aramids. Film photolysis of poly-(m-phenylene isophthalamide) (**49**)[46] gave some 2- and 4-aminobenzophenone (**50**) and (**51**) backbone units in low quantum yield (6×10^{-7} moles/einstein), as well as some m-substituted aniline backbone units (**52**).

Scheme 12

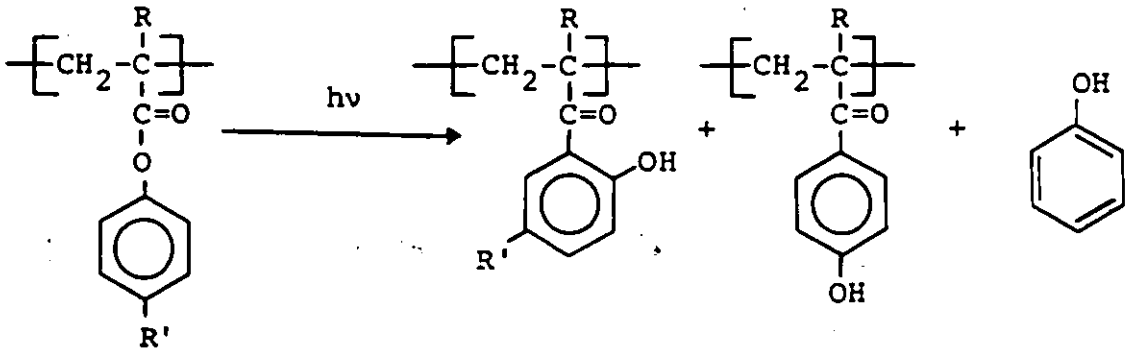


In the case of photoproduct **52**, permanent cleavage of the main chain results.

Considerable effort has been devoted to the study of the

photo-Fries rearrangement in polymer pendant groups. Okawara et al.[49], and Bellus et al.[44] studied the solution photochemistry of poly-(p-cresyl acrylate) (53a). The o-hydroxyphenone rearrangement product 54a and some phenol were the only photoproducts obtained in this case. The initial reaction which consisted of photorearrangement and polymer chain degradation with phenol production, subsided due to the photostabilizing effect of 54a. Solid-state irradiation of a film of 53a also gave the o-hydroxyphenone polymer unit (54a), phenol and some starting 53a[50,51].

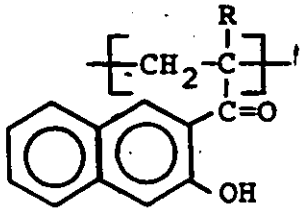
Scheme 13



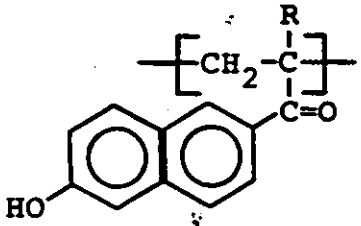
53a R=H, R'=CH_3 54a R=H, R'=CH_3

b R= CH_3, R'=H b R=CH_3, R'=H 55 R=CH_3

Similar film and solution photochemistry behavior has been reported for poly-(phenyl methacrylate) (PPMA) 53b[51,52] and various substituted aryl acrylates[52]. Guillet et al.[53] have illustrated the enhanced photostabilizing ability of the photo-Fries rearrangement products of naphthyl acrylates (R=H) and methacrylates (R=CH_3). This increased stability has been attributed to the high extinction coefficients of both the o- and p-photoproducts (56 and 57), and their ability to dissipate the absorbed light by non-photochemical pathways.



56



57

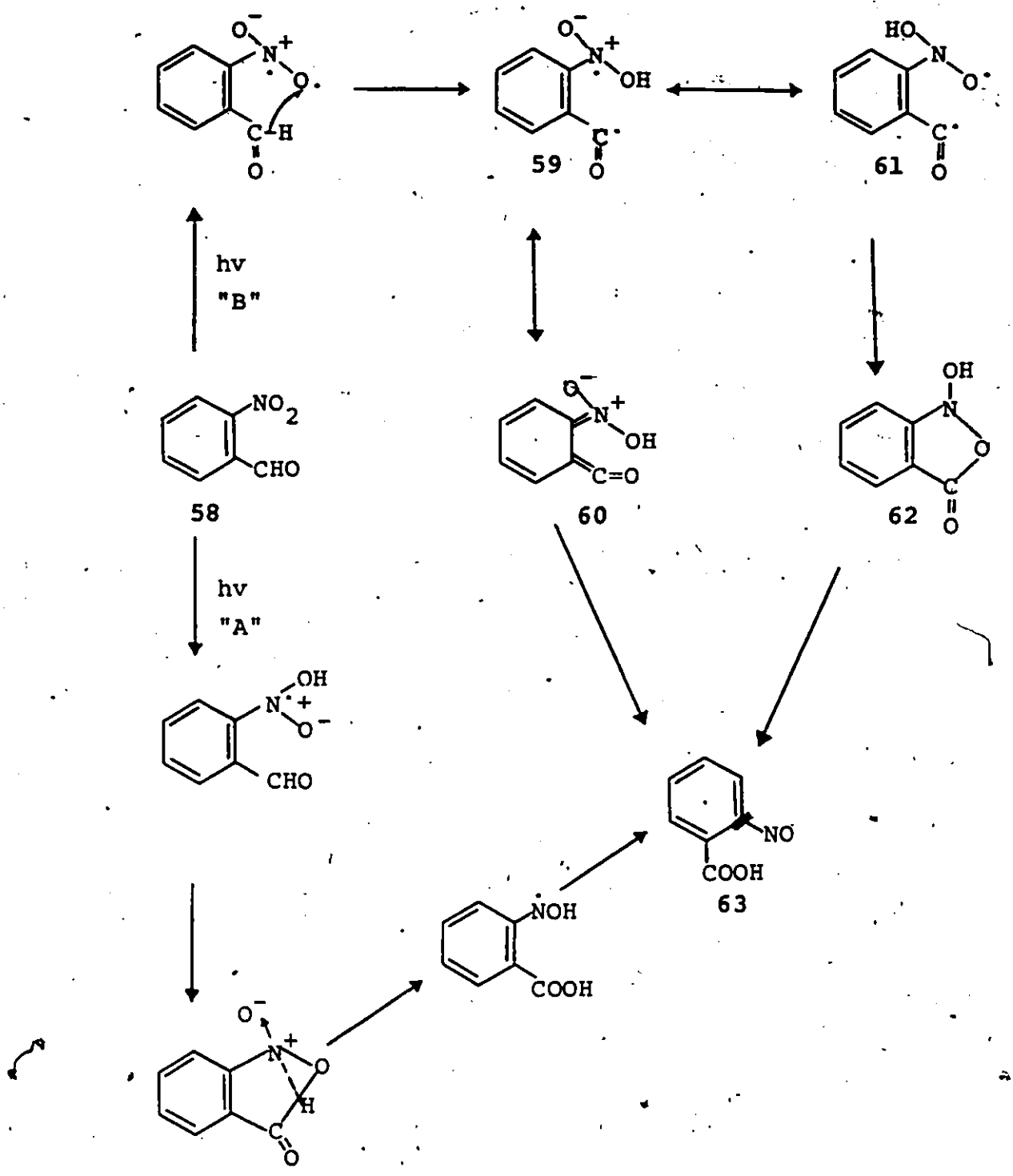
Although the photo-Fries rearrangement and degradation of a number of polymers has been reported in the literature[43-53], to our knowledge no attempts have been made at using this reaction as the basis for a lithographic imaging system. The expected increased solubility of the rearranged photoproducts in aqueous base due to the presence of a phenolic hydroxyl group should give rise to an image upon development in a suitable solvent. A similar result would be obtained for the NH_2 containing photoproducts of amides when developed in aqueous acid. The photodegradative component of the photo-Fries reaction reported by Bellus et al.[44], would also be expected to contribute to the solubility difference between exposed and unexposed areas of a polyester or polyamide film. Since the standard film thickness of a resist layer is only about 1 μm, the photostabilizing effects of the rearrangement products reported by Guillet and Li[50], and Bellus et al.[44] for 10 and 25 μm thick films of 53, may only be of marginal importance. Other sections of this thesis cover the synthesis, photochemical study and lithographic testing of polymers containing pendant ester or amide groups which are susceptible to the photo-Fries rearrangement.

Photorearrangement of O-Nitrobenzaldehyde:

The photoisomerization of o-nitrobenzaldehyde (o-NBA) (58) to nitrosobenzoic acid (63) as shown in Scheme 14, was first reported by Ciamician and Silber[54]. Tanasescu and Ionescu[55] have proposed that this reaction is intramolecular since it is concentration-independent and does not occur with m- and p-nitrobenzaldehydes in organic solvents. However, Wubbels et al.[56], have reported that rearrangement of the p-NBA does occur in water. Subsequent studies with 58 in the solid, liquid and gaseous phases have shown that the quantum yield of photoproduct 63 is invariably equal to 0.5[57,58]. Samokvalova and Krongauz[59] have shown that the rearrangement can proceed via the transfer of excitation energy from a solvent such as benzene to the aldehyde.

Although this photorearrangement has been known for over 80 years, very few researchers have studied its reaction mechanism. Calvert and Pitts[60] first suggested that the mechanism could involve scission of oxygen from the excited nitro group, followed by insertion into the C-H bond of the aldehyde, without initial detachment of the hydrogen atom. Pashayan et al.[61] have proposed a concerted mechanism for this oxygen scission and insertion as shown in pathway A of Scheme 14. The other possibility, which has received greater support in the literature, consists of abstraction of the aldehydic hydrogen by the excited nitro group. The resulting biradical 59 could give either ketene 60 or biradical 61. Transfer of the -OH group in 60 would give the product 63 directly[62,63]. Biradical 61 could give 63 by way of cyclic intermediate 62[64]. Conflicting ESR results supporting either one

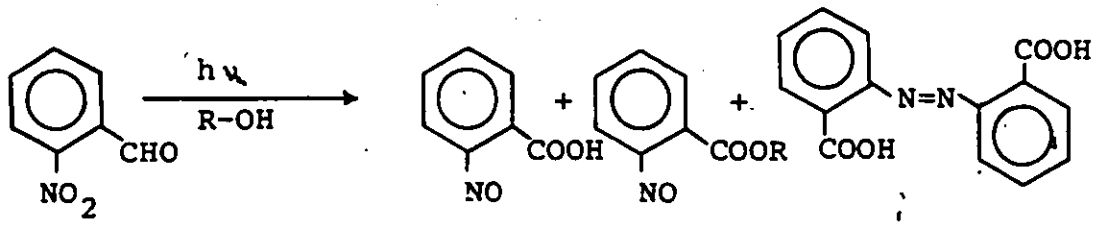
Scheme 14: Proposed Mechanisms for the Photorearrangement of o-Nitrobenzaldehyde



or the other of these pathways have been reported[65,66].

A number of other photoproducts can be formed as a result of side-reactions. The relative quantities of these various products have been found to vary according to the solvent used to carry out the photolyses.

Scheme 15



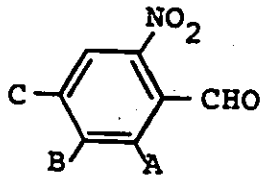
58 63 64 65

R= CH_3-; CH_3CH_2-; $(CH_3)_2CH$-

Photolysis of o-NBA in methanol or ethanol for example, gives the ester of o-nitrosobenzoic acid (**64**) and the azoxy derivative of **63** (**65**), whereas irradiation in isopropanol gives **63** as the major product[66]. In ethanol and methanol, o-NBA occurs to a large extent in the form of a hemiacetal, but in isopropanol the hemiacetal is not formed[66]. Pashayan et al.[61] have shown however, that the acetal and hemiacetal of o-NBA have almost identical photorearrangement quantum yields as o-NBA itself.

Pashayan et al.[68] have studied the quantum yields for the photoisomerization of o-NBA and some substituted o-NBA derivatives. Their findings are summarized in Table 3. The introduction of substituents para to the nitro substituent had little effect on the quantum yield. The greatest substituent effects are observed for the 6-nitro- and 6-methoxy-substituted

Table 3: Quantum Yield for the Photoisomerization of o-Nitrobenzaldehyde and It's Derivatives[68]



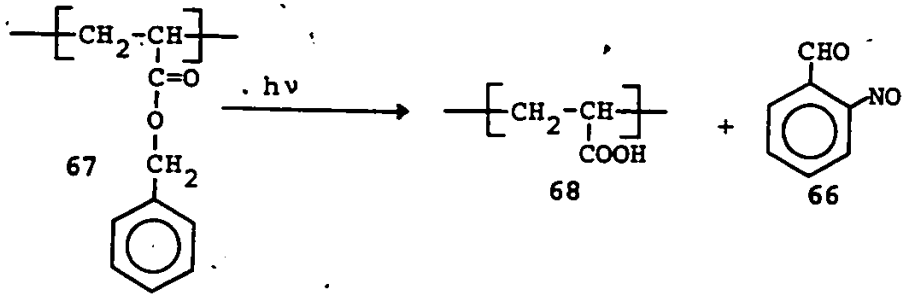
A	B	C	Quantum Yield* (mole/einstein)
H	H	H	0.50
H	OCH_3	H	0.56
OCH_3	H	H	0.30
NO_2	H	NO_2	0.67[58]
H	H	NO_2	0.56[58]

o-NBA. These authors have suggested[68] that an electron donating methoxy group at position 6 reduces the positive charge on the carbonyl carbon thereby decreasing the quantum yield of the photorearrangement to 0.30. Conversely, the electron withdrawing effect of the nitro group at position 6 results in an increase in the quantum yield to 0.67.

Photochemical oxygen transfer as seen for o-NBA, has also been reported for several aromatic nitro compounds possessing a benzylic hydrogen in the o-position[69,70]. Barzynski and Saenger[70] studied the photolysis of o-nitrobenzyl esters of a number of carboxylic acids. Oxygen transfer from the o-nitro substituent resulted in the production of o-nitrosobenzaldehyde (**66**) and the corresponding acid. While our work was in progress, a new o-nitrobenzylacrylate polymer **67** which also underwent this

same reaction (see Scheme 16) to give **66** and poly-(acrylic acid) (**68**) was reported[70].

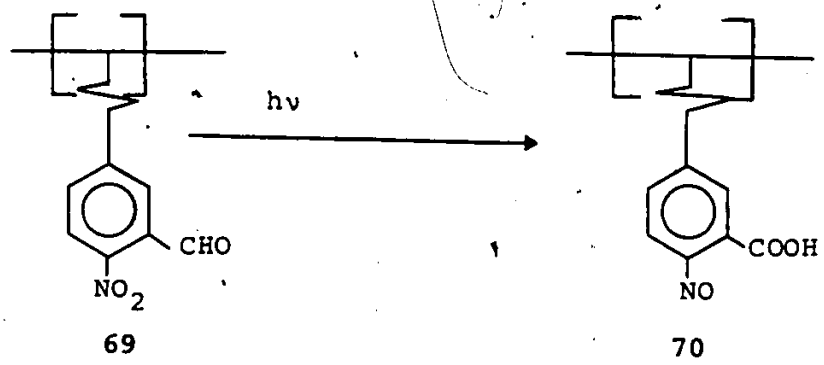
Scheme 16



The much greater solubility of **68** in aqueous base allowed the development of a three-dimensional relief image.

Another approach to using this oxygen transfer reaction in a one-component photoresist system could simply involve the introduction of o-nitrobenzaldehyde pendant groups into a polymer chain.

Scheme 17



Exposure of polymer films of the general type **69**, to light of an

appropriate wavelength should give the corresponding photoproduct **70.** A large difference in solubility would be expected between the exposed and unexposed polymers allowing access to three-dimensional imaging upon development in aqueous base. Synthetic approaches used to prepare polymers containing such o-NBA pendant groups, and the photochemistry of these polymers will be outlined.

RESULTS AND DISCUSSION

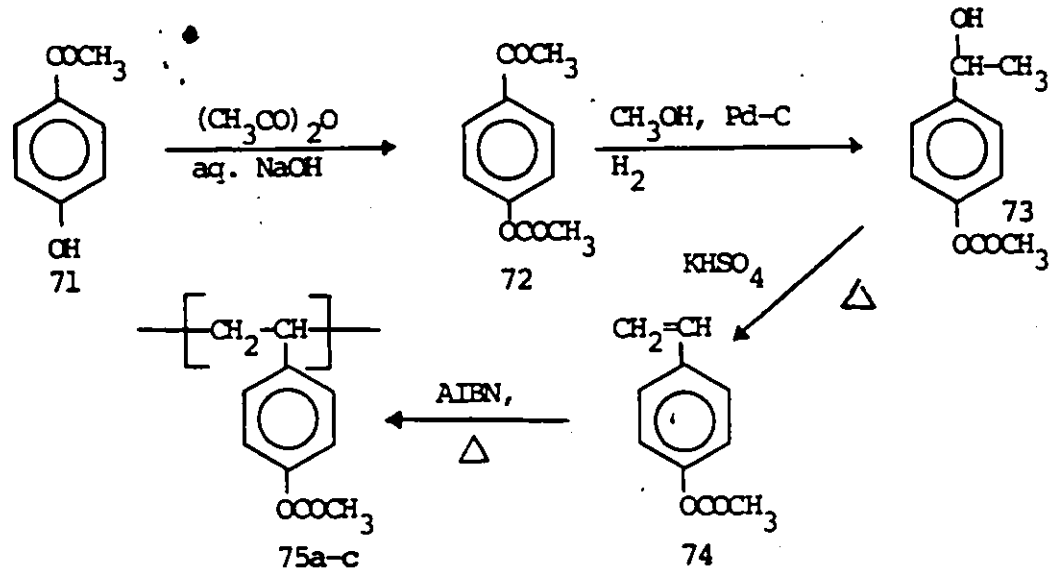
Photo-Fries Rearrangement

Preparation of the Polymers:

(a) Poly-(p-acetoxystyrene)(75)

Poly-(p-acetoxystyrene) was prepared as shown in Scheme 18.

Scheme 18



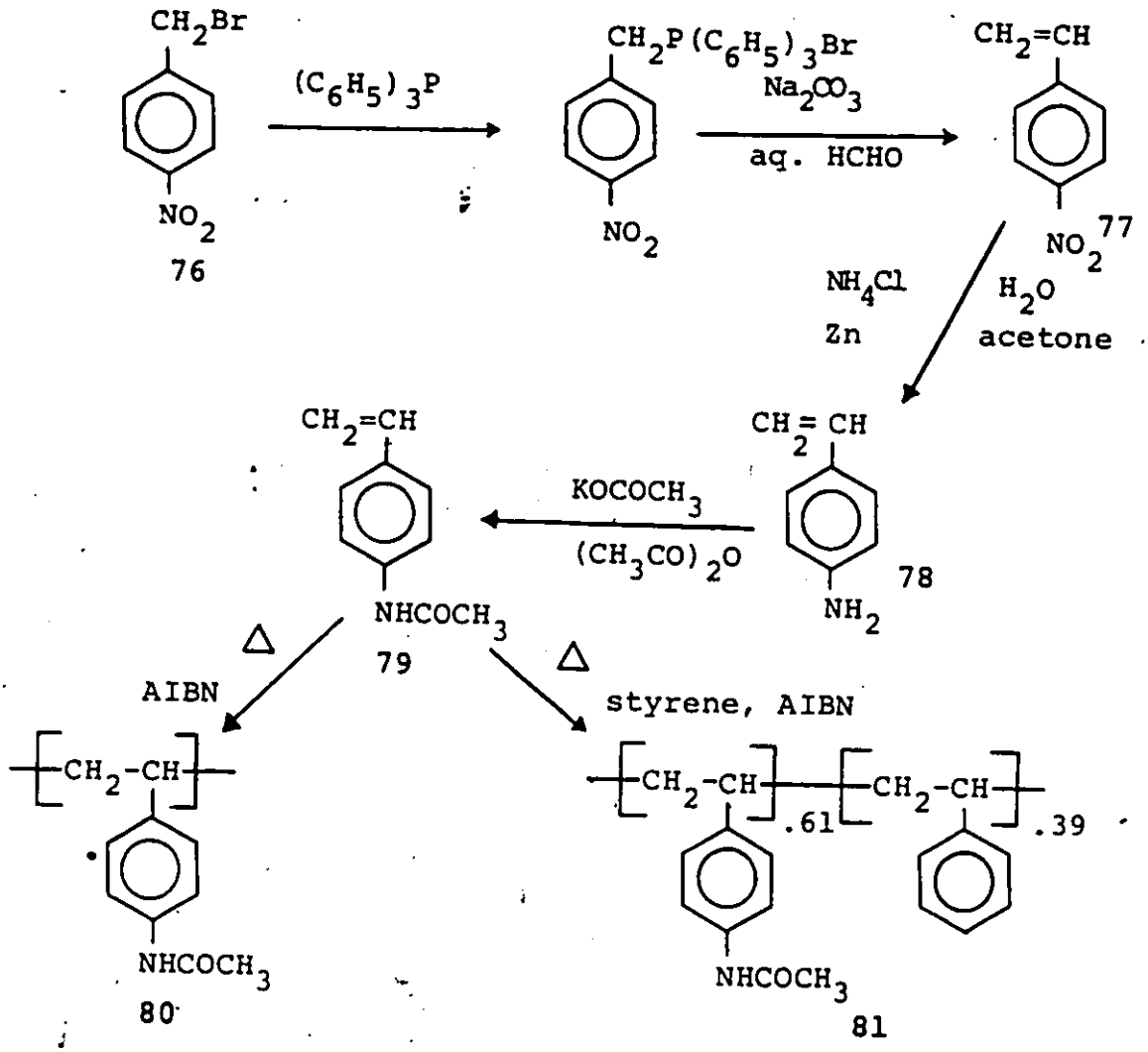
p-Acetoxystyrene (**74**) was obtained by the procedure of Corson et al.[71], using p-hydroxyacetophenone (**71**) as starting material. **71** was treated with acetic anhydride in aqueous sodium hydroxide to give p-acetoxyacetophenone (**72**). Hydrogenation of **72** in methanol with palladium on carbon led to the formation of p-acetoxyphenylmethylcarbinol (**73**) as the major product. The acetoxy group was resistant to the reduction conditions used, resulting in selective reduction to give intermediate **73**. Subsequent treatment of **73** with $KHSO_4$ at elevated temperatures in the presence of t-butyl catechol to inhibit polymerization, gave **74** in 46% overall yield. The polymerization of **74** was carried out in solu-

tion, and in bulk, using azobisisobutyronitrile (AIBN) as initiator, to give high yields of poly-(p-acetoxystyrene) (75a-c). Spectral data obtained confirmed the structural assignments of 75 and the various intermediates.

(b) Poly-(p-acetamidostyrene) (76) and its Styrene Copolymer (77)

Poly-(p-acetamidostyrene) (80) and copoly-(p-acetamidostyrene styrene) (81) were prepared as shown in Scheme 19.

Scheme 19



p-Nitrostyrene (77) was obtained by the procedure of Broos and

Anteunis[72]. A Wittig reaction on p-nitrobenzyl bromide (76) gave 77 in 78% yield. Reduction of 77 with ammonium chloride and zinc dust in a water-acetone mixture as reported by Boyer and Alul[71], gave p-aminostyrene (78). Crude 78 was treated with potassium acetate and acetic anhydride to give p-acetamidostyrene (79) in 60% yield. Free radical polymerization of 79 using AIBN as initiator gave homopolymer 80 which was insoluble in most organic solvents tested including methylene chloride, dioxane, acetonitrile, and ethanol, but was soluble in DMF, and DMSO.

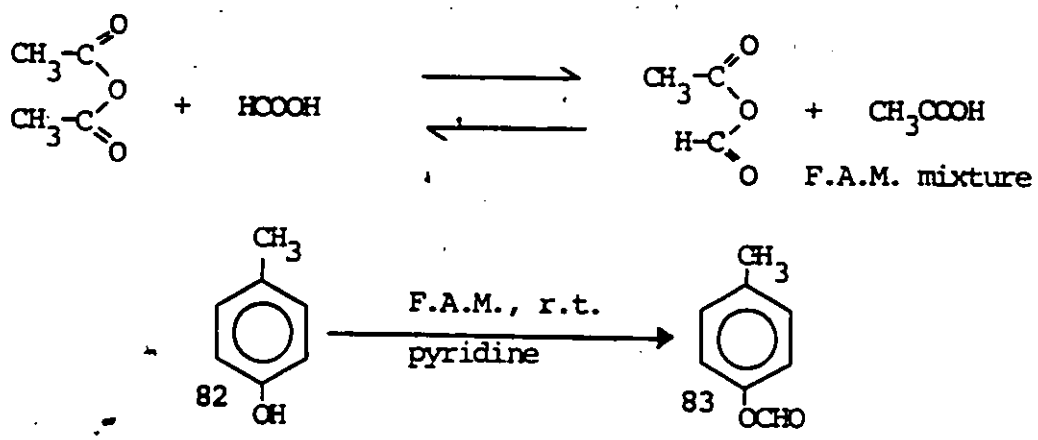
In an attempt to improve the solubility of the polymer, 79 was copolymerized with an equimolar amount of styrene. The copolymer which was obtained, 81, contained 61% of the acetamidostyrene units confirming the greater reactivity of this monomer as compared to styrene. Copolymer 81 also had poor solubility in most organic solvents, and although improved solubility properties might have resulted from the incorporation of more styrene units into copolymer 81, no other copolymerizations were attempted since a high incorporation of styrene would also result in markedly decreased photochemical activity.

(c) Poly-(p-formyloxystyrene) (89)

In order to assist with the characterization of the photo-Fries rearrangement and degradation products of poly-(p-formyloxystyrene), a low molecular weight model compound was synthesized. p-Tolyl formate (83)[74] was prepared via the formylation procedure of Stevens and Van Es[75] which utilizes a formic acid-acetic anhydride mixture (F.A.M.) as formylating agent. If the reaction temperature is kept near room temperature and pyridine

is used as the catalyst, this reaction proceeds very cleanly with little competing acylation[75] (less than 2%). This synthesis (Scheme 20) initially involves the production of an F.A.M. mixture followed by treatment of p-cresol (82) with this mixed anhydride for 1 day at room temperature in the presence of a catalytic amount of pyridine, to give 83 in 83% yield.

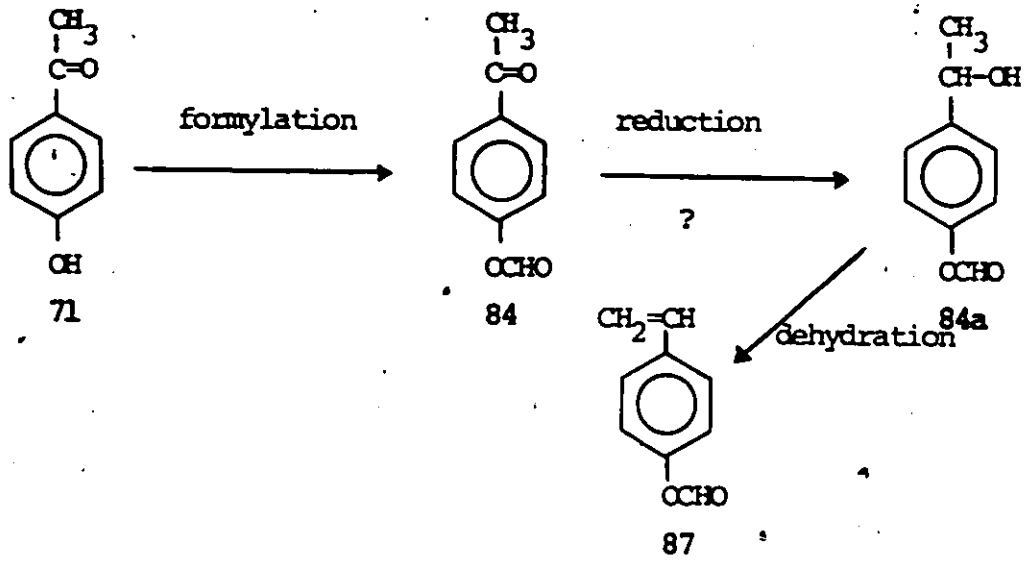
Scheme 20



Stevens and Van Es[75] have shown the great catalytic effect of pyridine on this formylation reaction. In the absence of pyridine, a 60 day reaction period was required to obtain a yield of 83 comparable to that obtained in one day with the catalyst[75,76].

Two basic methods were used to prepare poly-(p-formyloxystyrene) (89). The first approach involved synthesis of the monomer followed by polymerization, while the second involved chemical modification of poly-(p-hydroxystyrene) (88). At least two simple procedures for the preparation of p-formyloxystyrene from readily available starting materials may be conceived. The first of these outlined in Scheme 21, is analogous in concept to the procedure used by Corson et al.[71] to prepare p-acetoxystyrene.

Scheme 21

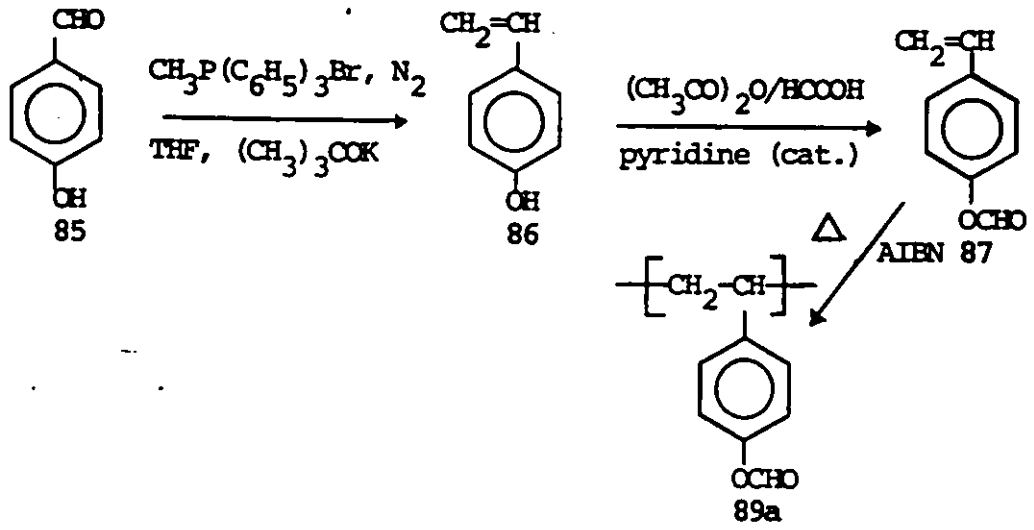


The starting material would be p-hydroxyacetophenone (**71**) which would be formylated under standard conditions to lead to **84**. The key step in this approach would be the selective reduction of the keto group of **84** in the presence of the reactive p-formyloxy group. A chemical dehydration of **84a** would then afford monomer **87**. Unfortunately, while **84** could be obtained in good yield, all attempts at the selective transformation of the keto group into the corresponding alcohol failed as the formyl group was lost in the reaction.

The second approach shown in Scheme 22 was much more successful, as the labile formyl group was added in the last step of the synthesis. This pathway involving the preparation and formylation of p-hydroxystyrene (**86**) gave p-formyloxystyrene (**87**) in good yield. **86** was readily prepared by a Wittig reaction on p-hydroxybenzaldehyde (**85**) using methyltriphenylphosphonium bromide and potassium tert-butoxide in THF. Formylation of **86** with the F.A.M. mixture gave **87** in 67% yield. Free-radical bulk polymeri-

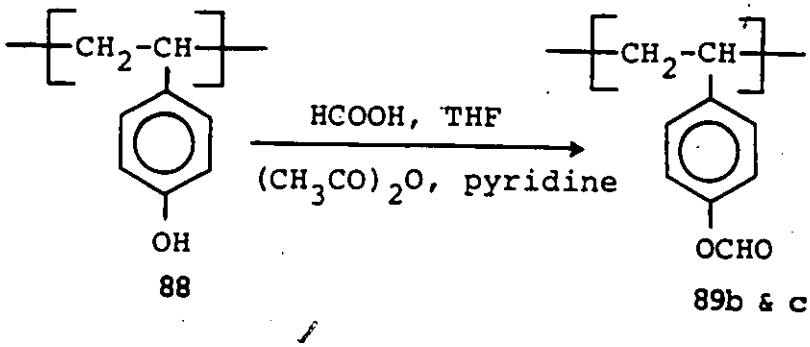
zation of **87** using AIBN as catalyst gave homopolymer **89a**.

Scheme 22



The last route to polymer **89** involved the chemical modification of poly-(p-hydroxystyrene) (**88**) as shown in Scheme 23.

Scheme 23



The main drawback with this procedure is the lack of availability of pure **88**. A low purity material is available commercially from the Maruzen Oil Company under the trade name "Resin M", however this material is heavily oxidized and highly coloured. High purity **88** was obtained by thermolysis or acidolysis of poly-(p-tert-butoxycarbonyloxystyrene) as described by Fréchet et al.[77] The treatment of a solution of **88** dissolved in THF, with an

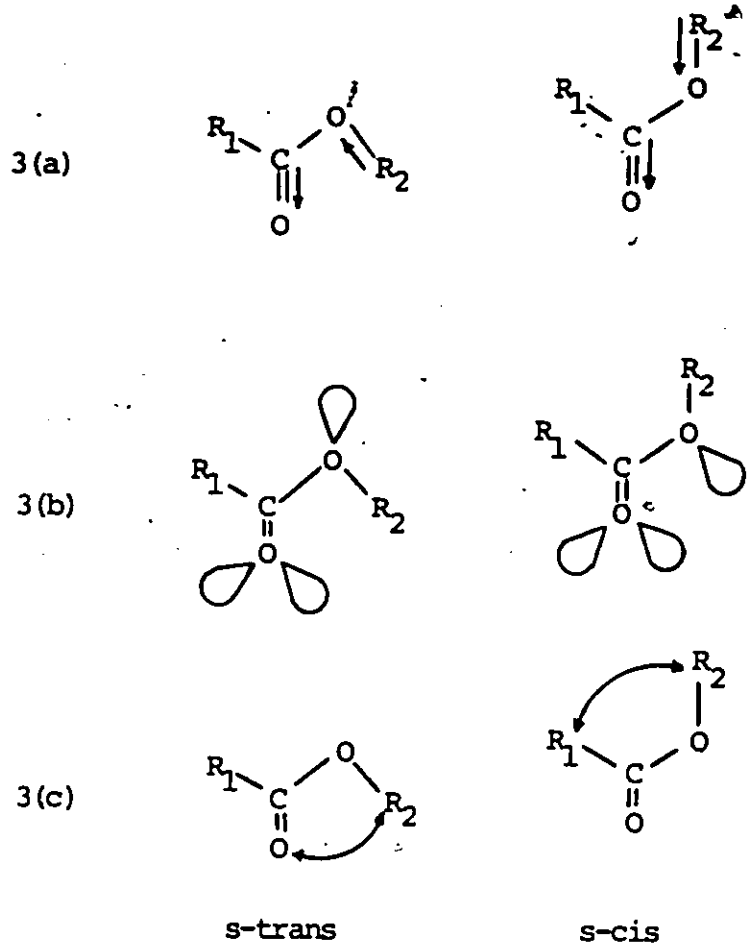
F.A.M. mixture and a catalytic amount of pyridine for 3 days led to nearly complete formylation of this polymer. The presence of a weak O-H band centered at 3424 cm^{-1} in the IR spectrum of **89** (see Figure 6) indicated that a small amount of unreacted units of **83** remained. Similarly, Stevens and Van Es[75] have reported that formylation of phenol by the same method does not go to completion (2% unreacted phenol remaining). The extent of formylation was not affected by increasing the reaction period to 6 days.

The formylated product **89** was found to be quite sensitive to moisture and heat. Prolonged storage of **89** in an unsealed vial at room temperature in the dark resulted in some decomposition as detected by the odour of formic acid. The decrease in C=O bands and increase in O-H band observed in the IR spectrum upon aging confirmed this degradative process. Storage of **89** in a sealed vial in a freezer provided improved shelf life.

All of the formates produced in this section showed two separate C=O absorptions above 1700 cm^{-1} due to the presence of both possible s-cis and s-trans conformations of formate group, as reported by Oki and Nakanishi[78]. The partial double bond character of the C-O bond due to delocalization of the electrons accounts for the observation of these two conformers. The presence of s-cis and s-trans conformers of many carboxylic acids[79] and amides[80] have also been reported.

Oki and Nakanishi[78] have outlined 3 theoretical reasons for the usual greater stability of the s-trans conformer.

Figure 3: Major Factors Governing the Conformation of Esters [78]



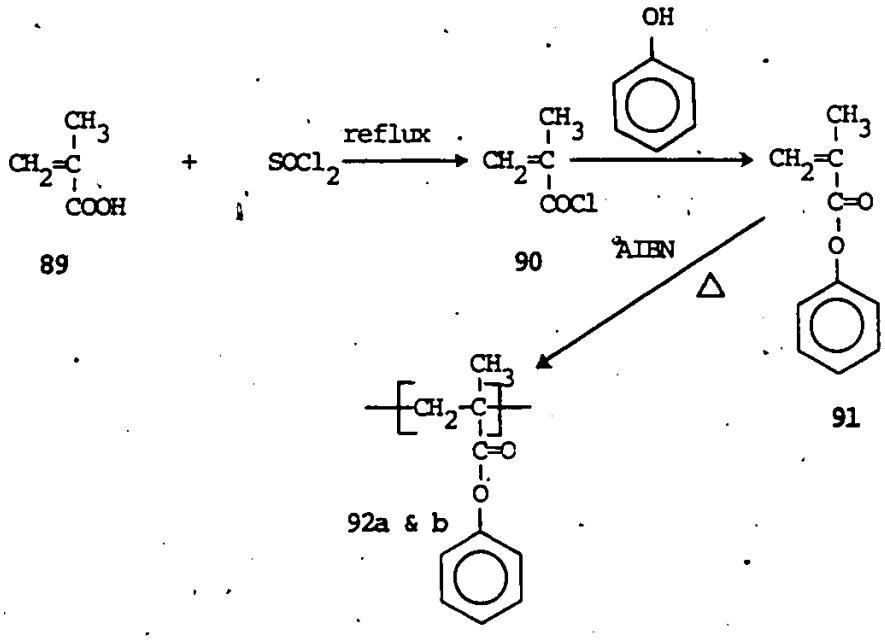
As seen in Figure 3(a), the direction of the dipoles of the two bonds is roughly antiparallel for the s-trans conformer and roughly parallel in the s-cis conformer. As a result, it would be expected that the s-trans conformer would be favoured in a less polar media. Secondly, as seen in Figure 3(b), the repulsion between lone pair electrons of the 2 oxygen atoms is greater in the case of the s-cis conformer. Thirdly, when R_1 is bulky, the steric repulsion between C=O and R_2 in the s-trans conformer should be smaller than that between R_1 and R_2 in the case of the s-cis conformer.

In order to observe both conformers, the stability of the s-trans conformer must be decreased and that of the s-cis increased. For formates, such as those that were prepared, containing a bulky R_2 group, the s-cis may be favoured due to increased interaction between R_2 and O relative to that between R_1 and R_2. There is no distinction between the two conformers in the NMR spectra of the formate esters produced. The NMR time scale at the normal operating conditions of the instrument allows interconversion between conformers. The shorter time scale of the IR allows for the detection of these two conformers. A low temperature NMR study carried out by Oki and Nakanishi[78] of t-butyl formate allowed the resolution of a single peak (8.04 ppm at 20°C) into two peaks at 8.88 and 8.03 ppm at -99°C.

(d) Poly-(phenyl methacrylate) (92)

Poly-(phenyl methacrylate) was prepared as shown in Scheme 24, according to the procedure of Sumrell et al.[81]

Scheme 24

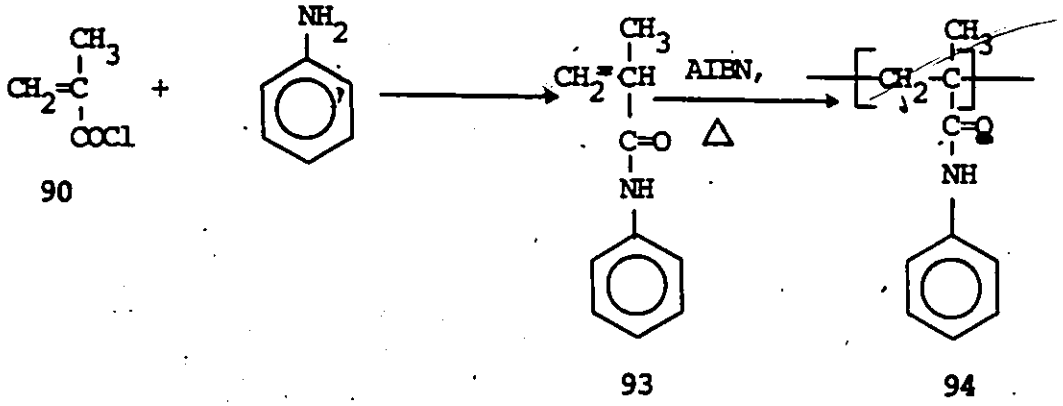


Refluxing a mixture of methacrylic acid and thionyl chloride gave methacryloyl chloride (90). Addition of phenol to the crude 90 with chlorine displacement, generated phenyl methacrylate (91) in reasonable yield. Free-radical polymerization of 91 in toluene using AIBN as initiator gave 92a and 92b.

(e) Poly-(methacryl anilide) (94)

Poly-(methacryl anilide) was prepared as shown in Scheme 25a, according to the procedure of Patai et al.[82]

Scheme 25a



The crude mixture of 90 was prepared as described in the preparation of 92. Aniline addition to the crude solution of 90 gave monomer 93 in 52% yield. Free-radical polymerization of 93 in benzene with AIBN as initiator gave 94.

Photochemical Studies and Imaging Experiments:

There are a number of difficulties in the study of the photochemistry of polymers. Unlike low molecular weight materials, no purification of the photoproducts can be carried out. Therefore, if a photochemical reaction only goes to 50% completion, a complex polymer incorporating both modified and unmodified units is obtained. This results in difficult monitoring of

the photoreactions, and complex or often impossible characterization of the photoproducts.

Solution and solid-state photochemical studies are routinely used to predict the resist potential of photosensitive polymers. Solid-state film studies are especially useful, since the reaction conditions can be carefully regulated so as to closely simulate the imaging process. For example, the thickness of the film studied should correspond to the thickness of resist that is required for a given application. This is critical since the reaction may only occur to a certain depth, especially if the photoproduct has a greater extinction coefficient than the starting material.

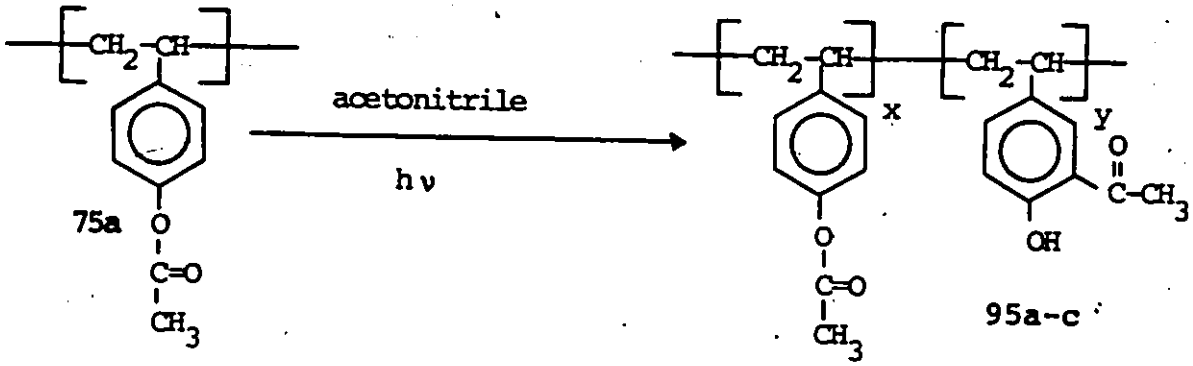
The study of the photo-Fries rearrangement and degradation in the solid-state was restricted to infrared and UV spectroscopy. Homogeneous polymer solutions were cast onto sodium chloride and/or quartz substrates so as to obtain 1 μm thick films, comparable to those routinely used as resists. Infrared and UV spectra were taken at regular intervals throughout the irradiations, allowing monitoring of the reactions. Recent advances in infrared spectroscopic technology (eg. FT-IR) allowing routine spectral subtraction and band integration facilitated this task.

Solution photochemistry was also useful since the larger amounts of photoproducts obtained allowed for more detailed product characterization. ^{13}C and ^{1}H NMR spectra of these photoproducts were used to support the results observed in the solid-state.

(a) Reactive Pendant Groups on Styrene Backbones:

Solution photochemistry studies of poly-(p-acetoxystyrene) (75a) in acetonitrile, showed that the expected rearrangement was indeed occuring (see Scheme 25b).

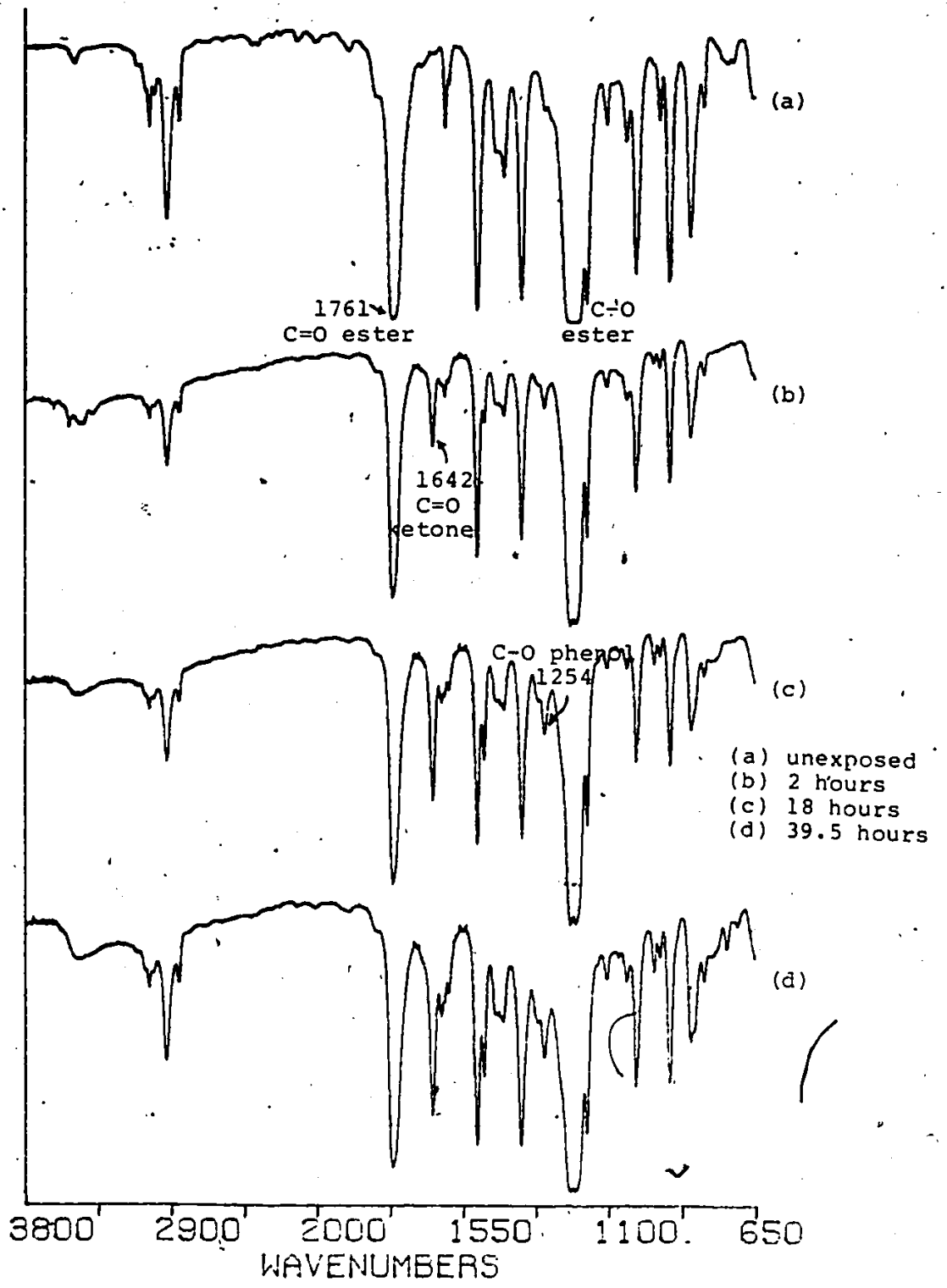
Scheme 25b



This is illustrated by Figure 4, which shows the change in intensity of the carbonyl absorption of a film of polymer **95a-c** cast onto a NaCl disk. The acetoxy peak at 1765 cm^{-1} slowly decreases in intensity, and is replaced by a new carbonyl band at 1643 cm^{-1} which corresponds to the o-rearranged ketone. The relative positions of the ester and o-hydroxyketone C=O bands correspond to those reported by Anderson and Reese[29] for phenyl acetate (**30**) and 2-hydroxyacetophenone. Due to the blocking of the p-position by the polymer backbone, the o-isomer was obtained exclusively. The emergence of a weak hydrogen-bonded O-H band at 3483 cm^{-1} suggests that little or no degradation has occured.

After the first two hours of irradiation, the presence of increasing amounts of photoproducts results in a drastic decrease in the reaction rate, as reported by Bellus and Hrdlovic[22]. Even after a total irradiation time of 39.5 hours, the reaction has

Figure 4: IR Spectral Changes During Solution Photochemistry of Polymeric Ester 75a



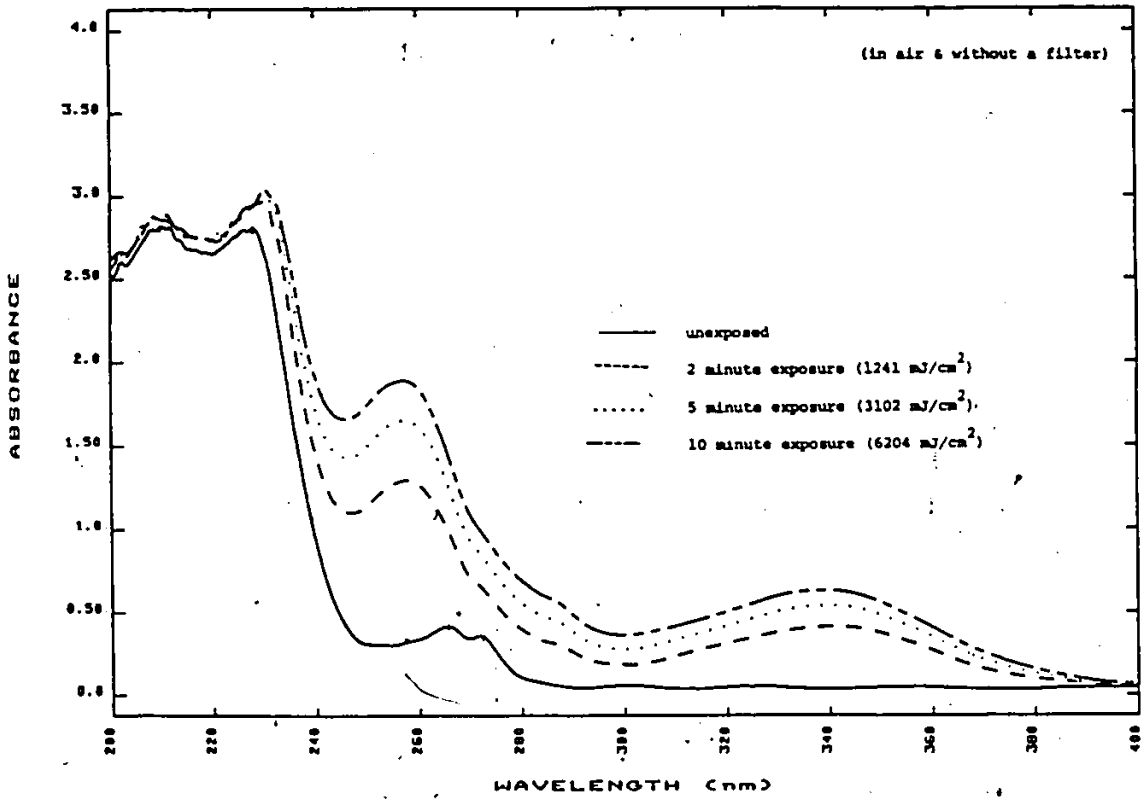
not gone to completion. The molar ratio of the resulting copoly-(p-acetoxystyrene 2-hydroxy-5-vinylacetophenone) (**95c**) is 0.52:0.48 as determined by ^{1}H NMR spectroscopy. Such prolonged periods of irradiation give rise to secondary polymer chain reactions such as cross-linking which result in an increase in the M_n value from 1.17×10^4 for **75a** to 4.50×10^4 for **95c**.

The photorearrangement of PACOST (**75a**) seen in solution is also found to occur in the solid-state. UV irradiation of a 1.26 μm thick film of **75b** on a NaCl substrate results in the same changes in the IR spectra with time of exposure as observed in solution. The quantum yield of the photorearrangement is low, with only a 40% conversion after a dose of 2.90 J/cm^2. The decrease in the rate of this reaction as the amount of photoproduct increases is shown in Figure 12.

The emergence of the weak O-H band at 3483 cm^{-1} in the IR spectra of films of copolymer **96**, as seen for the solution photochemistry products **95a-c**, indicates little degradation to p-hydroxystyrene units in the polymer. In the case of the solution photochemistry of PACOST, the absence of detectable amounts of the degradation product was attributed to the strong solvent cage provided by acetonitrile. This cage prevents escape of the acetyl radical, thereby favouring recombination of the radical pair to give either the starting material, or the o-rearranged product, as suggested by Kalmus and Hercules[32] for low molecular weight aryl esters. In the case of thin-film UV exposures, the low mobility of the acetyl radical in the solid polymer matrix also favours recombination of the radical pair.

The photostabilizing effect of the o-rearranged product observed in both solution (**95a-c**) and solid-state (**96**) photoproducts is demonstrated by the UV spectra of a film of copolymer **96** taken at given irradiation intervals and shown in Figure 5.

Figure 5. UV Spectral Changes Upon Irradiation of a Poly-(p-acetoxystyrene) Film (**75b**)



Before irradiation, the 1.10 μm thick PACOST **75b** film shows only a slight absorption near the 254 nm mercury emission line. Unfiltered irradiation of **75b** to doses ranging from 0 to 6.20 J/cm^2 gives copolymer **96** showing new UV absorptions at 256 and 340 nm, characteristic of the o-rearrangement photoproduct. The decrease in reaction rate with increased exposure time is explained

by the continuous formation of UV photostabilizing o-hydroxystyrene which absorbs strongly near 254 nm. Further irradiation beyond the 6.2 J/cm^2 dose has little effect on the UV spectrum, since the radiation is absorbed and dissipated non-photochemically by this photostabilizing group, as illustrated by Li and Guillet[50], and Gilazhov et al.[51] for 15-20 μm thick films of aryl acrylates and methacrylates. Since identical spectral results are obtained for film irradiation under nitrogen, photooxidation as reported by Hiraoka and Pacansky[84] for poly-(p-hydroxystyrene) is not a factor.

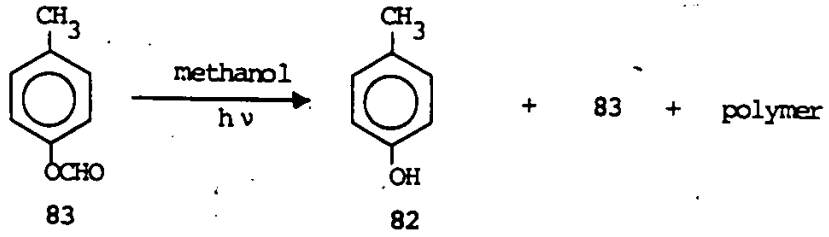
The photo-Fries rearrangement of poly-(p-acetamidostyrene) (**80**) was expected to proceed in the same way as shown in the literature for acetanilide (**37**)[27]. Since homopolymer **80** is only soluble in either DMF or DMSO, which have UV cut-offs around 270 nm[85], photochemical studies cannot be carried out in solution. As a result of the lack of improvement in the solubility of the copolymer with styrene (**81**), and the unavailability of an appropriate solvent, further attempts at carrying out solution photochemistry studies on either polymers **80** or **81** were discontinued. However, UV irradiation studies on 0.9 μm thick films of homopolymer **80** cast from DMF were carried out. No noticeable change in the IR spectra of these films was seen over the 0 to 3.16 J/cm^2 UV irradiation dose tested. These results indicate that the rate of the photorearrangement for poly-(p-acetamidostyrene) (**80**) is much slower than that observed for PACOST (**96**).

Although the acetate ester of poly-(p-hydroxystyrene) is more readily prepared than the corresponding formate, the

occurence of photostabilizing rearrangements make it ultimately unsuitable for use in imaging reactions. The photochemical studies on formyloxybenzene (29) reported by Horspool and Pauson[33] suggested that irradiation of formate esters would give phenols as the major photoproducts. Since phenols absorb much less in the deep UV range than o-rearrangement products such as o-hydroxyacetophenone[22], it was anticipated that the formate ester 89 would have a greater overall photochemical reactivity than was observed for the polymeric acetate ester.

The solution photochemistry of p-cresyl formate (83) was studied in order to confirm the results of Horspool and Pauson[33].

Scheme 26



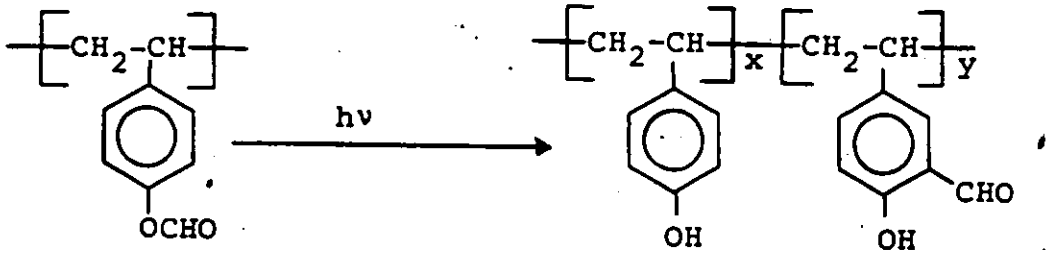
83 82

UV irradiation of an alcoholic solution of p-cresyl formate (83) (Scheme 26), with subsequent work-up gives p-cresol (82) in 68% isolated yield, as well as 4.8% unreacted 83. No corresponding o-rearranged product is observed by TLC. These results further suggest that poly-(p-formyloxystyrene) (83) would have a greater sensitivity to UV radiation than is observed for the acetate ester 75.

Irradiation of polymeric formate ester 89b in dioxane or acetonitrile gives essentially identical results, thus indicating that solvolysis reactions are minimal. IR spectroscopy was used

to monitor the progress of the reaction, as shown in Figure 6. As the UV exposure proceeds, the pair of formate ester carbonyl bands at 1761 and 1738 cm^{-1} decrease rapidly in intensity indicating the disappearance of the formyl groups by the decarbonylation reaction. The emergence of a strong O-H band at 3416 cm^{-1} confirms the expected formation of poly-(p-hydroxystyrene) (**88**), while a very weak carbonyl band at 1641 cm^{-1} suggests that a small amount of hydrogen-bonded, rearranged o-hydroxyaldehyde product **97** is also generated (see Scheme 27).

Scheme 27

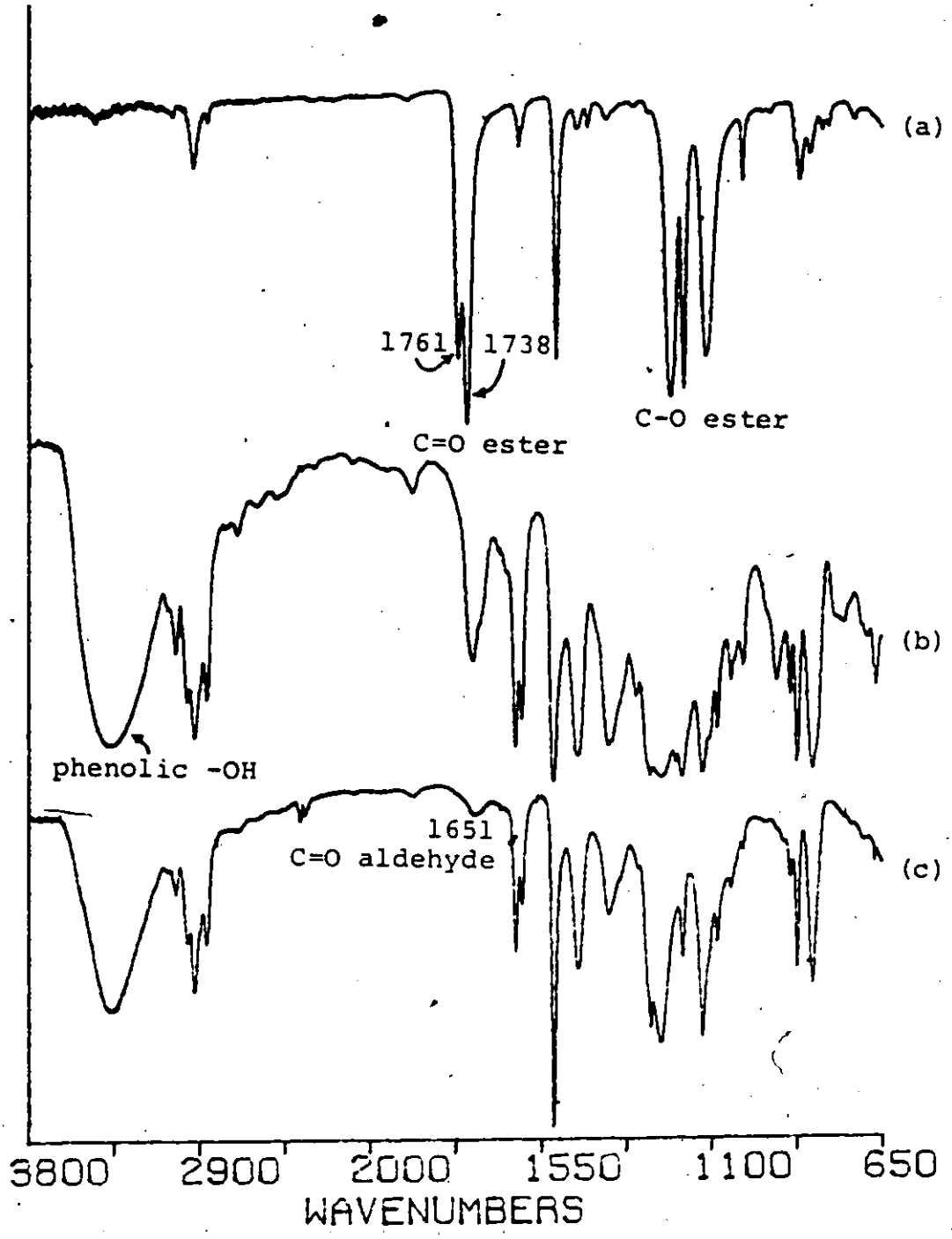


Solution	89b	88	97
Solid-State	89c	88	97

^{13}C and ^{1}H NMR spectra of the irradiated polymer confirm the regeneration of **88**, but does not confirm the presence of any of rearranged photoproduct **97**.

The carbonyl stretching absorption for the s-cis conformer is expected to occur at a higher frequency than the s-trans, since a higher energy is required to excite the molecule when its two dipoles are parallel. The C=O band located at 1761 cm^{-1}, is assigned to the s-cis isomer using this argument. In Figure 6, it is interesting to note that the intensity of the s-cis carbonyl band decreases at a faster rate upon irradiation than that

Figure 6: IR Spectral Changes During Solution Photochemistry of Polymeric Formate Ester 89b



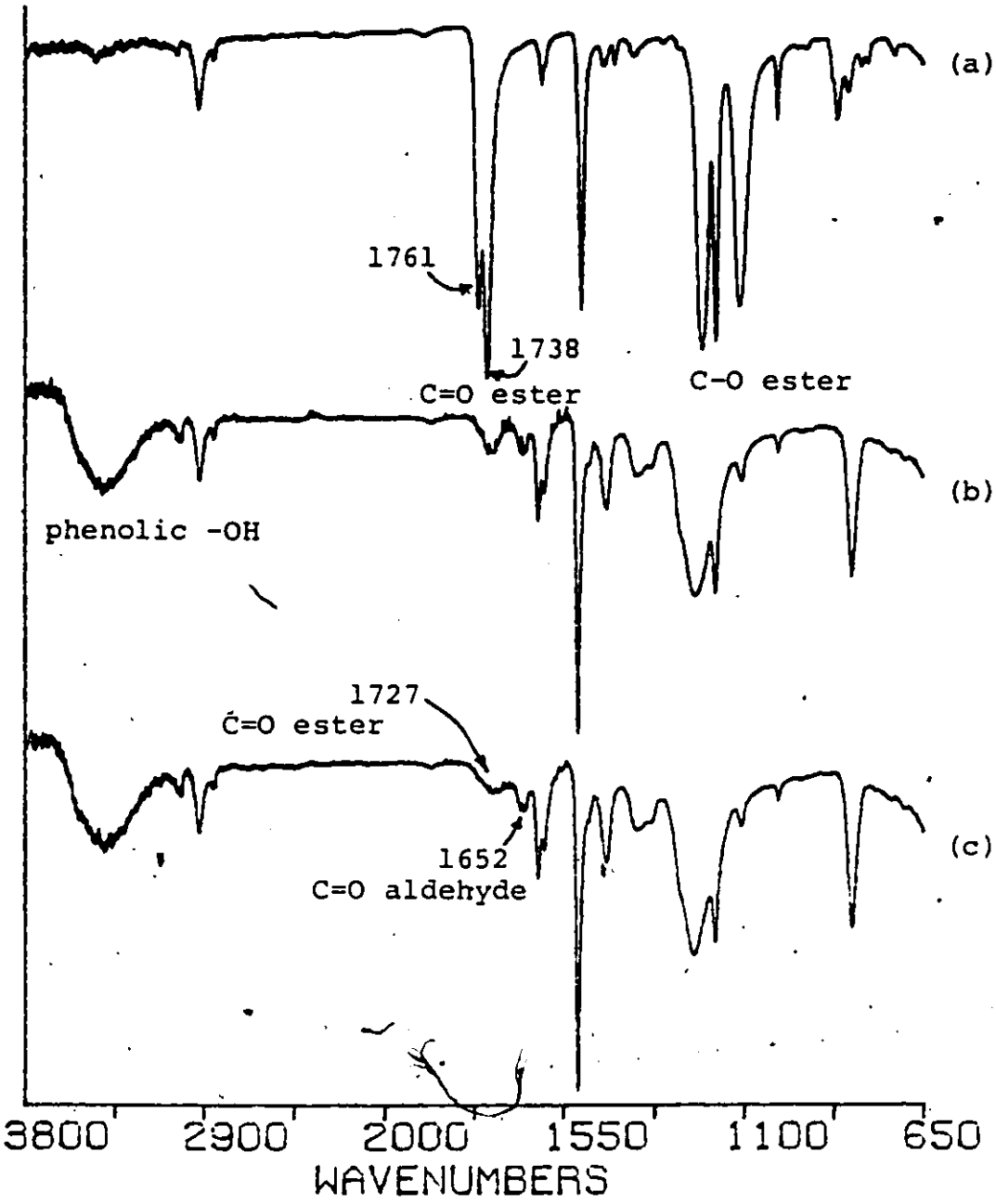
(a) unexposed; (b) 1 hour; (c) 6 hours

for the s-trans conformer. This suggests that the s-cis conformer is less stable to UV irradiation than the other conformer. Similarly, temperature dependence studies of phenyl formate has established that the s-cis isomer is the less stable isomer[78].

Solid-state photochemical studies were also carried out on 1 μm thick films of polymer **89c** on NaCl or quartz disks. As the UV spectrum of **89c** shows an absorption centered at 274 nm, a high pressure mercury lamp was used for exposure. The films were exposed to doses of unfiltered light ranging from 0 to 1.5 J/cm^2, and the reaction monitored by UV and IR spectroscopies. Near complete decarbonylation had occured after the initial 100 mJ/cm^2 dose, with little subsequent change in the IR spectra observed upon further irradiation, as shown in Figure 7. Only a very small amount of starting material and rearranged o-hydroxyaldehyde is observed in the product which has an IR spectrum almost identical to that of poly-(p-hydroxystyrene) (**88**). These observed IR changes are identical to those found for the irradiation of **89b** in solution.

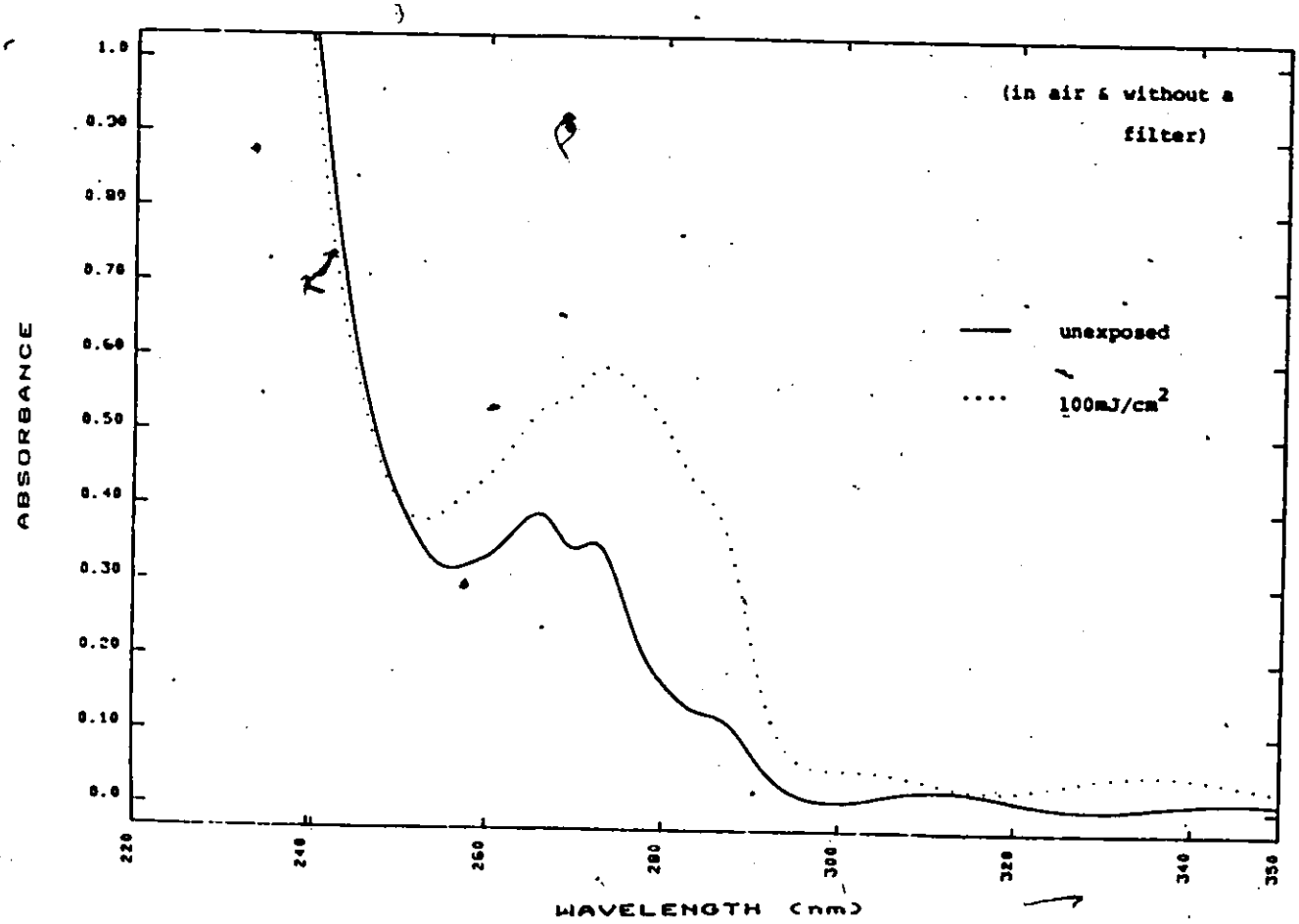
The UV absorption spectrum of the polymer also changes upon exposure, as shown in Figure 8. The phenolic photoproduct, although somewhat more strongly absorbing than the unirradiated formyl precursor polymer **89** in the 250 to 300 nm range, has a much lower absorbance than the o-rearranged product of PACOST. Consequently, degradation is the predominant photoreaction in this case and proceeds quickly to near completion.

Figure 7: IR Changes During Solid-State Photochemistry of Polymeric Ester **89c**



(a) unexposed; (b) 100 mJ/cm^2; (c) 300 mJ/cm^2.

Figure 8: UV Spectral Changes Upon Irradiation of Polymeric Ester **89c**



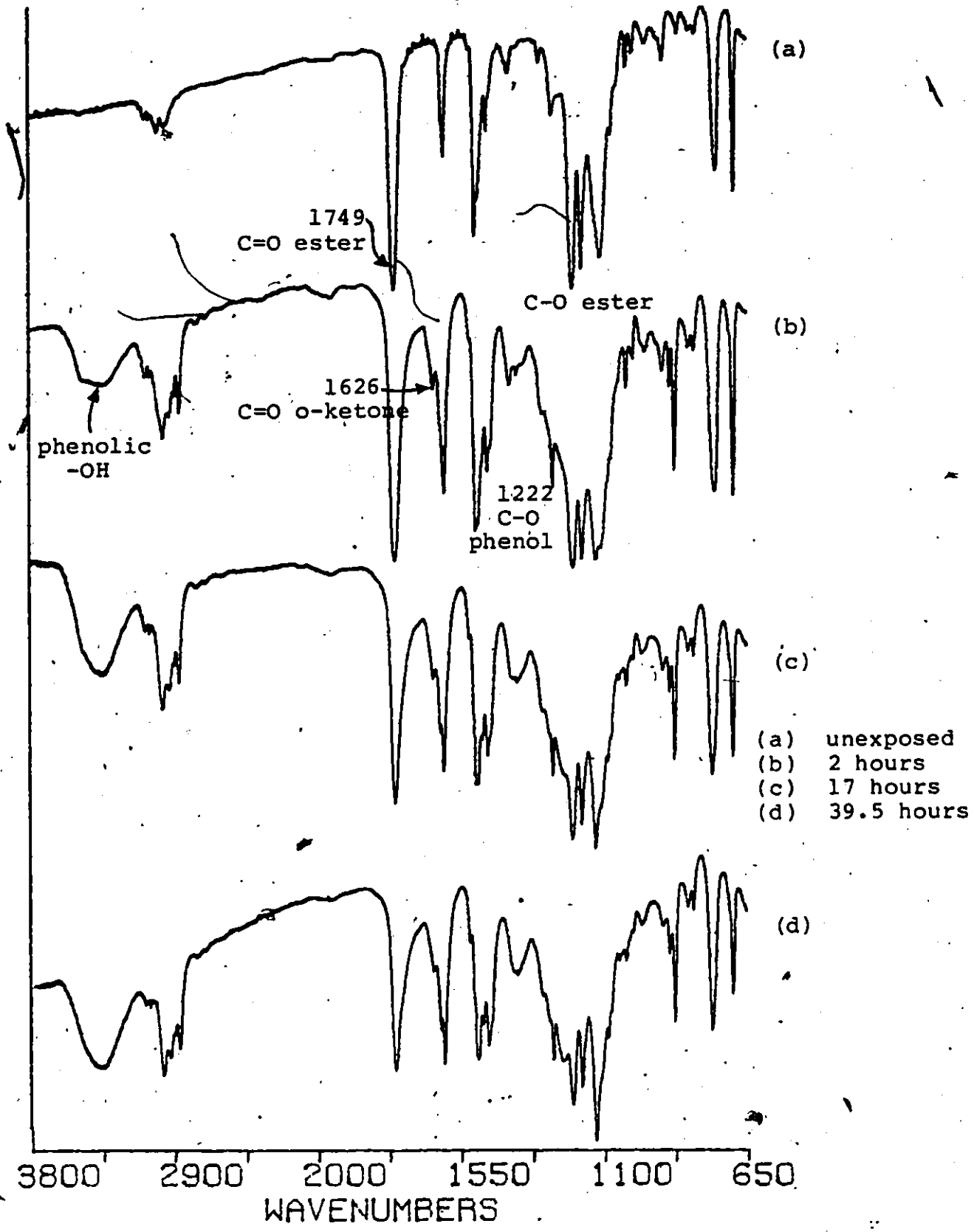
This study shows that large differences exist in the photochemical behavior of formate **89** and acetate **75**. In one instance, photodegradation is the main reaction route, while in the other, considerable photorearrangement is observed. In both cases solution studies were carried out in the same solvent, acetonitrile, which favours cage recombination. This implies that for the photolysis of **89**, the presence of this strongly caging solvent does not hinder generation of the phenolic photoproduct. Consequently, it appears likely that decomposition of the unstable

formyl radical occurs within the solvent cage, thereby preventing recombination of the radical pair. This proposal agrees with the observation[33] that a larger amount of carbon monoxide is detected after UV irradiation of formyloxybenzene (29), than is the case with other esters. Similarly, in the solid-state, decomposition of the formyl radical would give carbon monoxide, which could subsequently be dissipated easily through pores in the polymer film.

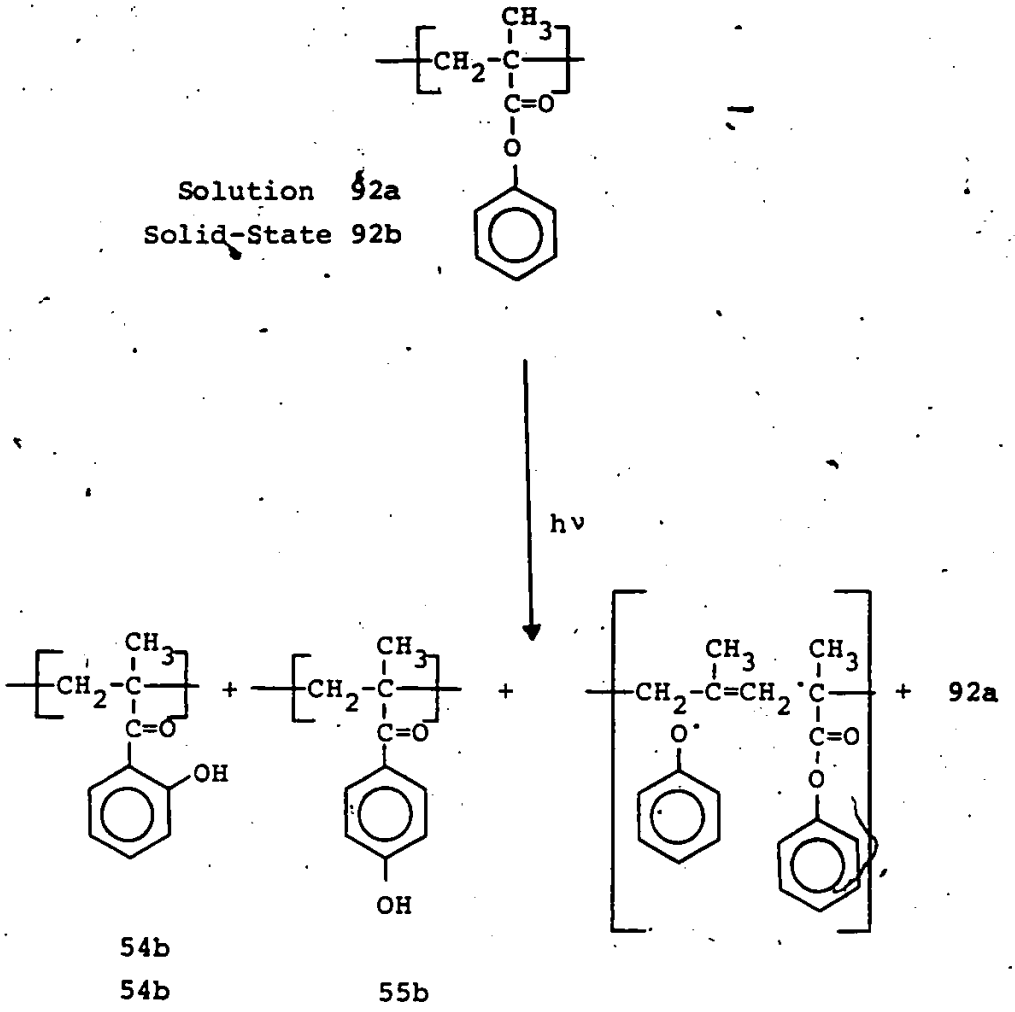
(b) Reactive Pendant Groups on Acrylic Backbones:

Solution photochemistry studies of poly-(phenyl methacrylate) (92a) in freshly distilled dioxane, show that the expected photorearrangement is indeed occurring as previously observed by Bellus et al.[44] and Okawara et al.[49] The IR spectra of films of the photoreaction mixture at various reaction times, cast onto NaCl disks, are shown in Figure 9. The ester carbonyl band of PPMA (92a) at 1747 cm^{-1} slowly decreases in intensity, and is replaced by a new carbonyl band at 1626 cm^{-1}, which corresponds to the o-rearranged ketone 54b (Scheme 13 and 28). The uncharacteristic shift of the ketone carbonyl in **54b** arises due to intramolecular hydrogen bonding. Although the p-position is unoccupied and available to rearrangement, no p-photoproduct is observed. This observation was also made in previous solution studies[44,49]. The expected emergence of an O-H band of medium intensity at 3384 cm^{-1} is also seen to occur.

Figure 9: IR Spectral Changes During Solution Photochemistry of Poly-(phenyl methacrylate) (92a)



Scheme 28



As observed in the solution studies of PACOST 75a, little change in the IR spectra is observed after the initial two hours of irradiation. Even after a total irradiation time of 56 hours, the phenyl methacrylate/o-hydroxyphenyl ketone molar ratio in copolymer **98** is approximately 0.75:0.25, as determined by ^{1}H NMR. This long exposure time results in a drop in M_n value from 7.10 x 10^3 to 8.40 x 10^2, indicating that some photo-Fries degradation resulting in formation of phenol is also occurring[44]. The mecha-

nism of this photodegradation appears to proceed via a pathway analogous to that proposed by Hiraoka[9] and others[1] for the radiolysis of PPMA (Scheme 3).

The ^{13}C NMR spectrum obtained for photoproduct **98** supports the assignment of the o-hydroxyphenyl ketone units, **54b**, with unreacted groups of **92a**. The aromatic peaks can be assigned by comparison with the calculated chemical shifts for phenyl acetate and o-hydroxyacetophenone using published tables[83]. As a result of the work-up procedure used, the small amount of phenol which is produced in the degradative process is removed from the polymer, and is therefore not seen in the ^{13}C NMR spectrum of copolymer **98**.

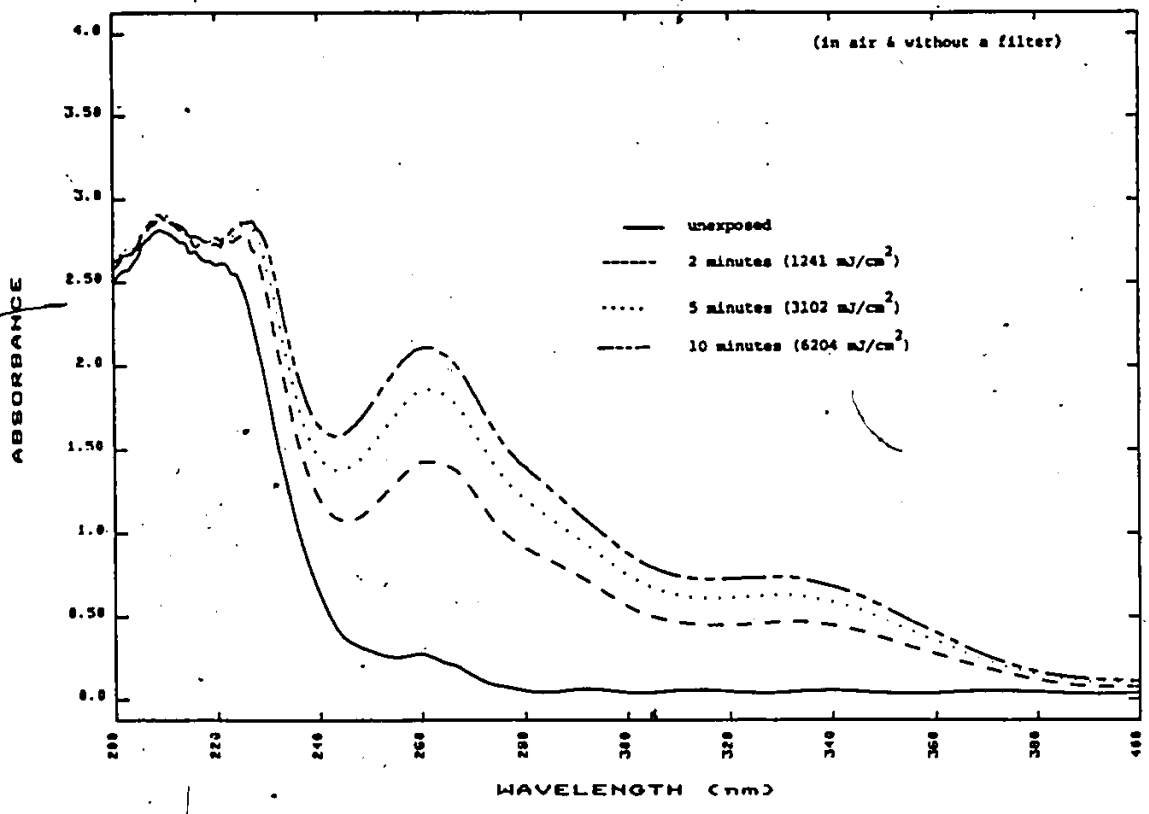
The photorearrangement of PPMA (**92b**) also occurs in the solid-state. UV irradiation of a 1.01 μm thick film of **92b** on NaCl substrate results in structural changes which can be monitored by IR spectroscopy. After a dose of 3.10 J/cm^2, 62% of the starting polymer units remain unchanged. The decrease in the rate of this reaction as the amount of photoproduct increases is shown in Figure 12.

Unlike the analogous photochemical study in solution, solid-state irradiation of **92b** gives the expected o-rearranged product **54b**, as well as a small amount of the p-product **55b** (Scheme 28). A weak carbonyl band at 1663 cm^{-1}, characteristic of **55b**, begins to emerge in the IR spectrum after a dose of approximately 1.29 J/cm^2 of unfiltered UV light. Similar results for the irradiation of 15-25 μm thick films of poly-(p-cresyl acrylate) (**53a**) have been reported in the literature[50,51]. In the case of thin-

film UV exposures, the low mobility of the polymer backbone radical and the phenoxyl radical in the solid polymer matrix favour recombination of the radical pair. Consequently, since the p-position is accessible through resonance and is not blocked, some p-product results, to give terpolymer **99**.

The photostabilizing effect of the photo-Fries rearrangement products observed in both solution (**98**) and solid-state (**99**) photoproducts is illustrated in Figure 10.

Figure 10: UV Spectral Changes Upon Irradiation of Films of **92b**



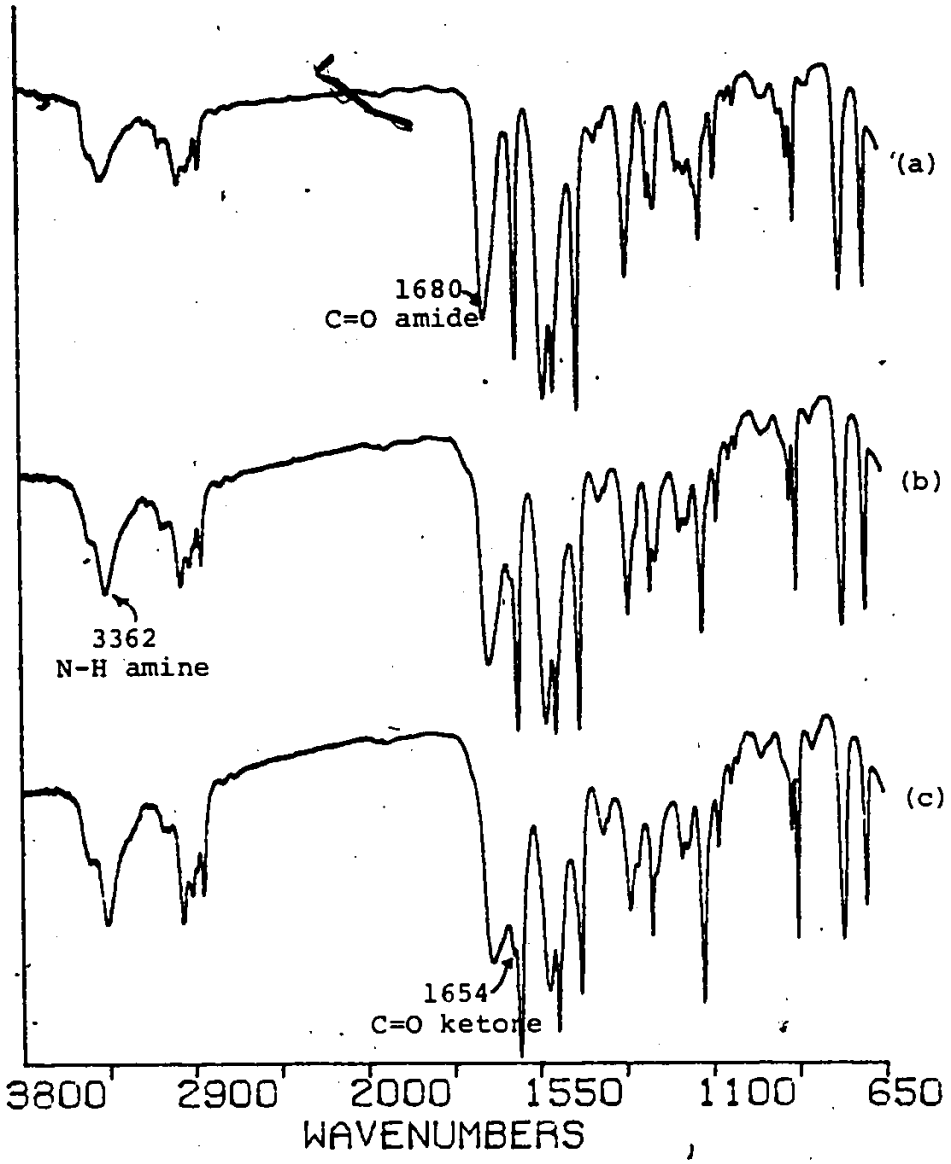
Before irradiation, the 1.10 μm thick PPMA **92b** film shows only slight absorption in the 254 nm region of the UV spectrum. Unfiltered irradiation of **92b** to doses ranging from 0 to 6.20 J/cm^2

gives terpolymer **99** showing new absorptions centered at 261 and 330 nm. As is the case in the photolysis of **75b**, the rearranged photoproducts absorb the incident light to an extent such that the photo-Fries reaction becomes almost totally inhibited. These results indicate that the photostabilizing effects observed by Li et al.[50], and Gilazhov et al.[51,52] for thicker poly-(aryl acrylate) films apply to 1 μm thick films as well. However, with thinner films, the effect of the photostabilizers is less restrictive as a larger proportion of the polymer bulk undergoes the photo-Fries reaction.

Photochemical studies of poly-(methacryl anilide) (**94**) dissolved in freshly distilled dioxane, show that the expected photorearrangement occurs as previously observed by Elad[27] and Chênevert and Plante[86] for acetanilide. The very slow rate of this photoreaction is illustrated by the IR study shown in Figure 11. The amide carbonyl band of polymer **94** located at 1679 cm^{-1} decreases very slowly in intensity for the first five hours of irradiation, with little subsequent change on further exposure. A weak shoulder on the amide C=O band, at 1654 cm^{-1} can be attributed to the rearranged products. Since both o- and p-aminoacetophenone show C=O absorptions[87] near 1650 cm^{-1}, assignment of the band to a particular photoproduct isomer could not be made.

The presence of a new N-H deformation band of medium intensity at 1615 cm^{-1} can be attributed to the o-rearranged photoproduct and/or aniline produced in the degradation reaction.

Figure 11: IR Changes During Solution Photolysis of Poly-(methacryl anilide) (94)



(a) unexposed; (b) 5 hours; (c) 55 hours

As expected, the 55 hour exposure time results in a considerable drop in the $\bar{M}_n$ value of the polymer, from 1.61×10^4 to 8.39×10^2, confirming the occurence of photo-Fries degradation with formation of aniline. The mechanism of this photodegradation is likely identical to that described for PPMA (92a) and PMMA[9].

The complex ^{13}C NMR spectrum obtained for the polymeric photoproduct **100** supports the presence of both the o- and p-aminophenyl ketone units in the polymer. As seen in the IR study, the bulk of the polymer remains unchanged after the prolonged period of irradiation. The weak aromatic peaks corresponding to the rearranged photoproducts can be assigned by comparison to the calculated chemical shifts for 2-aminoacetophenone and 4-aminoacetophenone using published tables[83]. The new carbonyl peaks expected between 190 and 210 ppm for the photoproducts are not detected.

Contrary to what had been observed for the photolysis of PPMA (92a), both the o- and p-rearranged products are obtained in this case. Similarly, irradiation of acetanilide has been reported to generate both o- and p-aminoacetophenone[86].

The photorearrangement of poly-(methacryl anilide) (**94**) also occurs in the solid-state but at a much slower initial rate than any of the polymeric esters tested. UV irradiation of 0.80 μm thick films of **94** results in only very subtle changes in the IR spectra. After a 2.50 J/cm^2 dose of unfiltered UV light only a very weak shoulder at 1654 cm^{-1} is seen in the IR spectrum, as well as a new weak N-H deformation band at 1615 cm^{-1}. Unirradiated 0.80 μm thick films of **92b** absorb very strongly in the UV,

with cut-off at 267 nm. Exposure of these films to doses ranging from 0 to 6.20 J/cm^2 gives rise to the emergence of a new absorption band centered at 309 nm, which is characteristic of the o- and/or p-rearranged products.

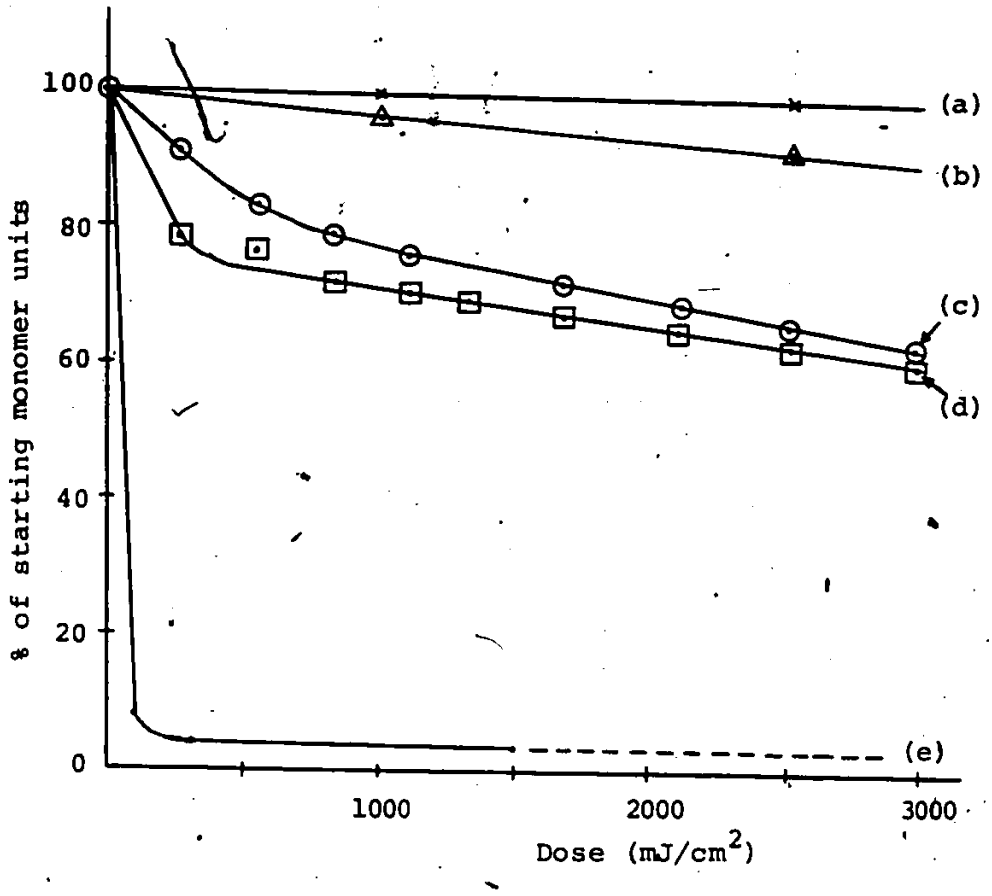
As is the case with polymeric amide **80**, poly-(methacryl anilide) (**94**) is much less sensitive to UV irradiation than the corresponding ester **92**. This lower sensitivity of aryl amides is in agreement with results reported for wholly aromatic polyamides[46]. Although the photo-Fries rearrangement of low molecular weight N-aryl amides has also been reported[88,89]; the low photochemical reactivity of analogous polymeric structures **80** and **92**, discouraged further work in this area.

(c) Comparison:

As shown in the previous sections, the types of polymeric photoproducts obtained in the photo-Fries reaction vary according to the nature of both the reactive pendant group, and the polymer backbone. Generally, when strongly UV absorbing o- and p-rearranged photoproducts are predominant, the reaction becomes inhibited as a result of photostabilization of the resulting polymer. Conversely, the degradation products show little UV absorption, and therefore have no inhibitory effect. The results observed for the various polymers tested are summarized graphically in Figure 12.

Quantitative FT-IR studies of the spectra accumulated for the solid-state film photochemical studies of the five polymers tested were carried out, to give the data shown in Figure 12.

Figure 12: Decrease in Starting Monomer Units in Photoflies Susceptible Polymers with UV Irradiation



(a) **80**; (b) **94**; (c) **92b**; (d) **75b**; (e) **89c**

The percentage of starting monomer units remaining in the polymer after a given dose is determined by comparing the integration of the ester or amide band(s) in the IR of the irradiated film with that for the unexposed film.

In the case of polymeric amides **80** and **94**, very little conversion to photoproducts is observed. This appears to result from the low sensitivity of aryl amides to UV irradiation. Al-

though the corresponding esters **75b** and **92b** show reasonable initial rates of conversion to photoproducts, the build-up of photostabilizing o-rearrangement products soon begins to inhibit the photo-Fries reaction. The formate ester **89c** shows a much faster rate of reaction than the other polymeric esters tested, with 93% conversion after a 100 mJ/cm^2 dose of unfiltered light. Almost exclusive conversion of the formate ester to weakly absorbing p-hydroxystyrene allows the photo-Fries degradation to proceed to near completion.

Since the photo-Fries reaction transforms a non-polar polymer (ester) into a very polar species (phenol), good image development was expected, as a result of their great differential solubility. The polar photoproducts should dissolve readily in polar solvents resulting in a positive image, whereas dissolution of the unexposed film in a non-polar solvent developer should result in a negative image.

The results shown in Figure 12 were used to predict the potential of these five polymers as photoresists. The higher photoconversion of the formate ester **89c** relative to the other polymers tested make it the most likely for use as a photoresist. The great difference in polymer polarity expected between the exposed and unexposed areas of a film of **89c** should facilitate image development. In the case of polymeric esters **75b** and **92b**, much greater doses are required to reach conversions of only 20-40%. As a result, the low conversions to phenolic units is expected to result in lower solubility differences between exposed and unexposed polymers with a concurrent decrease in image

quality. Of these two esters, **92b** is expected to have the greater differential solubility, since photo-Fries degradation results in a decrease in molecular weight of the polymer through main chain cleavage of the acrylic backbone. For the same reason, it might be possible to obtain an image from a film of poly-(methacryl anilide) **94** despite its low sensitivity.

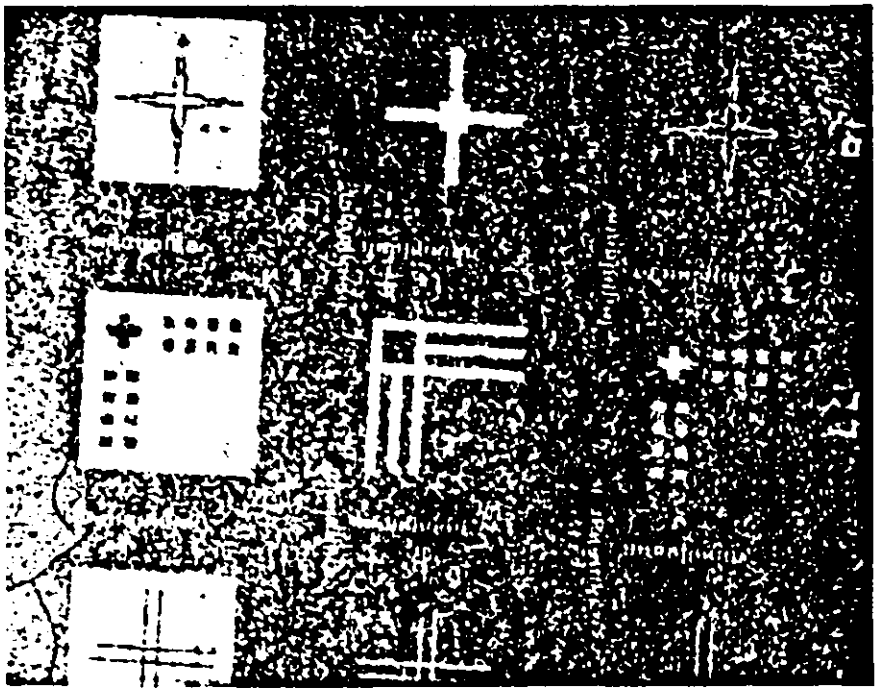
(d) Imaging Experiments:

The imaging experiments for all the photo-Fries susceptible polymers were carried out with unfiltered deep UV light, so as to duplicate the conditions used in the solid-state IR studies. It was impossible to pin-point the exact wavelength of light required to induce this photochemical reaction, however it appeared that transfer of energy was occuring, resulting in generation of the photoproducts.

One μm thick films of poly-(p-acetoxystyrene) (**75b**) were exposed through a contact "Wicked" mask to an unfiltered dose of 3.10 J/cm^2. Attempts at developing a negative image were made using a number of organic developers, but all failed as a result of the rapid decrease of the film thickness through dissolution of both exposed and unexposed areas. Dip development in a 1:1 3-heptanone/isopropanol mixture gives the fully developed positive image shown in Figure 13, having an unexposed film thickness of 0.48 μm. From these results, it is apparent that the polarity difference between polymers with 100% and 60% acetoxy pendant groups is inadequate to give a good quality image. For the same reason, commercial aqueous base developers MF-312 and AZ400K do not afford development, but cause extensive swelling and cracking

of the polymer film. Although an image was obtained, the low sensitivity and relative photostability of films of polymeric ester **75b** made it unsuitable as a photoresist.

Figure 13: Optical Micrograph of Resist Patterns in Poly-(p-acetoxystyrene)



x110

Dose: 3.10 J/cm^2; Developer: 1:1 3-heptanone/isopropanol

Films of poly-(p-formyloxystyrene) (**89c**) exposed to a 100 mJ/cm^2 dose of unfiltered UV light are readily developed in a 10:1:1 isopropanol/conc. ammonium hydroxide/water solution without any loss in the unexposed film thickness to give the fully developed positive images shown in the electromicrographs in Figure 14. The formate ester's near complete photo-Fries degradation to give highly polar poly-(p-hydroxystyrene) results in the great differential solubility responsible for the clean development of these patterns without loss of film thickness.

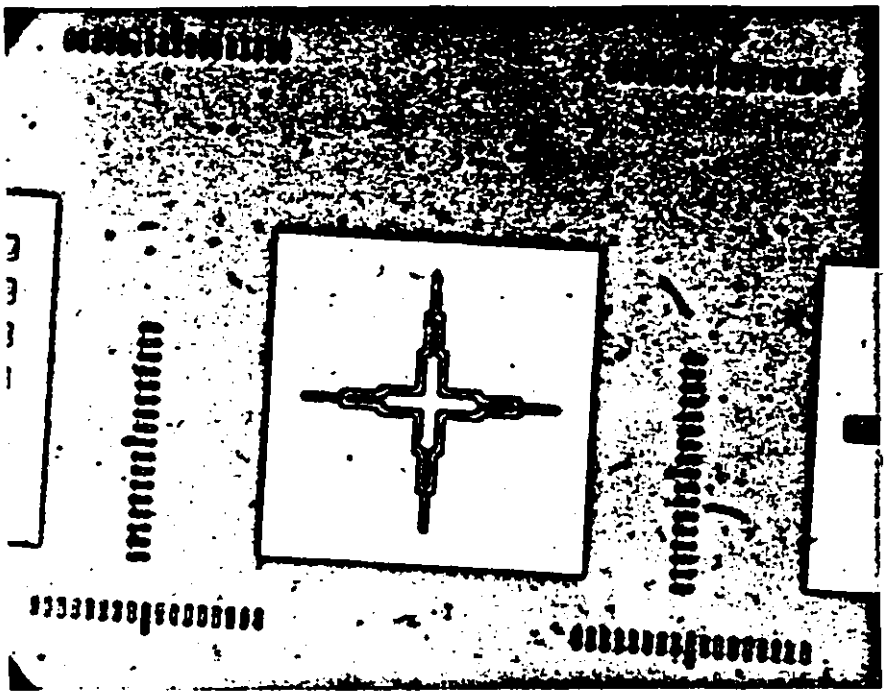
Figure 14: Electromicrographs of Resist Patterns in Poly-(p-formyloxystyrene)

Dose: 100 mJ/cm^2; Developer: 10:1:1 isopropanol/NH_4OH/water

Good quality negative images are also obtained when development of irradiated films of **89c** is carried out in methylene chloride or anisole-based developers. However, minor changes in developer composition result in swelling and poor resolution of images, as is very often the case with negative resists.

Films of poly-(phenyl methacrylate) (**92b**) were exposed in the same manner as that outlined for PACOST (**75b**) to doses of 3.10 and 7.76 J/cm^2. Attempts at developing a negative image in 4-methyl-2-pentanone, methyl ethyl ketone and n-propyl acetate resulted in complete loss of film thickness, without pattern development. Development in 3-heptanone however, gave fully developed positive images with a 30% loss in the unexposed film thickness for a 3.0 J/cm^2 exposure dose. Figure 15 shows an optical micrograph of the images obtained. The non-polar nature of the developing solvent suggests that the differential solubility in this case is predominantly the result of photo-Fries degradation and main chain cleavage. The selective dissolution of the lower molecular weight polymer chains in the unexposed areas would be expected to give the observed type of image development. The effect of chain scission overrides the photorearrangement effect, since the latter would tend to make the polymer more polar and would thereby favour dissolution in a more polar solvent. These subtle differences in solubility prevented image development in a number of commercially available aqueous developers.

Figure 15: Optical Micrograph of Resist Patterns in Poly-(phenyl methacrylate)



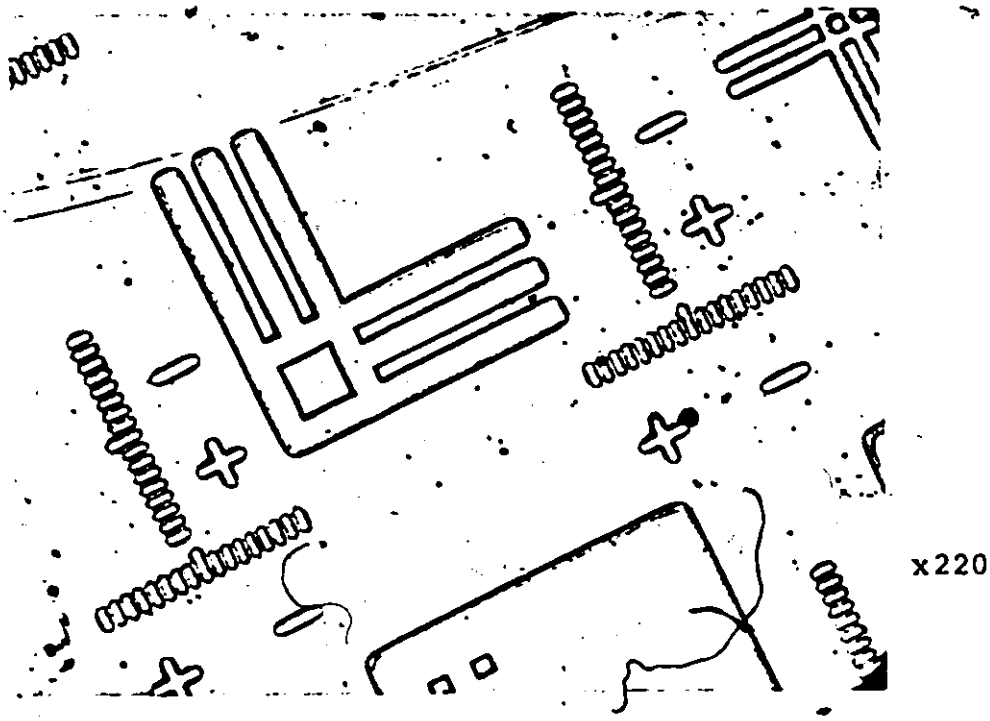
x220

Dose: 3.10 J/cm^2; Developer: 1:1 3-heptanone/isopropanol

As a result of the low UV sensitivity of the polymeric amides shown in Figure 12, films of poly-(methacryl anilide) (**94**) were exposed to doses of 6.27 and 12.55 J/cm^2. Attempts at developing a negative image using a number of organic developers were made. A 2:1 methylene chloride/chloroform mixture gives only partial development of a positive image for a dose of 12.55 J/cm^2 as shown in Figure 16. The lower dose exposure could not be developed in this same solvent system. Due to the small extent of photoconversion, the polarity of the polymer in the exposed and unexposed areas of the film is essentially identical. The partially developed image which is obtained with polymeric amide **94** is due to a molecular weight gradient, as seen with the

corresponding acrylic ester **92b**, resulting from photo-Fries induced main chain cleavage.

Figure 16: Optical Micrograph of Resist Patterns in Poly-(methacryl anilide)



Dose: 12.55 J/cm^2; Developer: 2:1 $CH_2Cl_2/CHCl_3$

The imaging experiments confirmed the predictions that were suggested from Figure 12. Of the polymers tested, the formate ester **89** shows the most potential for use as a photoresist. Although the sensitivity of this one-component photoresist is not higher than that of the classical Novolac-diazoquinone systems presently used commercially, **89** may nevertheless be adequate for some specialized applications. Of particular interest is the fact that it can be used in the mid and deep UV (<313 nm), where there is a great scarcity of useful materials. The recent development of high intensity excimer lasers could also enhance the usefulness of this photoresist.

o-Nitrobenzaldehyde Rearrangement

Preparation of the Polymers:

Two general methods were used to prepare polymers such as **69** having pendant o-nitrobenzaldehyde groups. The first approach involved synthesis of the monomer followed by polymerization, while the second involved chemical modification of an existing polymer. For both pathways, commercially available 5-hydroxy-2-nitrobenzaldehyde (**101**) was used, since the phenolic group was expected to be readily introduced into the molecule by either nucleophilic displacement or by addition. The various reaction conditions employed were optimized using less costly phenol and p-nitrophenol.

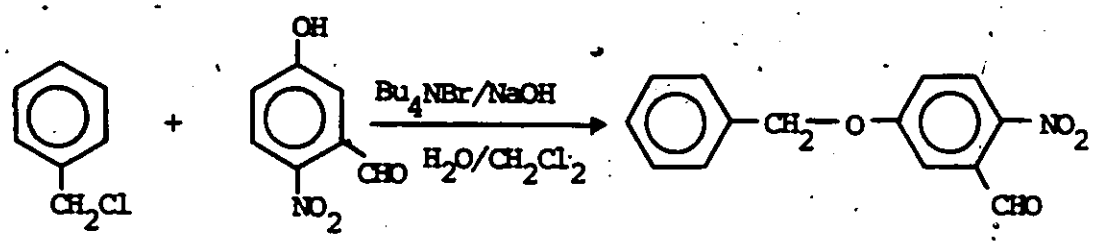
(a) Reactive Pendant Groups on Styrene Backbones:

Efforts at introducing the pendant group onto a styrene backbone were concentrated on chloride displacement from vinyl benzyl chloride (VBC) in both monomer and polymer. The commercially obtained VBC (Dow Chemicals Ltd.) used in this work consisted of a 60:40 mixture of the m- and p-isomers. Due to the high tendency of VBC to polymerize, low molecular weight model compounds were also prepared from benzyl chloride (**102**) to aid in the optimization of reaction conditions and in the characterization of the final polymers.

M^{c}Killop et al.[90] and D'Incan[91] have reported a general procedure for the synthesis of alkyl aryl ethers involving phase transfer catalysis. This method was used in the formation of 2-nitro-5-benzyloxybenzaldehyde (**104**) as shown in Scheme 29, by reaction of benzyl chloride (**102**) with 5-hydroxy-2-nitrobenzalde-

hyde (**101**) using Bu_4NBr and aqueous NaOH.

Scheme 29



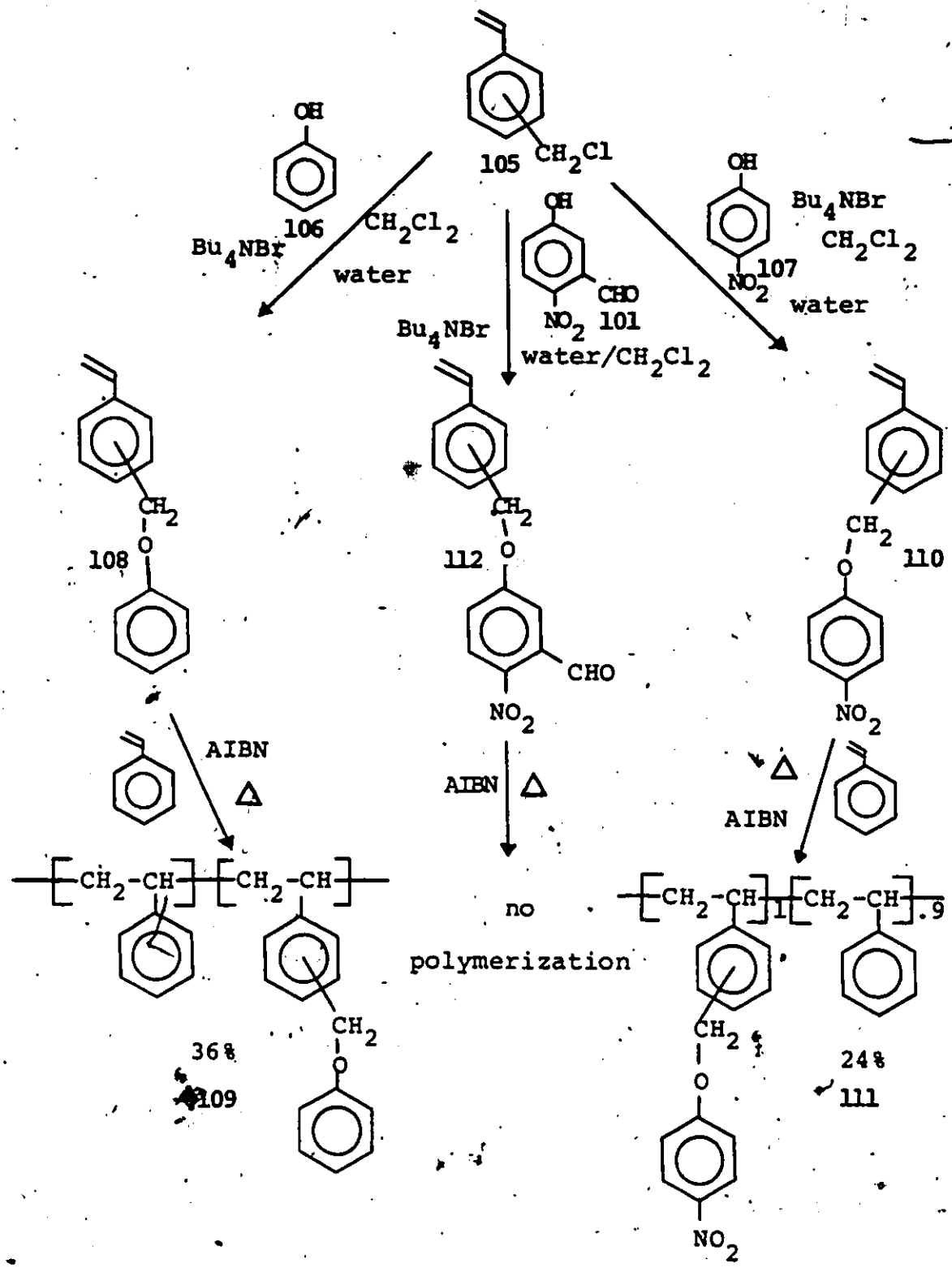
102 **101** **104**

This reaction proceeds satisfactorily despite the inhibitory effects of the electron withdrawing $-NO_2$ and -CHO groups on the phenolate displacement of chloride. **104** is also obtained in comparable yield without the use of a phase transfer catalyst by reacting **102** and **101** with NaOH in refluxing ethanol[93]. Although both methods are equivalent, the milder phase transfer route is preferred for the modification of the VBC isomeric mixture **105** in order to minimize unwanted polymerization in this step.

Using this same general procedure[90,91], **105** was reacted with phenol (**106**), p-nitrophenol (**107**) and **101** to give the corresponding benzyl phenyl ethers (**108**, **110**, **112**) in good yield as shown in Scheme 30. Copolymerization of these monomers with styrene was attempted with varying degrees of success. In all cases, the presence of phenolic benzyl ether groups is deleterious to the polymerizations, suggesting that chain transfer processes are prevalent and cause the destruction of the initiating radicals.

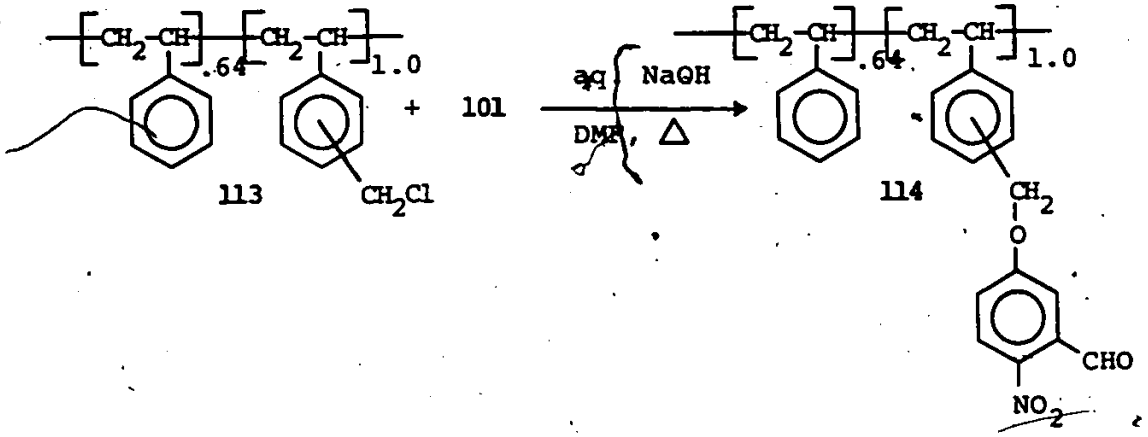
Greater success was achieved by chemical modification of a styrene VBC copolymer **113**. Reaction of copolymer **113** with **101** in DMF and aqueous sodium hydroxide for 24 hours at 60°C in the dark (see Scheme 31) gives the corresponding copoly-(styrene 2-nitro-

Scheme 30


OH
106
Bu4NBr
CH2Cl2
water
105 CH2Cl
OH
CHO
NO2 101
Bu4NBr
water/CH2Cl2
OH
Bu4NBr
CH2Cl2
NO2 107
water
CH2
O
108
112
110
CHO
NO2
AIBN
Δ
CH2-CH
CH2
36%
109
no
polymerization
.1
.9
24%
111

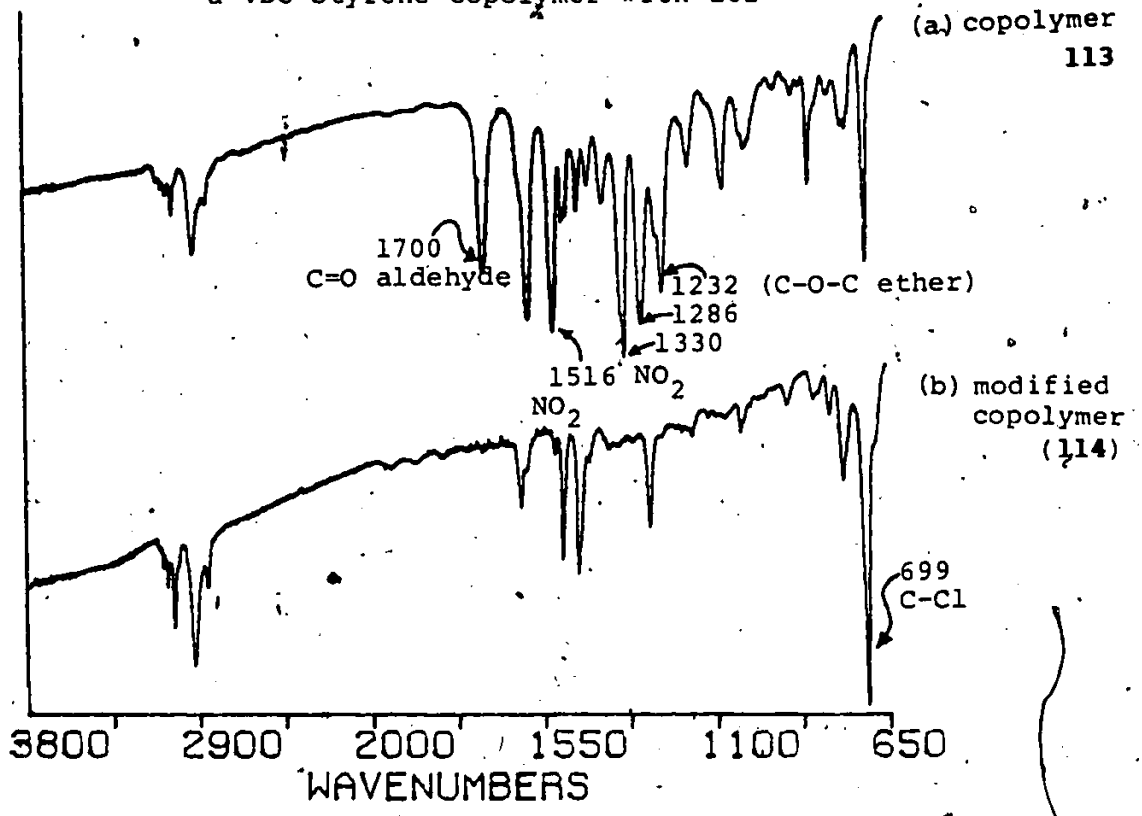
5-(m & p-vinylbenzyloxy)benzaldehyde)) (114) with no remaining chloride.

Scheme 31



The changes in the IR spectrum of the chemically modified polymer are shown in Figure 17.

Figure 17: IR Spectral Changes for the Chemical Modification of a VBC-Styrene Copolymer with 101



Attempted reactions at room temperature in the presence of a phase transfer catalyst such as Adogen 464 were unsuccessful.

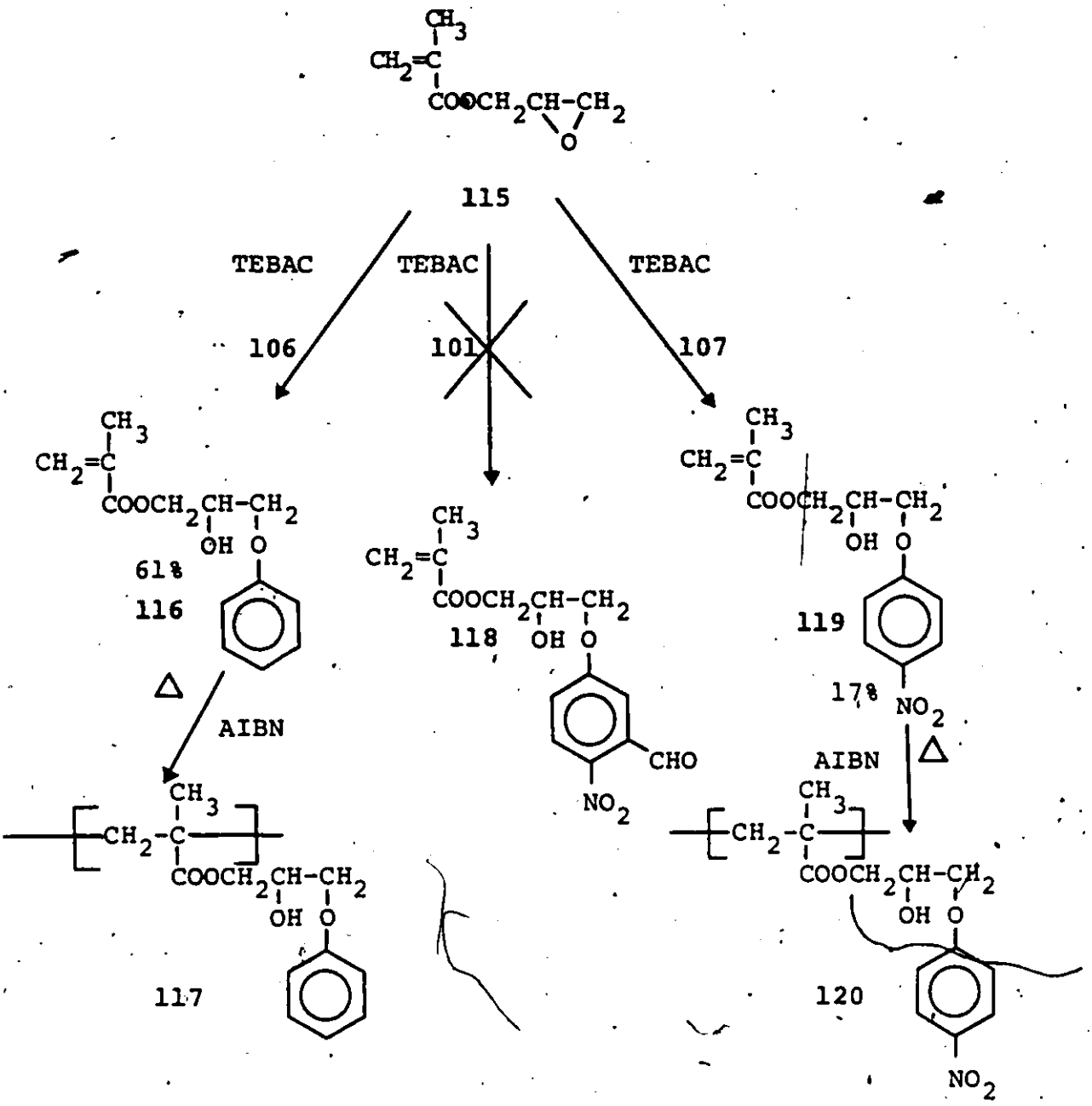
(b) Reactive Pendant Groups on Acrylic Backbones:

Two basic approaches were proposed for the introduction of o-NBA pendant groups into an acrylic backbone. The first involved addition of the phenolate of **101** to the epoxide rings of a monomer or polymer of glycidyl methacrylate. The other proposed method involved nucleophilic displacement of a labile leaving group.

Masuhara et al.[94] have reported the epoxide ring opening of glycidyl methacrylate (**115**) by phenolate addition in the presence of triethylbenzyl ammonium chloride (TEBAC) at 85°C to give 2-hydroxy-3-phenoxypropyl methacrylate (**116**). Monomer **115** was reacted with phenol (**106**), p-nitrophenol (**107**) and **101** under these same reaction conditions, as shown in Scheme 32, with varying degrees of success. In the case of phenol addition, a reasonable yield of monomer **116** was obtained (61%). However, the addition of the substituted phenols **107** and **101** to glycidyl methacrylate was much less efficient (17% and 0%), with an uncharacterized polymeric mass being the major product. In the case of the addition of **101** to monomer **115**, complete conversion to polymer occured, with no remaining starting material or expected product **118** visible by TLC. Reducing the reaction temperature to 70 or 50°C did not lower the amounts of polymeric products obtained.

This difference in the proportions of products obtained can be attributed primarily to the relative nucleophilicity of the

Scheme 32


CH3
CH2=C
COOCH2CH-CH2
O
115
TEBAC
TEBAC
TEBAC
106
101
107
OH O
61%
116
118
119
17%
NO2
CHO
AIBN
AIBN
117
120

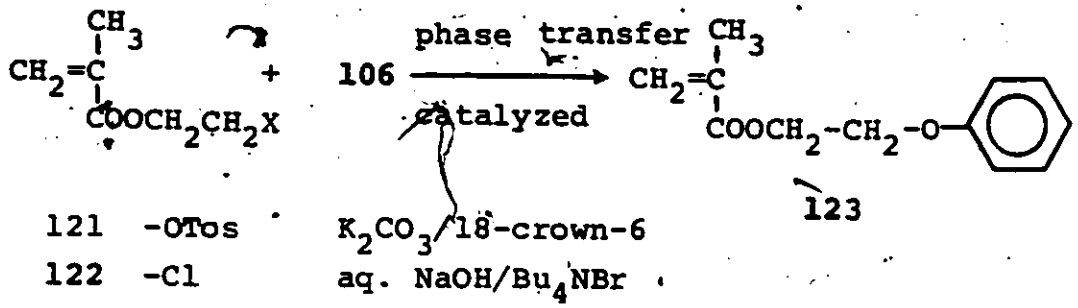
phenols. Since the phenolate of **106** is the strongest nucleophile of the three, its addition to the epoxide ring would be expected to be the most facile. The presence of the electron-withdrawing $-NO_2$ and -CHO substituents on the aromatic ring of the phenolates of **101** and **107** results in a reduced nucleophilicity, thereby slowing the rate of the reaction. In turn, the prolonged reaction times required for these phenolates to react with the epoxide allow for a more effective competition of the side reaction which results in the observed polymerization. The difficulty in reacting **101** with **115** is compounded by the possibility of o-nitrobenzaldehyde copolymerization in a basic medium[95].

Attempts at the modification of copoly-(glycidyl methacrylate-methyl methacrylate) (molar ratio 1.0:1.6) were made with little success using the following reaction conditions: NaH/THF; $(CH_3)_3COK$/THF; aq. NaOH/TEBAC; and pyridine/DMF.

The second method proposed for the introduction of o-NBA pendant groups into an acrylic backbone was by nucleophilic displacement of a halide or tosylate. 2-Tosyl ethyl methacrylate (**121**) was prepared by the classical procedure, as outlined by Pailer et al.[96]. 2-Chloroethyl methacrylate (**122**) was prepared in good yield by the esterification of methacrylic acid with 2-chloroethanol by the method of Askarov et al.[97]

Using the procedure of M^{c}Killop et al.[90], halide **122** was reacted with phenol under phase transfer conditions to give 2-phenoxyethyl methacrylate (**123**) in 56% yield. Tosylate **121** and phenol were reacted with anhydrous K_2CO_3/18-crown-6 in DMF to give **123** in comparable yield (see Scheme 33).

Scheme 33



Carrying out the tosylate displacement in the absence of phase transfer catalyst afforded only 11% of **123** after two days of reaction time at room temperature. Due to the disappointing photochemical results obtained for copolymer **114**, the synthesis of polymers containing the o-NBA pendant group was discontinued.

Photochemical Studies and Imaging Experiments:

Due to its high quantum efficiency of 0.5, the o-nitrobenzaldehyde photorearrangement was believed to be of potential use for a photoimaging system. Tomika et al.[98] have reported the use of o-NBA as a photoactive acid-producing compound, in a polyamide negative photoresist system. In our case, the photorearrangement was expected to introduce very polar nitrosocarboxylic acid pendant groups onto the polymer chain. In turn, this difference in polarity between the exposed and unexposed areas of the film was expected to allow for the formation of either a positive or a negative image upon development in a suitable solvent system.

Since copolymer **114** is only soluble in solvents such as DMF and DMSO, which absorb strongly in the deep UV, solution photochemical studies could not be performed. Films were cast onto NaCl and quartz wafers from DMF solution, allowing the solid-state film study of copolymer **114**. UV irradiation of a quartz

wafer results in a bathochromic shift in the C=O absorption from 324 to 342 nm. This shift corresponds to the conversion of the CHO to COOH groups. This observation is also made upon irradiation of the low molecular weight analog **104** in methanol.

UV irradiation of films of copolymer **114** results in the IR changes shown in Figure 18. The film was exposed to a total dose of 2.16 J/cm^2 (unfiltered light) with IR spectra recorded at regular intervals. After exposure to 166 mJ/cm^2, a new carboxylic acid C=O band is observed along with the other bands expected for the 2-nitroso-(5-(m & p)-vinylbenzyloxy)benzoic acid (**124**). Further irradiation, is accompanied by the appearance of a strong band at 1574 cm^{-1} which is due to the formation of the diazo-bridged cross-linked product (**125**) (see Scheme 34). A small amount of unreacted **114** polymer units remains even after the maximum applied dose.

Scheme 34

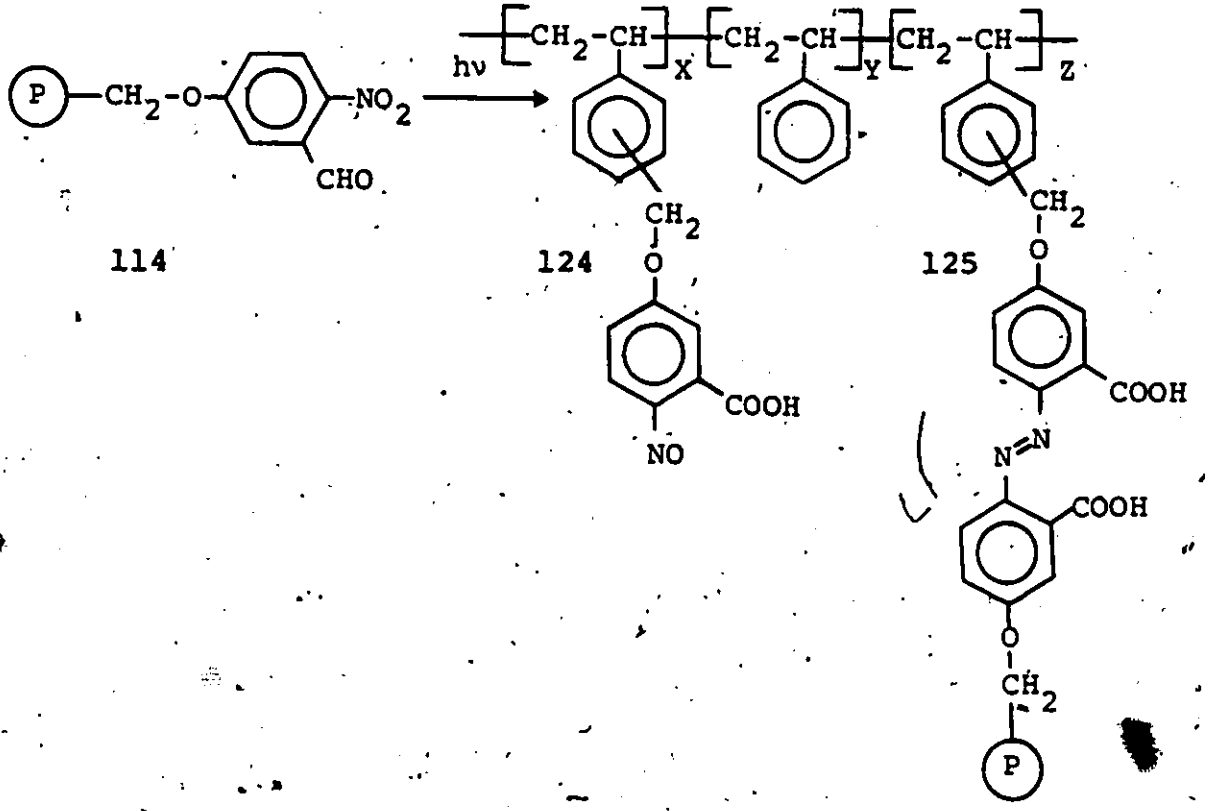
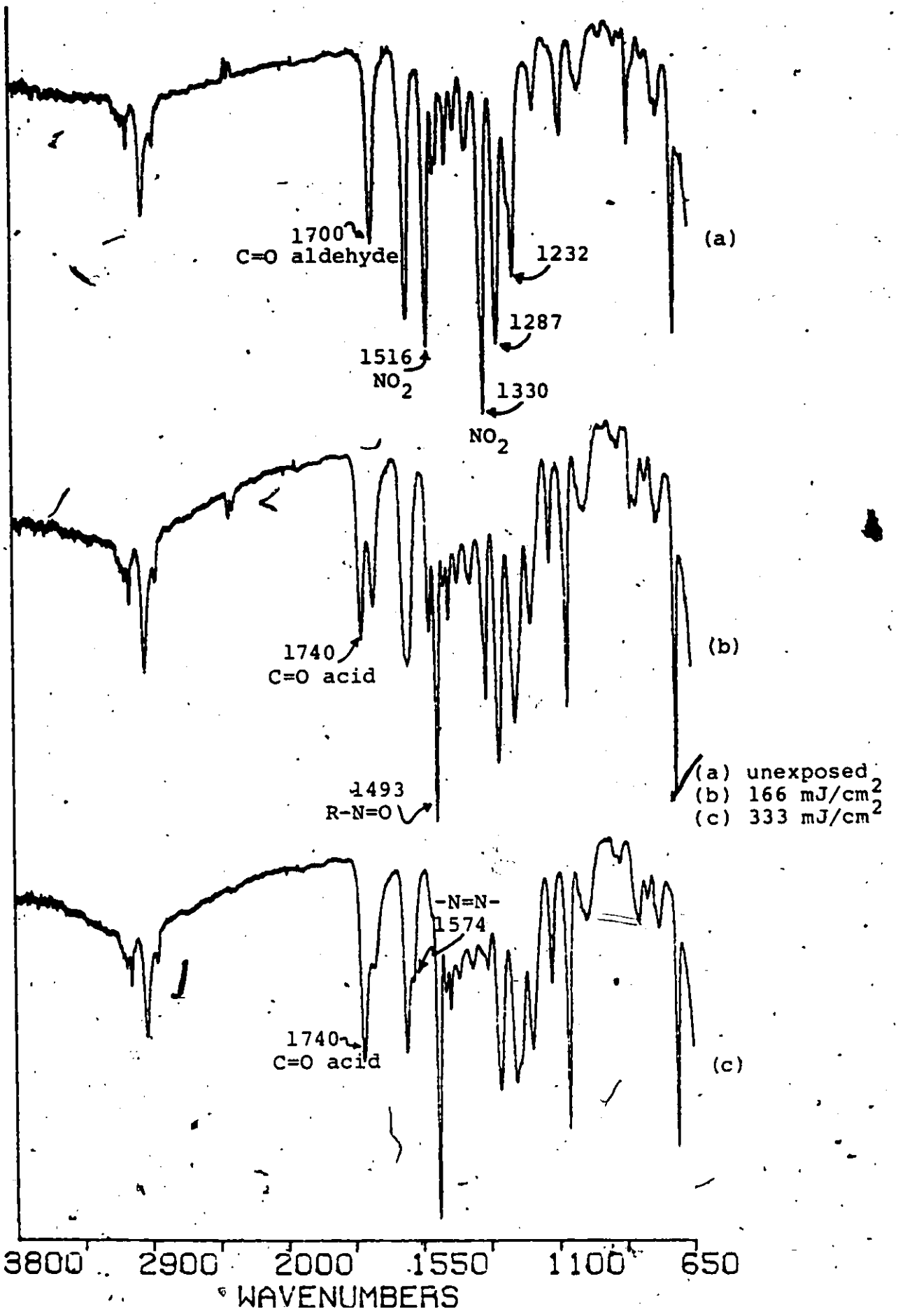


Figure 18: IR Spectral Changes Upon UV Irradiation of an o-NBA Pendant Group Containing Polymer Film (114).



It was anticipated that the occurence of the cross-linking side-reaction to give 125 might hamper the use of this polymer class as a positive photoresist system. Although Barzynski and Saenger[70] have also observed a similar photoinitiated diazo-coupling side reaction upon UV irradiation of their o-nitrobenzylacrylate polymer (67) (see Scheme 16), the initial detachment of the pendant group from the polymer backbone to give o-nitrosobenzaldehyde (66) eliminated the possibility of polymer chain cross-linking in the secondary process. Consequently, positive image development was possible from films of polymer 67[70].

Preliminary lithographic tests carried out under yellow light, involved casting films of copolymer 114 onto silicon wafers, prebaking for 0, 5 and 10 minutes at 100°C and studying the dissolution rate of these films in the casting solvent. In all cases, after 5 minutes in this solution, approximately 50% of the initial film thickness remained. This observation suggested that some cross-linking could be occurring even prior to "exposure" resulting in a reduced solubility in the casting solvent. Imaging experiments were attempted, using relatively low doses of 166 and 333 mJ/cm^2 of unfiltered light to minimize the diazo-coupling reaction. Poor quality incompletely developed negative images were observed upon development in a 2:1 n-butyl acetate/CH_2Cl_2 developer. Attempts at developing positive images using either a 5% aqueous NaOH solution or a 5% ethanolic NaOH solution gave no image development. From these results, it is apparent that the cross-linking side reaction to give units of 125 proceeds even at low dosage to give high molecular weight

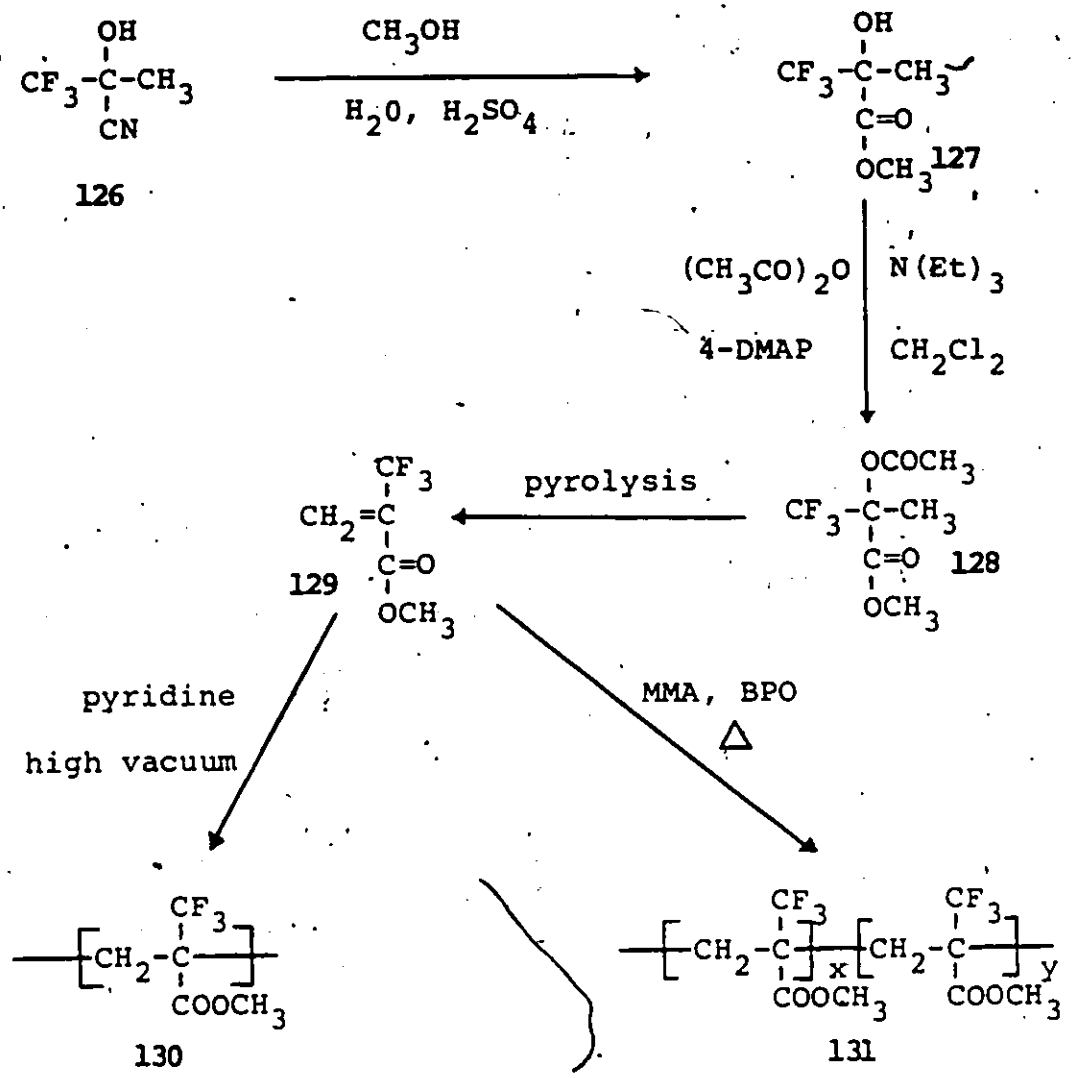
polymer networks, that override the systems differential polarity, thereby preventing the development of a positive image. Consequently, the only potential that the o-nitrobenzaldehyde pendant group polymer system may have is as a negative photoresist. Since the inherent problems with this system lie exclusively in the pendant group, the synthesis and testing of this class of polymers were discontinued.

E-Beam Degradable Methyl Methacrylate Analogs

Preparation of the Polymers:

Methyl α-(trifluoromethylacrylate) monomer (MTFMA) (129) was prepared by a modification of the method of Buxton et al.[99], as outlined by Ito et al.[17] (Scheme 35).

Scheme 35



Direct methanolysis of 1,1,1-trifluoroacetone cyanohydrin (126) gives methyl α-hydroxy-α-(trifluoromethyl) propionate (127) in good yield. Treatment of 127 with acetic anhydride, triethyl amine and 4-(dimethylamino)-pyridine in methylene chloride gives

methyl α-acetoxy-α-(trifluoromethyl) propionate (128), which upon pyrolysis afforded the MTFMA monomer 129. Anionic homopolymerization of monomer 129 under vacuum with pyridine as solvent/catalyst gave reasonable yields of poly-(methyl α-trifluoromethylacrylate) (PMTFMA) (130)[17]. Free-radical polymerization of monomer 129 with methyl methacrylate using benzoyl peroxide as initiator affords copoly-(methyl α-trifluoromethylacrylate methyl methacrylate) (P(MTFMA-MMA)) (131a)[17].

The classical copolymerization study on MMA and MTFMA reported by Ito et al.[17] shows that at very high MTFMA feed content, a copolymer with essentially 1:1 alternation can be produced, and that copolymers with greater than 50% MTFMA cannot be obtained by this procedure. The lack of polymerizability of MTFMA under radical initiation is explained in terms of the low reactivity of the monomer with a PMTFMA growing chain radical. However, as mentionned above, anionic polymerization of the monomer gives the desired homopolymer 130.

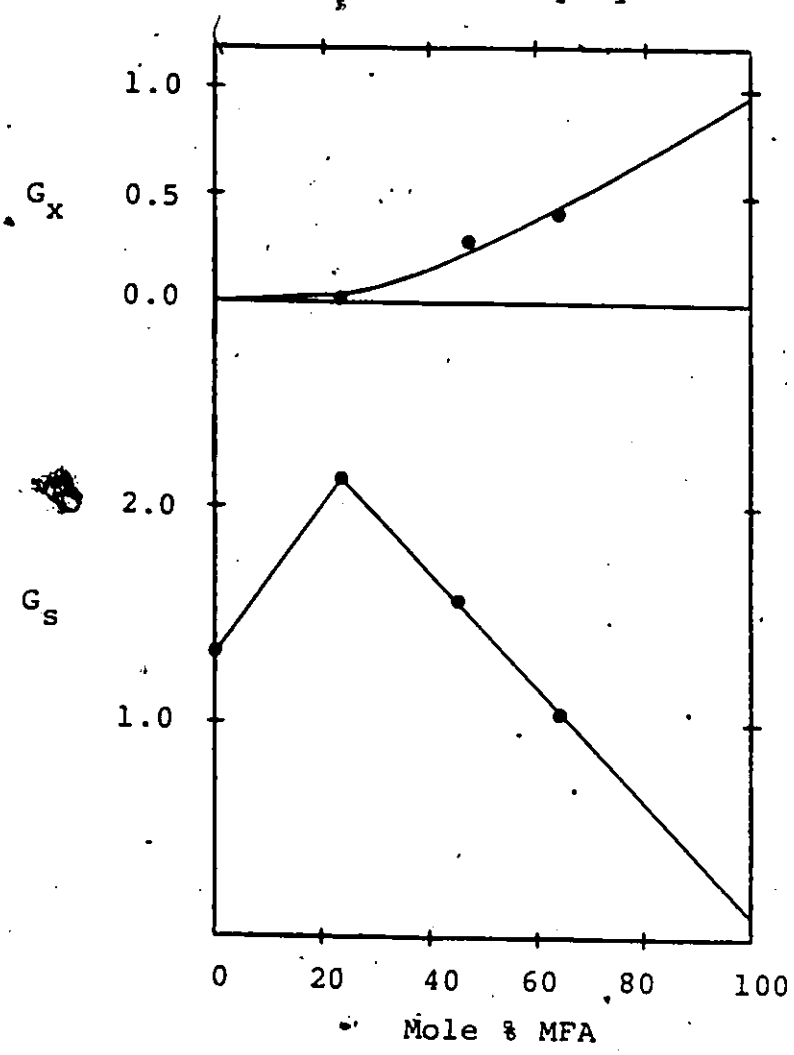
G-Value Study:

The effect of α-substituents on the scission efficiency of polyacrylates has been studied extensively by Pittman, Helbert and coworkers[12-16]. A review of their work leads to the conclusion that strongly inductive electron withdrawing α-substituted polyacrylates show increased scission efficiency (Gs) relative to poly-(methyl methacrylate) (PMMA). Unfortunately, in all the homopolymer analogs reported to date, an increase in the cross-linking efficiency (Gx) accompanies the increase in Gs. In some cases, the overall effect of this substitution has been to gene-

rate a negative resist[14,15].

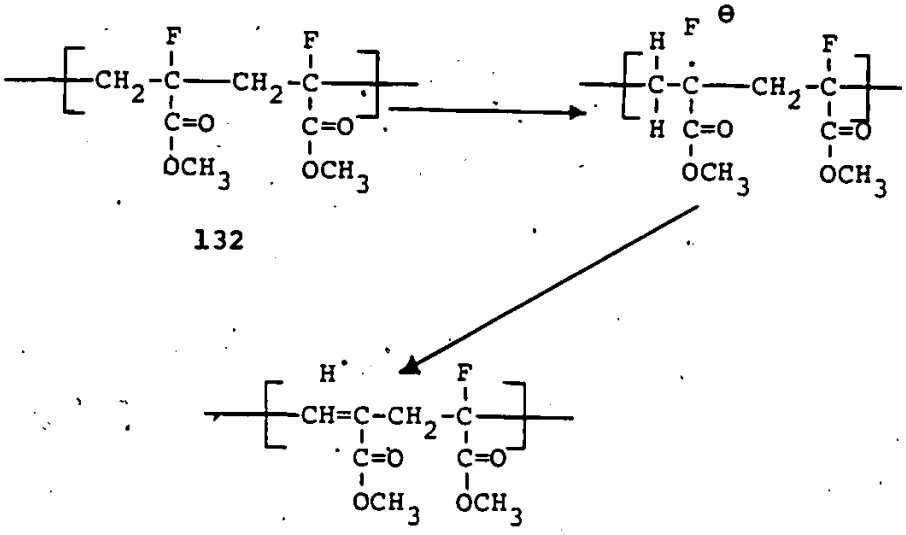
The generally accepted pathway proposed by Hiraoka[9] for the main chain degradation of PMMA under high energy exposure involves the generation of a tertiary radical on the polymer main chain followed by β-scission (Scheme 3). The presence of an electron withdrawing substituent in the α-position would serve to stabilize the initial backbone radical, as well as the tertiary radical which is generated upon chain cleavage. The expected enhanced stabilities of these radicals would explain the increase in Gs observed.

Figure 19: Gs and Gx versus Mole % of MFA in MFA/MMA Copolymers



The most thoroughly studied PMMA analogs with inductively withdrawing α-substituents are the poly-(alkylhaloacrylates). Pittman et al.[100] have shown that the α-fluoro substituent in 132 has an especially dramatic effect on both Gs and Gx. This is illustrated by a plot of Gs and Gx as a function of the mole fraction of the α-fluoro monomer in MMA copolymers (Figure 19). At low incorporation the Gs value increases drastically with little or no competing increase in Gx value. As the molar ratio of the α-fluoro monomer approaches one, Gx increases rapidly as Gs decreases, resulting in the predominance of crosslinking at moderate doses. This crosslinking tendency is probably brought about as a result of dissociative electron capture with the elimination of HF, leading to unsaturation in the polymer backbone as shown in Scheme 36.

Scheme 36



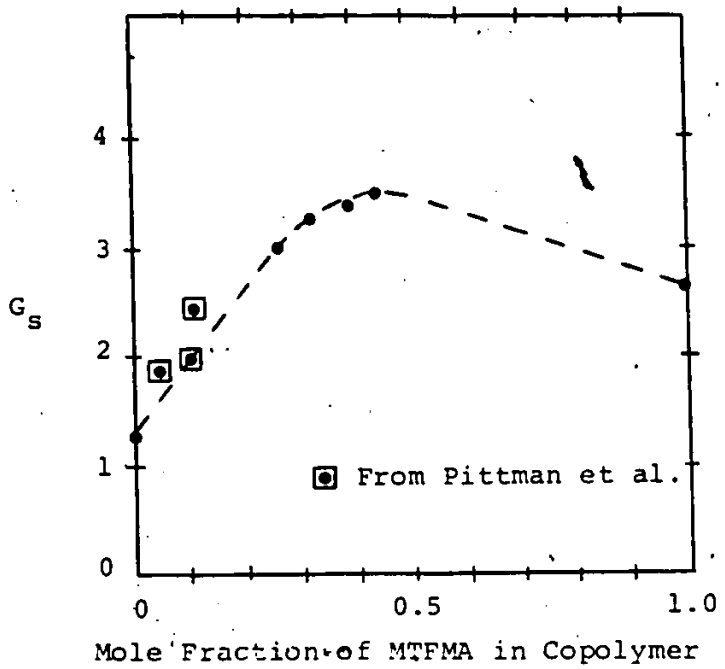
132

The resulting unsaturation in the polymer backbone can lead to the enhanced Gx observed by Pittman et al.[100] for homopolymer

130. The strongly electron withdrawing α-trifluoromethyl substituent of monomer **129** in polymers **130** and **131** was expected to increase Gs to a value greater than that of PMMA with Gx=0, since there are no hydrogens β to the fluorine substituents capable of participating in the elimination reaction.

Samples of PMTFMA and copolymers of MTFMA and MMA were subjected to ^{60}Co γ-radiolysis with monitoring of their molecular weights. From this data, Gs and Gx values were established as a function of polymer composition using standard analytical methods[102], and are shown in Figure 20 along with copolymer results reported by Pittman et al.[13]

Figure 20: Gs versus Mole % MTFMA in MTFMA/MMA Copolymers



The data indicates that Gs for homopolymer **130** is greater than Gs for PMMA, and that Gx cannot be measured. The absence of a Gx component for homopolymer **130** supports the suggested HF elimination crosslinking pathway which was proposed for homopolymer **132**. Since some copolymers of MMA and MTFMA have higher Gs values than either of the two homopolymers (see Figure 20), it was proposed that an MMA-MTFMA dyad may be more radiolabile than either an MMA-MMA or MTFMA-MTFMA dyad[101]. Further efforts to justify these observations were not undertaken.

Imaging Experiments:

The fact that the Gs values of homopolymer **130** and copolymer **131** are higher than that of PMMA suggests that for samples of these polymers having comparable molecular weight and dispersity, a developer solvent system allowing imaging of polymers **130** and **131** at lower e-beam doses than PMMA could be found. Although the developer search was not exhaustive, high resolution images for both homopolymer **130** and MMA copolymer **131** were obtained. Figure 21 shows scanning electron micrographs of images in PMTFMA produced in 1 μm thick films at 10, 15 and 20 $\mu C/cm^2$ at 20 KeV. Similarly, Figure 22 shows scanning electron micrographs of images in 0.38/0.62 P(MTFMA-MMA) copolymer films at 20 $\mu C/cm^2$ at 20 KeV. These images were obtained at doses well below the 50-100 $\mu C/cm^2$ working dose required for standard PMMA[1].

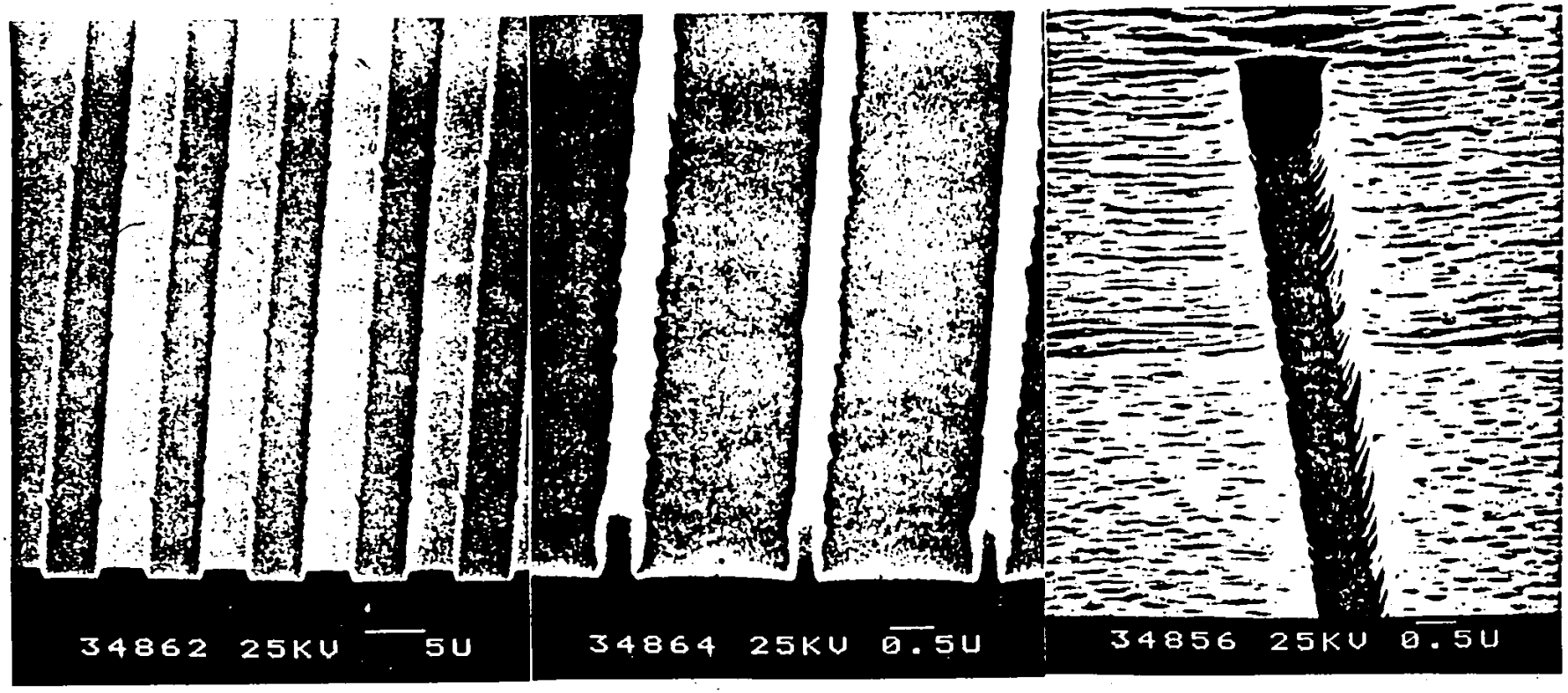


Figure 21: Resist Patterns in PMTFMA (a) 10 $\mu C/cm^2$; (b) 15 $\mu C/cm^2$; (c) 20 $\mu C/cm^2$

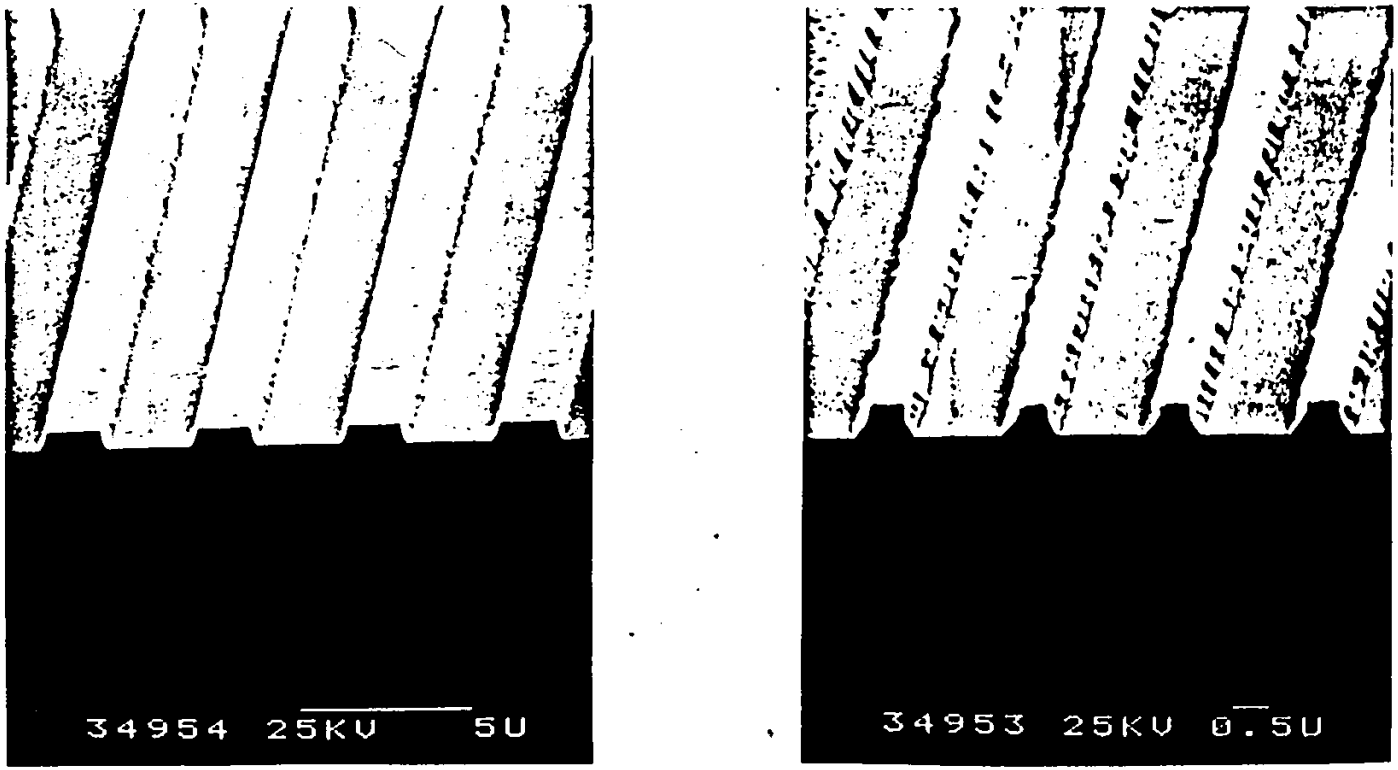


Figure 22: Resist Patterns in P(MTFMA-MMA) (Dose: 20 $\mu C/cm^2$)

EXPERIMENTAL

General Procedures:

The FT-IR studies were carried out using a Nicolet MX-1 spectrometer. Quantitative FT-IR studies were carried out using the quantitative software package supplied with the MX-1. The ^{1}H NMR spectra were taken on a Varian model EM360A spectrometer. UV spectra were run on a Hewlett-Packard UV-visible spectrophotometer. Molecular weight determinations were performed on a Waters Model 150 Gel Permeation Chromatograph equipped with 6 microstyragel columns using THF as the mobile phase and on a Wescan Model 231 recording membrane osmometer with toluene as solvent. Solution photochemistry was carried out in a 500 mL Hanovia reactor equipped with a water-cooled quartz insert, and an unfiltered 500 watt mercury arc source. Polymer solutions of the various samples dissolved in appropriate high boiling solvents were filtered through a 0.2 μm Millipore filter under yellow light. Polymer films were cast onto NaCl, quartz disks and silicon wafers, using a Headway Research Inc. spin-coater with 1" diameter chuck. Deep UV imaging experiments were carried out on silicon wafers using contact exposure through a quartz "Wicked" mask. Film thickness measurements were carried out using a Talystep Profilometer. Solid state irradiations were carried out using an Optical Associates Inc. (O.A.I.) deep UV source. The flux was measured using an O.A.I. model 354 exposure monitor and accompanying 254 nm probe. ^{60}Co γ-radiolyses of samples were performed at the National Bureau of Standards, Washington, DC. Electron beam irradia-

tions were carried out at the IBM San Jose Research Laboratory. Images were viewed and photographed using a Zeiss light microscope with polaroid photoattachment, and/or an electron microscope.

Photo-Fries Rearrangement

Preparation of p-Acetoxystyrene (74):

This compound was prepared by a modification of the procedure of Corson et al.[71]. To a stirred solution of 56.77 g p-hydroxyacetophenone (71) in 490 mL of 7.5% aqueous NaOH cooled in an ice bath was added 77.89 g acetic anhydride during 25 minutes. A white suspension formed as the mixture was stirred at 5 - 10°C for one hour. The suspension was filtered, washed with water and dried in the vacuum oven overnight. Recrystallization from ethyl acetate yielded 52.50 g of the desired intermediate, p-acetoxyacetophenone (72). To 250 mL of methanol was added the 52.50 g of 72 and 3.00 g of Pd-carbon catalyst. Hydrogenation under 380 psi of hydrogen resulted in the formation of a single product, as seen by TLC using an 8:2 hexane/ethyl acetate mixture as eluting solvent. The catalyst was removed by filtration through celite and washed with methanol. Evaporation of the combined filtrate fractions gave crude p-acetoxyphenylmethylcarbinol (73) which was added to 0.44 g t-butyl catechol and 0.44 g fused $KHSO_4$ in a distillation apparatus. The mixture was heated slowly to 190°C under a 20 mm Hg vacuum causing distillation of a colorless liquid. The distillate was diluted in ether, and the mixture extracted once with a 5% aqueous $NaCO_3$ solution and once with a saturated $CaCl_2$ solution. The ethereal solution was dried over

anhydrous $CaCl_2$, and the solvent evaporated. Fractional distillation of the crude residue gave 31.02 g (46%) of p-acetoxystyrene (74) (b.p. 69-72°C/0.5 mm Hg, lit. 73-75°C/0.6 mm Hg[71]).

FT-IR (NaCl, neat): 1765 cm^{-1} (vs, C=O ester); 1631 cm^{-1} (m, C=C vinylic); 1212, 1195 & 1014 cm^{-1} (s, C-O ester).

^1H NMR ($CDCl_3$): 2.13δ (3H, s, $-CH_3$), 6.96δ (2H, d, aromatic, J=8.5 Hz), 7.34 δ (2H, d, aromatic, J=8.5 Hz), AMX pattern for vinyl protons with δ_A=5.15, δ_M=5.59, δ_X=6.51 with J_{AM}=1.2 Hz, J_{AX}=11.0 Hz & J_{MX}=17.0 Hz.

M. S.: m/e 162 (M^+), 120 (base peak, C_8H_7OH), 43 (CH_3CO^+), 27 ($CH_2=CH^+$).

Polymerization of 74:

(a) Solution Polymerization:

9.95 g of monomer 74 and 0.0997 g AIBN were added to 60 mL of toluene in a 100 mL 2-necked round-bottomed flask equipped with a water-cooled condenser, nitrogen inlet and outlet. The mixture was heated to 70-75°C under nitrogen for 24 hours. Precipitation of the polymeric solution in methanol and subsequent filtering and washing with additional methanol gave a white powder. Drying in the vacuum oven overnight at room temperature, afforded 5.46 g (55%) of poly-(p-acetoxystyrene) (PACOST) (75). [(75a: M_n=1.17 x 10^4, M_w=2.06 x 10^4, polydispersity=1.76 (gpc); M_n=1.85 x 10^4 (osm)); (75b: M_n=6.30 x 10^3, M_w=1.38 x 10^4, PD=2.17 (gpc); M_n(osmometry)=1.19 x 10^4)]. (spectral data listed below)

(b) Bulk Polymerization:

To 7.45 g of monomer 74 in a 50 mL round-bottomed flask equipped with water-cooled condenser, nitrogen inlet and outlet

was added 0.0691 g (1%) azobisisobutyronitrile (AIBN). The mixture was heated at 75°C for 24 hours under a constant flow of nitrogen. The solid polymeric mass was dissolved in CH_2Cl_2 and precipitated in methanol. The polymer was filtered, washed with methanol and dried in a vacuum oven overnight at room temperature. 5.80 g of poly-(p-acetoxystyrene) (PACOST) (75c) was obtained for a 78% yield. [M_n(osmometry)=1.78 x 10^4]

FT-IR (KBr): 1761 cm^{-1} (vs, C=O ester); 1218, 1206 & 1017 cm^{-1} (vs, C-O ester), 846 cm^{-1} (s, C-H p-disubst. aromatic).

UV Spectrum (1 μm film): 234 nm (cut-off), 265 nm (A=0.41), 271 (A=0.35).

^1H NMR ($CDCl_3$): 1.03-1.97 δ (3H, bm, CH_2-CH), 2.19δ (3H, s, $-CH_3$), 6.23-7.13δ (4H, bm, aromatic).

^{13}C NMR ($CDCl_3$): 21.2δ (q, $-CH_3$), 40.01δ (d, α-CH), 40.1-49.4δ (bm, β-CH_2), 121.9δ (122.6, d, aromatic C3a), 129.3δ (127.0, d, aromatic C2a), 142.3δ (146.7, s, aromatic C1a), 148.7δ (149.1, s, aromatic C4a).

Preparation of p-Nitrostyrene (77):

p-Nitrostyrene was prepared by a modification of the procedure of Broos and Anteunis[72] as follows. 36.33 g p-nitrobenzyl bromide (76), 44.59 g triphenyl phosphine and 160 mL of chloroform were added to a 500 mL 3-necked round-bottomed flask equipped with a condenser, and nitrogen inlet and outlet. The mixture was refluxed for two hours, and then poured into ether resulting in the precipitation of the p-nitrobenzyltriphenyl phosphonium bromide salt. Washing the salt twice with ether, followed by filtration and drying in the vacuum oven overnight afforded 80.90

g of product. A solution of 44.6 g of sodium carbonate in 140 mL of water was slowly added to a 3-necked 1 L round-bottomed flask containing a stirred suspension of the salt in 400 mL of 37% aqueous formaldehyde solution. The reaction mixture was stirred for four hours at room temperature, and then extracted twice with 200 mL of ether. The ethereal portion was extracted once with water, and twice with brine. Drying of the organic phase with $MgSO_4$, followed by filtration and solvent evaporation on the flash evaporator gave an orange residue. Separation by silica gel column chromatography using a 9:1 hexane/ethyl acetate mixture as eluting solvent yielded 19.65 g (78%) of p-nitrostyrene (77).

FT-IR (NaCl, neat): 1597 cm^{-1} (vs, C=C aromatic); 1514 & 1344 cm^{-1} (vs, NO_2); 990 & 926 cm^{-1} (m, monosubst. alkene).

^1H NMR ($CDCl_3$): 7.45δ (2H, d, aromatic, J=9.0 Hz), 8.09δ (2H, d, aromatic, J=9.0 Hz), AMX pattern for vinyl protons with δ_A=5.41, δ_M=5.84, δ_X=6.73 ppm with J_{AM}=1.0 Hz, J_{AX}=10.6 Hz, and J_{mx}=17.0 Hz.

Preparation of p-Acetamidostyrene (79):

p-Acetamidostyrene was prepared by a modification of the procedure reported by Boyer and Alul[73]. To a solution of 21.00 g 77 in 225 mL of reagent grade acetone was added 15.00 g ammonium chloride in 60 mL of water. The reaction mixture was heated to reflux, and 45.00 g of zinc dust was slowly added. After refluxing the mixture for an additional 40 minutes, the zinc was removed by vacuum filtration, and the remaining orange solution concentrated to about 90 mL. The concentrate was slowly added to

a 250 mL round-bottomed flask containing 15.90 g of potassium acetate and 16.50 g of acetic anhydride with cooling in an ice bath. After complete addition, the mixture was allowed to react at room temperature for 45 minutes. Pouring the mixture in 400 mL of water gave a yellow precipitate. Recrystallization of the crude product in ethyl acetate, with drying in the vacuum oven for 24 hours afforded 13.08 g (60%) of p-acetamidostyrene (79) (m.p. 132.5°C, lit. 134°C[73]).

FT-IR (KBr pellet): 3287 cm^{-1} (m, NH); 1661 cm^{-1} (vs, C=O amide); 1625 cm^{-1} (s, C=C vinylic); 1599 cm^{-1} (vs, C=C aromatic); 1512, 1541 cm^{-1} (vs, N-H & C-N of 2° amide); 906 cm^{-1} (s, monosubst. alkene); 843 cm^{-1} (s, p-disubst. aromatic).

^1H NMR ($CDCl_3$): 2.13δ (3H, s, $-CH_3$); 7.27δ (2H, d, J=8.2 Hz), 7.44δ (2H, J=8.2 Hz, aromatic), 7.87δ (1H, bs, N-H), AMX pattern for vinyl protons with δ_A=5.15, δ_M=5.59, and δ_X=6.64 ppm with J_{AM}=1.5 Hz, J_{AX}=10.6 Hz, and J_{MX}=17.2 Hz.

M. S.: m/e 161 (M^+), 119 (base peak, $C_8H_7NH_2$), 43 ($C_2H_3O^+$), 27 ($C_2H_3^+$).

Solution Polymerization of p-Acetamidostyrene:

Into a 3-necked 100 mL round-bottomed flask equipped with condenser and nitrogen inlet and outlet, was dissolved 3.59 g of monomer 79 in 75 mL toluene. 0.0393 g AIBN was added, and the reaction stirred for 24 hours at 72°C under nitrogen. A heavy white suspension formed during the polymerization was dissolved by addition of DMF to the reaction mixture. Precipitation in methanol gave a yellow precipitate. The polymer was washed with methanol, and dried in the vacuum oven overnight at 65°C to give

2.54 g (71%) of poly-(p-acetamidostyrene) (**80**) containing 8.41% N (6.00 meq N/g-P). **80** was insoluble in methylene chloride, acetonitrile, dioxane, ethanol and soluble in only DMF and DMSO.

FT-IR (KBr pellet): 3299 cm^{-1} (m, N-H); 1667 cm^{-1} (vs, C=O amide); 1602 cm^{-1} (vs, C=C aromatic); 1536 & 1514 cm^{-1} (vs, N-H & C-N); 832 cm^{-1} (m, p-disubst. aromatic).

^{13}C NMR (DMSO-d6): 23.92δ (q, $-CH_3$), 119.14δ (118.6, d, aromatic C3a), 127.45δ (126.0, d, aromatic C2a), 136.83δ (137.1, s, aromatic C4a), 139.61δ (142.7, s, aromatic C1a), 168.02δ (s, C=O amide).

Solution Copolymerization of Styrene and p-Acetamidostyrene:

A mixture of 1.30 g of styrene, 1.96 g of **79**, 15 mL of ethanol, and 0.0208 g AIBN was loaded into a 50 mL three-necked round-bottomed flask equipped with condenser, and nitrogen inlet and outlet. The mixture was stirred under nitrogen at 76°C for 48 hrs, diluted with toluene and precipitated in ether. Washing with ether and drying the product in the vacuum oven overnight at room temperature gave 2.09 g (64%) of a poly-(p-acetamidostyrene styrene) copolymer (**81**) containing 6.10 %N (3.77 meq N/g-P) for a molar ratio of 0.61:0.39. Copolymer **81** was insoluble in methylene chloride, dioxane, tetrahydrofuran and acetonitrile, slightly soluble in ethanol and toluene, and very soluble in DMF.

FT-IR (KBr pellet): 3302 cm^{-1} (m, N-H); 1668 cm^{-1} (vs, C=O amide); 1602 cm^{-1} (vs, C=C aromatic); 1536 and 1514 cm^{-1} (vs, N-H & C-N); 832 cm^{-1} (m, p-disubst. aromatic); 761 & 701 cm^{-1} (m, monosubst. aromatic).

Preparation of p-Tolyl Formate (83):

This compound was prepared by a modification of the procedure of Stevens and Van Es[74]. 12.80 g of formic acid was slowly added to 28.30 g of acetic anhydride so as to keep the reaction mixture below 45°C. The formic acid-acetic anhydride mixture (F.A.M.) was heated to 45°C for 1 hour and then cooled to room temperature. 15.00 g of p-cresol (82) and 0.10 g pyridine were added to the cooled mixed anhydride solution and the combined mixture stirred in the dark at room temperature for 48 hours. The acids and anhydrides were distilled off under high vacuum at a temperature below 50°C. Fractional distillation of the remaining residue gave 15.68 g (83%) of p-tolyl formate (83) (b.p. 75°C/10 mm Hg, lit. 62-63°C/3 mm Hg[74]).

FT-IR (NaCl, neat): 1762 & 1742 cm^{-1} (vs, C=O ester); 1195, 1170 & 1109 cm^{-1} (vs, C-O ester).

^1H NMR ($CDCl_3$): 2.34δ (3H, s, $-CH_3$), 6.91δ (2H, d, aromatic, J=7.9 Hz), 7.15δ (2H, d, aromatic, J=7.9 Hz), 8.19δ (1H, s, OCHO).

M. S.: m/e 136 (M^+), 108 (C_7H_7OH), 29 (CHO^+).

Preparation of p-Formyloxyacetophenone (84):

An F.A.M. was prepared by combining 20.30 g formic acid with 45.12 g acetic anhydride as outlined for the preparation of 83. After cooling the mixture to room temperature, 40.00 g of p-hydroxyacetophenone (71) and 0.80 g of pyridine were added. The combined mixture was stirred in the dark at room temperature for 24 hours. Distillation of the green reaction mixture at 5 mm Hg left a red residue which crystallized in the freezer overnight.

47.05 g (96%) of crude p-formyloxyacetophenone (84) was obtained. RT-IR (KBr pellet): 1767 & 1742 cm^{-1} (vs, C=O ester); 1675 cm^{-1} (vs, C=O ketone); 1269, 1200, 1168 & 1107 cm^{-1} (vs, C-O ester). ^1H NMR ($CDCl_3$): 2.53δ (3H, s, $-COCH_3$), 7.16δ (2H, d, aromatic, J=9.5 Hz), 7.97δ (2H, d, aromatic, J=9.5 Hz), 8.26δ (1H, s, -OCHO).

Attempted Reduction of 84:

5.00 g of crude 84 was dissolved in 25 mL of reagent grade methanol and 1.17 g $NaBH_4$. A TLC obtained after two hours of stirring at room temperature indicated the absence of any remaining starting material. The excess $NaBH_4$ was destroyed by addition of water. Removal of the solvent left a white solid. Extraction of the solid twice with water and ether gave a solid white residue, which when isolated by column chromatography using a 90:10 hexane/ethyl acetate mixture gave as main product 3.24 g of p-hydroxyacetophenone (71)(m. p. 107°C).

^1H NMR ($CDCl_3$): 2.56δ (3H, s, $-COCH_3$), 5.12δ (1H, s, -OH), 6.92δ (2H, d, aromatic, J=8.0 Hz), 7.82δ (2H, d, aromatic, J=8.0 Hz). Separate experiments using catalytic hydrogenation (Pd/C) gave the same result.

Preparation of p-Hydroxystyrene (86):

17.85 g methyltriphenylphosphonium bromide in 10 mL THF was combined with 12.01 g potassium t-butoxide at room temperature under N_2. 6.10 g of p-hydroxybenzaldehyde (85) was added while maintaining the reaction temperature below 25°C. After one hour of stirring the reaction mixture was poured into 50 mL of ice water and extracted with ethyl acetate. The aqueous phase was

acidified to pH 4 and re-extracted with ethyl acetate. Evaporation of the solvent gave 18.60 g of a liquid residue. A silica gel column using a 6:4 hexane/ethyl acetate mixture as eluting solvent gave 5.02 g (83.6%) of pure p-hydroxystyrene (**86**) having a m. p. of 71-73°C (lit. 69-70°C[69]).

FT-IR (KBr pellet): 3383 cm^{-1} (s, O-H); 1629 cm^{-1} (m, C=C vinylic); 1261 & 1255 cm^{-1} (s, C-O alcohol).

^{1}H **NMR** ($CDCl_3$): 5.10 δ (1H, s, -OH), 6.86 δ (2H, d, aromatic, J=8.0 Hz), 7.35δ (2H, d, aromatic, J=8.0 Hz), AMX pattern for vinyl protons with δ_A=5.16, δ_M=5.62, δ_X=6.66 ppm, with J_{AM}=0.75 Hz, J_{AX}=11.0 Hz & J_{MX}=18.0 Hz.

^{13}C **NMR** ($CDCl_3$): 110.79 δ (t, $-CH_2$), 116.30δ (116.0, d, aromatic C3a), 128.37δ (127.9, d, aromatic C2a), 130.71δ (130.7, s, aromatic C1a), 137.74 δ (d, -CH), 158.37 δ (154.5, t, aromatic C4a).

M. S.: m/e 120 (M^+, base peak), 27 ($CH_2=CH^+$).

Preparation of p-Formyloxystyrene (87):

4.30 g of formic acid was combined with 9.54 g acetic anhydride as outlined in the preparation of **83**. After cooling the mixture to room temperature 5.20 g of **86** and 0.15 g pyridine were added. The mixture was stirred in the dark for 3 days. A TLC obtained of the crude reaction mixture using an 8:2 hexane/ethyl acetate mixture indicated the reaction had gone to completion. Removal of the acids and anhydrides at low temperature under vacuum left a yellow residue which upon fractional distillation gave 5.19 g (81.0%) of p-formyloxystyrene (87) (b. p. 83°C at 3 mm Hg).

FT-IR (NaCl, neat): 1763 & 1739 cm^{-1} (vs, C=O ester); 1631 cm^{-1}

(m, C=C vinylic); 1298, 1194, 1170 & 1105 cm^{-1} (vs, C-O ester).

^1H NMR ($CDCl_3$): 6.98 δ (2H, d, aromatic, J=8.6 Hz), 7.35 δ (2H, d, aromatic, J=8.6 Hz), 8.17 δ (1H, s, -OCHO), AMX pattern for vinyl protons with δ_A=5.17, δ_M=5.63, δ_X=6.55 ppm with J_{AM}=1.0 Hz, J_{AX}=10.6 Hz & J_{MX}=17.0 Hz.

M. S.: m/e 148 (M^+), 120 (base peak, C_8H_7OH), 29 (HCO^+), 27 ($CH_2=CH^+$).

Polymerization of p-Formyloxystyrene:

6.11 g p-formyloxystyrene (87) and 0.0652 g AIBN were combined in a 25 mL round-bottomed flask equipped with an air cooled condenser and N_2 bubbler, and heated at 80°C overnight. The resulting polymeric mass was dissolved in THF and precipitated in petroleum ether. Repeated washing, followed by drying of the polymer overnight in a vacuum oven at room temperature yielded 4.85 g (79%) of poly-(p-formyloxystyrene) (89a) [M_n=1.09 x 10^4, M_w=1.65 x 10^4, polydispersity=1.51 (gpc)] (spectral data listed below).

Formylation of Poly-p-(hydroxystyrene):

The F.A.M. was prepared by combining 3.87 g formic acid with 8.54 g acetic anhydride as outlined for the preparation of 83. 4.50 g of poly-(p-hydroxystyrene) (88) was dissolved in 30 mL of THF and added along with 0.10 g of pyridine to the F.A.M. The reaction mixture was stirred in the dark at room temperature for 3 days. The mixture was precipitated directly into water, filtered in a suction filter and washed four times with water. Drying for 48 hours at room temperature under vacuum gave 4.99 g (90%) of poly-(p-formyloxystyrene) containing a small number of

remaining p-hydroxystyrene units. [(89b: M_n=1.65 x 10^3, M_w=4.74 x 10^3, polydispersity=2.87 (gpc); (89c: M_n=1.80 x 10^4, M_w=4.10 x 10^4, polydispersity=2.28 (gpc)]

FT-IR (KBr pellet): 3424 cm^{-1} (w, O-H); 1761 & 1738 cm^{-1} (vs, C=O ester); 1205, 1169 & 1107 cm^{-1} (vs, C-O ester).

UV Spectrum (1 um film): 241 nm (cut-off), 266 nm (A=0.39), 272 nm (A=0.36), 286 nm (A=0.12).

^1H NMR ($CDCl_3$): 0.91-2.24 (3H, bm, CH_2-CH), 6.23-7.24 (4H, bm, aromatic), 8.22 (1H, s, -OCHO).

^{13}C NMR ($CDCl_3$): 40.0-49.5 (bm, CH_2-CH), 121.82 (122.6, d, aromatic C3a), 128.64 (127.0, d, aromatic C2a), 142.92 (146.7, s, aromatic C1a), 148.01 (149.1, s, aromatic C4a), 159.44 (s, -COO-).

Preparation of Phenyl Methacrylate (91):

This compound was prepared by a modification of the procedure of Sumrell et al.[81] as follows. 43.00 g of methacrylic acid (89) and 59.50 g of thionyl chloride were added to a 250 mL 3-necked flask equipped with a condenser and exit tube connected to a gas absorption trap. Evolution of bubbles of sulfur dioxide and hydrogen chloride was immediately observed. The solution was refluxed at 85-90°C for 1.5 hours to generate methacryloyl chloride (90). The orange coloured solution turned red upon cooling to room temperature and addition of 47.00 g of phenol. The reaction mixture was heated for 1 hour at 95°C after which time the bubble evolution had ceased. The mixture was extracted with water and chloroform. Drying of the chloroform layer with anhydrous magnesium sulfate followed by filtration and solvent evapo-

ration gave a yellow residue. A TLC obtained using an 8:2 hexane/ethyl acetate solution as the eluting solvent indicated the formation of a major fast-moving product as well as a non-moving spot at the origin. Separation by silica gel column chromatography using a 9:1 hexane/ethyl acetate solution as eluting solvent afforded 36.25 g (45%) of phenyl methacrylate (PMA) (**91**).

FT-IR (NaCl, neat): 1737 cm^{-1} (vs, C=O ester); 1638 cm^{-1} (m, vinylic C=C); 1199, 1164 & 1129 cm^{-1} (vs, C-O ester), 747 & 690 cm^{-1} (m, C-H monosubst. aromatic).

^1H NMR ($CDCl_3$): 2.04 δ (3H, s, $-CH_3$), 5.70 δ (1H, s, vinylic trans C-H), 6.33 δ (1H, s, vinylic cis C-H), 6.84-7.59 δ (5H, m, aromatic).

M. S.: m/e 162 (M^+), 94 (C_6H_5OH), 69 (base peak, $C_4H_5O^+$), 41 ($C_3H_5^+$).

Polymerization of Phenyl Methacrylate:

A mixture of 8.48 g of **91**, 0.0857 g of AIBN and 50 mL of toluene was placed into a 2-necked 100 mL round-bottomed flask equipped with a water-cooled condenser, and nitrogen inlet and outlet. The polymerization was allowed to proceed at 75°C under a constant nitrogen flow for 24 hours. After this time, the thick reaction mixture was precipitated in methanol. The white precipitate obtained was washed three times for 30 minutes and dried overnight at room temperature in the vacuum oven. 7.60 g (89%) of poly-(phenyl methacrylate) (PPMA) (**92**) was obtained. [(**92a**: M_n=7.10 x 10^3, M_w3.47 x 10^4, polydispersity=4.90 (gpc); M_n(osmometry)=1.90 x 10^4), (**92b**: M_n=9.40 x 10^3, M_w= 1.52 x 10^5, polydispersity=16.2 (gpc); M_n(osmometry)=2.05 x 10^4]

FT-IR (KBr pellet): 1747 cm^{-1} (vs, C=O ester); 1273, 1192, 1163 & 1106 cm^{-1} (vs, C-O ester), 752 & 687 cm^{-1} (m, C-H monosubst. aromatic).

UV Spectrum (1 μm film): 228 nm (cut-off), 260 nm (A=0.30), 266 nm (A=0.21).

^1H NMR ($CDCl_3$): 1.16-1.83δ (3H, bm, $-CH_3$), 2.00-2.87δ (2H, bm, $-CH_2-$), 6.87-7.47δ (5H, bm, aromatic H's).

^{13}C NMR ($CDCl_3$): 18.22 & 18.24δ (2 triplets, $-CH_3$), 45.73 & 45.91δ(s, α-C), 50.50-56.50δ (bm, $-CH_2-$), 120.98δ (122.50, d, aromatic C2a), 125.89δ (126.5, d, aromatic C4a), 129.49δ (129.50, d, aromatic C3a), 150.54δ (151.5, s, aromatic C1a), 174.86, 175.47 & 175.85δ (3 singlets, C=O).

Preparation of Methacryl Anilide (93):

Methacryl anilide was prepared by a modification of the procedure of Patai et al.[82]. 43.0 g methacrylic acid and 61.00 g thionyl chloride were added to a 250 mL 3-necked round-bottomed flask equipped with a condenser. The reaction mixture was refluxed for 2 hours, and then cooled to room temperature. The crude methacryloyl chloride (90) was slowly added with an addition funnel to a mechanically stirred solution of 95 mL aniline and 250 mL toluene in a 1 L 3-necked flask. A white precipitate formed upon addition of the acyl chloride. Mechanical stirring was continued for an additional 2 hours. Removal of the precipitate by filtration, and concentration of the filtrate yielded an orange residue which crystallized upon cooling. Recrystallization from hexane, and subsequent drying in the vacuum oven overnight yielded 42.04 g (52%) of methacryl anilide (93) (m.p.

84.5°C, lit. 85°C[82]).

FT-IR (KBr pellet): 3657 & 3295 cm^{-1} (m, N-H); 1658 cm^{-1} (vs, C=O amide); 1621 cm^{-1} (s, vinylic C=C); 1542 & 1527 cm^{-1} (s, N-H & C-N of 2° amide); 1244 cm^{-1} (m, trans amide linkage); 891 cm^{-1} (m, gem. disubst. alkene).

^1H NMR ($CDCl_3$): 1.93δ (3H, s, $-CH_3$), 5.27δ (1H, s, vinylic trans C-H), 5.65δ (1H, s, vinylic cis C-H), 6.73-7.63δ (5H, m, aromatic), 8.17δ (1H, bs, -NH).

M. S.: m/e 161 (M^+), 93 ($C_6H_5NH_2$), 69 ($C_4H_5O^+$), 41 (base peak, $C_3H_5^+$).

Polymerization of Methacryl Anilide:

8.50 g of monomer **93** was dissolved in 80 mL benzene in a 100 ml round-bottomed flask equipped with condenser and nitrogen inlet and outlet. After dissolution of the monomer, 0.0650 g AIBN was added, and the mixture was heated at 75°C for 24 hours. After about one hour, a white precipitate started forming in the polymerization mixture. After 24 hours, the polymeric precipitate was filtered with suction, washed with twice with each of benzene and ether. The precipitate was dissolved in chloroform and precipitated in ether. Drying the precipitate in the vacuum oven at room temperature overnight afforded 7.00 g (82%) of poly-(methacryl anilide) (**94**) containing 8.68 %N (6.19 meq N/g-P). [M_n=1.61 x 10^4, M_w=1.09 x 10^5, polydispersity=6.76 (gpc)]

FT-IR (KBr pellet): 3437 & 3354 cm^{-1} (m, N-H); 1680 cm^{-1} (s, C=O amide); 1524 & 1500 cm^{-1} (vs, N-H & C-N); 1239 cm^{-1} (s, trans amide linkage).

UV Spectrum (1 μm film): 268 nm (cut-off), 283 nm (A=0.44).

^{13}C NMR (acetone-d_6): 10.50-24.50 δ (bm, $-CH_3$), 46.74δ (s, α-C), 50.60-60.95 δ (bm, $-CH_2-$), 121.78 δ (118.5, d, aromatic C2a), 125.0δ (122.5, d, aromatic C4a), 129.87δ (128.5, d, aromatic C3a), 139.12δ (139.5, s, aromatic C1a), 175.82δ (s, C=O amide).

Solution Photochemistry of Poly-(p-acetoxystyrene) (75a):

2.576 g of 75a was dissolved in 350 mL of acetonitrile and placed in a 500 mL Hanovia reactor equipped with a water-cooled quartz finger and 500 watt mercury arc lamp, condenser and nitrogen inlet and bubbler. The solution was irradiated for a total of 39.5 hours with hourly aliquot samplings. The aliquots were concentrated on the flash evaporator. The residues were dissolved in CH_2Cl_2, and films cast on NaCl disks. The wafers were placed in a vacuum oven at room temperature for 30 minutes to remove trace solvent. FT-IR spectra of these aliquots were used to monitor the progress of the reaction. After 39.5 hours, the IR data indicated the photorearrangement had gone to about 50% completion. The acetonitrile was removed on the flash evaporator, and the yellow syrupy residue was dissolved in CH_2Cl_2. Precipitation in methanol afforded a light yellow powder. The precipitate was filtered, washed with additional methanol and dried overnight in the vacuum oven at 40°C to give 1.82 g of polymer (71% recovery). Spectral analysis of the product confirmed that it contained both p-acetoxystyrene and 2-hydroxy-5-vinylacetophenone repeating units in a molar ratio of 0.52:0.48 (^1H NMR) (95c). [M_n=4.50 x 10^4, M_w=3.62 x 10^5, polydispersity=8.06 (gpc)]. Spectral data listed below corresponds to product after 39.5 hrs. of irradiation and intermediate data presen-

ted in Figure 4.

FT-IR (NaCl, films): 3483 cm^{-1} (m, -OH); 1763 cm^{-1} (s, C=O ester); 1642 cm^{-1} (s, C=O ketone); 1615 cm^{-1} (m, C=C aromatic); 1254 cm^{-1} (s, C-O phenol); 1217 & 1201 cm^{-1} (vs, C-O ester); 912 & 850 cm^{-1} (m, C-H p-disubst. aromatic); 874 & 832 cm^{-1} (m, C-H 1,2,4-trisubst. aromatic).

^1H NMR ($CDCl_3$): 0.97-1.77δ (3H, bm, allylic H's), 2.20δ (1.57H, s, $-CH_3$ ester), 2.31δ (1.43H, s, $-CH_3$ ketone), 6.17-7.03δ (3.75H, bm, aromatic).

^{13}C NMR ($CDCl_3$): 21.60δ (q, $-CH_3$ ester), 26.53δ ($-CH_3$ ketone), 40.43δ (d, α-CH), 40.0-48.50δ (m, β-CH_2), 118.34δ (115.8, d, aromatic C5b), 122.06δ (122.6, d, aromatic C3a), 122.17δ (124.9, s, aromatic C3b), 129.32δ (127.0, d, aromatic C2a), 129.75δ (129.6, d, aromatic C2b), 135.44δ (133.7, d, aromatic C6b), 142.23δ (146.7, s, aromatic C1a), 148.75δ (149.1, s, aromatic C4a), 160.51δ (s, C-OH), 169.30δ (s, C=O ester), 204.62δ(s, C=O ketone).

Solid-State Photochemistry of Poly-(p-acetoxystyrene) (75b):

A 35% solution of PACOST (75b) in diglyme was prepared. 1.10 μm thick films on NaCl disks and quartz wafers were obtained by spin-coating at 2000 rpm for 30 seconds. Trace solvent was removed from the films by prebaking at 100°C for 30 minutes. The films of 75b were exposed using an unfiltered 500 watt OAI deep UV source, with the output measured using a 254 nm probe. The quartz wafers were exposed to doses ranging from 0 to 18.6 J/cm^2 with UV spectra recorded at regular intervals. A parallel FT-IR study was also carried out for doses between 0 and 2.94

J/cm^2. Spectral data confirmed the formation of a p-acetoxystyrene 2-hydroxy-5-vinylacetophenone copolymer (96). Quantitative FT-IR interpretation was used to evaluate the relative proportions of the starting and photorearranged polymer units as a function of exposure dose.

FT-IR (NaCl, 1.26 μm film, dose=2.94 J/cm^2): 3483 cm^{-1} (w, -OH); 1764 cm^{-1} (s, C=O ester); 1643 cm^{-1} (m, C=O ketone); 1615 cm^{-1} (w, C=C aromatic); 1254 cm^{-1} (w, C-O phenol); 1217 & 1201 cm^{-1} (vs, C-O ester); 912 & 846 cm^{-1} (m, C-H p-disubst. aromatic); 836 cm^{-1} (m, C-H 1,2,4-trisubst. aromatic)

UV Spectrum (1.10 μm, dose=3.10 J/cm^2): 238 nm (cut-off), 256 nm (A=1.63), 271 nm (A=0.79), 287 nm (A=0.95), 340 nm (0.55).

Solid-State Photochemistry of Poly-(p-acetamidostyrene):

Spin-coating a 20% solution of poly-(p-acetamidostyrene) (80) in DMF onto NaCl disks or quartz wafers at a spin-speed of 2500 rpm gave 0.9 μm thick polymer films. Trace solvent was removed from the films by a 30 minute prebake at 100°C. The films were exposed to unfiltered deep UV radiation, with the output measured using a 254 nm probe. Films of 80 were exposed to doses ranging between 0 and 3.16 J/cm^2. No change was observed in the IR spectrum upon irradiation.

Solution Photochemistry of p-Cresyl Formate:

2.50 g of 83 was dissolved in 325 mls of spectral grade methanol (cut-off 215 nm) and irradiated in the Hanovia cell. The reaction was monitored by TLC using an 8:2 hexane/ethyl acetate mixture as eluting solvent. After four hours the reaction was terminated and the solvent removed on the flash evaporator to

give a syrupy residue. The presence of a non-mobile polymeric component was also visible on TLC. Column chromatography using hexane as the eluting solvent gave 0.12 g (4.8%) unreacted p-cresyl formate and 1.70 g (68%) p-cresol (82). Spectral data confirmed p-cresol as the major product.

FT-IR (NaCl, neat): 3329 cm^{-1} (vs, O-H), 1235 cm^{-1} (vs, C-O phenolic).

^1H NMR ($CDCl_3$): 2.26δ (3H, s, $-CH_3$), 5.43δ (1H, bs, -OH), 6.68δ (2H, d, aromatic, J=9.0 Hz), 6.98δ (2H, d, aromatic, J=9.0 Hz).

Solution Photochemistry of Poly-(p-formyloxystyrene):

2.0 g of poly-(p-formyloxystyrene) (**89b**) was dissolved in 300 mls of spectral grade acetonitrile, and the solution irradiated in the Hanovia apparatus. Small aliquots of the irradiating polymer solution were withdrawn at regular intervals and concentrated by solvent evaporation on a flash evaporator. Polymer films were coated onto NaCl disks, and dried in the vacuum oven at room temperature for 20 minutes. In this way, the photochemical reaction was monitored by FT-IR. The irradiation was continued for a total of 14 hours, however no further significant changes were observed after 5 hours. Spectral data of the polymer obtained after the 14 hours of irradiation indicated almost exclusive conversion to poly-(p-hydroxystyrene) (**88**). [M_n=5.50 x 10^2, M_w=1.26 x 10^3, polydispersity=2.29 (gpc)]

FT-IR (NaCl, film): 3416 cm^{-1} (s, O-H); 1730 cm^{-1} (w, C=O ester); 1651 cm^{-1} (w, C=O aldehyde); 1219 & 1171 cm^{-1} (m, C-O phenolic).

^1H NMR (acetone-d_6): 0.65-2.23δ (3H, bm, CH_2-CH), 2.95δ

(1H, bs, -OH), 5.85-7.00δ (4H, bs, aromatic).

^{13}C NMR (acetone-d_6): 35.50-49.60δ (bm, β-CH_2), 40.40δ (d, α-CH), 115.64δ (115.9, d, aromatic C3b), 129.27δ (127.4, d, aromatic C2b), 137.51δ (141.4, s, aromatic C1b), 155.80δ (153.0, s, aromatic C4b).

Solid-State Photochemistry of Poly-(p-formyloxystyrene):

A 10% solution of poly-(p-formyloxystyrene) (89c) in diglyme was prepared under yellow light. The polymer solution was spin-coated onto NaCl disks and quartz wafers so as to obtain 1 μm thick films. The films were prebaked for 30 minutes at 100°C on a hot plate. The films were exposed to unfiltered deep UV doses of 100, 300 and 1500 mJ/cm^2 as measured by the 254 nm probe of the exposure monitor. The progress of the photochemistry was monitored by both FT-IR and UV spectrophotometry. The spectral data obtained indicated almost complete conversion to poly-(p-hydroxystyrene) (88) after the 100 mJ/cm^{-1} dose.

FT-IR (NaCl, film): 3414 cm^{-1} (s, O-H); 1727 cm^{-1} (w, C=O ester); 1652 cm^{-1} (w, C=O aldehyde); 1219 & 1170 cm^{-1} (s, C-O phenolic).

UV Spectrum (1 μm film): 241 nm (cut-off), 266 nm (A=0.52), 276 nm (A=0.59), 286 nm (A=0.41).

Solution Photochemistry of Poly-(phenyl methacrylate):

2,109 g of **92a** was dissolved in 300 mL of freshly distilled dioxane having a UV cut-off of 225 nm. The solution was placed in the Hanovia UV reactor and irradiated as outlined for the solution photochemistry of PACOST. Aliquots of the reaction mixture were withdrawn for a total of 56 hours at regular inter-

vals. The aliquots were evaporated on the flash evaporator at a temperature of 45°C and dissolved in CH_2Cl_2 for film coating onto NaCl disks. Solvent was removed by placing the films in the vacuum oven at room temperature for 30 minutes. After 10 hours of irradiation very little subsequent change in the IR was observed. The reaction was monitored for a total of 56 hours. The irradiation was terminated and the dioxane removed on the flash evaporator. The syrupy residue was dissolved in CH_2Cl_2 and precipitated in petroleum ether. Washing of the polymer in petroleum ether followed by filtration and drying of the polymer overnight in the vacuum oven at room temperature gave 1.44 g (69%) of a copolymer containing both phenyl methacrylate and the o-hydroxyphenyl ketone rearranged product (**54b**) in a molar ratio of 0.75:0.25 (^{1}H NMR). [after 56 hours, M_n=8.40 x 10^2, M_w=3.00 x 10^3, polydispersity=3.57 (gpc)] Figure 9 illustrates FT-IR spectral data for **98** at different times during the irradiation. Listed below are the spectral data for **98** after 56 hours of deep UV irradiation.

FT-IR (NaCl, film): 3384 cm^{-1} (s, O-H); 1749 cm^{-1} (s, C=O ester); 1626 cm^{-1} (m, C=O o-hydroxyketone); 1605 cm^{-1} (m, C=C o-subst. aromatic); 1222 & 1120 cm^{-1} (s, C-O phenol); 1192, 1163 & 1106 cm^{-1} (s, C-O ester).

^{1}H NMR ($CDCl_3$): 0.50-1.97δ (3H, bm, $-CH_3$), 3.10-4.13δ (2H, bm, $-CH_2-$), 6.20-7.61δ (4.70 H, bm, aromatic).

^{13}C NMR ($CDCl_3$): 18.00-22.80δ (bm, ester $-CH_3$), 24.58 δ (s, o-hydroxyketone $-CH_3$), 46.01δ (s, ester α -C), 51.20-56.40 δ (bm, CH_2), 66.59 δ (s, o-hydroxyketone α-C), 115.33δ (115.8, d, aroma-

tic C6b), 120.28δ (121.2, d, aromatic C4b), 121.25δ (124.9, s, aromatic C2b), 125.84δ (126.5, d, aromatic C4a), 129.52δ (129.5, d, aromatic C3a), 136.40δ (134.1, d, aromatic C5b), 150.65δ (151.5, s, aromatic C1a), 155.93δ (155.5, s, aromatic C1b), 163.00 δ (bs, C=O ketone), 175.60-178.00 δ (series of sharp singlets, C=O ester).

Solid-State Photochemistry of Poly-(phenyl methacrylate):

A 25% solution of **92b** in diglyme gave 1.01 μm thick films on NaCl disks and quartz wafers when spun at 8,000 rpm for 30 seconds. The films were prebaked and exposed as outlined for PACOST (**75b**). The quartz wafers were exposed to doses ranging from 0 to 18.6 J/cm^2, with UV spectra recorded at regular intervals. The NaCl wafers were exposed to doses ranging between 0 and 2.94 mJ/cm^2. Spectral data confirmed the formation of a copolymer containing both methyl methacrylate and the o-hydroxyphenyl ketone rearranged product units. Quantitative FT-IR interpretation was used to evaluate the relative proportions of the starting and photorearranged polymer units as a function of exposure dose for terpolymer **99**. Spectral data listed below corresponds to the film at the indicated doses.

FT-IR (NaCl, 1.01 μm film, dose=2.94 J/cm^2): 3433 cm^{-1} (w, -OH); 1749 cm^{-1} (vs, C=O ester); 1663 cm^{-1} (w, C=O p-hydroxyketone); 1626 cm^{-1} (w, C=O o-hydroxyketone); 1221 cm^{-1} (w, C-O phenol); 1191, 1163 & 1105 cm^{-1} (vs, C-O ester).

UV Spectrum (1.01 μm, dose=3.10 J/cm^2): 235 nm (cut-off), 261 nm (A=1.84), 330 nm (A=0.74).

Solution Photochemistry of Poly-(methacryl anilide):

2.01 g of **94** in 350 mL of dioxane was irradiated in a Hanovia reactor as outlined for the solution photochemistry of **92a**. Aliquots of the reaction mixture were withdrawn at regular intervals during the 55 hour irradiation period, concentrated and coated onto NaCl wafers as described for PPMA. After 8 hours, very little further rearrangement was observed. After 55 hours, the photolysis mixture was concentrated to 50 mL on the flash evaporator and precipitated into petroleum ether. Washing the precipitate twice with petroleum ether and drying in the vacuum oven overnight afforded 1.63 g (81%) of a copolymer containing primarily methacryl anilide, with a small amount of the o-rearranged product (**100**). [after 55 hours M_n=8.39 x 10^2, M_w=1.39 x 10^3, polydispersity=1.65 (gpc)] Listed below are the spectral results for **100** after 56 hours of deep UV irradiation.

FT-IR (NaCl, film): bands seen for **94** as well as 3362 cm^{-1} (w, increase in intensity due to N-H amine); 1654 cm^{-1} (ws, C=O ketone), 1615 cm^{-1} (m, N-H); 1524 cm^{-1} (reduced intensity of N-H & C-N band of 2^o amide); 1291 & 1254 cm^{-1} (m, C-N aromatic amide).

^{13}C **NMR** ($CDCl_3$): 15.90-33.20 δ (bm, ester & aminoketone $-CH_3$), 36.0-57.33δ(bm, ester & aminoketone β-CH_2), 45.93δ (s, amide α-C), 66.49 δ (bs, aminoketone α-C), 115.36 δ (115.2, d, o-product aromatic C6b & p-product aromatic C2b), 121.27δ (d, aromatic C2a), 127.18δ (s, p-product aromatic C3b), 128.15δ (d, aromatic C4a), 129.53δ(129.5, d, o-product aromatic C3b), 130.53δ (d, aromatic C3a), 138.78δ (s, aromatic C1a), 150.73δ (149.3, s, p-

product aromatic C1b), 155.92δ (151.3, s, o-product aromatic C1b), 168.49δ (s, C=O amide).

Solid-State Photochemistry of Poly-(Methacryl Anilide):

A 20% solution of **94** in diglyme gave 0.80 μm thick films on NaCl disks and quartz wafers when spun at 3000 rpm for 30 seconds. The films were prebaked and exposed as outlined for PACOST (**75b**). The quartz wafers were exposed to doses of unfiltered deep UV light ranging from 0 to 55.80 J/cm^2 with UV spectra recorded at regular intervals. The NaCl wafers were exposed to doses of 0 to 2.50 J/cm^2. Spectral data indicated the formation of only a very small amount of the o-rearranged product. Spectral data listed below corresponds to the film at the indicated doses.

FT-IR (NaCl, film, dose=2.50 J/cm^2): (same as for **94** except for the emergence of the following weak bands): 3362 cm^{-1} (w, N-H amine); 1654 cm^{-1} (s, C=O ketone), 1615 cm^{-1} (w, N-H 1° amine).

UV Spectrum (0.80 μm, dose=6.20 J/cm^2): 269 nm (cut-off), 282 nm (A=0.98), 309 nm (A=0.84).

Lithographic Testing of Poly-(p-acetoxystyrene) (**75b**):

A 37% solution of **75b** in diglyme gave 0.97 μm thick polymer films on silicon wafers for a spin-speed of 3500 rpm for 30 seconds. After a 30 minute prebake at 100°C, the films of **75b** were exposed to a deep UV dose of 3.10 J/cm^2 through a Wicked mask using a 500 watt OAI deep UV source, and then postbaked at 100°C for 15 minutes. Pattern development was attempted in various mixtures of 3-heptanone, 2-methoxyethylacetate and N-butyl acetate with little success due to rapid dissolution of the

unexposed areas of the film. Dip development for 90 seconds in a 1:1 3-heptanone/isopropanol mixture, followed by an isopropanol wash gave fully developed images, while reducing the unexposed film thickness to 0.48 μm. The surface of the film was visibly affected by the solvent, as shown in the optical micrograph in Figure 13. MF-312 and AZ-400K alkali developers were tried. After 3 minutes in these developers extensive film swelling and cracking occured without any apparent pattern development.

Lithographic Testing of Poly-(p-formyloxystyrene) (89c):

A 15% solution of **89c** in diglyme was used to coat silicon wafers with a 1.01 μm thick film. After a 30 minute prebake at 100°C, the films were exposed through a contact Wicked mask to varying doses of unfiltered deep UV light, measured with the 254 nm probe of the exposure monitor. For a dose of 100 mJ/cm^2, a clean positive image was obtained upon development in a 10:1:1 isopropanol/ammonium hydroxide/water solution for 90 seconds. Electron micrographs of these high resolution patterns are shown in Figure 14. MF-312 was also tried for positive image development. The prolonged development times of up to 600 seconds required for exposure doses ranging from 0 to 308 mJ/cm^2 resulted in loss of film thickness in the unexposed areas of the film. Negative image development of irradiated films of **89c** was achieved using methylene chloride or anisole-based developers, diluted with hexane.

Lithographic Testing of Poly-(phenyl methacrylate) (92b):

A 25% solution of **92b** in diglyme was used to coat silicon wafers at a spin speed of 4800 rpm for 30 seconds with a 0.97 μm

thick film. The films were prebaked and exposed through a Wicked mask as outlined for PACOST 75b. Films of 92b were exposed to doses of 3105 and 7760 mJ/cm^2. Development was attempted in a number of solvents. Attempts to use 4-methyl-2-pentanone, methyl ethyl ketone and propyl acetate failed due to rapid dissolution of the unexposed areas of the film, without pattern development. Development for 15 seconds in 3-heptanone gave well resolved patterns with the unexposed film thickness having been reduced to 0.68 μm (see Figure 15). When attempts were made to use the commercial alkali based developers such as AZ-400K and AZ-2401, patterns remained completely undeveloped after 3 minutes. During this time extensive swelling, cracking and lifting of the films occured in these developers.

Lithographic Testing of Poly-(methacryl anilide) (94):

A 20% solution of 94 in diglyme gave 1.0 μm thick films when spun at a spin speed of 2000 rpm for 30 seconds. The films were prebaked and exposed through a Wicked mask as outlined for PACOST (75b). 6,270 mJ/cm^2 and 12,550 mJ/cm^2 doses of unfiltered deep UV light were used. Development in methylene chloride, diglyme, 2-methoxyethyl ether and n-butyl acetate caused dissolution of the unexposed areas. A 2:1 methylene chloride/ chloroform mixture gave partial development of an image for the higher exposure dose only. After 120 seconds in this solvent, the unexposed film thickness was 0.57 μm and the exposed film thickness was 0.75 μm giving the image shown in Figure 16. Longer development times in this solvent caused extensive swelling of the polymer film with distortion of the patterns.

o-Nitrobenzaldehyde Rearrangement

Preparation of Benzyl Phenyl Ether (103):

This compound was prepared by a modification of the method of McKillop et al.[90] A solution consisting of 0.94 g NaOH, 3.22 g Bu_4NBr, and 0.94 g phenol (**106**) in 50 mL of water was added to 3.17 g benzyl chloride (**102**) in 50 mL of CH_2Cl_2. The reaction was allowed to proceed for 1 day at room temperature with continuous stirring. The 2 phases were then separated, and the aqueous phase extracted twice with 20 mL of CH_2Cl_2. Evaporation of the combined extracts yielded a colorless liquid residue. The residue was mixed with 50 mL water and extracted twice with 30 mL ethyl ether. The ethereal solution was washed twice with 25 mL 2N NaOH solution, and once with 50 mL brine. A TLC of the crude mixture, using an 8:2 hexane/ethyl acetate mixture as eluting solvent, indicated the presence of benzyl chloride and another slower moving component. The ethereal phase was washed with Na_2SO_4, and the solvent removed on the evaporator. Distillation at 2 mm Hg gave 3 fractions between 110 and 115°C (lit. 105-108°C, 1 mm Hg[92]) totalling 1.32 g (72%) of pure benzyl phenyl ether (**103**).

FT-IR (KBr pellet): 1599 cm^{-1} (s, aromatic C=C); 1247, 1171 & 1030 cm^{-1} (s, C-O-C ether); 744 & 697 cm^{-1} (m, C-H monosubst. aromatic).

^1H NMR ($CDCl_3$): 4.95δ (2H, s, $-CH_2-O-$), 6.77-7.60δ (5H, m, phenyl aromatic), 7.35δ (5H, s, benzyl aromatic).

M. S.: m/e 184 (M^+), 91 (base peak, $C_7H_7^+$), 65 ($C_5H_5^+$), 39 ($C_3H_3^+$).

Preparation of 2-Nitro-5-benzyloxybenzaldehyde (104):

Method #1:

To a solution of 6.33 g benzyl chloride (102) in 50 mL of CH_2Cl_2 was added a solution consisting of 50 mL water, 1.20 g NaOH, 6.44 g Bu_4NBr and 3.34 g of 5-hydroxy-2-nitrobenzaldehyde (101). The reaction was allowed to proceed in the absence of light for 1 day at room temperature with continuous stirring. The 2 phases were then separated, and the aqueous phase extracted twice with 30 mL of CH_2Cl_2. Evaporation of the combined extracts yielded a brownish oil. The oil was poured into cold water without significant product crystallization, and therefore the water was extracted with more CH_2Cl_2 and dried with anhydrous $MgSO_4$. Evaporation of the solvent and seed crystal addition resulted in the formation of crystals. Recrystallization from isopropyl ether gave 3.94 g (77%) of 2-nitro-5-benzyloxybenzaldehyde (104) (m.p. 73°C).

Method #2:

A mixture consisting of 2.78 g of 101, 2.13 g of 102 and 0.74 g NaOH dissolved in 4.3 mL water and 25 mL ethanol (95%) was refluxed for 8 hours in the dark. The alcohol was removed on the evaporator leaving a dark syrupy residue. Upon pouring the residue into 100 mL of cold water with stirring, a product crystallized out of solution. The crystals were isolated by suction filtration, washed several times with distilled water, and dried in the vacuum oven overnight. Recrystallization from isopropyl ether yielded 2.95 g (61%) of 104 (m.p. 73°C).

FT-IR (KBr pellet): 1697 cm^{-1} (s, C=O aldehyde); 1590 cm^{-1} (s,

aromatic C=C); 1514 cm^{-1} (s, N=O); 1333 & 1280 cm^{-1} (vs, NO_2), 1249 & 1070 cm^{-1} (s, C-O-C ether), 851 cm^{-1} (m, C-H 1,2,4-trisubst. aromatic); 753 & 696 cm^{-1} (m, C-H monosubst. aromatic).

^1H NMR ($CDCl_3$): 5.20 δ (2H, s, $-CH_2-O-$), 7.10-7.43 δ (2H, m, phenyl aromatic C2 & C6), 7.43 δ (5H, s, benzyl aromatic), 8.16 δ (1H, d, phenyl aromatic C5), 10.54 δ (1H, s, -CHO).

M. S.: m/e 257 (M^+), 91 (base peak, $C_7H_7^+$), 46 (NO_2), 30 (NO), 28 (CO).

Preparation of (3 & 4)-Vinylbenzyloxybenzene (108):

To a solution of 3.82 g of vinyl benzyl chloride (VBC) (105) in 50 mL of CH_2Cl_2 was added a solution consisting of 50 mL water, 0.94 g NaOH, 3.22 g Bu_4NBr and 0.94 g phenol (106). The reaction was allowed to proceed for 1 day at room temperature with continuous stirring. The 2 phases were then separated, and the aqueous phase extracted twice with 20 mL of CH_2Cl_2. Evaporation of the combined extracts yielded a yellow syrup. The residue was mixed with 50 mL water and extracted twice with 25 mL ethyl ether. The ethereal solution was washed two times with 50 mL 2N NaOH solution, once with 50 mL brine, and twice with 50 mL of distilled water. Drying of the organic phase with anhydrous Na_2SO_4, followed by solvent evaporation gave a yellow residue that crystallized upon standing. Recrystallization from methanol yielded 1.39 g (66%) of a mixture of (3 & 4)-vinylbenzyloxybenzene (108) (m.p. 111-112°C).

FT-IR (KBr pellet): 1625 cm^{-1} (w, vinylic C=C); 1605 & 1599 cm^{-1} (m, aromatic C=C); 1243, 1228 & 1029 cm^{-1} (s, C-O-C ether); 994 & 905 cm^{-1} (m, vinylic =CH); 875 cm^{-1} (m, C-H p-disubst. aromatic);

833 cm^{-1} (m, C-H m-disubst. aromatic); 751 & 690 cm^{-1} (s, C-H monosubst. aromatic).

^1H NMR ($CDCl_3$): 5.01δ (2H, s, $-CH_2-O-$), 6.82-7.33δ (4H, m, styryl aromatic H's of m- & p-isomers), 7.34δ (5H, s, phenyl aromatic), AMX pattern for vinyl protons with δ_A=5.19, δ_M=5.69 and δ_X=6.68 with J_{AM}=2.0 Hz, J_{AX}=11.0 Hz & J_{MX}=17.0 Hz.

M. S.: m/e 210 (M^+), 117 (base peak, $C_9H_9^+$), 91 ($C_7H_7^+$).

Copolymerization of Monomer **108** and Styrene:

A mixture of 0.515 g of **108**, 0.512 g freshly distilled styrene, and 0.0104 g of AIBN was added to 5 mL of toluene in a round-bottomed flask equipped with a condenser and a nitrogen bubbler. The polymerization was allowed to proceed at 75°C under nitrogen with stirring for 28 hrs. The reaction mixture was then cooled to room temperature and added dropwise to petroleum ether giving a white precipitate. The precipitate was washed 3 times with additional petroleum ether and dried in the vacuum oven overnight at room temperature. A yield of 0.37 g (36.1%) of copoly-(styrene (3 & 4)-vinylbenzyloxybenzene) (**109**) was obtained. [M_n=2.19 x 10^4, M_w=3.33 x 10^4, polydispersity=1.53 (gpc); M_n(osmometry)=1.72 x 10^4]

FT-IR (KBr pellet): 1599 & 1586 cm^{-1} (s, aromatic C=C), 1241, 1221 & 1171 cm^{-1} (s, C-O-C ether), 753 & 699 cm^{-1} (s, C-H monosubst. aromatic).

^{13}C NMR ($CDCl_3$): 40.41 δ (d, α-CH), 38.50-48.55δ (bm, β-CH_2), 69.84 δ (t, $-CH_2-O-$), 114.79δ (114.10, d, **108** aromatic), 120.82δ (120.80, d, **108** aromatic), 129.44δ (129.50, d, **108**, aromatic), complex peak patterns due to the presence of both m- and p-

isomers with peaks at 126.48δ (d), 127.91δ (d), 134.21δ (s), 145.76δ(s)

Preparation of (3 & 4)-Vinylbenzyloxy-p-nitrobenzene (**110**):

To a solution of 7.63 g of VBC (**105**) in 100 mL of CH_2Cl_2 was added a solution consisting of 100 mL water, 1.20 g NaOH, 6.44 g Bu_4NBr and 2.78 g p-nitrophenol (**107**). The reaction was allowed to proceed for 1 day at room temperature with continuous stirring and TLC monitoring. The 2 phases were then separated, and the aqueous phase extracted twice with 20 mL of CH_2Cl_2. Evaporation of the combined extracts yielded a yellow syrup. The residue was mixed with 50 mL water and extracted twice with 25 mL ethyl ether. The ethereal solution was washed twice with 20 mL 2N NaOH solution, and once with 20 mL brine. Drying of the organic phase with anhydrous Na_2SO_4, followed by solvent evaporation gave a syrupy yellow residue. Recrystallization from a hexane/ether mixture yielded 4.02 g (79%) of a mixture of (3 & 4)-vinylbenzyloxy-p-nitrobenzene (**110**) (m.p. 59-60°C).

FT-IR (KBr pellet): 1630 cm^{-1} (w, vinylic C=C); 1517 & 1500 cm^{-1} (s, N=O); 1340 & 1298 cm^{-1} (s, NO_2); 1250 & 1015 cm^{-1} (vs, C-O-C ether); 992 & 910 cm^{-1} (s, vinylic =C-H); 880 cm^{-1} (m, C-H p-disubst. aromatic); 844 cm^{-1} (m, C-H m-disubst. aromatic).

^1H NMR ($CDCl_3$): 5.13δ (2H, s, $-CH_2-O-$), 7.02δ (2H, d, phenyl aromatic C2a & C6a, J=10.5 Hz), 6.50-7.64δ (4H, m, styryl aromatic H's of m- and p-isomers), 8.14δ (2H, d, phenyl aromatic C3a & C5a, J=10.5 Hz).

M. S.: m/e 255 (M^+), 117 (base peak, $C_9H_9^+$), 91 ($C_7H_7^+$), 30 (NO).

Copolymerization of Monomer **110** and Styrene:

(a) In Solution:

A mixture of 0.625 g **110**, 0.512 g styrene, and 0.0130 g AIBN was copolymerized in solution as outlined for copolymer **109**. Precipitation and washing in petroleum ether gave 0.260 g (23%) g of poly-(styrene-(3 or 4)-styryloxy-p-nitrobenzene) (**111a**).

(b) In Bulk:

To a 10 mL round bottom flask preheated to 75°C, equipped with condenser and nitrogen inlet and outlet was added 2.53 g of monomer **110** and 1.03 g styrene. After the (3 or 4)-vinylbenzyl-oxy-p-nitrobenzene had dissolved and the monomer mixture brought to temperature, 0.0378 g AIBN was added. The mixture was heated under nitrogen at 75°C for 24 hrs. After this time the solution had become more viscous than originally, but could still be stirred. After 48 hrs. at this temperature the polymerization was terminated, and a TLC taken using an 8:2 hexane/ethyl acetate mixture as eluting solvent. The TLC indicated that unpolymerized styrene and monomer **110** remained in significant quantity. The polymer solution was precipitated and washed three times in ether. Drying in the vacuum oven overnight at room temperature afforded 0.830 g (24%) of copolymer (**111b**) containing 4.11% N (2.93 meq/g P) for a molar ratio of 1.0:0.9. [M_n=1.93 x 10^4, M_w=2.84 x 10^4, polydispersity=1.47 (gpc)]

FT-IR (KBr pellet): 1608 & 1592 cm^{-1} (vs, aromatic C=C); 1513 cm^{-1} (vs, N=O); 1342 & 1298 cm^{-1} (vs, $-NO_2$); 1260, 1243 & 1172 cm^{-1} (s, C-O-C ether); 856 cm^{-1} (s, C-H m-disubst. aromatic); 752 & 701 cm^{-1} (s, C-H monosubst. aromatic).

^{13}C NMR ($CDCl_3$): 40.52δ (d, α-CH), 37.50-47.54δ (bm, β-CH_2), 70.62δ (t, -CH_2-O-), 114.76δ (115.0, d, 110 aromatic), 126.41δ (125.9, d, styrene aromatic), 141.57δ (140.8, s, 110 aromatic), 163.66 δ (165.7, s, 110 aromatic); complex peak patterns due to the presence of both m- and p-isomers with peaks at 128.85δ (bs), 132.87 δ (s), 135.21δ (s), 145.43δ (bs).

Preparation of 2-Nitro-5-(m & p-vinylbenzyloxy)benzaldehyde (112):

To a solution of 15.26 g of VBC (105) in 100 mL of CH_2Cl_2 was added a solution consisting of 100 mL water, 2.40 g NaOH, 12.92 g Bu_4NBr and 6.68 g 5-hydroxy-2-nitrobenzaldehyde (101). The reaction was allowed to proceed in the absence of light for one day at room temperature with continuous stirring. The 2 phases were then separated, and the aqueous phase extracted twice with 80 mL of CH_2Cl_2. Evaporation of the combined extracts yielded a yellow oil. The residue was mixed with 50 mL water and extracted twice with 50 mL ethyl ether. The ethereal solution was washed 2 times with 100 mL 2 N NaOH solution, and once with 50 mL brine. Drying of the organic phase with anhydrous $MgSO_4$ followed by solvent evaporation gave a syrupy orange-red residue, which crystallized upon cooling. A double recrystallization from isopropyl ether yielded 9.24 g (82%) of a mixture of 2-Nitro-5-(m & p-vinylbenzyloxy)benzaldehyde (112) (m.p. 66-67°C).

FT-IR (KBr pellet): 1695 cm^{-1} (s, C=O aldehyde); 1626 cm^{-1} (m, vinylic C=C), 1510 cm^{-1} (s, N=O); 1327 & 1282 cm^{-1} (vs, NO_2); 1239, 1162 & 1072 cm^{-1} (s, C-O-C ether); 997 & 913 cm^{-1} (m, vinylic =CH); 863 cm^{-1} (m, C-H p-disubst. aromatic).

^{1}H NMR ($CDCl_3$): 5.14 δ (2H, s, $-CH_2-O-$), 7.01-7.56 δ (6H, m, phenyl aromatic C2, C6 & styryl aromatic H's of m- & p-isomers), 8.12 δ (1H, d, phenyl aromatic C5, J=9.0 Hz), 10.45 δ (1H, s, -CHO), AMX pattern for vinyl protons with δ_A=5.26, δ_M=5.73, δ_X=6.70 with J_{AM}=1.30 Hz, J_{AX}=9.00 Hz, J_{MX}=18.0 Hz.

M. S.: m/e 283 (M^+), 117 (base peak, $C_9H_9^+$), 91 ($C_7H_7^+$), 39 (HCO), 30 (NO).

Attempted Free-Radical Polymerization of Monomer 112:

1.50 g of monomer 112 was placed in a foil wrapped 10 mL round-bottomed flask preheated to 75°C, equipped with condenser and nitrogen inlet and outlet. After the monomer had melted, 0.0152 g of AIBN was added and the mixture was left to stir at 75°C under nitrogen in the dark for 2 days. After this time, the solution remained fluid, and a TLC obtained using an 8:2 hexane/ethyl acetate mixture as eluting solvent indicated that most of the monomer remained, except for a small component that sat at the origin. Attempted precipitation in ether, petroleum ether and methanol failed, further suggesting that essentially no polymerization had occured.

Copolymerization of VBC and Styrene:

A bulk polymerization tube was loaded with 6.00 g VBC (106), 6.00 g styrene and 0.1453 g of AIBN. The contents of the tube was frozen and thawed under vacuum three times and then sealed under vacuum. The polymerization was carried out in an oven at 80°C for 3 days. The tube was then opened and the solid material dissolved in chloroform. The polymer was precipitated and washed 3 times for 30 minutes in methanol and dried in the vacuum oven

at 40°C overnight. A white powdery polymer weighing 8.10 g (68%) was obtained which contained 7.1% Cl (2.09 meq Cl/g P). The molar ratio of the poly-(styrene VBC) copolymer (**113**) was calculated to be 0.64:1.0. [M_n=4.54 x 10^4, M_w=9.69 x 10^4, polydispersity=2.13 (gpc), M_n(osmometry)=5.60 x 10^4]

FT-IR (KBr pellet): 1602 cm^{-1} (m, aromatic C=C), 1266 cm^{-1} (s, CH_2-Cl), 699 cm^{-1} (vs, C-Cl).

Chemical Modification of Copolymer **113**:

To 100 mL DMF was added 6.015 g of copolymer **113**, 5.789 g 5-hydroxy-2-nitrobenzaldehyde (**101**) and 12.1 mL of a 3N NaOH solution under nitrogen. The mixture was stirred in the dark, under nitrogen at 60°C for 1 day. Upon dropwise addition of this solution to methanol a yellow precipitate formed. The polymer was washed four times with methanol until the filtrate was colorless, and dried in the vacuum oven overnight at room temperature. 7.73 g (85%) of copolymer **114** was obtained which contained 3.01% N (2.15 meq/gP), and no Cl. The modified polymer was only soluble in DMF and DMSO.[M_n=6.87 x 10^4 (calculated from **113**)]

FT-IR (KBr pellet): 1700 cm^{-1} (s, C=O aldehyde); 1583 cm^{-1} (vs, C=C); 1330 & 1286 cm^{-1} (vs, NO_2); 1232 & 1034 cm^{-1} (vs, C-O-C ether); 849 cm^{-1} (m, C-H p-disubst. aromatic); 759 & 700 cm^{-1} (s, C-H m-disubst. aromatic).

UV Spectrum (1.04 μm film): 265 nm (cut-off), 324 nm (A=2.00).

Preparation of 2-Hydroxy-3-phenoxypropyl Methacrylate (**116**):

This compound was prepared by a modification of the procedure of Masuhara et al.[94] Into a two-necked 25 mL round-bottomed flask equipped with an air condenser and nitrogen inlet and

outlet was added 5.00 g glycidyl methacrylate (115), 3.64 g phenol (106) and 0.10 g of triethylbenzyl ammonium chloride (TEBAC). The mixture was heated to 85 °C and allowed to react under nitrogen for three hours after which time a TLC using a 6:4 hexane/ethyl acetate mixture as eluting solvent, indicated the absence of starting material and the presence of a slower moving product. A non-mobile polymeric component was also observed using this same solvent system. The mixture was poured into benzene and extracted twice with 50 mL of 2N NaOH solution. The benzene layer was dried with $MgSO_4$ and the solvent evaporated off to give a colorless syrup. Column chromatography using a 70:30 hexane/ethyl acetate mixture as eluting solvent yielded 5.20 g (61%) of pure 2-hydroxy-3-phenoxypropyl methacrylate (**116**).

FT-IR (NaCl, neat): 3452 cm^{-1} (s, O-H); 1719 cm^{-1} (vs, C=O ester), 1638 cm^{-1} (m, C=C vinylic); 1321 cm^{-1} (s, C-O 1° alcohol), 1296 & 1172 cm^{-1} (vs, C-O ester), 1246 & 1046 cm^{-1} (s, C-O-C ether).

^1H NMR ($CDCl_3$): 1.95 δ(3H, s, $-CH_3$), 2.88δ (1H, s, -OH), 3.77-4.46δ (5H, m, propyl H's), 5.50δ (1H, s, vinylic trans C-H), 6.08δ (1H, s, vinylic cis C-H), 6.80-7.40δ (5H, m, aromatic).

M. S.: m/e 236 (M^+), 143 (base peak, $C_7H_{11}O_3^+$), 94 (C_6H_5OH), 69 (base peak, $C_4H_5O^+$), 41 ($C_3H_5^+$).

Polymerization of Monomer **116**:

Into a 15 mL three-necked round-bottomed flask equipped with nitrogen inlet and outlet was added 2.85 g monomer and 0.0285 g AIBN. The mixture was heated at 78°C for 24 hours. The solid polymeric mass was dissolved in CH_2Cl_2 and precipitated slowly

into petroleum ether. The precipitate so obtained was washed twice with additional petroleum ether, and dried in the vacuum oven overnight to give a white polymer weighing 2.70 g (95%). Elemental analysis for C and H gave results of 63.82 (64.10%) and 6.83% (6.82%) respectively for homopolymer 117.

FT-IR (KBr pellet): 3459 cm^{-1} (s, O-H); 1729 cm^{-1} (vs, C=O ester); 1297 (w), 1245 & 1047 cm^{-1} (vs, C-O-C ether); 1173 & 1155 cm^{-1} (vs, C-O ester).

^{13}C NMR ($CDCl_3$): 17.78 δ (bs, $-CH_3$), 30.91 δ (s, β-CH_2), 45.06 δ(s, α-C), 64.0-72.2 δ (m, propyl C's), 115.09 δ(114.1, d, aromatic C2a), 121.34 δ(120.8, d, aromatic C4a), 131.23δ(129.5, d, aromatic C3a), 158.26δ(159.9, s, aromatic C1a), 177.57 & 177.74δ(2 singlets, C=O).

Preparation of 2-Hydroxy-3-p-nitrophenoxypropyl Methacrylate (119):

5.00 g glycidyl methacrylate (115), 5.38 g p-nitrophenol (107) and 0.0890 g TEBAC were combined in a two-necked round-bottomed flask equipped with an air-cooled condenser and nitrogen inlet and outlet. The mixture was heated at 85°C for 3 hours with continuous stirring. During this time, the solution became very viscous. A TLC obtained using a 6:4 hexane/ethyl acetate mixture indicated the absence of starting material, the presence of a slower moving product and an intense polymeric non-mobile component. The viscous yellow reaction mixture was insoluble in benzene but dissolved readily in $CHCl_3$. Extraction with a 2% NaOH solution followed by drying with $MgSO_4$ and separation by column chromatography using a 10% solution of ethyl acetate in

hexane yielded 1.72 g (17%) of pure 2-hydroxy-3-p-nitrophenoxypropyl methacrylate (**119**).

FT-IR (KBr pellet): 3469 cm^{-1} (m, O-H); 1713 cm^{-1} (vs, C=O ester); 1631 cm^{-1} (m, C=C vinylic); 1507 & 1350 cm^{-1} (vs, NO_2); 1325 cm^{-1} (s, O-H); 1299 & 1175 cm^{-1} (s, C-O ester); 1262 & 1047 cm^{-1} (vs, C-O-C ether).

^1H NMR ($CDCl_3$): 1.96δ (3H, s, $-CH_3$), 3.18δ (1H, s, -OH), 3.90-4.51δ (6H, m, propyl H's), 5.60δ (1H, s, trans vinylic C-H), 6.14δ (1H, s, cis vinylic C-H), 6.96δ (2H, d, aromatic, J=9.0 Hz), 8.16δ (2H, d, aromatic, J=9.0 Hz).

M. S.: m/e 281 (M^+), 143 ($C_7H_{11}O_3^+$), 69 (base peak, $C_4H_5O^+$), 41 ($C_3H_5^+$), 30 (NO).

Polymerization of Monomer **119**:

To 10 mL of toluene was added 1.05 g of monomer **119** and 0.0110 g of AIBN. The mixture was heated to 75°C, and left stirring under nitrogen for 24 hrs. During this polymerization period, a polymer-like residue had precipitated onto the walls of the flask. The residue was redissolved upon addition of CH_2Cl_2 to the reaction mixture. Evaporation of the solvents gave a spongy light yellow residue. The residue was then dissolved in THF and precipitated in ether. Subsequent washing and overnight drying at room temperature gave 0.80 g (76%) of polymer (**120**) containing 4.90% C (4.98%), 55.40% H (55.53%) and 5.46% N (5.38%).

FT-IR (KBr pellet): 3486 cm^{-1} (s, O-H); 1730 cm^{-1} (vs, C=O ester); 1513 & 1344 cm^{-1} (vs, NO_2), 1299 & 1174 cm^{-1} (s, C-O ester); 1264 & 1034 cm^{-1} (s, C-O-C ether).

^{13}C NMR (Acetone-d_6): 15.61δ (q, $-CH_3$), 45.60 & 45.93δ (2 singlets, α-C), 66.10 δ (t, $-CH_2-O-$), 68.24δ (d, -CH-), 71.06 δ (t, $-CH_2-OCO-$), 115.73 δ (115.0, d, aromatic C2a), 126.59δ (124.7, d, aromatic C3a), 142.36δ (140.8, s, aromatic C4a), 164.80 δ (165.7, s, aromatic C1a), 178.14 & 178.32δ (2 singlets, C=O).

Attempted Preparation of 2-Hydroxy-3-(3-formyl-4-nitrophenoxy)-propyl Methacrylate (118):

1.25 g glycidyl methacrylate (115), 1.62 g 5-hydroxy-2-nitrobenzaldehyde (101) and 0.0890 g TEBAC were combined in a 10 mL round-bottomed flask equipped with a condenser and a nitrogen inlet-outlet. The reaction mixture was heated to 85°C for 1 hour, after which time a solid viscous mass was obtained. From a TLC obtained of the reaction mixture using a 6:4 hexane/ethyl acetate mixture as eluting solvent, it was apparent that no glycidyl methacrylate monomer remained, although some 5-hydroxy-2-nitrobenzaldehyde was detectable. An intense non-mobile spot at the origin confirmed polymerization had occured. When the reaction was repeated at a reaction temperature of 50 or 70°C, the same result was obtained.

Preparation of 2-Tosylethyl Methacrylate (121):

A solution of 6.10 g hydroxyethyl methacrylate in 85 mL of dry pyridine was cooled to 0°C in an ice bath and treated with 13.41 g p-tosyl chloride. The reaction mixture was placed in the refrigerator for 39 hours during which time pyridine hydrochloride crystallized out of solution. The solution was extracted with ether three times. Extraction of the combined ethereal extracts twice with 100 mL of a 1:1 hydrochloric acid/water

mixture was followed by a single water extraction. The ethereal solution was then dried over K_2CO_3/Na_2SO_4 and the solvent removed on the evaporator to yield the crude yellow tosylate oil. The residue was immiscible in petroleum ether. The tosylate was purified by addition of petroleum ether to the oil, then slowly cooling the mixture to -75°C, and decanting off the supernatant. Removal of the trace petroleum ether under high vacuum left 10.64 g (80%) of 2-tosylethyl methacrylate (121).

FT-IR (NaCl, neat): 1723 cm^{-1} (vs, C=O ester); 1637 cm^{-1} (m, C=C vinylic); 1360 cm^{-1} (s, S=O); 1320 & 1297 cm^{-1} (s, C-O ester); 923, 816 & 772 cm^{-1} (s, S-O).

^1H NMR ($CDCl_3$): 1.86 δ (3H, s, $-CH_3$), 2.39 δ (3H, s, tosyl $-CH_3$), 4.21δ (4H, s, $-CH_2-CH_2-$), 5.49 δ (1H, s, trans vinylic C-H), 5.96δ (1H, s, cis vinylic C-H), 7.22δ (2H, d, aromatic, J=8.6 Hz), 7.66δ (2H, d, aromatic, J=8.6 Hz).

M. S.: m/e 284 (M^+), 155 ($C_7H_7SO_2^o$, 112 (base peak,), 91 ($C_7H_7^+$), 69 (base peak, $C_4H_5O^+$), 41 ($C_3H_5^+$).

Preparation of 2-Chloroethyl Methacrylate (122):

30.00 g of methacrylic acid, 28.00 g of 2-chloroethanol, 0.52 g hydroquinone, 1.50 g H_2SO_4 and 50 mL toluene were loaded into a 200 mL round-bottomed flask equipped with an azeotropic side arm and condenser. The mixture was refluxed until 6.2 mL of water had been produced. The two phases were separated and the organic phase extracted two times with 50 mL of a 5% aqueous K_2CO_3 solution, followed by one extraction with a brine solution, and two water extractions. The organic mixture was then dried with anhydrous $MgSO_4$ and the toluene evaporated under vacuum to

give a yellow residue. Fractional distillation of the crude product gave 22.61 g (54%) of 2-chloroethyl methacrylate (**122**) (b.p. 56.5-57.5 °C, 5 mm Hg).

FT-IR (NaCl, neat): 1722 cm^{-1} (vs, C=O ester), 1639 cm^{-1} (s, vinylic C=C), 1324 & 1284 cm^{-1} (vs, C-O ester), 669 cm^{-1} (s, C-Cl).

^1H NMR ($CDCl_3$): 1.96δ (3H, s, $-CH_3$), 3.69δ (2H, t, $-CH_2-$), 4.38δ (2H, t, $-CH_2-$), 5.60δ (1H, s, trans vinylic C-H), 6.14δ (1H, s, cis vinylic C-H).

M. S.: m/e 148 (M^+), 113 ($C_6H_9O_2^+$), 69 (base peak, $C_4H_5O^+$), 41 ($C_3H_5^+$), 36 (HCl).

Preparation of 2-Phenoxyethyl Methacrylate (123):

(1) by chloride displacement:

0.94 g phenol, 0.60 g NaOH, 3.71 g of **122**, and 0.32 g of Bu_4NBr were added to 50 mL CH_2Cl_2 and 50 mL water in a 250 mL round-bottomed flask. The mixture was stirred magnetically at room temperature for 20 hours. The two phases were separated and the aqueous phase washed twice with 25 mL portions of CH_2Cl_2. Combining and flash evaporating the organic extracts gave a clear colourless liquid. This residue was dissolved in 40 mL of ether and then extracted twice with 25 mL of 2 N NaOH solution and once with brine. The ethereal solution was then dried with anhydrous $MgSO_4$, filtered to remove the drying agent and the solvent evaporated. Column chromatography of the crude mixture using hexane as the eluting solvent afforded 1.15 g (56%) of 2-phenoxyethyl methacrylate (**123**).

(2) by displacement of tosylate in DMF:

To 5 mL of DMF in a 25 mL 3-necked round-bottomed flask, equipped with a condenser and nitrogen inlet and outlet was added 0.76 g phenol and 3.30 g anhydrous K_2CO_3. The suspension was stirred for 5 minutes and then 2.25 g of 2-tosylethyl methacrylate was added. Stirring was left to continue for 44 hours at room temperature. A TLC obtained using a 6:4 hexane/ethyl acetate mixture as eluting solvent indicated the presence of a new faster moving product in small amounts with most of the starting material remaining. The reaction was dumped into 50 mL of water, and extracted four times with 50 mL of CH_2Cl_2. The organic phase was dried with $MgSO_4$, filtered, and the solvent evaporated, leaving a yellow residue. Isolation by column chromatography using a 20:80 hexane/ethyl acetate mixture as eluting solvent gave 0.60 g (10.5%) of **123.**

(3) by displacement of tosylate under phase transfer conditions:

0.38 g phenol, 5 mL DMF, 1.65 g K_2CO_3, 1.12 g of 2-tosylethyl methacrylate were combined with 0.0521 g 18-crown-6 and reacted as outlined above. Isolation of the desired product was carried out as outlined above. Column chromatography using an 8:2 hexane/ethyl acetate mixture as the eluting solvent gave 0.43 g (50%) of **123.**

FT-IR (NaCl, neat): 1721 cm^{-1} (vs, C=O ester); 1639 cm^{-1} (m, C=C vinylic); 1294 & 1164 cm^{-1} (s, C-O ester); 1248 & 1086 cm^{-1} (s, C-O-C ether); 754 & 692 cm^{-1} (s, C-H monosubst. aromatic).

^{1}H NMR ($CDCl_3$): 1.93 δ (3H, s, $-CH_3$), 4.15δ (2H, t, $-CH_2-$), 4.44δ (2H, t, $-CH_2-$), 5.50δ (1H, s, trans vinylic C-H), 6.09δ (1H, s, cis vinylic C-H), 6.67-7.46 δ (5H, m, aromatic).

M. S.: m/e 206 (M^+), 113 (base peak, $C_6H_9O_2^+$), 69 ($C_4H_5O^+$), 65 ($C_5H_5^+$).

Solid-State Photochemistry of Copolymer 114:

A 20% solution of copolymer **114** in DMF gave 1.04 μm thick films on NaCl disks and quartz wafers when spun at 4000 rpm for 30 seconds. The films were prebaked for 20 minutes at 100°C and exposed. The quartz wafers were exposed to doses of unfiltered light ranging from 0 to 259 mJ/cm^2, with UV spectra recorded at regular intervals. The NaCl disks were exposed to doses ranging between 0 and 2.16 J/cm^2. Spectral data confirmed the formation of the rearranged 2-nitroso-5-(m & p)-vinylbenzyloxybenzoic acid (**124**) with some subsequent formation of the diazo bridging cross-linked product (**125**), and some remaining unreacted monomer units of **114**. Little further change was observed in the IR spectra of the film after the initial 832 mJ/cm^2. The IR changes observed in this study are shown in Figure 18.

FT-IR (NaCl, 1.04 μm, dose=499 mJ/cm^2): 1740 cm^{-1} (s, C=O carboxylic acid); 1700 cm^{-1} (m, C=O aldehyde); 1574 cm^{-1} (m, N=N diazo group); 1516 & 1329 cm^{-1} (m, NO_2); 1493 cm^{-1} (vs, R-N=O nitroso); 1289 cm^{-1} (s, C-O carboxylic acid); 1234 & 1060 cm^{-1} (s, C-O-C ether).

UV Spectrum (1.01 μm, dose=259 mJ/cm^2): 268 nm (cut-off), 342 nm (A=1.98).

Lithographic Testing of Copolymer 114:

While under yellow light, 0.95 μm thick films of 114 were cast onto silicon wafers from a 15% diglyme solution using a spin-speed of 3000 rpm for 30 seconds. Films of 114 were pre-baked at 100°C for 5 and 10 minutes, and their dissolution rate in the casting solvent compared to that of an unbaked film. After 5 minutes time in diglyme, 50% of the film thickness remained in all three cases. Imaging experiments were attempted using both 166 and 333 mJ/cm^2 doses of unfiltered UV light. A faint distorted negative image was obtained upon development in a 2:1 n-butyl acetate/methylene chloride developer, although the films were not completely removed in the unexposed areas of the film. No image was obtained upon development in either a 5% aqueous NaOH solution or a 5% ethanolic NaOH solution. All of these experiments indicated that some spontaneous cross-linking reaction occurred even prior to exposure.

E-Beam Degradable Methyl Methacrylate Analogs

Polymerization of Methyl α-(trifluoromethyl)acrylate:

Methyl α-(trifluoromethylacrylate) (MTFMA) (**130**) was synthesized by a modification of the method of Buxton et al.[99], outlined in a recent publication by Ito, Willson, and Miller[17]. The monomer was polymerized in high vacuum under scrupulously anhydrous conditions using pyridine as catalyst as outlined in the above publication. Polymerization of 6.68 g of MTFMA yielded 2.5 g (37.4%) of poly-(methyl α-trifluoromethylacrylate) (PMTFMA) (**130**). [M_n=1.72 x 10^4 (osm. & gpc) and M_w=2.23 x 10^4, polydispersity=1.30 (gpc)]

Radical Copolymerization of MTFMA and Methyl Methacrylate:

Radical copolymerizations of MTFMA with methyl methacrylate (MMA) were carried out in bulk with benzoyl peroxide as initiator at 60°C as outlined by Ito et al.[17] For example, copolymerization of 1.30 g MTFMA with 0.39 g MMA gave 0.67 g (40%) of methanol insoluble copoly-(methyl methacrylate-methyl α-trifluoromethylacrylate) (P(MTFMA-MMA)) (**131a**). [M_n=1.06 x 10^5 (osm. & gpc), M_w=2.42 x 10^5, polydispersity=2.24 (gpc)] The mole fraction of MTFMA in this copolymer was 0.36 as determined by ^{13}C NMR.

Measurement of Gs and Gx for **130** and **131a-d**:

Samples of **130** and **131a-d** of varying compositions were sealed in glass tubes under high vacuum, and were subjected to varying doses of ^{60}Co γ-radiolysis. Molecular weight determination of the irradiated samples by osmometry and gpc, permitted the calculation of the Gs and Gx values as a function of composition. The results are shown in Figure 20.

E-Beam Lithographic Testing of PMTFMA (130):

A 30% solution of **130** in diglyme was prepared. Polymer films of approximately 1 μm in thickness were obtained by depositing a drop of polymer solution onto a silicon wafer and spinning at 2000 rpm for 30 seconds. The films were prebaked at 100°C for 30 minutes to remove any remaining solvent. The standard Kyser 5-Line e-beam pattern, consisting of grouped and isolated lines of varying line widths (4, 2, 1, 0.5, & 0.25 μm) was used. Exposure doses studied ranged between 5 and 20 $\mu c/cm^2$. Images were developed by either dip or spray development.

(a) Dip Development: Exposed 1.10 μm thick films of **130** on silicon wafers were developed in 3-heptanone at 40°C, rinsed in isopropanol, and dried in a nitrogen stream. After 1 minute in the developer, the 10 and 20 $\mu c/cm^2$ patterns were resolved down to 1 μm, with an unexposed film thickness of 0.95 μm. The same patterns were resolved down to a line width of 0.50 μm after 90 seconds in the developer. After 3 minutes, and a decrease in film thickness to 0.56 μm, the lower dose patterns remained undeveloped. Observation of the developed patterns using both light and electron microscopy indicated the presence of precipitated and redeposited blotches of polymer.

(b) Spray Development: Exposed 1.10 μm thick films of **130** on silicon wafers were spun on a spin-coater at 700 rpm and developed with a continuous stream of 3-heptanone at 25°C for the desired time. Rinsing was started with a stream of isopropanol, as the developer flow was slowly reduced, then stopped. The wafer was then dried by continued spinning in a nitrogen stream. After

1 minute in the developer, the 10 and 20 $\mu c/cm^2$ patterns were resolved down to 0.5 μm with an unexposed film thickness of 1.05 μm. Overdevelopment of the higher dose patterns occured after 1 minute. The 10 $\mu c/cm^2$ patterns were cleared down to 1 μm line width after a 2 minute development and an unexposed film thickness of 0.95 μm. Cleaner patterns were observed with spray development than were obtained in part (a). Electron micrographs of the 10, 15 and 20 $\mu c/cm^2$ images were obtained and are shown in Figure 21.

E-Beam Lithographic Testing of P(MTFMA-MMA) (131a):

A 10% solution of 131a in chlorobenzene gave 1.01 μm thick films on silicon wafers when deposited and prebaked as outlined above. Kyser 5-Line pattern exposures identical to those outlined above were prepared. A 2.5 minute spray development using the same procedures as above with a 3:1 hexyl acetate/3-heptanone solution and isopropanol wash gave resolution of the 15 and 20 $\mu c/cm^2$ patterns down to a line width of 1 μm. The corresponding unexposed film thickness was 0.93 μm. Further spraying resulted in overdevelopment of the higher dose patterns and extensive damage to the unexposed film surface, without resolution of the 5 and 10 $\mu c/cm^2$ doses. Electron micrographs of the 20 $\mu c/cm^2$ images were obtained, and are shown in Figure 22.

CLAIMS TO ORIGINAL RESEARCH

- Solid-state photochemical studies of the photo-Fries rearrangement.

- Design of novel photosensitive polymers containing o-nitrobenzyl moieties.

- Study of the imaging of methyl α-trifluoromethylacrylate e-beam resists.

REFERENCES

1) C. G. Willson. in Introduction to Microlithography. Edited by L. F. Thompson, C. G. Willson, and M. J. Bowden. ACS Symposium Series 219, Washington. 1983. p. 88.

2) O. Süs and W. Schaefer. U. S. Patent 3,092,494 (1963).

3) M. F. Drum and J. R. Leblanc. in Step-Growth Polymerizations. Edited by D. H. Solomon. Dekker Press, New York. 1973.

4) W. S. DeForest. Photoresist: Materials and Processes. McGraw-Hill, New York. 1975. p. 49.

5) O. Süs. Justus Liebigs Annalen der Chemie. **556**, 65 (1944).

6) J. Pacansky and J. R. Lyerla. IBM J. Res. Develop. **23**, 1 (1979).

7) I. Haller, M. Hatzakis, and R. Srinivasan. IBM J. Res. Develop. **12**, 251 (1968).

8) M. Dole. The Radiation Chemistry of Macromolecules. Vol. 1. Academic Press, New York. 1972.

9) H. Hiraoka. IBM J. Res. Develop. **21**, 121 (1977).

10) W. Moreau, D. Merritt, W. Moyer, M. Hatzakis, D. Johnson, and L. Pederson. J. Vac. Sci. Technol. **16**, 1989 (1979).

11) T. Tada. J. Electrochem. Soc. **126**, 1829 (1979); M. Kakuchi, S. Sugawara, K. Murase, and K. Matsuyama. J. Electrochem. Soc. **124**, 1648 (1977).

12) J. N. Helbert, E. H. Poindexter, G. A. Stahl, C. Y. Chen, and C. U. Pittman. J. Polym. Sci. Chem. Ed. **17**, 49 (1979).

13) J. N. Helbert, E. H. Poindexter, C. U. Pittman, and C. Y. Chen. Pol. Eng. Sci. 20 (1980).

14) J. N. Helbert, C. Y. Chen, C. U. Pittman, and G. L. Hagnauer, Macromolecules **11**, 1104 (1978).

15) C. U. Pittman, M. Ueda, C. Y. Chen, J. H. Kwiatkowski, C. F. Cook, and J. N. Helbert. J. Electrochem. Soc. **128**, 1758 (1981).

16) J. H. Lai, J. N. Helbert, C. F. Cook, and C. U. Pittman. J Vac. Sci. Technol. **16**, 1992 (1980).

17) H. Itō, D. C. Miller and C. G. Willson. Macromolecules **15**, 915 (1982).

18) A. H. Blatt. Org. Reactions. 1, 342 (1942).

19) H. J. Shine. MTP Int. Rev. Sci.: Org. Chem., Ser. One. **3**, 65

(1973).

20) J. C. Anderson and C. B. Reese. Proc. Chem. Soc. 217 (1960).

21) H. Kobsa. J. Org. Chem. **27**, 2293 (1962).

22) D. Bellus and P. Hrdlovic. Chem. Rev. **67**, 599 (1967).

23) D. Bellus. Adv. Photochem. **8**, 109 (1971).

24) C. Pac and S. Tsutsomi. Bull. Chem. Soc. Jpn. **37**, 1392 (1964).

25) D. P. Kelley and J. T. Pinkey. Tetrahedron Lett. 3427 (1964).

26) H. Obara, H. Takahashi, and H. Hirano. Bull. Chem. Soc. Jpn. **42**, 560 (1969).

27) D. Elad, D. V. Rao, and V. I. Stenberg, J. Org. Chem. **30**, 3252 (1965).

28) R. A. Finnegan and J. J. Mattice. Tetrahedron, **21**, 1013 (1965).

29) J. C. Anderson and C. B. Reese, J. Chem. Soc. 1781 (1963).

30) M. R. Sandner, E. Hedaya, and D. J. Trecker. J. Am. Chem. Soc. **89**, 5725 (1967).

31) J. W. Meyer and G. S. Hammond. J. Am. Chem. Soc. **94**, 2219 (1972).

32) C. E. Kalmus and D. M. Hercules. J. Am. Chem. Soc. **96**, 449 (1974).

33) W. M. Horspool and P. L. Pauson. J. Chem. Soc. 5162 (1965).

34) V. A. Kuz'min, I. V. Khudyakov, G. Hageman, P. P. Levin, K. De Jonge. Izv. Akad. Nauk SSR, Ser. Khim. 1148 (1979).

35) R. A. Finnegan and D. Knudson. Tetrahedron Lett. 3429 (1968).

36) H. J. Hageman. Tetrahedron **25**, 6015 (1969).

37) J. S. Bradshaw, E. L. Loveridge, and L. White. J. Org. Chem. **33**, 4127 (1968).

38) V. P. Pathak and R. N. Khanna. Synthesis **11**, 882 (1981).

39) C. E. Kalmus and D. M. Hercules. Tetrahedron Lett. 1575 (1972).

40) D. J. Carlsson, L. H. Gan, and D. M. Wiles. Can. J. Chem.

53, 2337 (1975).

41) J. S. Bradshaw, R. D. Knudsen and E. L. Loveridge. J. Org. Chem. 35, 1219 (1970).

42) H. Shizuka and I. Tanaka. Bull. Chem. Soc. Jpn. 41, 2343 (1968).

43) S. B. Maerov. J. Polym. Sci., Part A. 3, 487 (1965).

44) D. Bellus, P. Slama, P. Hrdkovic, Z. Manasek, and L. Durisinova. J. Polym. Sci., Part C. 22, 629 (1969).

45) S. M. Cohen, R. H. Young, and A. H. Markhart. J. Polym. Sci., Part A-1. 9, 3263 (1971).

46) D. J. Carlsson, L. H. Gan, and D. M. Wiles. J. Polym. Sci. Polym. Chem Ed. 16, 2353 (1978).

47) N. S. Allen. Polymer Photochemistry 3, 167 (1983).

48) B. Ranby and J. F. Rabek. Photodegradation, Photooxidation and Photostabilization of Polymers. Willey Press, New York. (1975).

49) M. Okawara, S. Tani, and E. Imoto. Kogyo Kagaku Zasshi. 68, 223 (1965).

50) S.-K. L. Li and J. E. Guillet. Macromolecules. 10, 840 (1977).

51) E. G. Gilazhov, N. P. Ivanova, N. V. Zubko, and I. A. Arbuzova. Akad. Nauk. Kaz. SSR, Ser. Khim. 28, 81 (1978).

52) E. G. Gilazhov, N. P. Ivanova, N. V. Zubko, and I. A. Arbuzova. Plast. Massy 6, 26 (1979).

53) J. E. Guillet, L. Merle-Aubry, D. A. Holden, and Y. Merle. Macromolecules 13, 1138 (1980).

54) G. Ciamician and P. Silber. Ber. 34, 2040 (1901).

55) I. Tanasescu and M. Ionescu. Bull. Soc. Chim. Fr. 84 (1946).

56) G. W. Wubbels, R. R. Hautala, and R. L. Letsinger. Tetrahedron Lett. 1689 (1970).

57) E. J. Bowen, H. Hartley, W. D. Scott, and H. G. Watts. J. Chem. Soc. 125, 1218 (1924).

58) P. Leighton and F. A. Lucy. J. Chem. Phys. 2, 756 (1934).

59) L. I. Samokhvalova and V. A. Krongauz. Dokl. Akad. Nauk. SSR. 177, 1134 (1967).

60) J. G. Calvert and J. N. Pitts. Photochemistry, John Wiley and Sons, New York. 1966. p. 478.

61) A. A. Pashayan, A. L. Prokhoda, S. A. Sarkisyan. Khim. Vys. Energ. **11**, 56 (1977).

62) P. de Mayo and W. Reid. Quart. Reviews **15**, 414 (1961).

63) R. O. Kan. Organic Photochemistry, M^{c}Graw Hill, New York. 1961. p 218.

64) D. C. Neckers. Mechanistic Organic Photochemistry. Reinhold Publishing Corp., New York. p. 207 (1967).

65) P. Coppens and A. J. Tench. U. S. At. Energy Comm. BNL-6161, 8 (1961). Chem. Abstr. 60:14356e.

66) W. G. Filby and K. Günther. Z. Naturforsch., Teil B. **28**, 810 (1973).

67) H. Mauser and H. Heitzer. Z. Naturforsch., Teil B. **21**, 109 (1966).

68) A. A. Pashayan, A. L. Prokhoda and V. A. Krongauz. Khim. Vys. Energ. **10**, 155 (1976).

69) E. Havinga, R. O. De Jongh and W. Dorst. Rec. Trav. Chim. Pays-Bas, **75**, 378 (1956).

70) H. Barzynski and D. Saenger. Angew. Makromol. Chem. **93**, 131 (1981).

71) B. B. Corson, W. J. Heintzelman, L. H. Schwartzman, H. E. Tiefenthal, R. J. Lokken, J. E. Nickels, G. R. Atwood, and F. J. Pavlik. J. Org. Chem. **23**, 544 (1958).

72) R. Broos and M. Anteunis. Synth. Comm. **6**, 53 (1976).

73) J. H. Boyer and H. Alul. J Am. Chem. Soc. **68**, 2136 (1946).

74) S. Sofuku, I. Muramatsu, and A. Hagitani. Bull. Chem. Soc. Jpn. **40**, 2942 (1967).

75) W. Stevens and A. Van Es. Rec. Trav. Chim. **84**, 1247 (1965).

76) W. Stevens and A. Van Es. Rec. Trav. Chim. **83**, 1294 (1964).

77) J. M. J. Frechet, E. Eichler, H. Ito, and C. G. Willson. Polymer. **24**, 995 (1983).

78) M. Oki and H. Nakanishi. Bull. Chem. Soc. Jpn. **43**, 2558 (1970).

79) M. Oki and M. Hirota. Bull. Chem. Soc. Jpn. **33**, 119 (1960). and Bull. Chem. Soc. Jpn. **34**, 374 (1961).

80) H. Kessler and A. Rieker. Ann. Chem. **708**, 57 (1967).

81) G. Sumrell, P. G. Campbell, G. E. Ham and C. H. Schramm. J. Am. Chem. Soc. **81**, 4310 (1959).

82) S. Patai, M. Bentov, and M. E. Reichman. J. Am. Chem. Soc. **74**, 845 (1952).

83) F. W. Wehrli and T. Wirthlin. Interpretation of Carbon-13 NMR Spectra. Heyden and Son Ltd., London. 1980. p. 47.

84) H. Hiraoka and J. Pacansky. J. Electrochem. Soc. **128**, 2645 (1981).

85) V. M. Parikh. Absorption Spectroscopy of Organic Molecules. Addison-Wesley Publishing Company, Toronto. 1974. p.18.

86) R. Chênevert and R. Plante. Can. J. Chem. **61**, 1092 (1983).

87) The Aldrich Library of Infrared Spectroscopy of Organic Molecules. Edited by C. J. Pauchert. Addison-Wesley Publishing, Toronto. 1974. p. 18.

88) M. Fischer. Tetrahedron Lett. 4295 (1968).

89) H. J. Hageman. Recueil **91**, 1447 (1972).

90) A. M^{c}Killop, J. C. Fiaud, and R. P. Hug. Tetrahedron. **30**, 1379 (1974).

91) E. D'Incan and P. Viout. Tetrahedron. **31**, 159 (1975).

92) N. Kornblum, P. J. Berrigan, and W. J. Le Noble. J. Am. Chem. Soc. **85**, 1141 (1963).

93) A. Ek and B. Witkop. J. Am. Chem. Soc. **76**, 5579 (1954).

94) E. Masuhara, N. Nakabayashi, K. Furuta. Yuki Gosei Kagaku Kyokai Shi. **33**, 53 (1975).

95) H. Ito and C. G. Willson. unpublished results.

96) M. Pauler and P. Bergthaller. Monatsh. Chem. **99**, 103 (1968).

97) M. A. Askarov and S. R. Pinkhasov. Khim. i Fiz-Khim. Prirodn. Sintetich. Polimerow, Akad. Nauk. Uz. SSR, **2**, 142 (1964).

98) F. Tomita, M. Shimizu, and S. Kiriyama. Japan Kokai 76 36,932.

99) W. Buxton, M. Stacey, and J. C. Tatlow. J. Chem. Soc. 366 (1954).

100) C. U. Pittman, C. Y. Chen, M. Ueda, and J. N. Helbert. Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem. **20**, 602 (1979).

101) C. G. Willson, H. Ito, D. C. Miller and T. G. Tessier. SPE 6th International Photopolymer Conference. Ellenville, New York. 1982.

102) C. U. Pittman, M. Iqbal, C. Y. Chen, and J. N. Helbert. J. Polym. Sci. Polym. Chem. Ed. 16, 2721 (1978).