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LIST OF ABBREVIATIONS

asym: asymmetric

CH_a-CH_a: axial-axial protons on adjacent carbons

CH_e-CH_e: equatorial-equatorial protons on adjacent carbons

^{13}C-NMR: carbon-13 nuclear magnetic resonance

D: polydispersity (Mw/Mn)

DB: double bond

deep UV: ultra-violet below 300 nm

DMF: dimethylformamide

DMSO-d_6: hexadeuterated dimethylsulfoxide

DSC: differential scanning calorimetry

EA: elemental analysis

e-beam: electron beam

GC-MS: gas chromatography-mass spectroscopy

GPC: gel permeation chromatography

IR: infrared

KeV: kiloelectron volt

^{1}H-NMR: proton nuclear magnetic resonance

PBOCST: poly(p-t-butyloxycarbonyloxystyrene)

PHOST: poly(p-hydroxystyrene)

PPA: polyphthalaldehyde

min: minute

mJ/cm^2: millijoules per centimeter square

mm Hg: millimetre of mercury

mmoles: millimoles

Mn: number-average molecular weight

MS: mass spectroscopy

MW: molecular weight

Mw: weight-average moleculat weight

N: normality

RPM: revolution per minute

sym: symmetric

t-BOC: t-butyloxycarbonyl group

Tc: ceiling temperature

Tg: glass transition temperature

TGA: thermogravimetric analysis

THF: tetrahydrofuran

Tm: crystalline melting temperature

$\mu C/cm^2$: microcoulombs per centimetre square

wt: weight

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ABSTRACT

Linear polycarbonates containing tertiary, secondary benzylic or allylic carbonate units are synthesized using catalyzed phase-transfer polycondensation of biscarbonylimidazolides or bis-p-nitrophenylcarbonate derivatives of active diols with a variety of diols.

These polymers undergo depolymerization when exposed to thermolytic or acidolytic conditions.

The thermal degradation of these polycarbonates is studied by thermogravimetry as well as gas chromatography-mass spectroscopy.

INTRODUCTION

Recent advances in the fabrication of microelectronic devices have required the development of new resist material which incorporate both improved resolution and increased sensitivity to meet the need for the production of smaller and smaller devices while maintaining acceptable throughput. At the present time, state of the art microelectronic devices have minimum features which approach 1 μm in production environment. The printing of such small three-dimentional features which are only twice the wavelength of visible light requires new developments in the design of resist materials.

One approach to higher resolution has been to develop materials which are sensitive to electron beams or X-rays; however, the very complex exposure systems which are required currently have a low intrinsic productivity.

Another approach to increased resolution is to use materials which can be exposed using shorter wavelength "deep-UV" radiation. A major limitation with such an approach is again that the flux available from conventional sources, such as those used in projection printing devices, is very low in the deep-UV (figure 1). To maintain high productivity while operating in the deep-UV requires that high resolution resists with greatly improved sensitivities be designed.

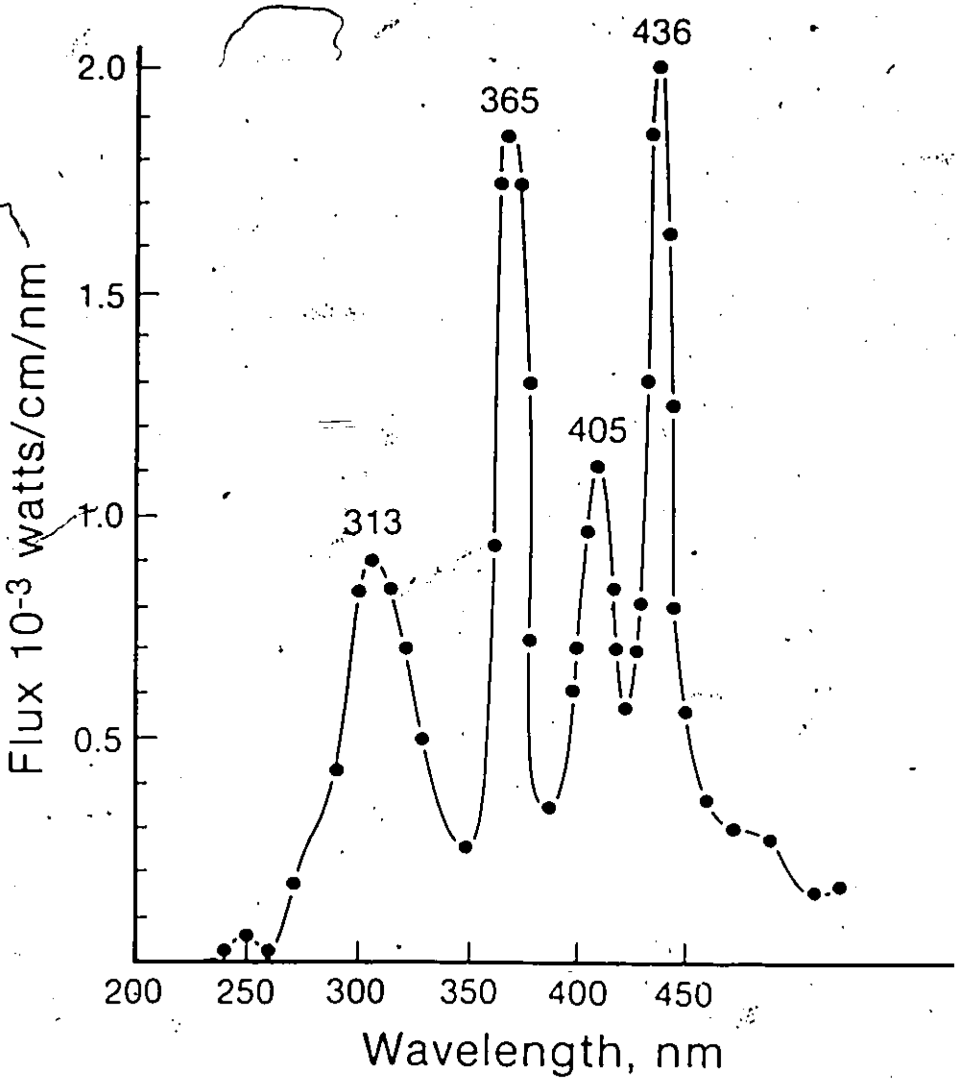


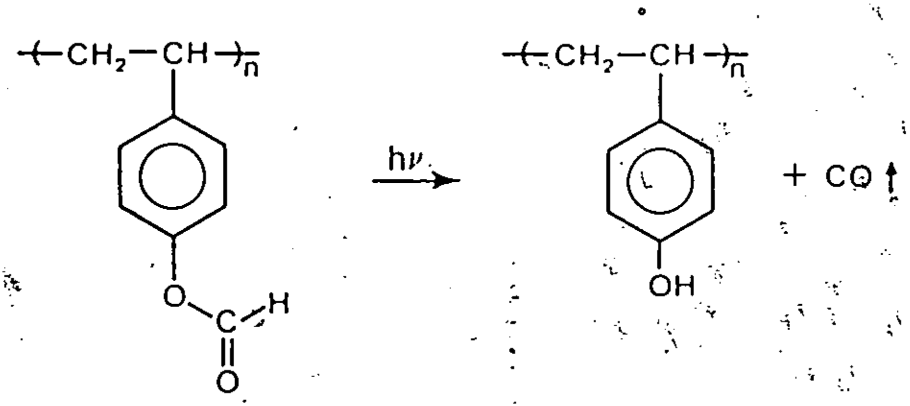
Figure 1 UV lamp spectrum

One approach towards the design of novel radiation-sensitive polymers has been to develop systems which incorporate chemical amplification (1). Some interesting new developments in the chemistry of negative tone photoresists have resulted in the optimization of high sensitivity systems such as the halogenated polystyrenes which operate on the basis of radiation-induced crosslinking (2-5). However, these systems suffer from a serious limitation in resolution which limits their usefulness. Exposure to radiation results in the crosslinking of the polymers in the exposed areas, while image development consists in the dissolution of the unexposed polymer. The problem which arises is that, although insoluble, the crosslinked polymer still shows a great affinity for the developing solvent and their interaction causes swelling to occur which results in loss of resolution through image distortion.

A convenient way to avoid the problem of swelling during image development is to design new materials which operate on the basis of radiation-induced changes in solubility due to changes in the chemical, rather than the physical (crosslinked vs linear), structure of the polymer (6-12). Another potentially simpler approach, which will be explored further in this thesis, involves the design of materials in which irradiation results in the occurrence of chain depolymerization processes (8, 13-15).

The first system based on the principle of radiation induced differential solubility was reported in 1980 by Hofer and coworkers (6). The basic design incorporated modification of the polarity of the side chain of a functionalized styrene polymer and was extended recently by more practical work on polymers such as poly(p-formyloxystyrene) (10-11) which are susceptible to a photo-Fries degradation when exposed to UV radiation (scheme 1).

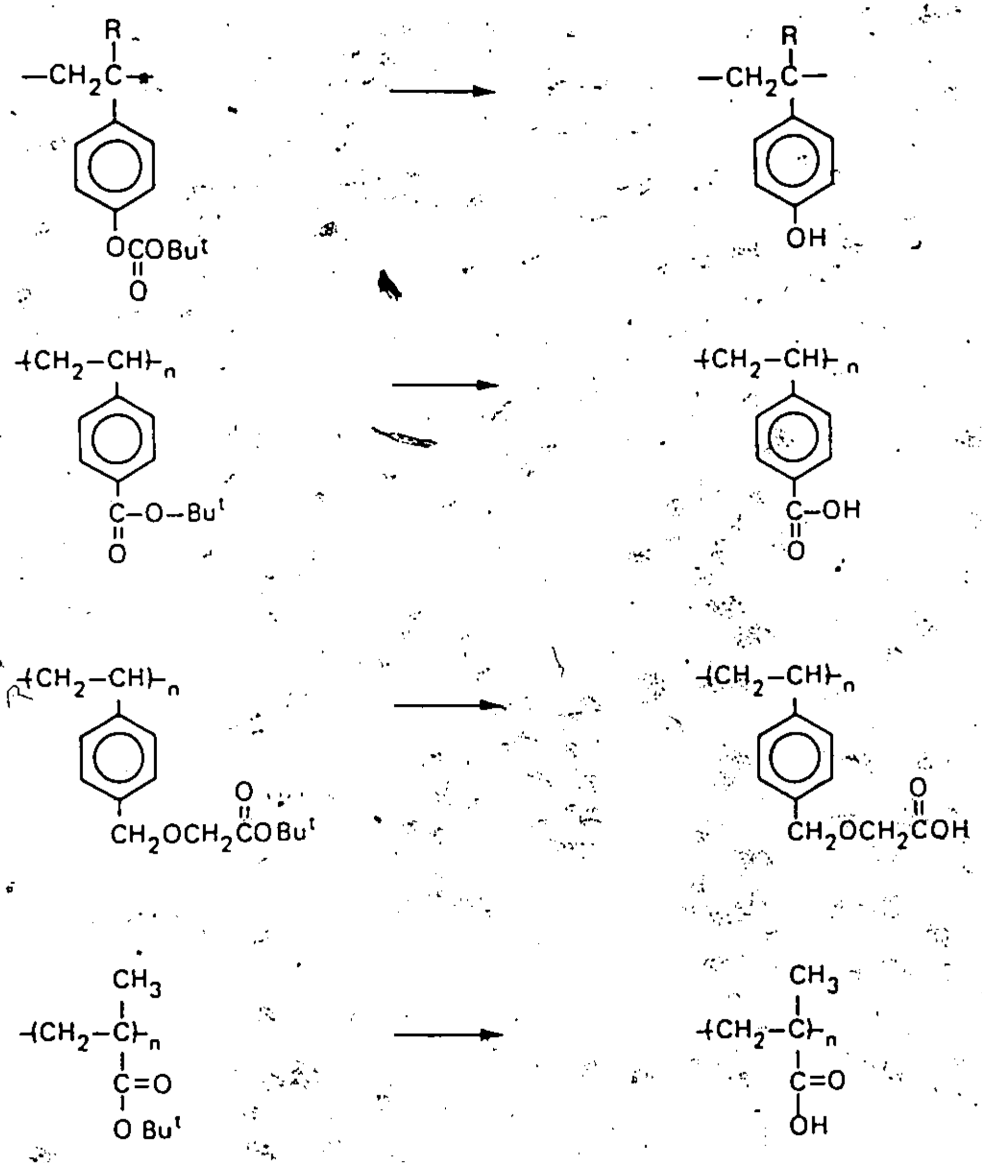
Irradiation of the polymer results in a drastic change in the side-chain polarity which allows for imaging either in positive or negative tone. In the positive mode, the exposed areas which contain the phenolic material can be dissolved in polar solvents such as alcohol or aqueous base while in the negative mode it is the unexposed areas which are selectively dissolved without swelling using such non-polar solvents as chlorobenzene. Clearly a material such as poly(p-formyloxystyrene) should be a valuable addition to the tools available to the resist chemist due to its dual tone versatility and the improvement in resolution it provides. However, while a definite increase in resolution is achieved through exposure in the deep-UV, the flux which is available from classical exposure systems at 254 nm is to low to allow the use of any but the most sensitive resist systems. It is such a consideration which dictates the need to design for chemical amplification (1).



Scheme I. Photo-Fries Degradation of Poly(p-formyloxystyrene).

A very attractive design for new resist materials incorporates both radiation-induced side-chain modification for processing without resolution loss due to swelling, and chemical amplification for very high sensitivity. Most notable among these new materials are those which operate on the basis of acid-catalyzed thermolysis of side-chain protecting groups (7-9). The polymer structures (9) shown in scheme 2 meet this design requirement. For example, poly(p-t-butyloxycarbonyl-oxystyrene) [PBOCST] undergoes thermolysis near 200° in a rapid reaction which produces two gaseous products, carbon dioxide and 2-methyl-propene, in addition to the polar phenolic polymer poly(p-hydroxy-styrene) (16, 17). In the presence of an acid catalyst, the thermolysis reaction occurs at a much lower temperature as confirmed by the thermogravimetric data shown in figure 2. Therefore, addition of a "sensitizer" molecule that produces acid upon irradiation allows efficient imaging of PBOCST and similar polymers (7-9). The "sensitizers" which have been used are onium salts such as diphenyl iodonium or triphenyl sulfonium hexafluoroantimonate which are known (18-19) to produce strong Bronsted acids upon irradiation in the deep-UV (scheme 3).

When a film of PBOCST, mixed with 5-20% of diphenyliodonium hexafluoroarsenate is subjected to UV irradiation no significant change is detected by infrared spectroscopy, however after post-baking at 100°C for 1 minute the t-BOC protecting group is removed as



R
—CH₂C—
OCOBu^t
O
OH
(CH₂—CH)ₙ
C—O—Bu^t
C—OH
CH₂OCH₂COBu^t
CH₂OCH₂COOH
CH₃
(CH₂—C)ₙ
C=O
O Bu^t
OH

Scheme 2

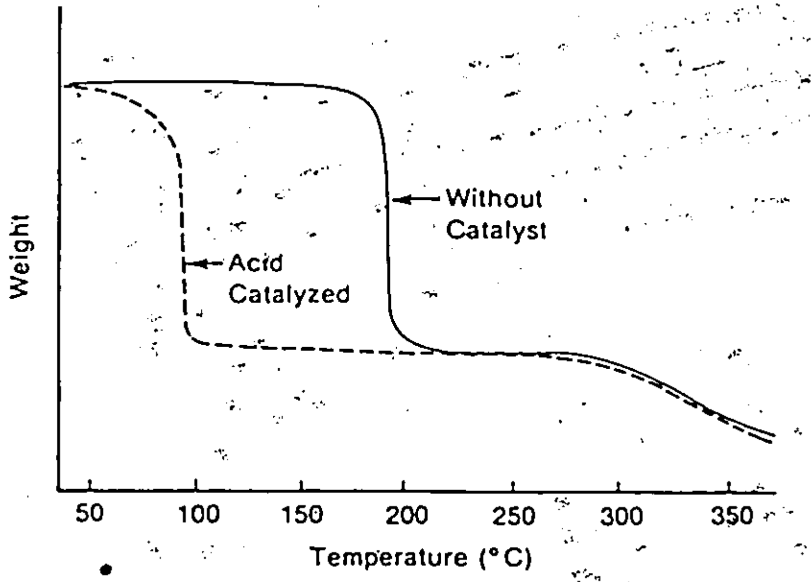


Figure 2. Thermogram of PBOCST with and without added acid catalyst.

$$Ar_3S^+ X^- \xrightarrow{h\nu} [Ar_3S^+ X^-]^{*}$$

$$[Ar_3S^+ X^-]^{\bullet} \longrightarrow Ar_2S^{+\bullet} + Ar^{\bullet} + X^-$$

$$Ar_2S^{+\bullet} + YH \longrightarrow Ar_2S^+\text{-}H + Y^{\bullet}$$

$$Ar_2S^+\text{-}H \longrightarrow Ar_2S + H^+$$

$$2\,Ar^{\bullet} \longrightarrow Ar\text{-}Ar$$

$$Ar^{\bullet} + YH \longrightarrow ArH + Y^{\bullet}$$

ϕ = 0.19 at 313 and 365 nm

Scheme 3

indicated by IR spectroscopy which shows disappearance of the carbonyl band while a strong absorption corresponding to the hydroxyl functionality appears (7-9). The infrared spectra for this process are shown in figure 3. Thus in the imaging process, the exposed areas of the polymer are transformed to poly(p-hydroxystyrene), while the masked areas remain unchanged, the development of the image is done according to the solubility differences of those areas. A polar solvent selectively dissolves the poly(p-hydroxystyrene) areas to give a positive tone image. A negative image can also be obtained if a non polar solvent is used to dissolve only the PBOCST portions of the film. The ability of PBOCST and similar t-butyl ester polymers to form positive and negative images (20) is schematized in figure 4.

The catalyzed acidolysis of the t-BOC pendant groups is believed to proceed via unimolecular acid hydrolysis with an alkyl-oxygen bond fission (21-22). The tertiary carbocation formed subsequently eliminates a proton to form the more stable 2-methyl-propene. The alkyl-oxygen bond fission is followed by the evolution of carbon dioxide from the monoester of carbonic acid leaving a phenolic moiety (scheme 4). Note that a molecule of the acid regenerated during the catalytic process can cleave many t-BOC groups, thus providing a chain reaction often referred to as "chemical amplification" in the context of resist materials.

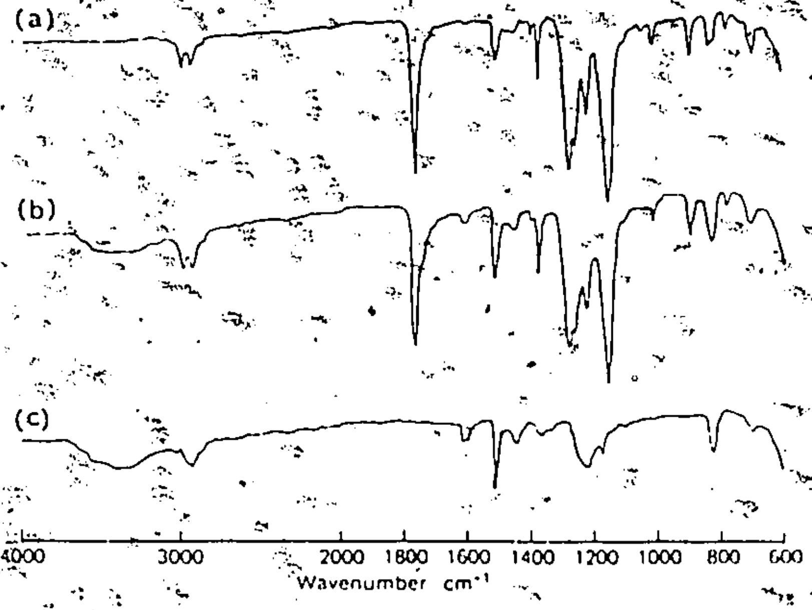


Figure 3 IR spectra of PBOCST/Ph_2IAsF_6 (a) unexposed, (b) exposed, (c) post-baked

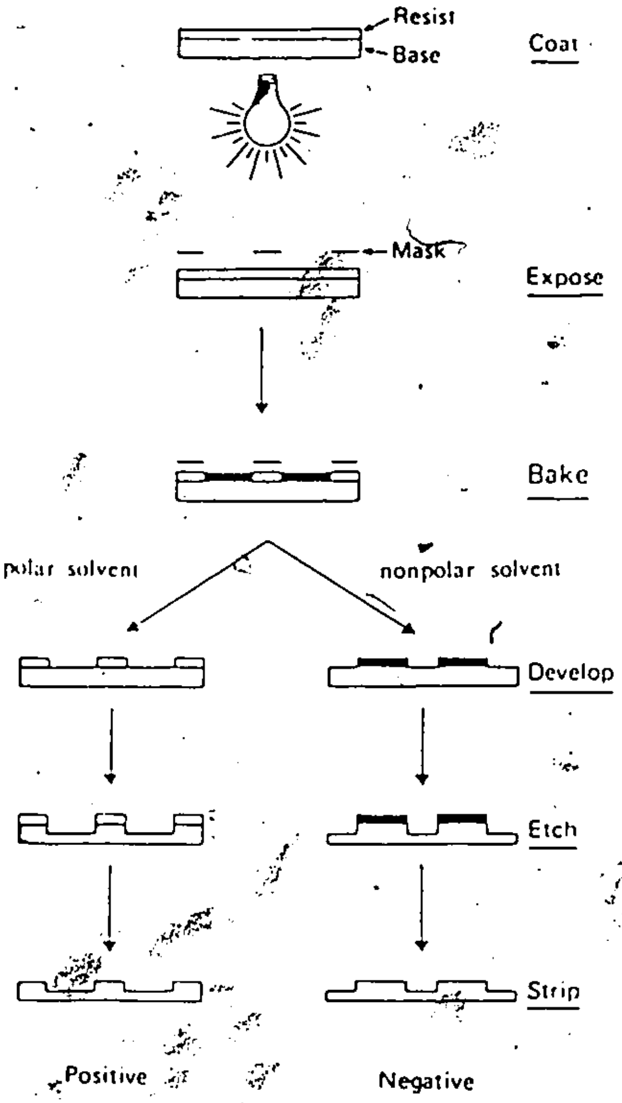
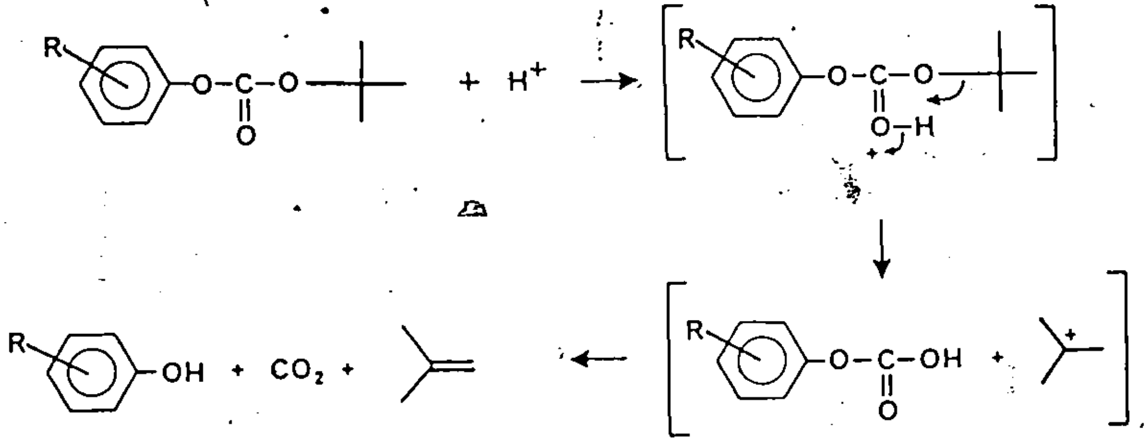


Figure 4 Representation of positive and negative imaging of PBQCST and similar t-butyl ester polymers

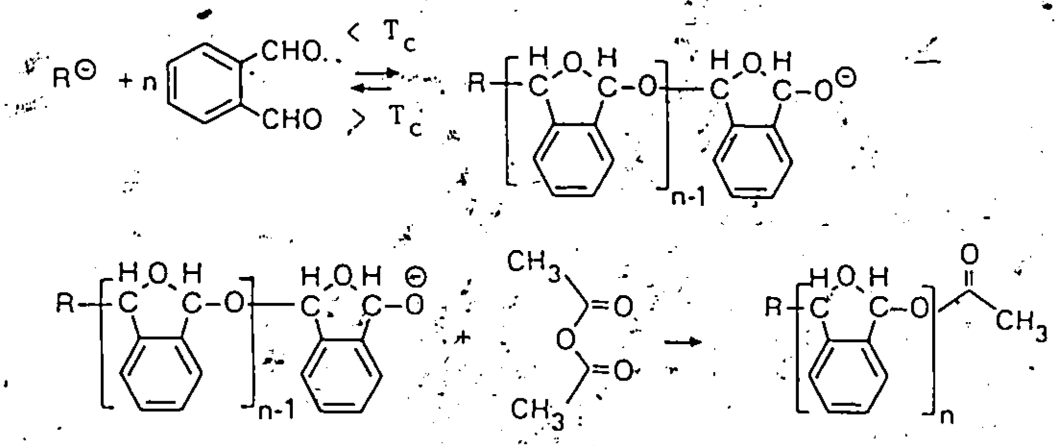


Scheme 4

Of particular relevance to this work are the earlier reports on imaging systems that operate on the basis of light-induced depolymerization processes (8, 13-14). For example, it is well known that although polyphtalaldehyde (PPA) has a ceiling temperature of -40^{o} a PPA polymer stable to ca. 180^{o} can be obtained by the simple device of end-capping the polymer as shown in scheme 5 (23, 24).

The stability of the end-capped PPA polymer is entirely dependent on the presence of these stabilizing end groups and any process which effectively removes them or exposes an uncapped moiety through chain cleavage will result in spontaneous depolymerization of the PPA at room temperature. Thus, a resist material has been formulated (8, 13-14) by combining end-capped PPA with a radiation-sensitive onium salt which produces strong acid upon exposure (18-19). Irradiation of a film of the PPA resist results in the formation of a local concentration of acid which causes chain cleavage to occur in the exposed areas. The PPA resist is characterized by its very high sensitivity due to chemical amplification of the initial photoevent through two distinct but cumulative processes.

- A single photogenerated acid moiety cleaves a PPA chain thereby reverting the effect of the end-capping process with depolymerization of the entire chain due to a ceiling temperature phenomenon.



Scheme 5

- The photogenerated acid catalyst is not consumed in the overall process and may become further involved in the cleavage of neighboring chains thereby providing a second stage of chemical amplifications. This process is however limited by the low mobility of the reactive catalytic species within the solid matrix and by other process-terminating side-reactions.

In addition to its high sensitivity, the PPA resist has the property of dry development. This feature is interesting as it can contribute to a reduction in the number of processing steps, but, in this case, the design of the material is such that exposure results in the immediate liberation of volatile phtalaldehyde monomer within the exposure tool. Such spontaneous depolymerization process, though attractive in principle, is less desirable in practice due to the possibility of contamination of the exposure tool via vapor deposition. An alternate approach towards the same goal involving the acid catalyzed deprotection-degradative rearrangement of certain polycarbonate derivatives of glycidol (15,25) is also not fully satisfactory as the activation energy required for the entropy-driven process to occur is such that processing is extremely difficult and full image development is not achieved.

Our laboratory has developped a new approach to imaging systems incorporating chemical amplification using a catalyzed depolymerization reaction as shown in figure 5, which contrasts the

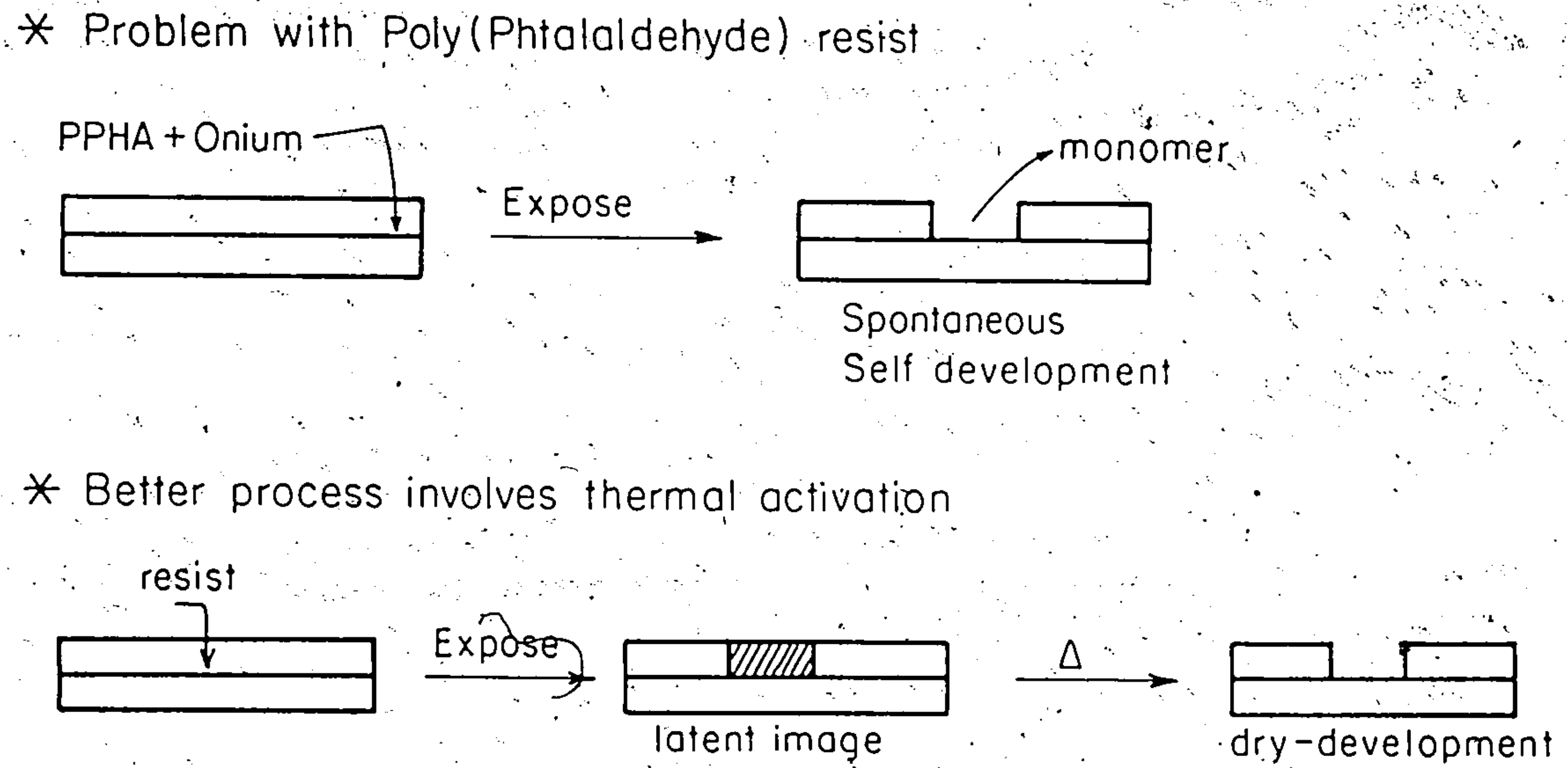
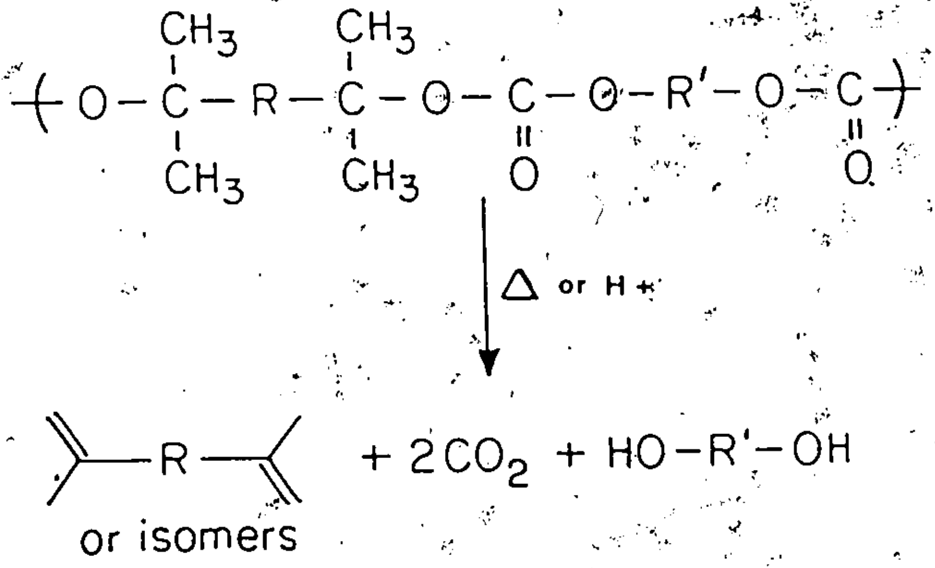


Figure 5 Need for a thermal activation in the development process

process with that used for the polyphtalaldehyde resist described above. Both systems involve the use of polymers which are used in combination with a small amount of photosensitive onium salt. However, while in the case of the PPA resist generation of catalytic amounts of acid by exposure to radiation results in the immediate spontaneous depolymerization of the unstable PPA over its ceiling temperature, the new resist material should remain stable to the acid catalyst which is formed in the photolysis of the onium salt and thus should only form a latent image consisting of protons dispersed in a polymer matrix. Image development by depolymerization will only result from a subsequent baking of the image as the design of the polymer is such that catalyzed acidolysis can only occur above room temperature yet below the normal thermolysis temperature of the polymer as was the case for PBOCST (figure 2).

Recent work in our laboratory (25-27) involves the development of linear polycarbonates containing tertiary carbonate units in their backbone. These polymers undergo irreversible catalytic depolymerization when exposed to UV radiations in the presence of onium salts in a process which is analogous to the cleavage of the side-chains of PBOCST. Scheme 6 shows the acidolysis products of tertiary polycarbonates. These polymers constitute a new class of polymers since tertiary polycarbonates had not been synthesized before. Because tertiary chloroformates are known to be highly susceptible to thermal elimination (28), attempts to polymerize

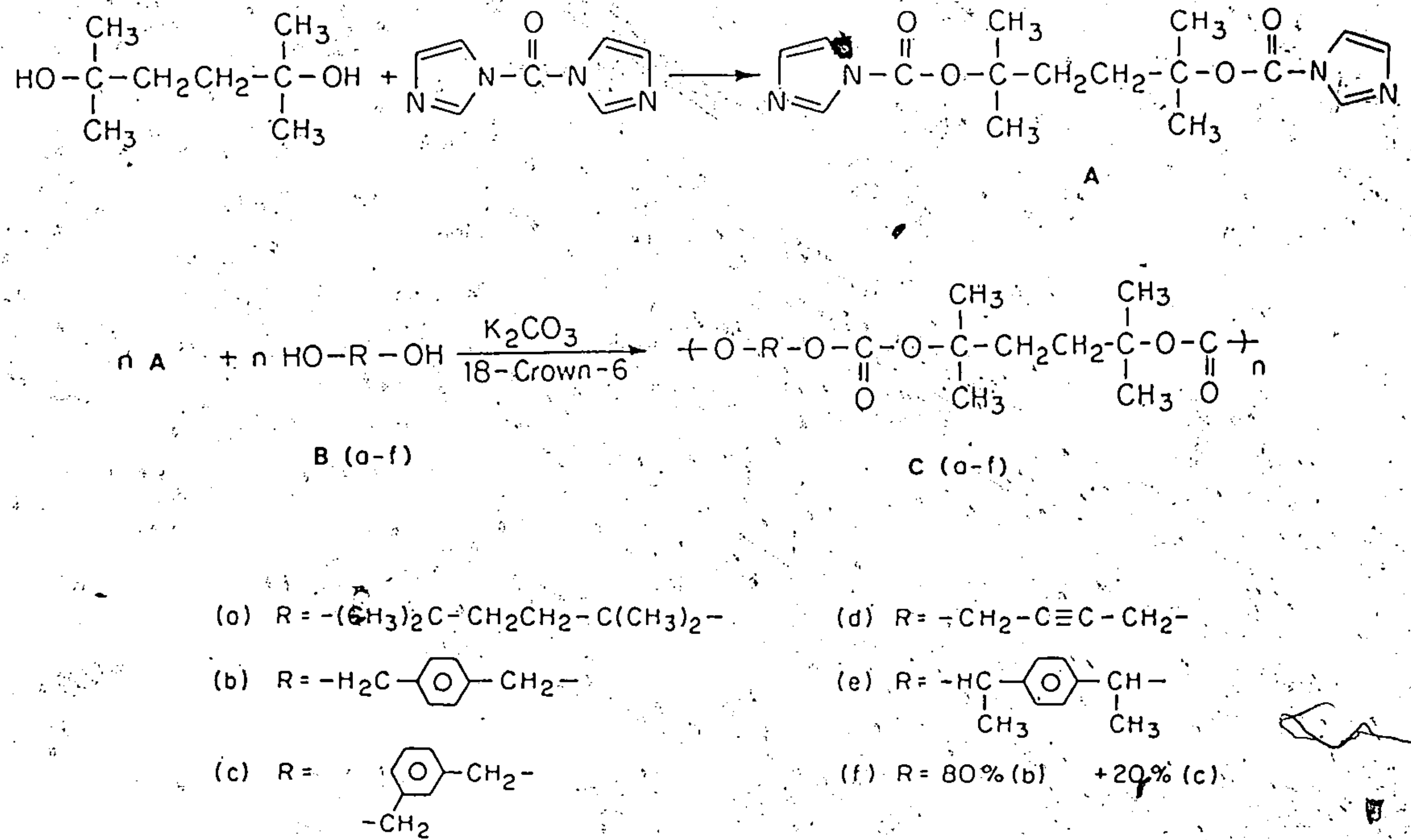


Scheme 6

tertiary polycarbonates through condensation of dihydroxy compounds with bifunctional tertiary chloroformates would only give oligomeric materials at best. Also reaction between a tertiary diol and a bifunctional chloroformate would probably only lead to formation of oligomers due to the low reactivity of the tertiary diols with chloroformate functionalities. The approach of Houlihan (25) to the synthesis of tertiary polycarbonates was to use the tertiary carbonylimidazoyl groups which had been previously reported by Staab as activating groups in the synthesis of t-butylcarbonates (29).

Solid-liquid phase-transfer catalyzed polycondensation of bifunctional carbonylimidazoyl derivatives of tertiary diols with a variety of diols in the presence of potassium carbonate affords tertiary polycarbonates with acceptable molecular weights (scheme 7).

The thermogravimetric analyses (TGA) of these polycarbonates suggest that they are all stable to approximately 200°C. Upon reaching their critical decomposition temperature, the polymers decompose to form small molecules while leaving no solid residue. As a representative example, the copolycarbonate of 2,5-dimethyl-2,5-hexanediol and p-benzenedimethanol thermolyzes at 200°C (figure 6, curve a) to produce carbon dioxide, p-benzenedimethanol and three dienes corresponding to the possible dehydration products of 2,5-dimethyl-2,5-hexanediol. A small amount of 2,5-dimethyl-hex-5-ene-2-ol originating from the end chain segments of the polymer is also formed (scheme 8). The presence


A
n A + n HO–R–OH
K_2CO_3
18-Crown-6
B (a-f)
C (a-f)
(a) R = $-(CH_3)_2C-CH_2CH_2-C(CH_3)_2-$
(b) R = $-H_2C-$
$-CH_2-$
(c) R =
$-CH_2-$
$-CH_2$
(d) R = $-CH_2-C\equiv C-CH_2-$
(e) R = $-HC$
CH_3
$CH-$
CH_3
(f) R = 80% (b) + 20% (c)

Scheme 7

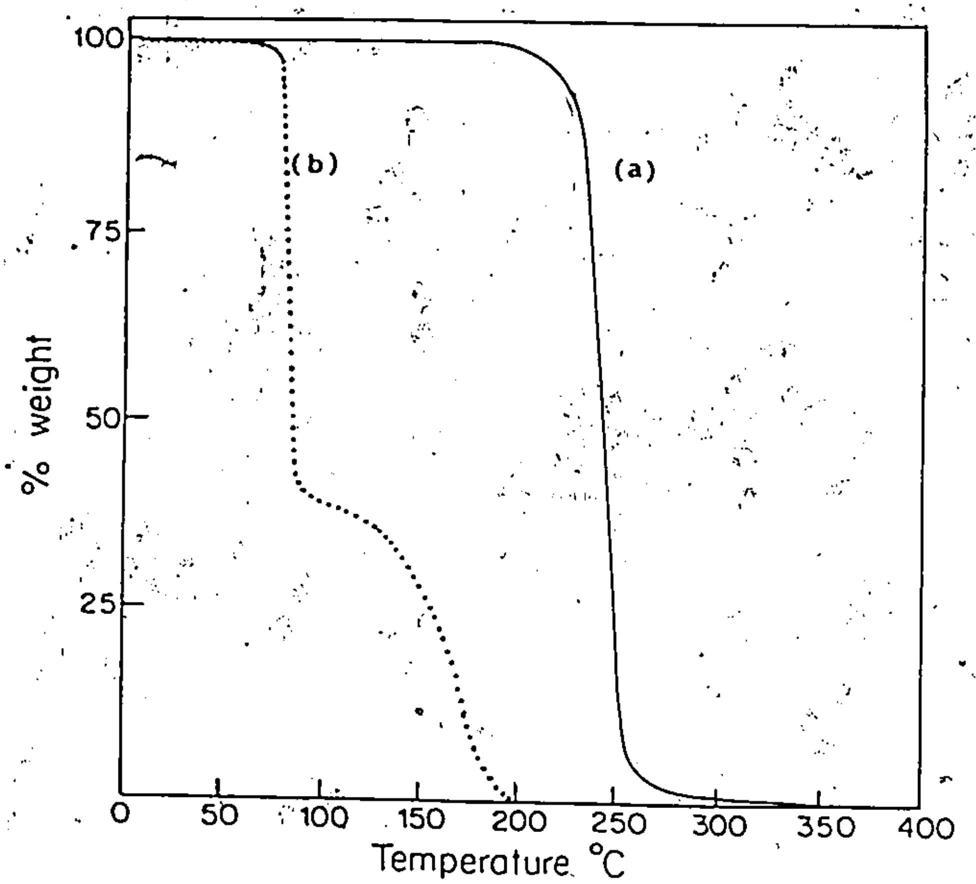
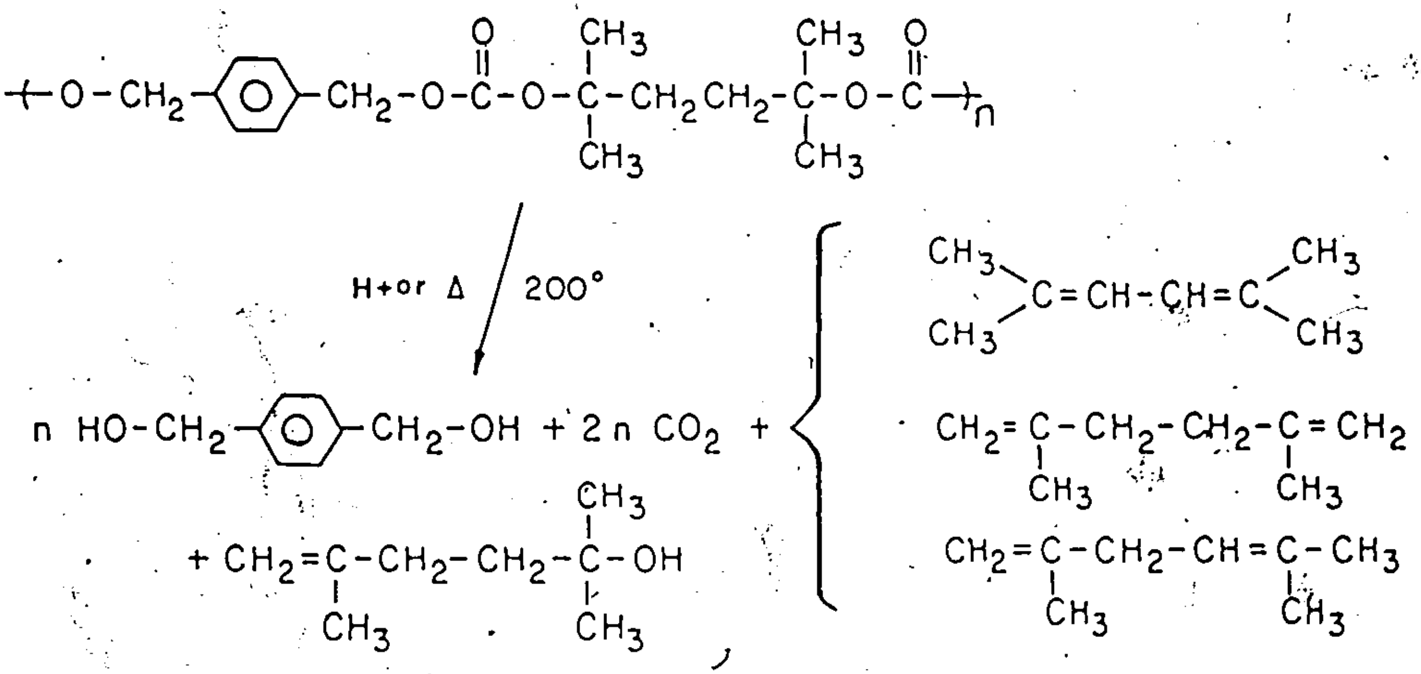


Figure 6 TGA of copolycarbonate of p-benzenedimethanol and 2,5-dimethyl-2,5-hexanediol (a) thermolysis, (b) acid-catalyzed thermolysis



Scheme 8

of these thermolysis products was confirmed by further analysis in a process which combines thermolysis gas chromatography, and mass spectroscopy (27).

The thermal degradation aspect of such polymers is interesting as they eventually could be used as matrix materials which would be stable under a given set of conditions, but could liberate the chemicals they are carrying in a controlled manner, simply by heating to a defined temperature. Potential applications can be envisionned in areas as varied as paints, coatings, explosives, propellants and controlled-release pharmaceuticals.

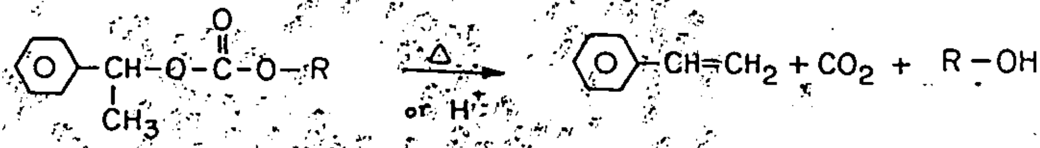
As was observed in the case of PBOCST, the thermolysis reaction is acid-catalyzed and addition of a small amount of acid to the copolycarbonate of 2,5-dimethyl-2,5-hexanediol and p-benzenedimethanol causes a shift of the thermolysis curve (figure 6, curve b) to lower temperatures. The exact shape of the curve is dependent on the reaction conditions used for this measurement.

This thesis presents further work on the design, chemistry and testing of polycarbonates which can undergo depolymerization by thermolysis or acidolysis. Catalyzed phase-transfer polycondensation is used in the preparation of new tertiary polycarbonates with improved physical properties. Polycarbonates with benzylic and allylic moieties are also synthesized and shown to have potential as sensitive photoresists materials.

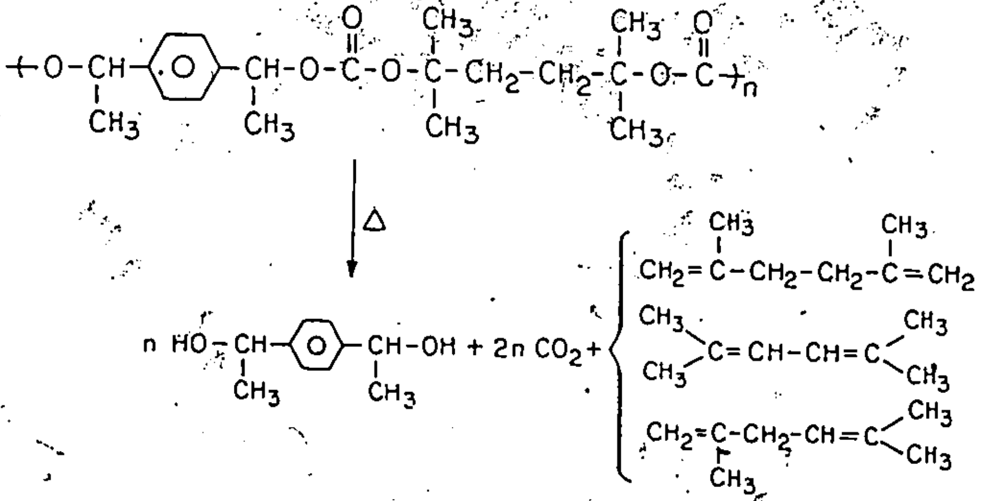
RESULTS AND DISCUSSION

As pointed out earlier, the synthesis of tertiary polycarbonates has been successfully achieved via the phase-transfer catalyzed polycondensation of diols and bis-carbonylimidazoyl derivatives of tertiary diols. These polymers show the expected behavior when subjected to acidolysis or thermolysis conditions releasing carbon dioxide, a diol, and a mixture of dienes derived from the tertiary diol biscarbonylimidazolide. This decomposition mechanism depends on the ability of the tertiary moiety to form a stable tertiary intermediate which can subsequently eliminate to form an alkene. For example in an acidolytic process a tertiary carbocation is formed initially and eliminates a proton located on an adjacent carbon. This mechanism suggest that any species which is capable of forming a stable intermediate with an available proton on the alpha position, could be incorporated into a polycarbonate which would decompose in the same manner as the tertiary polycarbonates.

This hypothesis was verified by a study of model compounds (30) where thermolysis or acidolysis of carbonates of 1-hydroxyethyl benzene releases styrene (scheme 9), thus confirming the formation of a secondary benzylic intermediate. The copolycarbonate of p-bis(1-hydroxyethyl) benzene and 2,5-dimethyl-2,5-hexanediol has been prepared (25). It depolymerizes at 220°C as indicated by TGA; analysis of the thermolysis products by mass spectroscopy, shows that the polymer decomposes via the formation of a tertiary intermediate to give p-bis(1-hydroxyethyl) benzene, carbon dioxide and a mixture of



Scheme 9

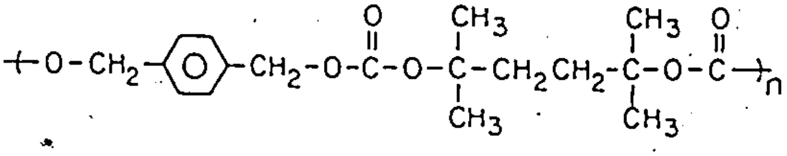
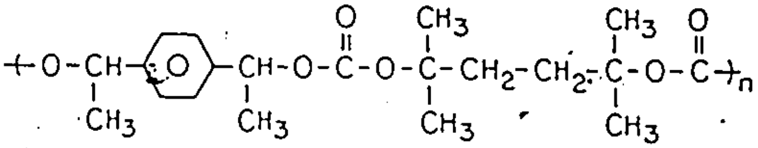
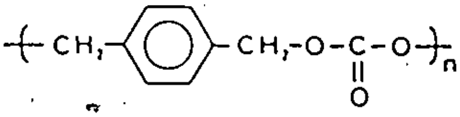
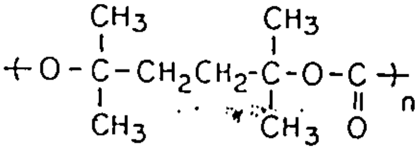
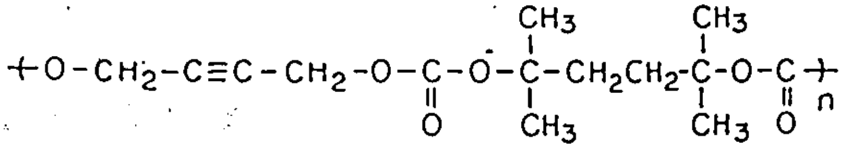


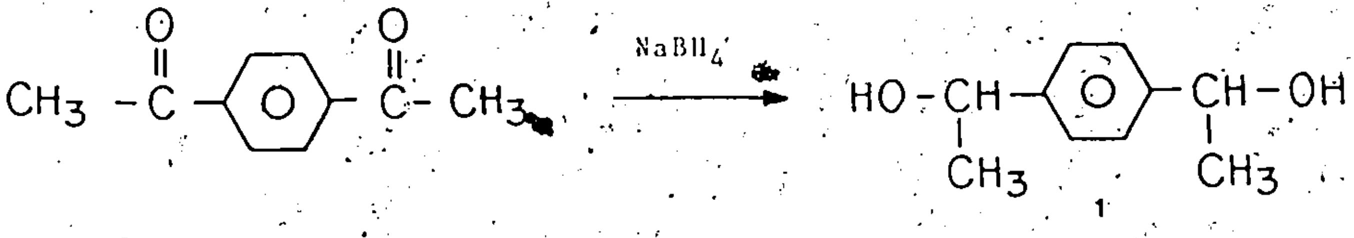
Scheme 10

dienes resulting from the dehydration of 2,5-dimethyl-2,5-hexanediol (scheme 10). The decomposition via a secondary benzyl intermediate is probably not seen in this case simply because the formation of the tertiary intermediate is a lower energy process. This copolymer has a better solubility than the copolycarbonate of 2,5-dimethyl-2,5-hexanediol and p-benzenedimethanol due to the methyl substituents which prevent the close packing of polymer chains which is observed with the analogous polymer containing p-benzenedimethanol. Incorporation of aromatic moieties is desirable in order to obtain a high melting polymer (see Table I). The homopolycarbonate of p-bis(1-hydroxyethyl) benzene should give access to a material of even higher melting point than its copolymer with the aliphatic tertiary diol, while good solubility in organic solvents should be preserved due to the presence of the methyl substituents.

The synthesis of p-bis(1-hydroxyethyl) benzene, 1, is the first step to the synthesis of the homopolymer. The diol is obtained by reduction of p-diacetylbenzene with sodium borohydride (scheme 11). The corresponding bis-carbonylimidazolide, I-a, is obtained in 35% yield by reaction of p-bis(1-hydroxyethyl) benzene with 1,1'-carbonyldiimidazole in the presence of a catalytic amount of potassium metal.(scheme 13). The product is a white solid which has to be stored below room temperature to avoid any slow thermal degradation process. This bis-carbonylimidazolide is allowed to react under phase-transfer conditions (scheme 14) with p-bis(1-hydroxyethyl) benzene to give 73% yield of the desired polycarbonate, II-a. The polymer is soluble in common solvents, and its DSC shows a Tg at 78°C

Table I. Melting point of linear polycarbonates

	Tm	ref
	150	(25)
	93	(25)
	195	(37)
 $\left[O-C(CH_3)_2-CH_2CH_2-C(CH_3)_2-O-C(=O) \right]_n$	<rt	(25)
 $\left[O-CH_2-C\equiv C-CH_2-O-C(=O)-O-C(CH_3)_2-CH_2CH_2-C(CH_3)_2-O-C(=O) \right]_n$	<rt	(25)



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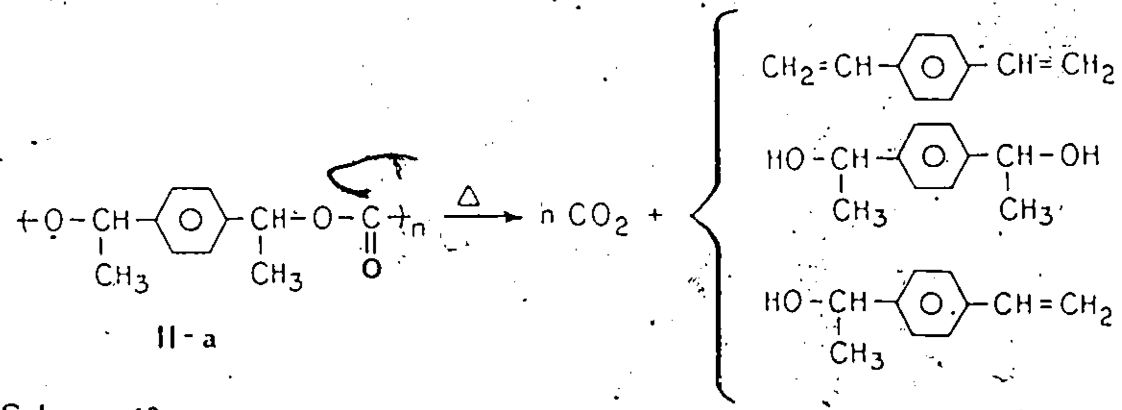
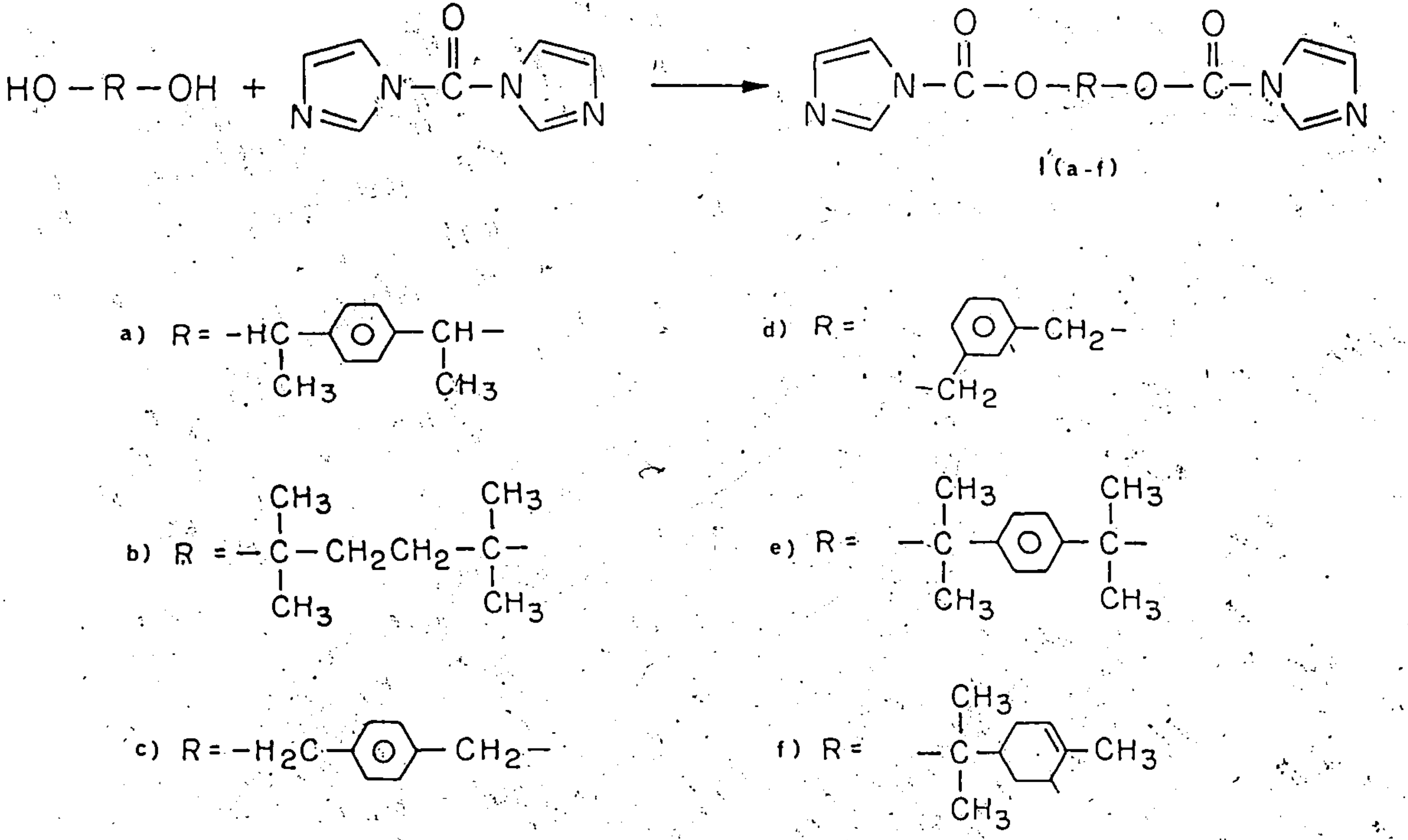
Scheme 11

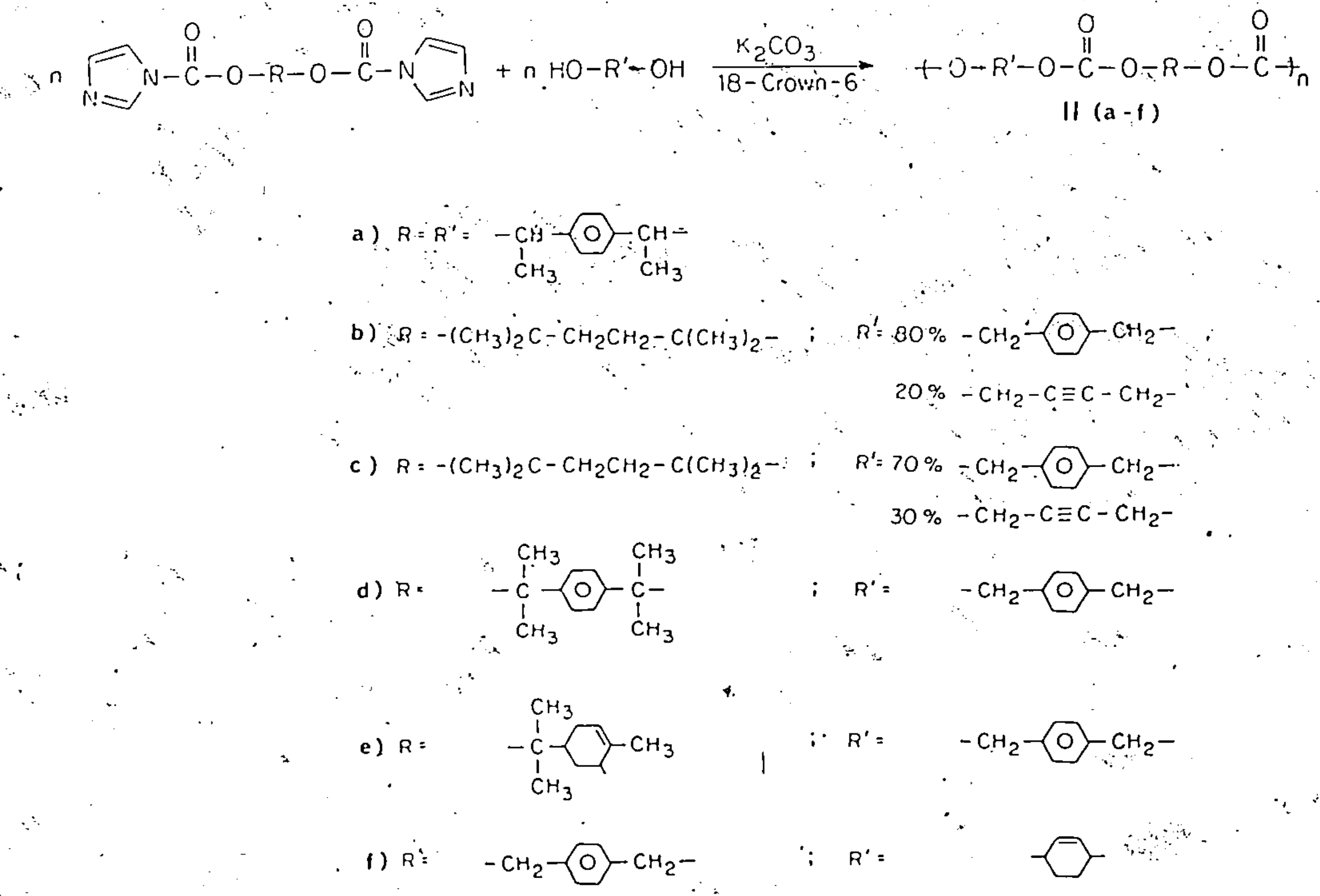


II - a

Scheme 12



Scheme 13


n
K2CO3
18-Crown-6
+ n HO–R'–OH
II (a - f)
a) R = R' =
b) R = -(CH3)2C-CH2CH2-C(CH3)2- ; R' = 80 % -CH2-⟨O⟩-CH2-
20 % -CH2-C≡C-CH2-
c) R = -(CH3)2C-CH2CH2-C(CH3)2- ; R' = 70 % -CH2-⟨O⟩-CH2-
30 % -CH2-C≡C-CH2-
d) R =
; R' =
e) R =
; R' =
f) R =
; R' =

Scheme 14

and a melting point at 105°C (figure 7). As expected this melting point is higher than that observed for the corresponding copolycarbonate with 2,5-dimethyl-2,5-hexanediol which is 93°C. A preliminary study by TGA (figure 8) indicates that the polymer is stable up to 230°C and then suffers a weight loss of 79% over a range of 50°C. The residual 21% might be an oligomer or polymer of the divinyl benzene which is produced in the reaction as confirmed by mass spectroscopy (figure 9). The other products of the depolymerization being carbon dioxide, vinyl(1-hydroxyethyl) benzene and bis(1-hydroxyethyl) benzene (scheme 12). The residual polymer eventually thermolyses at 400°C. The acidolysis of a thin film (0.9 μm) of this polycarbonate was studied by infrared spectroscopy. An exposure of 20 mJ and a post-bake of 1 min. at 100°C are necessary to observe the complete disappearance of the carbonyl band of the starting polymer. Figure 10 shows the IR spectra before and after exposure, and after baking. No poly(divinylbenzene) residue is observed by IR after the post-bake step.

Previous studies have shown that the incorporation of aromatic rings in the polycarbonate structure is an important consideration to obtain a polymer with a high melting point. The polycarbonate of p-benzenedimethanol and 2,5-dimethyl-2,5-hexanediol has a melting of 150°C but its solubility is relatively low and it is difficult to form a useful film of this polymer. An attempt was made to increase its solubility by replacing the aromatic diol by 1,4-butynediol. As expected the solubility of the polymer is increased effectively by the incorporation of 1,4-butynediol in the polycarbonate chains, however

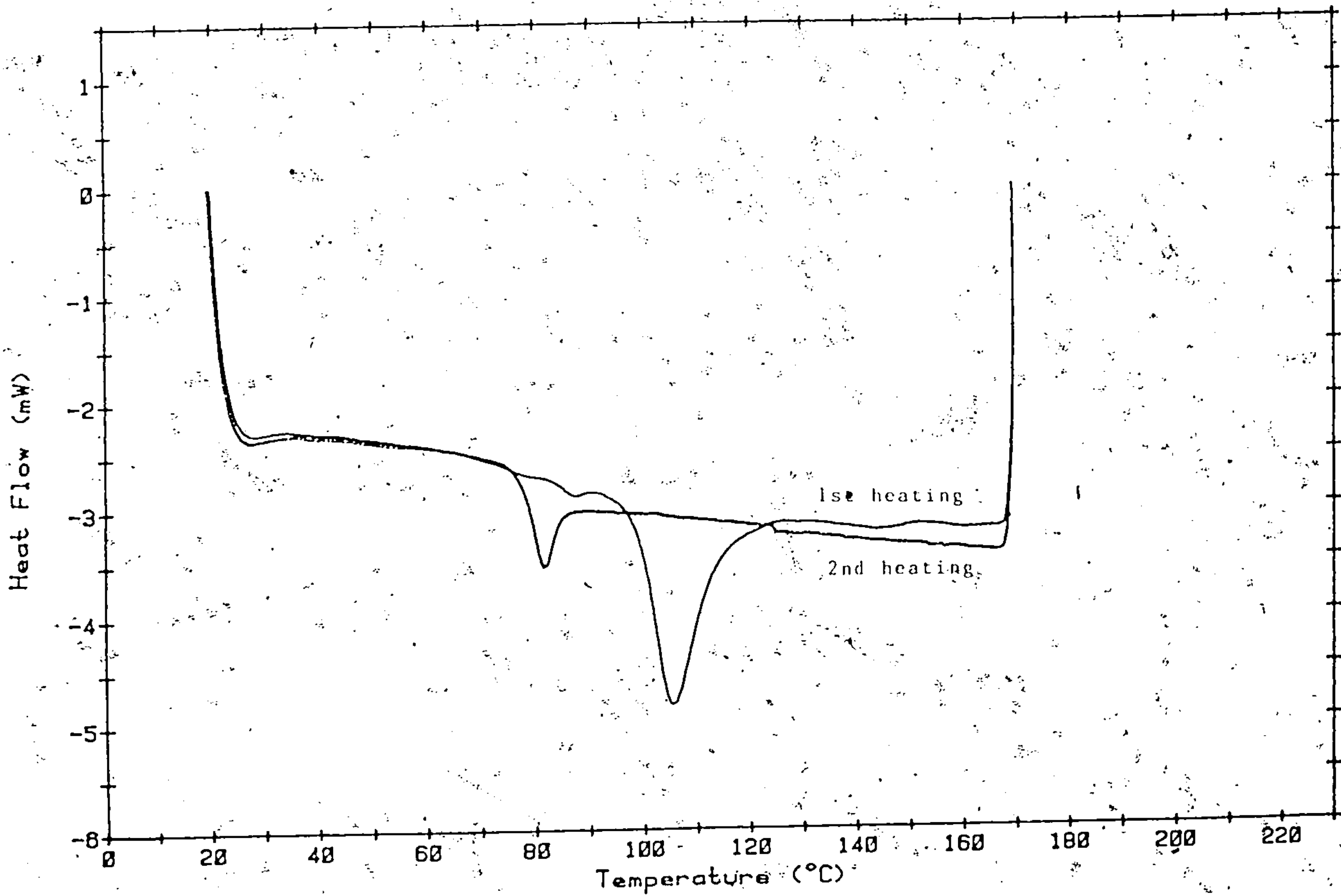


Figure 7 DSC of II-a

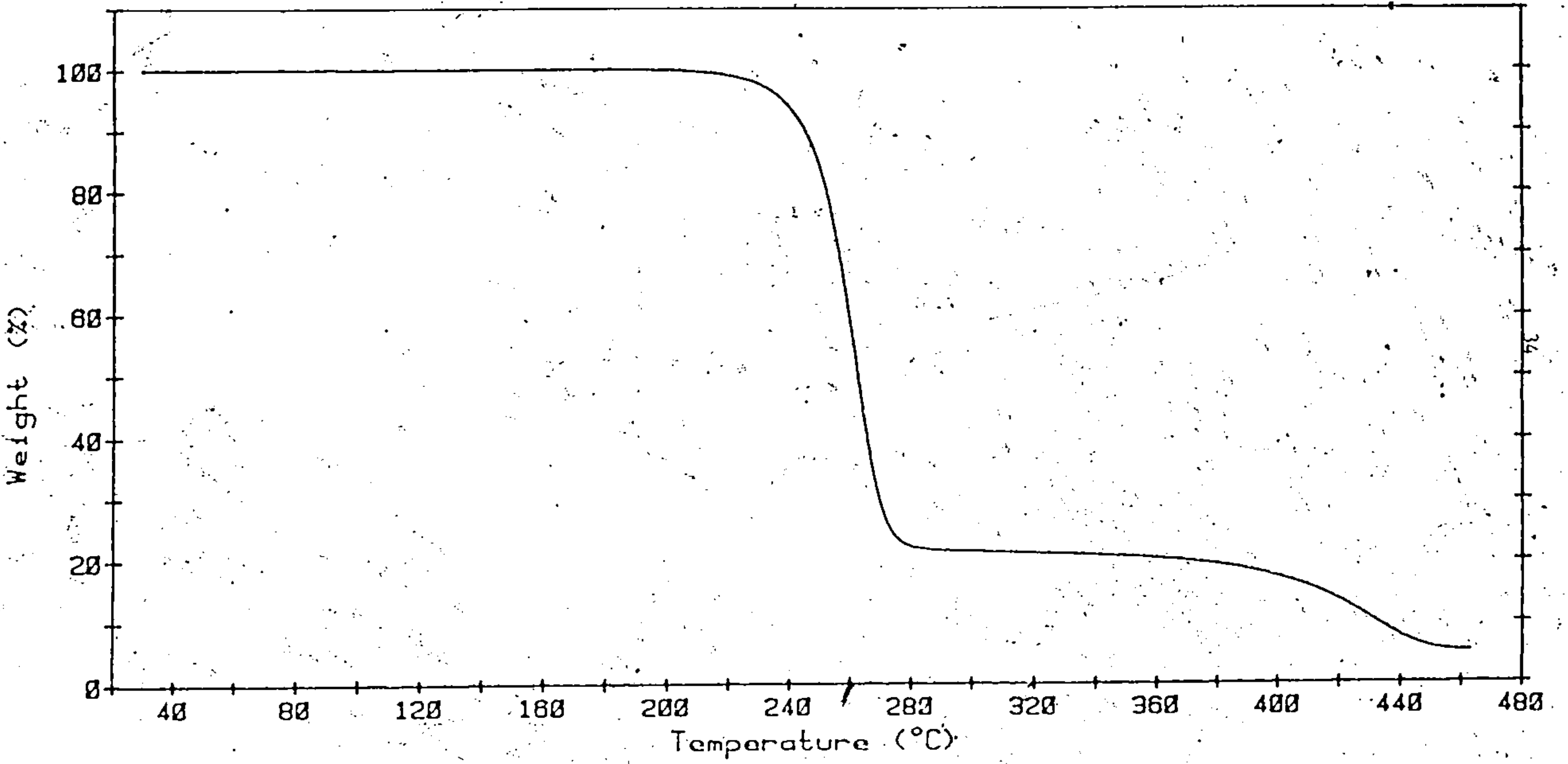


Figure 8 TGA of II-a

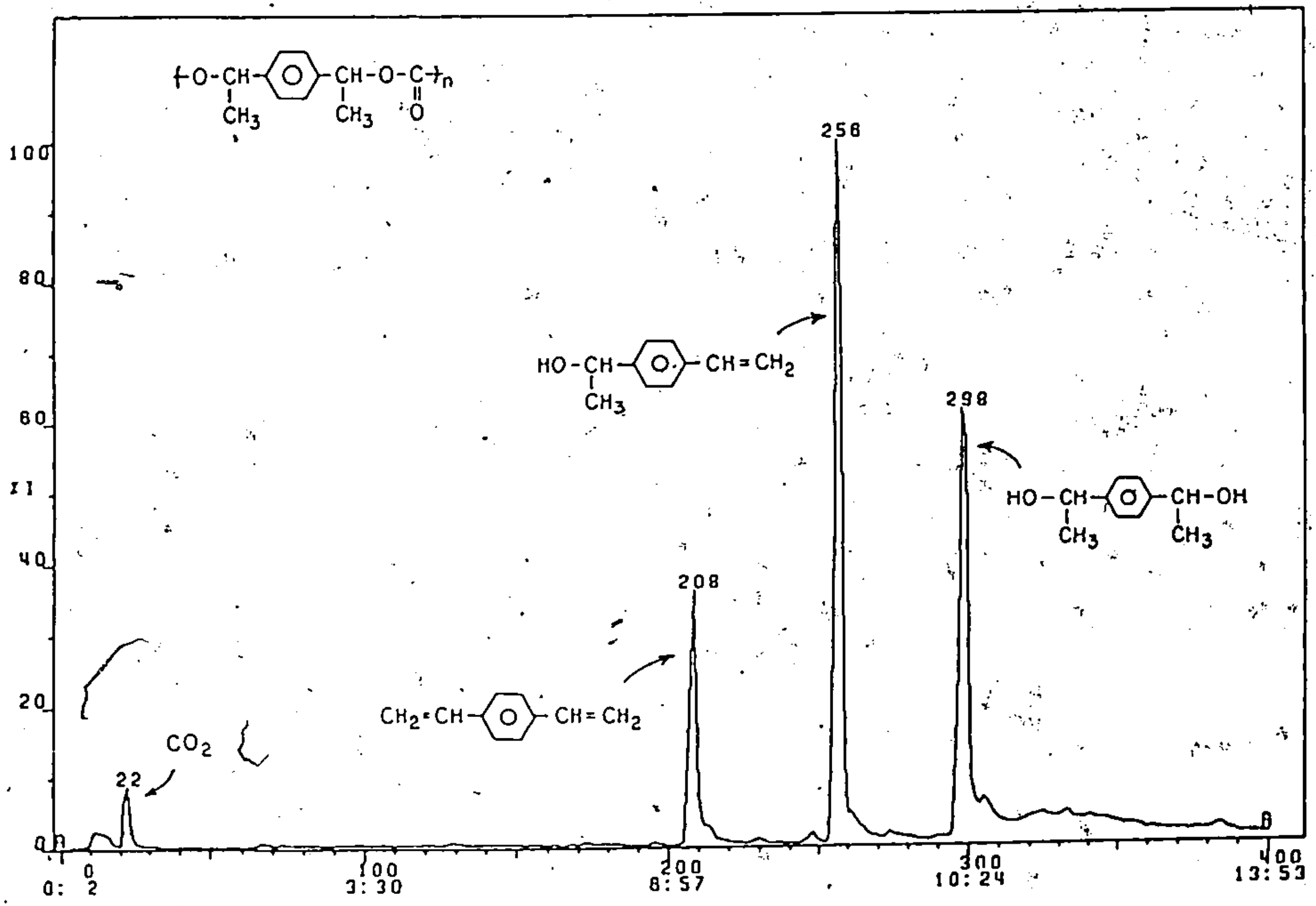


Figure 9 GC-MS of II-a

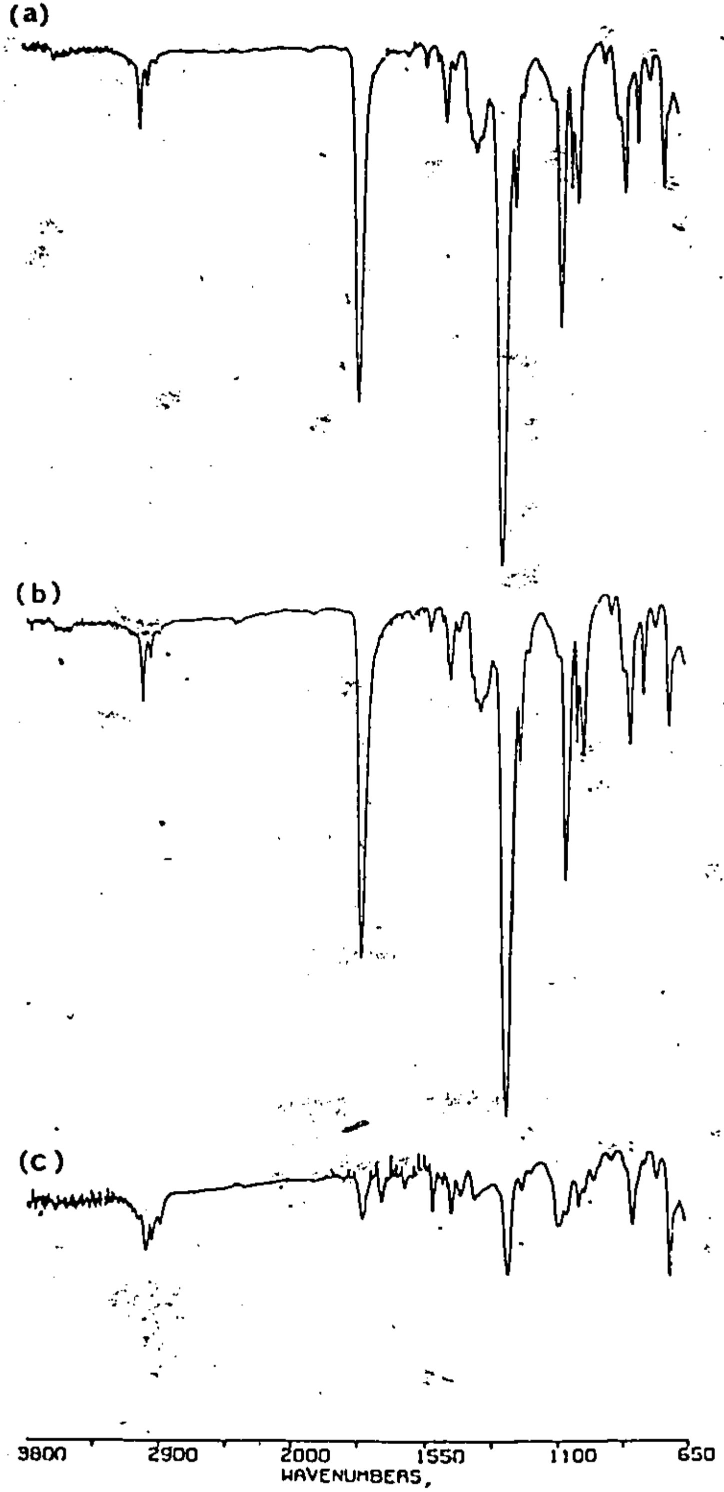


Figure 10 IR spectra of II-a/Ph_2IAsF_6 (a) unexposed, (b) exposed, (c) post-baked

the material obtained has poor mechanical properties and has a melting point below room temperature which makes it unsuitable for application as a coating material (25). Since aromaticity tends to contribute to the obtention of high melting properties and incorporation of the alkyne increases solubility it is expected that incorporation of both in the same polymer in alternation with 2,5-dimethyl-2,5-hexanediol should give a polycarbonate with balanced solubility and melting properties.

The bis-carbonylimidazolide of 2,5-dimethyl-2,5-hexanediol, I-b, is obtained in 71% yield by treating the diol with 1,1'-carbonyldiimidazole in the presence of potassium metal (scheme 13). A terpolymer, II-c, having a diol ratio of 70:30 p-benzenedimethanol:1,4-butynediol is prepared with the bis-carbonylimidazolide, I-b, under phase-transfer conditions as shown in scheme 14. The polymer is obtained in 80% yield as a white solid that shows good solubility in a variety of organic solvents. DSC indicates a Tg at 25°C, a Tm at 117°C and two other endotherms at 66°C and 100°C which are probably due to conformational changes of the polymer chains. Note that the Tm value is intermediate to the melting points of the copolymers of 2,5-dimethyl-2,5-hexanediol with p-benzenedimethanol (150°C) and with 1,4-butynediol (below room temperature). The TGA curve for this polymer shows that the polymer decomposes almost completely between 190°C and 215°C (figure 11). A study of the products given-off during the thermal degradation indicates the evolution of 1,4-butynediol, p-benzenedimethanol, 2,5-dimethyl-hex-5-ene-2-ol, and a mixture of three dienes corresponding to all possible dehydration products of 2,5-

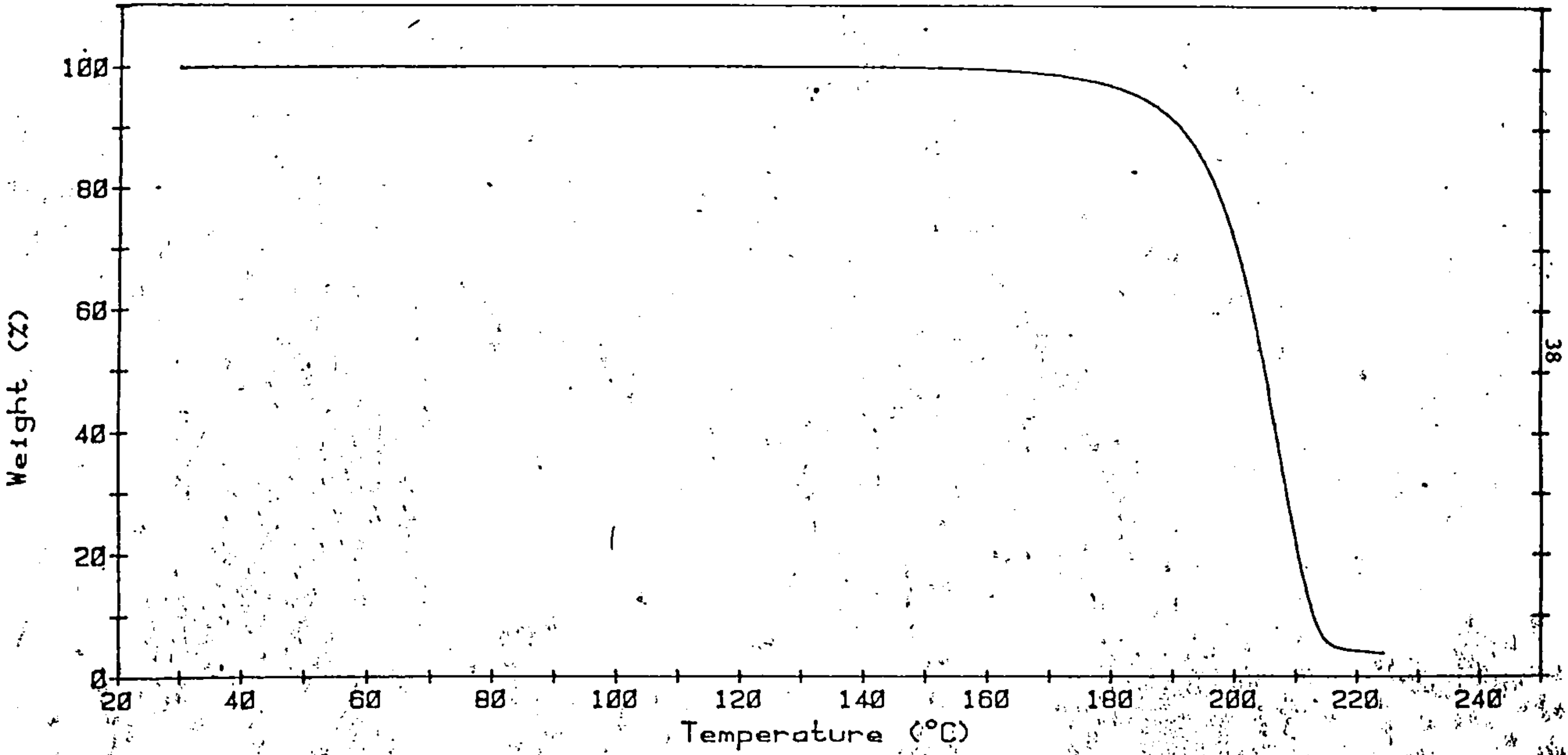
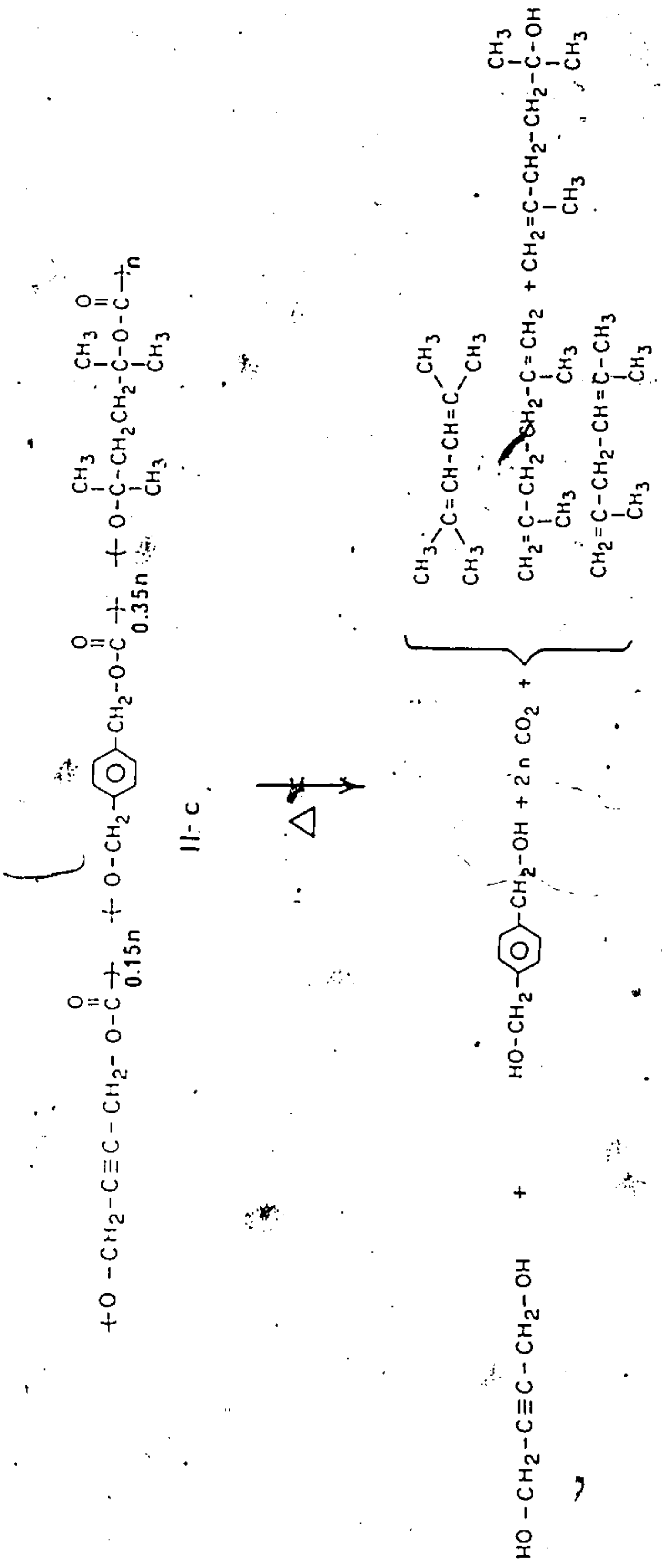


Figure 11 TGA of II-c

dimethyl-2,5-hexanediol (scheme 15). The thin film (1.2 μm) acidolysis of this terpolymer, followed by infrared spectroscopy reveals that the carbonyl band disappears gradually after consecutive exposure of 5 mJ and 1 min. post-bake at 100°C. A total exposure of 100 mJ is necessary to observe the complete disappearance of the carbonyl absorption (figure 12).

The preparation of a terpolymer, II-b having a diol ratio of 80:20 p-benzenedimethanol:1,4-butynediol with 2,5-dimethyl-2,5-hexanediol was attempted, but only 60% yield of an oligomer was isolated. The low extent of the reaction might have been caused by the use of impure starting material, or of improper reaction conditions. The reaction was however not repeated in view of other more significant developments reported below.

In the study of polymers containing tertiary diols, it was desirable to see whether the use of pinacol instead of 2,5-dimethyl-2,5-hexanediol in a copolymer with an aromatic diol would give a higher melting polymer because of the greater rigidity of the pinacol moiety. The first approach to the preparation of a copolycarbonate containing pinacol was to attempt the synthesis of the corresponding bis-carbonylimidazolide. The reaction of pinacol with 1,1'-carbonyldiimidazole does not afford the desired product. The only compound isolated is the 5-membered ring carbonate, 1,1,2,2-tetramethylethane carbonate, 2, resulting from the competing ring closure side reaction (scheme 16). The alternative route to the desired polycarbonate involves a condensation of pinacol with bis-



Scheme 15

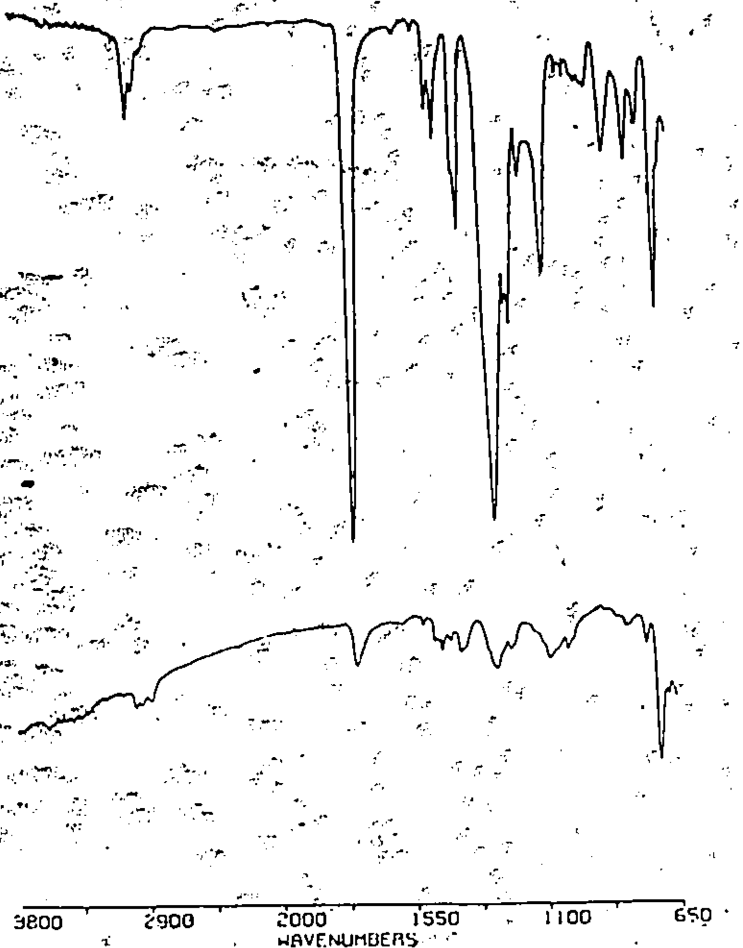
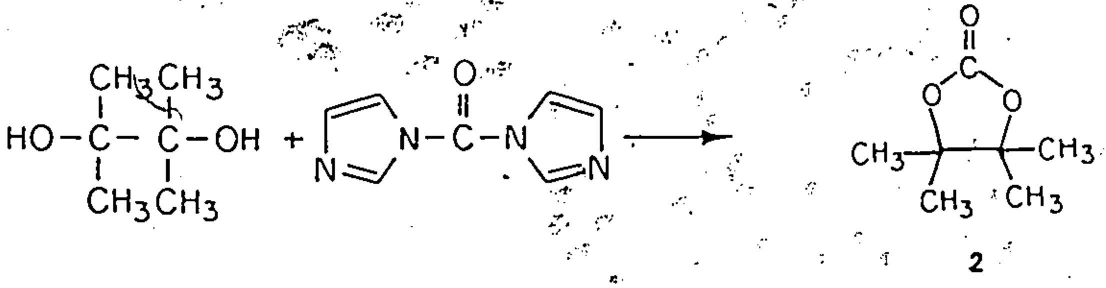


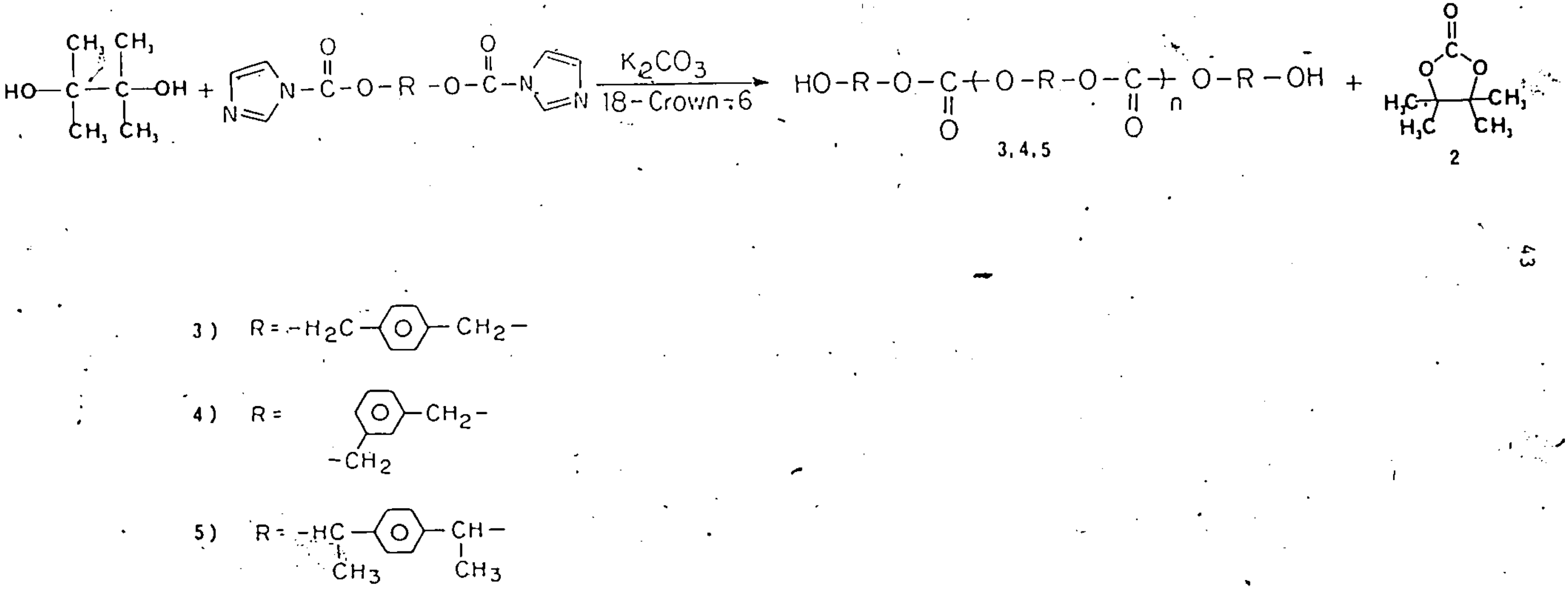
Figure 12 IR spectra of II-c/Ph_2IAsF_6 (a) unexposed, (b) After exposure and post-bake



Scheme 16

carbonylimidazolide derivative of an aromatic diol. The bis-carbonylimidazolides of para and meta-benzenedimethanol, I-c, and I-d, can be prepared by treating each diol with a catalytic amount of base, then adding the resulting alcoholate solution to a suspension of 1,1-carbonyldiimidazole (scheme 13). The very pure para isomer is obtained in only 29% yield by successive recrystallizations from dichloromethane and petroleum ether. Attempts to wash a dichloromethane solution of the para isomer with distilled water or to purify through chromatography on silica gel, leads to hydrolysis or partial decomposition of the product. On the other hand, the meta isomer is purified more easily by washing a CCl_4 solution of the crude compound with distilled water. No hydrolysis occurs in this case and the product is isolated in 63% yield. Purification of the crude material by chromatography on silica is impossible as total decomposition occurs on the column. The bis-carbonylimidazolide of the para isomer is not soluble enough in carbon tetrachloride to be purified in the same manner as the corresponding meta derivative.

The reactions of the bis-carbonylimidazolides of meta-benzenedimethanol, para-benzenedimethanol or p-bis(1-hydroxyethyl)benzene with pinacol do not give the expected polycarbonates. Oligomers of the polycarbonates of meta-benzenedimethanol, 4, para-benzenedimethanol, 3, and p-bis(1-hydroxyethyl)benzene, 5, are isolated respectively. Formation of the cyclic carbonate, 2, is also detected by proton NMR analysis of the reaction product (scheme 17).

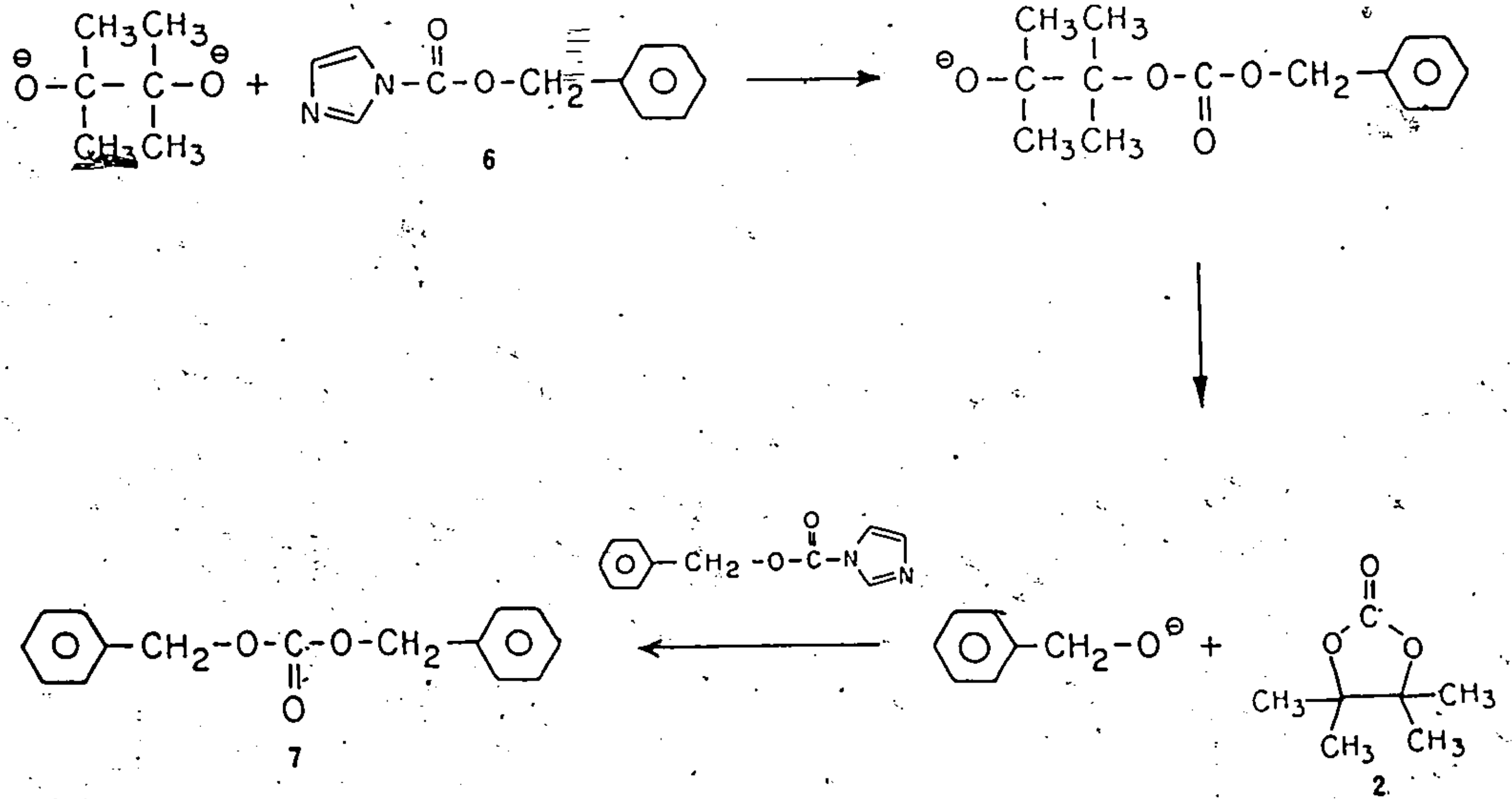

K$_2$CO$_3$
18-Crown-6
3,4,5
2
n
3) R = –H$_2$C–C$_6$H$_4$–CH$_2$–
4) R =
–CH$_2$
–CH$_2$–
5) R = –HC(CH$_3$)–C$_6$H$_4$–CH(CH$_3$)–

Scheme 17

A model study of these reactions using the carbonylimidazoyl derivative of benzyl alcohol with pinacol confirms that the pinacol fragment once attached to one benzylic unit through a carbonate moiety undergoes a ring-closure side-reaction leading to the 5-membered ring cyclic carbonate instead of attacking another imidazolide molecule to form a linear bis-carbonate. Again the major products obtained are 1,1,2,2-tetramethylethane carbonate, 2, and bis-benzyl carbonate, 7. Upon ring closure of the pinacol carbonate units, the benzylic alcoholate which is eliminated is able to react with the surrounding carbonylimidazolide to form the bis-benzyl carbonate (scheme 18). The formation of aromatic homo-oligomers in the polymer preparations can be explained by a similar mechanism.

It was decided to use α,α'-dihydroxy-p-diisopropyl-benzene as a substitute for pinacol, since this molecule has the potential of increasing even more the melting point of the polymer because of its aromatic character. It is expected that its copolycarbonate with p-benzenedimethanol should have a good solubility because of the methyl substituents which prevent close packing of the chains. The polymer should also depolymerize by acidolysis or thermolysis because of its ability of forming a stable tertiary benzylic intermediate with protons available for elimination on adjacent carbons.

The polycondensation of this tertiary diol with the bis-carbonylimidazolide of benzenedimethanol is not expected to be most suitable for the obtention of a high molecular weight polymer because tertiary diols react slowly with carbonylimidazolides due to steric constraints



Scheme 18

(25) and also because tertiary diols are susceptible to dehydration under the reaction conditions. A better approach is to use the bis-carbonylimidazolide of α,α'-dihydroxy-p-diisopropyl-benzene to prepare the desired polymer. The bis-carbonylimidazolide, <u>I-e</u>, prepared following the usual procedure (scheme 13), is obtained as a white solid in 29% yield after purification by recrystallization. The polycondensation of <u>I-e</u> with p-benzenedimethanol, (scheme 14), gives polymer <u>II-d</u> in 80% yield. As expected, the polymer is soluble in a variety of organic solvents. DSC indicates that the polymer has a Tg of 46°C, but no melting point is observed while another endotherm at 140°C stands for the decomposition of the polymer (figure 13). This fact is confirmed by a TGA curve which shows a loss of 50% of the weight between 140°C and 150°C, followed by a slow decrease in weight from 150°C to 240°C where the weight loss reaches 90% (figure 14). Additional analysis by mass spectroscopy (figure 15) reveals the formation of p-benzenedimethanol, 1,4-diisopropenyl-benzene and 4-(2-hydroxypropyl-α-methylstyrene as expected from the proposed mechanism of depolymerization (scheme 19). The latter product is obtained from the units located at the end of the polymer chains.

A brief study of the acidolysis of a 1.5 μm thick film of the polymer, followed by infrared spectroscopy, shows that the carbonyl band disappears after an exposure of 20 mJ, with no heating being necessary (figure 16). But it seems that the diene which is given-off during the process crosslinks, as a thin insoluble residue is observed during imaging testing on silicon wafers. The crosslinking of 1,4-diiso-

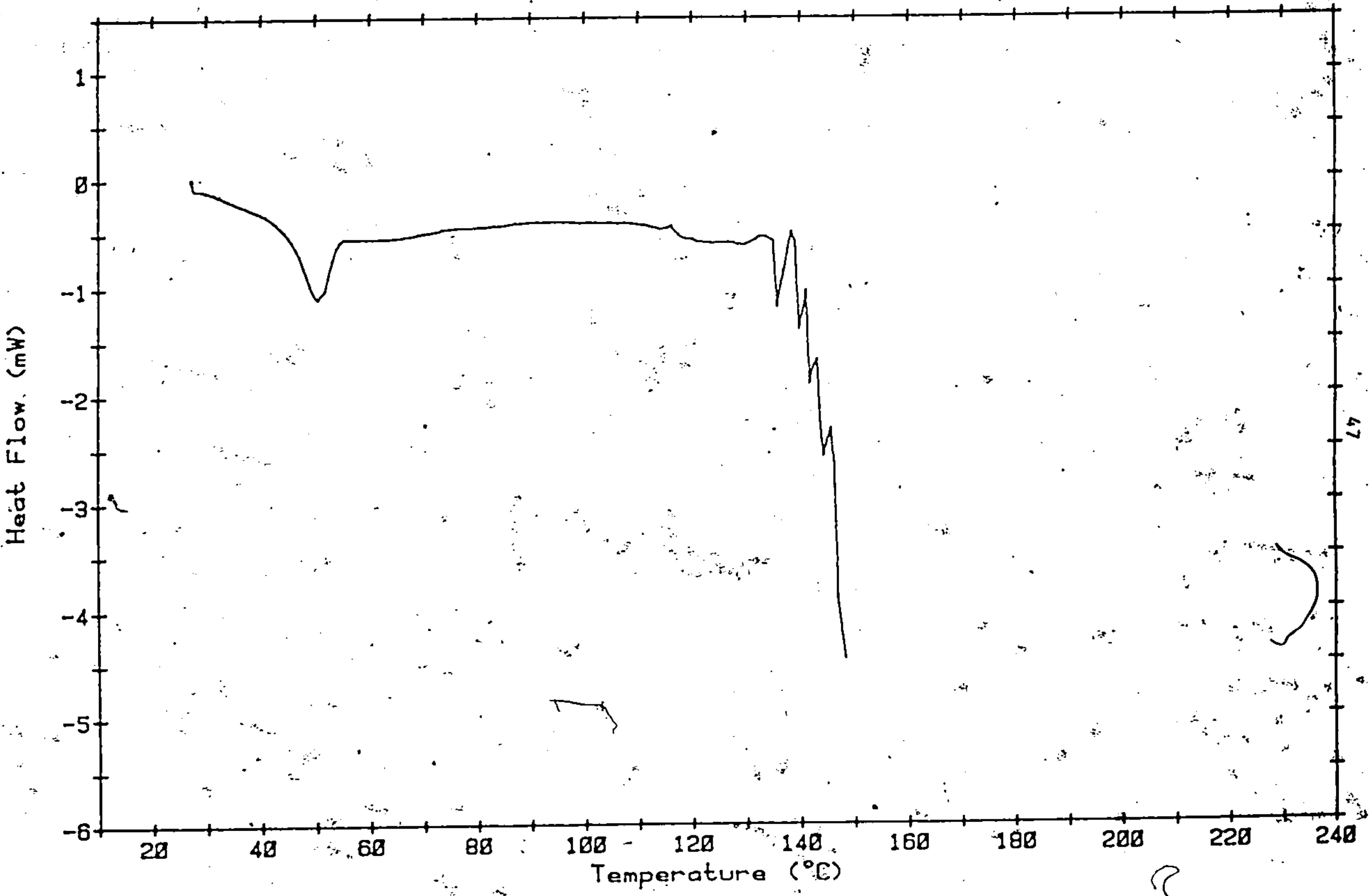


Figure 13 DSC of II-d

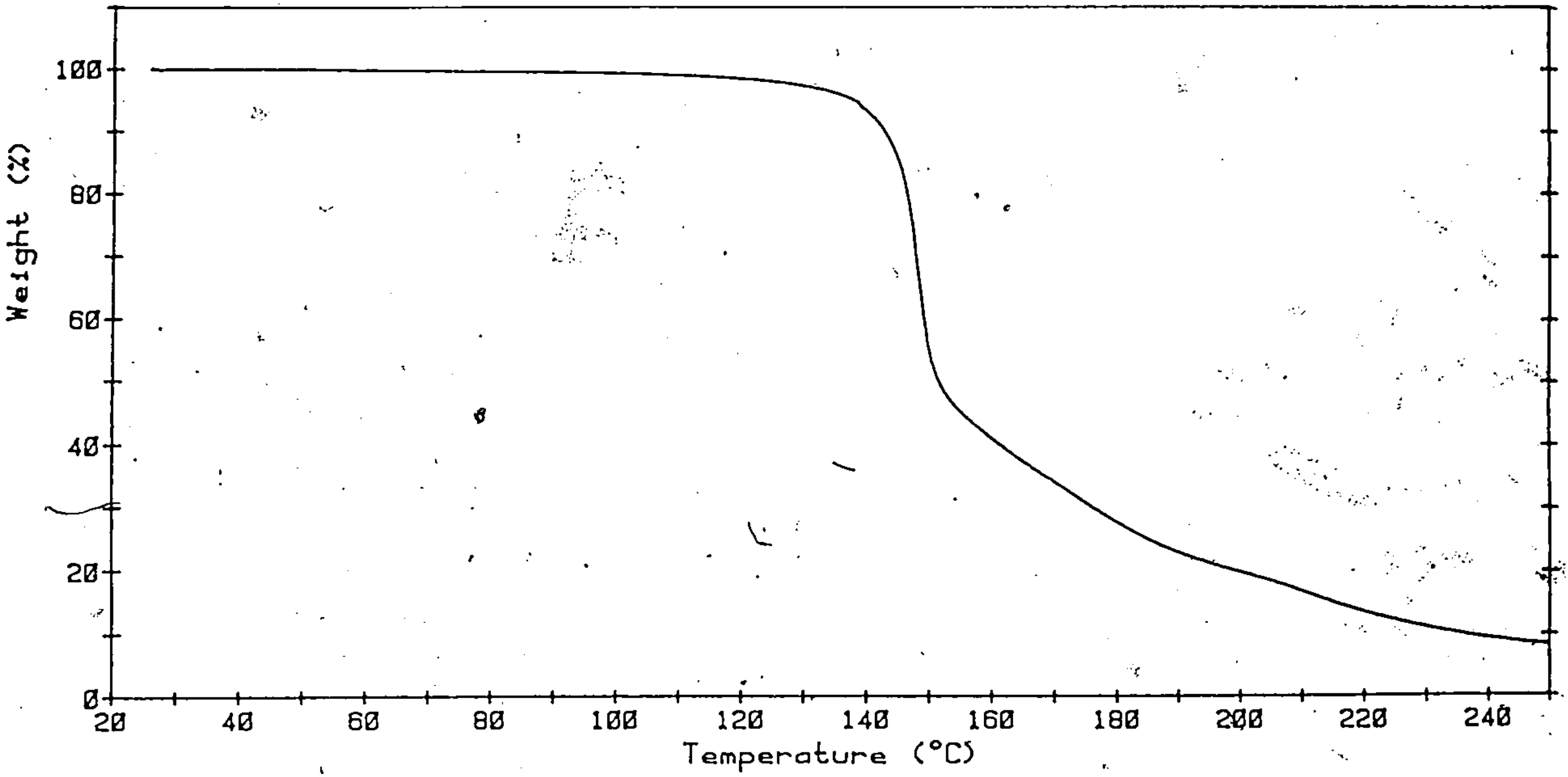


Figure 14 TGA of II-d

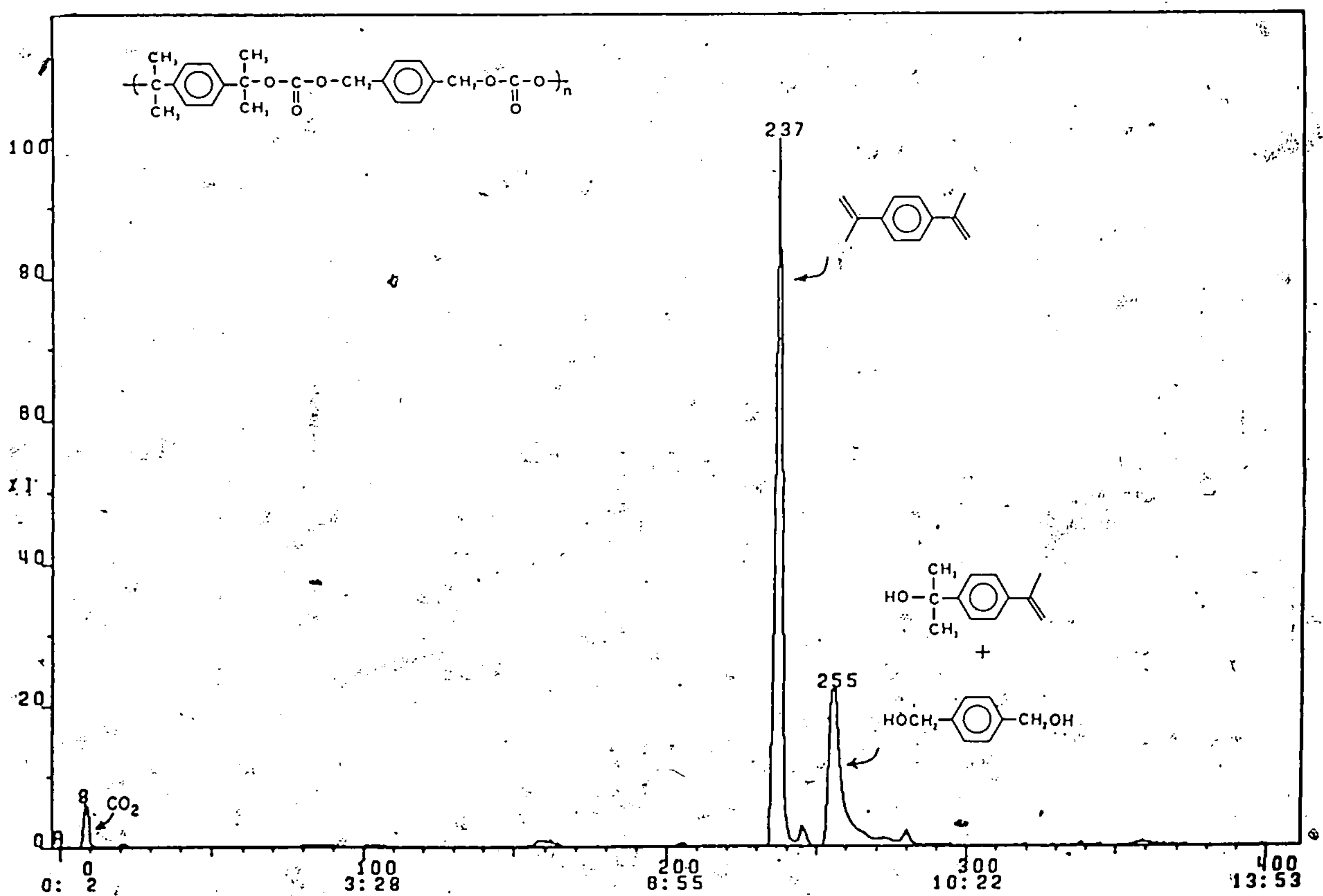
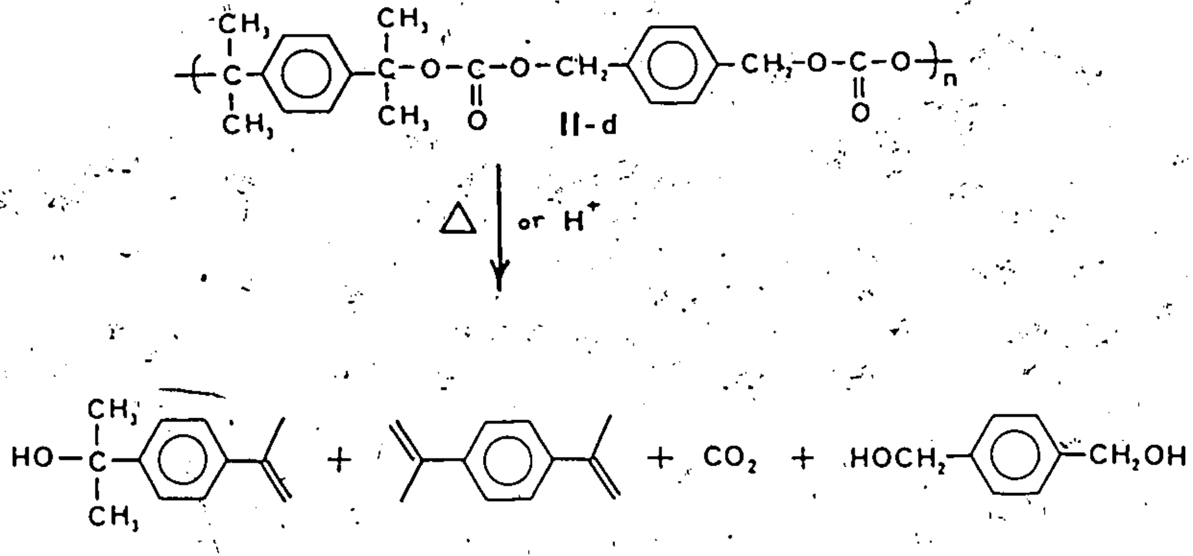
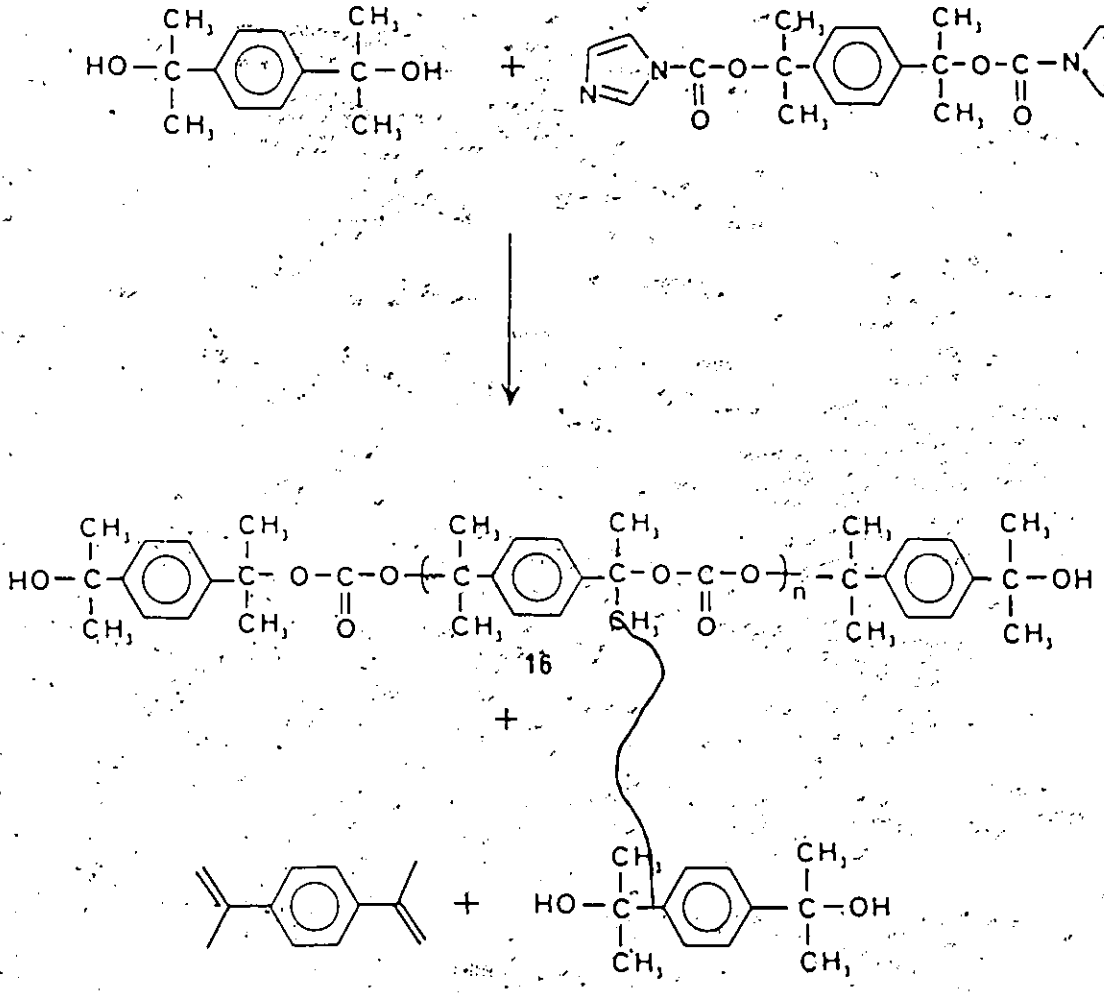


Figure 15 GC-MS of II-d



Scheme 19



Scheme 20

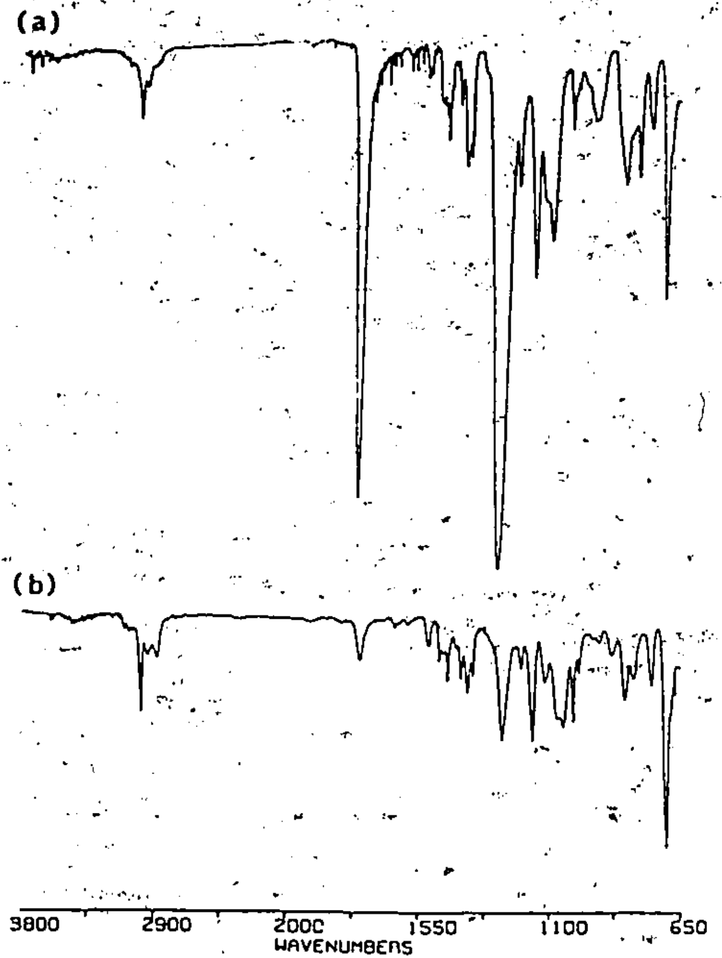
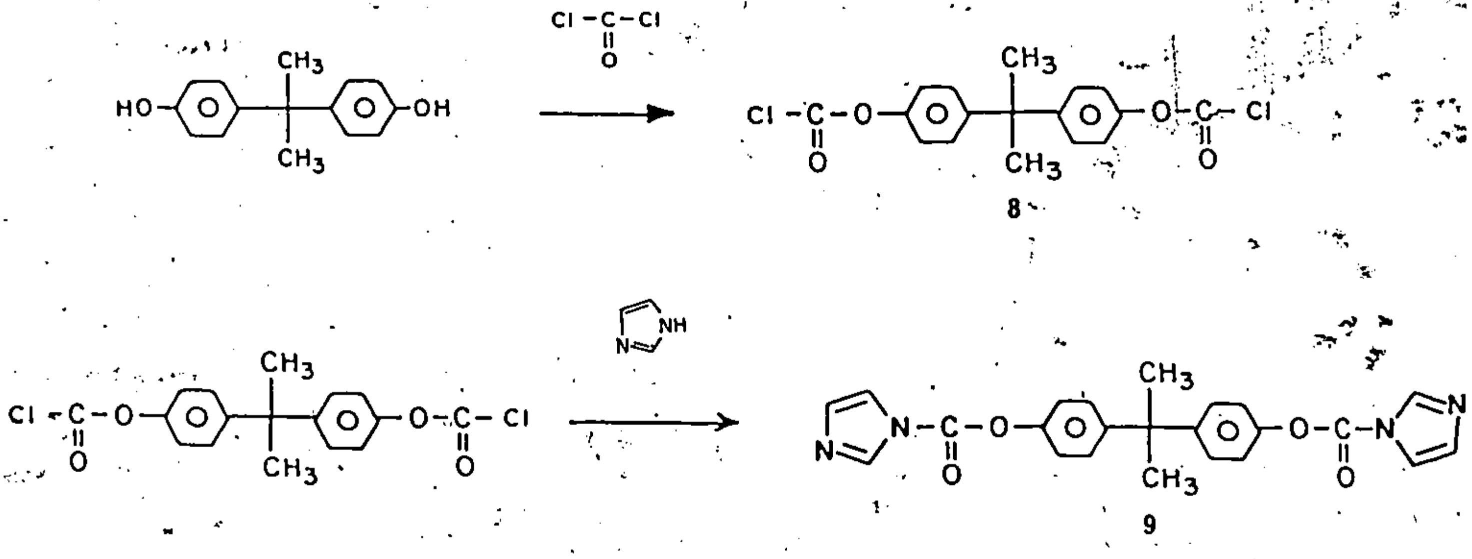


Figure 16 IR spectra of II-d/Ph_2IAsF_6 (a) unexposed, (b) exposed



Scheme 21

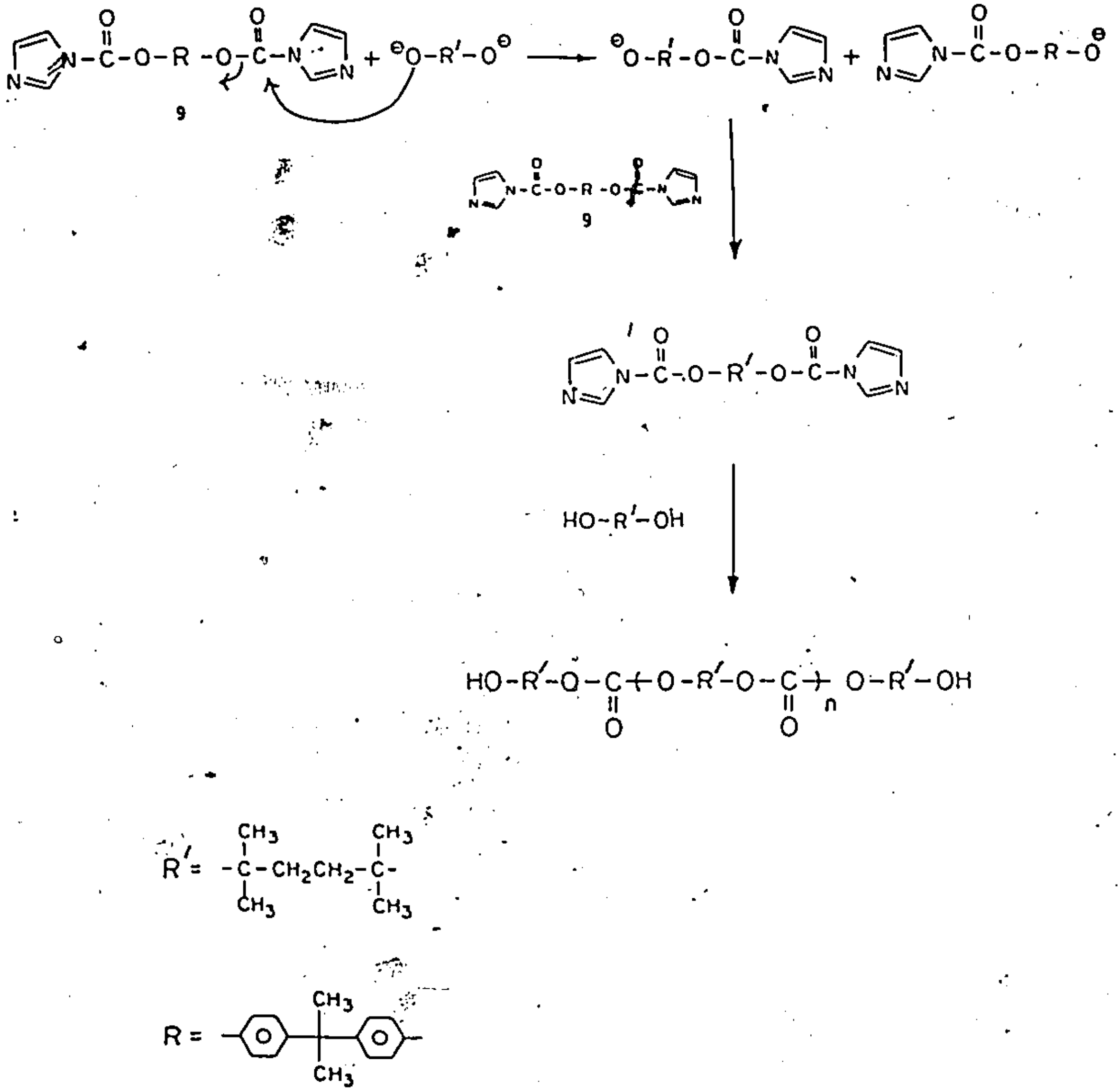
propyl-benzene could explain the ~ 10% residue which is observed in the thermogravimetric analysis.

Attempts to polymerize the bis-carbonylimidazolide of α,α'-dihydroxy-p-diisopropyl-benzene with its parent tertiary benzylic diol only gave the starting diol, a small amount of the corresponding oligomer 16, and some 1,4-diisopropenyl-benzene, thus confirming the low reactivity of tertiary diols and their susceptibility to elimination (scheme 20).

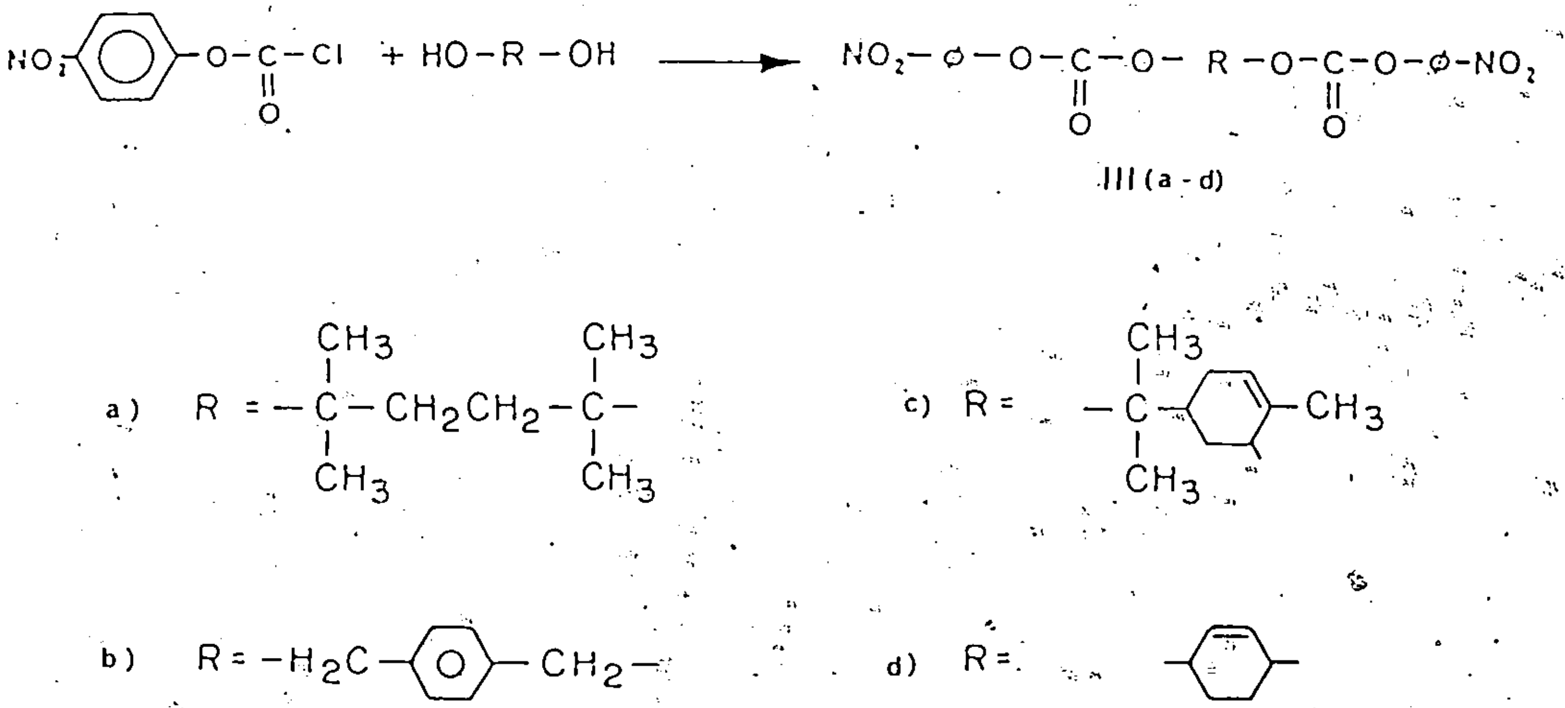
The reactivity of bisphenol A with the bis-carbonylimidazolide of 2,5-dimethyl-2,5-hexanediol under phase-transfer catalysis was previously tested (25), hoping that the resulting polycarbonate having a backbone with a structure analogous to that of the t-BOC group would behave as a highly reactive photoresist. But that polymerization was not successfull due to the fact that the phenolate anion is a better leaving group than the imidazoyl anion and, therefore, displacement of the imidazoyl anion cannot occur under the basic conditions used in the reaction.

Reacting the bis-carbonylimidazolide of bisphenol A with 2,5-dimethyl-2,5-hexanediol seemed to provide a better route to the synthesis of that polymer. The synthesis of the bis-carbonylimidazolide of bisphenol A is achieved by a two-step reaction involving the formation of the bischloroformate intermediate using phosgene, followed by displacement with imidazole (scheme 21). Unfortunately, this approach does not provide a good polymerization since the aliphatic diol displaces the better leaving group phenolate to form the carbonylimidazolide of 2,5-dimethyl-2,5-hexanediol. The reaction of the latter with a second molecule of bisphenol A bis-carbonylimidazolide leads to the formation of the bis-carbonylimidazolide of 2,5-dimethyl-2,5-hexanediol. The subsequent reaction of the aliphatic bis-carbonylimidazolide formed "in-situ" with the parent diol can explain the presence of the oligomer recovered in the reaction mixture (scheme 22). The presence of bisphenol A and 2,5-dimethyl-2,5-hexanediol in the reaction product was also observed by ^{1}H-NMR.

The next alternative to the preparation of a polycarbonate incorporating bisphenol A, was to use a derivative having a better leaving group than a phenolate. We chose to prepare the bis-p-nitrophenylcarbonate of 2,5-dimethyl-2,5-hexanediol, III-a, which can be synthesized in a 65% yield by reaction with p-nitrophenylchloroformate (scheme 23). The product is easily purified by recrystallization and is stable for long periods of time if kept below room temperature. During the polymerization of III-a with bisphenol A (scheme 24), a yellow coloration due to the formation of p-nitrophenol is observed, and the white polymer incorporating bisphenol A, IV-a, is obtained in 94% yield. DSC indicates that the polymer has a melting point of 166°C and a Tg of 87°C (figure 17). A strong endotherm at 180°C corresponds to the decomposition temperature of the polymer which is confirmed by a TGA curve (figure 18) showing a weight loss of 46% from 175°C to 180°C, this loss is attributed to carbon dioxide and the mixture of aliphatic dienes formed by the elimination process. The residual bisphenol A sublimes from 180°C to 225°C; it should be noted that the exact shape of the TGA curve is a function of experimental

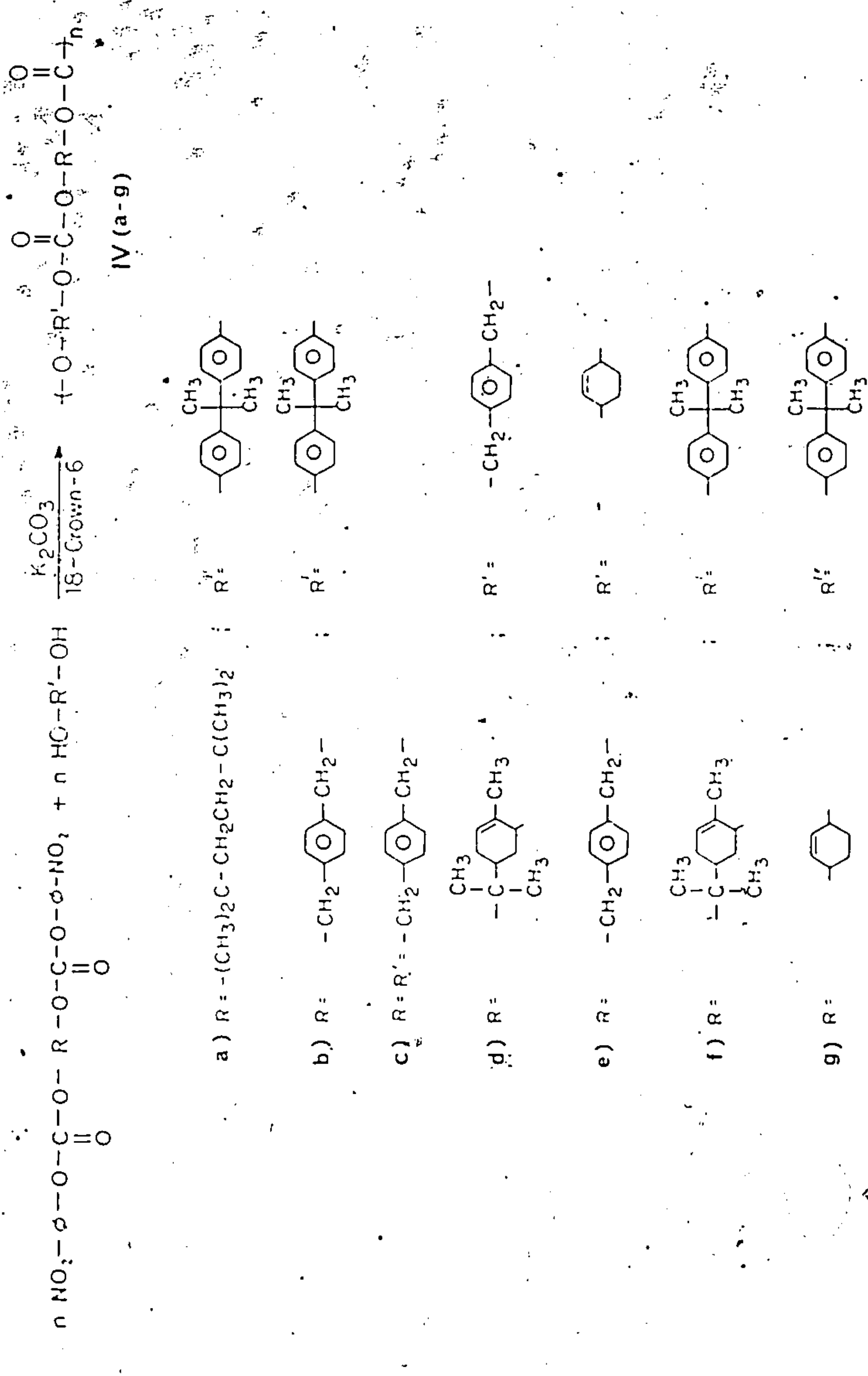


Scheme 22



III (a - d)

Scheme 23


n NO₂–φ–O–C(=O)–O– R –O–C(=O)–O–φ–NO₂ + n HO–R′–OH
K₂CO₃
18-Crown-6
IV (a-g)
a) R = -(CH₃)₂C-CH₂CH₂-C(CH₃)₂ ; R′ =
b) R = ; R′ =
c) R = R′ =
d) R = ; R′ =
e) R = ; R′ =
f) R = ; R′ =
g) R = ; R′ =
CH₃
CH₂

Scheme 24

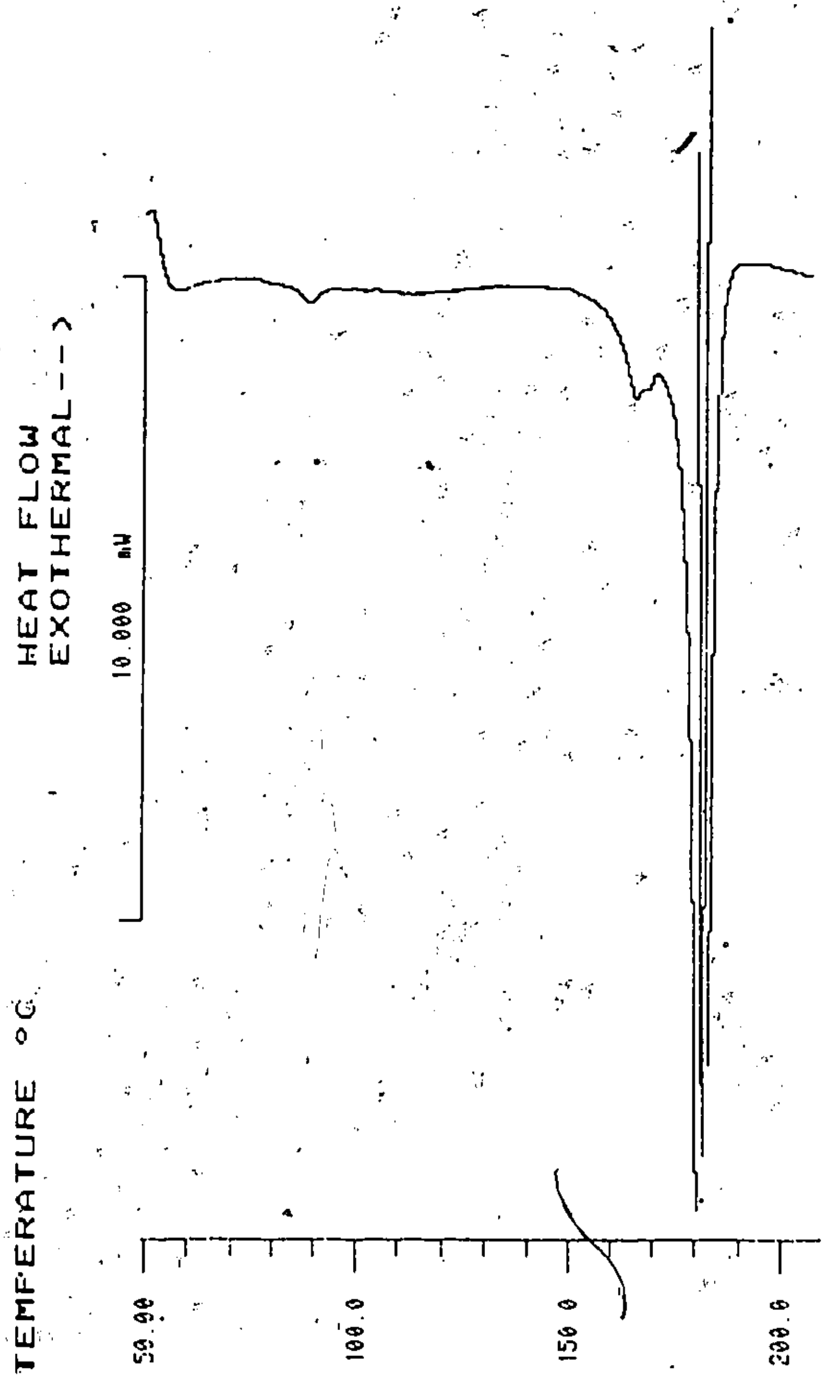


Figure 17 DSC of IV-a

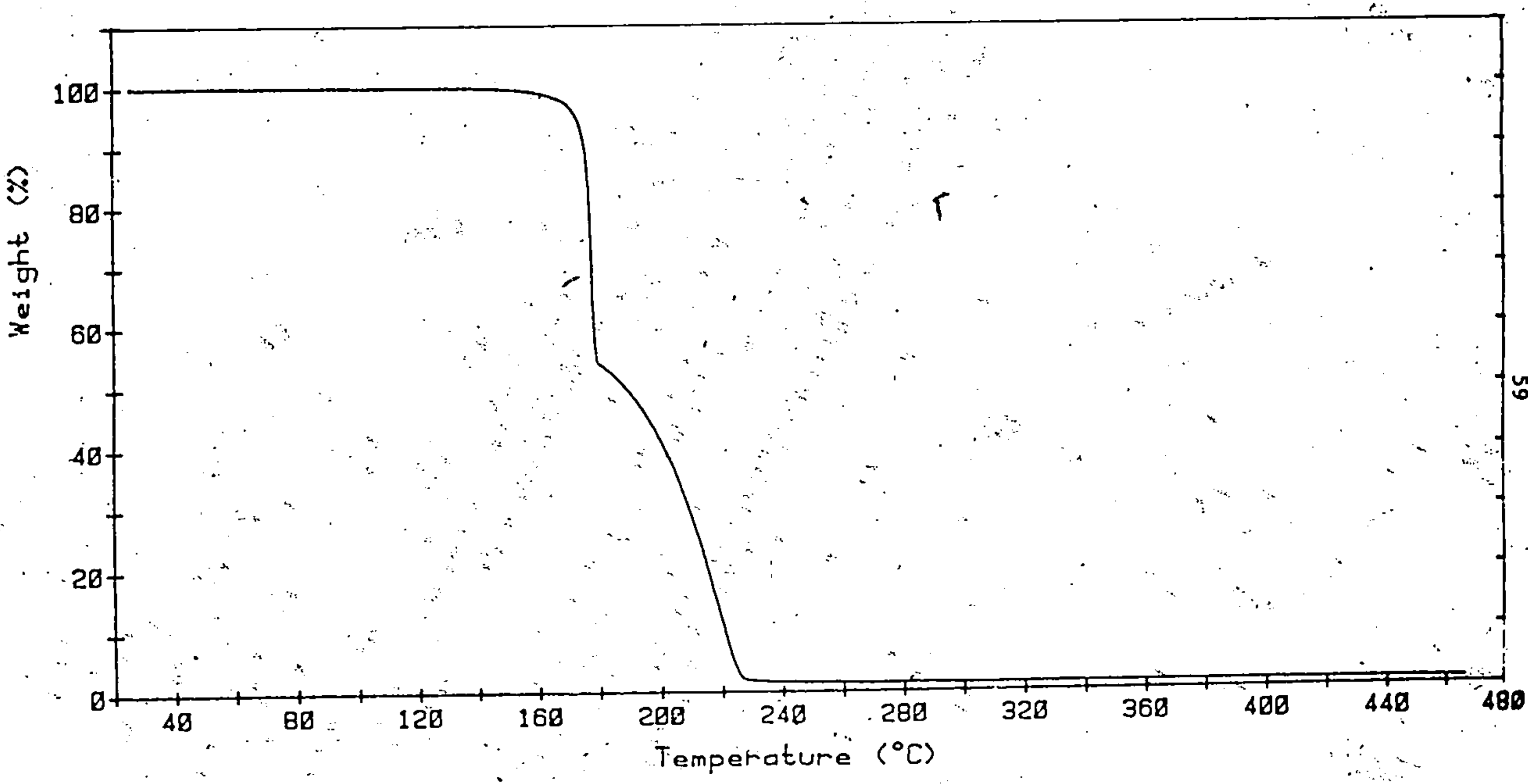
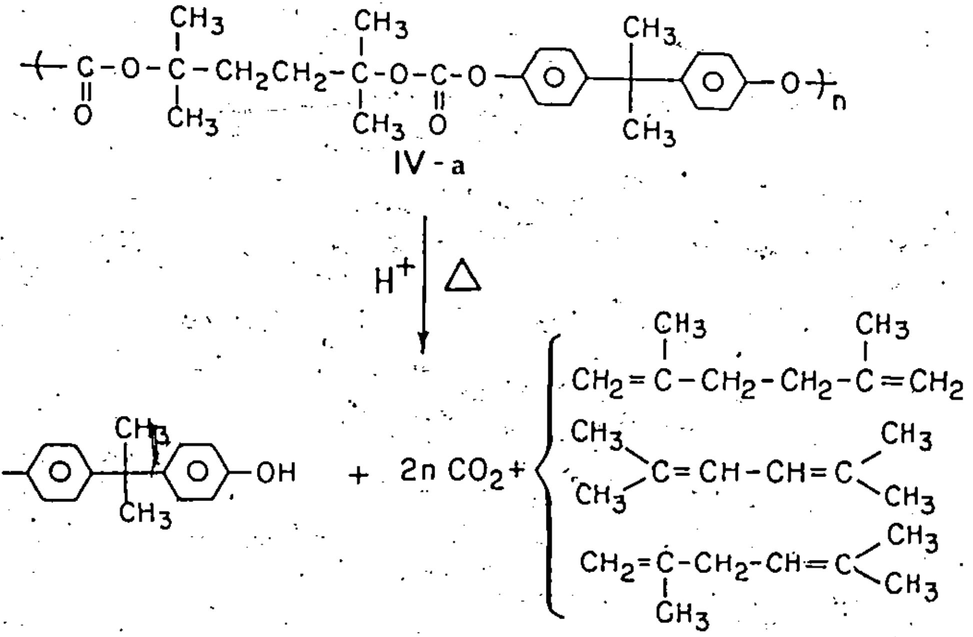


Figure 18 TGA of IV-a

conditions including in particular the flow rate of inert gas through the furnace. A thermolysis study followed by gas chromatography and mass spectroscopy confirms that the thermal decomposition results in the formation of bisphenol A and various dienes derived from 2,5-dimethyl-2,5-hexanediol (scheme 25).

The behavior of a film of polymer IV-a containing a catalytic amount of onium salt upon irradiation in the deep UV (254 nm) is monitored by infrared spectroscopy as a preliminary step for imaging study. The behavior of this polymer should be similar to that of PBOCST which requires a post-bake of 1 min. at 100°C after exposure in order to remove the protecting groups. A solution of the linear polycarbonate, IV-a, in dichloroethane containing 15% of triphenylsulfonium hexafluoroarsenate is cast on a NaCl disk to a thickness of 0.85 µm. An IR spectrum shows that the polymer is stable to baking at 100°C before irradiation; upon exposure to 10 mJ/cm^2 of 254 nm UV light, the bands attributed to the polycarbonate gradually disappear without the need of a post-bake. The carbonyl peak has completely disappeared after 15 min., leaving a residue on the NaCl disk which was identified as bisphenol A (figure 19). It should be noted however that post-bake does accelerate the decomposition process and that complete disappearance of the carbonyl peak is observed upon exposure to 5 mJ/cm^2 followed by 3 min. postbake at 60°. In actual imaging development, post-bake would not be sufficient to remove the bisphenol A residue since it is not volatile enough at 60° and atmospheric pressure. The production of an image from this system would have to involve wet development unless development under high vacuum can be implemented.



Scheme 25

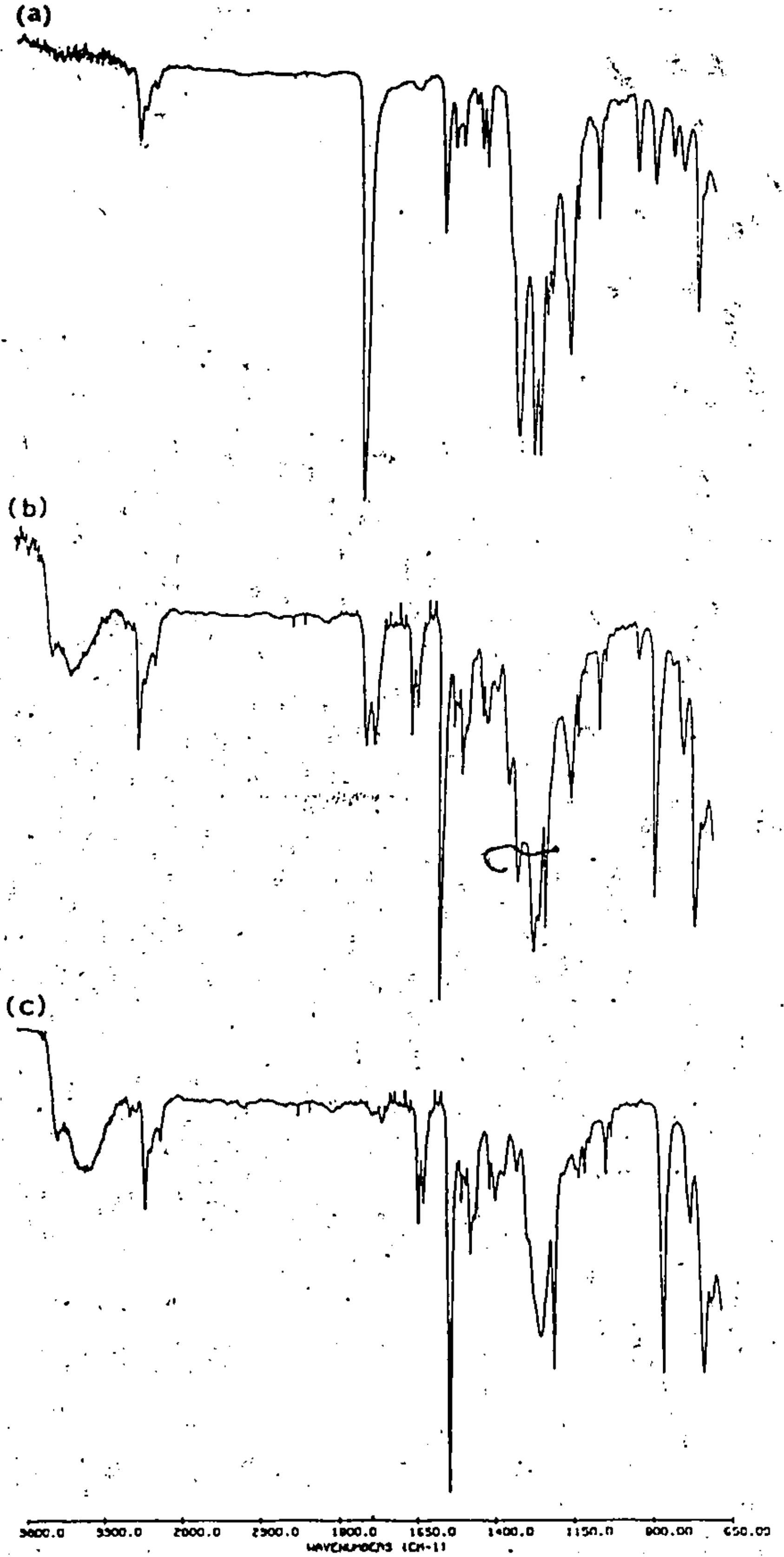


Figure 19 IR spectra of IV-a/Ph_2IAsF_6 (a) unexposed, (b) exposed, (c) 15 min. after exposure

The bis-p-nitrophenylcarbonate of a tertiary diol proved to be a stable but reactive monomer in the formation of polycarbonates. It was desirable to test whether a reactive derivative of a benzylic diol could also be made and used in the preparation of polycarbonates. The synthesis of the bis-p-nitrophenylcarbonate of 1,4-benzenedimethanol, III-b, is achieved (scheme 23) in a yield of 56% after purification by recrystallization. This derivative is much easier to prepare and purify, and is obtained in a better yield (56% vs 29%) than the corresponding bis-carbonylimidazolide. This material can be used in polycondensations reactions with bisphenol, benzylic, secondary and tertiary diols. The reaction with the secondary diol, cyclohexenediol, will be discussed later.

The white soluble polymer, IV-b, which is obtained in 91% yield by reaction between bisphenol A and compound III-b (scheme 24), has a DSC showing a Tg at 90°C (figure 20). This polymer is expected to be more stable than the polycarbonates forming a stable intermediate with an alpha hydrogen available for elimination. Indeed, TGA indicates a decomposition temperature of 260°C (figure 21) which is 85°C higher than that of the polycarbonate of bisphenol A with 2,5-dimethyl-2,5-hexanediol. Thermolysis followed by mass spectroscopy reveals that the polymer decomposes to release bisphenol A, but no p-benzenedimethanol is observed as the depolymerization mechanism is different in this case due to the lack of alpha hydrogens.

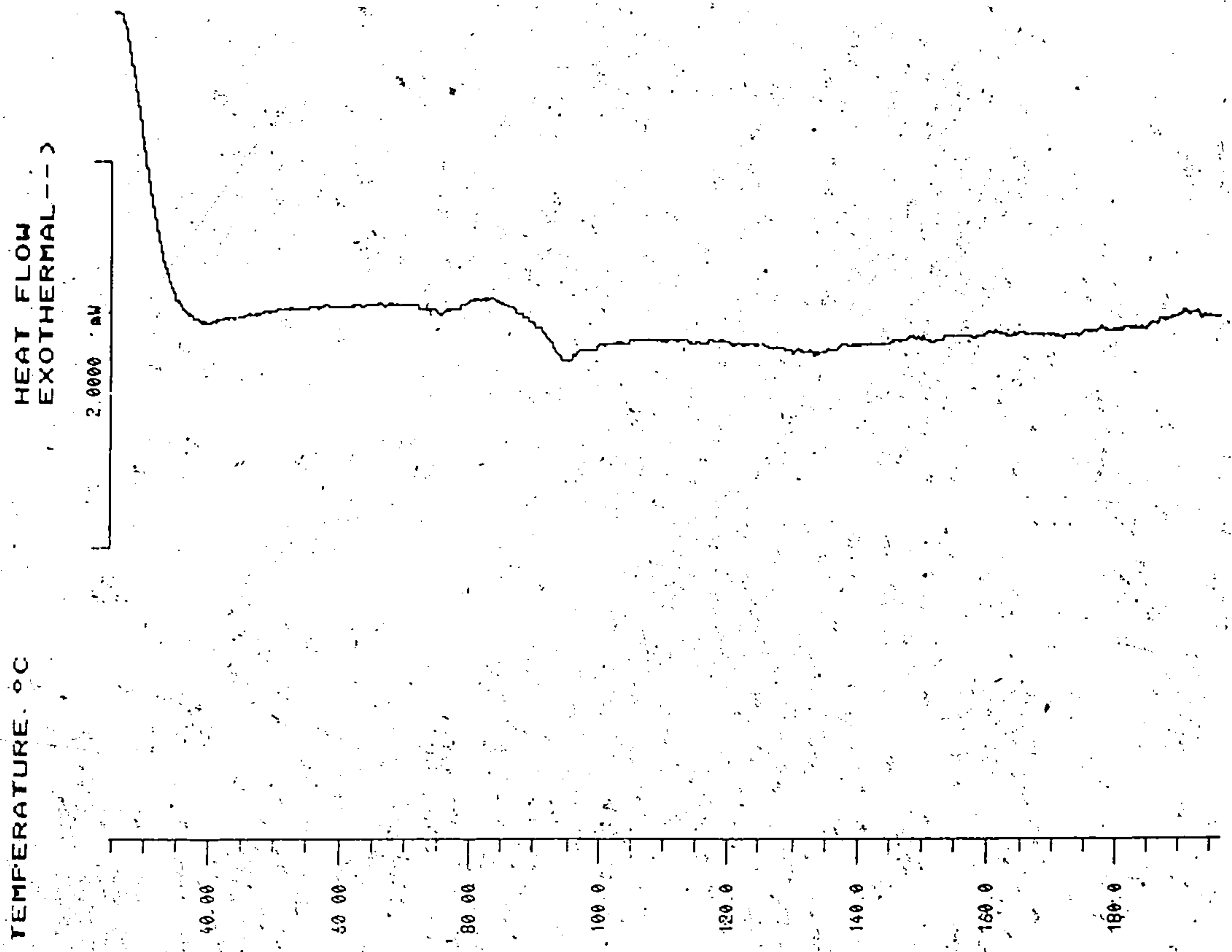


Figure 20 DSC of IV-b

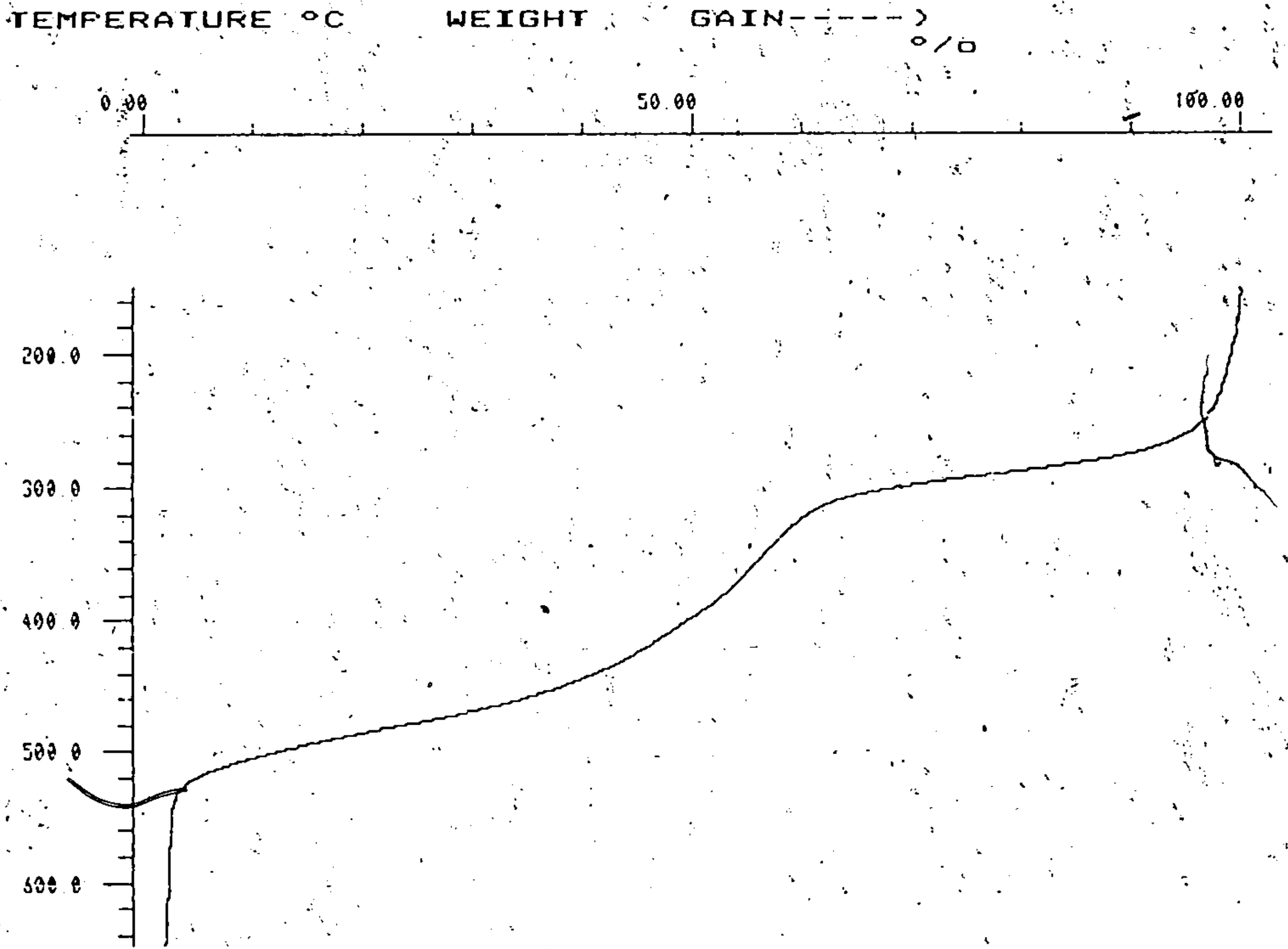


Figure 21 TGA of IV-b

The formation of a polycarbonate using the bis-p-nitrophenylcarbonate, III-b, with the corresponding diol (scheme 24) gives the desired polymer, IV-c, in a 93% yield. The polymer melts at 230°C and has another endotherm at 205°C as detected by DSC (figure 22). The aromatic homopolymer has a very low solubility and is expected to decompose at a high temperature. As can be seen in figure 23, thermogravimetric analysis confirms this expectation as the polymer thermolyses near 300°. Mass spectroscopy does not detect any p-benzenedimethanol after thermolysis, as in the previous example with polymer, IV-b, due to a different mechanism of depolymerization which does not allow for simple elimination of stable molecules as is the case with polymer IV-a, and other polycarbonates of similar design.

As seen previously, the synthesis of a polymer by condensation of a tertiary diol and a bis-carbonylimidazolide derivative does not give good results since the elimination of the tertiary diol seems to occur before the polymerization can take place. It was worthwhile trying whether a tertiary diol would be more reactive in a polycondensation with a diol bis-p-nitrophenylcarbonate. The polymerization of 2,5-dimethyl-2,5-hexanediol and bis-p-nitrophenylcarbonate, III-b, did not yield to the desired copolycarbonate incorporating tertiary units. Instead an insoluble polymer identified as the homopolycarbonate of 1,4-benzenedimethanol, 10, was isolated (scheme 26). We can conclude from our experiments that neither bis-carbonylimidazolides nor diol bis-p-nitrophenylcarbonates are suitable for polycondensation with tertiary diols. When it is necessary to introduce a tertiary alcohol fragment in a polycarbonate, the best results are obtained by using

Figure 22 DSC of IV-c

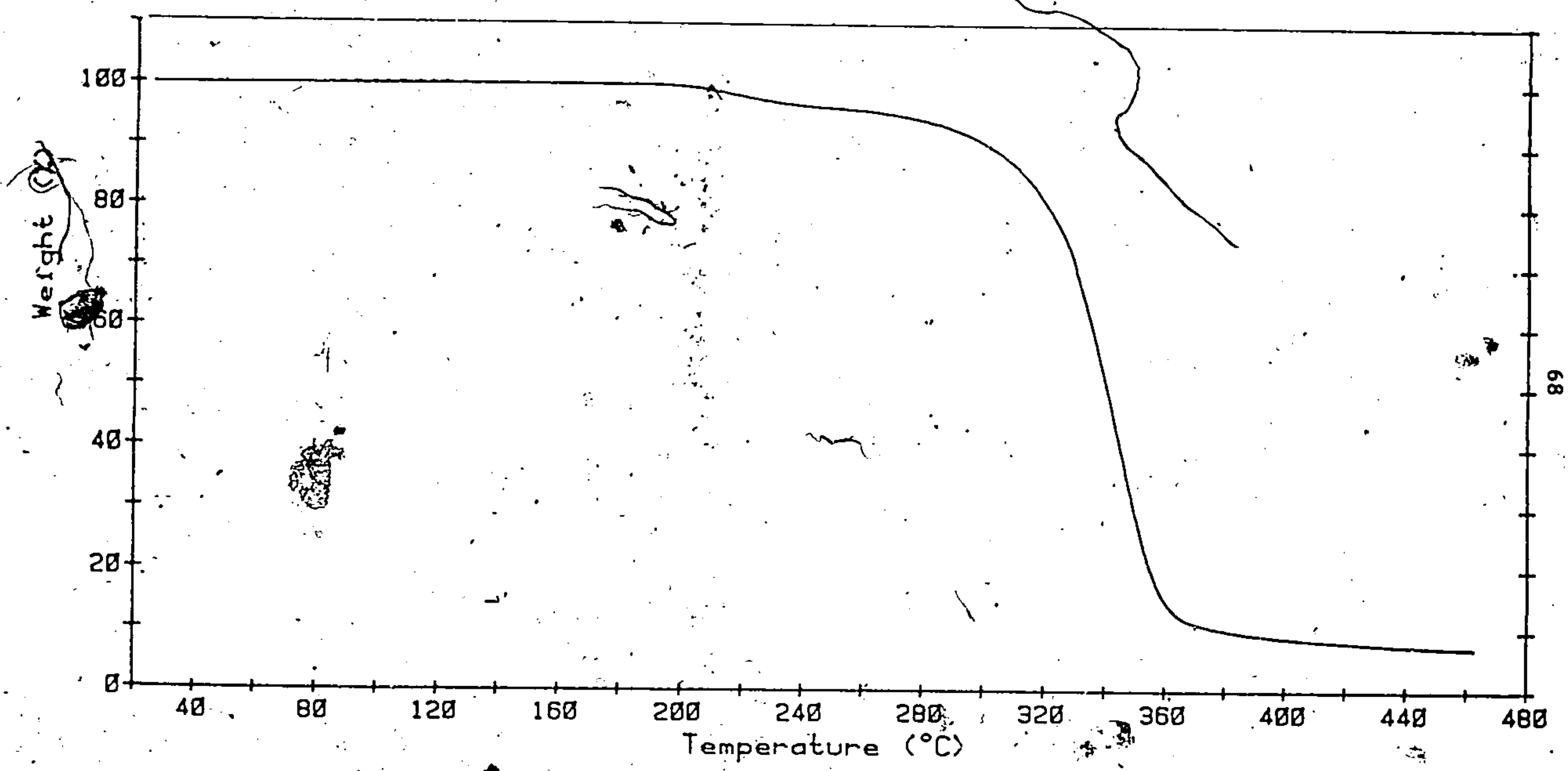
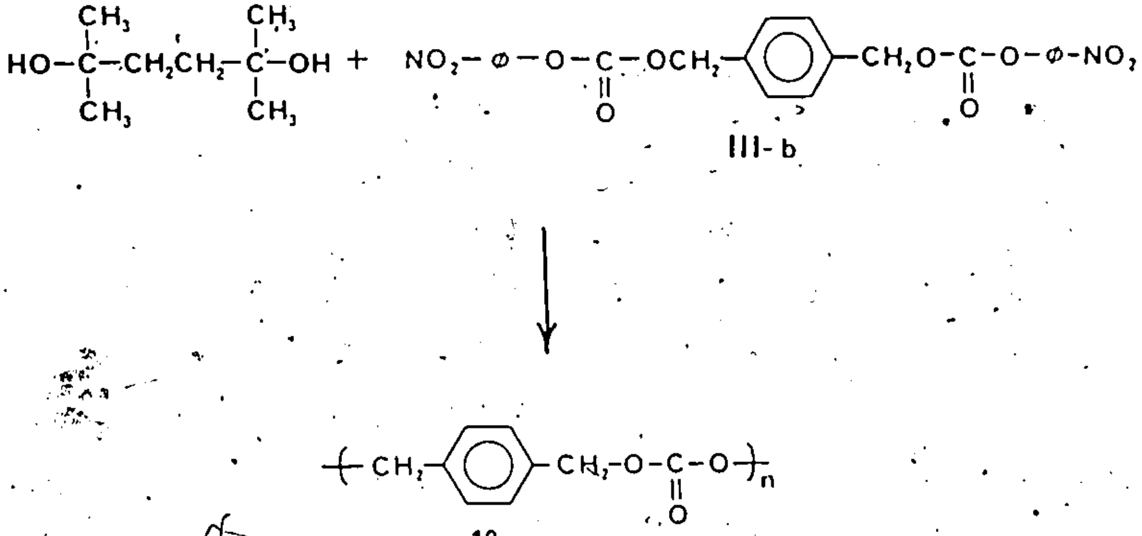


Figure 23 TGA of IV-c



III-b

10

Scheme 26

the bis-carbonylimidazolide or bis-p-nitrophenylcarbonate derivative of the tertiary diol together with primary, secondary, or phenolic diols.

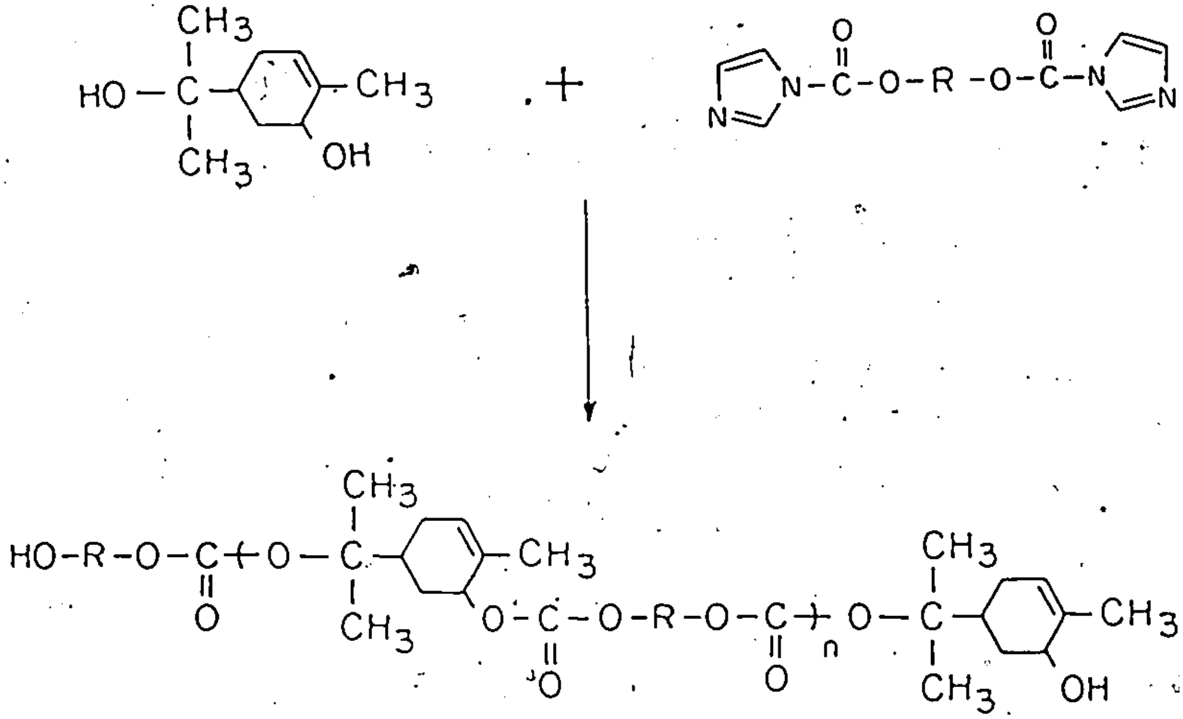
The bis-p-nitrophenylcarbonates provide a route to the synthesis of polycarbonates containing bisphenols. Their use can also be extended to replace the bis-carbonylimidazolides in all condensations with diols since they are easier to prepare and are obtained in better yields in the case of the benzylic derivatives.

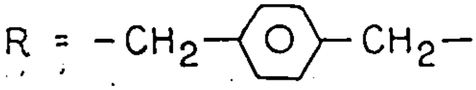
We have already demonstrated that polycarbonates containing units of any diol capable of forming a stable intermediate and having at least one hydrogen on the alpha position, are susceptible to depolymerization via catalytic acidolysis or thermolysis through processes which have relatively low activation energies. This was shown to be the case for certain polycarbonates incorporating tertiary or benzylic units. We can also design a new class of polycarbonates which would contain substituted allylic diols. The intermediate which would be formed during the depolymerization of such polycarbonates would possess allylic stabilization and would produce conjugated molecules after elimination of an alpha hydrogen, thus facilitating the overall depolymerization process. For example, a polymer containing cyclohexenediol should break down to produce benzene molecules upon acidolysis or thermolysis.

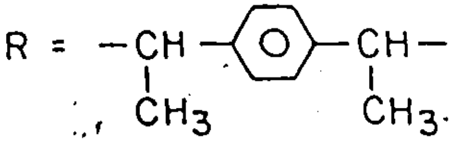
The first unsaturated diol available to us was sobrerol*, which contains both an allylic and a tertiary hydroxyl group and could give

* p-menth-6-ene-2,8-diol

a volatile triene as a result of elimination. Attempts to polymerize sobrerol with the bis-carbonylimidazolide of benzylic diols, 1,4-benzenedimethanol and p-bis(1-hydroxyethyl)benzene, were not successfull as only a small amount of oligomeric materials were obtained (scheme 27). This illustrates once more that a molecule having a tertiary alcohol site is not very reactive in phase-transfer catalyzed polycondensations. The alternative route was to synthesize the bis-carbonylimidazolide of sobrerol, I-f (scheme 13). Compound I-f obtained in 60% yield as a crystalline solid, can be used in a polycondensation with a diol such as p-benzenedimethanol under phase-transfer catalysis (scheme 14). The desired polymer, II-e, is obtained in 75% yield but can be shown to be only oligomeric by its infrared spectrum which contains both carbonyl and hydroxyl bands. Molecular weight determination by GPC confirms this finding since the GPC number average molecular weight is lower than 1000. The low extent of the polymerization can be attributed to the difference in reactivity of the aromatic diol towards the secondary and tertiary reactive sites of the bis-carbonylimidazolide. The bis-p-nitrophenylcarbonate of sobrerol, III-c, (scheme 23), synthesized in 60% yield, proved to be a better reactant for the preparation of a polymer with p-benzenedimethanol (scheme 24). Indeed, polymer IV-d was obtained in 80% yield from the polycondensation of those starting materials. A typical polymer obtained by this method has an number average molecular weight of 11,000 as determined by osmometry measurement. The low melting point of 80°C, observed by DSC (figure 24), reflects the asymmetry of the polymer. This asymmetry prevents the close packing of the chains thus lowering the crystallinity. The high asymmetry of



12) 

11) 

Scheme 27

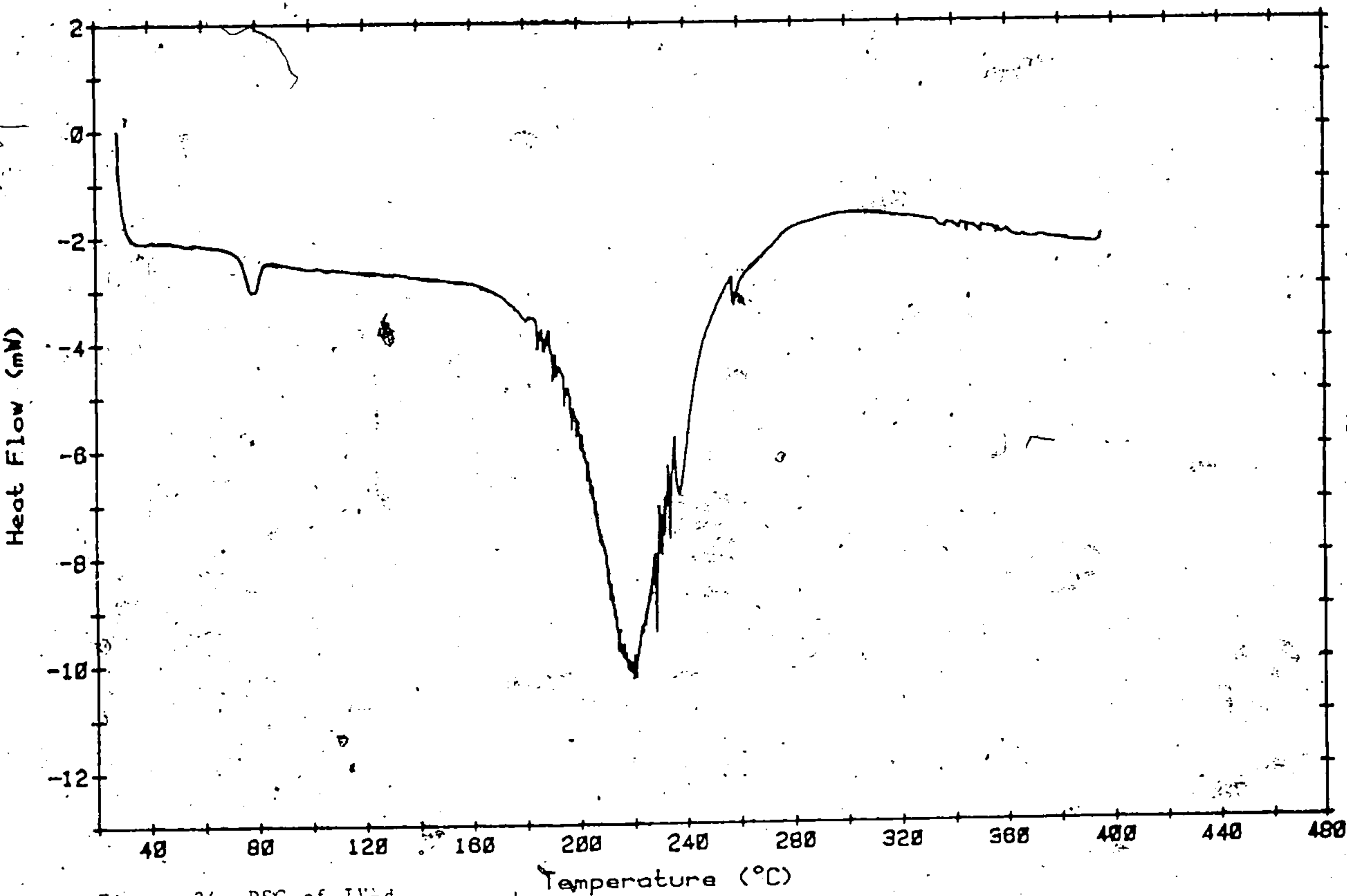


Figure 24 DSC of IV-d

sobrerol units also imparts a very good solubility to the polymer. Thermogravimetric analysis reveals that the polymer falls apart rapidly from 190°C to 250°C, leaving no residue (figure 25). The species formed during the thermolysis have been identified by mass spectroscopy (figure 26) as being the expected p-benzenedimethanol, 2-methyl,5-isopropylidene-1,3-cyclohexadiene and 2-methyl,5-isopropenyl-1,3-cyclohexadiene which partially isomerizes to p-cymene. In acidic conditions, 2-methyl,5-isopropenyl-1,3-cyclohexadiene is known to isomerize readily to p-cymene (31). The presence of 4'-methyl-α-methylstyrene was detected and attributed to air oxidation of the chain end fragments, 2-methyl, 5-isopropanol-1,3-cyclohexadiene, to p-cymene-8-ol which subsequently undergoes dehydration (scheme 28) (31). The air oxidation is possible since the bulb thermolysis - GC-MS experiment was conducted in the presence of air at 250°C. In order to eliminate the compound assumed to be produced by air oxidation, the thermolysis experiment was done under vacuum. Although greatly reduced, the oxidation product was still detected as well as a new compound which was positively identified by mass spectroscopy as limonene, the reduced product of 2-methyl,5-isopropenyl-1,3-cyclohexadiene. Thus the formation of a small amount of 4'-methyl-α-methylstyrene in the absence of oxygen can still be explained by the fact that 2-methyl,5-isopropenyl-1,3-cyclohexadiene acts as an oxidant (scheme 29). It is noted that in the absence of oxygen, the gas chromatogram shows an approximate 1:1 ratio for 4'-methyl-α-methylstyrene and limonene. The presence of ether fragments is also revealed by mass spectrometry, suggesting that under thermolysis, the carbonate units can lose carbon dioxide first to form an ether mole-

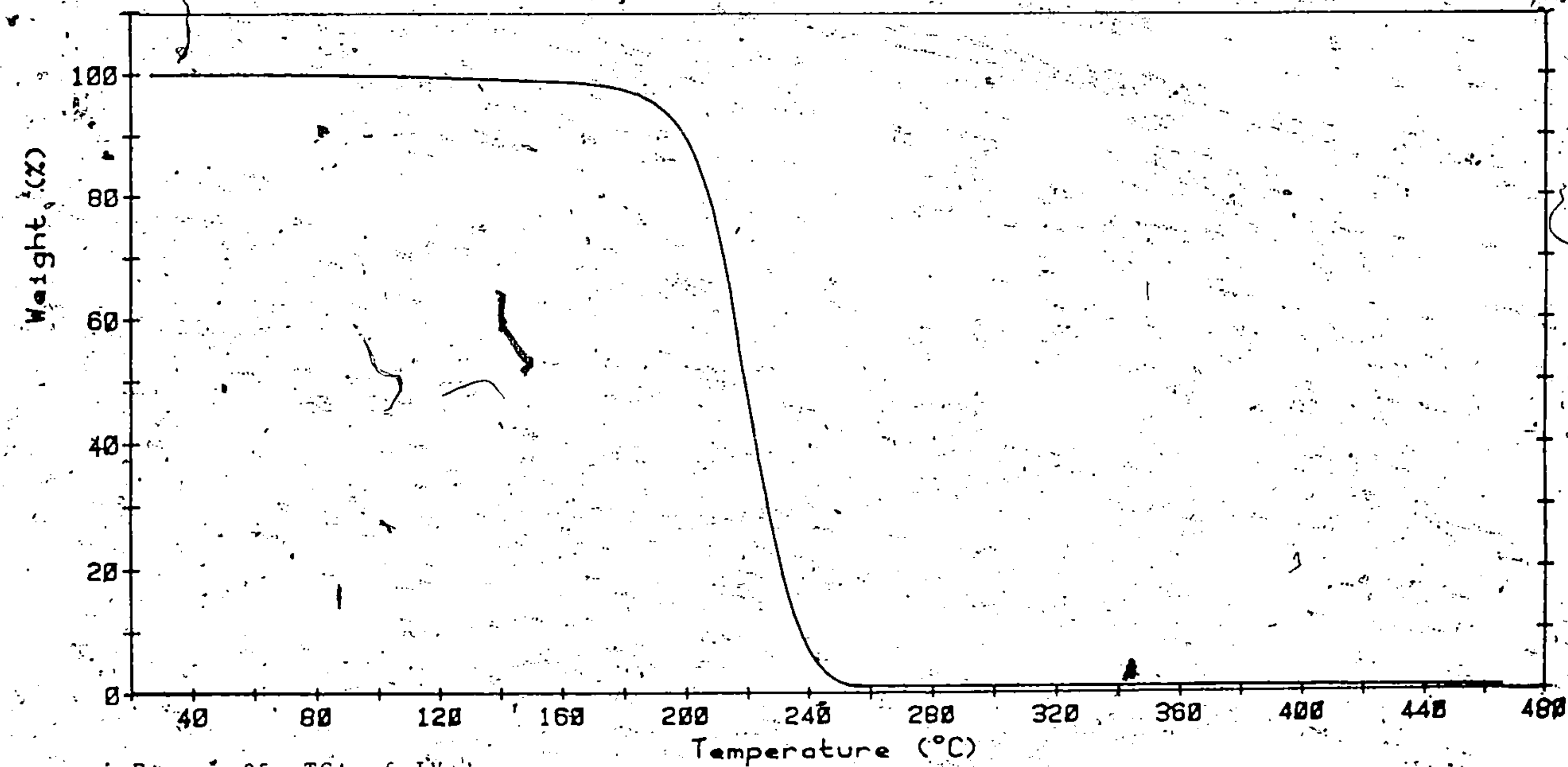


Figure 25 TGA of IV-d

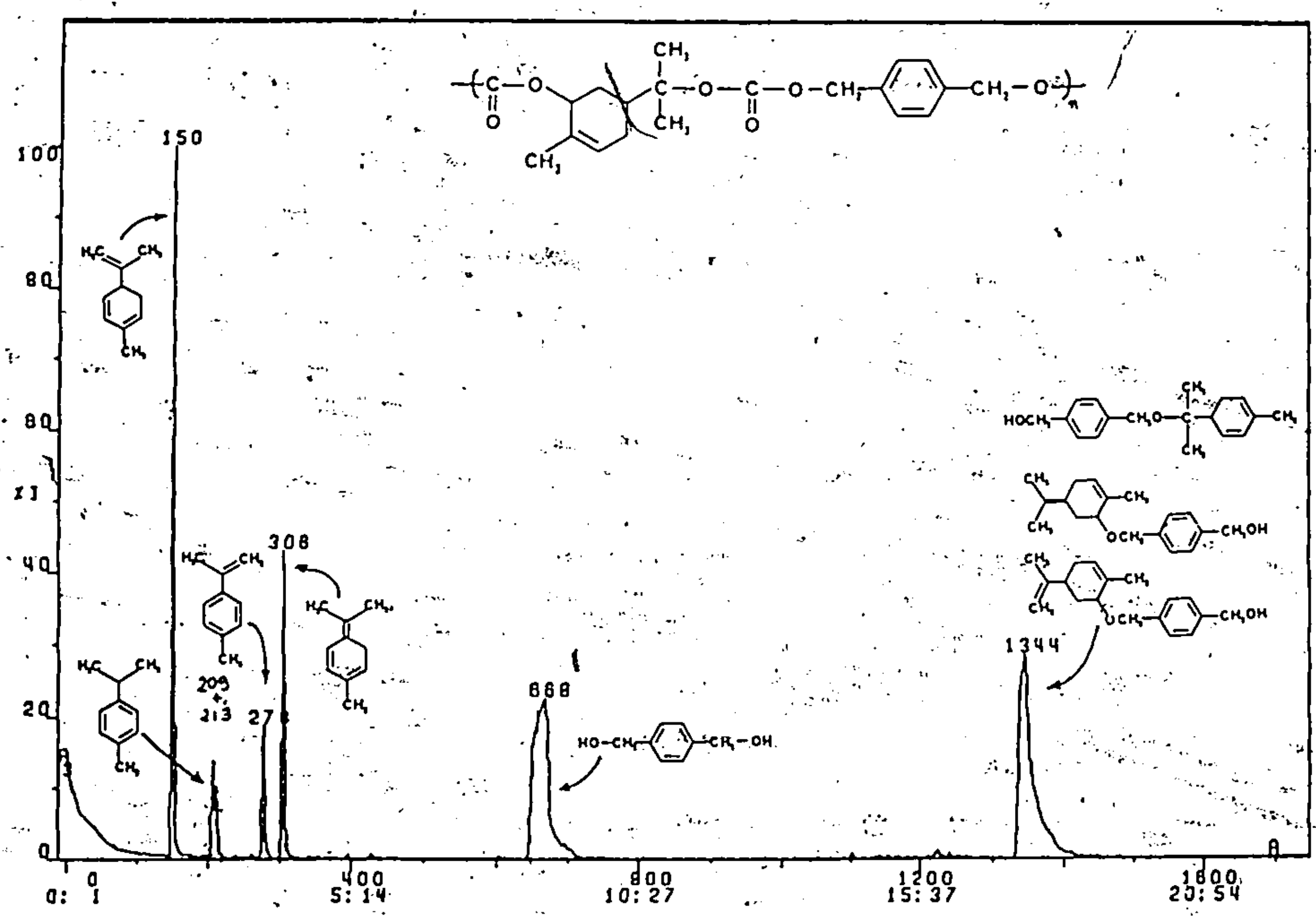
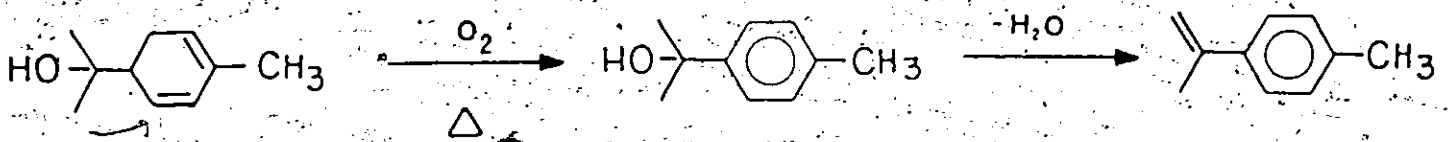
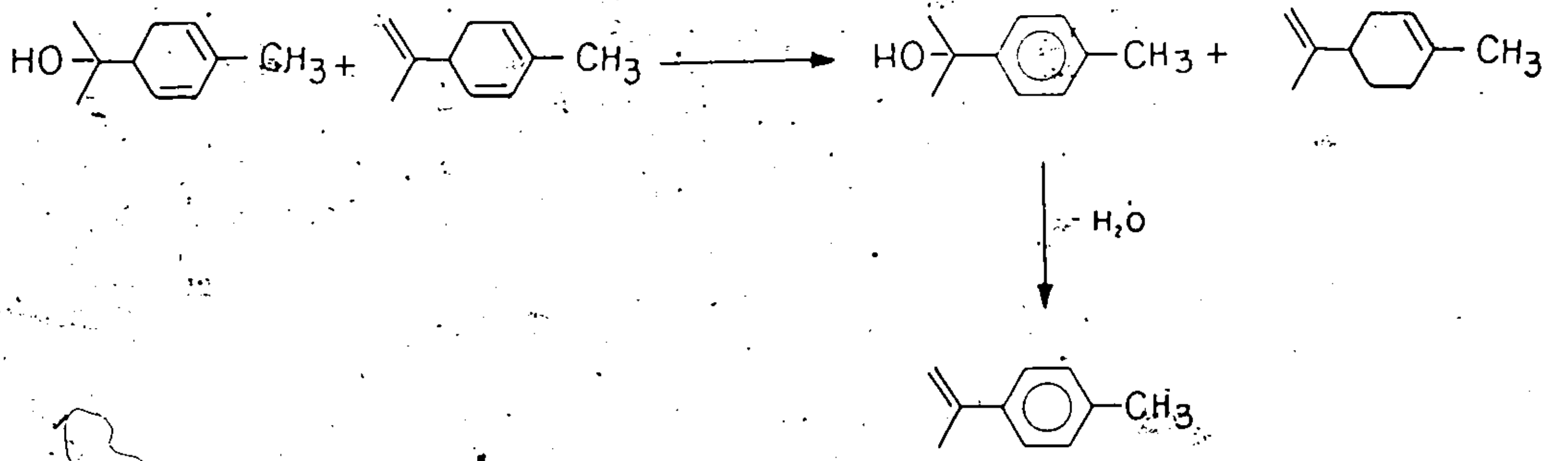


Figure 26 GC-MS of IV-d



Scheme 28

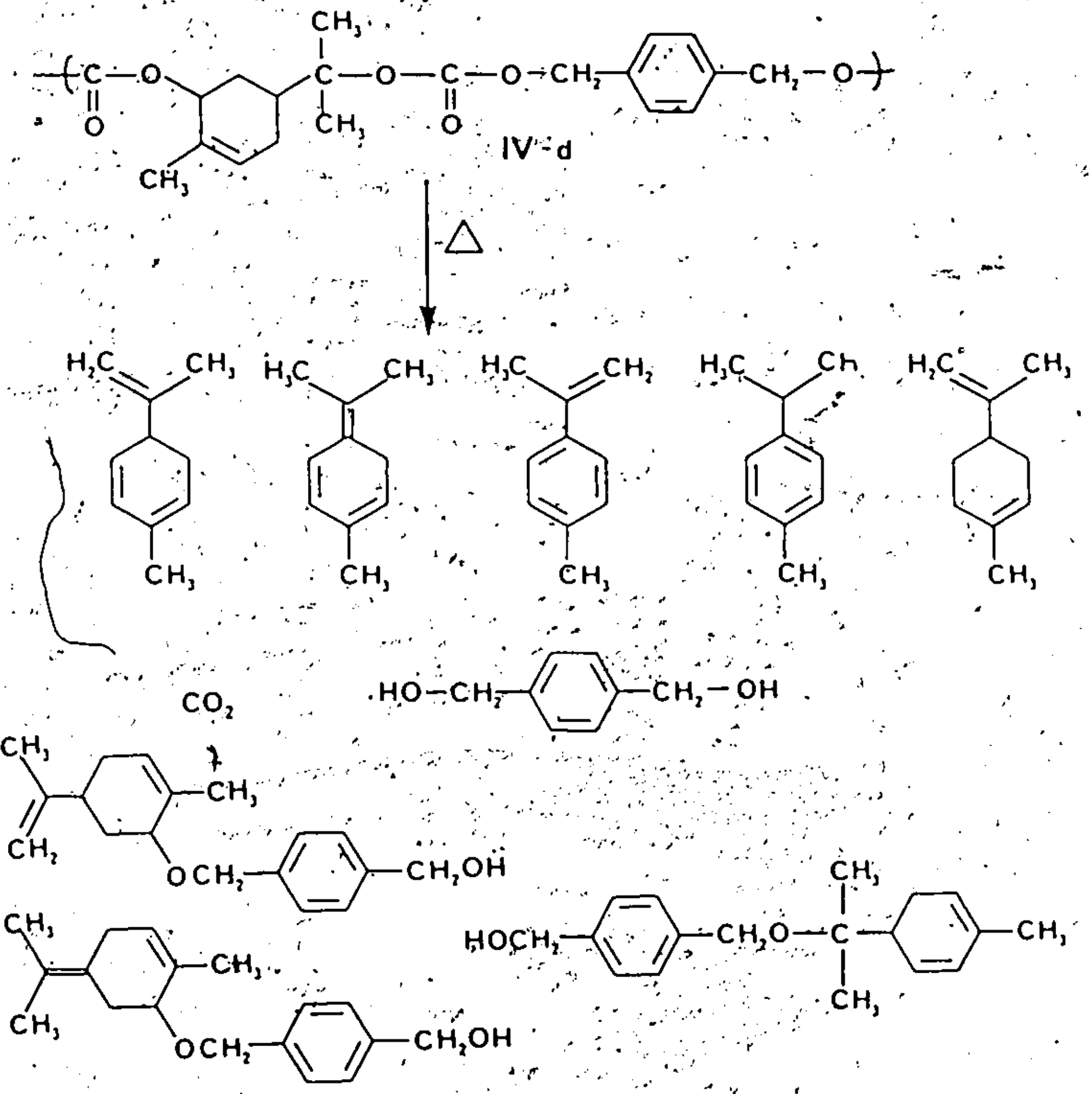


Scheme 29

cule. Scheme 30, shows the three ether isomers which could be formed along with the other thermolysis products. It is not easy, on the basis of mass spectrometric data alone, to identify which ether isomer is the major one assuming that all three are produced. ^{1}H-NMR analysis of the thermolysis products would be necessary to positively assign the structure of the ether; this experiment was not attempted.

The light initiated acidolysis of a 1.2 µm thick film of the polymer containing a catalytic amount of onium salt can be followed by infrared spectroscopy. This study shows that the carbonyl band disappears after exposure to 50 mJ and 5 min. post bake at 100°C. A residue identified as p-benzenedimethanol is found on the NaCl disk after post-bake (figure 27).

The bis-p-nitrophenylcarbonate of sobrerol was also copolymerized with bisphenol A using the usual procedure (scheme 24). The white polymer, IV-f, obtained in 79% yield has a DSC indicating a Tg at 135°C and another endotherm at 190°C corresponding to the decomposition temperature (figure 28). A study of the degradation of the polymer indicates loss of 23% of the weight from 180°C to 190°C. The total weight loss reaches 83% from 190°C to 280°C. At that point, the sample mass decreases very slowly and it finally reaches zero when the temperature gets as high as 450°C (figure 29). Further study of thermolysis by gas chromatography and mass spectroscopy (figure 30) indicates the formation of bisphenol A, p-cymene, 4'-methyl-α-methylstyrene, 2-methyl,5-isopropenyl-1,3-cyclohexadiene and 2-methyl,5-isopropylidene-



Scheme 30

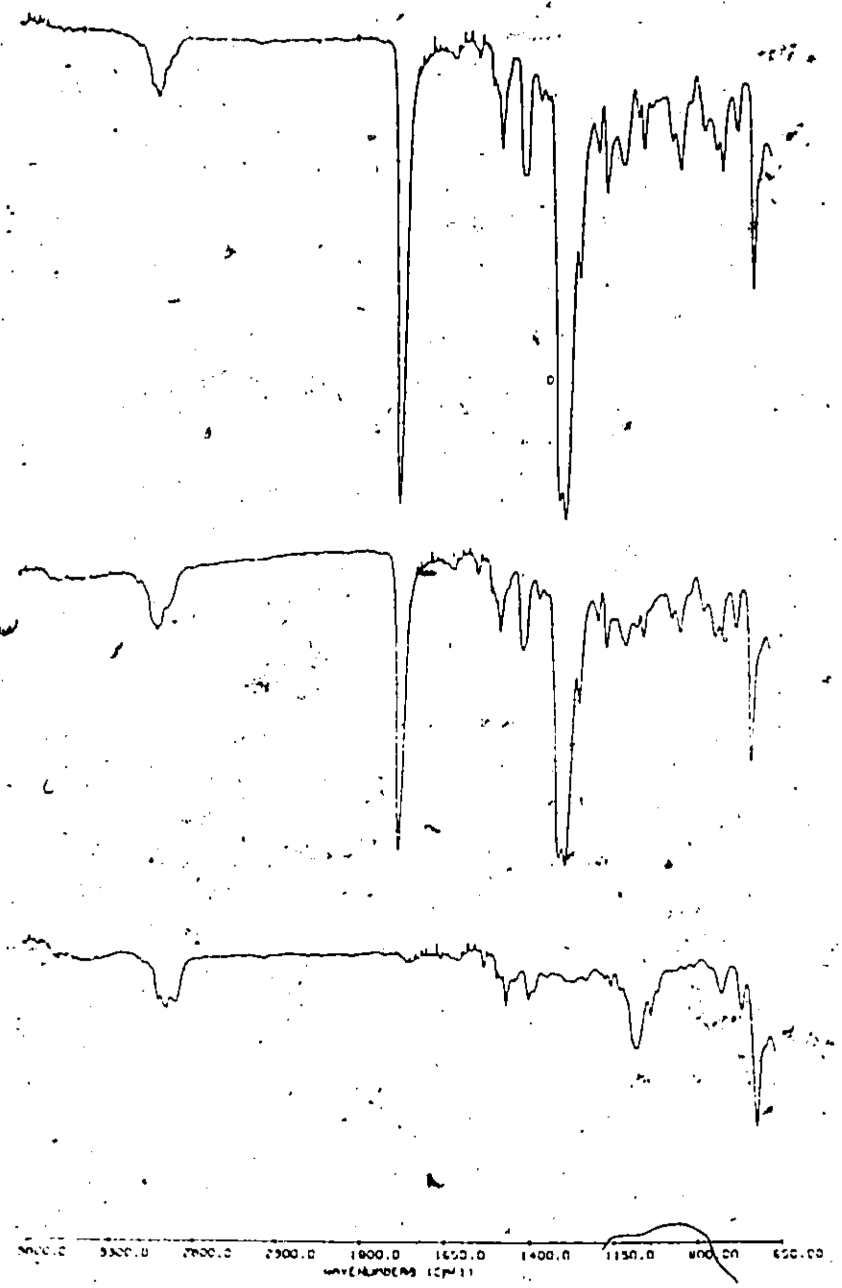


Figure 27 IR spectra of IV-d/Ph_2IAsF_6 (a) unexposed, (b) exposed, (c) post-baked

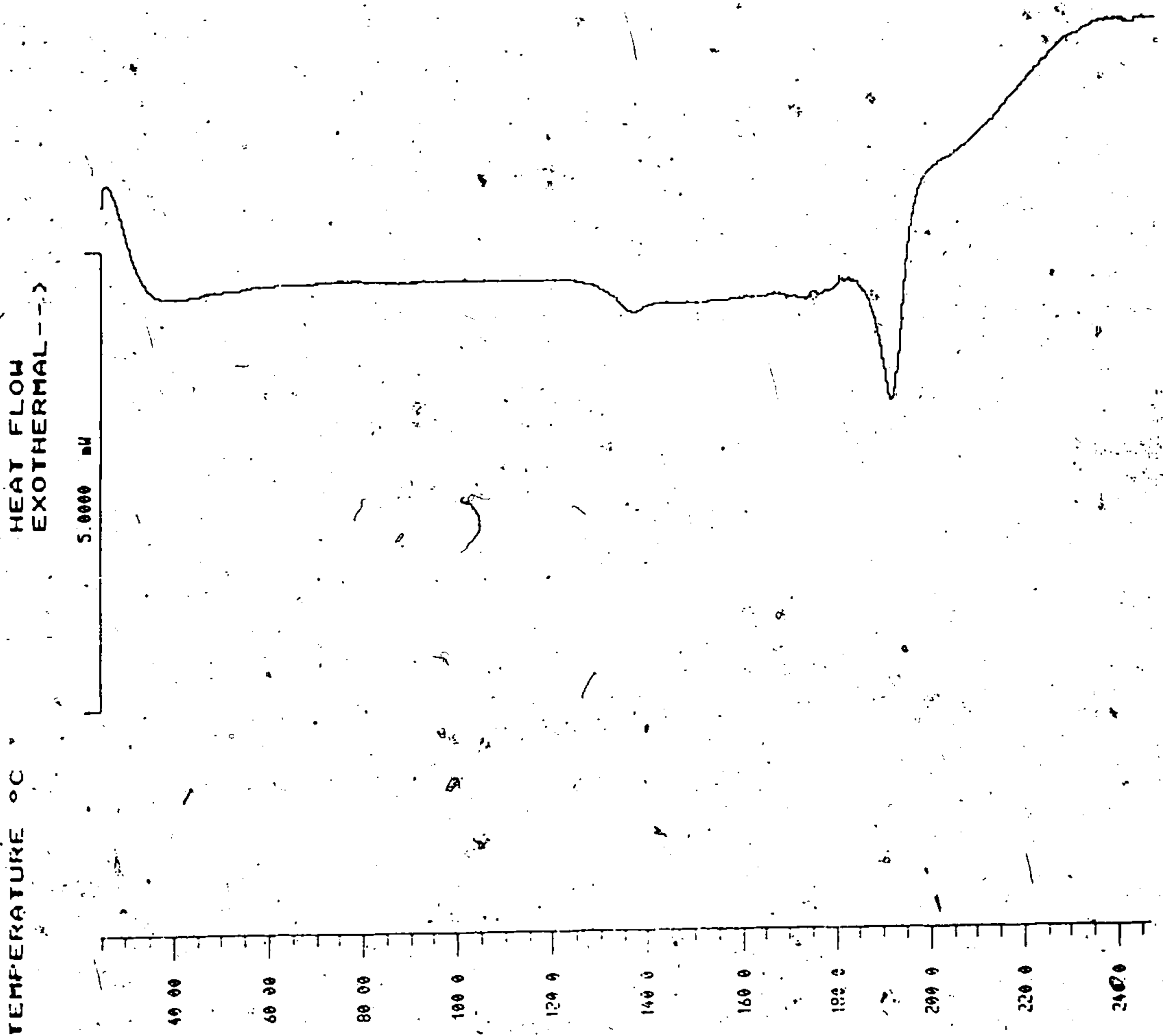


Figure 28 DSC of IV-f

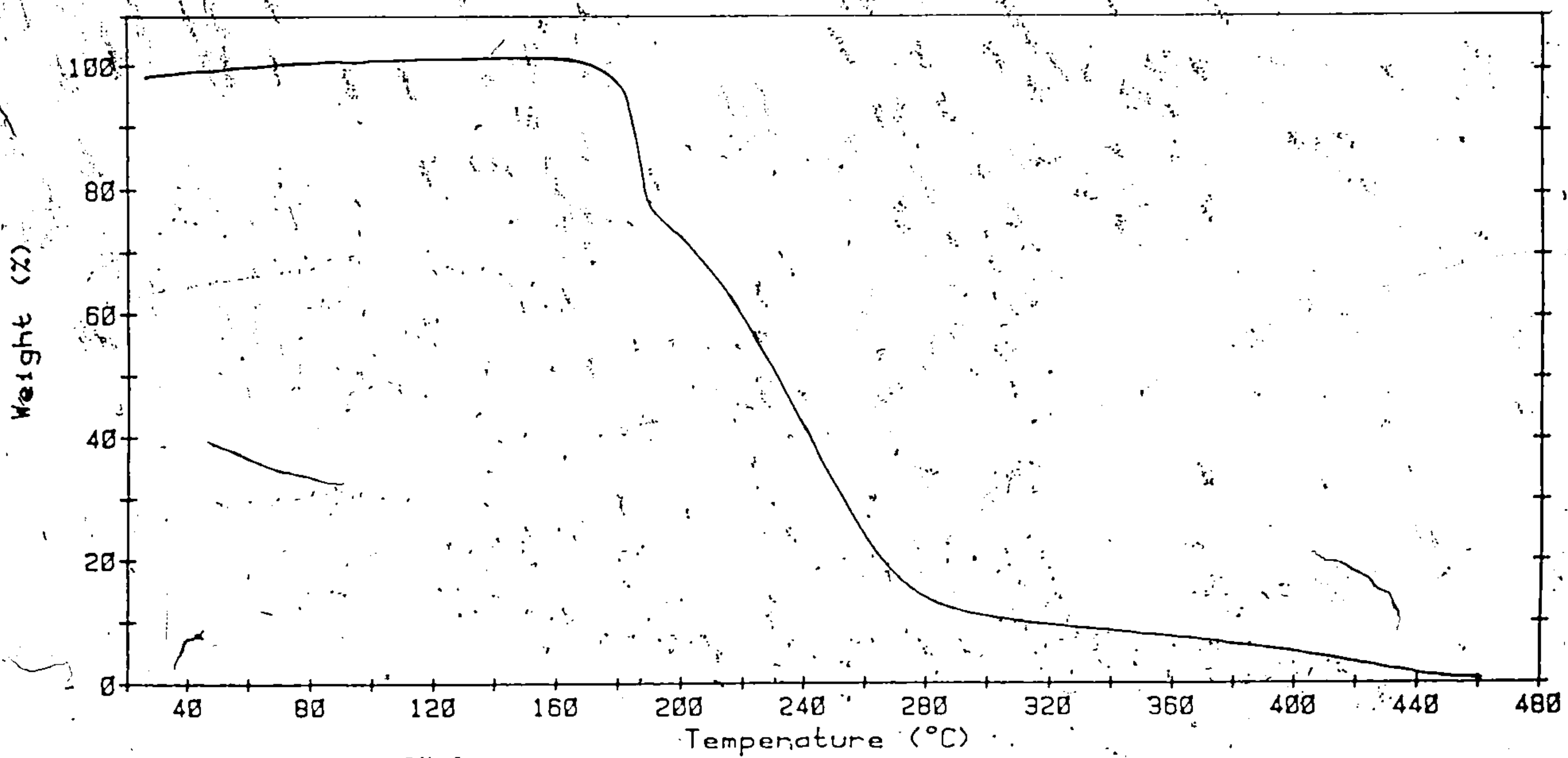


Figure 29 TGA of IV-f

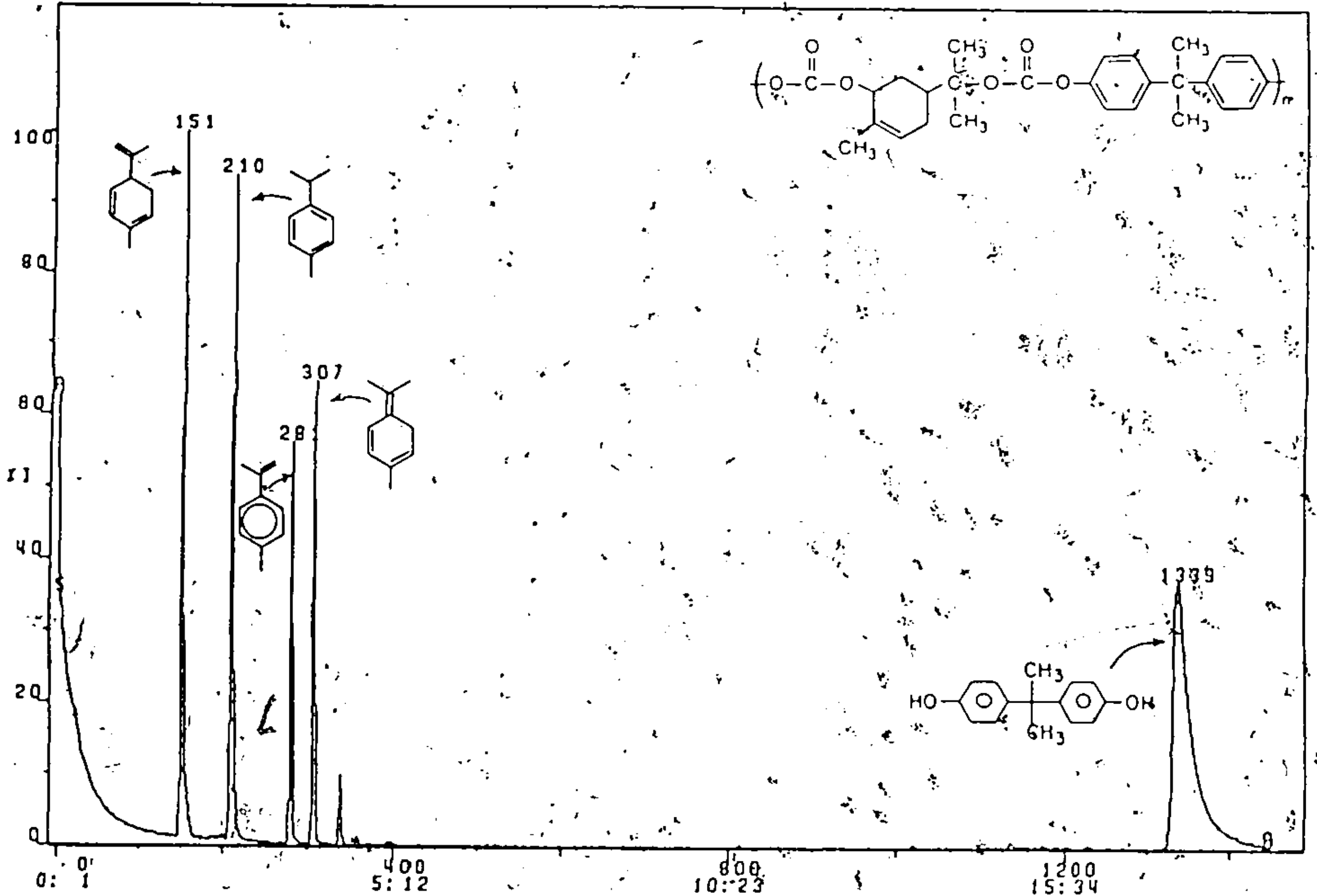
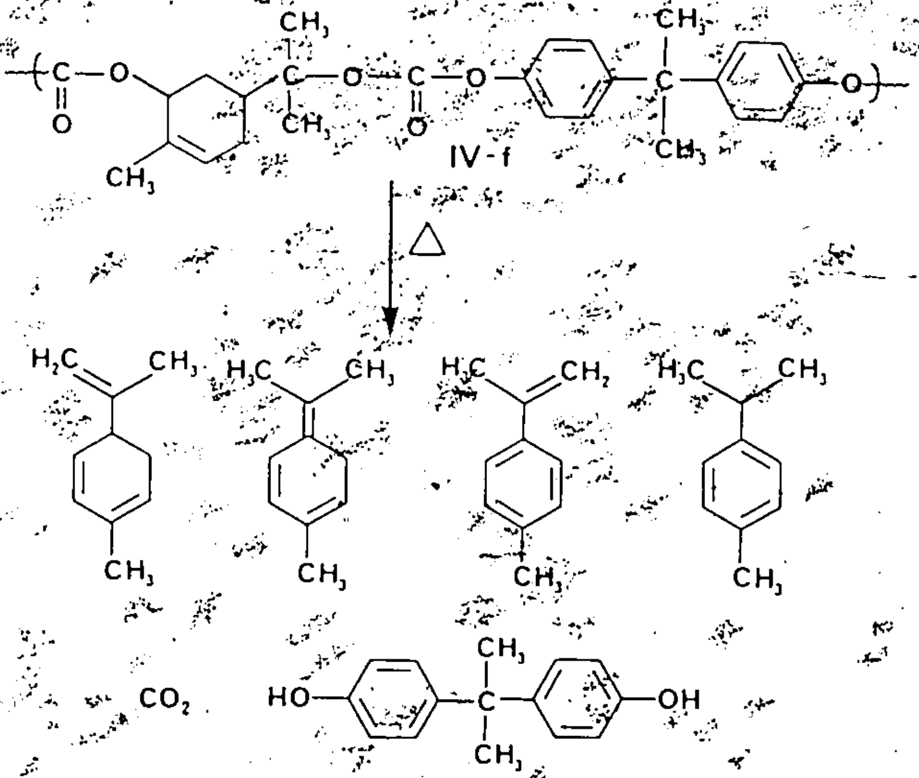


Figure 30 GC-MS of IV-f

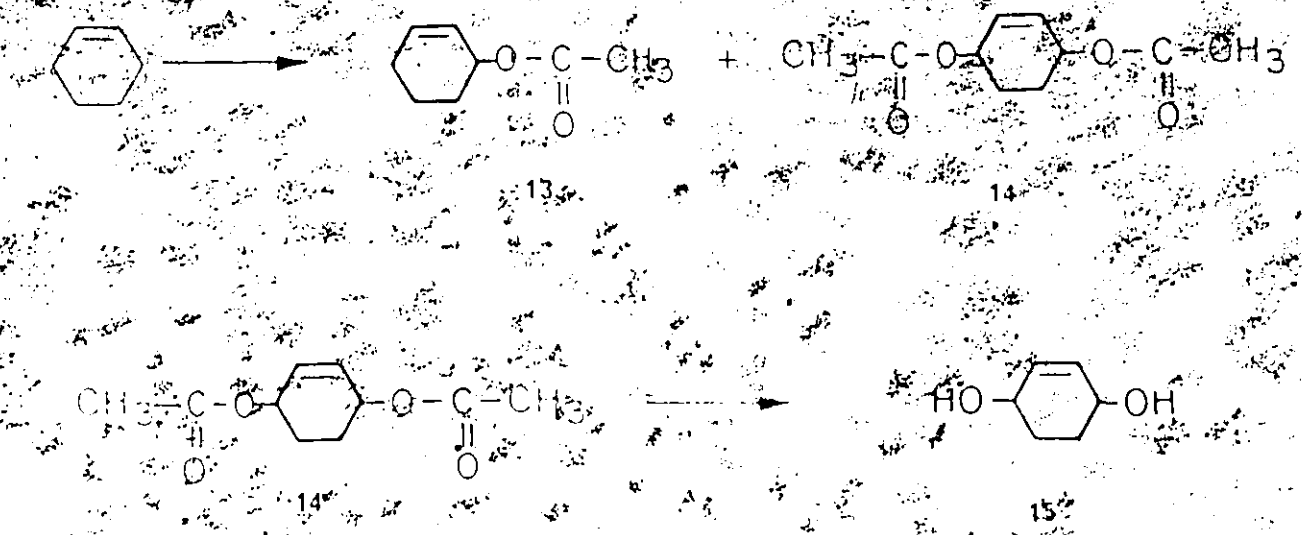
1,3-cyclohexadiene (scheme 31). Note that no ether intermediate is observed in this case.

The allylic diol of choice for incorporation into a depolymerizable polycarbonate is 3,6-cyclohexenediol; this should produce benzene upon depolymerization. This allylic diol is made through the intermediacy of 3,6-diacetoxycyclohexene, 14, which is obtained in 30% yield along with 35% of the monoacetate by-product, 13, by the oxidation of cyclohexene with t-butylhydroperoxide in the presence of acetic acid. Subsequent base hydrolysis of the diacetate leads to the desired unsaturated diol 15 in 60% yield (scheme 32).

The polymer of 3,6-cyclohexenediol with the bis-carbonylimidazolide of p-benzenedimethanol is only recovered in low yield (56%) after 45 hours of reaction under phase transfer conditions and it consists mainly of low molecular weight chains (scheme 14, II-f). The low extent of the reaction may be attributed to the low reactivity of the secondary diol towards the bis-carbonylimidazolide reactant. If the same reaction is carried out substituting the bis-p-nitrophenyl-carbonate of p-benzenedimethanol, III-b, for the bis-carbonylimidazolide, the reaction is more successful (scheme 24), due to the higher reactivity of III-b with the secondary diol. Thus, after 90 hours of reaction, a white polymer, IV-e, is obtained in 91% yield; this polymer has an average number molecular weight of 17,600 as determined by osmometry. Differential scanning calorimetry indicates a Tg at 65°C and three small endotherms at 73, 87 and 123°C (figure 31). A TGA curve (figure 32) shows that the polymer decomposes rapidly from 200



Scheme 31



Scheme-32

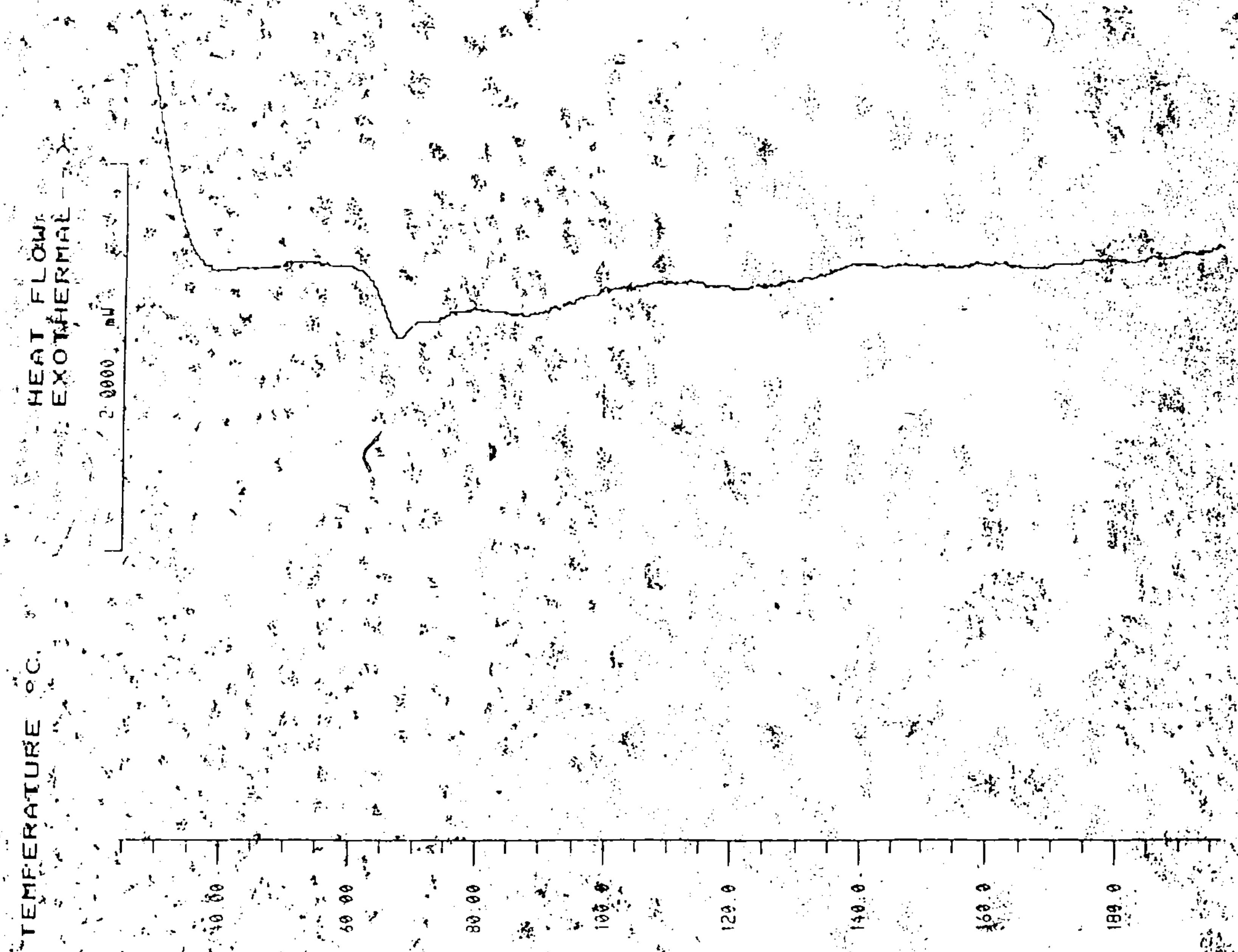


Figure 31 DSC of IV-e

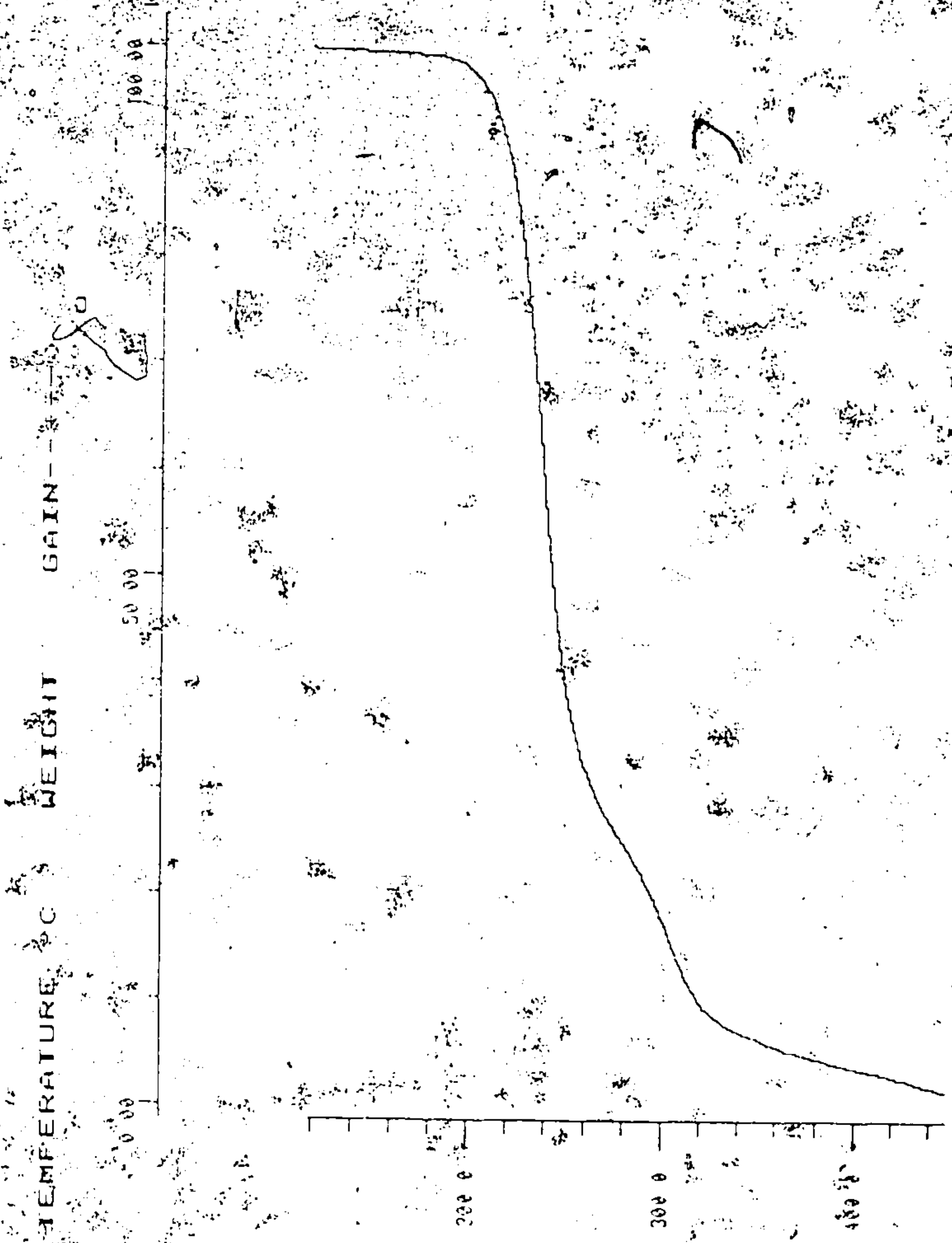


Figure 32 TGA of IV-e

to 270°C to lose 72% of its weight, the weight loss reaches 90% on further heating to 310°C and 100% loss is only observed at 450°C.

The GC-mass spectroscopic study (figure 33) of the thermal process for this polymer, conducted in the absence of oxygen, shows (scheme 33) p-benzenedimethanol, benzene and four isomers of the compound coming from the cyclohexenediol fragments which are located at the ends of the polymer chains: 2-cyclohexene-1-one, 3-cyclohexene-1-one, 1,4-cyclohexadiene-3-ol and 1,3-cyclohexadiene-5-ol. Scheme 35 shows the mechanisms by which the formation of these isomers can occur. The first one is positively identified by comparison with the MS of an authentic sample. Note that the molecular peak is relatively strong for ketones in general and that this isomer fragments by losing ethylene, leaving a very stable species at m/e 68. The assignment for the second one is made on the basis of the strong molecular peak and of the fragmentation pattern involving the favorable loss of CH_2CO explaining the strong peak at 54. The 1,4-cyclohexadiene-3-ol is susceptible to the loss of acetylene to form a stable species at m/e 70 and its very weak molecular peak is characteristic of secondary alcohols. The fourth isomer is assigned to a secondary diol due to the weak molecular peak and the presence of the strong peak at m/e 55 which is attributed to the loss of C_3H_5 radical. An unambiguous assignment of the two alcohols isomers would require comparison with the mass spectra of the actual alcohol molecules; unfortunately, these do not appear to have been reported in the literature.

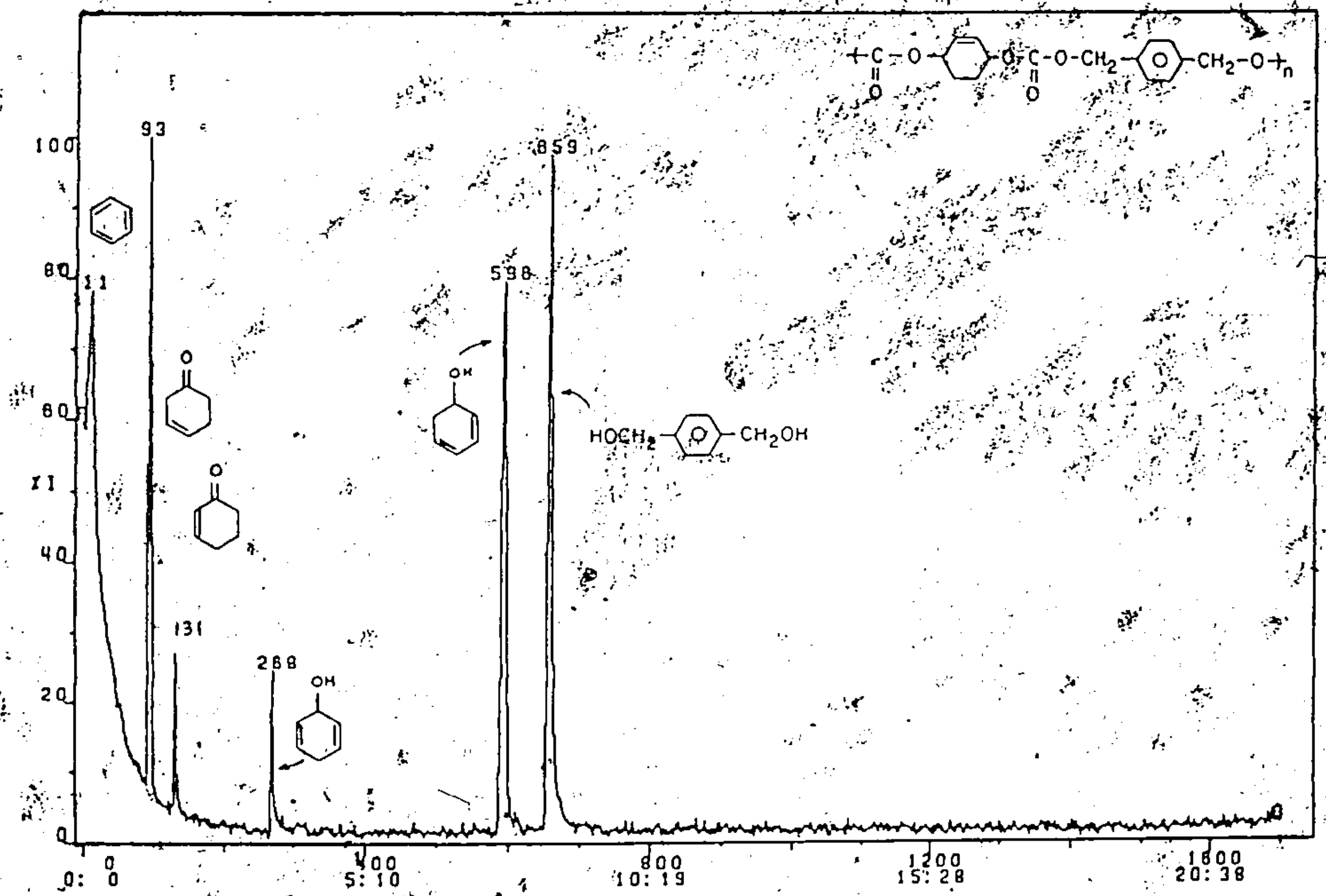
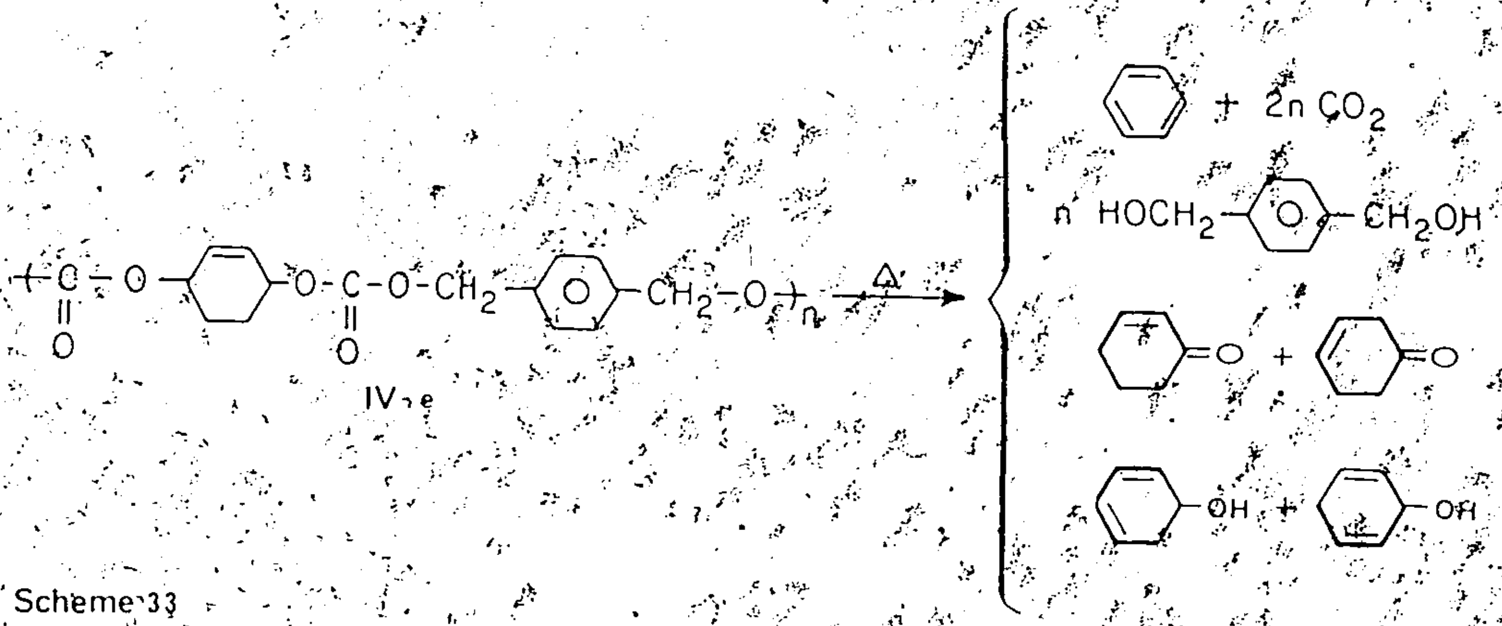
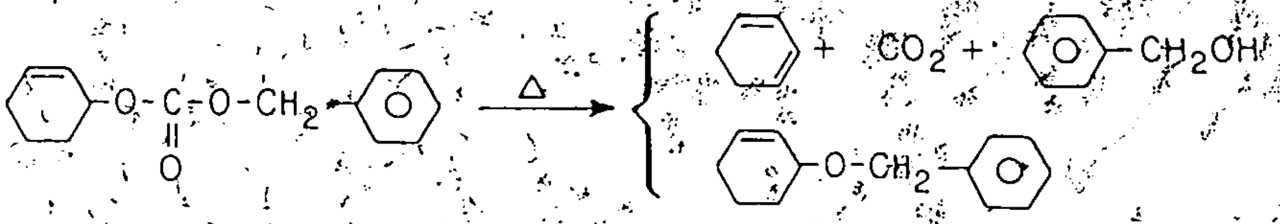


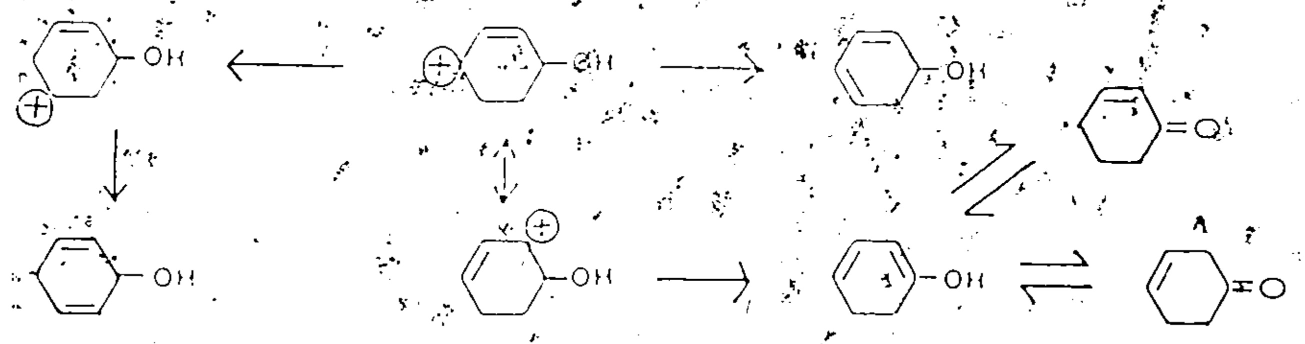
Figure 33 GC-MS of IV-e



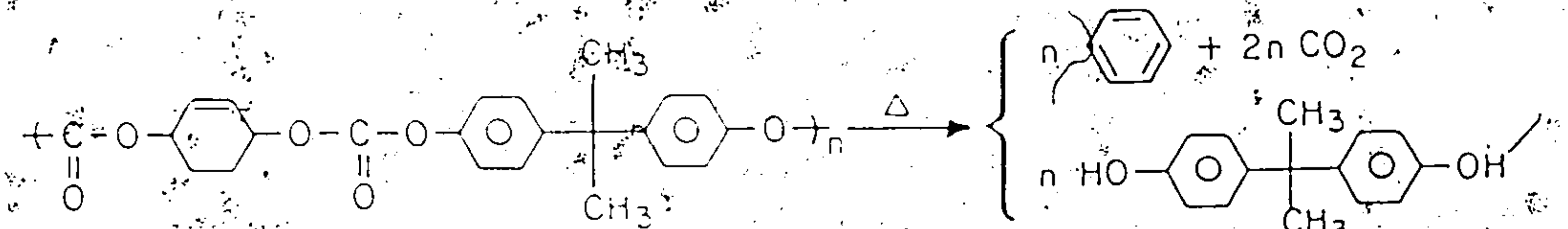
Scheme 33



Scheme 34



Scheme 35



IV- g

Scheme 36

Conducting thermolysis under vacuum eliminated the formation of phenol and 4-methanolbenzaldehyde which were observed when the thermolysis was done in the presence of oxygen. Note that no ether formation is observed as is the case with the corresponding sobrerol polymer although a model compound study of solution acidolysis produces the corresponding ether (Scheme 34) (30).

A study of the acidolysis of a film of the polymer containing cyclohexenediol and p-benzenedimethanol, reveals that when a film of 0.75 µm thickness is exposed to 50 mJ of UV radiations in the presence of onium salt and then post-baked to 100°C for 5 min, the carbonyl absorption completely disappears leaving a residue of p-benzenedimethanol (figure 34).

A polymer IV-g incorporating cyclohexanediol and bisphenol A was also prepared from bisphenol A and the bis-p-nitrophenylcarbonate of the unsaturated diols (scheme 24). Monomer III-d prepared by the usual method (scheme 23) in 61% yield after purification by recrystallization from a dichloromethane-petroleum ether mixture. The new polymer, IV-g, recovered in 90% yield has a Tg of 150°C by DSC (figure 35). The polycarbonate undergoes rapid thermal degradation from 220 to 280°C, losing 80% of its weight. The remaining 20% of weight disappears from 330 to 400°C (figure 36). The GC-MS analysis (figure 37) of the thermolysis products shows carbon dioxide, benzene, and bisphenol A (scheme 36).

Figure 34. IR spectra of IV-e/Ph_2IAsF_6 (a) unexposed, (b) exposed, (c) post-bake

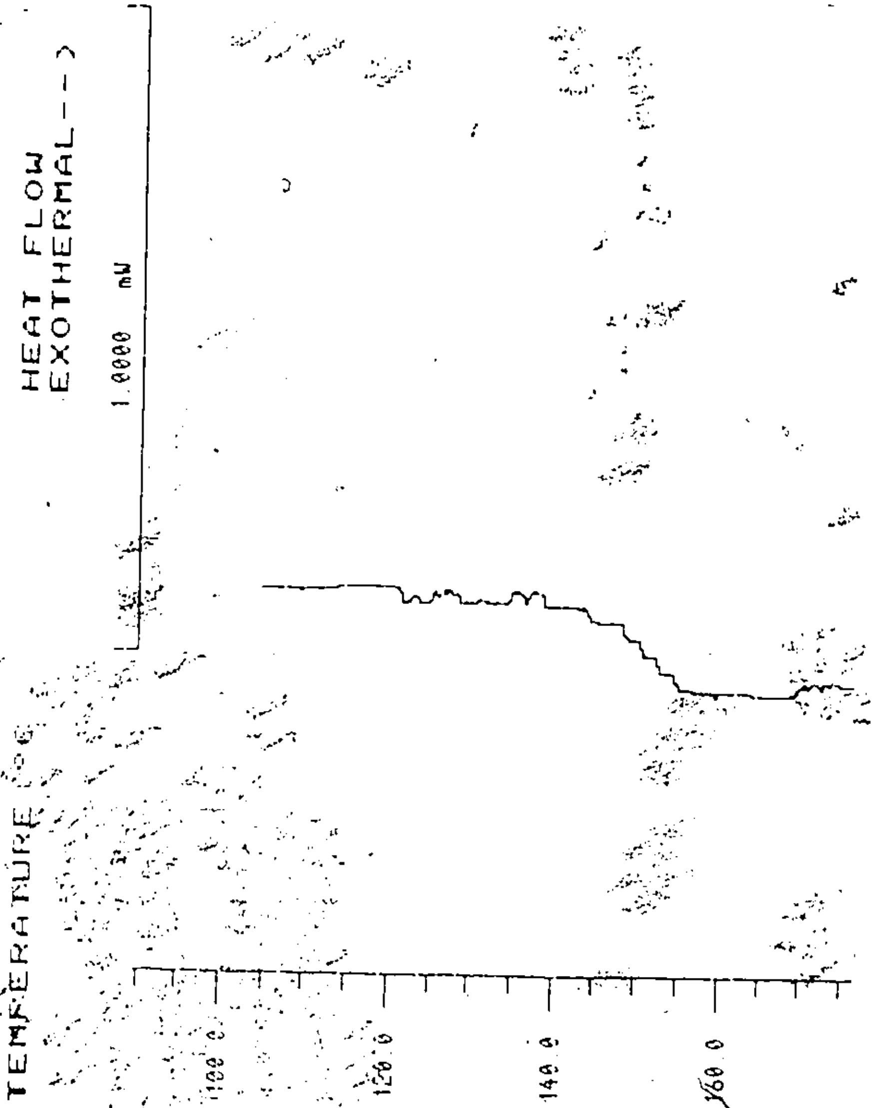


Figure 35 DSC of IV-g

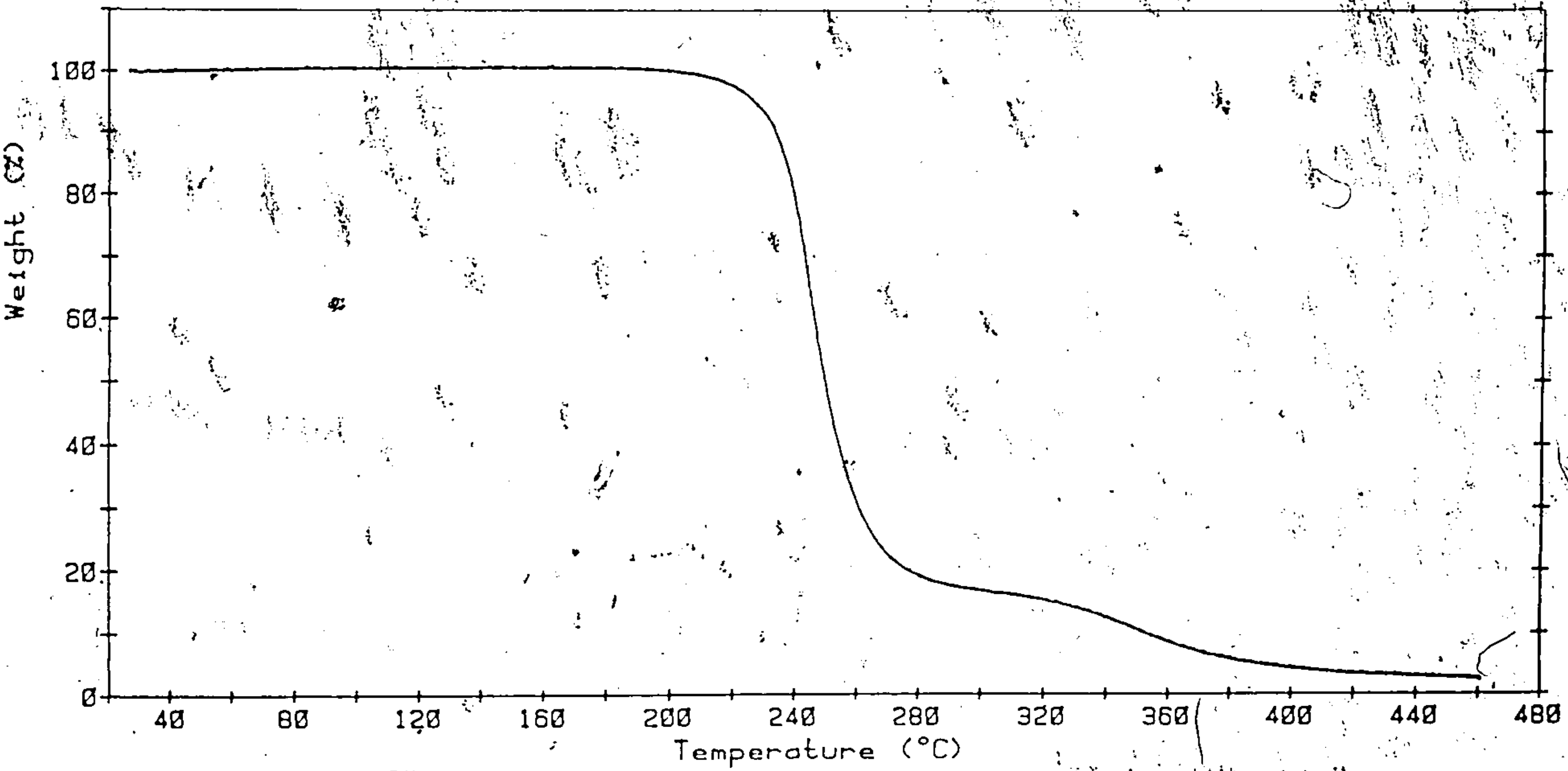


Figure 36 TGA of IV-g

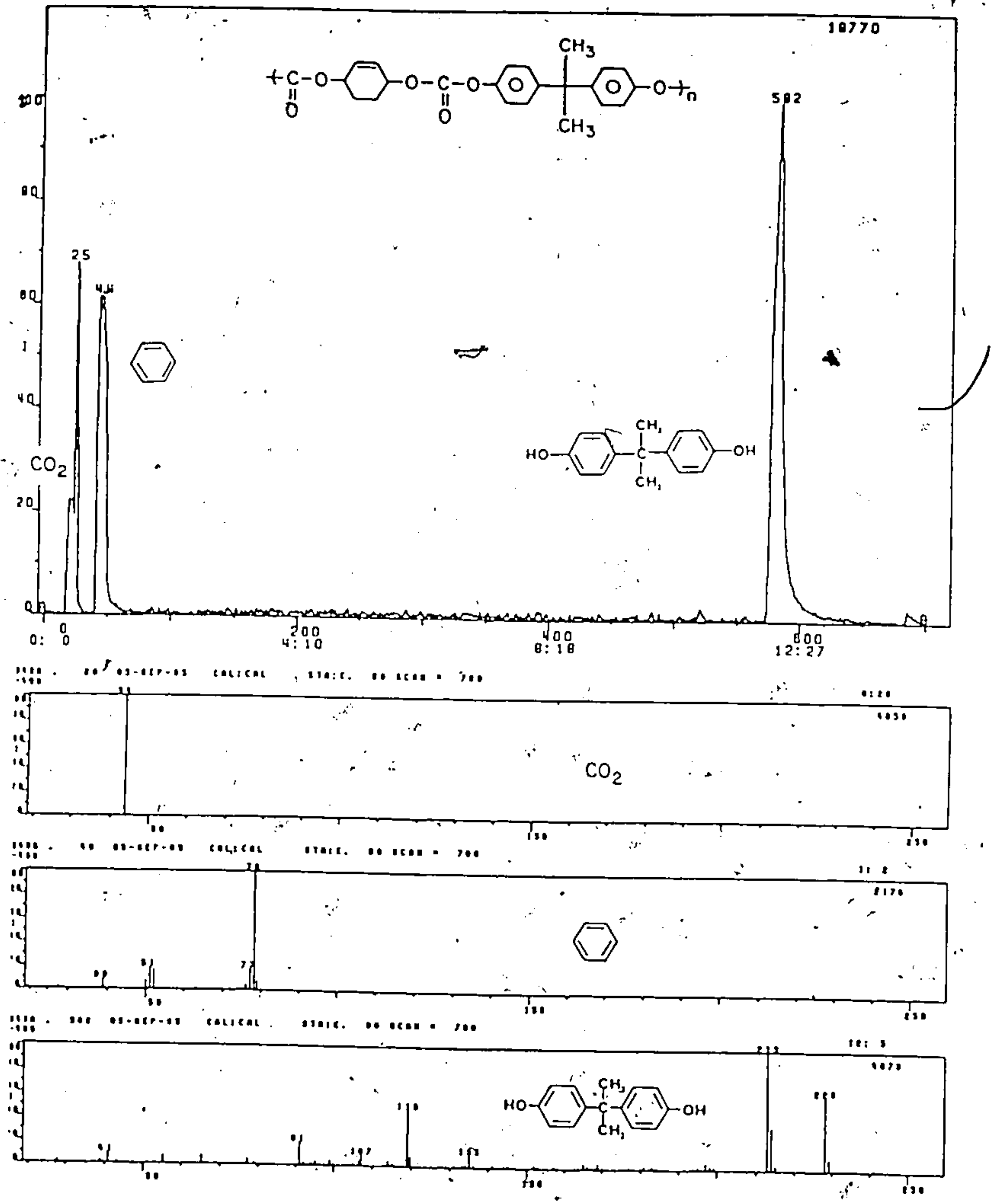


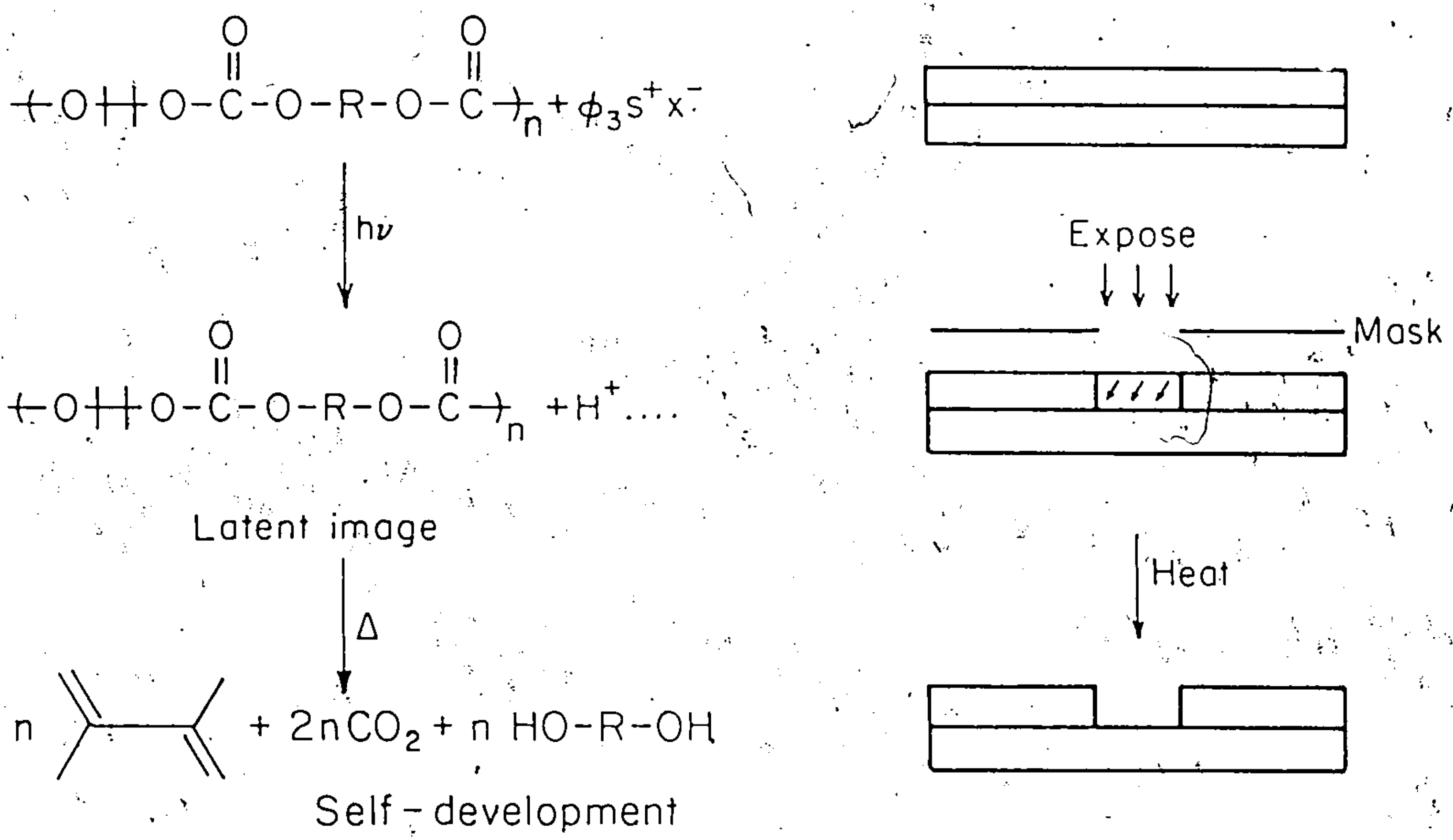
Figure 37 GC-MS of IV-g

IMAGING EXPERIMENTS

Only preliminary imaging experiments could be carried out to test the potential of the various materials as resist materials. Further testing required the use of projection printing equipment and was done by others (32). The results which were obtained are described briefly below since they are relevant to this thesis.

In general, the polymers containing 5-10 weight % of triphenylsulfonium hexafluoroarsenate are dissolved in an appropriate amount of solvent to afford a 20% solution. After filtration through 0.5 μm Millipore filter, the solutions are spin-coated onto 5" silicon wafers, adjusting the spinning speed to obtain coatings of approximately 1 μm thickness. The coating step is then followed by a short baking period during which most of the remaining solvent is evaporated.

Exposure is accomplished using a Perkin-Elmer 500 deep-UV projection printing tool with an appropriate chromium on quartz mask. The scanning speed of the instrument is related to the UV dose provided to each image in the process. This exposure step results in the formation of a latent image only which consists of the intact polycarbonate matrix with a local concentration of acid in the areas which have been exposed to radiation (scheme 37).

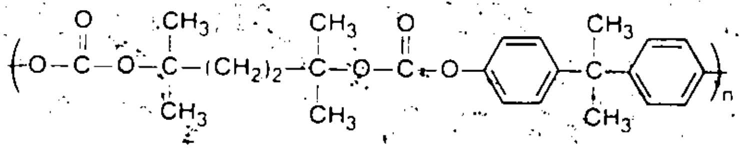


Scheme 37

Following exposure, the wafers are removed from the projection printing tool and image development is accomplished through baking the exposed wafers at an appropriate temperature, sufficient to provide the energy required for the catalyzed depolymerization to occur, but below the temperature at which the polycarbonate begins to flow (scheme 37). With all the polycarbonates described in this thesis, this post-exposure baking step results in the appearance of a partly developed image only as the low moleeular weight diols or bisphenols which result from the depolymerization have a low volatility at atmospheric pressure and at the 60-80° baking temperatures.

Although full development could conceivably be achieved in vacuo, these experiments required specialized equipment which was not available at the time of testing. Therefore, for those polymers which produce bisphenol A upon catalyzed thermolysis, full development was achieved by a rapid washing with 2-propanol or similar polar solvents which do not dissolve or swell the unexposed polycarbonate.

Once development is complete the images can be inspected by optical as well as scanning electron microscopy. Figure 38 shows a scanning electron micrograph of a positive image obtained from polymer IV-a which confirms that this polymer has potential as a resist material. Figures 39 and 40 show similar positive tone images obtained with polymer IV-g. The apparent defect seen in figure 40 is the result of sample preparation which involves cracking of a silicon wafer along its crystal axis to expose the edge of an image to the beam of the



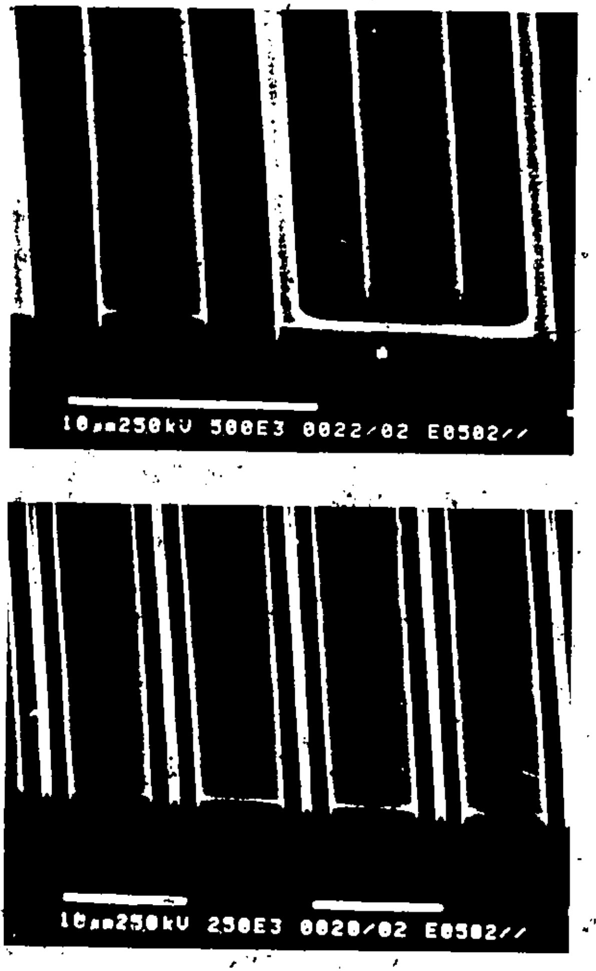


Figure 38. Scanning electron micrograph of a positive image of polymer IV-a

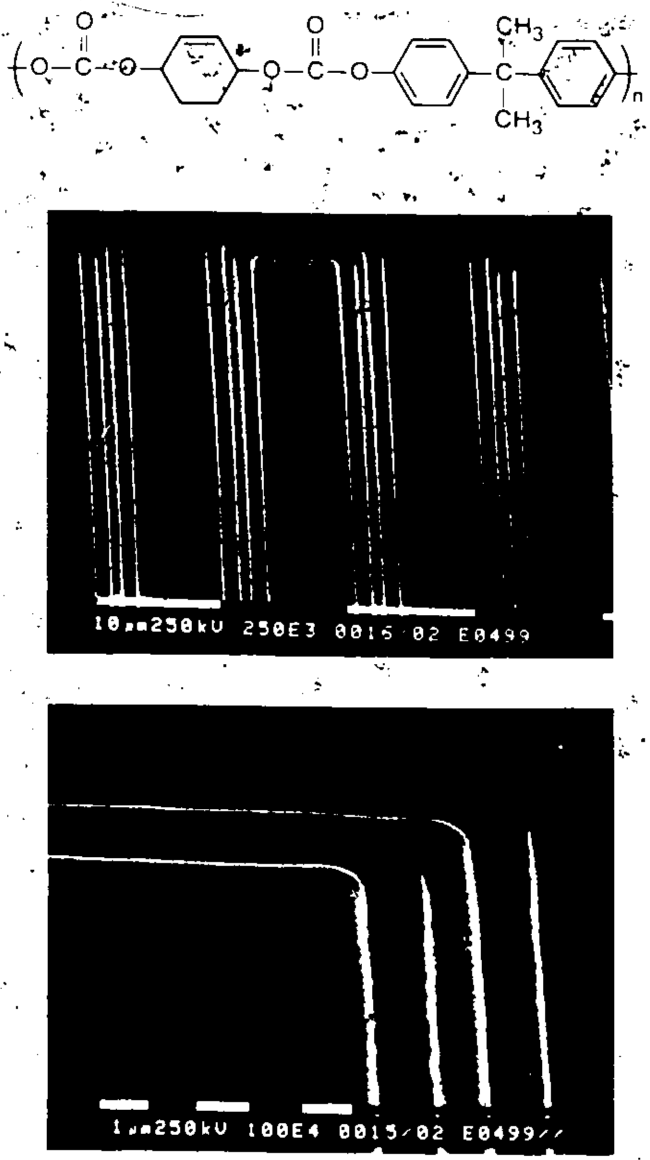
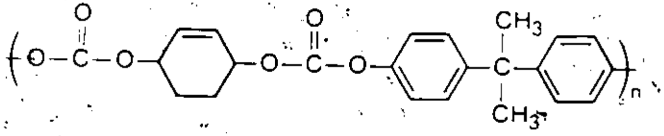


Figure 39 Scanning electron micrograph of a positive image of polymer IV-g



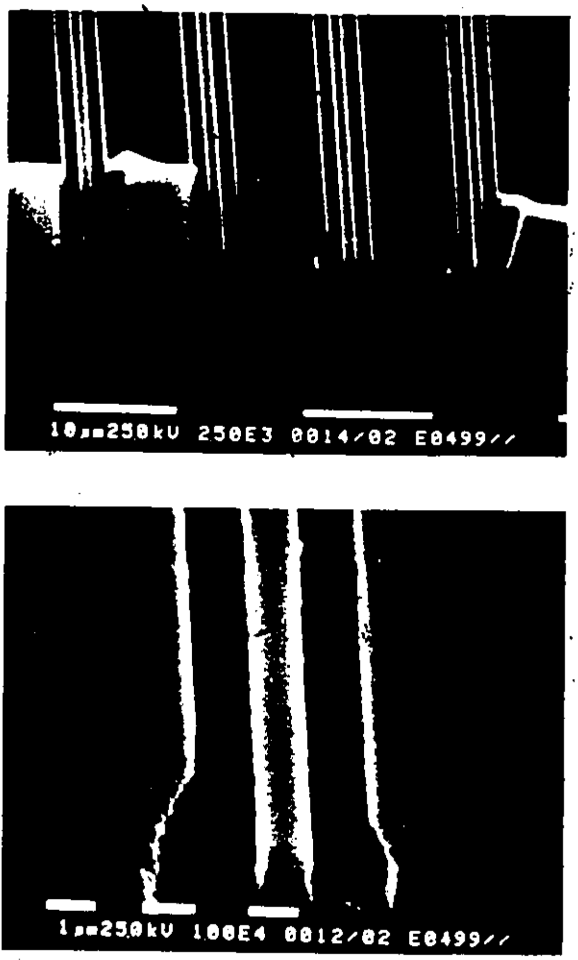


Figure 40 Scanning electron micrograph of a positive image of polymer IV-g

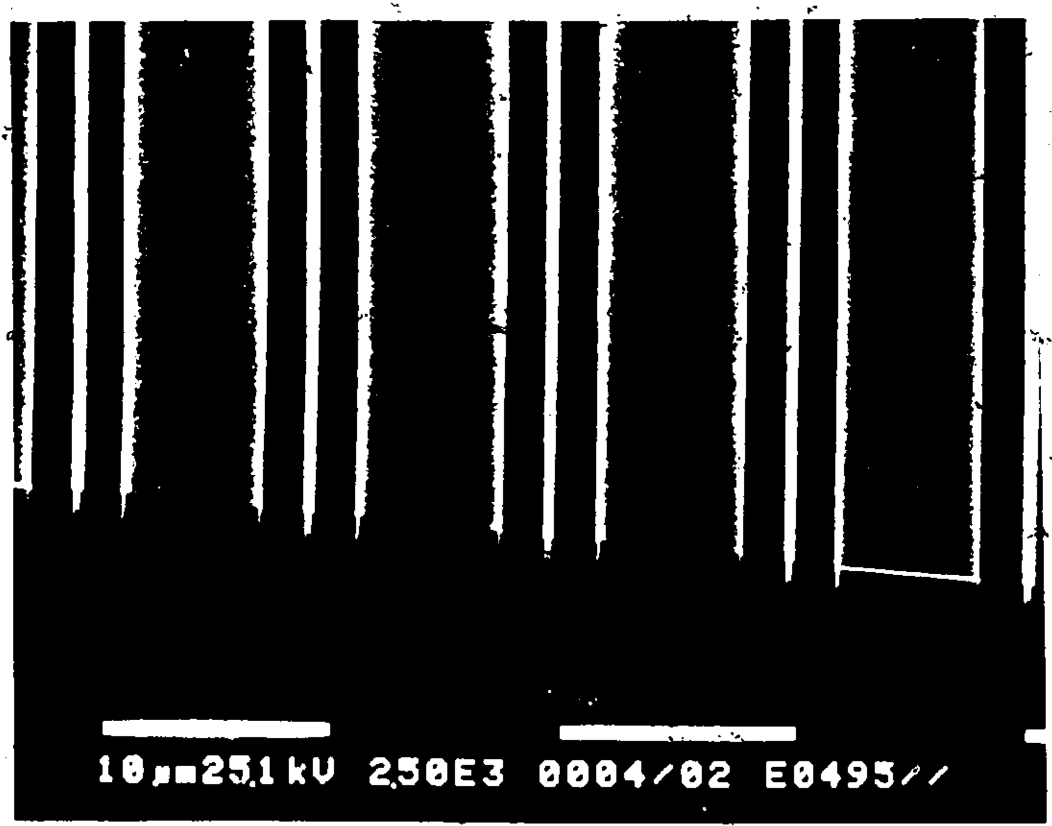
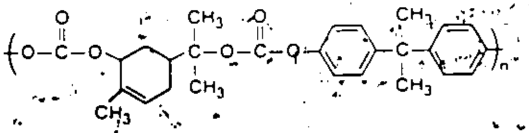


Figure 41 Scanning electron micrograph of a positive image of polymer IV-f



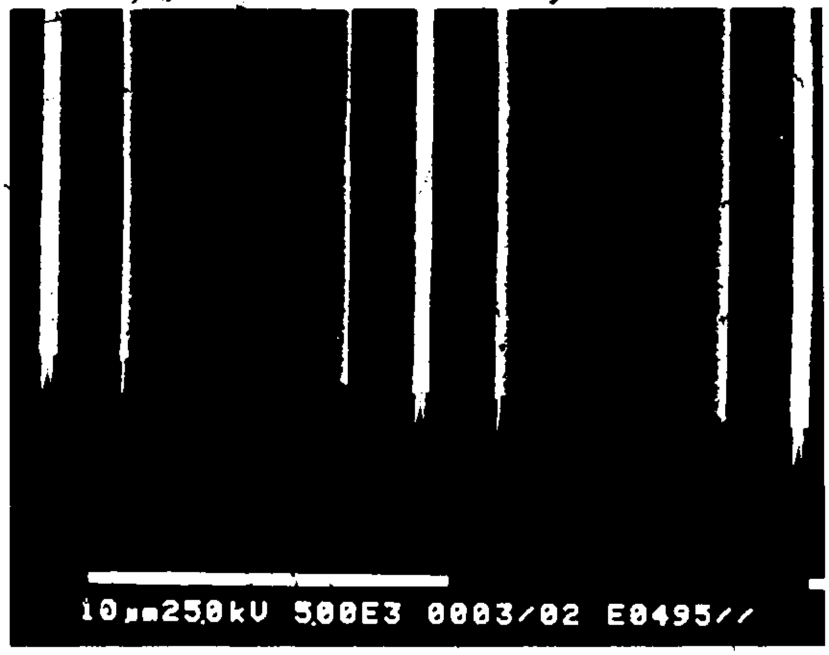


Figure 42. Scanning electron micrograph of a positive image of polymer IV-f

scanning electron microscope. The strain lines seen on this photograph are typical of those observed for a thermoplastic material stretched to its yield point.

Figures 41 and 42 obtained with the polymer IV-f containing both Sobrerol and bisphenol A confirm the particular quality of this material which has a good solubility yet is high melting and can be used to print extremely high resolution positive images. It should be noted that the smallest feature seen on these images is only slightly larger than the wavelength of the exposing light (254 nm).

Several other polycarbonates reported in this thesis can also be imaged, some affording negative tone images, but numerous technical problems relating to their solubilities and imaging characteristics remain to be studied.

CONCLUSION

The design of new resist materials which can operate on the basis of radiation-induced catalyzed depolymerization has been extended significantly through the development of new appropriately substituted allylic and benzylic copolycarbonates.

The most successful synthetic routes involve polycondensation reactions with active p-nitrophenylcarbonate or carbonylimidazoyl derivatives of the tertiary, allylic or benzylic diols and other diols or bisphenols under phase-transfer conditions.

Attempts to use unactivated tertiary diols directly only lead to oligomers because tertiary diols react slowly due to steric constraints and also because they tend to eliminate water molecules under phase-transfer conditions.

To obtain a copolymer incorporating bisphenol A, under phase-transfer polycondensation, it is necessary to use the bis-p-nitrophenylcarbonate of the other diol fragment to be introduced, and to react it with the bisphenol. Attempts to use a bis-carbonylimidazolide derivative with bisphenol-A are not successfull due to the relative basicities of the phenol and imidazole. The use of bisphenol A bis-carbonylimidazolide with another diol is also not satisfactory due to basicity considerations which suggest the possible formation of irregular structures. Thus, the bis-p-nitrophenylcarbonate of bisphenol A is not expected to give satisfactory results when employed with a non phenolic diol because the latter could displace the bisphenolate as well as the p-nitrophenolate anions.

In general bis-p-nitrophenylcarbonate derivatives are easier to prepare, obtained in higher yield, and more reactive than the corresponding bis-carbonylimidazolides.

The results obtained with bis-carbonate derivatives of 1,4-cyclohexenediol are particularly interesting since both acidolysis and thermolysis result in aromatization. This novel aromatization procedure could conceivably be used in a variety of other applications. Although only preliminary imaging tests have been carried out, the results which have been obtained are very encouraging. Our design objective has been met as thermal activation is required for development following radiation-induced creation of a latent image in a depolymerizable material.

EXPERIMENTAL

DL-sobrerol, 1,1'-carbonyldiimidazole, and p-nitrophenyl chloroformate were obtained from Sigma Chemicals and used without further purification. Para-benzenedimethanol, meta-benzenedimethanol, para-diacetylbenzene, 4,4'-isopropylidenediphenol, pinacol, benzyl alcohol, imidazole, and tert-butyl hydroperoxide were purchased from Aldrich Chemicals and used without further purification; 2-butyne-1,4-diol was also obtained from Aldrich Chemicals but was purified by chromatography over silica gel using ethyl acetate as eluent. α,α'-dihydroxy-p-diisopropylbenzene was commercially available from Tokyo Kasei Inc.; cyclohexene was purchased from Fisher and phosgene was obtained from Matheson. These were all used without further purification.

All experiments involving the synthesis of the bis-carbonylimidazolides, bis-p-nitrophenylcarbonates and polycarbonates were done using dried solvents. The solvents were purified as follows: tetrahydrofuran was distilled over benzophenone-sodium under nitrogen; dichloromethane was distilled over phosphorus pentoxide under nitrogen; hexanes and ethyl acetate used for chromatography were distilled. Weighings were performed to the accuracy indicated ± 0.1 mg to ensure that stoichiometric balance was achieved.

Infrared spectra were taken using a Nicolet 10-DX spectrometer, using KBr pellets for solid samples, neat films between NaCl disks for liquids, and films coated on NaCl disks for polymers. Nuclear magnetic resonance spectra were recorded on Varian EM-360A, CFT-80 and XL-300 instruments, using $CDCl_3$ as solvent (unless otherwise indicated) and tetramethylsilane as a standard. Mass spectra were taken using a VG-7070E double-focusing mass spectrometer using either the normal thermal probe, or chemical ionization with methanol.

Molecular weight of polymers were determined using a Wescan Model 231 recording membrane osmometer with 1,2-dichloroethane as the solvent or using a Waters Model 150 Gel permeation chromatography equipped with a series of five microstyragel columns of different exclusion volumes using tetrahydrofuran as the mobile phase. Thermogravimetric analysis (TGA) and differential scanning calorimetry were done using a DuPont 1090 instrument at a heating rate of 10°C/min. under nitrogen atmosphere or a Mettler TA 3000 System. For the IR study of the acidolysis of polymers, polymer films were cast on NaCl disks using a Headway Research Inc. spin-coater with a 1 inch diameter chuck at 2-5000 RPM. Film thickness was measured on silicon wafers using a Tencor Sigmascan profilometer. Deep UV irradiations were carried out using an Optical Associates Inc.(O.A.I.) Series 30 deep UV light source. The radiation flux was measured using a model 354 exposure monitor fitted with a 254nm probe.

The UV testing of the polymers, followed by infrared spectroscopy provides a way to see whether the polycarbonates undergo the expected changes when subjected to acidolytic conditions. The procedure for this testing involves the preparation of a solution of the polymer with 10-15 mole % of an onium salt (e.g. triphenylsulfonium hexafluoroarsenate) in dichloroethane. This polymer solution is then spin coated on a NaCl disk, using a spin-coater in order to obtain a film of 1 μm thickness (measured with a profilometer). After a pre-bake at 70-100°C for 15 min., an infrared spectrum is taken and referred to as "unexposed" polymer. A given arbitrary dose (generally 50 mJ) of UV radiations (254 nm) is applied to the film and another infrared spectrum is taken, this is referred to as "exposed" polymer. A third infrared spectrum which represents the polymer after a post-bake at 70-100°C for a few minutes (1-5 min.) is referred to as "post-baked". Comparison of the three spectra allows the observation of the changes which occur when acid alone is generated in the polymer film or when acidolysis is combined with thermolysis. Note that this procedure is only done to test the photochemical behavior of the polycarbonate. The exact conditions for dose, baking and development have to be determined in actual lithographic experiments in order to obtain optimal resolution of the image.

The depolymerization products obtained in the thermolysis process have been studied using a gas chromatograph coupled to a mass spectrometer system (Table II). The polymer sample is thermolyzed in a glass bulb heated to 300-350°C and a solution of the products which are formed is injected into the GC/MS system. This technique allows the identification of the products formed upon thermolysis. The products obtained after the acidolysis of the same polymers have not been studied in such details. Although model studies as well as infrared monitoring suggest that a similar range of products are obtained. However no attempt has been made to fully characterize the acidolysis products.

Figures 43-51 refer to the assignments of peaks reported in the ^{13}C and ^{1}H-NMR spectra for a number of molecules used in this study.

Symbols used in the experimental section are as follows:

^{1}H-NMR = nuclear magnetic resonance spectrum for protons. When reporting this data, the number before the parenthesis refers to the chemical shift as measured in ppm from tetramethylsilane; the multiplicity of a peak is indicated by the first term in the parenthesis, where s = singlet, d = doublet, t = triplet, q = quartet, p = pentet and m = multiplet; the integration is given by the second term in parenthesis; the assignment for the peak is given by the last term, in some cases the peak is numbered and refers to a figure appearing below.

IR = infrared spectrum. When reporting this data, the number before the parenthesis refers to the infrared frequency of a given band expressed in reciprocal centimeters. The term inside the parenthesis assigns the structural unit responsible for the band.

MS = mass spectrum. When reporting this data, the number before the parenthesis indicates the value of *m/e* for a given peak. The first term in parenthesis refers to the intensity of the peak, where VW = very weak, W = weak, M = medium, S = strong and VS = very strong. The second term in parenthesis assigns the origin of the peak, M+ referring to the parent molecular ion. Data obtained by chemical ionization is designated by an asterix.

^{13}C-NMR = nuclear magnetic resonance spectrum for carbon-13. When reporting this data, the number before the parenthesis indicates the position of a peak expressed in ppm from tetramethylsilane. The first term in parenthesis indicates the multiplicity of the peak in the partially decoupled spectrum, where s = singlet, d = doublet, t = triplet and q = quartet. The second term refers to peak assignment, in some cases the peak is numbered and refers to a figure appearing below. The assignments of the carbons are made with the help of spectral parameters reported in literature(33,34) or by comparison with the spectral data already reported in the literature for model compounds(35).

EA = Elemental analysis, where C= carbon, H= hydrogen, N= nitrogen.

MW = Molecular weight determination for polymer, where Mn is the number average molecular weight, Mw is the weight average molecular weight and D the polydispersity (Mw/Mn). GPC refers to gel permeation chromatography data.

DSC = Differential scanning calorimetry, where Tg is the glass transition temperature.

TGA = Thermogravimetric analysis.

Assignments for proton and carbon-13 NMR

Figure 43

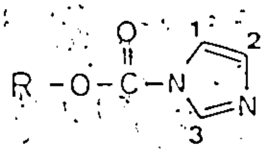


Figure 44

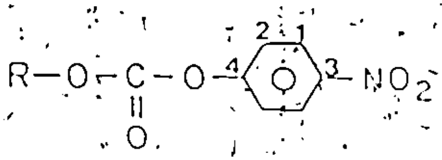


Figure 45

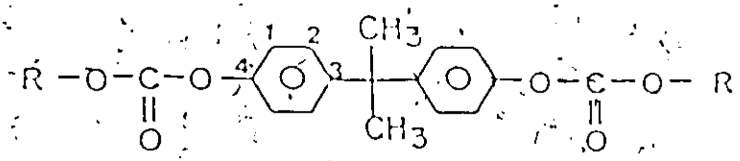


Figure 46

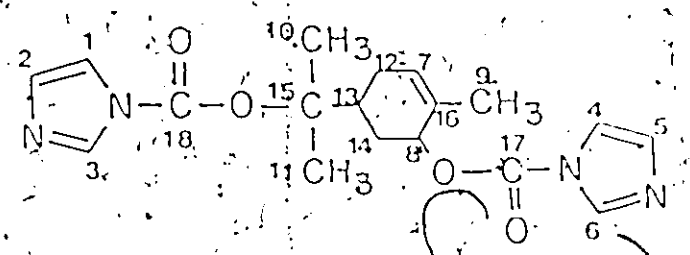
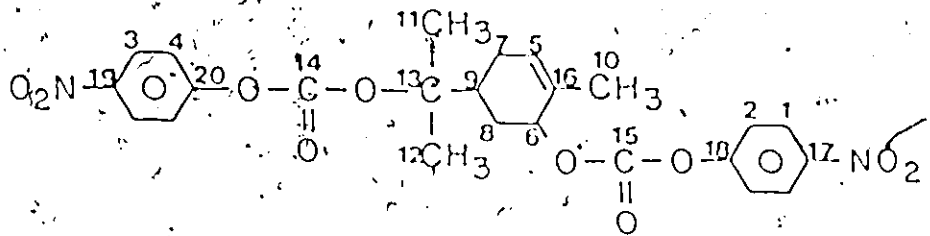


Figure 47



N.B.: The numbering system used herein is not based on systematic nomenclature; it is used *ad hoc* to facilitate the reading of the experimental section.

Figure 48

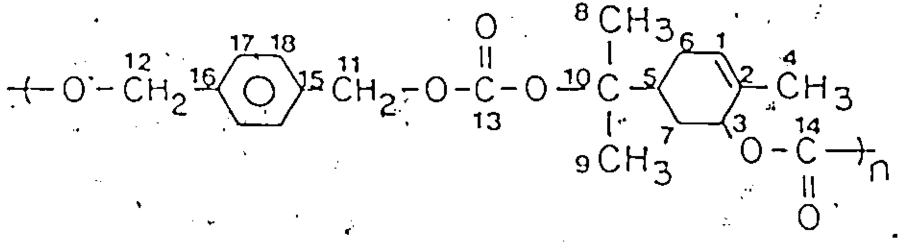


Figure 49

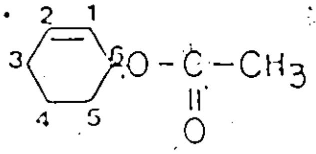


Figure 50

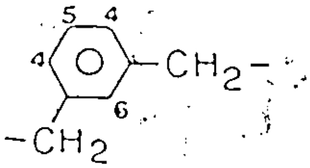
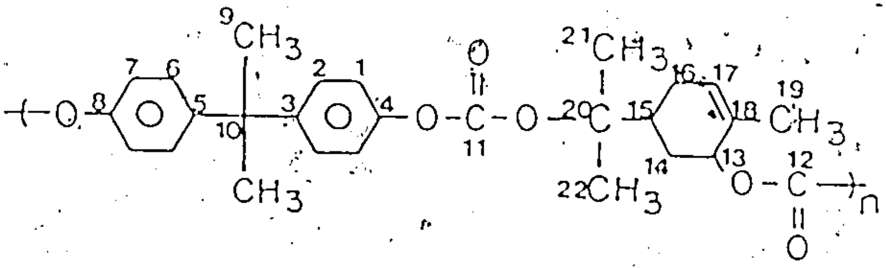


Figure 51



N.B.: The numbering system used herein is not based on systematic nomenclature; it is used <u>ad hoc</u> to facilitate the reading of the experimental section.

1-1) Reduction of p-diacetylbenzene with sodium borohydride

The reduction of p-diacetylbenzene is done using a procedure adapted from that for the reduction of nitrobenzaldehyde as described by Vogel (36). A solution is prepared consisting of 20.0 g (123 mmoles) of p-diacetylbenzene dissolved in 250 mL of methanol. To this solution is added slowly, while stirring and cooling (keeping the temperature between 18 °C and 25 °C), 2.5 g of sodium borohydride in 50 mL of a 0.2N aqueous solution of sodium hydroxide. The reaction mixture is stirred at room temperature for a further hour. The work-up is done by removing the methanol on the rotatory evaporator, diluting the residue in distilled water, and extracting the diol with ether. After drying the organic phase over magnesium sulfate and removal of the solvent, the crude product is purified by recrystallization from ethyl acetate and petroleum ether. A yield of 79% (13.0 g) of a white compound is obtained and its spectral data are consistent with the desired p-bis(1-hydroxyethyl)benzene, <u>1</u>.

^{1}H-NMR (in DMSO-d_6): 1.37(d, 6H, CH_3); 4.06(d; disappears in D_2O, 2H, OH); 4.72(q, 2H, CH); 7.23(s, 4H, CH aromatic).

IR: 3289(OH stretch); 1085(C-OH stretch); 1370 and 1453(CH_3, asymmetric and symmetric bending); 832(= CH, out-of-plane bending, aromatic).

1-2) Synthesis of the bis-carbonylimidazolide of p-bis(1-hydroxy ethyl)-benzene, I-a

A mixture of 15.95 g (95.96 mmoles) of the diol 1 dissolved in 70 mL of dry THF is treated with 0.56 g of potassium metal, and is refluxed until all the metal is dissolved. The solution is then cooled and added under argon atmosphere to a suspension of 31.12 g (192 mmoles) of 1,1-carbonyldiimidazole in 40 mL of dry THF. After two hours of reflux, thin layer chromatography shows the disappearance of the diol. The solvent is removed on an evaporator fitted with a $CaCl_2$ drying tube, and the residue is dissolved in chloroform. The solution is filtered to remove insoluble impurities and the crude material obtained after evaporation of the solvent is applied on a silica gel column (600 g) using ethyl acetate as eluent to give 11.9 g (35% yield) of a white crystalline solid. This material is the desired compound I-a as seen by spectroscopic and elemental analysis.

EA: found (C:60.76, H:5.17, N:15.61); calculated (C:61.01, H:5.12, N:15.81).

^{13}C-NMR: 147.95(s, C = O); 140.28(s, C aromatic); 137.06(d, CH imidazolide C#3); 130.66(d, CH imidazolide C#2); 126.71(d, CH aromatic); 117.09(d, CH imidazolide C#1); 76.71(d, CH-O); 21.87(q, CH_3). For assignment of numbered carbons see figure 43.

^{1}H-NMR: 8.04(m, 2H, CH imidazolide, H#3); 7.36(s, 4H, CH aromatic); 7.30(m, 2H, CH imidazolide, H#1); 6.96(m, 2H, CH imidazolide, H#2); 6.00(q, 2H, CH-O); 1.70(d, 6H, CH_3). For assignment of numbered protons see figure 43.

IR: 1748(C = O); 1634 and 1525(C = C and C = N); 1478 and 1456(CH_3 asymmetric deformation); 1291, 1263, 1172, 1097, 1064 and 1001(C-O-C, C-N=C and N-C-C stretch); 837(=C-H out-of-plane bending, aromatic).

MS*: 355(M, M+1); 311(M, loss of CO_2); 267(M, loss of $2CO_2$); 243(M, loss of CO_2 and imidazole); 199(VS, loss of imidazole and $2CO_2$); 149(S, loss of 2 imidazolyl radicals, CO_2 and CO); 131(VS, loss of $2CO_2$ and 2 imidazoles).

I-3) Reaction of the bis-carbonylimidazolide of p-bis(1-hydroxy ethyl)-benzene with p-bis(1-hydroxy ethyl)-benzene

A mixture consisting of 7.5057 g (21.193 mmoles) of the bis-carbonylimidazolide I-a, 3.5181 g (21.193 mmoles) of the diol, 0.6 g of 18-crown-6, 11 g of potassium carbonate and 15 mL of dry dichloromethane is prepared under argon atmosphere. The reaction mixture is stirred and refluxed for 19 hours. After this time, tlc shows no starting material remaining and the polymer is worked-up by diluting with dichloromethane, and centrifugating the suspension. The decanted solution is concentrated on an evaporator and precipitated in methanol to afford 5.97 g (73% yield) of a white polymer which has spectroscopic and elemental analysis consistent with a linear polycarbonate of p-bis(1-hydroxy ethyl)-benzene. The polymer, II-a, is soluble in THF, 2-methoxyethyl acetate, bis-(2-methoxyethyl) ether, ethylene glycol dimethyl ether, 1,2-dichloroethane, chloroform and dichloromethane.

EA: found (C:69.20, H:6.39); calculated (C:68.74, H:6.29).

MW; Osmometry: Mn = 7490

GPC: Mn = 2700, Mw = 13700, D = 5.1

DSC: Tg: 78°C, Tm: 105°C

^{13}C-NMR: 153.87(s, C = O); 140.98(s, C aromatic); 126.26(d, CH aromatic); 76.04(s, CH benzyl); 22.25(q, CH_3).

^{1}H-NMR: 7.20(m, 4H, CH aromatic); 5.55(q, 2H, CH benzyl); 1.46(d, 6H, CH_3).

IR: 1741(C = O); 1517(C = C stretch); 1452 and 1360(CH_3 asym. and sym. bending); 1255 and 1058(C-O-C stretch); 836(= C-H out-of-plane bending, aromatic)

2-1) Synthesis of the bis-carbonylimidazolide of 2,5-dimethyl-2,5-hexanediol, I-b

A solution of 4.00 g (27.4 mmoles) of 2,5-dimethyl-2,5-hexanediol dissolved in 40 mL of dry THF, to which is added 0.16 g of potassium metal is prepared under argon atmosphere. The reaction mixture is refluxed until all the metal is dissolved; the alcoholate solution is then cooled to room temperature and transferred under argon atmosphere to a flask containing a stirred suspension of 8.86 g (54.7 mmoles) of 1-1'-carbonyldiimidazole in 20 mL of dry THF. The mixture is stirred and refluxed for one hour after which time, tlc shows no remaining starting material. The work-up is done by adding ethyl acetate to the reaction mixture and washing the resultant solution several times with distilled water. After drying, the organic layer over anhydrous magnesium sulfate, the solvents are removed to yield the crude product which is purified by chromatography on silica gel (300 g) using ethyl acetate as an eluent. This affords 6.50 g (71% yield) of a white crystalline solid which has a melting point of 94-96°C. This material has spectroscopic and elemental analyses consistent with the desired product, I-b.

EA: found (C: 57.31, H: 6.59, N: 16.93); calculated (C: 57.47, H: 6.63, N: 16.75).

^{13}C-NMR: 25.92 (q, CH_3); 34.41 (p, CH_2); 86.83 (s, C–O); 117.09 (d, CH imidazolide, C #1); 130.38 (d, CH imidazolide, C #2); 137.01 (d, CH imidazolide, C #3); 146.96(s, C = O). For assignment of numbered carbons see figure 43.

^{1}H-NMR: 1.63 (s, 12H, CH_3); 2.03 (s, 4H, CH_2); 6.98 (d, 2H, CH imidazolide, H #2); 7.03 (t, 2H, CH imidazolide, H #1); 8.06 (d, 2H, CH imidazolide, H #3). For assignment of numbered protons see figure 43.

IR: 1746(C = O); 1624 and 1530 (C = C and C = N); 1478 (CH_2 scissoring and CH_3 asymmetric bending); 1385 and 1382 (CH_3 gem-dimethyl symmetric bending); 1254, 1220, 1179, 1161, 1098, 1061 and 1000 (C-O-C, C-N-C and N-C-C stretches); 665 and 650 (ring deformation imidazolide).

MS: M+ absent; 223 (VW, loss of CO_2 and imidazolyl radical); 222 (W, loss of CO_2 and imidazole); 179 (W, loss of 2 CO_2 and imidazolyl radical); 178 (VW, loss of 2 CO_2 and imidazole); 163 (W, loss of 2 CO_2, imidazolyl and CH_3 radicals); 111 (S, loss of 2 CO_2, imidazole and imidazolyl radical); 110 (S, loss of 2 CO_2 and 2 imidazoles); 95 (S, loss of 2 CO_2, 2 imidazoles and CH_3); 69 (VS, protonated imidazole); 68 (S, imidazole).

2-2) Reaction of the bis-carbonylimidazolide of 2,5-dimethyl-2,5-hexanediol I-b with 1,4-benzenedimethanol and 1,4-butynediol (70:30): Preparation of Polymer II-c

A mixture of 3.3940 g (10.149 mmoles) of the bis-carbonylimidazolide I-b, 0.9776 g (7.075 mmoles) of 1,4-benzenedimethanol, 0.2671 g (3.106 mmoles) of 1,4-butynediol, 0.25 g of 18-crown-6, 6.8 g of potassium carbonate and 8 ml of dry dichloromethane is prepared under argon atmosphere. The reaction mixture is stirred and refluxed for 24 hours. After this time, tlc shows no remaining starting material and the polymer is worked-up by diluting with CH_2Cl_2 and centrifugating the suspension to remove the insoluble salts. The decanted solution is concentrated on rotatory evaporator and precipitated in methanol to afford 2.61 g (80% yield) of a white polymer, which has spectroscopic and elemental analyses consistent with the polycarbonate, II-c.

EA: found (C: 63.27, H: 6.97); calculated (C: 63.03, H: 7.33)

^{1}H-NMR: 1.47 (s, 12H, CH_3); 1.85 (s, 4H, CH_2 hexanediol); 4.72 (s, 1.2H, CH_2 butynediol); 5.10 (s, 2.8H, CH_2 benzenedimethanol); 7.40 (s, 2.8H, CH aromatic).

^{13}C-NMR: 25.72 (q, CH_3); 34.27 (t, CH_2 hexanediol); 54.51 (t, CH_2 butynediol); 68.30 (t, CH_2 benzenedimethanol); 80.92 (s, C butynediol); (83.84 (s, C hexanediol, end chain units)); 84.54 (s, C hexanediol); 128.39 (d, CH benzenedimethanol);

135.80 (s, C benzenedimethanol); (152.54 (s, C = O, end chain units)); 153.21 (s, C = O)).

IR: 1740 (C = O); 1476 (C = C stretch); 1443 (CH_3 asym. bending); 1372 and 1380 (CH_3 sym. bending); 1258, 1262, 1207, 1167 and 1085 (C-O-C).

MW; GPC: Mw = 13500, Mn = 7900, D = 1.7

DSC: T_g = 25°C; 2 endotherms at 66° and 100°C

T_m = 117°C

2-3) Reaction of the bis-carbonylimidazolide of 2,5-dimethyl-2,5-hexanediol with 1,4-benzenedimethanol and 1,4-butynediol (80:20): Preparation of II-b

A mixture of 3.4216 g (10.233 mmoles) of the bis-carbonylimidazolide I-b, 1.1808 g (7.8946 mmoles) of 1,4-benzenedimethanol, 0.1936 g (2.2512 mmoles) of 1,4-butynediol, 0.22 g of 18-crown-6, 6.8 g of potassium carbonate and 8 mL of dry dichloromethane is prepared under argon atmosphere. The reaction mixture is stirred and refluxed for 24 hours. After this time, tlc shows no remaining starting material and the polymer is worked-up as usual and, after precipitation in methanol, 1.96 g (60% yield) of a foamy white oligomer is obtained. The ^1H-NMR spectrum reveals the presence of significant amounts of end-groups in the oligomer and the IR shows C = O band as well as terminal O-H absorption.

3-1 Attempted synthesis of the bis-carbonylimidazolide of pinacol

A solution of 1.00g (8.5 mmoles) of pinacol dissolved in 15 mL of dry THF is prepared under argon atmosphere. To this solution is added 0.05 g of potassium metal, and the mixture is refluxed while stirring until all the metal is dissolved. The alcoholate solution is then cooled and added, under argon atmosphere pressure through a teflon tubing, to a stirred suspension of 2.76 g (17 mmoles) of 1,1'-carbonyldiimidazole in 15 mL of dry THF. After refluxing for three hours, the solvent is removed on rotatory evaporator and the crude product is applied on a silica-gel column (80 g) using ethyl acetate as the eluting solvent. The pure compound, melting at 183°C and in 82% yield (1.02 g) is identified by spectroscopic means as being 1,1,2,2-tetramethyl ethylcarbonate, 7.

^{1}H-NMR: 1.40 (s,CH_3)

^{13}C-NMR: 153.94 (s,C = O); 86.08 (s,C); 22.31 (q,CH_3)

IR: 1778 (C = O); 1286 (C-O-C); 1466 (CH_3 asym. bending);
1389 and 1378 (CH_3, gem-dimethyl sym. bending)

*MS: 145(VS,M +1); 101(M,loss of CO_2); 83(M,loss of CO_2 and CH_3); 59(M,loss of CO_2 and isopropyl radical)

3-2 Synthesis of the bis-carbonylimidazolide of 1,4-benzenedimethanol, I-c

A suspension of 10.0 g (72 mmoles) of 1,4 benzenedimethanol in 100 mL of dry THF is prepared under argon atmosphere. To this solution is added 0,6 g of potassium metal and the mixture is stirred and refluxed until all the metal is dissolved. At this point the yellow suspension obtained is added to a suspension of 23.4 g (144 mmoles) of 1,1'-carbonyldiimidazole in 50 mL of dry THF affording a yellow solution which is refluxed for 4 hours. The solvent is removed on rotatory evaporator, and the crude product is recrystallized from CH_2Cl_2/petroleum ether. A 29% yield (6.90 g) of pure compound is recovered. The spectroscopic and elemental analysis are consistent with the desired compound, I-c.

E.A.: found (C:58.75, H:4.43, N:16.95); calculated (C:58.89, H:4.32, N:17.17)

^{1}H-NMR: 8.10 (m,2H,CH imidazolide, H#3); 7.48 (s,4H,CH aromatic); 7.38 (m,2H,CH imidazolide H#1); 7.03 (m,2H,CH imidazolide, H#2); 5.40 (s,4H,CH_2). For assignment of numbered protons see Figure 43.

^{13}C-NMR: 148.56 (s,C = O); 137.14 (d,CH imidazolide, C#3); 135.09 (s,C aromatic); 130.76 (d,CH imidazolide, C#2); 129.16 (d,CH aromatic); 117.15 (d,CH imidazolide, C#1); 69.20 (t,CH_2). For assignment of numbered carbons see figure 43.

IR: 1746 (C = O); 1526 (C = N); 1635 and 1478 (C = C); 1456 (CH_2 scissoring); 1295, 1254, 1174, 1099, 1060 and 1007 (C-O-C, C-N-C and N-C-C); 857 (= C-H out-of-plane, aromatic p-disubst.).

MS: 326 (W,M+); 282 (VW,loss of CO_2); 238 (W,loss of 2 CO_2); 215 (M,loss of CO_2 and imidazoyl radical); 171 (S,loss of 2 CO_2 and imidazoyl radical); 104 (VS, loss of 2 CO_2 and 2 imidazoyl radicals).

3-3 Reaction of the bis-carbonylimidazolide of 1,4-benzenedimethanol with pinacol

A mixture of 0.2041 g (1.727 mmoles) of pinacol, 0.5635 g (17.27 mmoles) of the bis-carbonylimidazolide I-c, 0.08 g of 18-crown-6, 2 g of anhydrous potassium carbonate and 3 mL of dry dichloromethane is prepared under argon atmosphere. This reaction mixture is stirred and refluxed for 18 hours. Tlc shows no starting material remaining. The work-up is done by diluting with CH_2Cl_2 and centrifugating the suspension. Since no polymer is found in the decanted organic solution, the insoluble material is poured into distilled water in order to dissolve

K_2CO_3. The white insoluble solid which remains in suspension in water, is dried and identified as the polycarbonate of 1,4-benzenedimethanol, 3, by comparing its IR spectrum to that found in literature (37). The polymer is not soluble in any of the usual organic solvents including in hot DMSO, hot DMF, hot ortho-dichloro-benzene, and others.

IR: 1742 (C = O); 1455 (CH_2 scissoring); 1254 and 1231 (C-O-C); 850 (=C-H out-of-plane bending, aromatic p-disubst.).

3-4 Synthesis of the bis-carbonylimidazolide of 1,3-benzenedimethanol, I-d

A solution of 8.0 g (57.9 mmoles) of 1,3-benzenedimethanol in 80 mL of dry THF is prepared under argon atmosphere. To this solution is added 0.34 g of potassium metal and the mixture is refluxed until all the metal is dissolved. The cooled alcoholate solution is then added to a suspension of 20.6 g (127 mmoles) of 1,1'-carbonyldiimidazole in 40 mL of dry THF and the reaction mixture is stirred and refluxed for three hours. The solvent is removed on rotatory evaporator and the crude product is dissolved in CCl_4 and washed with distilled water. After drying the organic phase over magnesium sulfate and removal of the solvent, 63% (11.9 g) yield of pure product is obtained. Spectroscopic data show that the desired product, I-d, has been obtained.

^{1}H-NMR: 8.10 (m,2H,CH imidazolide, H#3); 7.47(s,4H,CH aromatic); 7.41 (m,2H,CH imidazolide, H#1); 7.05 (m,2H,CH imidazolide, H#2); 5.43 (s,4H,CH$_2$). For assignment of numbered protons see figure 43.

^{13}C-NMR: 148.31 (s,C = O); 136.89 (d,CH imidazolide, C#3); 134.60 (s,c aromatic); 130.53 (d,CH imidazolide, C#2); 129.28 (d,CH aromatic, C#5); 129.23 (d,CH aromatic C#4); 128.75 (d,CH aromatic, C#6); 116.92 (d,CH imidazolide C#1); 69.06 (t,CH$_2$). For assignment of numbered carbons see figure 43 and 50.

IR: 1751 (C = O); 1526 (C = N); 1476 (C = C); 1457 (CH$_2$ scissoring); 1298, 1287, 1253, 1169, 1093, 1062 and 998 (C-O-C, C-N-C and N-C-C); 892 and 763 (= C-H out-of-plane bending, aromatic m-disubst.); 707 (C = C out-of-plane ring bending).

MS: 326 (W,M+); 282 (W,loss of CO$_2$; 238 (W,loss of 2 CO$_2$); 215 (W,loss of CO$_2$ and imidazolyl radical); 171 (VS,loss of 2 CO$_2$ and imidazolyl radical.); 104 (S,loss of 2 CO$_2$ and 2 imidazolyl radical).

3-5 Reaction of the bis-carbonylimidazolide of 1,3-benzenedimethanol with pinacol

A mixture of 0,2198 g (1.860 mmoles) of pinacol, 0,6069 g (1.860 mmoles) of the bis-carbonylimidazolide I-d, 0,07 g of 18-crown-6, 2 g of potassium carbonate and 3 mL of dry CH_2Cl_2 is prepared under argon atmosphere. This reaction mixture is stirred and refluxed for 24 hours. The work-up is done by diluting with CH_2Cl_2 and centrifugating the suspension. The clear decanted solution is concentrated and precipitated into methanol. Only a few mg of a gummy material is obtained which is identified by spectroscopy as being a carbonate oligomer of 1,3-benzenedimethanol, 4.

^{1}H-NMR: 7.26 (m,4H,CH aromatic); 5.07 (s,4H,CH_2)

IR: 3389 (O-H stretch, terminal hydroxyls); 1747 (C = O); 1612 and 1490 (C = C stretch); 1452 (CH_2 scissoring); 1259 (C-O-C stretch); 889 and 791 (= C-H out-of-plane bending, aromatic); 700 (C = C ring out-of-plane bending).

The methanol is evaporated and the residue, analysed by ^{1}H-NMR, contains:

- pinacol 1.23 (s,CH_3);
- 1,1,2,2,-tetramethyl ethyl carbonate, 7, 1.40 (s,CH_3);
- 1,3-benzenedimethanol 7.25 (m,4H,CH aromatic); 4.54 (s,4H,CH_2)
- 18-crown-6 and imidazole

3-6 Reaction of the bis-carbonylimidazolide of p-bis(1-hydroxyethyl)-benzene with pinacol

A mixture of 0,2350 g (1.989 mmoles) of pinacol, 0.7044 g (1.989 mmoles) of the bis-carbonylimidazolide 1-a, 0.07 g of 18-crown-6, 2 g potassium carbonate and 3 mL of dry CH_2Cl_2 is prepared under argon atmosphere. This reaction mixture is stirred and refluxed for 22 hours. After dilution with CH_2Cl_2 and centrifugation, precipitation of the concentrated organic solution into methanol affords 0.3 g of a white polymer which is identified as the polycarbonate of p-bis(1-hydroxyethyl)-benzene, 5.

^1H-NMR: 7.20 (m,4H,CH aromatic); 5.55 (q,2H,CH benzyl); 1.46 (d,6H,CH_3)

IR: 1741 (C = O); 1451 and 1347 (CH_3, asym. and sym. bending); 1255 and 1058 (C-O-C stretch); 858 (=C-H out-of-plane bending, aromatic)

3-7 Synthesis of the carbonylimidazolide of benzyl alcohol, 6

A solution of 3.0 g (27.7 mmoles) of freshly distilled benzyl alcohol in 20 mL of dry THF is prepared under argon atmosphere. To this solution is added 0.11 g of potassium metal and the mixture is refluxed until all the metal is dissolved. The cooled solution is added to a suspension of 5.0 g (30.8 mmoles) of 1,1'-carbonyldiimidazole in 15 mL of dry THF and the mixture is refluxed for two hours. At this time thin layer chromatrography shows that the reaction is complete. The solvent is evaporated and the crude liquid product is applied on a silica gel column (65 g) using 40:60 ethyl acetate: hexanes as eluent. A white solid is obtained in 38% (2.14 g) yield and its spectroscopic and elemental analysis are characteristic of the desired compound, 6.

EA: found (C:65.09, H:5.09, N:13.93); calculated (C:65.34; H:4.98, N:13.85)

^{1}H-NMR: 8.10 (m,1H,CH imidazolide, H#3); 7.40 (s,6H,CH aromatic and CH imidazolide, H#1); 7.03 (m,1H,CH imidazolide; H#2); 5.36 (s,2H,CH_2). For assignment of numbered protons see figure 43.

MS: 202 (W,M^+); 158 (M,loss of CO_2); 91 (VS,loss of CO_2 and imidazolyl radical).

3-8 Reaction of the carbonylimidazolide of benzyl alcohol with pinacol

A mixture of 0.70 (3.5 mmoles) of the carbonylimidazolide of benzyl alcohol, 6, 0,20 g (1.7 mmoles) of pinacol, 0.07 g of 18-crown-6, 2 g of potassium carbonate and 4 mL of dry dichloromethane is prepared under argon atmosphere. After three hours of reflux, the reaction mixture is cooled to room temperature and, after dilution with CH_2Cl_2, filtered to remove K_2CO_3. The organic phase is washed with distilled water, dried, and after removal of the solvent, the main products are separated by column chromatography on silica (25 g) and identified by spectroscopy as being 1,1,2,2-tetramethylethyl carbonate, 2, and bis-benzyl carbonate, 7. Some unreacted pinacol is also found in the aqueous phase.

Bis-benzyl carbonate, 7:

^{1}H-NMR: 7.33 (s,10H,CH aromatic); 5.10 (s,4H,CH_2)

IR: 1748 (C = O); 1456 (CH_2 scissoring); 1264 (C-O-C); 749 (= C-H out-of-plane bending); 695 (C = C out-of-plane ring bending)

MS: absent (M+); 151 (M,loss of benzyl radical); 107 (S,loss of CO_2 and benzyl radical); 91 (VS,benzyl radical).

4-1 Synthesis of the bis-carbonylimidazolide of α,α'-dihydroxy-p-diisopropyl-benzene, I-e

A solution is prepared under argon atmosphere, consisting of 5.00 g (25.7 mmoles) of α,α'-dihydroxy-p-diisopropyl-benzene dissolved in 70 mL of dry THF. To this solution is added 0,15 g of potassium metal, and the solution is brought to reflux while stirring until all the metal is dissolved. The solution is then cooled and added, under argon atmosphere, to a stirred suspension of 8.35 g (51.5 mmoles) of

1,1'-carbonyldiimidazole in 30 mL of dry THF. This reaction mixture is then refluxed for three hours at which time thin layer chromatography indicates that the reaction is complete. The solvent is removed on rotatory evaporator and the crude product is purified by recrystallization from dichloromethane/petroleum ether to afford 2.87 g (29%) of pure compound which has spectroscopic and elemental analyses consistent with the desired bis-carbonylimidazolide, I-e.

EA: found (C:63.09, H:5.77, N:14.46); calculated (C:62.82, H:5.80, N:14.65)

^{1}H-NMR: 8.10 (m,2H,CH imidazolide H#3); 7.39 (m,6H,CH imidazolide H#1 and CH aromatic); 7.02 (m,2H,CH imidazolide H#2); 1.97 (s,12H,CH_3). For assignment of numbered protons see figure 43.

^{13}C-NMR: 146.72 (s,C = O); 143.41 (s,C aromatic); 137.09 (d,CH imidazolide,C#3); 130.53 (d,CH imidazolide,C#2); 124.82 (d,CH aromatic); 117.18 (d,CH imidazolide,C#1); 86.17 (s,C benzyl); 28.27 (q,CH_3). For assignment of numbered car see figure 43.

IR: 1755 (C = O); 1525 (C = N); 1475 (C = C); 1384 and 1370 (CH_3 gem-dimethyl sym. bending); 1295, 1251, 1200, 1177, 1149, 1095, 1061 (C-O-C, C-N-C, N-C-C) 843 (=C-H out-of-plane bending aromatic).

MS: absent (M+); 227 (VW,loss of 2 CO_2 and imidazolyl radicals); 160 (W,loss of 2 CO_2 and imidazolyl radicals); 158 (VS,loss of 2 CO_2 and 2 imidazole); 159 (S,loss of 2 CO_2, imidazolyl radical and imidazole); 143 (M,loss of 2 CO_2,2 imidazole and CH_3); 68 (VS,imidazole); 44 (VS,CO_2)

4-2 Reaction of the bis-carbonylimidazolide of α,α'-dihydroxy-p-diisopropyl-benzene with 1,4-benzenedimethanol

A mixture of 12.0019 g (31.3841 mmoles) of the bis-carbonylimidazolide, I-e, 4.3363 g (31.3841 mmoles) of 1.4-benzenedimethanol, 0,66 g of 18-crown-6, 20 g of anhydrous potassium carbonate and 27 mL of dry dichloromethane is prepared under an argon atmosphere. The reaction mixture is stirred and refluxed for 24 hours at which time tlc shows no remaining starting material. The work-up is done by diluting the reaction mixture with dichloromethane, and centrifugating the suspension. The solvent of the decanted solution is removed and the residue dissolved in THF. After precipitation in distilled water, 9.65 g (80% yield) of a white polymer is obtained. The polymer, II-d, is characterized by its spectroscopic and elemental analyses.

EA: found (C:68.63, H:6.48); calculated (C:68.74, H:6.29)

^{1}H-NMR: 1.78 (s,12H,CH_3); 5.00 (s,4H,CH_2); 7.31 (m,8H,CH aromatic)

^{13}C-NMR: 152.97 (C = O); 143.81 (s,C aromatic, α,α'-dihydroxy-p-diisopropyl-benzene); 135.61 (s,C aromatic, benzenedimethanol); 128.33 (d,CH aromatic, benzenedimethanol); 124.47 (d,CH aromatic, α,α'-dihydroxy-p-diisopropyl-benzene); 83.34 (s,C benzylic, α,α'-dihydroxy-p-diisopropyl-benzene); 68.47 (t,CH_2); 28.30 (q,CH_3).

IR: 1748 (C = O); 1466 (CH_2 scissoring); 1457 (CH_3 asym. bending); 1385 and 1366 (CH_3 gem-dimethyl sym. bending); 1256, 1201, 1142, 1109 and 1084 (C-O-C); 837 (= C-H out-of-plane bending, aromatic).

MW; Osmometry: Mn = 14000

GPC: Mn = 2418, Mw = 6153, D = 2.5

DSC: Tg = 46°C

4-3 Reaction of the bis-carbonylimidazolide of α,α'-dihydroxy-p-diisopropyl-benzene with α,α'-dihydroxy-p-diisopropyl-benzene

A mixture of 0.9326 g (4.800 mmoles) of the diol, 1.8358 g (4.800 mmoles) of the bis-carbonylimidazolide, I-e, 0.2 g of 18-crown-6, 3 g of potassium carbonate and 5 mL of dry CH_2Cl_2 is prepared under argon atmosphere. The reaction mixture is stirred and refluxed for 45 hours. After centrifugation of the suspension and evaporation of the solvent, the ^{1}H-NMR of the crude mixture shows mainly the starting diol, a small amount of oligomer, 16, and some 1,4-diisopropenylbenzene indicating that the tertiary diol underwent elimination.

5-1) Synthesis of the bischloroformate of 4,4'-isopropylidene diphenol, 8

A solution is prepared by bubbling 2.91 g (29 mmoles) of phosgene ($COCl_2$) into 20 mL of dichloromethane which is kept cool by using a ice-water bath. 4,4'-isopropylidenediphenol (2.96 g, 13 mmoles) is added to the phosgene solution, and then 3.15 g (26 mmoles) of N,N-dimethylaniline diluted in 10 mL of dichloromethane is added dropwise to the reaction mixture over a period of 30 minutes. After the addition is complete, the reaction mixture is stirred for three hours after which time thin layer chromatography monitoring indicates completion of the reaction. Dry nitrogen is bubbled through the green solution in order to remove the excess of phosgene which is then trapped into a KOH/ethanol solution. The solution turns colorless upon removal of excess phosgene. The work-up is done by washing the solution with distilled water and dilute hydrochloric acid. The washed organic layer is dried over magnesium sulfate and, after evaporation of the solvent on rotatory evaporator, the product, 8, is obtained as a white solid in a 95% yield (4.35 g). ^{1}H-NMR and infrared spectroscopy suggest that the product is sufficiently pure to be used without further purification in the next step.

^{1}H-NMR: 1.67(s, 6H, CH_3), 7.13(m, 8H, CH aromatic).

IR: 1776(C=O); 1466(CH_3 asym. bending); 1385 and 1364(CH_3 gem-dimethyl sym. bending); 1197, 1167 and 1129(C-O-C stretch); 875(C-H out-of-plane bending, aromatic); 675(C-Cl stretch).

5-2) Synthesis of the bis-carbonylimidazolide of 4,4'-isopropylidenediphenol, 9

A solution of 3.05 g (8.6 mmoles) of the bischloroformate, 8, dissolved in 10 mL of dry THF is added dropwise to a solution of 2.35 g (34.6 mmoles) of imidazole dissolved in 25 mL of dry THF. The reaction mixture is then allowed to stir at room temperature for two hours. The white precipitate which is observed is filtered and dissolved in chloroform; then, the insoluble imidazolium chloride is filtered and the crude product is recovered by evaporating the organic solvent on rotatory evaporator. Purification is achieved by crystallization from chloroform / ethyl acetate to afford 67% yield (3.44 g) of a material which has spectroscopic and elemental analyses consistent with the desired bis-carbonylimidazolide, 9.

EA: found (C:66.14, H:4.89, N:13.29); calculated (C:66.34, H:4.84, N:13.45).

^{1}H-NMR: 1.70(s, 6H, CH_3); 7.08(m, 2H, CH imidazolide, H#2); 7.18(m, 8H, CH aromatic); 7.47(m, 2H, CH imidazolide, H#1); 8.18(m, 2H, CH imidazolide, H#3). For assignment of numbered protons see figure 30.

IR: 1786(C=O); 1595 and 1478(C = C stretch); 1526(C = N stretch); 1462(CH_3, asym. bending); 1385 and 1364(CH_3, gem-dimethyl sym. bending); 1290, 1254, 1200, 1175, 1099 and 1060(C-O-C, C-N-C and N-C-C); 875(=C-H out-of-plane bending, aromatic).

MS: 416(S, M+); 401(VS, loss of CH_3); 307(S, loss of CH_3, CO, and imidazolyl radical + H); 306(W, loss of CH_3, CO, and imidazolyl radical); 213(M, loss of CH_3, 2 CO and 2 imidazolyl radicals + 2H); 28(S, CO); 44(W, CO_2).

5-3) Reaction of the bis-carbonylimidazolide of 4,4'-isopropylidenediphenol with 2,5-dimethyl-2,5-hexanediol

A mixture of 0,8326 g (2,000 mmoles) of the bis-carbonylimidazolide 9, 0.2925 g (2.000 mmoles) of 2,5-dimethyl-2,5-hexanediol, 0.1 g of 18-crown-6, 2.0 g of anhydrous potassium carbonate, and 7 mL of dry THF is prepared under argon atmosphere. After stirring and refluxing for 19 hours none of the desired polymer is isolated, but the presence of the starting diol, 4,4'-isopropylidenediphenol and a little amount of oligomer, 17, is detected by ^{1}H-NMR and IR. Replacing THF by dichloromethane does not improve the outcome of the reaction.

5-4) Synthesis of bis-p-nitrophenylcarbonate of 2,5-dimethyl-2,5-hexanediol, III-a

A solution of 12.10 g (60 mmoles) of p-nitrophenylchloroformate in 30 mL of dry dichloromethane is added over a period of 45 minutes to a solution of 4.39 g (30 mmoles) of 2,5-dimethyl 2,5-hexanediol in 4.74 g (60 mmoles) of dry pyridine and 85 mL dry dichloromethane. The stirred solution is refluxed for 15 hours. After cooling to room temperature, 150 mL of CH_2Cl_2 is added to the reaction mixture in order to bring the white precipitate into solution. Afterwards, the organic solution is washed twice with 100 mL of distilled water, once with 50 mL of a 5% solution of hydrochloric acid and once more with 50 mL of distilled water. After drying over magnesium sulfate, the organic solvent is removed on rotatory evaporator. The crude product is recrystallized using dichloromethane and petroleum ether. The pure product obtained in a 65% yield (9.23 g), is identified by spectroscopic and elemental analysis as being the desired compound, III-a.

EA: found (C: 55.48, H: 5.18, N: 5.77); calculated (C: 55.46, H: 5.08, N: 5.88).

^{1}H-NMR: 1.56(s, 12H, CH_3); 1.97(s, 4H, CH_2); 7.26(d, 4H, CH aromatic H#2); 8.15(d, 4H, CH aromatic H#1). For the assignment of numbered protons see figure 44.

^{13}C-NMR: 25.77(q, CH_3); 33.87(t, CH_2); 85.98(s, C hexanediol); 122.00(d, CH aromatic, C#2); 125.09(d, CH aromatic, C#1); 145.18(s,C aromatic, C#3); 155.51(s, C aromatic, C#4); 150.39(s, C=O). For assignment of numbered carbons see figure 44.

IR: 1757(C = O stretch); 1622 and 1489(C = C stretch); 1530 and 1351(NO_2 stretch); 1456(CH_2, scissoring); 1389 and 1376(CH_3 gem-dimethyl sym. bending); 1278, 1191, 1155 and 1099(C-O-C stretch); 859(= C-H out-of-plane bending, aromatic).

MS: absent(M+); 139(VS, p-nitrophenol); 111(M, loss of $2CO_2$, p-nitrophenol and p-nitrophenyl radical); 110(M, loss of $2CO_2$ and 2 p-nitrophenol); 95(S, loss of $2CO_2$, 2 p-nitrophenol and CH_3); 55(S, loss of $2CO_2$, 2 p-nitrophenol and C_4H_7 radical); 44 (VS, CO_2).

5-5) Reaction of bis-p-nitrophenylcarbonate of 2,5-dimethyl 2,5-hexanediol with 4,4-isopropylidenediphenol: Preparation of polymer IV-a

A mixture of 0.6758 g (2.9607 mmoles) of 4,4'-isopropylidene diphenol, 1.41058 g (2.9607 mmoles) of the bis-p-nitrophenylcarbonate, III-a, 0.1 g of 18-crown-6, 2 g of potassium carbonate and 5 mL of dry dichloromethane is prepared under argon atmosphere. A yellow coloration due to p-nitrophenol, appears as soon as all the reactants are mixed together. After stirring and refluxing for 48 hours, the work-up of the polymer is done by diluting the reaction mixture with dichloromethane and centrifugating the suspension. The decanted clear solution is then concentrated to about 20 mL. After three precipitations into 500 mL of methanol and drying in vacuo, the white polymer is obtained in 94% yield (1.18 g). The spectroscopic and elemental analyses of the polymer are consistent with a linear alternating polycarbonate of 2,5-dimethyl 2,5-hexanediol and 4,4-isopropylidenediphenol, <u>IV-a</u>.

MW; Osmometry: Mn = 13500

GPC: Mn = 10200, Mw = 24600, D = 2.4

DSC: Tg = 87°C; Tm = 166°C

EA: found (C: 70.34, H: 7.07); calculated (C: 70.40, H: 7.09)

^{1}H-NMR: 1.51(s, 12H, CH_3 hexanediol); 1.59(s, 6H, CH_3 4,4-isopropylidenediphenol); 1.91(s, 4H, CH_2); 7.03(d, 4H, CH aromatic, H #2); 7.18(d, 4H, CH aromatic, H #1). For assignment of numbered protons see figure 45.

^{13}C-NMR: 25.59(q, CH_3, hexanediol); 30.92(q, CH_3, 4,4'-isopropylidenediphenol); 34.54(m, CH_2); 42.41(s, benzylic C); 84.90(s, C, hexanediol); 120.60(d, CH aromatic, C #1); 127.73(d, CH aromatic, C #2); 147.78(s, C aromatic, C #3);

148.91(s, C aromatic, C #4); 151.89(s, C=O). For assignment of numbered carbons see figure 45.

IR: 1755(C=O stretch); 1595 and 1509(C=C stretch); 1469(CH_3 asym. bending); 1456(CH_2 scissoring); 1396 and 1370(CH_3 gem-dimethyl sym. bending); 1263, 1204, 1196 and 1110(C-O-C stretch); 838(= C-H out-of-plane bending, aromatic).

Imaging of IV-a

A solution of 1.57 g of polymer in 13.6 g tetrachloroethane containing 0.160 g of triphenylsulfonium hexafluoroantimonate is used to coat 5" silicon wafers by spin coating at 4000 RPM to produce a 0.85 μm thick film. Pre-bake must not exceed 70°C as the film flows at 80°C. After exposure at scan speed 360, the wafers are post-baked 2 min at 60°C. A visible underexposed positive image which is difficult to develop fully is obtained. The exposure is increased to scan speed 1000, then baked at 60°C for 2 min. A 60% dry-developped image is obtained. The image can be fully developped using a 5:4:1 mixture of isopropanol: n-amyl alcohol:anisole. Figure 38 shows the positive image obtained from polymer IV-a.

5-6) Synthesis of the bis-p-nitrophenylcarbonate of 1,4-benzenedimethanol, III-b

A solution of 14.1 g (70 mmoles) of p-nitrophenylchloroformate in 40 mL of dry dichloromethane is added over a period of one hour to a solution of 4,80 g (35 mmoles) of 1,4-benzenedimethanol in 5.53 g (70 mmoles) of dry pyridine and 60 mL of dry dichloromethane. After stirring at room temperature overnight, enough dichloromethane is added to the reaction mixture to bring the white compound formed into solution. The organic phase is then washed successively with distilled water, a 5% solution of hydrochloric acid and once more with distilled water. After drying the organic phase over anhydrous magnesium sulfate and removal of the solvent on rotatory evaporator, a white solid is recovered. Recrystallization from dichloromethane affords 9.11 g (56% yield) of pure product which is shown to be the desired compound, III-b, by spectroscopic and elemental analysis.

^{1}H-NMR: 5.32(s, 4H, CH_2); 7.53(s, 4H, CH, benzenedimethanol); 7.40(d, 4H, CH nitrophenol, H #2); 8.30(d, 4H, CH nitrophenol, H #1). For assignment of numbered protons see figure 44.

^{13}C-NMR: 70.35(CH_2); 121.72(CH, nitrophenol, C #2); 125.32(CH, nitrophenol, C #1); 128.98(CH, benzenedimethanol); 135.08(C, benzenedimethanol); 145.43(C, nitrophenol, C #3); 155.40(C, nitrophenol, C #4); 152.40(C=O). For assignment of numbered carbons see figure 44.

IR: 1767(C = O); 1617 and 1494(C = C); 1521 and 1345(NO_2 stretch); 1458(CH_2 scissoring); 1253,1215 and 1167(C-O-C); 863(= C-H out-of-plane bending, aromatic).

MS: absent(M+); 286(VS, loss of CO_2 and nitrophenyl radical); 242(W, loss of $2CO_2$ and nitrophenyl radical); 139(W, nitrophenol); 104(s, loss of $2CO_2$ and 2 nitrophenyl radicals).

EA: found (C: 56.29, H: 3.70, N: 5.84); calculated (C: 56.42, H: 3.44, N: 5,98).

5-7) Reaction of bis-p-nitrophenylcarbonate of 1,4-benzenedimethanol with 4,4'-isopropylidenediphenol: Preparation of Polymer IV-b

A mixture of 0.48077 g (2.1060 mmoles) of 4,4'-isopropylidenediphenol, 0.98637 g (2.1060 mmoles) of the bis-p-nitrophenylcarbonate, III-b, 0.2 g of 18-crown-6, 2 g of anhydrous potassium carbonate and 5 mL of dry dichloromethane is prepared under argon atmosphere. After stirring and refluxing for 24 hours, tlc shows no remaining starting material, the work-up and recovery of the polymer are done as reported in section 5-5 affording 0.80 g (91% yield) of a white polymer. The recovered polymer has spectroscopic and elemental analysis consistent with a linear copolycarbonate, IV-b, of 4,4'-isopropylidenediphenol and 1,4-benzenedimethanol.

MW; Osmometry: Mn = 12200

DSC: Tg = 90°C

EA: found (C: 71.86, H: 5.50); calculated (C: 71.76, H: 5.30).

^{1}H-NMR: 1.63(s, 6H, CH_3); 5.28(s,4H, CH_2); 7.08(d, 4H, CH 4,4'-isopropylidenediphenol, H #2); 7.23(d, 4H, CH 4,4'-isopropylidenediphenol, H #1); 7.50(s, 4H, CH benzenedimethanol). For assignment of numbered protons see figure 45.

^{13}C-NMR: 153.69(C=O); 149.01(C 4,4'-isopropylidenediphenol, C #4); 148.08(C 4,4'-isopropylidenediphenol, C #3); 135.34(C benzenedimethanol); 128.78(CH, benzenedimethanol); 127.85(CH 4,4'-isopropylidenediphenol, C #2); 120.40(CH 4,4'-isopropylidenediphenol, C #1); 69.78(CH_2); 42.48(benzylic C, 4,4'-isopropylidenediphenol); 30.90(CH_3). For assignment of numbered carbons see figure 45.

IR: 1760(C = O); 1606 and 1506(C = C); 1464(CH_3 asym. bending); 1452(CH_2 scissoring); 1412 and 1377(CH_3 gem-dimethyl sym. bending); 1254,1214 and 1178(C-O-C); 835(= C-H out-of-plane bending, aromatic).

6-1 Reaction of the bis-p-nitrophenyl carbonate of 1,4-benzenedimethanol with 2,5-dimethyl 2,5-hexanediol

A mixture of 0.47942 g (3.2786 mmoles) of the diol, 1.53550 g (3.2786 mmoles) of compound III-b, 0.2 g of 18-crown-6, 2 g of potassium carbonate and 4 mL of dry THF is prepared under argon atmosphere. The reaction mixture is stirred and refluxed for 21 hours. A polymer which is unsoluble in CH_2Cl_2 is isolated and identified by IR spectroscopy as the polycarbonate of 1,4-benzenedimethanol, 10.

6-2 Reaction of 1,4-benzenedimethanol with the bis-p-nitrophenyl carbonate of 1,4-benzenedimethanol: Preparation of Polymer IV-c

A mixture of 0.64538 g (4,6709 mmoles) of 1,4-benzenedimethanol, 2.18772 g (4.6709 mmoles) of the bis-p-nitrophenylcarbonate III-b, 0,3 g of 18-crown-6, 3.0 g of anhydrous potassium carbonate and 8 mL of dry THF is prepared under an argon atmosphere. After stirring and refluxing for 24 hours, the polymer is worked-up by adding 250 mL of THF to the reaction mixture and by decanting the suspension obtained from the K_2CO_3 lying at the bottom of the beaker. The suspension is then poured and stirred into 300 mL of methanol to afford a solid which is filtered and washed five times with methanol. Water is added to the K_2CO_3 residue and the insoluble material obtained is filtered and washed five times with methanol. The two crops of polymer are combined and dried in vacuo to afford 1.42 g (93% yield) of a white polymer which has the spectroscopic and elemental analyses consistent with a polycarbonate of 1,4-benzenedimethanol, IV-c. The polymer is not soluble, not even in hot DMSO, hot acetonitrile and hot $CHCl_3$.

EA: found (C:65.64, H:5.02); calculated (C:65.85, H:4.91)

IR: 1741 (C = O); 1455 (CH_2 scissoring); 1259 and 1231 (C-O-C); 850 (= C-H out-of-plane, aromatic)

DSC: Tm = 230°C, endotherm at 205°C

7.1 Reaction of DL-Sobrerol with the bis-carbonylimidazolide of p-bis(1-hydroxyethyl)-benzene

A mixture of 0.7881 g (4.629 mmoles) of DL-Sobrerol, 1.6394 g (4.629 mmoles) of the bis-carbonylimidazolide, I-a, 0,18 g of 18-crown-6, 2 g of potassium carbonate and 4 mL of dry dichloromethane is prepared under argon atmosphere. After stirring and refluxing for 25 hours, the reaction mixture is worked-up in the usual way. Precipitation from THF into water gives a gummy material which is identified as being the oligomeric carbonate, 11. This is particularly indicated in the IR spectrum by a strong C=O absorption along with a strong OH band belonging to the terminal hydroxyls.

7-2 Reaction of DL-Sobrerol with the bis-carbonylimidazolide of 1,4-benzenedimethanol

A mixture is prepared under argon atmosphere, consisting of 0.30734 g (1.8053 mmoles) of DL-Sobrerol, 0.58907 g (1.8053 mmoles) of the bis-carbonylimidazolide, I-c, 0.15 g of 18-crown-6, 2 g of potassium carbonate and 4 mL of dry THF. The reaction mixture is stirred and refluxed for 43 hours. After centrifugation of the suspension, only a gummy material is obtained from precipitations. This material was dissolved in CH_2Cl_2 and extracted with water. The aqueous phase contains mostly sobrerol and the organic phase consists mainly of the oligomeric carbonate 12 as shown by ^1H-NMR and especially IR spectra which shows the C=O groups along with the OH absorption of the terminal hydroxyls.

7-3 Synthesis of the bis-carbonylimidazolide of DL-Sobrerol, I-f

5.10 g (30 mmoles) of DL-Sobrerol is dissolved in 40 mL of dry THF under argon atmosphere. To this solution is added 0.13 g of potassium metal, and the solution is brought to reflux while stirring until all the metal is dissolved. The solution is cooled to 30°C and added, under argon atmosphere, to a stirred suspension of 9.73 g (60 mmoles) of 1,1'-carbonyldiimidazole in 30 mL of dry THF. The reaction mixture is refluxed for two hours. The solvent is removed on rotatory evaporator and the residue recrystallized from ethyl acetate/petroleum ether. The pure compound is isolated in a 60% yield (6.37 g) and the spectroscopic and elemental analyses are consistent with structure <u>I-f</u>.

EA: found (C:60.14, H:6.04, N:15.63); calculated (C:60.32, H:6.19, N:15.63)

^{1}H-NMR: 8.18 (s,1H,imidazolide H#6); 8.03 (s,1H,imidazolide H#3); 7.46 (s,1H,imidazolide H#4); 7.27(s,1H,imidazolide H#1); 7.10 (s,1H,imidazolide H#5); 7.03 (s,1H,imidazolide H#2); 5.86 (m,1H,alkene,H#7); 5.45 (broad singlet,1H,H#8); 1.78 (s,3H,CH_3,H#9); 1.58 and 1.62 (2s,6H,CH_3,H#10,H#11); 1.62 to 2.56 (m,5H,H#12,13,14). For assignment of numbered protons see figure 46.

^{13}C-NMR: 148.37 (C = 0, C#17); 146.62 (C = 0, C#18); 136.92 and 136.64 (CH imidazolide, C#3,6); 130.54 and 130.30 (CH imidazolide, C#2,5); 129.68 (C alkene, C#16); 128.71 (CH alkene, C#7); 116.93 and 116.69 (CH imidazolide, C#1,4); 88.90 (C, C#15); 75.26 (CH, C#8); 37.49 (CH,C#13); 29.61 (CH_2,C#12); 26.55 (CH_2,C#14); 20.41 (CH_3,C#9); 22.94 and 23.33 (CH_3,C#10,11). For assignment of numbered carbons see figure 46.

IR: 1769 and 1755 (C = 0 stretches); 1618 and 1480 (C = C); 1529 (C=N); 1454 (CH_2 scissoring); 1378 and 1390 (CH_3 gem-dimethyl sym. bending); 1293, 1253, 1222, 1184, 1174, 1127, 1091, 1063 and 1003

(C-O-C, C-N-C, N-C-C stretch); 851 (=C-H out-of-plane bending for trisubst. D.B.).

MS: 359 (VW, M+1); 315 (VW, loss of CO_2); 204 (W, loss of 2 CO_2 and imidazolyl radical); 203 (VS, loss of 2 CO_2 and imidazole); 137 (VW, loss of 2 CO_2 and 2 imidazolyl radicals); 135 (M, loss of 2 CO_2 and 2 imidazoles).

7-4 Reaction of the bis-carbonylimidazolide of DL-Sobrerol with 1,4-benzene dimethanol

A mixture is prepared under argon atmosphere consisting of 0.63291 g (4.6386 mmoles) of 1,4-benzenedimethanol, 1.66246 g (4.6386 mmoles) of the bis-carbonylimidazolide I-f, 0.2 g of 18-crown-6, 2 g of anhydrous potassium carbonate and 5 mL of dry dichloromethane. This mixture is stirred and refluxed for 48 hours. The work-up is done by diluting the reaction mixture with dichloromethane, and centrifugating the suspension. The decanted solution is concentrated and precipitated into methanol but only a gummy polymer is obtained. The tacky polymer is dissolved in CH_2Cl_2 and washed with distilled water. After drying the organic phase over magnesium sulfate, the solvent is evaporated and the residue dried in vacuo to give 1.26 g (75%) of a white foamy polymer which, when examined by ^{1}H-NMR and IR spectroscopy is seen to consists mainly of the oligomeric carbonate, II-e. This can best be seen in the IR spectrum of the foamy material, which shows the characteristic bands for the carbonate group, along with that of the hydroxyl groups.

IR: 3456 (O-H stretch, terminal hydroxyls); 1739 (C = O stretch, carbonate); 1452 (CH_2 scissoring); 1387 and 1371 (CH_3 gem-dimethyl sym. bending); 1271, 1254, 1211, 1160, 1136, 1087 and 1025 (C-O-C stretch, carbonate).

MW; GPC: Mn = 866, Mw = 1695, D = 1.96.

7-5 Synthesis of the bis-p-nitrophenylcarbonate of DL-Sobrerol, III-c

A solution of 12.10 g (60 mmoles) of p-nitrophenyl-chloroformate in 30 mL of dry dichloromethane is added over a period of 30 min to a solution of 5.10 g (30 mmoles) of DL-Sobrerol in 75 mL of dry dichloromethane and 4.74 g (60 mmoles) of dry pyridine. The stirred reaction mixture is refluxed for four hours. After cooling at room temperature, the solution is diluted with 100 mL of dichloromethane, washed once with 75 mL of distilled water, twice with 50 mL of a 5% solution of hydrochloric acid and several times with distilled water, until the aqueous phase is no more acidic. After drying over magnesium sulfate, the organic solvent is removed on rotatory evaporator. Recrystallisation from dichloromethane/petroleum ether affords 9.0 g (60% yield) of pure compound III-c which is identified by spectroscopic and elemental analyses.

EA: found (C:57.82, H:4.93, N:5.75); calculated (C:57.60, H:4.83, N:5.60)

^{1}H-NMR: 8.23 and 8.21 (2d,4H,CH nitrophenol, H#1,3); 7.32 and 7.36 (2d,4H,CH nitrophenol, H#2,4); 5.78 (m,1H,CH alkene, H#5); 5.18 (broad singlet,1H,H#6); 1.56 to 2.37 (m,5H,H#7,8,9); 1.76 (s,3H,CH_3,H#10); 1.52 and 1.54 (2s,6H,CH_3,H#11,12). For assignment of numbered protons see figure 47.

^{13}C-NMR: 155.53 (s,C aromatic, C#18,20); 152.27 (s,C = 0, C#15); 150.36 (s,C = 0, C#14); 145.24 (s,C aromatic, C#17,19); 129.67 (s,C alkene, C#16); 128.64 (d,CH alkene, C#5); 125.14 (d,CH aromatic, C#1,3); 121.84 and 121.61 (2d,CH aromatic C#2 and C#4); 87.97 (s,C, C#13); 76.69 (d,CH,C#6); 37.44 (d,CH,C#9); 29.33 (t,CH_2,C#7); 26.46 (t,CH_2,C#8); 20.59 (q,CH_3,C#10); 22.63 and 23.17 (2q,CH_3,C#11 and C#12). For assignment of numbered carbons see figure 47.

IR: 1765 and 1749 (C = 0); 1614 and 1492 (C = C stretch); 1515 and 1348 (NO_2); 1458 (CH_2 scissoring); 1374 and 1382 (CH_3 gem-dimethyl sym. bending); 1259, 1221, 1162, 1133 and 1110 (C-O-C stretches); 858 (=C-H out-of-plane bending, aromatic), 848 (=C-H out-of-plane bending for tribsubst. D.B.).

MS: absent (M+); 318 (W,loss of CO_2 and nitrophenoyl radical); 317 (W,loss CO_2 and nitrophenol); 274 (W,loss of 2 CO_2 and nitrophenyl radical); 273 (W,loss 2 CO_2 and nitrophenol); 136

(W,loss of 2 CO_2 and 2 nitrophenyl radical); 135 (M,loss of 2 CO_2 nitrophenyl radical and nitrophenol); 134 (W,loss of 2 CO_2 and 2 nitrophenol); 139 (M,nitrophenol); 107 (VS,loss of 2 CO_2, 2 CH_3, nitrophenol and nitrophenyl radical).

7-6 Reaction of the bis-p-nitrophenyl carbonate of DL-Sobrerol with 1,4-benzenedimethanol: Preparation of Polymer, IV-d

A mixture of 1.22073 g (2.4392 mmoles) of compound III-c, 0.33703 g (2.4392 mmoles) of the diol, 0.23 g of 18-crown-6, 2.0 g of anhydrous potassium carbonate and 5 mL of dry dichloromethane is prepared under argon atmosphere. This reaction mixture is stirred and refluxed for 41 hours until all starting materials have been consumed, and after cooling at room temperature, is worked-up by diluting with CH_2Cl_2 and centrifugating the suspension. The decanted solution is then concentrated on rotatory evaporator to 10 mL and precipitated four times into 600 mL of methanol. After drying in vacuo, 0.70 g (80%) of a white polymer is recovered. The polymer IV-d is characterized by spectroscopy and elemental analyses.

EA: found (C:66.79, H:6.99); calculated (C:66.65, H:6.71).

^{1}H-NMR: 7.28 (m,4H,CH aromatic); 5.62 (broad singlet,1H,H alkene, H#1); 5.03 (m,5H,CH_2 benzenedimethanol and CH, H#3); 1.64 (s,3H,CH_3,H#4); 1.48 to 2.11 (s,5H,H#5,6,7); 1.38 and 1.42

(2s,6H,CH_3,H#8,9). For assignment of numbered protons see figure 48.

^{13}C-NMR: 155.04 (s,C = 0, C#14); 153.28 (s,C = 0, C#13); 135.78 and 135.65 (2s,C aromatic, C#15,16); 130.05 (s,C alkene,C#2); 128.28 and 128.16 (2d,CH aromatic, C#17,18); 128.05 (d,CH alkene, C#1); 85.36 (s,C,C#10); 75.01 (d,CH,C#3); 68.91 (t,CH_2 benzenedimethanol,C#12); 68.25 (t,CH_2. benzenedimethanol,C#11); 37.69 (d,CH,C#5); 29.54 (t,CH_2,C#6); 26.19 (t,CH_2,C#7); 20.58 (q,CH_3,C#4); 23.06 and 23.25 (2q,CH_3,C#8 and C#9). For assignment of numbered carbons see figure 48.

IR: 1740 (C = 0); 1452 (CH_2 scissoring); 1379 (CH_3 sym. bending), 1265, 1247, 1211, 1160, 1136, 1084 and 1025 (C-O-C stretch); 847 (= C-H out-of-plane bending for trisub. D.B.); 790 (= C-H out-of-plane, aromatic)

MW; Osmometry: Mn = 11100

GPC: Mn = 6100, Mw = 10000, D = 1.6

DSC: Tm = 80°C

7-7 Reaction of bis-p-nitrophenylcarbonate of DL-Sobrerol with Bisphenol A: Preparation of polymer IV-f

A suspension of 5.00461 g (0.01000 mole) of bis-p-nitrophenyl carbonate LII-c, 2.28294 g (0.01000 mole) of bisphenol A, 0.68 g of 18-crown-6, 6.8 g of potassium carbonate and 20 mL of dry dichloromethane chloride is prepared under argon atmosphere. This preparation is stirred and refluxed over a period of 48 hours until all starting materials have been consumed. After usual dilution and centrifugation, the decanted solution is concentrated and precipitated three times into four liters of methanol in order to remove all the p-nitrophenol. After drying in vacuo, 3.56 g (79%) of a white polymer is recovered. The spectroscopic and elemental data confirm that the structure of the polymer IV-f corresponds to the desired one.

E.A.: found (C:72.07, H:6.79); calculated (C:71.98, H:6.71).

^{1}H-NMR: 7.14(m,4H,CH aromatic,H#1); 7.00(m,4H,CH aromatic,H#2); 5.72(m,1H,CH alkene,H#17); 5.14(m,1H,CH-O,H#13); 1.76(s,3H,CH_3,H#19); 1.60(m,6H,CH_3,bisphenol A,H#9); 1.53 and 1.51(2s,3H each,$2CH_3$,H#21 and H#22); 1.65-2.28(m,5H,H#14,15,16). For assignment of numbered protons see figure 51.

^{13}C-NMR: 153.74(C = O, C#12); 151.90(C = O, C#11); 148.95(C aromatic, C#4,8); 147.78(C aromatic, C#3,5); 129.99(C alkene, C#18); 128.30(CH alkene, C#17); 127.75 and 127.70(CH aromatic, C#2,6); 120.64 and 120.37(CH aromatic, C#1,7); 86.45(C-O, C#20); 75.68(CH-O, C#13); 42.41(C, bisphenol A, C#10); 37.81(CH, C#15); 30.90(CH_3, bisphenol A, C#9); 29.52(CH_2, C#16); 26.34(CH_2, C#14); 23.06 and 22.96(CH_3, C#21,22); 20.65(Ch_3, C#19). For assignment of numbered carbons see figure 51.

IR: 1758(vs, C = O); 1600 and 1508(w and m, C = C aromatic ring); 1249, 1215, 1128(vs, C-O-C stretch); 835(m, = C-H, out-of-plane bending aromatic).

MW; Osmometry: Mn = 15400

GPC: Mw = 32200, Mn = 15300; D = 2.1

DSC: Tg = 135°C

Imaging of IV-f

A solution of 0.5 g of polymer in 5 g tetrachloroethane containing 0.055 g of triphenylsulfonium hexafluoroantimonate is used to coat 5" silicon wafers by spin coating at 3000 RPM to produce a 1 μm thick film. The polymer solution does not wet adequately the silicon wafer and poor film quality is observed. Addition of a small amount of methyl cellosolve acetate does not resolve the problem.

A new solution is prepared from 1.08 g of polymer and 0.106 g of triphenylsulfonium hexafluoroantimonate in 8 g methyl cellosolve acetate. Poor films are again obtained by coating on virgin 5" silicon wafers but the quality of the coatings improves following washings of the wafers in HF. The wafers are pre-baked at 80°C for 5-15 min. then exposed through a test mask using a Perkin-Elmer deep-UV projection printing tool operating at scan speed 2000-4000. Other wafers exposed at lower scan speeds (360 or 1000) are underexposed. Upon post-baking of the wafers at 80°C a visible positive image appears immediately but this image is only incompletely developed as some of the material which is produced by the catalyzed thermolysis reaction is not very volatile at the post-bake temperature under atmospheric pressure. Full development is achieved by brief immersion or spraying of the exposed wafers in isopropanol followed by rapid drying under a stream of nitrogen. Although post-baking was done at the relatively low temperature of 80°C, the imaged material can be post-baked at higher temperature as the polymer starts to flow (thereby destroying the image) only when the temperature reaches 140°C.

Figures 41 and 42 show scanning electron micrographs of positive images obtained from polymer <u>IV-f</u> by the process described above. It is noteworthy that high resolution images having dimensions barely larger than the wavelength of the exposing radiation (254 nm) can be obtained. Although precise sensitivity measurements are still not completed it appears that polymer <u>IV-f</u> has a sensitivity essentially equal to the best currently known deep-UV resist materials.

8-1 Synthesis of cis- and trans- 3,6-diacetoxycyclohexene, 14

The synthesis of 3,6-diacetoxycyclohexene is the first step to the synthesis of 3,6-cyclohexenediol using a procedure described by Rosenthal (38). A mixture of 32 g (0.39 mole) of cyclohexene, 72 g (1.2 mole) of acetic acid and 0.8 g of cuprous chloride is heated to 80-85°C while stirring. Then, 100 g of 70 weight percent purity tertiary butyl hydroperoxide (0.78 mole) is slowly added and the reaction mixture heated to 80°C for 16 hours. After cooling to room temperature, the solution is diluted with hexane and washed with distilled water. The organic phase is dried over magnesium sulfate and most of the solvent is removed on rotatory evaporator prior to distillation at 10 mm Hg pressure. The 3,6-diacetoxycyclohexene boiling at 113-117°C is obtained in a 30% yield (23.5 g) and the 19.3 g (35%) of by-product 3-acetoxycyclohexene, 13, is recovered at 58-67°C. The desired 3,6-diacetoxycyclohexene, 14, is obtained as a yellow liquid and shows the following spectroscopic and elemental analyses.

EA: found (C;60.43, H:7.07); calculated (60.59, H:7.12).

^{1}H-NMR(39): 5.93 (broad singlet,0.7H,CH alkene,cis isomer); 5.91 (broad singlet,1.3H,CH alkene,trans isomer); 5.32 (m,1.3 H,CH-O,trans isomer); 5.24 (m,0.7 H,CH-O,cis isomer); 2.12 (m,1.3H,CH_e-CH_e,trans isomer); 2.08 (s,2.1 H,CH_3,cis isomer); 2.06 (s,3.9 H,CH_3,trans isomer); 1.88 (m,1.4 H,CH_2,cis isomer); 1.70 (m,1.3 H,CH_a-CH_a,trans isomer).

^{1}H-NMR also shows that the ratio of the cis:trans diastereoisomers is 35:65.

^{13}C-NMR: 170.54 (s,C = 0); 130.27 (d,CH alkene); 67.57 and 67.25 (2d, CH-0 trans and cis isomers); 25.74 and 24.82 (2t,CH_2, trans and cis isomers); 21.20 (q,CH_3).

IR: 1735 (C = 0); 1459 (CH_2 scissoring); 1454 (CH_3 asym. bending); 1372 (CH_3 sym. bending); 1234 (C-0-C); 791 (=C-H out-of-plane bending, cis 1,2-disubst. D.B.)

MS: absent (M+); 139 (V.W., loss of CH_3COO); 96 (VS, loss of CH_3COO and CH_3CO); 79 (W,C_6H_5 + 2H); 78 (W;C_6H_6); 77 (W,$C_6H_5^+$); 43 (VS,CH_3CO)

3-acetoxycyclohexene, 13.

^{1}H-NMR: 5.79 (m,2H,CH alkene); 5.20 (m,1H,CH); 2.03 (s,3H,CH_3); 1.72 (m,6H,CH_2)

^{13}C-NMR: 170.70 (s,C = 0); 132.61 (d,CH alkene,C#1); 125.78 (d,CH alkene,C#2); 68.08 (d,CH-0,C#6); 28.32 (t,CH_2,C#5); 24.89 (t,CH_2,C#3); 21.38 (q,CH_3); 18.89 (t,CH_2,C#4). For assignment of numbered carbons see figure 49.

IR: 1732 (C = 0); 1454 (CH_2 scissoring); 1438 (CH_3 asym. bending); 1372 (CH_3 sym. bending); 1241 (C-0-C); 728 (= C-H out-of-plane bending cis-1,2-disubst. D.B.)

MS: 140 (W,M+); 98 (VS,3-cyclohexenol); 97 (M,loss of CH_3CO); 81 (M,loss of CH_3COO); 80 (S,cyclohexadiene); 79 (VS,C_6H_5 + 2H); 78 (W,C_6H_6); 77 (W,C_6H_5 +); 43 (VS,CH_3CO)

8-2 Synthesis of cis- and trans- 3,6-cyclohexenediol, 15

The 3,6-diacetoxycyclohexene, 14, (18.0 g, 91 mmoles) is stirred at room temperature with 11.0 g of potassium hydroxide dissolved into 100 g of ethanol 99% for a period of three days. After which time, the ethanol is removed on rotatory evaporator and the brown residue washed in a soxhlet with ether. After most of the organic solvent is removed on rotatory evaporator, the diol is distilled at 130-132°C at 10 mm Hg pressure and is obtained in 60% yield (6.2 g). Upon standing for a few days the viscous transparent product becomes semi-solid. Care must be taken to wash the distillation apparatus just before the desired compound begins to distill, in order to remove any lower boiling viscous impurities which would otherwise contaminate the diol. The ^{1}H-NMR spectrum of 15 shows that the ratio of the cis:trans diastereoisomers is 45:55.

EA: found (C:63.15, H:8.88); calculated (C:63.14, H:8.83).

^{1}H-NMR(39): 5.86 (s,0.9H,CH alkene,cis isomer); 5.81 (s,1.1H,CH alkene,trans isomer); 4.23 (m,1.1H,CH-O,trans isomer); 2.11 (m,1.1H,CH_e-CH_e,trans isomer); 4.13 (m,0.9H, CH-O,cis isomer); 1.47 (m,1.1H,CH_a-CH_a,trans isomer); 1.78 (m,1.8H,CH_2,cis isomer), 1.64 (broad singlet,2H,OH).

^{13}C-NMR: (in Dioxan with external lock) 132.78 and 132.43 (2d,CH alkene,trans and cis isomers); 66.42 and 65.45 (2d,CH,trans and cis isomers); 29.90 and 27.70 (2t;CH_2,trans and cis isomers).

IR(neat): 3320 (H-bonding,OH); 1450 (CH_2 scissoring); 1062 (C-O stretch); 742 (=C-H out-of-plane bending for cis 1,2-disubst. D.B.).

MS: 114 (V.W., M+); 113 (W,loss of H); 96 (M,loss of H_2O); 86 (W,loss of C_2H_4); 78 (W,loss of $2H_2O$); 70 (VS,loss of C_2H_4O); 57 (loss of C_3H_5O)

8-3 Reaction of 3,6-cyclohexenediol with the bis-carbonylimidazolide of 1,4-benzenedimethanol

A mixture of 0.22755 g (1.9936 mmoles) of the diol 0.65053 g (1.9936 mmoles) of the bis-carbonylimidazolide I-c, 0.1 g of 18-crown-6, 2 g of anhydrous potassium carbonate and 3 mL of dry dichloromethane is prepared under argon atmosphere. This reaction mixture is stirred and refluxed for 45 hours. After the usual work-up the polymer is precipitated in methanol and only 0,34 g (56% yield) of a white polymer is recovered. This polymer is shown to consist of chains of low molecular weight of the desired polycarbonate, II-f. This can best be seen in the IR spectrum which show the characteristic bands for the carbonate group, along with that of the hydroxyl groups.

IR: ν 3475 (O-H stretch, terminal hydroxyls); 1741 (C = O, carbonate); 1454 (CH_2 scissoring); 1242, 1196 and 1079 (C-O-C); 792 (=C-H out-of-plane bending, cis, 1,2-disubst. D.B.)

MW; GPC: Mn = 2800, Mw = 3900, D = 1.4.

8-4 Reaction of the bis-p-nitrophenylcarbonate of 1,4-benzenedimethanol with 3,6-cyclohexenediol

A mixture is prepared under argon atmosphere, consisting of 1.13478 g (9.9542 mmoles) of the diol, 4.66225 g (0.9542 mmoles) of the bis-p-nitrophenyl carbonate III-b, 0.63 g of 18-crown-6, 7 g of potassium carbonate and 15 mL of dry dichloromethane. The reaction mixture is stirred and refluxed for 90 hours, after which time it is worked-up by the usual method. Three precipitations into 1.5 liter of methanol are necessary to obtain 2.76 g (91% yield) of the pure white polymer. This polymer, IV-e, shows the following spectroscopic and elemental analysis. The cis:trans ratio of the cyclohexenediol is shown to be 35:65 by ^{1}H-NMR.

EA: found (C:63.36, H:5.49); calculated (C:63.12, H:5.30).

^{1}H-NMR: 7.36 (s,4H,CH aromatic); 5.96 (m,2H,CH alkene); 5.14 (m,6H,CH-O and CH_2 benzenedimethanol); 2.15 (m,1.3H,CH_e-CH_e,trans isomer); 1.92 (m,1.4H,CH_2,cis isomer); 1.76 (m,1.3H,CH_a-CH_a, trans isomer)

^{13}C-NMR: 154.51 (C = O); 135.47 (s,C aromatic); 129.97 (d,CH alkene); 128.51 (d,CH aromatic); 71.09 (d,CH alicyclic); 69.14 (t,CH_2,benzenedimethanol); 25.25 (t,CH_2 alicyclic,trans isomer); 24.57 (t,CH_2 alicyclic, cis isomer)

IR: 1742 (C = O); 1452 (CH_2 scissoring); 1244, 1196 and 1029 (C-O-C); 792 (= C-H out-of-plane bending, cis 1,2-disubst. D.B.)

DSC: Tg = 65°C; 3 endotherms at 73,87 and 123°C

MW; Osmometry: Mn = 17600

GPC: Mn = 7900, Mw = 15000, D = 1.9

8-5 Synthesis of bis-p-nitrophenylcarbonate of 3,6-cyclohexenediol, III-d

A solution of 31.82 g (158 mmoles) of p-nitrophenyl chloroformate in 100 mL of dry dichloromethane is added dropwise, over a period of 1 hour, into a solution of 9.01 g (79 mmoles) of 3,6-cyclohexenediol and 12.48 g (158 mmoles) of pyridine in 70 mL of dichloromethane. A suspension appears ans is allowed to gently reflux overnight. The product in suspension is brought in solution by adding more methylene chloride. The solution is washed with distilled water, twice with 5% HCl solution and again with water until there is no more trace of acid. The organic layer is then dried over magnesium sulfate, filtered and evaporated on rotatory evaporator. The crude material is recrystallized from dichloromethane and petroleum ether mixture. After drying in vacuo, 21.05 g (61%) of desired compound is recovered. Integration of ^{1}H-NMR shows a cis:trans ratio of the cyclohexenediol of 10:90.

E.A.: found (C:53.95, H:3.68, N:6.21); calculated (C:54.06, H:3.63, N:6.30).

^{1}H-NMR: 8.29(d,4H,CH aromatic, H#1); 7.40(d,4H,CH aromatic, H#2); 6.17(m,2H,CH alkene); 5.34(m,2H,CH-O); 2.32(m,1.8H,CH_e-CH_e, trans isomer); 2.08(m,0.4H,CH_2, cis isomer); 1.98(m,1.8H,CH_a-CH_a, trans isomer)*. For assignment of numbered protons see figure 44.

^{13}C-NMR: 155.35(C aromatic, C#4); 151.96(C=O); 145.39(C aromatic, C#3); 129.93(CH alkene); 125.29(CH aromatic, C#1); 121.68(CH aromatic, C#2); 72.13(CH-O); 24.93(CH_2). For assignment of numbered carbons see figure 44.

IR: 1754(vs, C=O); 1521 and 1346(s, NO_2 sym. and asym. stretch); 1256,1214(s, C-O-C stretch); 861(m, =C-H out-of-plane bending, aromatic)

MS: M+(absent); 262(W, loss of CO_2 and nitrophenyl radical); 218(W, loss of 2 CO_2 and nitrophenyl radical); 217(W, loss of 2 CO_2 and nitrophenol); 139(M, nitrophenol); 80(M, loss of 2 CO_2 and 2 nitrophenyl radical); 79(VS, loss of 2 CO_2 , nitrophenyl radical and nitrophenol); 78(M, loss of 2 CO_2 and 2 nitrophenols); 44(M, CO_2).

8-6 Reaction of bis-p-nitrophenylcarbonate of 3,6-cyclohexenediol with bisphenol A

Under argon atmosphere, a mixture of 8.01780 g (18.0436 mmoles) of bis-p-nitrophenylcarbonate III-d, 4.11922 g (18.0436 mmoles) of bisphenol A, 12 g of anhydrous potassium carbonate, 1.2 g of 18-crown-6 and 40 mL of dry dichloromethane is stirred and allowed to reflux for 3 days to ensure that all starting materials are consumed. The reaction mixture is diluted with more dichloromethane and centrifugated. The decanted clear solution is concentrated and precipitated four times into 4 litres of methanol. The white polymer IV-g, is obtained in 90% yield (6.36 g) after drying in vacuo. The cis:trans ratio of cyclohexenediol is 12:88 as shown by ^{1}H-NMR.

E.A.: found (C:69.86, H:5.51); calculated (C:70.04, H:5.62).

^{1}H-NMR: 7.21(d,4H,CH aromatic, H#1); 7.05(d,4H,CH aromatic, H#2); 6.10(m,2H,CH alkene); 5.26(m,1.75H,CH-O, trans isomer); 5.17(m,0.25H,CH-O, cis isomer); 2.26(m,1.75H,CH_e-CH_e, trans isomer); 2.06(m,0,5H,CH_2, cis isomer); 1.90(m,1.75H,CH_a-CH_a, trans isomer); 1.64(s,6H,CH_3). For assignment of numbered protons see figure 45.

^{13}C-NMR: 153.27(C = O); 148.92(C aromatic, C#4); 148.05(C aromatic, C#3); 130.01(CH alkene); 127.84(CH aromatic, C#2); 120.37(CH aromatic, C#1); 71.61(CH_2-O); 42.46(C, bisphenol A); 30.89(CH_3); 25.15(CH_2). For assignment of numbered carbons see figure 45.

IR: 1757(vs,C = O); 1600 and 1508(w and m,C = C aromatic ring); 1247,1214,1082(vs, C-O-C stretch); 835(m, = C-H out-of-plane bending, aromatic)

MW; Osmometry: Mn = 13900

GPC: Mw = 40300, Mn = 20600, D = 1.96

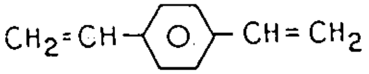
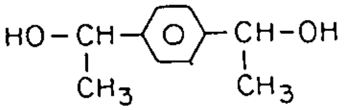
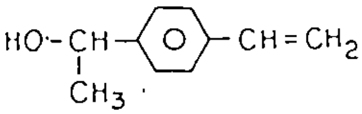
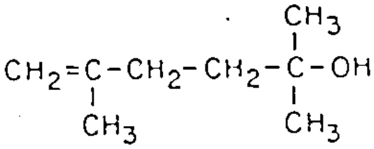
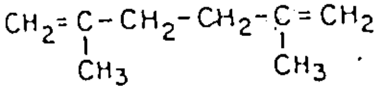
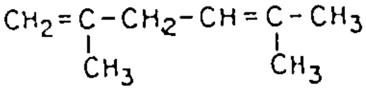
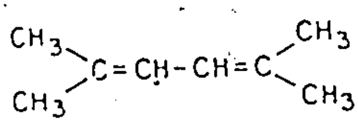
DSC: Tg = 150°C

Imaging of <u>IV-g</u>

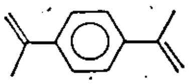
A solution of 2 g of polymer in 34 g tetrachloroethane containing 0.220 g of triphenylsulfonium hexafluoroantimonate is used to coat 5" silicon wafers (no HF wash necessary) by spin-coating at 2700 RPM to produce 1 µm thick film. The wafers are pre-baked at 70°C for 5-15 min. then exposed through a test mask at scan speed 2000. After a post-bake at 80°C a partially developed image is observed. Complete development is obtained after washing in isopropyl alcohol (aqueous base A2 developpers leave a small residue).

Figures 39 and 40 show scanning electron micrographs of positive image obtained from polymer IV-g by the process described above.

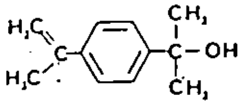
TABLE II MS data of the thermolysis products of linear polycarbonates

Polymer	thermolysis fragments	characteristic peaks (m/e)
II-a		M+ = 130(VS); 129(W); 128(W); 127(W); 115(W); 77(VW)
		M+ = 166(W); 151(VS); 133(W); 130(W); 121(W); 105(VS); 79(M); 77(W); 45(M); 43(VS)
		M+ = 148(W); 133(VS); 130(W); 105(VS); 79(W); 77(W); 43(M)
II-c		M+ = 138(M); 121(VW); 107(VS); 91(M); 79(VS); 77(M)
	$HOCH_2C\equiv CCH_2OH$	M+ = 86(VW); 68(W); 57(VS); 55(M); 39(S)
	 $CH_2=C(CH_3)-CH_2-CH_2-C(CH_3)_2-OH$	M+ = (absent); 113(VW); 110(W); 95(M); 70(M); 59(VS); 55(M); 43(S)
	 $CH_2=C(CH_3)-CH_2-CH_2-C(CH_3)=CH_2$	M+ = 110(W); 95(S); 81(M); 77(W); 68(S); 67(M); 55(VS)
	 $CH_2=C(CH_3)-CH_2-CH=C(CH_3)-CH_3$	M+ = 110(M); 95(VS); 81(W); 77(W); 68(W); 67(M); 55(M)
		M+ = 110(S); 95(VS); 81(W); 77(W); 68(W); 67(M); 55(M)

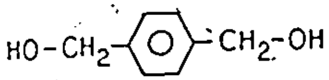
II-d



M+ = 158(VS); 143(M); 128(W); 115(W); 91(VW); 77(VW); 41(W)

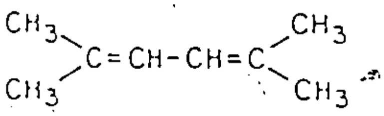


M+ = 176(W); 161(S); 158(W); 143(W); 91(VW); 77(VW); 43(VS)

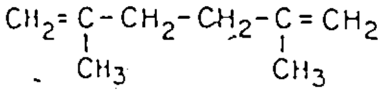


as in II-c

IV-a

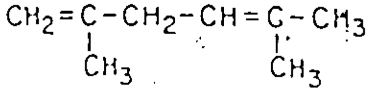


as in II-c



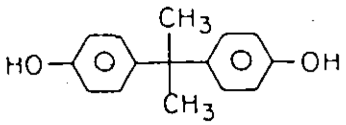
$CH_2=C(CH_3)-CH_2-CH_2-C(CH_3)=CH_2$

as in II-c



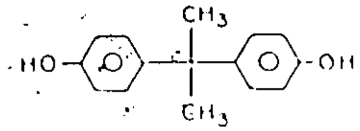
$CH_2=C(CH_3)-CH_2-CH=C(CH_3)-CH_3$

as in II-c



M+ = 228(M); 213(VS); 198(W); 119(M); 91(W)

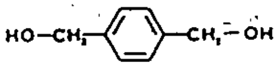
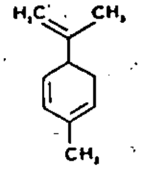
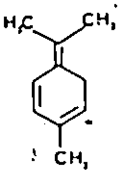
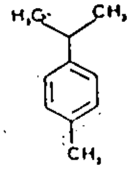
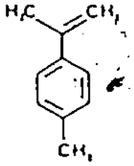
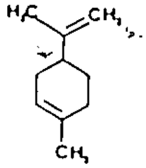
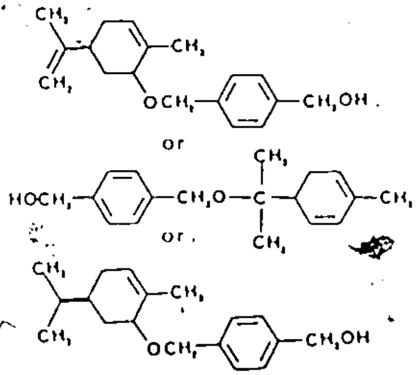
IV-b

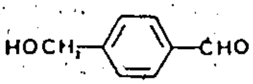
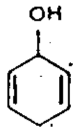
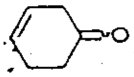
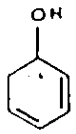
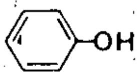
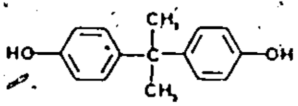
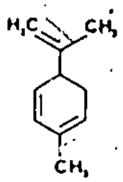
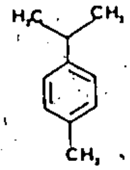
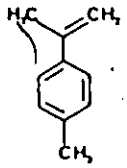
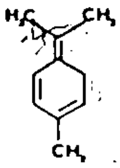


as in IV-a

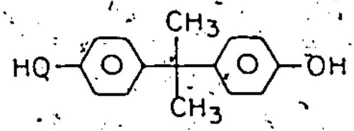
IV-c no fragments observed

?

IV-d		as in II-c
		M+ = 134(S); 119(VS); 105(M); 93(W); 92(W); 91(VS); 79(W); 77(W)
		M+ = 134(VS); 119(VS); 105(M); 93(W); 92(W); 91(VS); 79(W); 77(W); 65(W)
		M+ = 134(M); 119(VS); 117(W); 91(W); 77(W)
		M+ = 132(S); 117(S); 115(M); 92(W); 91(M); 77(VW)
		M+ = 136(W); 121(W); 107(W); 93(M); 68(VS); 55(W); 39(M)
		M+ = 272(VW); 151(W); 121(VS); 119(W); 104(S); 93(M); 91(M); 79(W); 77(M); 55(M)

IV-c		as in II-c
		* M+ = 136(S); 135(M); 107(VS); 79(VS); 77(S)
		M+ = 96(VW); 70(VS); 69(W); 55(VW); 39(W)
		M+ = 96(M); 68(VS); 43(W); 39(W)
		M+ = 96(S); 68(W); 67(W); 54(VS); 43(S); 39(M)
		M+ = 96(VW); 95(W); 68(M); 67(M); 55(VS); 39(M)
		* M+ = 94(VS); 66(M); 65(M); 51(W); 39(M)
		M+ = 78(VS); 77(W); 52(W); 51(W); 50(W); 39(W)
IV-f		as in IV-a
		as in IV-d
		as in IV-d
		as in IV-d
		as in IV-d

IV-g



as in IV-a

M+ = 78(VS); 77(W); 52(W); 51(W); 50(W); 39(W)

* observed in the presence of oxygen

Statement of original research

- Synthesis of novel depolymerizable polycarbonates containing allylic diol fragments in their main chain sensitive to acidolysis and thermolysis.

- A novel method of aromatization based on thermolysis or acidolysis of biscarbonates of 1,4-cyclohexenediol.

- Use of bis-p-nitrophenylcarbonates in the preparation of copolycarbonates using using phase-transfer catalyzed polycondensation.

- Use of thermolysis combined to GC-MS for the study of depolymerizable polycarbonates.

- Implementation of a novel type of chemical amplification in a new, potentially useful, type of resist material.

Statement of future possible extensions of the work

- Study of the products formed during the acidolysis of the polycarbonates and comparison with the thermolysis products.

- Synthesis of other derivatives having good leaving groups which could be used in phase-transfer polycondensations such as: polyhalophenylcarbonates and N-hydroxysuccinimide carbonates.

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