This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Characterization of Bis(Isopropenylphenoxy)Alkanes and Bis(Vinylphenoxy)Alkanes: Two Classes of Highly Reactive, Photopolymerizable Monomers

J. V. Crivello[a]; A. Ramdas[a]
[a] Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York

To cite this Article Crivello, J. V. and Ramdas, A.(1992) 'Synthesis and Characterization of Bis(Isopropenylphenoxy)Alkanes and Bis(Vinylphenoxy)Alkanes: Two Classes of Highly Reactive, Photopolymerizable Monomers', Journal of Macromolecular Science, Part A, 29: 9, 753 — 774

To link to this Article: DOI: 10.1080/10601329208054114

URL: http://dx.doi.org/10.1080/10601329208054114

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J.M.S.—PURE APPL. CHEM., A29(9), pp. 753–774 (1992)

SYNTHESIS AND CHARACTERIZATION OF BIS(ISOPROPENYLPHENOXY)ALKANES AND BIS(VINYLPHENOXY)ALKANES: TWO CLASSES OF HIGHLY REACTIVE, PHOTOPOLYMERIZABLE MONOMERS

J. V. CRIVELLO* and A. RAMDAS

Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12180

Key Words: Photopolymerization; Cationic photopolymerization; Bis(isopropenylphenoxy)alkanes and bis(vinylphenoxy)alkanes

ABSTRACT

A novel and facile synthesis of difunctional, aromatic vinyl ether analogs is reported. These materials, which are conveniently prepared by the condensation of 4-acetoxystyrene or 4-isopropenylphenyl acetate with α,ω-dihaloalkanes in the presence of base, can be cationically polymerized using diaryliodonium or triarylsulfonium salts as photoinitiators to produce crosslinked polymers. Relative reactivities of the monomers toward cationic polymerization were studied using differential scanning photocalorimetry. The thermal stabilities of the polymers resulting from the photopolymerization of the difunctional, aromatic vinyl ether analogs were studied using thermogravimetric analysis.

INTRODUCTION

The discovery of diaryliodonium [1] and triarylsulfonium [2, 3] salts as classes of stable, efficient, and commercially attractive photoinitiators for cationic polymerization has led to the widespread use of photoinitiated cationic polymerization in coating, adhesive, and printing applications. Primarily because of their commercial availability and their previously established use in coating applications, most of the development in photoinitiated cationic polymerization has focused on commercially available multifunctional epoxy monomers. While such monomers offer an excellent combination of chemical, physical, and electrical properties in crosslinked films, their photopolymerization rates are slow as compared to those of free-radically photopolymerized acrylates. For this reason, current efforts in this laboratory have been directed toward the synthesis of epoxy monomers which exhibit higher reactivities in photoinitiated cationic polymerization [4]. Multifunctional alkyl vinyl ethers were also explored and shown to be considerably more reactive than epoxides in cationic photopolymerization [5]. However, their mechanical properties are rather poor. It was these limitations in epoxy and vinyl-ether-based coatings, together with a desire to expand the range of application of photoinitiated cationic polymerization in UV curing, that has led us to explore the development of alternative monomer systems.

EXPERIMENTAL

Materials

Bisphenol-A (4,4′-isopropylidenediphenol) and α,ω-dibromoalkanes were purchased from the Aldrich Chemical Company. 4-Acetoxystyrene was a gift of the Hoechst Celanese Company, while 2-chloroethyl vinyl ether was received as a gift from the Maruzen Oil Company. The above chemicals were used as received. The solvent, dimethylsulfoxide (DMSO), was purified by fractional distillation. The photoinitiators, (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate [6] and diphenyl(4-thiophenoxyphenyl)sulfonium hexafluoroantimonate [7], were prepared as previously described.

^{1}H- and ^{13}C-NMR data were obtained in $CDCl_3$ with a Varian Model XL 200 spectrometer equipped with a Fourier transform accessory. Thermogravimetric analyses were obtained with the aid of a Perkin-Elmer TGA-7 Thermal Analysis System. Measurements were made at a heating rate of 20°C/min in nitrogen. Infrared studies were performed on a Perkin-Elmer Model 298 Infrared Spectrometer.

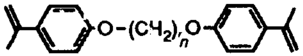
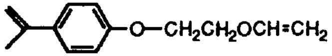
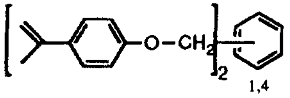
General Synthetic Method for the Synthesis of α,ω-Bis(4-isopropenylphenoxy)alkanes

The following general synthetic method shown for 1,4-bis(4-isopropenylphenoxy)butane was used for the preparation of all of the monomers shown in Table 1.

A. Synthesis of 4-Isopropenylphenyl Acetate

Into a 250-mL round-bottomed flask fitted with a distillation head, air condenser, and receiver were placed 50 g bisphenol-A and 0.5 g potassium hydroxide. The mixture was heated slowly to 200°C under nitrogen, and the products, a mix-

TABLE 1. Bis(4-Isopropenylphenoxy)alkanes

Structure	Notation	*n*	mp, °C	Yield, %	MW	Elemental analysis		
						%C	%H	%O
	III	4	156–157	60	322.5	81.6	8.0	10.4 (calc)
						82.0	8.1	9.9 (theor)
	IV	5	106–107	33	308.4	82.4	8.4	9.2 (calc)
						82.1	8.4	9.5 (theor)
	V	6	141–143	60	350.5	81.2	8.5	10.3 (calc)
						81.1	8.4	10.5 (theor)
	VI	8	135–136	47	378.6	82.5	9.1	8.4 (calc)
						82.2	8.9	8.9 (theor)
	VII	10	131–132	32	406.6	82.7	9.4	7.9 (calc)
						82.7	9.3	8.0 (theor)
	VIII		54–56	62	204.3	76.2	7.8	16.0 (calc)
						76.4	7.9	15.7 (theor)
	IX		191–194	89	370.5	84.4	7.0	8.6 (calc)
						84.3	7.1	8.6 (theor)

ture of phenol and 4-isopropenylphenol (46 g), were collected by vacuum distillation [8, 9]. To this mixture was added 51 g acetic anhydride and 0.25 mL pyridine. The mixture was stirred at 100°C for 3 h. The reaction products were poured into 100 mL distilled water and extracted with 100 mL ether. The organic layer was washed three times with 50 mL portions of a 10% solution of Na_2CO_3 and dried over anhydrous $MgSO_4$. After removal of the $MgSO_4$ by filtration, the ether was removed on a rotary evaporator. The mixture of acetates was fractionally distilled to give the desired 4-isopropenylphenyl acetate with a boiling point of 98°C/5 mmHg.

B. Condensation of 4-Isopropenylphenyl Acetate With α,ω-Dibromoalkanes

To a 250-mL, three-necked round-bottomed flask equipped with a magnetic stirrer, condenser, thermometer, nitrogen inlet, and addition funnel, were added 20 mL DMSO, 4.41 g (0.025 mol) 4-isopropenylphenyl acetate, and 0.96 (0.04 mol) powdered NaOH. An additional 15 mL DMSO was added and the temperature of the oil bath raised to 75°C. The reaction mixture was allowed to stir for an hour and 2.7 g (0.0125 mol) 1,4-dibromobutane dissolved in 15 mL DMSO was added dropwise over 2.5 h. After 5 h the heat was turned off and the reaction mixture was allowed to stir overnight at room temperature.

The reaction mixture was poured into 100 mL water and extracted with a 3:1 mixture of ether and toluene. The organic layer was washed 5 times with water. After stirring with anhydrous $MgSO_4$, the organic layer was filtered and the solvent removed on a rotary evaporator to give the desired monomer as a crystalline solid (yield of crude product = 3.33 g or 83% theory). The product was dissolved in chloroform and precipitated by the addition of a few drops of hexane. After filtering and vacuum drying, a yield of 2.40 g (60%) of pure product having a melting point of 156–156.5°C was obtained.

^1H NMR ($CDCl_3$) δ (ppm) = 6.8–7.5 (dd, 4H, aromatic protons A_2B_2 pattern); 5.2–5.3 (dd, 1H, *trans* $C\underline{H}_2{=}C$); 4.9–5.0 (d, 1H, *cis* $C\underline{H}_2{=}C$); 4.0–4.1 (t, 2H, $-O-C\underline{H}_2-$); 1.9–2.0 (m, 2H, $-O-CH_2-C\underline{H}_2-$); 2.1–2.2 (s, 3H, $C\underline{H}_3-C{=}$).

Synthesis of 1,6-Bis(4-Isopropenylphenoxy)hexane Using Phase-Transfer Catalysis

To a 250-mL, three-necked round-bottomed flask, equipped with a magnetic stirrer, condenser, thermometer, nitrogen inlet, and addition funnel, were added 60 mL toluene, 5.29 g (0.03 mol) 4-isopropenylphenyl acetate, 3.66 g (0.015 mol) 1,6-dibromohexane, 0.4 g tetrabutylammonium bromide (phase-transfer catalyst), and 35 mL of a 20% aqueous solution of NaOH. The mixture was refluxed overnight under nitrogen. After addition of 60 mL toluene, the organic and aqueous layers were separated. The organic layer was dried over anhydrous $MgSO_4$. After removal of the $MgSO_4$ by filtration, the organic solvent was removed on a rotary evaporator. The product was recrystallized from hot ethanol to give 2.36 g (44.9% yield) 1,6-bis(4-isopropenylphenoxy)hexane (mp 139–140°C).

^1H NMR ($CDCl_3$) δ (ppm) = 6.7–7.4 (dd, 4H, aromatic protons A_2B_2 pattern); 5.1–5.2 (dd, 1H, *trans* $C\underline{H}_2{=}C$); 4.8–4.9 (d, 1H, *cis* $C\underline{H}_2{=}C$); 3.8–3.9 (t, 2H, $-O-C\underline{H}_2-$); 2.0 (s, 3H, $C\underline{H}_3-C{=}$); 1.3–1.8 (m, 4H, $-O-CH_2-C\underline{H}_2-C\underline{H}_2$).

Synthesis of 2-(4-Isopropenylphenoxy)ethyl Vinyl Ether

To a 250-mL, three-necked round-bottomed flask, equipped with a magnetic stirrer, condenser, thermometer, nitrogen inlet, and addition funnel, were added 30 mL DMSO, 7.05 g (0.04 mol) 4-isopropenylphenyl acetate, and 4.8 g (0.12 mol) powdered NaOH. An additional 15 mL DMSO was added and the temperature of the oil bath was raised to and maintained between 75 and 80°C. The reaction mixture was stirred for 1 h and then 4.26 g (0.04 mol) 2-chloroethyl vinyl ether dissolved in 15 mL DMSO was added dropwise over 2.5 h. After 5 h the heat was turned off and the reaction mixture was allowed to stir overnight at room temperature. The reaction mixture was poured into 100 mL water and extracted with a 3:1 mixture of ether and toluene. The organic layer was washed 5 times with water. After stirring with anhydrous $MgSO_4$, the organic layer was filtered and the solvent removed on a rotary evaporator (yield of crude product = 5.67 g or 69% theory). The crude product was recrystallized from ethanol, filtered, and dried to yield 5.1 g (62%) of pure 2-(4-isopropenylphenoxy)ethyl vinyl ether (mp 54-56°C).

^{1}H NMR ($CDCl_3$) δ (ppm) = 6.85-7.5 (dd, 4H, aromatic protons A_2B_2 pattern); 6.5-6.6 (dd, 1H, $-O-C\underline{H}=CH_2$); 5.3 (dd, 1H, *trans* $Ar-C=C\underline{H_2}$); 5.0 (d, 1H, *cis,cis* $Ar-C\underline{H}=CH$); 4.05 (tt, 4H, $-O-C\underline{H_2}-$); 4.25 (m, 2H, $-O-CH=C\underline{H_2}$); 1.9-2.0 (m, 2H, $-O-CH_2-C\underline{H_2}-$); 2.1-2.2 (s, 3H, $C\underline{H_3}-CH=$).

General Synthetic Method for the Synthesis of α,ω-Bis(4-vinylphenoxy)alkanes

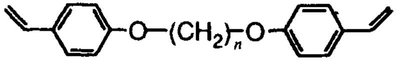
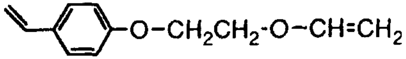
The following general synthetic method, exemplified for 1,4-bis(4-vinylphenoxy)butane, was used for the preparation of all of the monomers shown in Table 2.

Synthesis of 1,4-Bis(4-vinylphenoxy)butane

To a 250-mL, three-necked round-bottomed flask, equipped with a magnetic stirrer, condenser, thermometer, nitrogen inlet, and addition funnel, were added 30 mL DMSO, 5.19 g (0.032 mol) 4-acetoxystyrene, and 3.84 g (0.096 mol) powdered KOH. The reaction mixture was heated in an oil bath to 75°C and held for 1 h. Then 3.45 g (0.016 mol) 1,4-dibromobutane dissolved in 15 mL DMSO was added dropwise over the course of 2.5 h. After 5 h reaction time the heater was turned off and the reaction mixture was allowed to stir overnight. The reaction mixture was poured into 100 mL water and extracted with a 3:1 volume mixture of ether and toluene. The organic layer was washed 5 times with distilled water. After stirring with anhydrous $MgSO_4$, the organic layer was filtered and the solvent removed on a rotary evaporator, giving a yield of crude product of 3.45 g (72% theory). The product was dissolved in chloroform and triturated by the addition of hexane to yield 2.74 g (58%) of pure product having a melting point of 127-128.5°C.

^{1}H NMR ($CDCl_3$) δ (ppm) = 6.8-7.4 (dd, 4H, aromatic protons A_2B_2 pattern); 6.5-6.6 (dd, 1H, $CH_2=C\underline{H}$); 5.55-5.65 (d, 1H, *trans* $C\underline{H_2}=CH$); 5.1-5.2 (d, 1H, *cis* $C\underline{H_2}=CH$); 4.0-4.1 (t, 2H, $-O-C\underline{H_2}-$); 1.9-2.0 (m, 2H, $-O-CH_2-C\underline{H_2}-$).

TABLE 2. Bis(4-Vinylphenoxy)alkanes

Structure	Notation	*n*	mp, °C	Yield, %	MW	Elemental analysis		
						%C	%H	%O
	X	4	127–128	58	294.4	81.3	7.4	11.3 (calc)
						81.6	7.5	10.9 (theor)
	XI	5	80–82	30	308.4	81.2	7.7	11.1 (calc)
						81.8	7.8	10.4 (theor)
	XII	8	110–112	62	350.5	81.9	8.7	9.4 (calc)
						82.2	8.6	9.2 (theor)
	XIII	10	111–112	63	378.6	82.0	9.1	8.9 (calc)
						82.5	9.1	8.4 (theor)
	XIV		63-65	41	189.2	75.8	7.4	16.8 (calc)
						75.4	7.2	17.4 (theor)

Synthesis of 2-(4-Vinylphenoxy)ethyl Vinyl Ether

To a 250-mL, three-necked round-bottomed flask, equipped with a magnetic stirrer, condenser, thermometer, nitrogen inlet, and addition funnel, were added 30 mL DMSO, 4.05 g (0.025 mol) 4-acetoxystyrene, and 3.0 g (0.075 mol) powdered NaOH. An additional 15 mL DMSO was added and the temperature of the oil bath raised to and maintained between 75 and 80°C. The reaction mixture was stirred for 1 h and 2.66 g (0.025 mol) 2-chloroethyl vinyl ether dissolved in 15 mL DMSO was added dropwise over 2.5 h. After 5 h the heat was turned off and the reaction mixture was stirred overnight. The reaction mixture was poured into 100 mL water and extracted with a 3:1 mixture of ether and toluene. The organic layer was washed 5 times with water. After stirring with anhydrous $MgSO_4$, the organic layer was filtered and the solvent removed on a rotary evaporator. The product was dissolved in hot ethanol and cooled to yield 1.95 g (41%) of pure product (mp 63-65°C).

^1H NMR ($CDCl_3$) δ (ppm) = 6.8–7.4 (dd, 4H, aromatic protons A_2B_2 pattern); 6.5–6.7 (m, 2H); 5.55–5.7 (d, 1H, *trans* $C\underline{H}_2{=}CH$); 5.1–5.2 (d, 1H *cis* $C\underline{G}_2{=}CH$); 4.3–4.0 (m, 6H).

Synthesis of 4-Methoxy-α-methylstyrene

To a 250-mL, three-necked round-bottomed flask, equipped with a magnetic stirrer, condenser, thermometer, nitrogen inlet, and addition funnel, were added 30 mL DMSO, 7.05 g (0.04 mol) 4-isopropenylphenyl acetate, and 4.8 g (0.12 mol) powdered NaOH. An additional 15 mL DMSO was added, and the temperature of the oil bath was raised to and maintained between 75 and 80°C. The reaction mixture was stirred for 1 h and then 5.68 g (0.04 mol) methyl iodide dissolved in 15 mL DMSO was added dropwise over 2.5 h. After 5 h the heat was turned off and the reaction mixture was poured into 100 mL water and extracted with a 3:1 mixture of ether and toluene. The organic layer was washed 5 times with water. After stirring with anhydrous $MgSO_4$, the organic layer was filtered and the solvent removed on a rotary evaporator. The crude product was recrystallized from ethanol, filtered, and dried to yield 2.1 g (36%) pure 4-methoxy-α-methylstyrene (mp 27–28°C).

Model Compound Studies

A 0.5-mol% solution of (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate in 4-methoxy-α-methylstyrene was diluted to a concentration of approximately 10% in a quartz NMR tube and the ^1H NMR of the solution taken on a Varian Model XL 200 spectrometer. The solution was then irradiated using a GE H3T7 medium pressure mercury arc lamp for specific time periods until the reaction was complete as indicated by NMR.

Photopolymerizations

Differential Scanning Photocalorimetry Studies

The photoinitiated cationic polymerizations of the monomers listed in Tables 1 and 2 were monitored at their respective melting points using a Perkin-Elmer DSC-7 Differential Scanning Calorimeter equipped with a Photocalorimeter Accessory fitted with a Hanovia 200W Mercury-Xenon lamp as the UV-light source. The polymerizations were carried out on 2-3 mg samples of the monomer which contained 0.5 mol% photoinitiator; either (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate or (4-thiophenoxyphenyl)diphenylsulfonium hexafluoroantimonate.

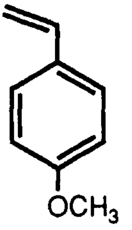
Infrared Studies

Infrared spectra were recorded on a Perkin-Elmer 298 Infrared Spectrometer. Solutions composed of 0.5 mol% (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate and the indicated monomer were diluted to approximately 10% in tetrachloroethane and placed between salt plates. Spectra were recorded before and after irradiation for specific time periods using a General Electric H3T7 medium pressure mercury arc lamp ballasted at 200 W. Characteristic vinyl peaks at 880-900 cm^{-1} were monitored.

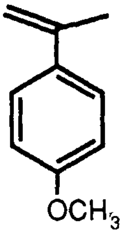
RESULTS AND DISCUSSION

Synthesis of the Aromatic Analogs of Vinyl Ethers

The goal of these investigations was to prepare novel monomers that would display the high reactivity of vinyl ethers while having better mechanical properties through the introduction of aryl groups. Alkoxy-substituted styrenes and α-methylstyrenes such as 4-methoxystyrene (I) and 4-methoxy-α-methylstyrene (II) can be regarded, respectively, as phenylogous vinyl and isopropenyl ethers in which the unsaturated group and the ether portions of the molecule can communicate electronically by inductive and resonance interaction through the phenyl group.



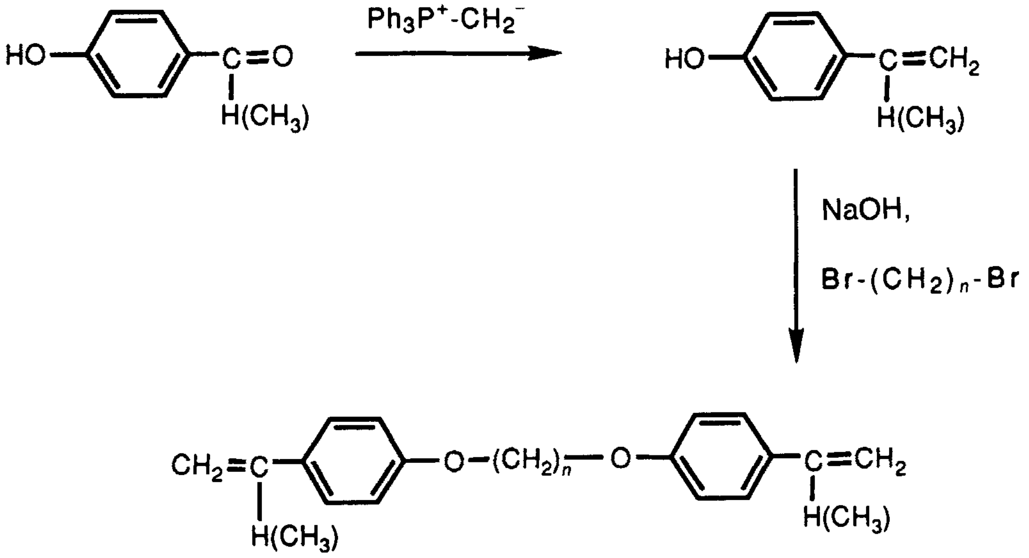
I



II

Consequently, the chemical reactivity of these compounds is similar to vinyl and isopropenyl ethers, and these monomers have been observed to undergo cationic polymerization at very high rates [2, 10-15]. Based on these considerations, it appeared desirable to attempt the preparation of monomers incorporating two or more alkoxy-substituted styrene or α-methylstyrene moieties. A review of the literature showed that this approach had been already explored by two research groups [14, 15] who employed the same basic synthetic approach shown in Scheme 1 for their preparation.

Although the synthetic route shown in Scheme 1 is reasonably straightforward, the overall yields of the products are rather low and, additionally, the Wittig reaction is impractical for other than the preparation of small-scale reactions. Furthermore, the intermediates in this synthesis, 4-hydroxystyrene and 4-isopropenyl-



(1)

(2)

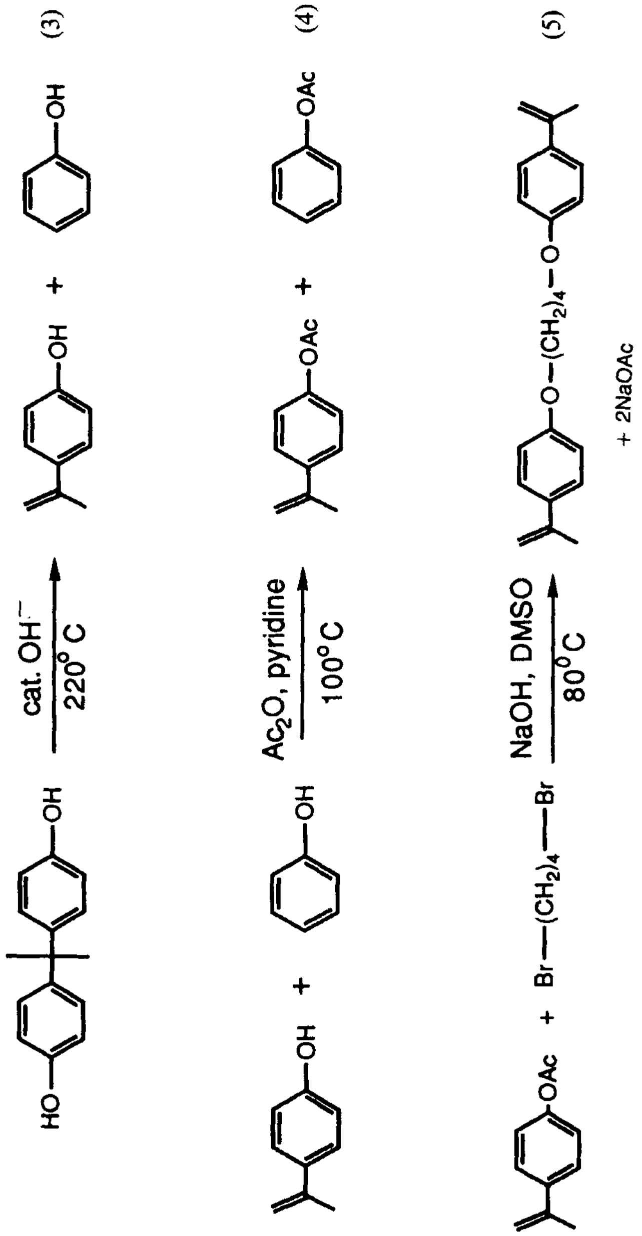
SCHEME 1.

phenol, are very unstable and tend to oxidize and oligomerize on standing. Accordingly, we have undertaken the development of novel, general synthetic routes to these monomers which circumvent these problems. The synthesis of a series of α,ω-bis(4-isopropenylphenoxy)alkanes using a novel preparative method developed in this laboratory is depicted in Scheme 2.

This synthesis involves the simple, direct preparation of 4-isopropenylphenol (4-hydroxy-α-methylstyrene) by the base-catalyzed decomposition of the readily available bisphenol-A at 200°C [8, 9]. Simple vacuum distillation of the reaction mixture during this reaction yields a mixture of phenol and 4-isopropenylphenol. Attempts to further separate the two products by distillation yields only small amounts of the desired 4-isopropenylphenol due to a variety of oligomerization and condensation side reactions. Instead, it was found convenient to carry out the acetylation of the entire mixture and then to carry out a fractional distillation to separate the resulting acetate esters. 4-Isopropenylphenyl acetate (4-acetoxy-α-methylstyrene), in contrast to its corresponding phenolic precursor, is stable and can be conveniently stored indefinitely at room temperature.

The desired difunctional vinyl ether analogs can be prepared in good yield as shown in Eq. (5) by the direct condensation of 4-isopropenylphenyl acetate with α,ω-dibromoalkanes in DMSO in the presence of sodium hydroxide. Gathered in Table 1 are the structures of the α,ω-bis(4-isopropenylphenoxy)alkanes prepared during the course of this work together with their yields, melting points, and elemental analyses.

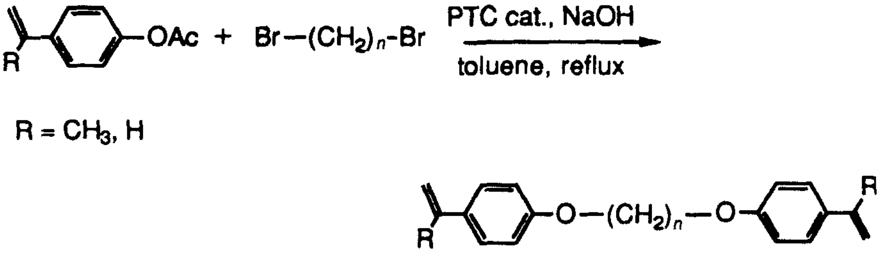
In a similar fashion, 4-acetoxystyrene, which is now readily available from commercial sources, can be smoothly reacted with α,ω-dibromoalkanes in DMSO in the presence of sodium hydroxide to yield a series of α,ω-bis(4-vinylphenoxy)alkanes. Table 2 gives the structures and data for a series of these monomers prepared


HO
OH
cat. OH⁻
220° C
OH
+
OH
(3)
OH
+
OH
Ac2O, pyridine
100°C
OAc
+
OAc
(4)
OAc
+
Br—(CH2)4—Br
NaOH, DMSO
80°C
O—(CH2)4—O
+ 2NaOAc
(5)

SCHEME 2.

during the course of this research. Two of the monomers, namely, 1,4-bis(4-vinylphenoxy)butane (**X**) and 1,10-bis(4-vinylphenoxy)decane (**XIII**), have been prepared before [14].

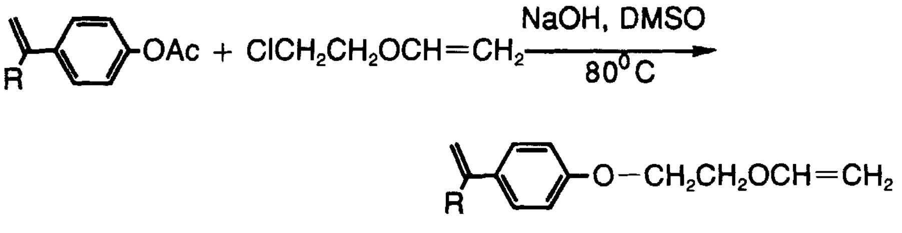
These two classes of monomers were also prepared in this laboratory by an alternate method involving phase-transfer catalysis which is shown in Eq. (6). 4-Acetoxystyrene and 4-isopropenylphenyl acetate were converted by an *in-situ* hydrolysis to the corresponding phenoxide by treatment with base and then coupled with the halo compound in the presence of NaOH and the phase-transfer catalyst, tetra-*n*-butylammonium bromide, to give the desired aromatic vinyl ether analogs.



(6)

Yields of difunctional monomers by both synthetic methods were uniformly good, but the reactions could be further optimized. In the case of monomer **IV**, addition of excess 1,5-dibromopentane (>1.5 mol) to 4-isopropenylphenyl acetate in the presence of NaOH and DMSO more than doubled the yield of 1,5-bis(4-vinylphenoxy)pentane. Since aliphatic halides are known to undergo elimination reactions in the presence of base, presumably the addition of excess halide compensated for the loss of the starting halo compound due to these elimination reactions.

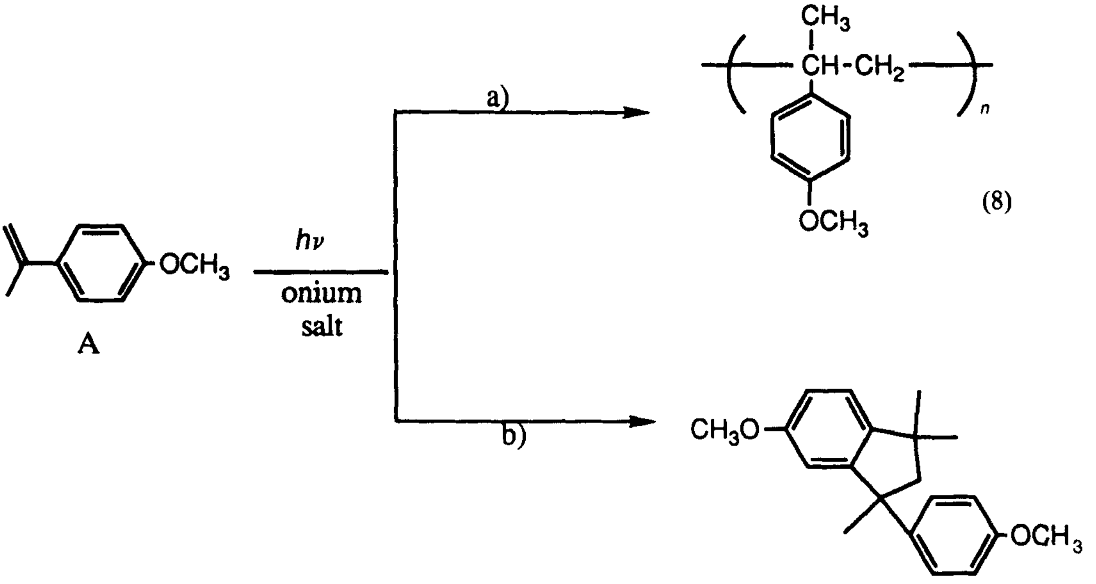
Two additional very highly reactive monomers, **VIII** and **XIV**, appearing respectively in Tables 1 and 2 were prepared as shown in Eq. (7) by the base-catalyzed condensation of the appropriate unsaturated aryl acetate with 2-chlorethyl vinyl ether.



(7)

Model Photoinitiated Cationic Polymerization Studies

Initial experiments showed that the monomers in both Tables 1 and 2 were readily photopolymerized in the presence of onium salt photoinitiators. To elucidate the mechanism of the photoinduced cationic polymerization of these monomers, a brief investigation was conducted with the aid of a model compound. For this study, we chose 4-methoxy-α-methylstyrene (4-isopropenylanisole) as a simple model for the study. Two pathways as depicted in Scheme 3 for the reaction of this monomer appeared possible: a) typical polymerization across the double bond, as is usually observed in the cationic polymerization of α-methylstyrene; or b) an intramolecular Friedel-Crafts cyclization to give a dimer containing an indane group.



SCHEME 3. (9)

The model compound, 4-methoxy-α-methylstyrene (A), was prepared by the reaction of 4-acetoxy-α-methylstyrene with methyliodide in DMSO/NaOH. When a solution of 4-methoxy-α-methylstyrene in $CDCl_3$ was irradiated with UV light in the presence of 0.5 mol% photoinitiator (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate, a polymer was not obtained, indicating that Path a) was not being followed. Instead, only low molecular weight species were formed. The progression of ^{1}H-NMR (in $CDCl_3$) spectra shown in Fig. 1 of the reaction mixture showed the rapid disappearance of the protons associated with the isopropenyl double bond (δ = 4.98–5.05 and 5.27–5.35 ppm) with the concurrent formation of resonances at δ = 4.68–4.74 and 5.05–5.10 ppm due to the presence of a new double bond. After irradiation for a longer time, these double bond resonances disappeared altogether. This was accompanied by an increase in the number of peaks in the aliphatic region (δ = 0.9–2.2 ppm).

These observations are consistent with the mechanism shown in Scheme 4. Initial protonation of the monomer (A) by the photogenerated acid yields the tertiary carbocation (B). Cation (B) then attacks another molecule of (A) to give a dimer cation (C). At this stage, (C) may directly cyclize to give (E) or undergo elimination to give the dimer olefin (D). Although (D) is stable and observed in our NMR studies, in the presence of the strong acid it is in equilibrium with (C) and is eventually irreversibly converted to indane (E). Considerable precedent for this mechanism exists in the literature. 4-Methoxy-α-methylstyrene has been shown to undergo dimerization to the unsaturated dimer (D) in the presence of strong acids [16]. In these latter studies, the structure of the dimer was established by degradation and infrared analysis. In addition, 4-isopropenylbenzoic acid and 4-isopropenylaniline have also been shown to form intermediate unsaturated dimers analogous to (D) in the presence of strong acids which further react to give substi-

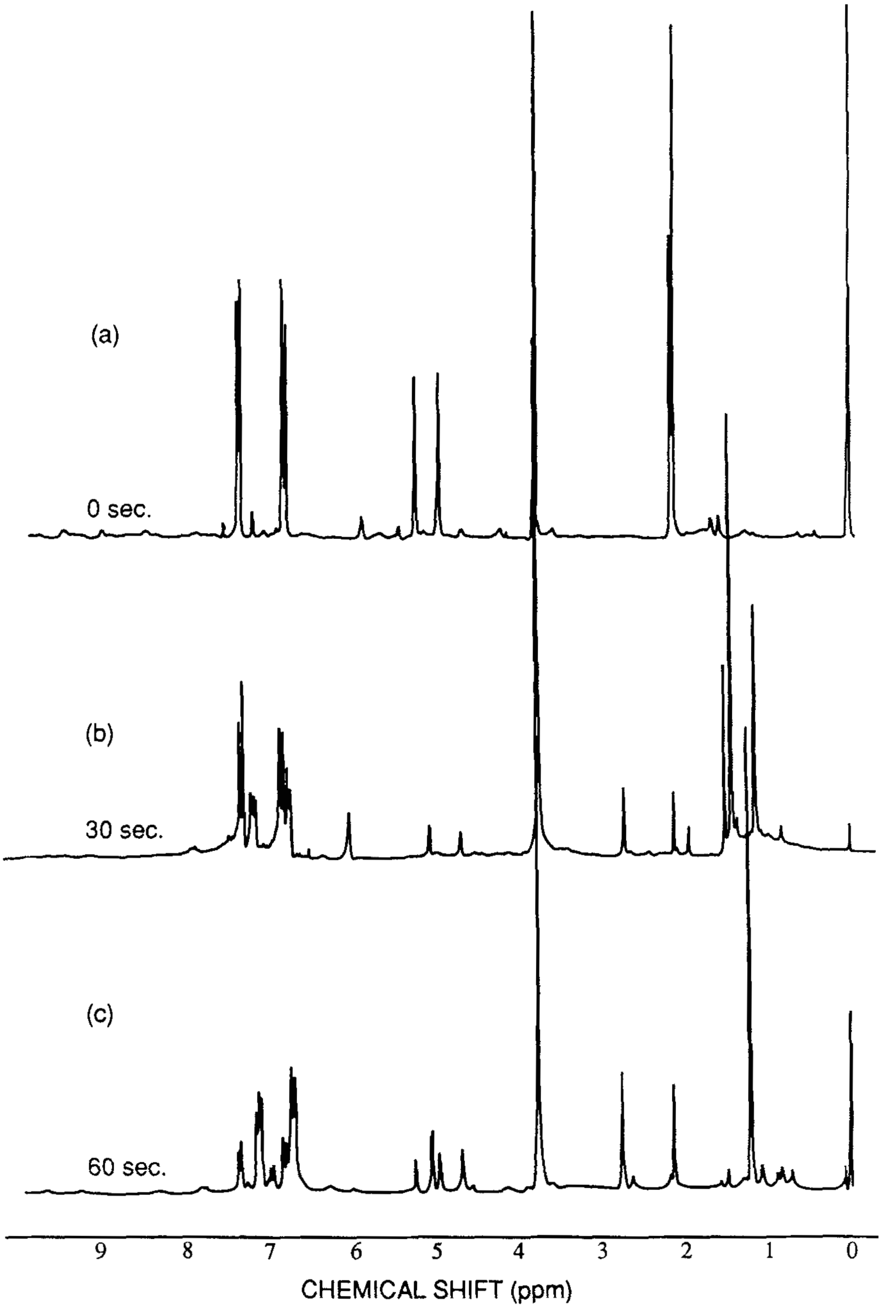
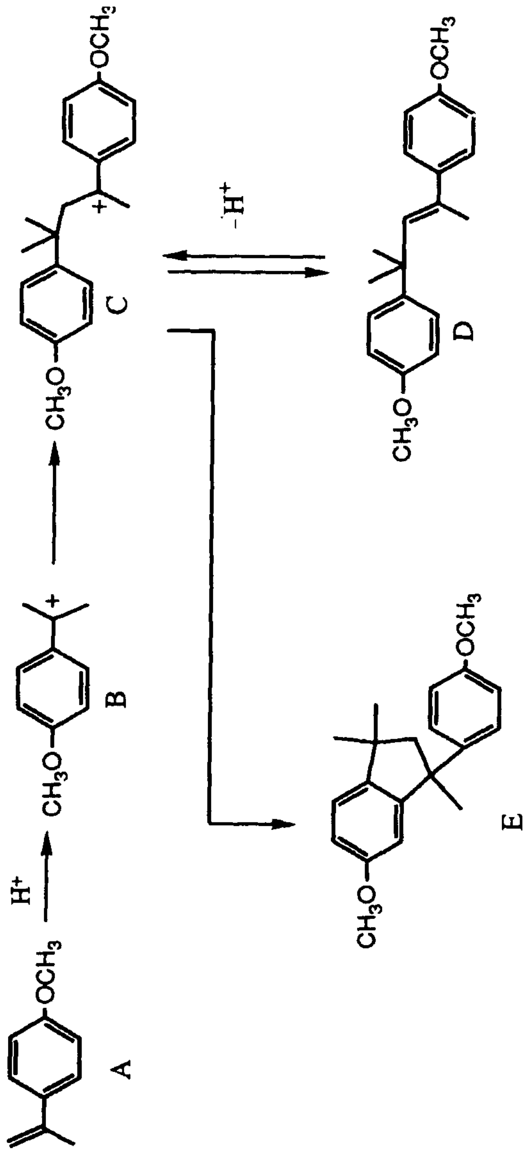


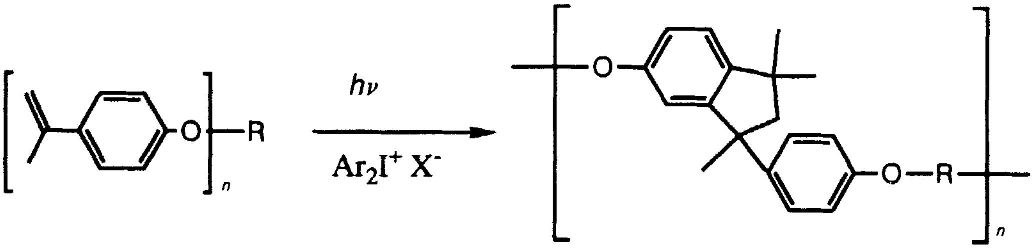
FIG. 1. ^1H NMR ($CDCl_3$) of the cationic photopolymerization of 4-methoxy-α-methylstyrene after (a) 0 seconds, (b) 30 seconds, and (c) 60 seconds irradiation in the presence of 0.5 mol% (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate.



(10)

SCHEME 4.

tuted indanes [17]. Based on these studies, the polymerization of the bis(isopropenylphenoxy)alkane monomers in Table 1 can be expected to yield polymers containing mainly indane groups in the backbone on photoinduced cationic polymerization in the presence of onium salts as depicted in Eq. (11).

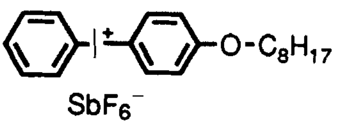


(11)

The fact that the polymer films obtained by the cationic photopolymerization of bis(4-isopropenylphenoxy)alkane monomers are insoluble in all solvents indicates that some crosslinking by conventional cationic olefin polymerization (Path a) must also be occurring in competition with the above process.

Photopolymerization

The aromatic vinyl ether analogs shown in Tables 1 and 2 are poor solvents for most simple aryl-substituted diaryliodonium and triarylsulfonium salt photoinitiators. Thus, it was not possible to evaluate the reactivity of these monomers using these conventional photoinitiators. Previous work by Crivello and coworkers [6] showed that diaryliodonium salts possessing long alkoxy substituents attached to one or both of the rings were very soluble in nonpolar organic solvents and monomers. A comparative study of the rates of polymerization of the aromatic vinyl ether analogs with different alkoxy substituted diaryliodonium salts indicated that (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate is an extremely good photoinitiator for such monomers.



Studies of the reactivities of various monomers were then conducted using differential scanning photocalorimetry in which the exothermic heat of the polymerization was monitored as a function of reaction time [18]. For example, the differential scanning photocalorimetric curves of liquid monomers **VIII** and **XIV** are given in Figs. 2 and 3. Both of these monomers are exceptionally reactive in photoinitiated cationic polymerization. It may be seen from these curves that when the shutter is opened at 1 min, polymerization occurs nearly instantaneously with the peak maximum appearing after 0.11 to 0.12 min irradiation. In both cases the peaks are very sharp and return rapidly to the baseline, indicating rapid and efficient polymerization.

The polymerization of several of the difunctional monomers was followed by infrared spectroscopy. Shown in Fig. 4 is a study of the polymerization of

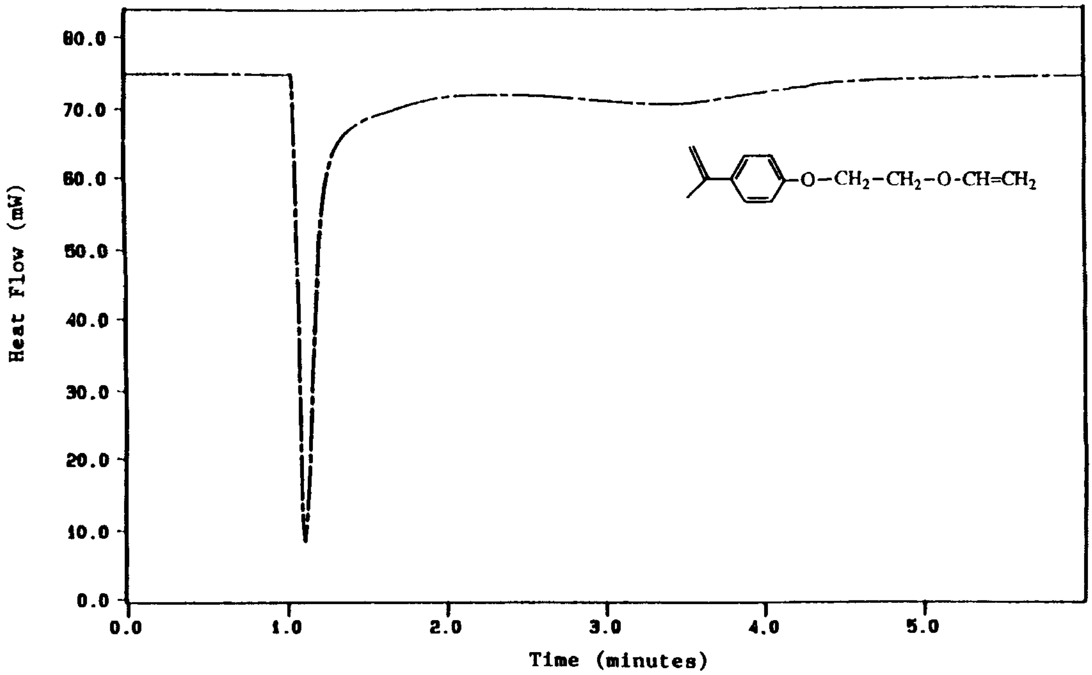


FIG. 2. Photo-DSC spectrum of the exothermic polymerization of 1-(4-isopropenylpenoxy)ethyl vinyl ether (**VIII**) in the presence of 0.5 mol% (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate.

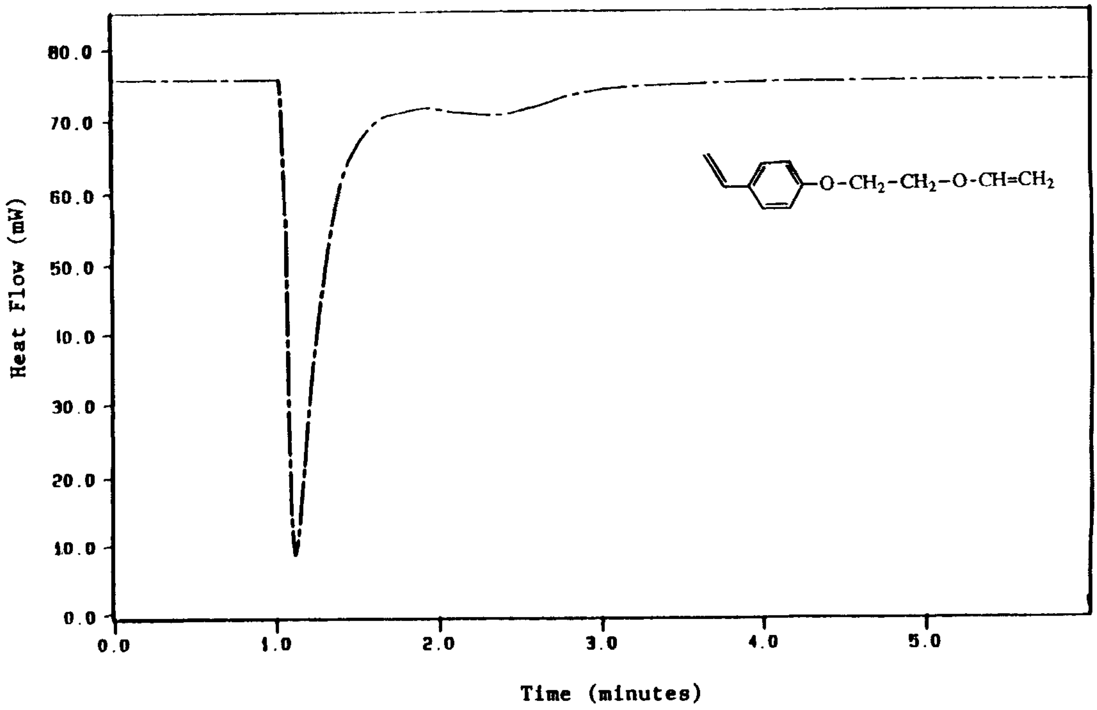


FIG. 3. Photo-DSC spectrum of the exothermic polymerization of 2-(4-vinylphenoxy)ethyl vinyl ether (**XIV**) in the presence of 0.5 mol% (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate.

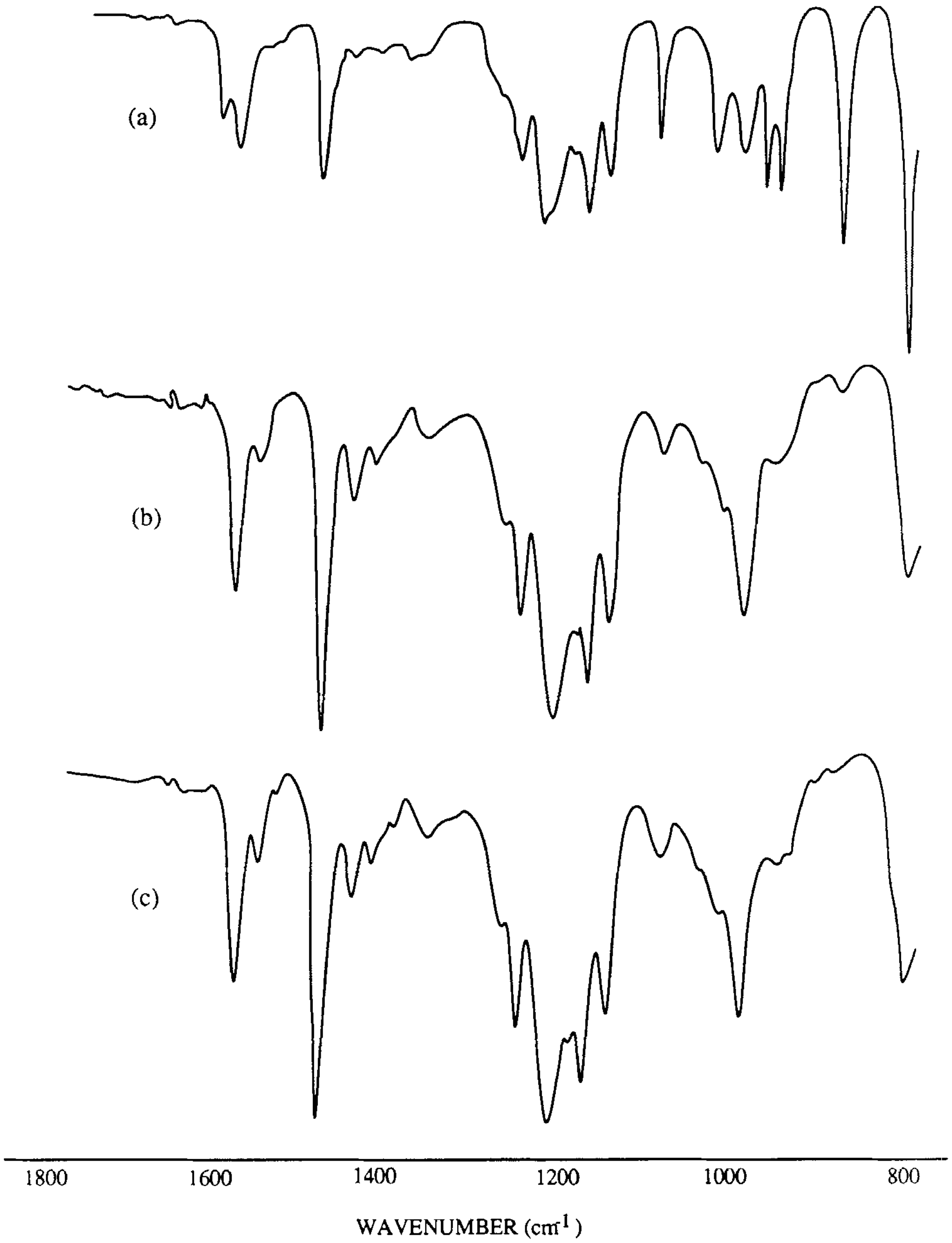


FIG. 4. Infrared spectra of 1,4-bis(4-vinylphenoxy)butane (**XI**) in the presence of 0.5 mol% (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate after (a) 0 seconds, (b) 30 seconds, and (c) 45 seconds UV irradiation.

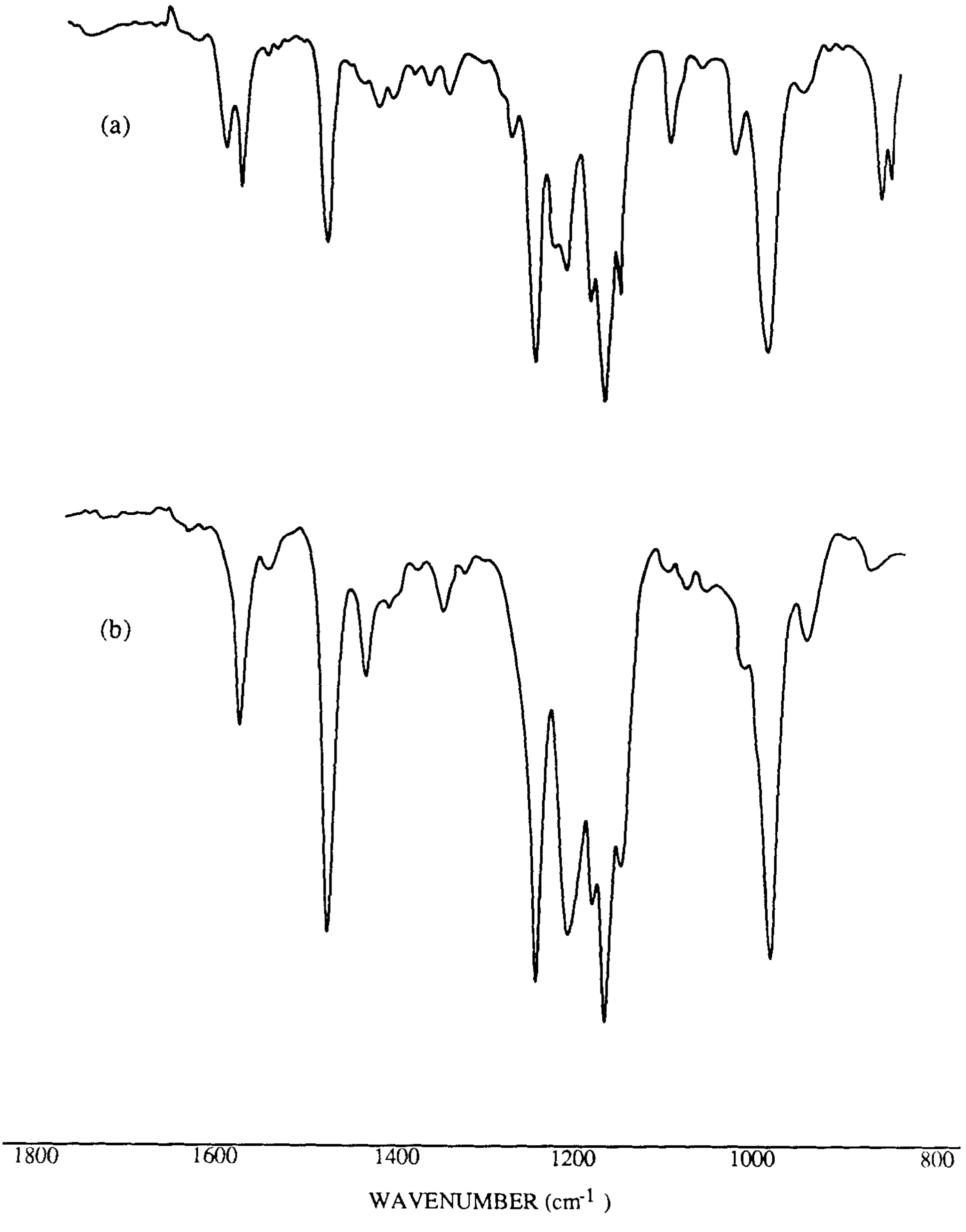


FIG. 5. Infrared spectra of 1,4-bis(4-isopropenylphenoxy)butane (**III**) in the presence of 0.5 mol% (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate after (a) 0 seconds and (b) 60 seconds UV irradiation.

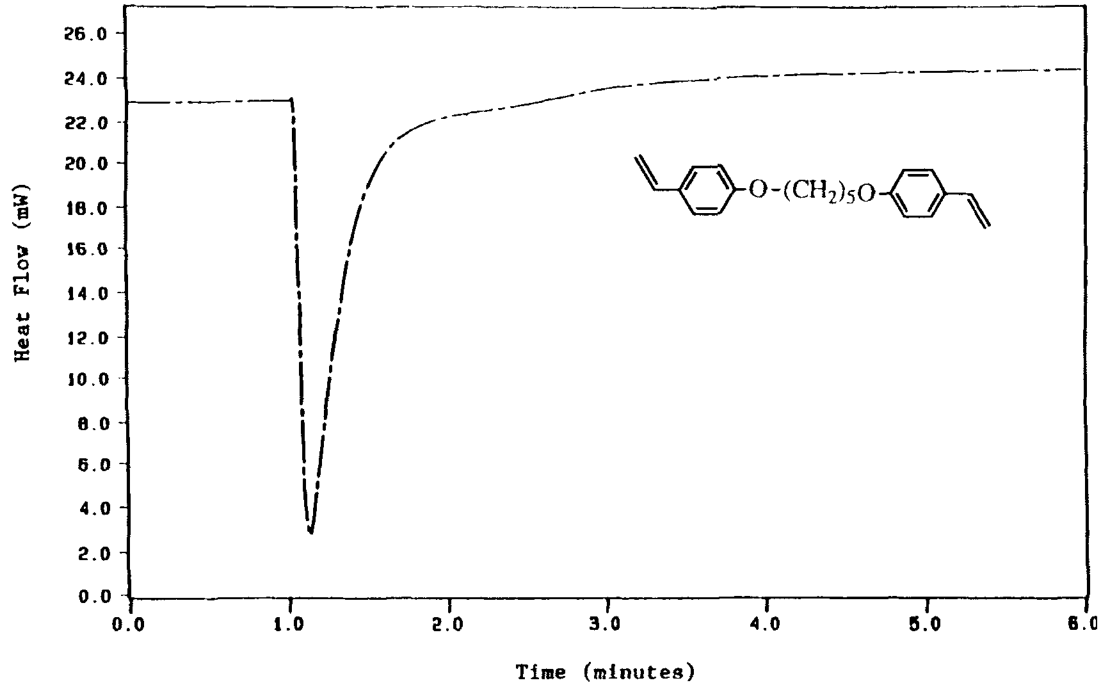


FIG. 6. Photo-DSC spectrum of the exothermic polymerization of 1,5-bis(4-vinylphenoxy)pentane (XI) in the presence of 0.5 mol% diphenyl(4-thiophenoxyphenyl)sulfonium hexafluoroantimonate.

1,4-bis(4-vinylphenoxy)butane (XI) using 0.5 mol% of the above described diaryliodonium salt photoinitiator. The double bonds at 900 cm^{-1} were monitored. As the spectra show, the reaction reaches a 91% conversion after only 30 s of UV irradiation, which increases to 96% after an additional 15 s irradiation and then does not change further on continued irradiation. The high reactivity of the multifunctional monomer toward cationic polymerization results in the swift formation of a highly crosslinked or vitrified polymer in which the remaining double bonds do not have sufficient mobility to react further. A similar series of IR spectra are shown for 1,4-bis(4-isopropenylphenoxy)butane (III) in Fig. 5. In this case the conversion reaches 87% after 60 s irradiation with no further increase on additional irradiation. Thus, the polymers derived from monomers containing the 4-isopropenylphenoxy groups appear to have a higher percentage of unreacted double bonds than those from the corresponding monomers containing 4-vinylphenoxy groups. As suggested previously, the structures of the polymers derived from the two series of monomers are different. The results can be rationalized by suggesting that polymers derived from monomers containing 4-isopropenylphenoxy groups give the more rigid indane backbone structure which inhibits mobility in the polymer chains and keeps the end groups from finding one another.

Since the bis(isopropenylphenoxy)alkanes and bis(vinylphenoxy)alkanes shown in Tables 1 and 2 are solids, the reactivity of these monomers in photopolymerization was studied using differential scanning photocalorimetry only at their melting points. To avoid possible complications due to competing thermally induced

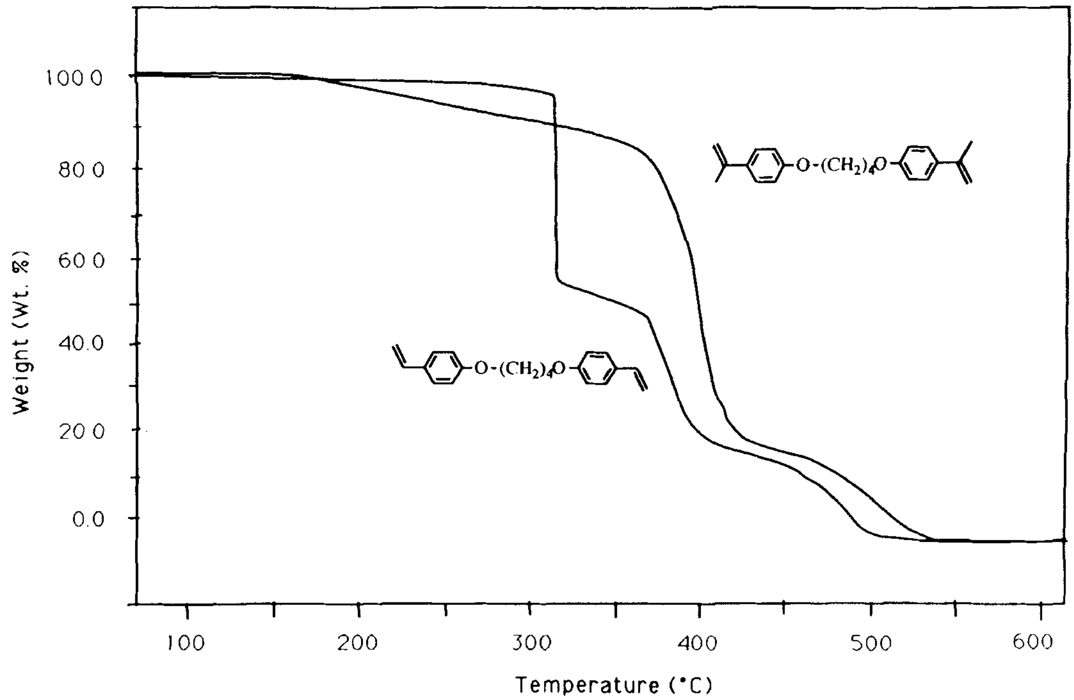
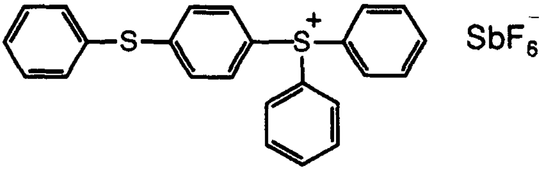


FIG. 7. Thermogravimetric analysis curve for photopolymerized films of monomers (III) and (X) in nitrogen at 20°C per minute.

cationic polymerization, the extremely thermally stable initiator, diphenyl(4-thiophenoxyphenyl)sulfonium hexafluoroantimonate, with the structure shown below was used in these studies.



The response of all of these difunctional vinyl ether analogs to UV irradiation is very high, as predicted. Figure 6 presents a typical differential scanning photocalorimetry curve obtained for the photopolymerization of 1,5-bis(4-vinylphenoxy)-pentane carried out at 115°C in the presence of 0.5 mol% of the aforementioned photoinitiator. As shown, the response of the monomer to UV irradiation is very fast, with the peak maximum occurring within 0.11 min and the entire polymerization completed after approximately 1 min irradiation time.

Figure 7 shows the thermogravimetric analysis curves of photopolymerized monomers **III** and **X**, carried out in nitrogen at 20°C/min. The polymers appear to be stable to approximately 350–400°C under these conditions. The initial loss of mass in the bis-isopropenylphenyloxy monomer, **III**, may be due to loss of residual unreacted monomer. It is anticipated that these monomers will find applications as electronic materials where their thermal stability is compatible with the thermal processing steps usually employed in integrated circuit fabrication.

CONCLUSIONS

A series of reactive, multifunctional monomers that can be readily photopolymerized in the presence of diaryliodonium and triarylsulfonium salt cationic photoinitiators have been prepared. The high sensitivity of these aromatic analogs of vinyl ethers toward photoinduced cationic polymerization has been demonstrated. Model studies indicate that the bis(isopropenylphenoxy)alkanes may be expected to yield polymers containing indane groups.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support of this research by the IBM Corporation.

REFERENCES

[1] J. V. Crivello and J. H. W. Lam, *Macromolecules, 10*, 1307 (1977).
[2] J. V. Crivello and J. H. W. Lam, *J. Polym. Sci., Polym. Chem. Ed., 17*, 977 (1979).
[3] J. V. Crivello and J. H. W. Lam, *Ibid., 17*, 1047 (1979).
[4] J. V. Crivello and J. L. Lee, *Ibid., 28*, 479 (1990).
[5] J. V. Crivello, J. L. Lee, and D. A. Conlon, *J. Radiat. Curing, 1*, 6 (1983).
[6] J. V. Crivello and J. L. Lee, *J. Polym. Sci., Polym. Chem. Ed., 27*, 3951 (1989).
[7] J. V. Crivello and J. H. W. Lam, *Ibid., 18*, 2687 (1980).
[8] J. V. Crivello, M. Deptolla, and H. Ringsdorf, *Liq. Cryst., 3*, 235 (1988).
[9] J. Kahovec, H. Pivcova, and J. Pospisil, *J. Collect. Czech. Chem. Commun., 36*, 1986 (1971).
[10] C. E. Schildknecht, *Vinyl and Related Polymers*, Wiley, New York, 1952, p. 620.
[11] N. Kanoh, A. Gotoh, T. Higashimura, and S. Okamura, *Makromol. Chem., 63*, 115 (1963).
[12] R. Cotrel, G. Sauvet, J. P. Vairon, and P. Sigwalt, *Macromolecules, 9*, 931, (1976).
[13] A. M. Goka and D. C. Sherrington, *Polymer, 16*, 819 (1975).
[14] J. Ericcson and A. Hult, *Polym. Bull., 18*, 295 (1987).
[15] J. Woods, J. M. Rooney, and J. H. Harris, U.S. Patent 4,543,397 (1985).

[16] J. M. Van Der Zanden and Th. R. Rix, *Rec. Trav. Chim.*, *75*, 1166 (1956).
[17] J. C. Petropoulos and J. J. Fisher, *J. Am. Chem. Soc.*, *80*, 1938.
[18] J. E. Moore, in *UV Curing Science and Technology* (S. P. Pappas, ed.), Technology Marketing Corp., Stamford, Connecticut, 1978.

Received February 14, 1992