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THE SYNTHESIS AND CATIONIC PHOTOPOLYMERIZATION OF NOVEL MONOMERS

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Key Words: Vinyl ether analogues; Monomer synthesis; Allyl-propenyl isomerizations; Cationic photopolymerization; Poly(indanes)

ABSTRACT

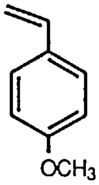
A series of aromatic monomers bearing two, three, four, and six cationically polymerizable vinyl, isopropenyl, or propenyl functional groups were prepared using readily available starting materials and characterized. The reactivity of the resulting monomers in photoinitiated cationic polymerization was studied using differential scanning photocalorimetry. The results of mechanistic investigations suggest that the polymerizations involve a stepwise condensation of the monomers followed by an intramolecular ring closure to form indane repeating units along the backbone of the polymer chains.

INTRODUCTION

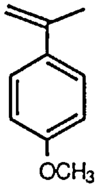
Over the past several years, interest in this laboratory has centered on the development of novel photoinitiators for cationic polymerizations [1]. As a result, several series of highly efficient cationic photoinitiators were developed and their use for the polymerization of a wide variety of monomer types investigated. At the present time, there is much current industrial interest in both photo and e-beam induced polymerizations because of their many potential benefits including; low energy consumption, lack of the use of polluting solvents, and high rates of polymerization. While many interesting cationically polymerizable monomers are commercially available and can be subjected to photopolymerization, few of these materials have the combination of mechanical properties, chemical resistance and high rates of polymerization desired for commercial photopolymerizations. Accordingly, in this laboratory we have undertaken the synthesis of several new classes of monomers designed specifically for cationic photopolymerization.

Of special interest for use in photoinduced cationic polymerizations are multifunctional alkyl vinyl and propenyl ethers since they are readily prepared and undergo facile photopolymerization at the highest rates of any monomers yet investigated [2–4]. However, these monomers have some significant drawbacks [5]. Alkyl vinyl and propenyl ethers hydrolyze rapidly in dilute aqueous acids, and although they undergo very rapid cationic polymerization, the polymers formed from these monomers often possess rather poor mechanical characteristics. Consequently, current efforts in this laboratory have centered on the synthesis of alternate, related monomers which posses high reactivity, hydrolytic stability, and potentially good mechanical properties.

It is well known that compared to styrene, 4-methoxystyrene (**A**) and 4-methoxy-α-methylstyrene (**B**) undergo anomalously high rates of cationic polymerization [6–8]. The high reactivity of these two monomers can be rationalized if they are considered to be, respectively, phenylogous vinyl and isopropenyl ethers. In both of these compounds the unsaturated group and the ether portions of the molecule can communicate electronically by inductive and resonance interaction through the phenyl groups. Thus, their reactivity more closely resembles that of methyl vinyl ether and isopropenyl methyl ether than, respectively, the corresponding styrene and α-methylstyrene monomers.



A

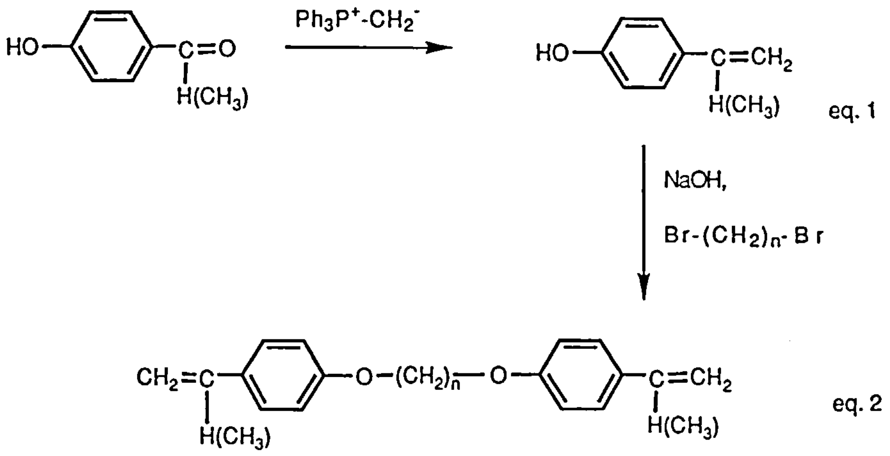


B

BIS(VINYLPHENOXY)ALKANES AND BIS(ISOPROPENYLPHENOXY)ALKANES

Based on the above 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 [9, 10] who employed the same basic synthetic approach shown in Scheme 1 for their preparation.

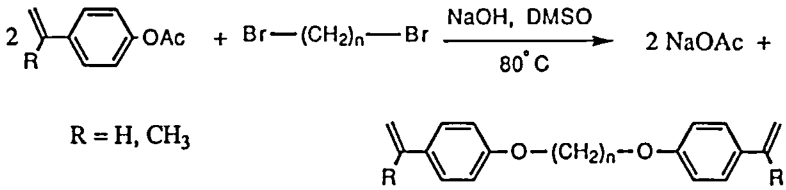
Although the synthetic route in Scheme 1 is reasonably straightforward, the overall yields of the products are rather low and, additionally, the Wittig reaction is



SCHEME 1.

impractical other than for small-scale reactions. In addition, the intermediates in this synthesis, 4-hydroxystyrene and 4-isopropenylphenol, 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 [11].

In Eq. (3) is shown the general route by which these monomers were prepared.



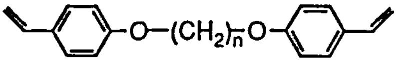
eq. 3

4-Acetoxystyrene, which is now available from commercial sources, undergoes smooth displacement reactions with α,ω-dibromoalkanes in DMSO in the presence of sodium hydroxide to yield a series of α,ω-bis(4-vinylphenoxy)alkanes. Table 1 gives the structures and data for a series of these monomers prepared during the course of this research.

A similar series of α,ω-bis(4-isopropenylphenoxy)alkanes, shown in Table 2, were prepared using a novel preparative method developed in this laboratory for 4-isopropenylphenyl acetate (4-acetoxy-α-methylstyrene). The synthesis of this intermediate compound is depicted in Scheme 2.

The base-catalyzed decomposition of bisphenol-A proceeds readily at 220°C [12, 13]. Simple 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 yielded only small amounts of the desired 4-isopropenyl-

TABLE 1. Bis(4-Vinylphenoxy)alkanes



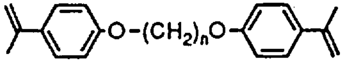
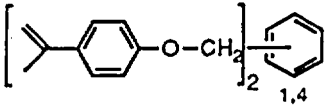
Notation	n	mp, °C	Yield, %	MW	Elemental analysis	%C	%H	%O
III	4	127–128	58	294.4	Found:	81.3	7.4	11.3
					Calculated:	81.6	7.5	10.9
IV	5	80–82	30	308.4	Found:	81.2	7.7	11.1
					Calculated:	81.8	7.8	10.4
V	8	110–112	62	350.5	Found:	81.9	8.7	9.4
					Calculated:	82.2	8.6	9.2
VI	10	111–112	63	378.6	Found:	82.0	9.1	8.9
					Calculated:	82.5	9.1	8.4

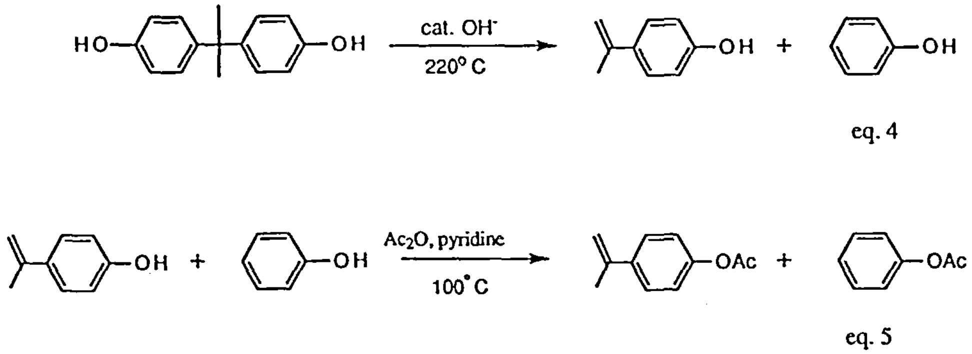
phenol due to a variety of oligomerization and condensation side reactions. Instead, it was found convenient to carry out the acetylation of the entire mixture and then to carry out a fractional distillation to separate the resulting acetate esters. 4-Isopropenylphenyl acetate, in contrast to its corresponding phenolic precursor, is stable and can be conveniently stored indefinitely at room temperature until use.

Table 2 gives the structures, characteristics, and elemental analysis data for a series of bis(4-isopropenylphenoxy)alkanes prepared according to Eq. (3). Both classes of monomers presented in Tables 1 and 2 are colorless crystalline solids which can be readily purified by chromatographic and recrystallization techniques. These monomers also undergo facile cationic photopolymerization in the presence of onium salt photoinitiators such as diaryliodonium and triarylsulfonium salts. Using differential scanning photocalorimetry (DSP), one can observe that polymerizations are virtually complete within 0.5 minutes. A typical DSP scan is shown in Fig 1. The sharp curve which was obtained indicates that this monomer is highly reactive and that cationic polymerization proceeds very exothermically. To elucidate the mechanism of the photoinduced cationic polymerization of these monomers, a brief investigation was conducted with the aid of model compound **B** (4-methoxy-α-methylstyrene, 4-isopropenylanisole). Two potential pathways are depicted in Scheme 3 for the reaction of this monomer: 1) typical cationic vinyl polymerization as is usually observed in the polymerization of α-methylstyrene, or 2) an intramolecular Friedel-Crafts cyclization to give a dimer containing an indane group.

When a solution of 4-methoxy-α-methylstyrene in $CDCl_3$ was irradiated with UV-light in the presence of 0.5 mol% (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate as a photoinitiator, a polymer was not obtained, indicating that Path 1) was not being followed. Instead, only low molecular weight species were formed. The progression of the ^{1}H-NMR (in $CDCl_3$) spectra shown in Fig. 2 of the reaction mixture showed the rapid disappearance of the protons associated with the isopro-

TABLE 2. Bis(4-Isopropenylphenoxy)alkanes

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



SCHEME 2.

penyl 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 **B** by the photogenerated acid yields the tertiary carbonation **C**. Cation **C** then attacks another molecule of **B** to give dimer cation **D**.

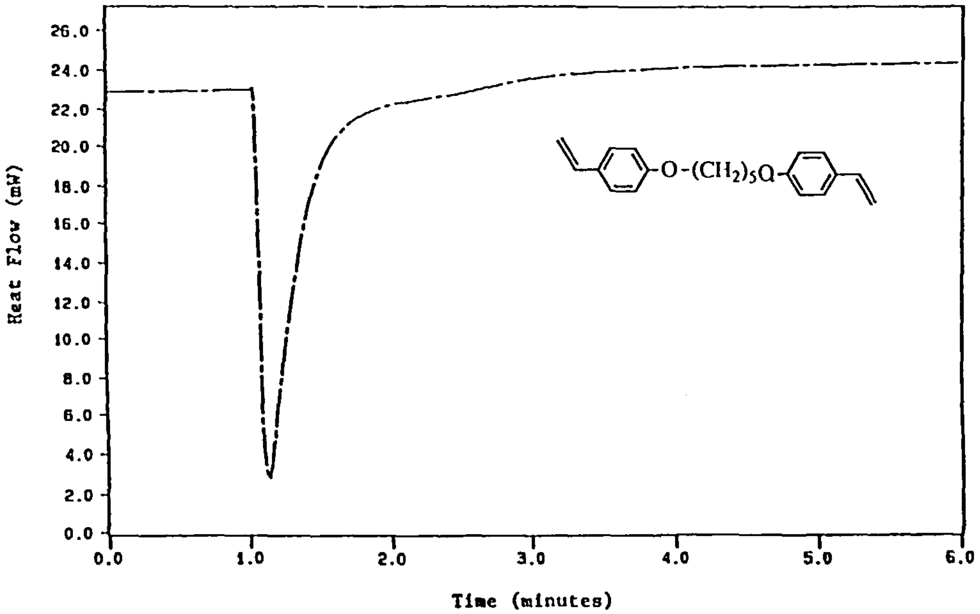
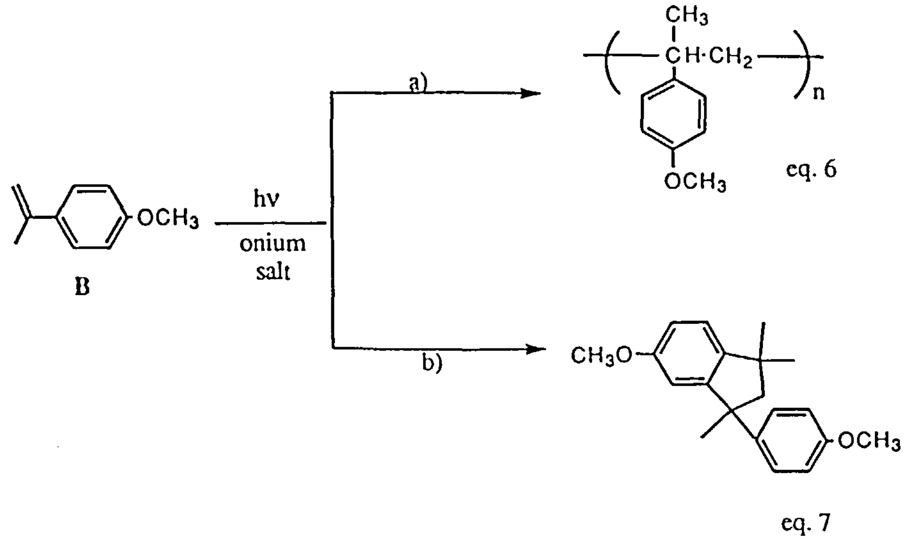
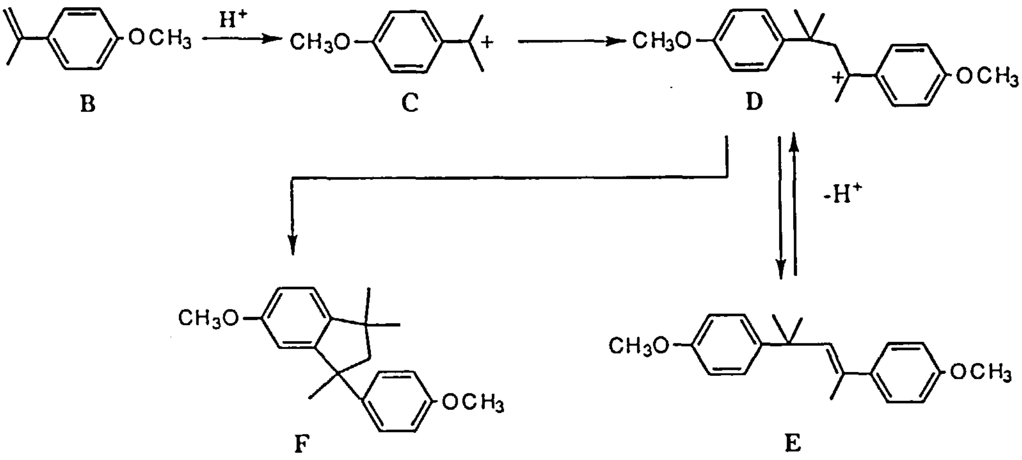


FIG. 1. DSP curve for the exothermic polymerization of 1,5-bis(4-vinylphenoxy)pentane (II) in the presence of 0.5 mol% diphenyl(4-thiophenoxyphenyl)sulfonium hexafluoroantimonate. Sample run isothermally at 80°C with the shutter opened at 1.0 minute.



SCHEME 3.

At this stage, **D** may directly cyclize to give **F** or undergo elimination to give the dimer olefin **E**. Although **E** is stable and observed in our NMR studies, in the presence of the strong acid it is in equilibrium with **B** and is eventually irreversibly converted to indane **F**. Considerable precedence for this mechanism exists in the literature. 4-Methoxy-α-methylstyrene has been shown to undergo dimerization to the unsaturated dimer **E** in the presence of strong acids [14]. In these latter studies



eq. 8

SCHEME 4.

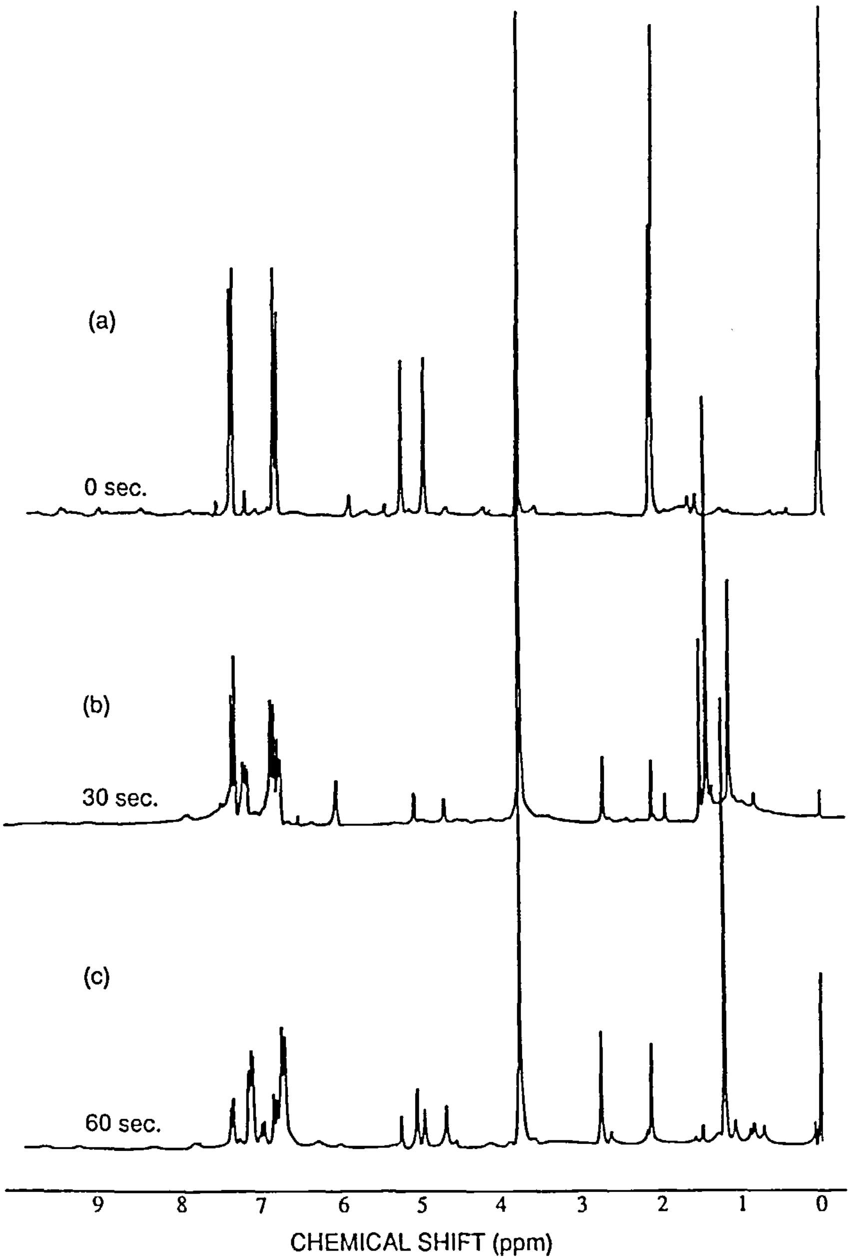
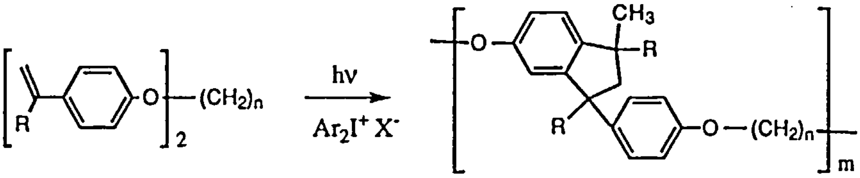


FIG. 2. ^1H NMR ($CDCl_3$) of the cationic photopolymerization of 4-methoxy-α-methylstyrene after (a) 0 seconds, (b) 30 seconds, and (c) 60 seconds irradiation in the presence of 0.5 mol% (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate.

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 E in the presence of strong acids which further react to give substituted indanes [15]. Based on these studies, the polymerization of the bis(vinylphenoxy)alkane and bis(isopropenylphenoxy)alkane monomers in Tables 1 and 2 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. (9).

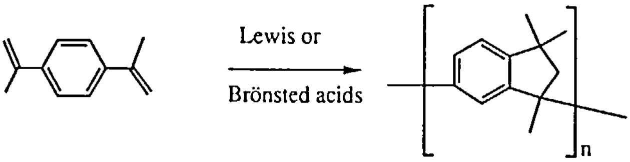


eq. 9

The observation that the polymer films obtained by the cationic photopolymerization of the two classes of difunctional monomers at room temperature are insoluble in all solvents indicates that some small amount of crosslinking by conventional cationic olefin polymerization (Path 1) may also be occurring in competition with the above process or that interchain Friedel-Crafts alkylation by isopropenyl cations may also be taking place.

1.3-DIISOPROPENYBENZENE

Previously, D'Onofrio [16] and Nuyken et al. [17–19] reported that the Lewis or Brønsted acid-catalyzed polymerization of 1,4-diisopropenylbenzene leads to poly(*p*-indane):

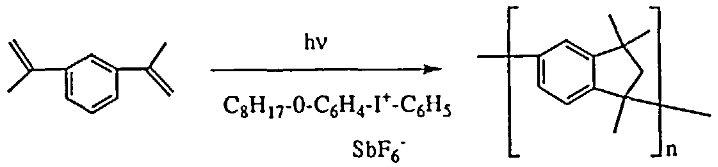


eq. 10

These two groups further reported that the poly(*p*-indane) prepared by either catalytic method exhibited excellent thermal characteristics. Polyindane synthesized from 1,4-diisopropenylbenzene has a glass transition temperature of 210°C and a decomposition temperature of 450°C in air.

In this laboratory we have been investigating the photoinitiated cationic polymerization of the isomeric 1,3-diisopropenylbenzene. This compound is a colorless, mobile liquid with a boiling point of 231 °C. Initial attempts to carry out the photoinitiated cationic polymerization of this monomer using (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate are shown in the differential scanning photocalorimetry curve of Fig. 3. Photopolymerization proceeds rapidly and exothermically over the course of 1.5–2.0 minutes irradiation using 0.5 mol% of the photoinitiator. The DSP results indicate that this monomer is extraordinarily reactive. When films of the same solution were drawn onto glass plates and irradiated using a 200-W medium pressure mercury arc lamp, dry, tack-free films were obtained within 20 seconds irradiation. Films prepared under these conditions were insoluble in both polar and nonpolar solvents. In contrast, it was observed that linear, soluble, low molecular weight poly(*m*-indane) (M_w = 19,170 g/mol) could be prepared by simply carrying out the cationic photopolymerization of 1,3-diisopropenylbenzene slowly over the course of several days under normal laboratory lighting conditions.

Spectroscopic investigations of the structure of the polymer derived from the photoinduced cationic polymerization of 1,3-diisopropenylbenzene suggest that the structure is analogous to that from its 1,4-isomer:



eq. 11

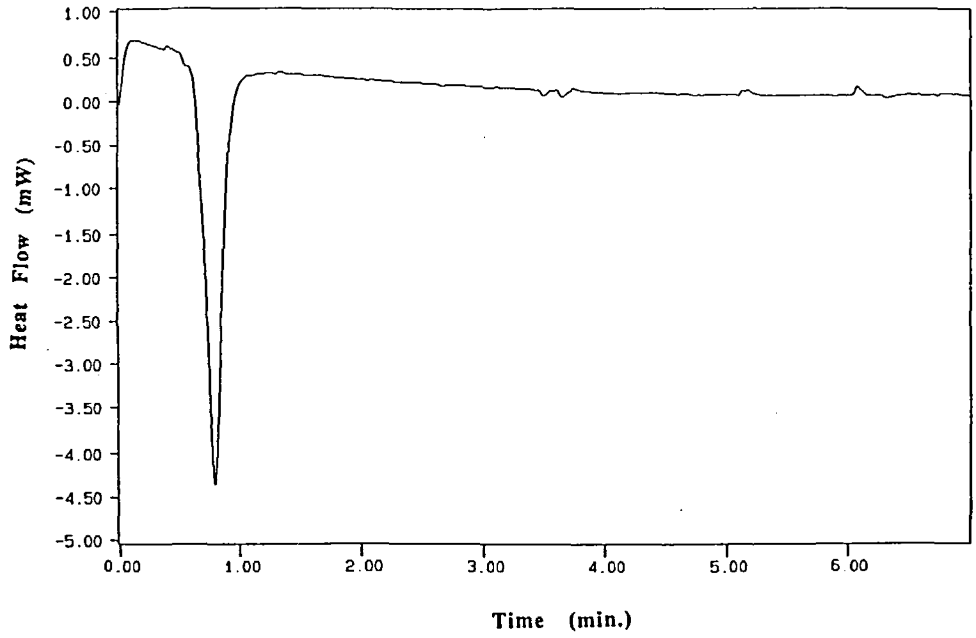
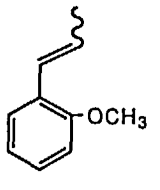


FIG. 3. DSP curve of the photopolymerization of 1,3-diisopropenylbenzene in the presence of 0.5 mol% (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate. Sample run isothermally at 30°C with the shutter opened at 0.5 minute.

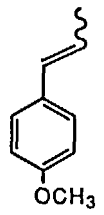
Poly(*m*-indane) prepared by photopolymerization has very interesting properties. The T_g appears to be above the decomposition temperature of the polymer (>350°C). The dielectric constant was found to be 2.6, and the coefficient of thermal expansion (CTE) in the temperature range of 25 to 250°C was 20×10^{-6} ppm/°C. Both of these properties indicate that this polymer may have very interesting uses as dielectric materials in electrical and microelectronic applications.

BIS(PROPENYLPHENOXY)ALKANES

While it has already been mentioned that compounds **A** and **B** can be considered to be phenylogous vinyl and isopropenyl ethers, respectively, the monomers **G** and **H** shown below can be regarded as phenylogous propenyl ether analogs. It was therefore proposed that these compounds as well as multifunctional monomers having related structures should undergo facile cationic photopolymerization.



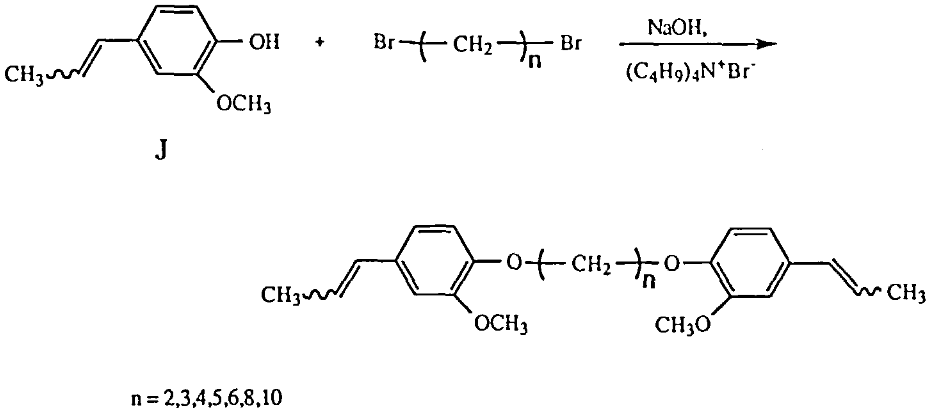
G



H

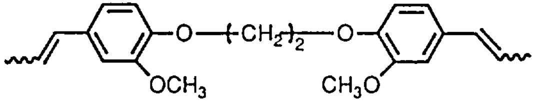
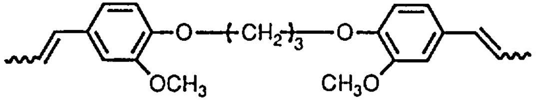
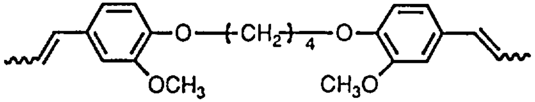
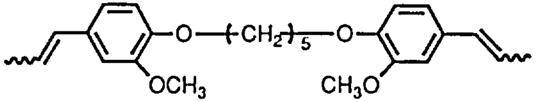
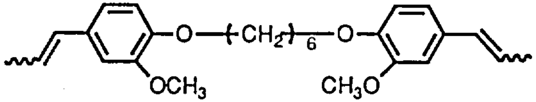
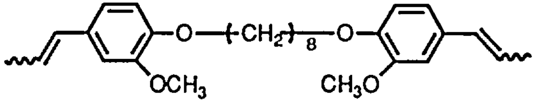
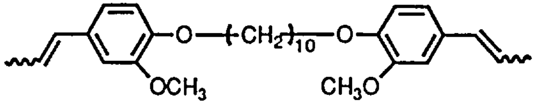
Based on these assumptions, the synthesis of two series of difunctional monomers containing propenyl phenyl ether groups was undertaken employing two different synthetic approaches [20].

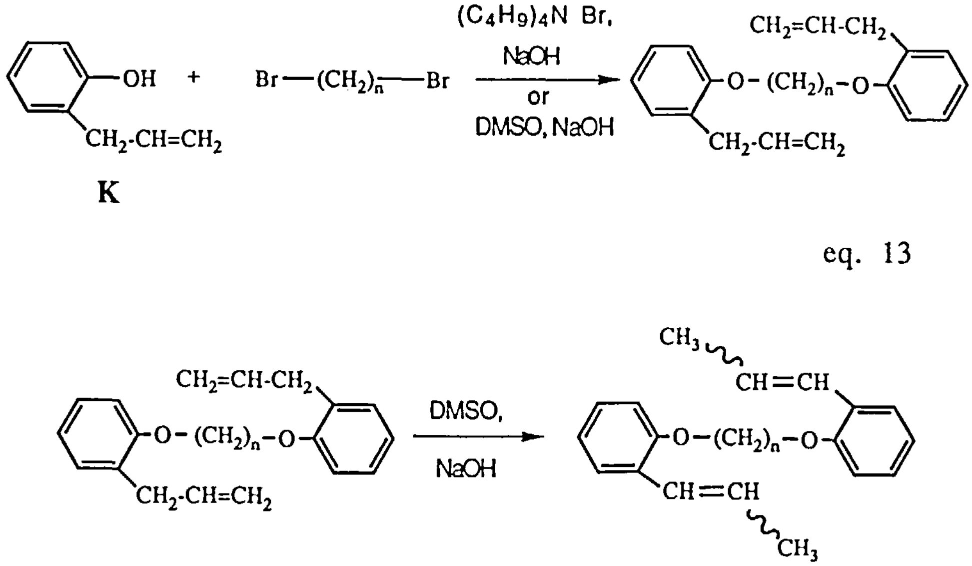
Isoeugenol (**J**) (a mixture of *cis* and *trans* isomers) was condensed with a series of α,ω-dibromoalkanes under phase-transfer conditions to give the series of difunctional monomers shown in Table 3. This chemistry is depicted in Eq. (12).



eq.12

TABLE 3. Difunctional Propenyl Ether Analogues Prepared from Isoeugenol and α,ω-Dibromoalkanes

Notation	Structure	MW	Elemental analysis			
				%C	%H	%O
XI		354	Found:	74.18	7.38	18.16
			Calculated:	74.55	7.39	18.06
XII		368	Found:	74.70	7.77	17.53
			Calculated:	74.97	7.66	17.37
XIII		382	Found:	75.12	7.78	17.10
			Calculated:	75.36	7.91	16.73
XIV		396	Found:	75.68	8.12	16.20
			Calculated:	75.73	8.13	16.14
XV		410	Found:	76.00	8.38	15.62
			Calculated:	76.06	8.35	15.59
XVI		438	Found:	76.21	8.77	15.02
			Calculated:	76.68	8.73	14.59
XVII		466	Found:	76.86	9.05	14.09
			Calculated:	77.21	9.07	13.71



K

eq. 13

eq. 14

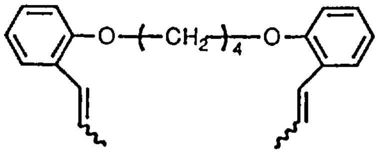
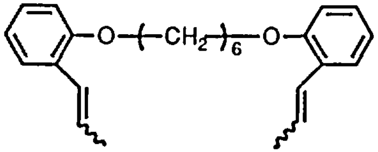
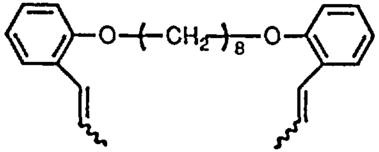
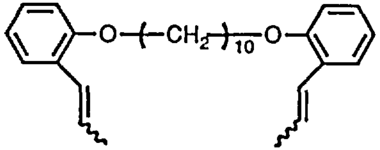
SCHEME 5.

The monomers prepared using the above method are a mixture of isomeric compounds (*cis-cis*, *cis-trans*, and *trans-trans*) due to the presence of the two propenyl double bonds. No effort was made to separate the individual isomers. The compounds shown in Table 3 are all pale yellow to colorless solids with broad melting points ranging from 90 to 130°C. These monomers showed no tendency to polymerize on storage at room temperature.

A second series of monomers was prepared by a two-step route shown in Scheme 5 starting with 2-allylphenol (**K**). 2-Allylphenol is readily available from the Claisen rearrangement of allyl phenyl ether. The monomers in Table 4 were prepared by first reacting 2-allylphenol with dibromoalkanes under phase-transfer conditions or in the presence of base and DMSO. The resulting bisethers were formed in nearly quantitative yields and were thereafter subjected to further reaction in the presence of sodium hydroxide and DMSO. Within 5–6 hours at 75–95°C, the allyl groups of the bisethers were quantitatively isomerized to the corresponding propenyl compounds. The resulting monomers shown in Table 4 are colorless to pale yellow solids which were readily recrystallized from toluene, ethanol, or pentane. Moderate to good yields were obtained for all the monomers, and no attempt was made to optimize the yields. As in the previous case, the monomers shown in Table 4 are mixtures of isomers resulting from *cis* and *trans* isomerism at the two propenyl double bonds.

The monomers shown in Tables 3 and 4 undergo facile photoinitiated cationic polymerization in the presence of onium salt photoinitiators. Shown in Figs. 4 and 5 are two typical DSP traces for difunctional monomers **XIV** and **XVII** obtained in an isothermal mode at 100°C. Both compounds proved to be quite reactive toward

TABLE 4. Difunctional Propenyl Ether Analogs Prepared from *o*-Allylphenol and α,ω-Dibromoalkanes

Notation	Structure	MW		Elemental analysis %C	%H	%O
XVIII		322	Found:	81.86	8.18	9.96
			Calculated:	81.95	8.13	9.92
XIX		350	Found:	81.94	9.10	8.96
			Calculated:	82.24	8.63	9.13
XX		378	Found:	82.20	9.12	8.68
			Calculated:	82.49	9.05	8.45
XXI		406	Found:	82.39	9.45	8.16
			Calculated:	82.71	9.42	7.87

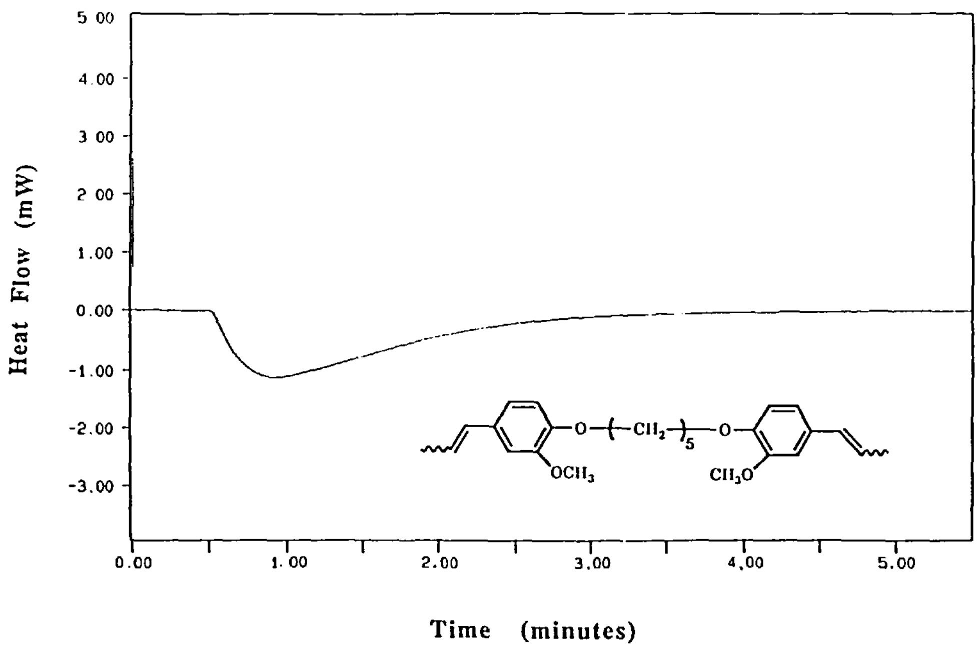
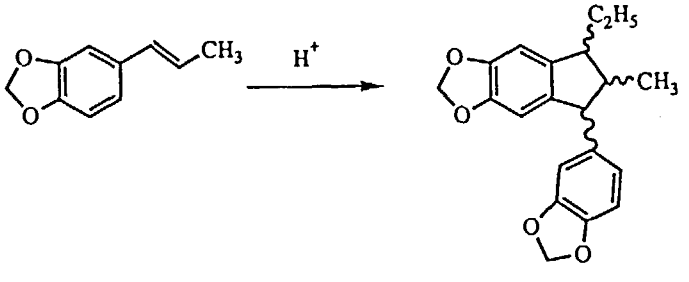


FIG. 4. DSP curve of the photopolymerization of **XIV** in the presence of 0.5 mol% (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate. Sample run isothermally at 30°C with the shutter opened at 0.5 minute.

photoinitiated cationic polymerization. As in the previous cases, the polymer films formed are clear, colorless, and insoluble in all solvents.

The structure of the latter polymers prepared by photoinduced cationic polymerization was investigated spectroscopically. On the basis of those studies it was concluded that the major process involved in the cationic photopolymerization consisted of an intramolecular cyclization to form polymers containing indane repeating units. Previously, Stevenson et al. [21] had shown that the treatment of aryl-2-propenes bearing electron donating groups with acids gives indanes. An example of this reaction is shown in Eq. (15) for the cyclization of isosaffrole (L).



L eq. 15

Likewise, such cyclizations are the predominant processes occurring in the polymerization of the monomers shown in Tables 3 and 4. In addition, crosslinking

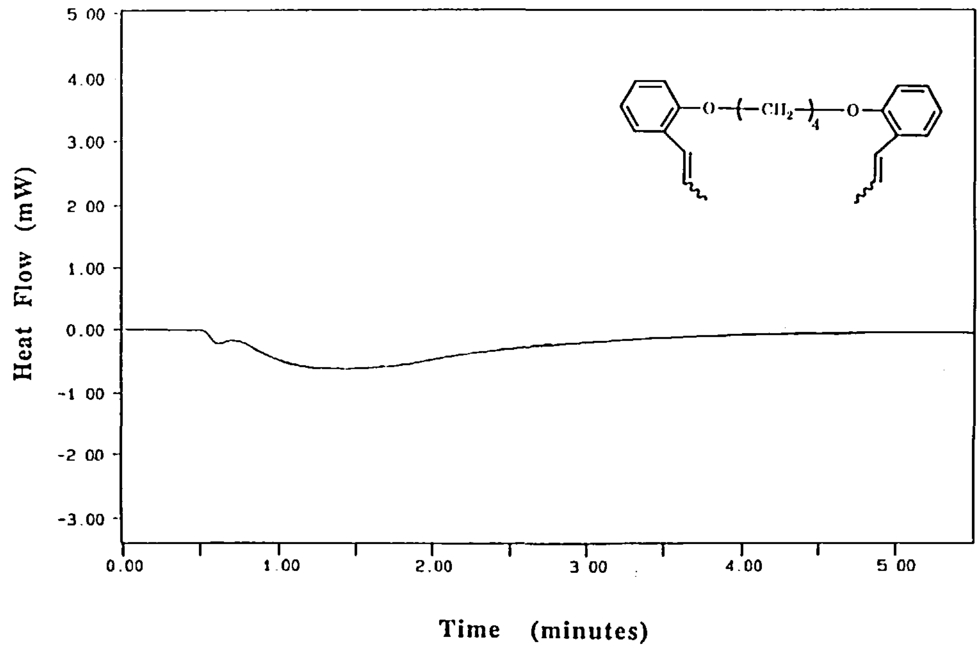
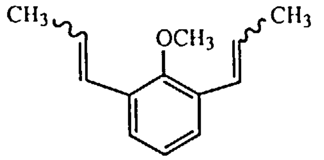


FIG. 5. DSP curve of the photopolymerization of XVIII in the presence of 0.5 mol% (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate. Sample run isothermally at 30°C with the shutter opened at 0.5 minute.

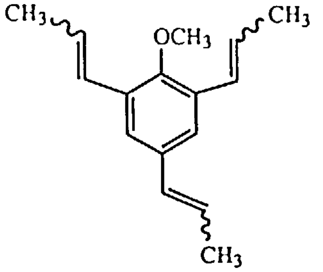
takes place with either independent polymerization of the two propenyl groups or by an interchain Friedel-Crafts reaction in which the activated, electron-rich aromatic groups are alkylated by protonated propenyl groups.

MULTIFUNCTIONAL AROMATIC MONOMERS CONTAINING PROPENYL GROUPS

The observation that propenyl ether analogs undergo facile cationic polymerization suggested that even simpler monomers than those described above could be prepared [22]. For example, 2,6-di(propenyl)phenyl methyl ether (M and 2,4,6-tri(propenyl)phenyl methyl ether (N) as well as other alkyl ether derivatives may also be regarded, respectively, as di- and trifunctional propenyl ether analogs.



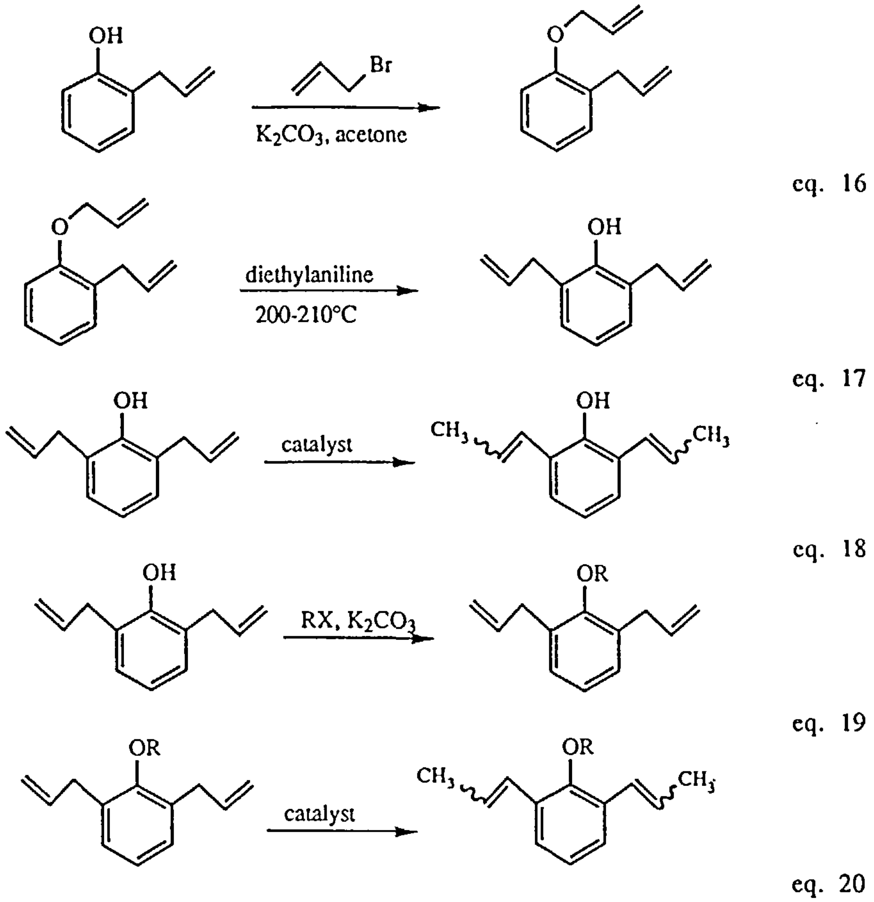
M



N

Preliminary investigations showed that, indeed, both of these compounds could be polymerized using various cationic initiators.

Shown in Scheme 6 are two general synthetic pathways which were used for the preparation of the above and related compounds. A similar series of reactions may be used for the synthesis of trifunctional propenyl derivatives such as N. The synthesis begins with the *O*-allylation of the commercially available 2-allylphenol as shown in Eq. (16). Claisen rearrangement (Eq. 17) of the 1-allyloxy-2-allylbenzene to 2,6-diallylphenol can be readily achieved in good yield by simply heating at 200–210°C for 24 hours in the presence of diethylaniline as catalyst and solvent. In the case of N, these first two steps were again repeated to give the 2,4,6-triallylphenol. Next, as depicted in Eq. (18), the 2,6-diallylphenol was isomerized to the corresponding 2,6-di(propenyl)phenol. Alternatively, a better route consists of first alkylating the phenol (Eq. 19) and then carrying out the isomerization of the alkyl ether to the corresponding di(propenyl)phenyl alkyl ether (Eq. 20). This latter reaction is optimally carried out at 120°C using tris(triphenylphosphine)ruthenium(II)dichloride as a catalyst. Under these conditions, the isomerization reaction proceeds cleanly

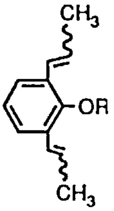
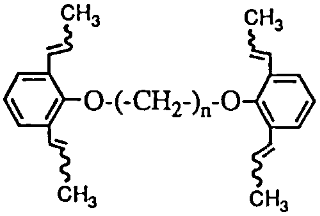
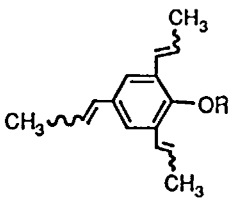
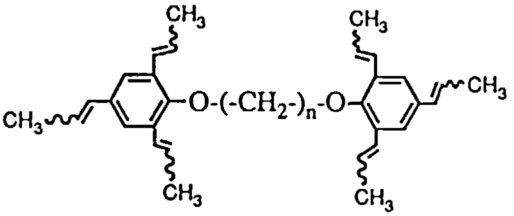


SCHEME 6.

to yield the desired propenyl derivatives with essentially no major by-products. Again, the propenyl compounds which are formed consist of both *cis* and *trans* isomers.

In Table 5 are given the structures and elemental analyses of a number of multifunctional propenyl ether analogs prepared using similar synthetic approaches. Besides simple di- and trifunctional compounds, tetra- and hexafunctional monomers were prepared by etherification of the corresponding di- and triallyl phenols with dibromoalkanes in the presence of a strong base followed by isomerization with $[(C_6H_5)_3P]_3RuCl_2$. Typically, the yields are very high, and in many cases they are quantitative. These eight monomers were liquid mixtures of isomers with both *cis* and *trans* configurations about the propenyl double bonds. The monomers were

TABLE 5. Structure of Multifunctional Propenyl Ether Analogues

Structure	R or *n*	Notation	MW
	CH_3 CH_2CH_3	XXII XXIII	188 202
	$n = 6$ $n = 8$	XXIV XXV	430 458
	CH_3 CH_2CH_3	XXVI XXVII	228 242
	$n = 6$ $n = 8$	XXVIII XXIX	510 538

purified prior to their use in cationic photopolymerization by column chromatography.

All of the monomers undergo photopolymerization to give solid, crosslinked films after 1 to 5 minutes UV irradiation in the presence of onium salt photoinitiators. Studies of the reactivities of the monomers were conducted using DSP. For example, the DSP curve for monomer **XXIII** is shown in Fig. 6. After the shutter is opened at 0.5 minute, polymerization takes place rapidly and is completed over the course of 1.5–2.0 minutes UV irradiation.

By monitoring the photopolymerization of 2,6-di(propenyl)phenyl ethyl ether (XXIII) by infrared spectroscopy, one may note a decrease in double bond absorption at 980 cm^{-1}. Other changes in the double bond and aromatic absorption bands at 1580–1620 cm^{-1} also take place, and there is a general broadening of all of the major absorption bands as the polymerization proceeds. During photopolymerization, it was noted that despite the high functionality of the monomers, the polymers remained soluble and only underwent crosslinking upon prolonged irradiation.

Based on these observations and the previous results, it is proposed that the structure of the polymers generated by the photopolymerization of the monomers shown in Table 5 also contain indane moieties as part of their backbones. Thus, for example, the polymerization of difunctional monomer **XXIII** would yield a polymer with a partial backbone structure as depicted in Eq. (21).

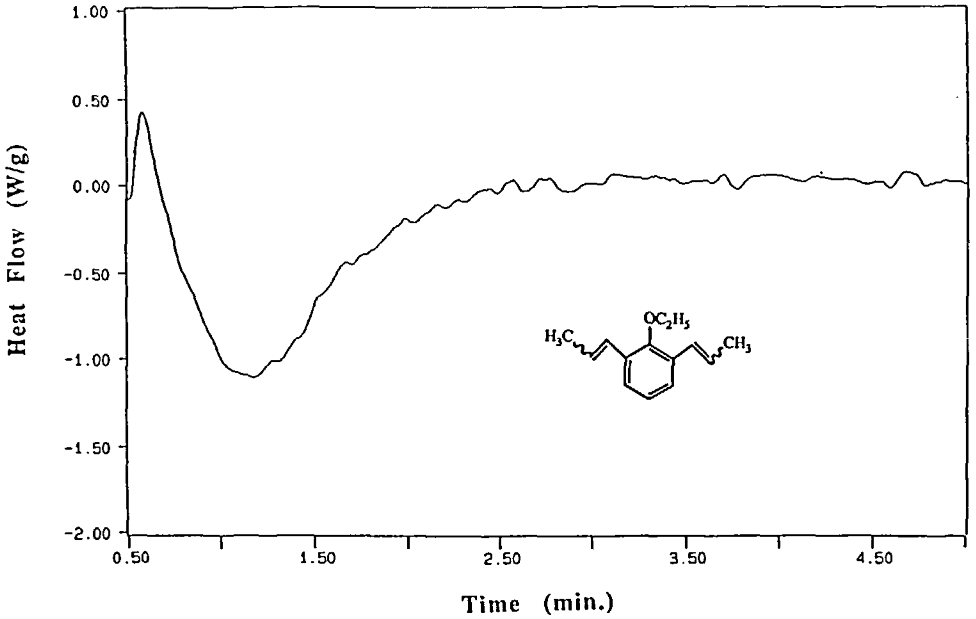
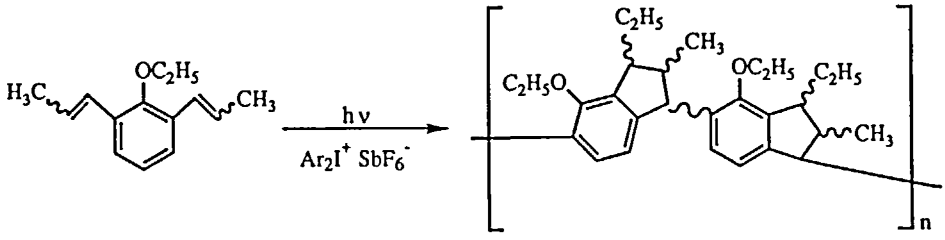


FIG. 6. DSP curve of the photopolymerization of XXIII in the presence of 0.5 mol% (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate. Sample run isothermally at 30°C with the shutter opened at 0.5 minute.



XXIII

eq. 21

Since network formation is noted during the latter stages of the photopolymerization, crosslinks can also be generated by normal, vinyl-type polymerization and perhaps also by intermolecular Friedel-Crafts alkylation processes between the polymer chains.

Efforts are currently in progress to prepare other vinyl, isopropenyl, and propenyl ether analogs and to examine their reactivity in photo and thermally initiated cationic polymerization.

CONCLUSIONS

Electron-rich alkoxy substituted aromatic compounds containing vinyl, isopropenyl, or propenyl groups may be regarded as phenylogous, isopropenyl, or propenyl ethers, respectively, with respect to their ability to undergo cationic polymerization. Based on this concept, several series of novel multifunctional monomers have been prepared and subjected to photoinitiated cationic polymerization. The monomers are prepared by simple, straightforward chemical reactions employing vinyl, isopropenyl, or propenyl phenols as starting materials. In addition, allyl-substituted aromatic compounds can be readily isomerized to the corresponding propenyl isomers by a base- or ruthenium-catalyzed rearrangement. All the monomers described here undergo facile photoinduced cationic polymerization on irradiation in the presence of onium salt photoinitiators. Investigation of the structure of the polymers formed indicates that intramolecular cyclization takes place as part of the chain extension process to yield polymers containing indane groups.

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