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CURING REACTIONS IN ACETYLENE TERMINATED RESINS—I. UNCATALYZED CURE OF ARYLPROPARGYL ETHER TERMINATED MONOMERS

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Abstract—Two arylpropargyl ether terminated monomers have been synthesized, (pHC≡CCH$_2$OC$_6$H$_4$)$_2$CMe$_2$ (**I**) and the analogous model monomer pHC≡CCH$_2$OC$_6$H$_4$CMe$_2$Ph (**II**) having a single arylpropargyl ether group. DSC, i.r., ^{1}H- and ^{13}C-NMR analysis of the products resulting from partial cure of **I** and complete cure of **II** showed that the crosslinking involves prior sigmatropic rearrangement of the arylpropargyl ether groups to 2*H*-1-benzopyran structures which subsequently polymerize. The various intermediate 2*H*-1-benzopyran-containing species were isolated and characterized.

INTRODUCTION

Resins formed from acetylene-terminated monomers (ATMs) are of interest as replacements amongst other things for epoxies especially for use under hot wet conditions [1–3]. ATMs fall into two main categories, viz. those terminated by arylacetylene and those by arylpropargyl ether groups. The uncatalyzed curing mechanism of the former type has been found to involve a free radical reaction resulting in a network for which the crosslink sites are linear conjugated polyenes formed from 6–8 ethynyl groups [4] together with some cyclotrimerization of acetylene end-groups [5]. However, until the results of the present study were made known [6], the reactions taking place during the uncatalyzed cure of arylpropargyl ether type ATMs were unelucidated. Since our initial preliminary communication showing the unexpected formation of 2*H*-1-benzopyran rings and their subsequent polymerization [6], other workers have reported similar observations [7]. We give here in detail the results of our study of the uncatalyzed cure of two monomers of the arylpropargyl ether type, (pHC≡CCH$_2$OC$_6$H$_4$)$_2$CMe$_2$ (**I**) and the analogous model monomer pHC≡CCH$_2$OC$_6$H$_4$CMe$_2$Ph (**II**) having a single arylpropargyl ether group. The reactions occurring are quite different from those for catalyzed cure of either arylpropargyl ether or arylacetylene ATMs [8, 9].

EXPERIMENTAL PROCEDURES

i.r. Spectra were recorded as Nujol mulls or CsI discs by use of a Perkin–Elmer 728 spectrometer connected to a Perkin–Elmer 360 data station. ^{1}H-NMR spectra were run on either a Perkin–Elmer R32 90 MHz CW or a Bruker WP-80-SY 80 MHz FT spectrometer, and ^{13}C-NMR spectra on this latter instrument operating at 20.115 MHz. Mass spectra were obtained by use of an AE1 MS9 mass spectrometer. DSC was performed on a Mettler TA 3000 System. Molecular weights were determined by VPO in toluene at 45° using a Knauer instrument calibrated with benzil. Elemental analyses were carried out by Butterworth Laboratories, Twickenham.

Preparation of I

The literature preparation [10] was adapted as follows. To a solution of bisphenol-A (228 g; 1 mol) and 92% NaOH (87 g; 2 mol) in 1 l. of water was added 80% propargyl bromide in toluene (295 g; 2 mol) and the mixture was refluxed under N_2 for 4 hr. It was then concentrated and the crude product was precipitated by addition of 600 ml of propan-2-ol. Purification by flash chromatography on neutral alumina (1:1 n-hexane:dichloromethane eluant) followed by recrystallization from propan-2-ol afforded colourless crystals of **I** in 50% yield, m.p. 84–85°.

^{1}H-NMR ($CDCl_3$, TMS): δ 1.63 (s, 6H; (C$\underline{H}_3$)$_2$CAr$_2$), 2.49 (tr, J = 2.4 Hz, 2H; CH$_2$C≡C$\underline{H}$), 4, 65 (d, J = 2.4 Hz, 4H; C$\underline{H}_2$C≡CH), 6.7–7.3 (m, 8H; C$_6\underline{H}_4$) ppm.

^{13}C-NMR ($CDCl_3$, TMS): δ 30.9 (C^2), 41.7 (C^1), 55.7 (C^7), 75.4 (C^9), 78.9 (C^8), 114.3 (C^5), 127.6 (C^4), 143.8 (C^3), 155.4 (C^6) ppm.

i.r.: 3280s 3260s [ν(≡C—H)], 2118w [ν(C≡C)] cm^{-1}.

MS (70 eV): m/e 304 (M^+).

Analysis: calculated for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62; O, 10.51. Found: C, 82.22; H, 6.91; O, 10.87.

Preparation of II

A mixture of p-cumyl phenol (42.4 g; 0.2 mol), 80% propargyl bromide in toluene (29.8 g; 0.2 mol) and 95% NaOH (8.4 g; 0.2 mol) in 150 ml of water were heated under reflux for 4 hr. After cooling, the organic layer was thoroughly washed with 1 M NaOH (aq) and then water, dried over $MgSO_4$, passed through a bed of neutral alumina and distilled under reduced pressure at 131–132° to give **II** as a colourless oil in 63% yield.

^{1}H-NMR ($CDCl_3$, TMS): δ 1.63 (s, 6H; (C$\underline{H}_3$)$_2$CAr$_2$), 2.39 (tr, J = 2.4 Hz, 1H; CH$_2$C≡C$\underline{H}$), 4.56 (d, J = 2.4 Hz, 2H; C$\underline{H}_2$C≡CH), 6.7–7.4 (m, 9H; C$_6\underline{H}_4$ and C$_6\underline{H}_5$) ppm.

^{13}C-NMR ($CDCl_3$, TMS): δ 30.8 (C^6), 42.2 (C^5), 55.6 (C^{11}), 75.3 (C^{13}), 78.8 (C^{12}), 114.3 (C^9), 125.5 (C^1), 126.6 (C^3), 127.7 (C^8), 127.9 (C^2), 143.6 (C^7), 150.6 (C^4), 155.5 (C^{10}) ppm.

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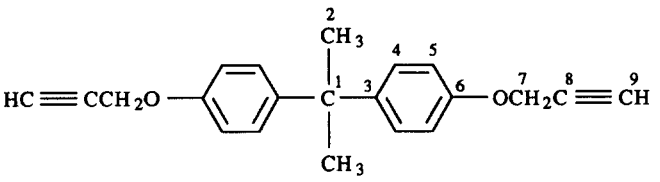
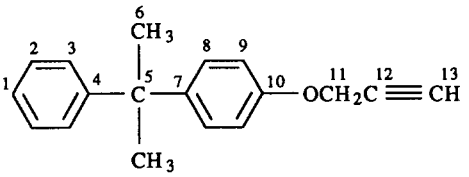
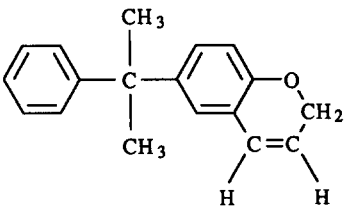


I



II



III

Structures I–III

i.r. 3280 m [ν(≡C—H)], 2120 w [ν(C≡C)] cm^{-1}.

MS (70 eV): *m/e* 250 (M^+).

Analysis: calculated for $C_{18}H_{18}O$: C, 86.36; H, 7.25; O, 6.39. Found: C, 86.32; H, 7.22; O, 6.46.

Preparation of 6-cumyl-2H-1-benzopyran (III)

The literature preparation of 2*H*-1-benzopyrans from arylpropargyl ethers [11] was adapted as follows. Benzoic acid (12.1 g; 0.1 mol) and **II** (7.5 g; 0.03 mol) in decalin (50 ml) were heated under reflux for 36 hr under N_2. Aqueous 0.1% $NaHCO_3$ (200 ml) and n-hexane (100 ml) were added to the cooled reaction mixture, and the organic layer was washed thoroughly with water and dried over $MgSO_4$. After removal of decalin under vacuum, the product was purified by chromatography on silica gel (1/1 n-hexane/CH_2Cl_2 eluant), the first band being pure **III** isolated as a colourless oil in 72% yield.

^{1}H-NMR ($CDCl_3$, TMS): δ 1.62 (s, 6H; $(C\underline{H}_3)_2CAr_2$), 4.72 (dxd, $J_{2,3}$ = 3.3 Hz, $J_{2,4}$ = 2.0 Hz, 2H; $OC\underline{H}_2CH{=}CHAr$), 5.65 (dxtr, $J_{3,4}$ = 10 Hz, $J_{2,3}$ = 3.3 Hz, 1H; $OCH_2C\underline{H}{=}CHAr$), 6.30 (dxtr, $J_{3,4}$ = 10 Hz, $J_{2,4}$ = 2.0 Hz, 1H; $OCH_2CH{=}C\underline{H}Ar$), 6.5–7.4 (m, 8H; $C_6\underline{H}_3$ and $C_6\underline{H}_5$) ppm.

^{13}C-NMR ($CDCl_3$, TMS): δ 30.9, 42.3, 65.5, 115.1, 121.7, 125.0, 125.6, 126.7, 127.5, 127.9, 143.5, 150.8, 152.0 ppm.

MS (70 eV): *m/e* 250 (M^+).

Analysis: calculated for $C_{18}H_{18}O$: C, 86.36; H, 7.25; O, 6.39. Found: C, 86.30; H, 7.24; O, 6.46.

Polymerization of I

I (5 g) was heated under N_2 at 220° for 3 hr (^{1}H-NMR spectrum of reaction mixture shown in Fig. 1). The product dissolved in 70 ml of CH_2Cl_2 was added dropwise to 400 ml of methanol and the resulting precipitate of brown polymer was separated by filtration and washed with methanol. This precipitation procedure was repeated to yield 1.06 g (21% yield) of methanol-insoluble polymer after drying to constant weight under vacuum at 60° (^{1}H-NMR spectrum shown in Fig. 2).

Analysis: calculated for $(C_{21}H_{20}O_2)_n$: C, 82.86; H, 6.62; O, 10.51. Found: C, 82.31; H, 6.71; O, 10.98.

A portion (0.82 g) of the methanol-soluble fraction was separated into three components by column chromatography on silica gel. Elution with 80/20 n-hexane/acetone separated initially the di-2*H*-1-benzopyran derivative (**V**) as a colourless oil (0.15 g; 16% of methanol-soluble fraction).

^{1}H-NMR ($CDCl_3$, TMS): δ 1.62 (s, 6H; $(C\underline{H}_3)_2CAr_2$), 4.72 (dxd, $J_{2,3}$ = 3.3 Hz, $J_{2,4}$ = 2.0 Hz, 4H; $OC\underline{H}_2CH{=}CHAr$), 5.65 (dxtr, $J_{3,4}$ = 10 Hz, $J_{2,3}$ = 3.3 Hz, 2H; $OCH_2C\underline{H}{=}CHAr$), 6.33 (dxtr, $J_{3,4}$ = 10 Hz, $J_{2,4}$ = 2.0 Hz, 2H; $OCH_2CH{=}C\underline{H}Ar$), 6.5–7.3 (m, 6H; $C_6\underline{H}_3$) ppm.

^{13}C-NMR ($CDCl_3$, TMS): δ 31.0, 41.8, 65.6, 115.1, 121.7, 125.5, 127.5, 143.7, 152.0 ppm.

Analysis: calculated for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62; O, 10.51. Found: C, 82.98; H, 6.62; O, 10.40.

Further elution with 80/20 n-hexane/acetone separated the mono-2*H*-1-benzopyran derivative (**IV**) as a colourless oil (0.09 g; 11% of methanol-soluble fraction).

^{1}H-NMR ($CDCl_3$, TMS): δ 1.62 (s, 6H; $(C\underline{H}_3)_2CAr_2$), 2.49 (tr, J = 2.4 Hz, 1H; $C{\equiv}C\underline{H}$), 4.65 (d, J = 2.4 Hz, 2H; $OC\underline{H}_2C{\equiv}CH$), 4.72 (dxd, $J_{2,3}$ = 3.3 Hz, $J_{2,4}$ = 2.0 Hz, 2H; $OC\underline{H}_2CH{=}CHAr$), 5.65 (dxtr, $J_{3,4}$ = 10 Hz, $J_{2,3}$ = 3.3 Hz, 1H; $OCH_2C\underline{H}{=}CHAr$), 6.30 (dxtr, $J_{3,4}$ = 10 Hz, $J_{2,4}$ = 2.0 Hz, 1H; $OCH_2CH{=}C\underline{H}Ar$), 6.5–7.3 (m, 7H; $C_6\underline{H}_3$ and $C_6\underline{H}_4$) ppm.

i.r.: 3280 m [ν(≡C—H)], 2120 w [ν(C≡C)] cm^{-1}.

Analysis: calculated for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62; O, 10.51. Found: C, 83.01; H, 6.61; O, 10.38.

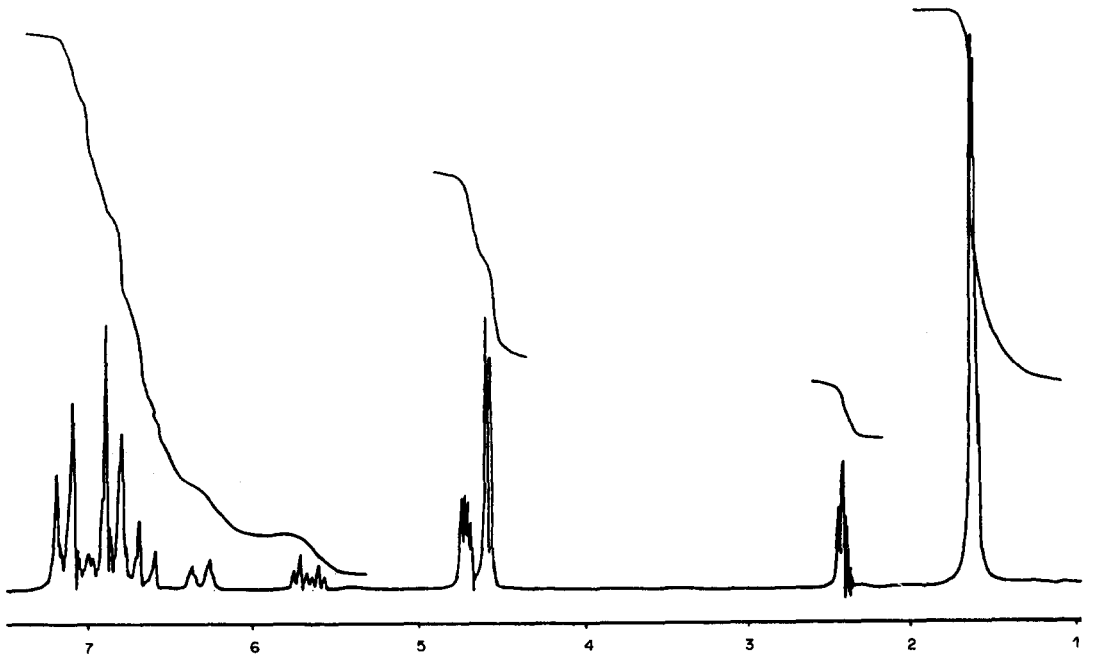


Fig. 1. ^{1}H-NMR spectrum (90 MHz) of I after being heated at 220° for 3 hr under N_2.

Finally, elution with 70/30 n-hexane/acetone separated unreacted I (^{1}H-NMR; m.p. 84–85°) as the only other compound (0.39 g; 48% of methanol-soluble fraction).

Polymerization of II

II (3 g) was heated at 220° under N_2 for 10 hr. The product dissolved in 30 ml of CH_2Cl_2 was added dropwise to 150 ml of methanol and the resulting precipitate of brown polymer was separated by filtration and washed with methanol. This precipitation procedure was repeated to yield 2.37 g (79% yield) of methanol-insoluble polymer after drying to constant weight under vacuum at 60° (^{1}H-NMR spectrum shown in Fig. 3 and ^{13}C-NMR in Fig. 4).

Analysis: calculated for $(C_{18}H_{18}O)_n$: C, 86.40; H, 7.25; O, 6.40. Found: C, 86.51; H, 7.11; O, 6.38.

The methanol-soluble fraction was dissolved in 100 ml of toluene and washed with hot 1 M aq. NaOH (4 × 10 ml). The NaOH extracts were neutralized with dil. HCl and the resulting mixture extracted with Et_2O. The combined Et_2O extracts were dried over $MgSO_4$. Evaporation afforded colourless crystals of *p*-cumyl phenol (0.18 g; 6% yield).

^{1}H-NMR ($CDCl_3$, TMS): δ 1.64 (s, 6H; $(C\underline{H}_3)_2CAr_2$), 4.66 (s, 1H; Ar$O\underline{H}$), 6.6–7.3 (m, 9H; $C_6\underline{H}_5$ and $C_6\underline{H}_4$) ppm.

m.p. 71–73° [mixed m.p. with authentic sample (Aldrich)].

i.r.: 3510 m (br) cm^{-1}.

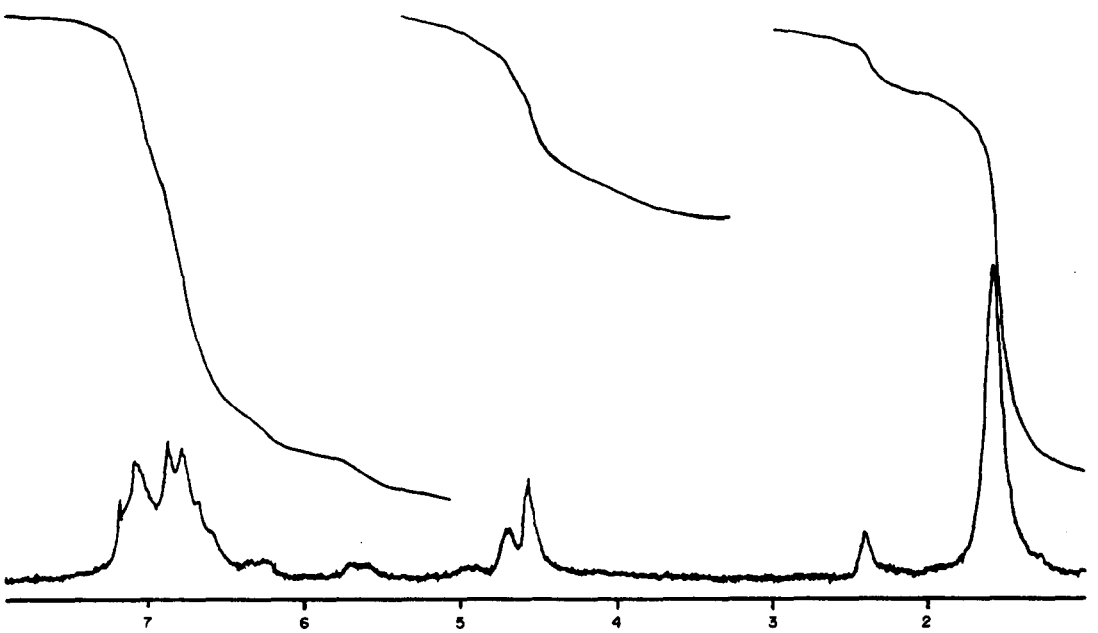


Fig. 2. ^{1}H-NMR spectrum (90 MHz) of the methanol-insoluble polymer obtained by heating I at 220° for 3 hr under N_2.

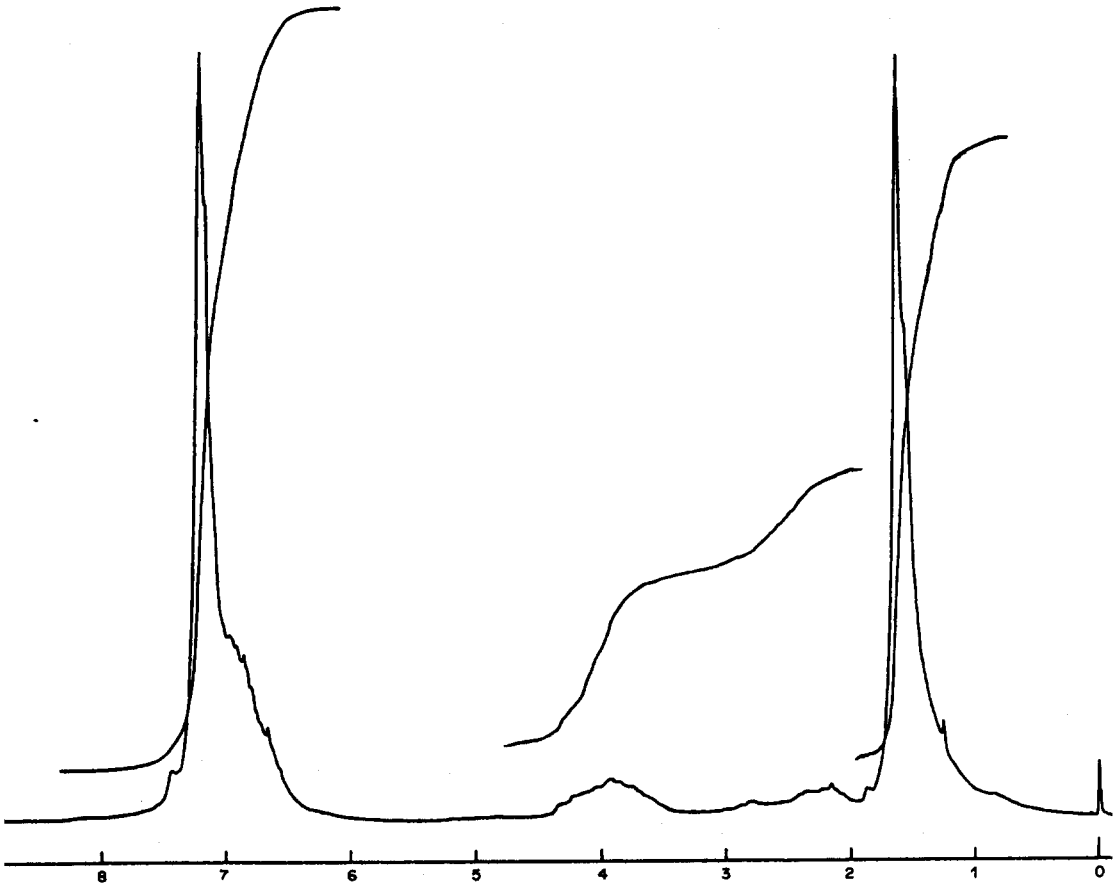


Fig. 3. ^{1}H-NMR spectrum (80 MHz) of the methanol-insoluble polymer obtained by heating II at 220° for 10 hr under N_2.

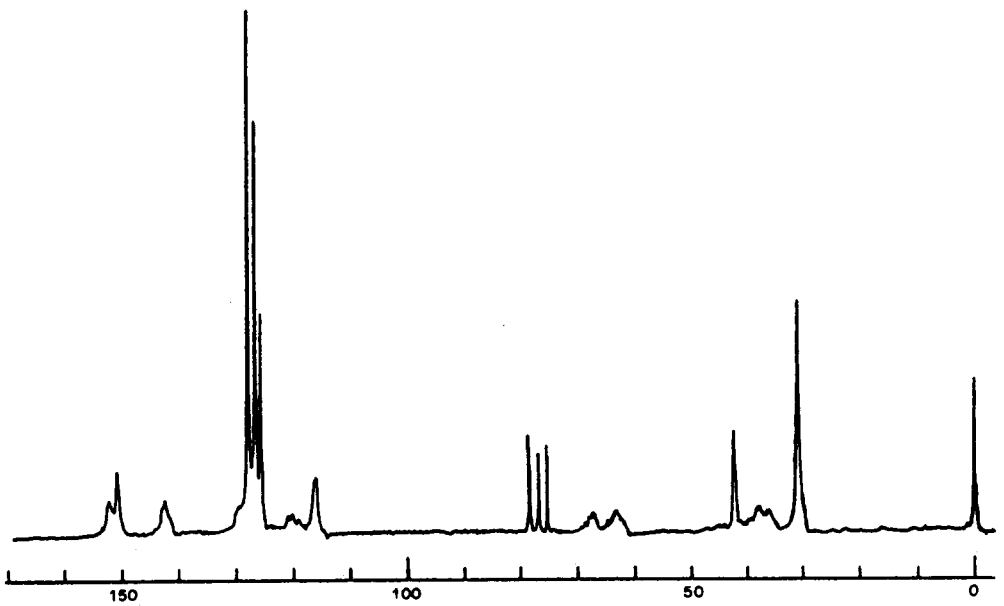


Fig. 4. ^{13}C-NMR spectrum (20.115 MHz) of the methanol-insoluble polymer obtained by heating II at 220° for 10 hr under N_2.

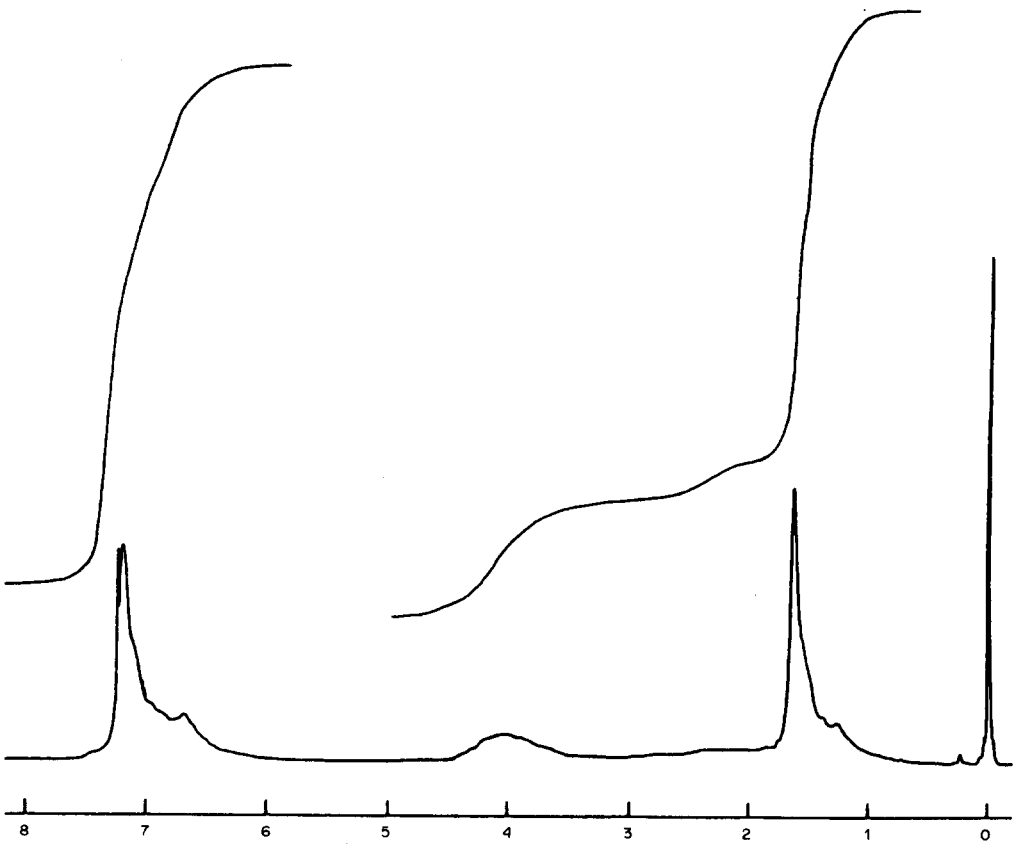


Fig. 5. ^{1}H-NMR spectrum (80 MHz) of the methanol-insoluble polymer obtained by heating **III** at 220° for 10 hr under N_2.

Analysis: calculated for $C_{15}H_{16}O$: C, 84.87; H, 7.60; O, 7.54. Found: C, 84.82; H, 7.61; O, 7.57.

Polymerization of III

III (3 g) was heated at 220° under N_2 for 10 hr. The product dissolved in 40 ml of CH_2Cl_2 was added dropwise to 180 ml of methanol and the resulting precipitate of yellow polymer was separated by filtration and washed with methanol. This precipitation procedure was repeated to yield 1.62 g (54% yield) of methanol-insoluble polymer after drying to constant weight under vacuum at 60° (^{1}H-NMR spectrum shown in Fig. 5 and ^{13}C-NMR in Fig. 6).

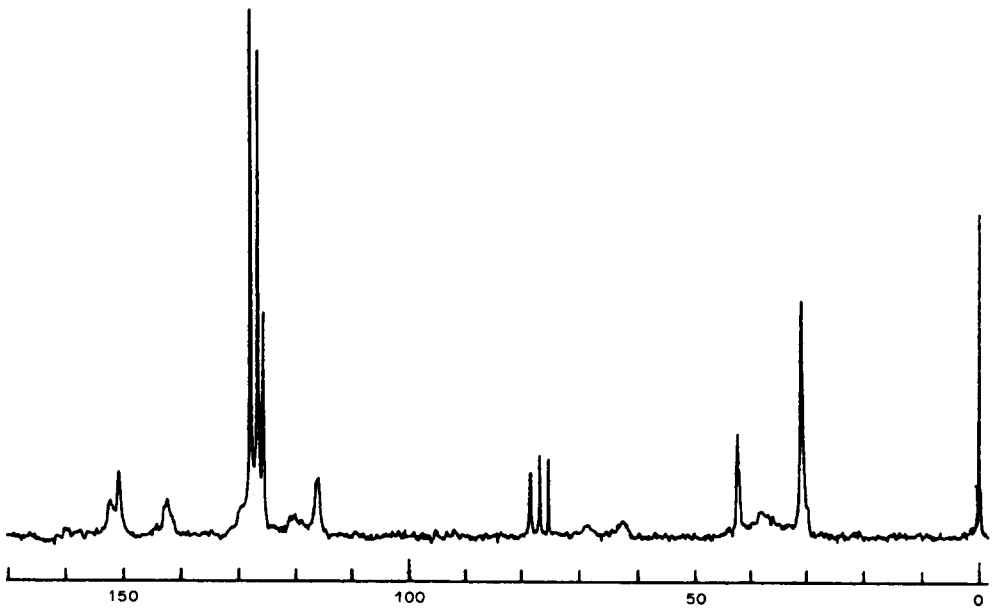
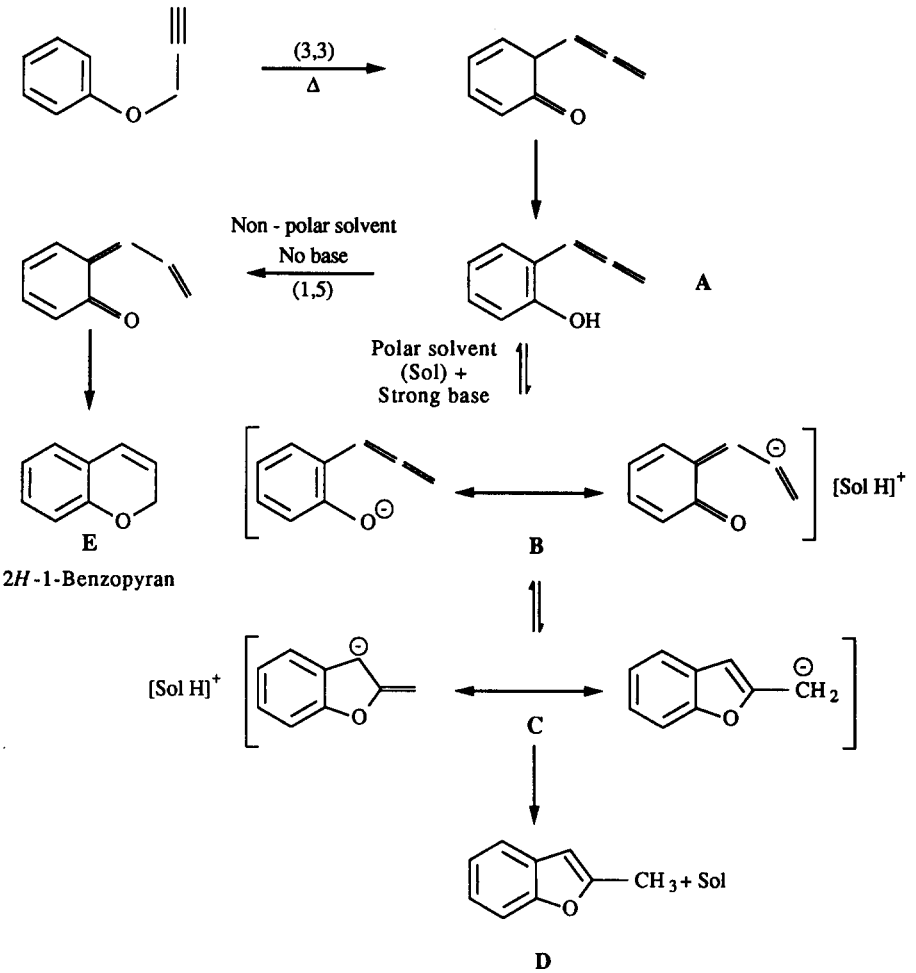


Fig. 6. ^{13}C-NMR spectrum (20.115 MHz) of the methanol-insoluble polymer obtained by heating **III** at 220° for 10 hr under N_2.



Scheme 1

Analysis: calculated for $(C_{18}H_{18}O)_n$: C, 86.40; H, 7.25; O, 6.40. Found: C, 86.55; H, 7.15; O, 6.30.

The methanol-soluble fraction afforded a yellow oil on evaporation, identified as being unreacted **III** from its ^{1}H-NMR and i.r. spectra.

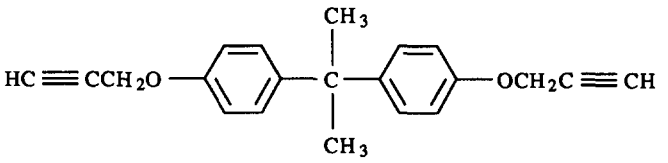
RESULTS AND DISCUSSION

Di-arylpropargyl ether terminated monomers are cured by being heated at temperatures above 200° for several hours [10]. Until the results of the present study were made known [6], the reactions during curing were unidentified. However, it was known [11–13] that in solution arylpropargyl ethers undergo thermal sigmatropic rearrangement reactions (Scheme 1) giving the phenol (**A**), 2*H*-1-benzopyran (**E**) or benzofuran (**D**) depending on the reaction conditions. The equilibrium between **B** and **C** favours the former, and if the mixture is treated with a strong acid the phenol (**A**) can be isolated. In the case of rearrangement in a non-polar solvent such as decalin in the absence of base, the dissociation of the phenol **A** giving the phenoxide **B** is very unfavourable and so the reaction leads to the 2*H*-1-benzopyran **E**. On the other hand, in a polar solvent in the presence of a strong base (e.g. sulpholane/K_2CO_3) the phenoxide **B** is readily formed and leads to benzofuran **D** as the product. It should be noted that this is what occurs in solution whereas, in the case of the bulk polymerization of arylpropargyl ether terminated monomers, the only solvent present is the molten mixture itself.

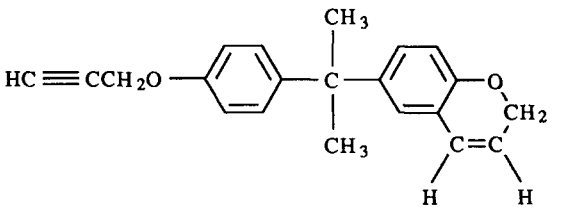
The di-arylpropargyl ether terminated monomer **I** was synthesized in 50% yield by reaction between bisphenol-A and propargyl bromide in aqueous base following the method described [10]. In the same way, the model mono-arylpropargyl ether terminated monomer **II** was prepared for study of the curing reactions.

Dynamic DSC (16°/min) of **I** showed a sharp m.p. at 85° and a large exotherm beginning at 220°, reaching a maximum at 278° and finishing at 320° [8]. The enthalpy of polymerization was 185 ± 8 kJ/mol ethynyl group. Isothermal DSC at 220° revealed polymerization to be complete after 10 hr and the enthalpy of polymerization was confirmed as being 180 ± 8 kJ/mol ethynyl group.

A sample of **I** was heated at 220° for 3 hr until just before gelation occurred. The ^{1}H-NMR spectrum (Fig. 1) shows a decrease of 55 ± 5% in the acetylene signal at δ 2.49 ppm and the appearance of CH_2

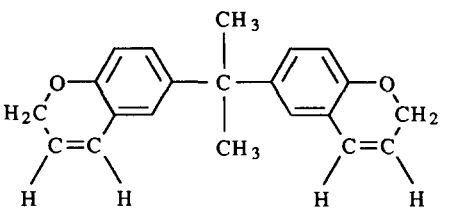


I



Mono-2*H*-1-Benzopyran

IV



Di-2*H*-1-Benzopyran

V

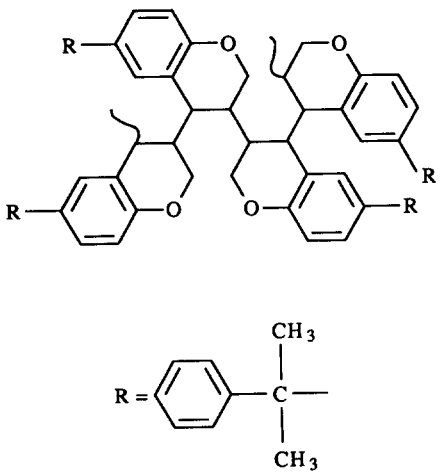
Polymer

Scheme 2

signals at δ 4.72 ppm together with vinyl resonances at δ 5.65 ppm and δ 6.33 ppm. These CH_2 and vinyl signals demonstrate formation of 2*H*-1-benzopyran groups [13] during polymerization (Scheme 2). The alternative rearrangement giving benzofuran groups does not occur as shown by the absence of signals at *ca* δ 2.3 ppm assigned to the Me group [13]. However, the i.r. spectrum provides evidence for some phenol formation although this is not visible in the NMR.

The partly polymerized sample was separated into a methanol-insoluble polymer and a methanol-soluble fraction. From the latter, three compounds were isolated by chromatography: unreacted I (48% yield), the mono-2*H*-1-benzopyran (IV) (11% yield) and the di-2*H*-1-benzopyran (V) (16% yield) which were identified from their ^{13}C-NMR and/or ^{1}H-NMR spectra.

The ^{1}H-NMR spectrum of the methanol-insoluble polymer (Fig. 2) shows signals characteristic of acetylene and 2*H*-1-benzopyran groups. TLC indicated that none of the three components in the methanol-soluble fraction was present. DSC showed an exotherm beginning at 200° and reaching a maximum at 270° with an enthalpy of polymerization of 203 J/g. The intermediate polymer is thus probably highly branched possessing both acetylene and 2*H*-1-benzopyran groups which undergo further polymerization on heating. At this stage in the investigation, 2*H*-1-benzopyran groups appeared to be precursors to the final polymer. In order to study this further, the



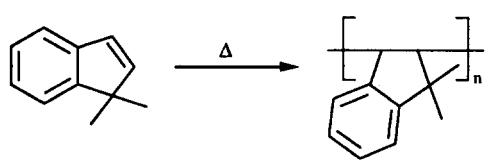
Scheme 3

curing reactions of the model monomer *p*-cumylpropargyl ether **II** were examined since unlike **I** it should be possible to polymerize **II** to high conversion without gelation. In addition, the resulting polymer should be free of 2*H*-1-benzopyran and acetylene groups except for those occurring at chain-ends.

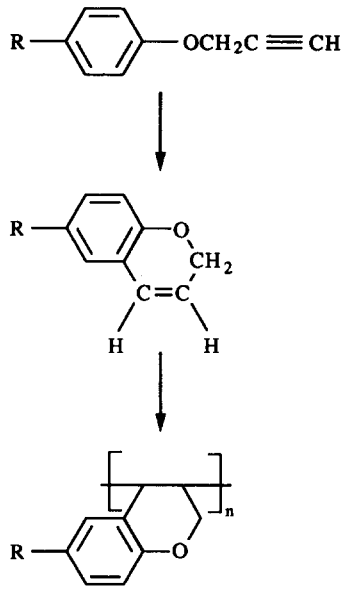
A sample of **II** was polymerized at 220° under N_2 for 10 hr. The disappearance of acetylene and appearance of 2*H*-1-benzopyran proton resonances, and subsequent disappearance of the latter, was followed in the ^{1}H-NMR spectrum. The reaction mixture was separated by precipitation into a pale-brown methanol-insoluble polymer (79% yield) and a methanol-soluble fraction.

The methanol-soluble fraction was found to contain 6% *p*-cumylphenol identified by i.r. and ^{1}H-NMR spectra, elemental analysis and mixed m.p. with an authentic sample. This formation of a small amount of phenol can be compared to that occurring during polymerization of **I** (*vide supra*).

The methanol-insoluble polymer had $\bar{M}_n$ of 1900 g mol^{-1} ($\overline{DP}_n$ 7.6) as determined by VPO. DSC showed a T_g at 89° but no exotherm below 320°. The absence of both an exotherm and also acetylene and 2*H*-1-benzopyran proton signals in the ^{1}H-NMR spectrum (Fig. 3) suggests that no polymerizable groups remain in the polymer. The ^{1}H- (Fig. 3) and ^{13}C-NMR spectra (Fig. 4) provide some information as to the structure of the main chain of the polymer. The broad proton signal between δ 1–3 ppm and the broad ^{13}C signal in the range δ 28–40 ppm are characteristic of aliphatic $R_{4-n}CH_n$ groups, whilst the δ 3.5–4.5 ppm proton signals and the broad ^{13}C resonances centred at δ 62 and 68 ppm are characteristic of phenoxide —CH_2OAr groups. The spectroscopic data suggest that the polymer has the structure shown in Scheme 3.



Scheme 4



Scheme 5

Finally, the 2*H*-1-benzopyran monomer **III** was synthesized by thermal cyclization of **II** in decalin in the presence of benzoic acid. The polymer obtained on curing **III** at 220° for 10 hr under N_2 was compared with that from cure of **I**. The ^{1}H-NMR spectrum showed that unreacted monomer was still present, and it was separated as a methanol-soluble fraction. The yellow methanol-insoluble polymer precipitated on addition of methanol (54% yield) had M_n of 1600 g mol^{-1} as determined by VPO ($\overline{DP}_n$ 6.4). DSC showed a T_g at 85° but no exotherm below 320°. The ^{1}H- (Fig. 5) and ^{13}C-NMR (Fig. 6) are virtually identical to those for the polymer obtained from **I**.

In summary, the results of this study have shown that polymerizations of the arylpropargyl ether terminated monomers **I** and **II** at 220° involve initial rearrangement to 2*H*-1-benzopyran groups which subsequently polymerize. Such sigmatropic rearrangements are observed for arylpropargyl ether groups in non-polar solvents in the absence of base [11–13]. In the case of **I** and **II**, the only solvent present is the molten mixture itself and the conditions should therefore approximate to those for a non-polar solvent. As regards subsequent polymerization of the 2*H*-1-benzopyran groups, it is known that indene, which has a similar reactive double bond, polymerizes at 200° to give a low molecular weight polymer with the structure shown in Scheme 4 [14]. We therefore propose that the uncatalyzed curing reactions of arylpropargyl ether terminated monomers are those shown in Scheme 5.

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