New Types of Cross-Linkable Polymers Containing the *trans*-1,2-Diphenylcyclopropane Moiety

Chunping Gao and Allan S. Hay*

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 2K6

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ABSTRACT: High molecular weight poly(ether sulfone)s, polyformals, and polyesters have been synthesized from the monomer *trans*-1,2-bis(4-hydroxyphenyl)cyclopropane by solution polycondensation. Characterization of and cross-linking studies on these polymers were carried out utilizing DSC, TGA, TMA, GPC, and solution and solid state NMR. The polymers can be thermally cross-linked when heated to 350 °C, and the glass transition temperatures (T_g) of the polymers increase after cross-linking. The resulting cross-linked networks are insoluble in all solvents tried. It was confirmed by MAS-^{13}C NMR that the cyclopropane rings were opened on heating. Thermogravimetric analysis shows that no significant weight loss accompanies the cross-linking reaction.

Introduction

Cross-linkable polymers are an important class of materials used in fiber-reinforced plastics, thermosetting molding compounds, elastomers, coatings, adhesives, ion exchange resins, matrix resins for advanced composites, and many other applications. A great deal of effort has been expended on the introduction of reactive functionality into polymers which will act as sites for cross-linking polymers when heated.

The largest effort has been centered on the synthesis of polymers which contain terminal reactive groups such as acetylene-containing moieties. Generally, this involves the preparation of oligomers[1–5] with reactive end groups which can subsequently be thermally chain extended to produce a highly cross-linked polymer matrix. Polymers containing reactive pendent groups have also been synthesized, and these polymers have also been thermally cured.[6,7]

Polymers containing internal reactive groups have been less studied.[1,8] High-temperature cross-linkable polymers containing reactive groups such as acetylene, benzocyclobutene, ethylene, and epoxide have been investigated. A recent paper[9] reported the synthesis of polymers derived from 1,1-bis(hydroxymethyl)cyclopropane. The polymerization and characterization of elastomeric polyethers containing the cyclopropane group were described. They found that the cyclopropane-containing polymers show no exothermic reaction below 200 °C and exhibit TGA stability characteristic of aliphatic hydrocarbon polymers with a break point of approximately 220 °C under a nitrogen atmosphere.

Our effort[10,11] has been directed toward the synthesis of monomers which contain a reactive functionality which can be incorporated into high molecular weight linear polymers and copolymers which can then be cross-linked on heating or by photochemical means. The pyrolysis of small ring hydrocarbons has been very extensively investigated.[12] The use of cyclopropane moieties in polymers for cross-linking which is the subject of the present report does not appear to have been studied up to now. We synthesized the reactive monomer *trans*-1,2-bis(4-hydroxyphenyl)cyclopropane (**2**) (Scheme 1) designed to lie dormant throughout synthesis and processing but which can then be triggered to a reactive state at a later point. Poly(ether sulfone)s, polyformals, and polyesters have been synthesized.

Experimental Section

***trans*-1,2-Bis(4-hydroxyphenyl)cyclopropane (2).** *trans*-1,2-Bis(*p*-methoxyphenyl)cyclopropane[13,14] (**1**; 20.0 mmol, 5.08 g) was dissolved in methylene chloride (10 mL). The resulting solution was cooled with an acetone–dry ice bath, and 60 mL of a solution of 1 M BBr_3 in CH_2Cl_2 was added carefully to the stirred solution. When the addition was complete, the reaction temperature was slowly raised to room temperature with continued stirring. The reaction mixture was then hydrolyzed with water, and the aqueous phase was extracted with ether. The organic layer was separated and extracted with 2 N sodium hydroxide. The alkaline extract was neutralized with dilute hydrochloric acid and extracted with ether, and the ether extract was dried over anhydrous magnesium sulfate. On removal of the ether, the product was further purified by recrystallization from acetic acid, mp 190–192 °C. MS (*m/e*, relative intensity %): 226 (M^+, 100). ^{1}H-NMR (200 MHz, DMSO): δ 9.10 (s, 2H), 6.90 (d, 4H), 6.60 (d, 4H), 1.90 (t, 2H), 1.20 (t, 2H). Anal. Calc: C, 79.62; H, 6.24. Found: C, 79.40; H, 6.24.

Homopolymer 3. A mixture of *trans*-1,2-bis(4-hydroxyphenyl)cyclopropane (**2**; 3.0 mmol, 0.6788 g), K_2CO_3 (5.6 mmol, 0.774 g), and 4,4′-difluorodiphenyl sulfone (3.0 mmol, 0.7628 g) in toluene (4 mL) and *N,N*′-dimethylacetamide (8 mL, freshly purified) was heated with stirring under nitrogen atmosphere with azeotropic removal of water for 3 h. Some toluene was bled continuously from the Dean-Stark trap until the temperature rose to 155 °C. The reaction mixture was lightly colored and was maintained at this temperature for 2 h. At this time the reaction was assumed to be complete. The reaction mixture was cooled to 100 °C, diluted with *N,N*′-dimethylacetamide (5 mL), and filtered. The filtrate was neutralized with acetic acid and coagulated into methanol. The precipitate was filtered and washed with methanolic water and finally with water. It was then boiled in distilled water for 1 h to remove any trapped salts, filtered, and dried in a vacuum oven at 80 °C; yield >90%. ^{1}H-NMR (200 MHz, DMSO): δ 7.89 (d, 4H), 7.22 (d, 4H), 7.04 (m, 8H), 2.23 (t, 2H), 1.45 (t, 2H).

Copolymers 4–7. A mixture of *trans*-1,2-bis(4-hydroxyphenyl)cyclopropane (**2**; 0.6 mmol, 0.1359 g), the other bis(phenol) (2.4 mmol), K_2CO_3 (0.774 g), 4,4′-difluorodiphenyl sulfone (3.0 mmol, 0.7628 g), toluene (4 mL) and *N,N*′-dimethylacetamide (8 mL, freshly purified) was treated as described for the synthesis of the homopolymer.

Homopolymer 8. A mixture of *trans*-1,2-bis(4-hydroxyphenyl)cyclopropane (**2**; 10.0 mmol, 2.26 g), 4-*tert*-butylphenol (0.15 mmol, 0.0225 g), reagent grade methylene chloride (3.09 mL), and *N*-methyl-2-pyrrolidinone (5 mL) was stirred under nitrogen until a homogeneous solution was obtained. At this point 0.849 g of NaOH pellets was added and the mixture exothermed to 37

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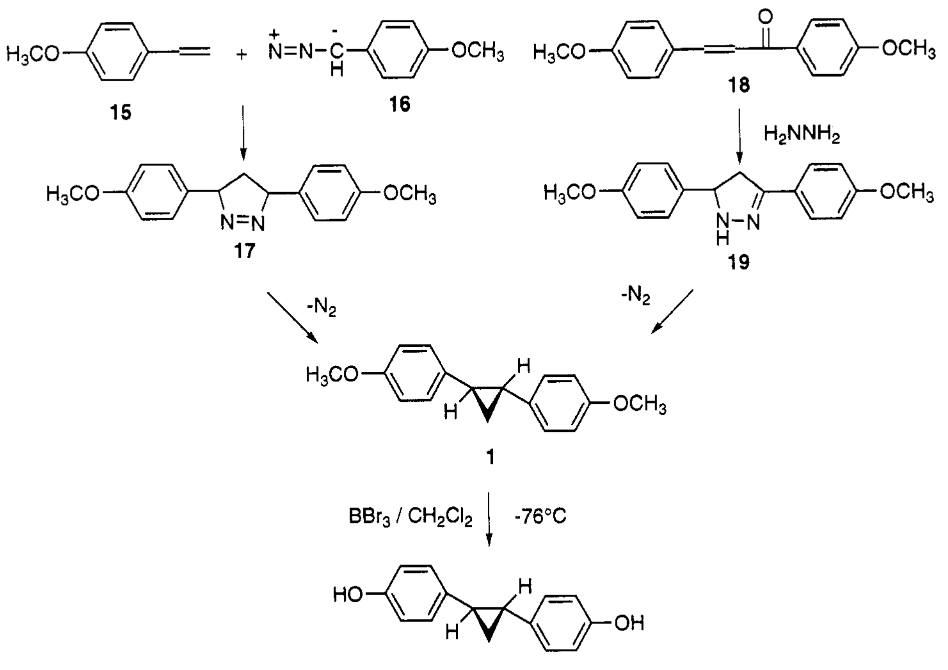
Scheme 1



°C. The mixture was placed in a 90 °C oil bath, and the solution was refluxed for 2 h, after which the solution was cooled and diluted with NMP. The mixture was allowed to cool to room temperature and the white solid (NaCl) was removed by filtration. The polymer was isolated by a reverse precipitation. This procedure involved the addition of a 50:50 (v/v) MeOH:acetone mixture to the polymer solution with stirring. The resulting solid was filtered and dried in a 75 °C vacuum oven; yield >90%. ^{1}H-NMR ($CDCl_3$): δ 7.00 (s, 8H), 5.65 (s, 2H), 2.00 (t, 2H), 1.30 (t, 2H).

Copolymers 9–11. The copolymers were made by the procedure described for the synthesis of the homopolymer using 2,2-bis(4-hydroxyphenyl)propane (BPA) and *trans*-1,2-bis(4-hydroxyphenyl)cyclopropane.

Polyesters 12–14. A solution of bis(phenol(s)) (2.5 mmol) and sodium hydroxide (0.2 g) in water (15 mL) was prepared in a blender. A second solution containing acid chloride(s) (2.5 mmol) in chloroform (7.5 mL) was prepared in a beaker. A solution of Duponol ME (sodium lauryl sulfate, 0.15 g) detergent in water (1.5 mL) was added to the slowly stirred aqueous solution in the blender, and the blender was run at maximum speed. The acid chloride solution was added as rapidly as possible, and the emulsion so formed was stirred for 5 min. The reaction mixture was filtered, and the polymer was washed well with methanol and dried.

Characterization of Polymers. Glass transition temperatures of the polymers were obtained using a Seiko 220 DSC instrument at a heating rate of 10 °C/min in nitrogen (50 mL/min) and a Seiko 220 TMA instrument at a heating rate of 3 °C/min. When T_g values were recorded, samples were never heated above 300 °C, to avoid cross-linking, and the values recorded were from the second scan. The T_g was taken from the midpoint of the change in slope of the baseline. The weight loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 10 °C/min in nitrogen and air. Polymer samples were cured at 350 °C under nitrogen in the TGA instrument. A DSC was then employed to determine the T_g increase. Inherent viscosity data were obtained with a calibrated Ubbelohde viscometer. The measurements were performed in $CHCl_3$ at 25 or 50 °C with a 1B(205) instrument. Molecular weights were obtained by gel permeation chromatography (GPC) relative to polystyrene standards in chloroform solution using a Waters 510 HPLC instrument equipped with μ-Styragel columns (500, 10^3, 10^4, and 100 Å) arranged in series and a UV detector. ^{1}H-NMR spectra were recorded at 200 MHz using a Varian XL-200 spectrometer in $CDCl_3$ with $(CH_3)_4Si$ as the internal standard.

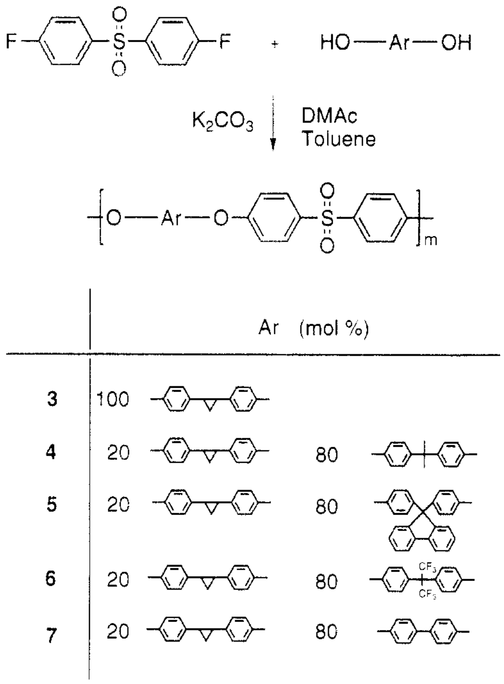
Solid State NMR. CP-MAS ^{13}C-NMR spectra and DP-MAS ^{13}C-NMR spectra were obtained in zirconium rotors on a Chemagnetics CMX-300 spectrometer at 75 MHz with spinning speeds of 5 kHz. All experiments were performed with a contact time of 1 ms and recycle delays of 1 s. The ^{1}H p/2 pulse width was 4 ms. The number of transients varied from 60 000 to 80 000. A sensitivity enhancement of 50 Hz was applied to the FID prior to Fourier transformation.

Swelling. Film strips with dimensions of ca. 0.1 × 3 × 10 mm were cured at 320 °C in a vacuum oven. The cured film strips were put into chloroform, and the change in area of the films was measured at specific time intervals.

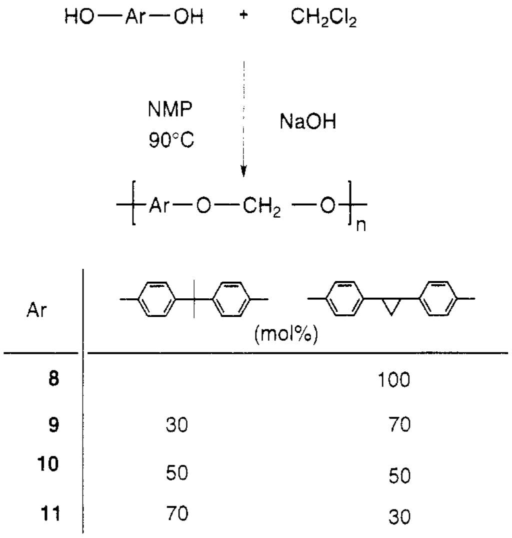
Results and Discussion

Monomer Synthesis. Overberger[13] reported a synthesis of *trans*-1,2-bis(4-methoxyphenyl)cyclopropane (**1**) (Scheme 1) by thermal and photolytic decomposition of 3,5-bis(4-methoxyphenyl)-1-pyrazoline (**17**) which was made by the reaction of (4-methoxyphenyl)diazomethane (**16**) with 4-methoxystyrene (**15**). The yield of the reaction to make 3,5-bis(4-methoxyphenyl)-1-pyrazoline (**17**) was only 35%. We found the method of Hamada[14] to be superior (Scheme 1). 4,4′-Dimethoxybenzylideneacetophenone (**18**) reacts with hydrazine hydrate to afford 3,5-bis(4-methoxyphenyl)-2-pyrazoline (**19**) which was converted to *trans*-1,2-bis(4–methoxyphenyl)cyclopropane (**1**) by base-catalyzed decomposition. Demethylation of **1** with BBr_3 in methylene chloride gave *trans*-1,2-bis(4-hydroxyphenyl)cyclopropane (**2**) in quantitative yield. The product was purified by recrystallization from acetic acid. This monomer was designed with several criteria in mind. First, the monomer's reactivity was chosen such that it would not interfere with polymer synthesis and processing methods typically employed for poly(ether sulfone)s, polyformals, and polyesters. This required a cross-linkable group that would be stable to alkali up to 200 °C. Second, the functional group should be thermally stable up to the T_g in order that cross-linking could be carried out in the melt. Third, cross-linking should occur without evolution of volatile byproducts and should involve a highly reactive intermediate in order to maximize conversion. Monomer **2** which contains the 1,2-diphenylcyclopropane moiety was chosen for this study.

Scheme 2



Scheme 3



Polymer Synthesis. Poly(ether sulfone)s have been studied since the 1960s. Two major methods have been developed for the synthesis of poly(ether sulfone)s. One method involves the base-mediated nucleophilic displacement of aromatic bis(phenols) with activated aromatic bis(halides). The second major method involves a Friedel–Crafts type polysulfonylation of aromatic substrates with aromatic bis(sulfonyl chlorides). For the first method, dimethyl sulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP), and tetramethylene sulfone have been used as the solvent. NMP or tetramethylene sulfone is used if the polymerization needs to be carried out at a higher temperature. In the present case, polymer hydrolysis and bis(phenolate) insolubility posed a problem in the synthesis when DMSO was used as solvent. Therefore the potassium carbonate/DMAc route was chosen because, in this system, excess potassium carbonate does not prevent the synthesis of high molecular weight macromolecules.

trans-1,2-bis(4-hydroxyphenyl)cyclopropane (**2**) was polymerized with 4,4′-difluorodiphenyl sulfone to give a poly(ether sulfone) by employing standard conditions in DMAc in the presence of excess (20%) anhydrous potassium carbonate. A series of copolymers was also synthesized from *trans*-1,2-bis(4-hydroxyphenyl)cyclopropane (**2**), bis(phenols), and 4,4′-difluorodiphenyl sulfone (Scheme 2) under the same conditions. All polymers were characterized by ^{1}H NMR. In the ^{1}H-NMR spectrum of polymer **3**, two triplets at 2.23 and 1.45 ppm were observed for the benzylic protons and the methylene protons in cyclopropane and a doublet at 7.89 ppm for protons ortho to the sulfone group, a doublet at 7.22 ppm for protons ortho to the cyclopropane group, and a multiplet for protons ortho to the ether linkage were observed. It can be concluded from these results that monomer **2** is stable under the polymerization conditions.

We previously developed a very simple method for the synthesis of polyformals[15] by the reaction of bis(phenols), such as Bisphenol A (BPA), and methylene chloride or methylene bromide in the presence of a phase-transfer catalyst or in an aprotic dipolar solvent. For this method, one does not need to control the stoichiometry of the starting monomers as in the usual nucleophilic displacement polymerization reactions because the first intermediate formed in the reaction between the phenoxide anion and methylene chloride is much more reactive than methylene chloride. When a phase-transfer catalyst was used, methylene chloride can be both solvent and reactant. The T_g of the polyformal from BPA is only 96 °C which limits its usefulness. Reaction of *trans*-1,2-bis(4-hydroxyphenyl)cyclopropane (**2**) in a 60:40 NMP/methylene chloride mixture in the presence of NaOH gave a high molecular weight polymer. It was found that there were some cyclics formed if the reaction temperature is maintained below 70 °C. The sodium or potassium salts of BPA are quite insoluble at lower temperatures; therefore, the reaction proceeds as if it were being carried out under high dilution conditions as a result of the slow dissolution of the salt. At 90 °C the salts are more soluble, the reaction is rapid, and cyclic formation is minimized. 4-*tert*-Butylphenol is used as the end-capping agent to avoid formation of extremely high molecular weight polymers. A series of copolymers from **2**, BPA, and methylene chloride were prepared under similar conditions (Scheme 3). The polymers were characterized by ^{1}H NMR. In the ^{1}H-NMR spectrum of polymer **8** two triplets at 2.00 and 1.30 ppm were observed for the benzylic protons and methylene protons in the cyclopropane group and a singlet for the formal protons and a singlet for the aromatic protons were observed.

Interfacial polycondensation[16] was used to synthesize the poly(aryl ester)s. Homopolymers and high molecular weight copolymers were prepared from **2**, BPA, and isophthaloyl and terephthaloyl chloride by interfacial polycondensation using typical conditions, as described in the literature (Scheme 4).[16]

Properties of Polymers. The properties of the poly(ether sulfone)s are listed in Table 1. All the uncured polymers are soluble in chloroform. Flexible and transparent films can be obtained by casting from chloroform solution at room temperature. When films of these polymers are heated, they maintain good mechanical properties above 200 °C. Poly(ether sulfone)s with inherent viscosities in the 0.35–0.62 range and with T_g's in the range from 189 to 261 °C were prepared. The T_g of poly(ether sulfone) **3** is 189 °C, which is almost the same as that of the poly(ether sulfone) from Bisphenol A. The molecular weight distribution of the polymers was determined by GPC on the basis of polystyrene standards. GPC results are consistent with their inherent viscosities. Polydispersities of these polymers are less than 3, sug-

Table 1. Properties of Polysulfones

polymers	T_g(uncured), °C DSC/tan δ[a]	T_g(cured), °C[b]	η_{inh},[c] dL/g	TGA,[d] °C N_2 (−5%)	M_w/M_n[e]
3	189/180	ND	0.35	450	39 976/19 988
4	184/148	207	0.41	438	63 375/22 080
5	261/248	293	0.56	449	88 404/44 294
6	183/152	222	0.60	428	95 534/44 990
7	230/216	246	0.62	451	91 967/46 758

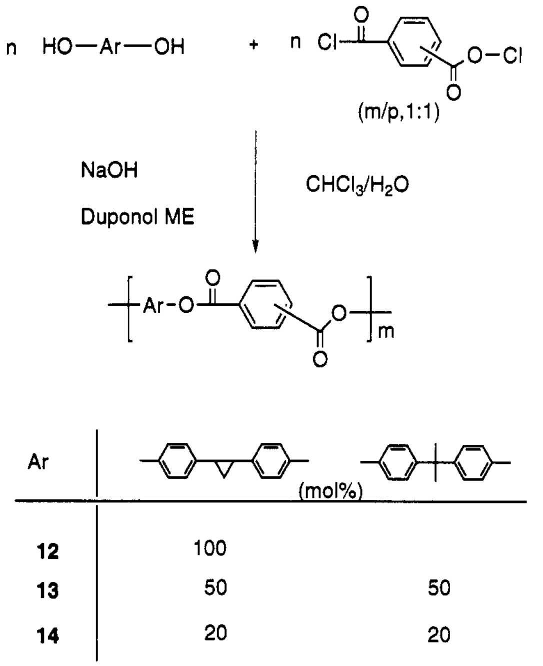
[a] DSC, heating at 10 °C/min. TMA, temperatures were recorded where the tan δ curve shows a maximum. [b] After curing for 2 h at 350 °C under nitrogen. [c] 5 g/dL in $CHCl_3$ at 25 °C. [d] TGA, heating at 10 °C/min. ND means that no T_g was detected in DSC. [e] GPC, based on polystyrene standards.

Table 2. Properties of Polyformals

polymers	η_{inh},[a] dL/g	T_g, °C[b] DSC/tan δ	T_g, °C[c] (cured)	TGA, °C[d] N_2/air (−5%)	solubility	M_w/M_n[a]
8	0.58	98.5/85.0	ND	433/411	DMAc	
9	0.40	92.9/76.0	ND	438/416	$CHCl_3$	36 253/21 632
10	0.45	95.0/75.0	128.0	444/405	$CHCl_3$	35 169/20 576
11	0.40	95.3/78.0	116.0	433/411	$CHCl_3$	33 138/18 294

[a] 5 g/dL in $CHCl_3$ at 25 °C or in DMAc at 50 °C. [b] DSC heating at 10 °C/min. [c] After curing for 2 h at 350 °C under nitrogen. [d] TGA, heating at 10 °C/min. [e] GPC, based on polystyrene standards.

Scheme 4



gesting that the polymerization reaction proceeds without any unusual termination reactions that might be ascribed to the cyclopropane moiety. Thermogravimetric analyses of these polymers show no significant weight loss (−5%) occurs before 430 °C, which is similar to the poly(ether sulfone) from BPA.

Properties of the polyformals are summarized in Table 2. The polyformal homopolymer 8 with inherent viscosity 0.58 dissolves with difficulty in chloroform and is very soluble in DMAc at higher temperatures, while all the copolymers are soluble in chloroform at room temperature. The T_g of the polyformal 8 from *trans*-1,2-bis(4-hydroxyphenyl)cyclopropane (2) is 98.9 °C, which is slightly higher than that of the polyformal from BPA. Films can be readily cast from chloroform which are all very tough and flexible. Molecular weights of these polymers obtained by GPC relative to polystyrene standards are consistent with their inherent viscosities in chloroform solution. There is no significant weight loss (−5%) by TGA before 430 °C in nitrogen which is similar to the homopolyformal from BPA which is very thermally stable in both nitrogen and air.

Table 3. Properties of Polyesters

polymers	η_{inh},[a] dL/g	T_g, °C[b] (uncured)	T_g, °C[c] (cured)	TGA, °C[d] N_2/air (−5%)	solubility
12				435/420	
13	1.38	208.2	ND	426/421	DMAc
14	1.51	208.0	236	464/430	DMAc

[a] 5 g/dL in DMAc at 50 °C. [b] DSC, heating at 10 °C/min. [c] After curing for 2 h at 350 °C under nitrogen. [d] TGA, heating at 10 °C/min.

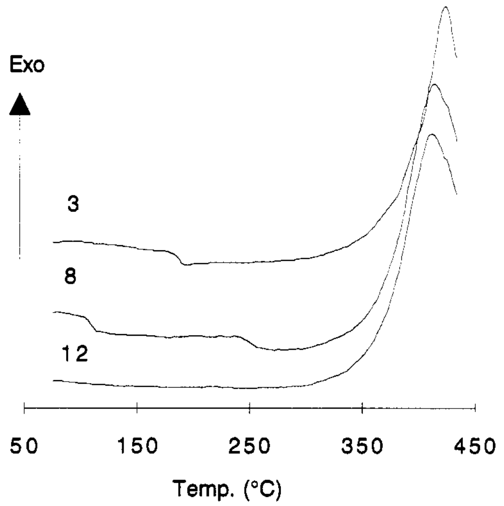


Figure 1. DSC thermograms of polymers 3, 8, and 12.

The properties of the polyesters are listed in Table 3. The polyester homopolymer precipitates from the reaction mixture during the polymerization and is infusible and insoluble in all organic solvents tried. High molecular weight copolymers 13 and 14 which are soluble in DMAc at higher temperatures can be readily prepared. Polymers 13 and 14 are amorphous with a glass transition at 208 °C, and no melting points are observable in the DSC scans. No significant weight losses (−5%) are observed by TGA for the polyesters before 426 °C in nitrogen.

Cross-Linking Studies. The DSC scans of homopolymers 3, 8, and 12 are shown in Figure 1. For poly(ether sulfone) 3 and polyformal 8 a T_g was observed, while no T_g was found in the DSC scan of polyester 12. Exotherms which are associated with the cross-linking reaction begin at 300 °C and reach maxima at 415 °C for all of the polymers. The cross-linking reaction proceeds readily at 350 °C. In the DSC scans of the homopolymers 3, 8, and

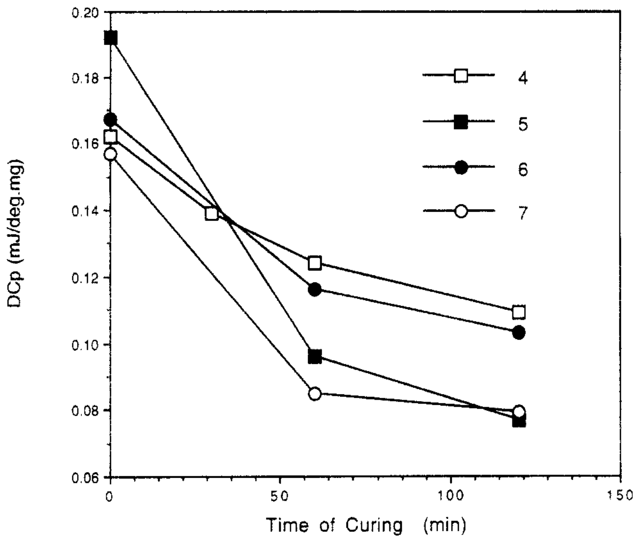


Figure 2. Effect of curing time on DCp at T_g (350 °C under N_2). DCp at T_g was obtained in a DSC.

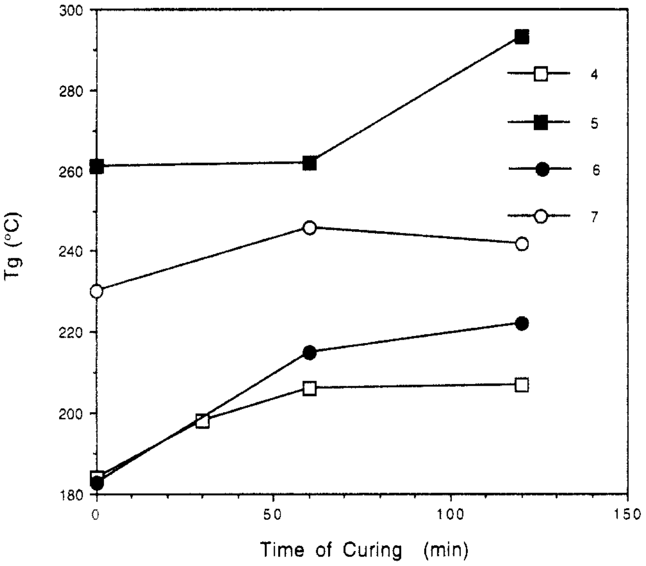


Figure 3. DSC scans showing the effect of curing time on T_g (350 °C under N_2, heating rate 10 °C/min).

12 no T_g is detected if they are cured at 350 °C under nitrogen for longer than 30 min.

Thermal analysis is frequently used to characterize cross-linked polymers. It is well-known that the T_g rises while the difference in specific heat capacity (DCp) at T_g decreases with increasing numbers of cross-links. The effect of curing time on the difference in specific heat capacity (DCp) at T_g (Figure 2) and on the T_g (Figure 3) of the poly(ether sulfone) copolymers containing 20 mol % of cyclopropane moieties has been studied. After copolymers 4–7 were cured at 350 °C under nitrogen in TGA for different time periods, the cured polymers were examined in the DSC to determine the T_g increase and DCp decrease. It was found that DCp decreased rapidly and T_g increased as curing time increased as a result of the cross-linking of the polymers. Among the copolymers 4–7, the DCp of copolymer 5 decreased most and its T_g increased most with increased curing time. After 1 h the changes in DCp and T_g slowed down significantly.

The effect of curing time on DCp and T_g of polyformals and polyesters containing different amounts of cyclopropane groups was also studied. As expected, for the same curing time the higher the content of cyclopropane group in the polymers, the larger the change in T_g and DCp. No

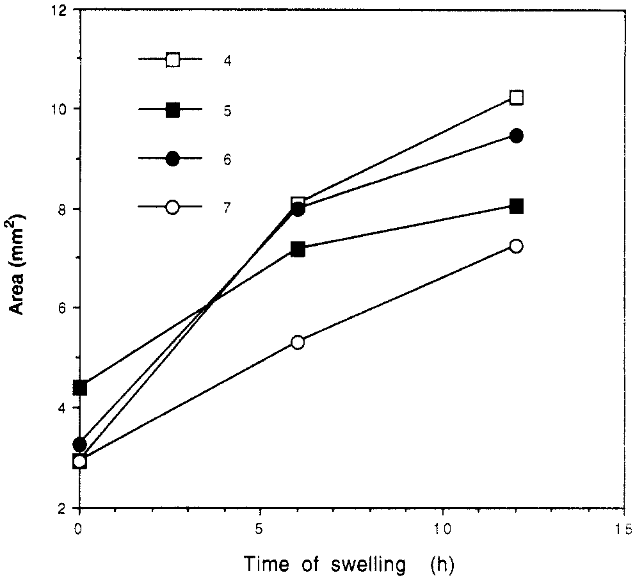


Figure 4. Swelling of polymers in chloroform (25 °C after curing for 2 h at 320 °C under N_2).

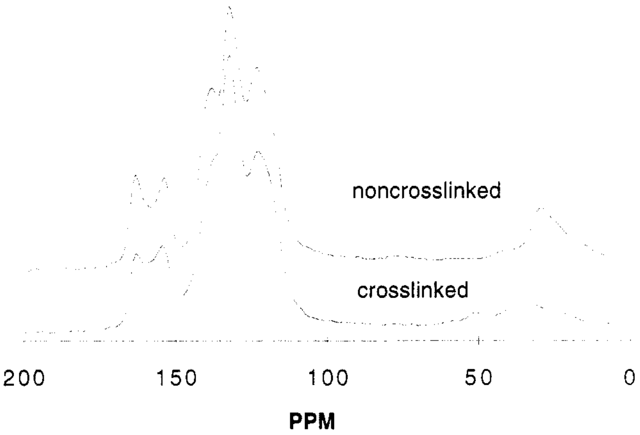


Figure 5. CP-MAS ^{13}C-NMR spectra of non-cross-linked and cross-linked polymer 3. Cross-linking reaction at 350 °C for 2 h under N_2.

T_g is detected by DSC after 2 h of curing at 350 °C in nitrogen when the content of the cyclopropane group in polyformals is higher than 70% and that in the polyesters is higher than 50%.

The cured polymers were insoluble in chloroform. The polymer films which were cured at 350 °C for 2 h were placed in chloroform at room temperature to test solubility and swelling. Homopolymers 3, 8, and 12 show no observable swelling over 24 h in chloroform, while all the copolymers swell to a certain degree. The swelling of polymers 4–7 in chloroform is shown in Figure 4. The area of their films rises with the time of swelling. After swelling for 6 h, the area of the polymer films increases by 16–47%. Polymer 5 swells least among them. Swelling studies of polymers 9–11, 13, and 14 show that the greater the content of diphenylcyclopropane moiety in its backbone, the less the polymer swells after cross-linking.

CP-MAS ^{13}C-NMR Studies. In an attempt to better understand the cross-linking chemistry of the polymers, CP-MAS ^{13}C-NMR spectra were taken for non-cross-linked and cross-linked polymers 3, 8, and 12. Typical spectra for non-cross-linked and cross-linked polymers 3 are presented in Figure 5. We also obtained dipolar dephasing magic angle spin (DP-MAS) ^{13}C solid state NMR spectra of non-cross-linked and cross-linked polymers 3, 8, and 12 to use as an assignment tool. Typically, after a 60 μs delay, most of the methylene and methine carbon signals disappear from the spectrum; only nonprotonated carbons and methyl carbons remain in the DP-MAS ^{13}C solid state NMR spectra since they are weakly coupled to the protons. By a combination of dipolar dephasing- and cross-polarized-MAS ^{13}C solid NMR the assignments for the solid state NMR spectra of the polymers was possible.

Peaks at 162.69, 152.91, and 136.90 ppm, which were the signals of nonprotonated carbons, were observed in the DP-MAS ^{13}C NMR spectrum of polymer **3**. The peak at 162.69 ppm is assigned to the aromatic carbons bonded to the sulfonyl groups, the peak at 152.91 ppm is the signal of the aromatic carbons connected to the oxygen atoms, and the peak at 136.90 ppm is due to the aromatic carbons bonded with the cyclopropane group. The other protonated carbon signals overlap to give peaks at 130.25, 121.66, and 116.97 ppm. The peak at 28.68 ppm is assigned to the aliphatic cyclopropane carbons.

After cross-linking polymer **3**, the signals of the cyclopropane aliphatic carbons, peaks at 26.68 ppm, disappear, and three new aliphatic peaks are generated. The peak at 136.90 ppm for polymer **3** corresponds to the aromatic carbons bonded with the cyclopropane ring which are shifted to high field. Similar changes are observed for the polyformals and polyesters. These are believed to be the result of opening of cyclopropane rings in the polymers at 350 °C and formation of aliphatic chains.

Conclusions

High molecular weight poly(ether sulfone)s, polyformals, and polyesters prepared from *trans*-1,2-bis(4-hydroxyphenyl)cyclopropane have been synthesized by solution polycondensation. The polymers can be cross-linked well above their glass transition temperature by treatment in nitrogen at 350 °C. The glass transition temperatures increase and the differences in specific heat capacity (DCp) at T_g decrease after cross-linking. The resulting cured polymers were insoluble in all solvents. It was confirmed by MAS-^{13}C NMR that the cyclopropane rings were opened on heating. Thermogravimetric analysis shows that no significant weight loss accompanies the cross-linking reaction.

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