BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 21, pp. 4141–4146, 1995

0032-3861/95/$10.00 + 0.00

New crosslinkable cyclic aryl ether ketones containing the *trans*-1,2-diphenylcyclopropane moiety

Chunping Gao and Allan S. Hay*
Department of Chemistry, McGill University, Montreal, Quebec H3A 2K6, Canada
(Received 1 March 1995; revised 27 April 1995)

Cyclic aryl ether oligomers containing the *trans*-1,2-diphenylcyclopropane moiety were synthesized in high yield from 1,2-bis(*p*-hydroxyphenyl)cyclopropane and 1-(3-hydroxyphenyl)-2-(4′-hydroxyphenyl)cyclopropane by reaction with 1,2-bis(4-fluorobenzoyl)benzene or 1,2-di(4-fluorobenzoyl)-3,6-diphenylbenzene. These oligomers undergo melt polymerization readily to give a crosslinked polymer in the presence of a phenolate salt as catalyst. The cyclic oligomers were characterized utilizing gel permeation chromatography, nuclear magnetic resonance and matrix-assisted laser desorption ionization mass spectrometry. Thermal analysis was conducted by differential scanning calorimetry and thermogravimetric analysis.

(Keywords: cyclic aryl ether ketone; 1,2-diphenylcyclopropane; crosslinking)

INTRODUCTION

In the fabrication of thermoplastic composites starting with high-molecular-weight linear polymers, problems like poor fibre wetting and breakage of the fibres are difficult to avoid. These problems are a direct result of the extremely high viscosity typical of thermoplastics in the melt. The attractiveness of using cyclo-oligomers to prepare linear polymers results from the unique combination of low melt viscosity for processing and polymerization in the melt without the liberation of volatile by-products[1–5]. Workers at General Electric have developed low-molecular-weight aromatic carbonate cyclo-oligomers for this purpose[6]. Poly(aryl ethers), which have superior thermo-oxidative stability[4], have been synthesized by the ring-opening polymerization of macrocyclic ethers. Mullins found that, with a proper choice of process conditions, aryl ether cyclo-oligomers are surprisingly easy to prepare on a laboratory scale. Some crosslinkable cyclic oligomers were prepared from 2,4-difluorobenzonitrile and 1,3-dihydroxybenzene. The product mixture polymerized readily to give a crosslinked polymer.

We have recently described a synthesis for cyclic aryl ether oligomers, which proceeds in high yield by reaction of 1,2-bis(4-fluorobenzoyl)benzene with a number of bisphenols[7]. These oligomers undergo melt polymerization readily at 340°C, in the presence of an anionic catalyst, to give high-molecular-weight polymers with high T_g values (up to 260°C). However, these polymers typically have limited solvent resistance, which may restrict the utility of composites based on such polymers. One way we are investigating to overcome this problem is to synthesize cyclic aryl ether oligomers that polymerize readily to give cross-linked polymers. For many composite applications some crosslinking is desirable. Crosslinking systems are often used in these applications when resistance to solvents, resistance to high temperatures, and high mechanical performance are required.

Recently we have developed new types of crosslinkable polymers containing the *trans*-1,2-diphenylcyclopropane moiety[8]. The polymers, which have been synthesized from the monomer *trans*-1,2-bis(4-hydroxyphenyl)cyclopropane by solution polycondensation, can be thermally crosslinked when heated above the glass transition temperature without producing volatile by-products. The resulting crosslinked networks are insoluble in all solvents tried.

Herein, we report the synthesis, ring-opening polymerization and crosslinking of cyclic aryl ethers containing the *trans*-1,2-diphenylcyclopropane moiety.

RESULTS AND DISCUSSION

The monomers 1,2-bis(4-hydroxyphenyl)cyclopropane (**1a**) and 1-(3-hydroxyphenyl)-2-(4′-hydroxyphenyl)-cyclopropane (**1e**) were synthesized by catalytic decomposition of the corresponding hydroxyl-substituted 3,5-diphenyl-2-pyrazolines, which were the products of the reaction between hydroxychalcones and hydrazine monohydrate according to the simple method we reported recently[9]. Linear high-molecular-weight poly(ether sulfone)s, polyformals and polyesters have been synthesized from 1,2-bis(4-hydroxyphenyl)cyclopropane (**1a**)[8].

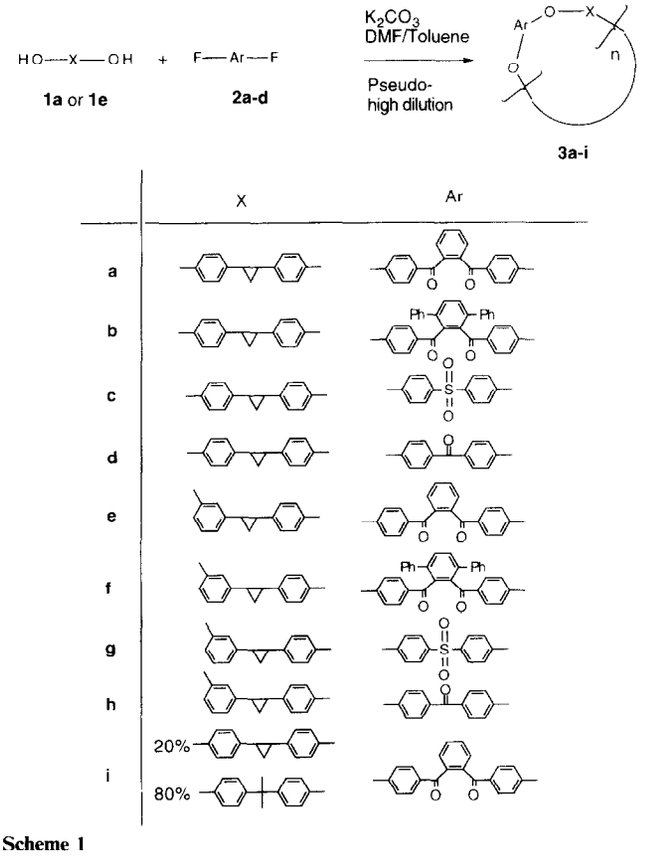
1,2-Bis(4-fluorobenzoyl)benzene (**2a**) and 1,2-di(4-fluorobenzoyl)-3,6-diphenylbenzene (**2b**) were synthesized utilizing the method recently described[10]. The monomers were isolated in very high yield. These fluoro monomers undergo reactions with bisphenols in

* To whom correspondence should be addressed

the presence of excess anhydrous potassium carbonate in an aprotic solvent (*N,N*-dimethylacetamide) to give high-molecular-weight amorphous poly(aryl ether ketone)s with high glass transition temperatures that are very soluble in solvents such as chloroform and toluene at room temperature.

Cyclic aryl ether oligomers (**3a, 3b, 3e, 3f** and **3i**) containing the *trans*-1,2-diphenylcyclopropane moiety were synthesized in high yield from 1,2-bis(*p*-hydroxyphenyl)cyclopropane (**1a**) and 1-(3-hydroxyphenyl)-2-(4′-hydroxyphenyl)cyclopropane (**1b**) by reaction with 1,2-bis(4-fluorobenzoyl)benzene (**2a**) or 1,2-di(4-fluorobenzoyl)-3,6-diphenylbenzene (**2b**) (*Scheme 1*). An efficient pseudo-high-dilution method[6] was used to achieve a high yield of cyclic oligomers. Thus, a concentrated dimethylformamide (DMF) solution of reactants (0.6 M) is pumped into the reaction vessel containing solvent (DMF) and base (K_2CO_3) over a period of 8 h. Toluene is used for continuous azeotropic removal of water generated during the reaction. Following the addition of the reactants, the mixture is heated at reflux for another 8 h to ensure a complete reaction. In this way, the concentrations of reactants in solution was maintained at high dilution by slow addition of starting materials, in the correct stoichiometry, and using conditions where the displacement reaction is as fast as possible. In this manner, cyclic aryl ether oligomers (**3c, 3d, 3g** and **3h**) containing the *trans*-1,2-diphenylcyclopropane moiety were also synthesized from 1,2-bis(4-hydroxyphenyl)-cyclopropane (**1a**) and 1-(3-hydroxyphenyl)-2-(4′-hydroxyphenyl)cyclopropane (**1e**) by reaction with bis(4-fluorophenyl)sulfone (**2c**) and 4,4′-difluorobenzophenone (**2d**) (*Scheme 1*).

The cyclic oligomers were characterized by the combination of g.p.c. and matrix-assisted laser desorption



Scheme 1

ionization mass spectrometry (m.a.l.d.i.-m.s.), which indicates that the range of oligomerization of 1,2-bis(*p*-hydroxyphenyl)cyclopropane (**1a**) with the activated aromatic bisfluorides **2a** and **2b** is from 2 up to about 9. Maldi-ms of cyclic oligomers **3a** and **3b** are shown in *Figure 1*. All cyclic oligomers with degree of polymerization from 2 to 9 can be seen clearly in the maldi-ms spectra of cyclic oligomers **3a** and **3b**. Potassium chloride in 2,5-dihydroxybenzoic acid was used as the matrix material in the analyses, and the mass numbers in the maldi-ms spectra correspond to oligomer ions with K^+ attachment that usually occurs when a spectrum is recorded using a matrix. The signal of some oligomer ions can also be observed in the spectra. The second highest peak, which is very close to the highest peak, is the signal of the dimer ion. It also can be seen that the content of linear oligomers in the mixture is not significant. The molecular weights of cyclic oligomers **3a** and **3b** determined by maldi-ms are listed in *Table 1*.

The compositions of cyclic oligomers determined by g.p.c. are summarized in *Table 2*. A g.p.c. trace of cyclic oligomer **3a** is shown in *Figure 2*, which indicates along with maldi-ms data that the smallest ring is the easiest formed.

Attempts to make cyclic oligomers from 1,2-bis(4-hydroxyphenyl)cyclopropane (**1a**) and bis(4-fluorophenyl)sulfone (**2c**) or 4,4′-difluorobenzophenone (**2d**) using the same method were not as successful. G.p.c. traces of those oligomers show that the mixture contains significant amounts of linear polymers along with the desired cyclic oligomers. As suggested from a study of molecular models, bis(4-fluorophenyl)sulfone (**2c**) or 4,4′-difluorobenzophenone (**2d**) are less prone to cyclo-oligomer formation than 1,2-bis(4-fluorobenzoyl)benzene (**2a**) or 1,2-di(4-fluorobenzoyl)-3,6-diphenylbenzene (**2b**).

In the oligomerization of *trans*-1-(3-hydroxyphenyl)-2-(4-hydroxyphenyl)cyclopropane **1c** and activated aromatic bisfluorides **2a** and **2b**, 22% of the monocyclic ($n = 1$) and no cyclic aryl ether oligomers with degree of polymerization higher than 5 were formed. A g.p.c. trace of cyclic oligomer **3c** is shown in *Figure 2*. Cyclic oligomers were synthesized from 1-(3-hydroxyphenyl)-2-4-hydroxyphenyl)cyclopropane (**1c**) and bis(4-fluorophenyl)sulfone (**2c**) or 4,4′-difluorobenzophenone (**2d**) under the same conditions. It was found that no cyclic oligomers with degree of polymerization higher than 5 were formed. The cyclic aryl ether oligomers from 1-(3-hydroxyphenyl)-2-(4′-hydroxyphenyl)cyclopropane have high melting points.

Cocyclic oligomers **3i** were also prepared by reaction of 20 mol% of 1,2-bis(4-hydroxyphenyl)cyclopropane and 80 mol% of 2,2-bis(4-hydroxyphenyl)propane (BPA) with bis-1,2-(4-fluorobenzoyl)benzene (**2a**).

All the cyclic oligomers are readily soluble in chloroform. The residual potassium salts in the cyclics were removed by twice precipitating a DMF solution into a large excess of aqueous 0.2 M HCl.

The results of the termal analysis of the cyclic oligomers are summarized in *Table 3*. The cyclic oligomers **3a, 3c, 3d** and **3i** exhibit a T_g but no observable melting endotherm, while **3b** shows a moderate melting endotherm at 325°C after a T_g at 179°C. In the d.s.c. scans of the cyclic oligomers **3e, 3f, 3g** and **3h** only melting endotherms and no T_g were observed. An

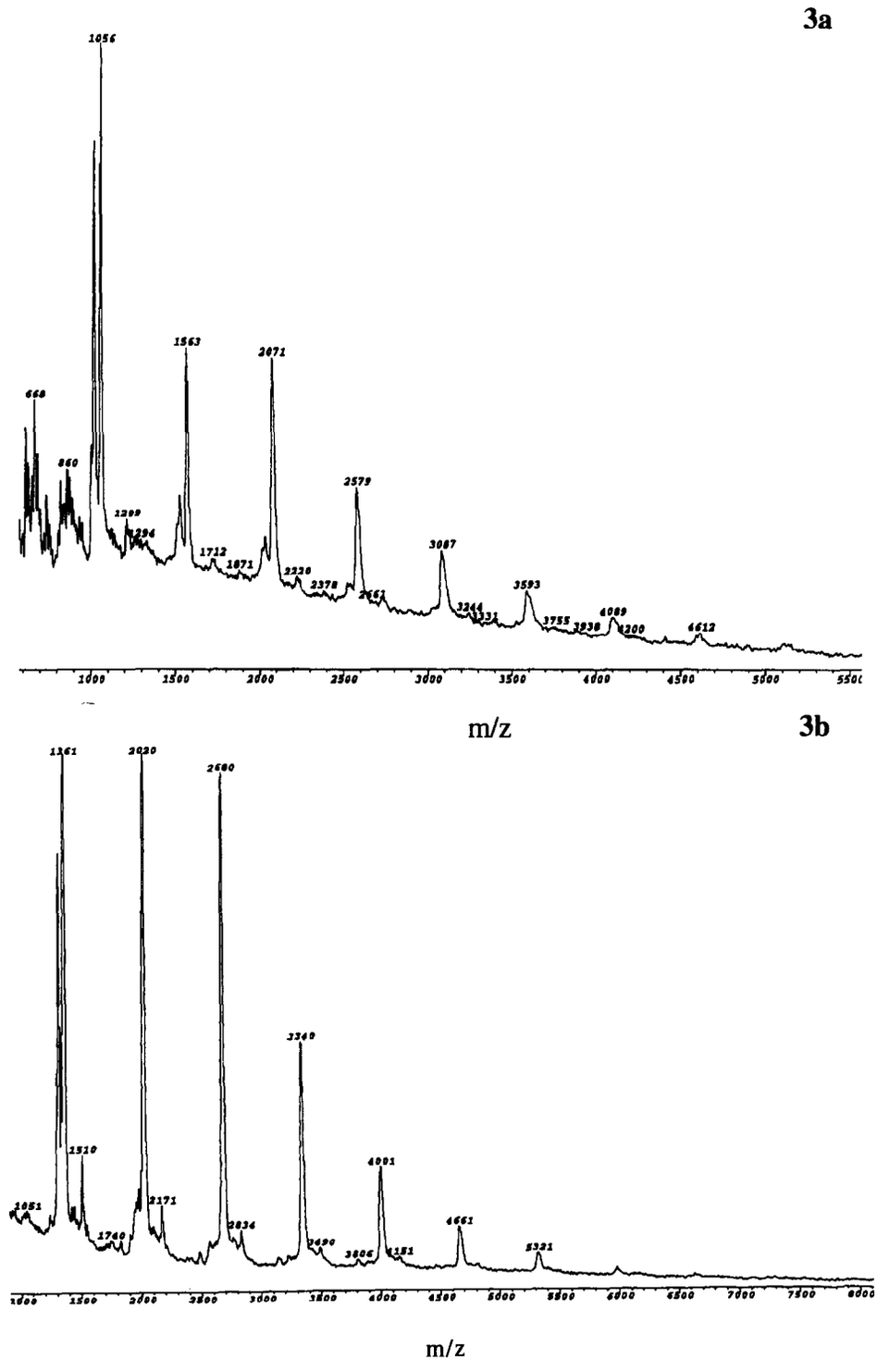


Figure 1 M.a.l.d.i.-m.s. spectra of cyclic oligomers **3a** and **3b**

Table 1 Molecular weights determined by maldi-ms

Degree of polymerization n	Cyclics **3a** determined/calculated	Cyclics **3b** determined/calculated
2	1016/1017	1321/1321
3	1023/1026	1980/1982
4	2031/2034	2640/2643
5	2539/2543	3300/3304
6	3047/3051	3961/3965
7	3553/3560	4621/4625
8	4060/4068	5281/5286

Table 2 Composition (%) of cyclics by g.p.c. analysis

Cyclic oligomer	Mono-cyclic $n = 1$	Dimer $n = 2$	Trimer $n = 3$	Tetramer $n = 4$	Pentamer $n = 5$	Higher homologues
3a	0	40.5	11.1	8.6	4.9	34.9
3b	0	38.1	12.4	7.2	11.7	30.6
3c	0	25.4	11.4	6.4	4.6	52.3
3d	0	33.6	14.3	7.7	4.7	39.7
3e	21.7	42.3	23.8	12.2	0	0
3f	21.9	36.0	22.0	8.7	11.4	0
3g	0	55.4	22.1	11.1	11.4	0
3h	0	40.9	26.0	13.0	20.1	0
3i	0	37.7	14.9	7.4	7.1	32.9

Table 3 Properties of cyclic oligomers containing 1,2-diphenylcyclopropane

Cyclic oligomer	T_g[a] (°C)	T_m[a] (°C)	Exotherm[a] T_{onset}/T_{max}	T.g.a.(−5%)[b] (°C)
3a	154		300/401	431
3b	185	325	302/404	430
3c	183		300/397	404
3d	139		300/409	437
3e		363	–/405	401
3f		370	–/415	426
3g		356	–/420	395
3h		394	–/420	380
3i	163		302/404	409

[a] Measured by d.s.c. under nitrogen atmosphere, heating rate 10°C min^{-1}
[b] Reported 5% weight loss under nitrogen atmosphere, heating rate 10°C min^{-1}

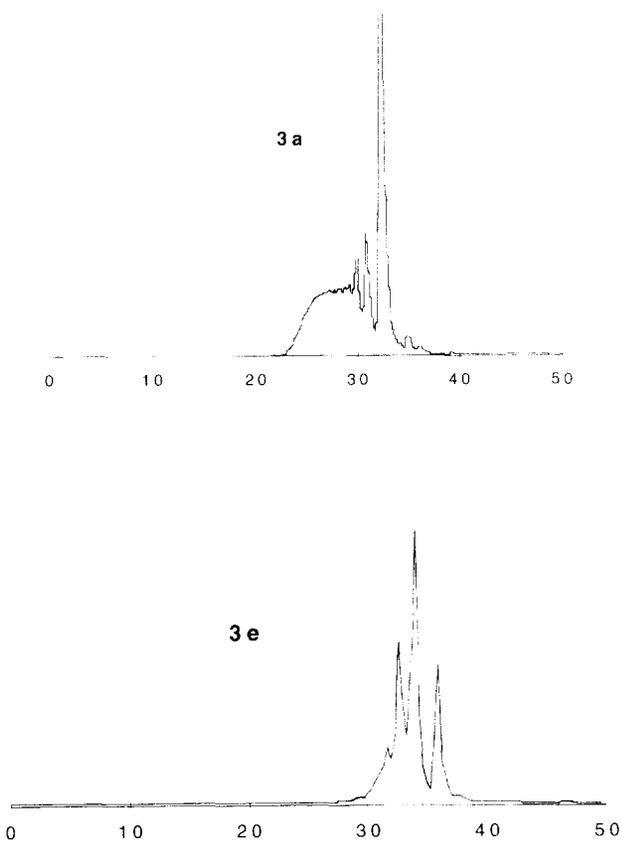


Figure 2 G.p.c. trace of cyclic oligomers **3a** and **3e**

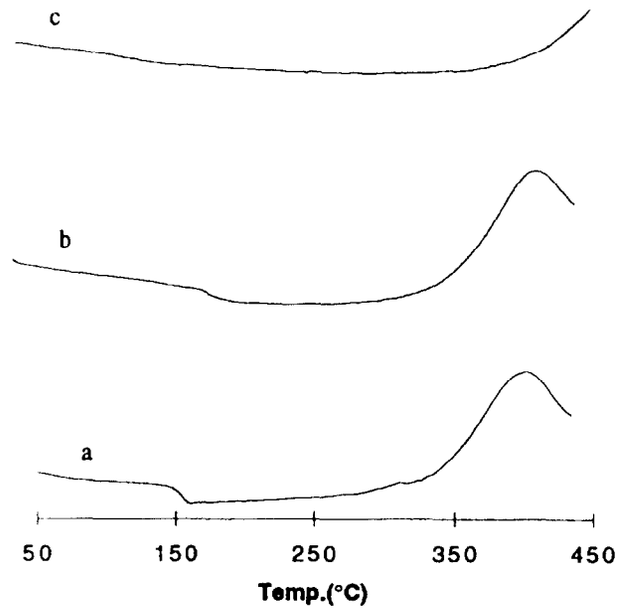


Figure 3 D.s.c. scans of cyclic oligomers **3a**: (a) first scan, (b) after heating at 300°C for 30 min, and (c) after heating at 350°C for 30 min

exotherm at about 400°C, which is associated with the crosslinking reaction, was observed in the d.s.c. scans of all cyclic oligomers. The exotherms of cyclic oligomers are consistent with those of linear polymers described previously[8].

The d.s.c. scans of cyclic oligomers **3a** are shown in *Figure 3*. Curve a is the d.s.c. thermogram of cyclic oligomer **3a**, curve b is the d.s.c. scan of cyclic oligomer **3a** after being heated at 300°C for 30 min in nitrogen, and curve c is the result after being heated at 350°C for 30 min in nitrogen. A T_g at 154°C and an exotherm at 401°C were observed in scan a. A T_g at 188°C and an

exotherm at 406°C were shown in scan b. Only an exotherm, starting from 360°C, appears in curve c. These results suggest that curing at 350° for 30 min can provide efficient crosslinking while curing at 300°C is not sufficient to achieve significant crosslinking in 30 min.

Ring-opening polymerization of the cyclic oligomers can be initiated with a phenolate catalyst. Since the aryl ether linkage is activated by an electron-withdrawing group, it will undergo ether exchange reaction readily[11]. The potassium salt of 4,4′-biphenol has been shown to be an effective catalyst for the polymerization of cyclic oligomers from 1,2-bis(4-fluorobenzoyl)benzene and BPA[6].

It was found that ring-opening polymerization and crosslinking occurred simultaneously when cyclic aryl ether oligomers of 1,2-bis(4-hydroxyphenyl)cyclopropane were cured above 280°C. After they were cured at 280°C or above, the resulting materials were no longer soluble in organic solvents, and T_g values increased significantly. Compared to the thermally cured products, a large increase in T_g was obtained when the cyclic oligomers were cured in the presence of the potassium salt of 4,4′-biphenol. The results are listed in *Table 4*.

The results from ring opening of cyclic oligomers **3e, 3f, 3g** and **3h** in dimethylacetamide (DMAc) at 160°C in the presence of a catalytic amount of the sodium salt of biphenol show that these cyclics can readily undergo ring-opening polymerization. Attempts to cure cyclic oligomers **3e, 3f, 3g** and **3h**, which are extremely high-melting solids, at 280 and 300°C were unsuccessful. In order to induce polymerization and crosslinking, the materials have to be cured above their melting points.

No T_g is detected by d.s.c. after 30 min curing of all homocyclics above 350°C in nitrogen. The cured materials also show no observable swelling over 24 h in chloroform. Curing of all cyclic oligomers at 350°C in nitrogen gave highly crosslinked materials with high solvent resistance.

Heating cyclic oligomer **3a** at 280°C with and without catalyst (potassium salt of 4,4-biphenol) on a glass plate afforded films. Only the film obtained from curing of cyclic oligomer **3a** at 280°C in the presence of the catalyst had enough integrity to be tested by thermomechanical analysis (t.m.a.). The Young's modulus of the film at 25°C is 1.0 GPa. The film maintains mechanical properties to temperatures close to the T_g. These results indicate that, in the presence of catalyst, ring-opening polymerization and curing occur simultaneously.

EXPERIMENTAL

Materials

1,2-Bis(4-hydroxyphenyl)cyclopropane **1a**. It was synthesized according to the method previously described[9]. *trans*-3,5-Bis(4-hydroxyphenyl)-2-pyrazoline (1.0 g, 3.9 mmol) was mixed with 1.0 g of powdered sodium hydroxide. The mixture was heated to 250°C under nitrogen and the decomposition proceeded for 30 min. The cooled reaction product was dissolved in water, neutralized with hydrochloric acid, and extracted with ether. The ether layer was washed with water to remove the salt. Removal of the ether left a residue, which was crystallized from acetic acid. Yield > 90%. M.p. 190–191°C. ^{1}H n.m.r. (DMSO-d_6) δ (ppm) = 1.16–1.22 (t, 2H), 1.80–1.98 (t, 2H), 6.60–6.70 (d, 4H), 6.90–6.96 (d, 4H), 9.15 (s, 2H). M.s. m/z = 226 (M^+, 100), 131 (15), 121 (45), 107 (20). Calculated for $C_{15}H_{14}O_2$ (226.27): C, 79.62; H, 6.24. Found: C, 79.40; H, 6.24.

trans-1-(3-Hydroxyphenyl)-2-(4-hydroxyphenyl)cyclopropane ***1e***. M.p. 123–125°C. ^{1}H n.m.r. (DMSO-d6) δ (ppm) = 1.23–1.30 (t, 2H), 1.94–2.07 (m, 2H), 6.50–7.06 (m, 8H), 9.16 (s, 1H), 9.25 (s, 1H). M.s. m/z = 226 (M^+, 100), 131 (31), 120 (16), 107 (27). Calculated for $C_{15}H_{14}O_2$ (226.27): C, 79.62; H, 6.24. Found: C, 79.08; H, 6.33.

*1,2-Bis(4-fluorobenzoyl)benzene (**2a**)*. M.p. 90–91°C. ^{1}H n.m.r. (500 MHz, $CDCl_3$) δ (ppm) = 7.06 (dd, 4H), 7.62 (s, 4H), 7.74 (dd, 4H). M.s.(e.i.) m/e = 322.

*1,2-Di(4-fluorobenzoyl)-3,6-diphenylbenzene (**2b**)*. M.p. 157–158°C. ^{1}H n.m.r. (500 MHz, $CDCl_3$) δ (ppm) = 6.84 (dd, 4H), 7.14–7.29 (m, 10H), 7.57 (dd, 4h), 7.62 (s, 2H). M.s(e.i.) m/e = 474.

Characterization

G.p.c. analyses were performed on a Waters 510 HPLC equipped with 5μ Phenogel columns (linear 3 × 500 Å) arranged in series with choloroform as solvent, and a u.v. detector. D.s.c. scans were obtained using a Seiko 220 DSC instrument at a heating rate of 10°C min^{-1} in N_2 (160 ml min^{-1}). When recording T_g values samples were never heated above 300°C, to avoid crosslinking, and the values recorded are 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 using a Seiko 220 TG/DTA instrument at a heating rate of 10°C min^{-1} in nitrogen. Polymer samples were cured under nitrogen in the t.g.a. instrument. A

Table 4 T_g values (°C) of cyclic oligomers cured at 280 and 300°C

	Without salt		With salt[a]	
Cyclic oligomer	280°C	300°C	280°C	300°C
3a	176	188	215	242
3b	214	223	224	260
3c	196	198	228	242
3d	157	162	165	173
3i	174	180	176	200

[a] 1.0 mol % of KOPhPOK was used

d.s.c. was then employed to determine the T_g increase. Potassium chloride in 2,5-dihydroxybenzoic acid was used as the matrix material to record the laser time-of-flight (t.o.f.) mass spectra. Gram S and insulin were used as external calibrations. Sample concentration was 1 mg ml^{-1}, polarity was positive, acceleration voltage was 25 kV and reflection voltage was N/A. ^{1}H and ^{13}C n.m.r. spectra were recorded at 500 MHz using a Varian XL-500 spectrometer in $CDCl_3$ with $(CH_3)_4Si$ as the internal standard. Measurements of mechanical properties were made on the films using a Seiko TMA/SS 120. Maldi-ms was obtained in a TofSpec MALDI-TOF mass spectrometer.

General procedure for cyclization reaction

The cyclization reaction was conducted in a 100 ml three-necked, round-bottomed flask, equipped with a mechanical stirrer, Dean–Stark trap, condenser, thermometer and nitrogen inlet. The flask was charged with 50 ml of DMF, 10 ml of toluene and 5.0 g of K_2CO_3. The mixture was magnetically stirred and heated to reflux at 140°C and kept there for 1 h. Then, a solution of difluoro monomer (2.2 mmol) and bisphenol (2.2 mmol) was added over 8 h via a syringe pump. At the end of addition, the resulting solution was refluxed for another 10 h at 150°C. The reaction mixture was cooled and filtered to remove the salt. The solution was concentrated by rotary evaporation. The concentrated solution was added dropwise to a large excess of 0.2 N hydrochloric acid solution (200 ml) with vigorous stirring. The precipitate was filtered and washed several times with water to remove any residue. The solid was then dried at 100°C under vacuum overnight.

ACKNOWLEDGEMENTS

We thank the Natural Sciences and Engineering Research Council of Canada and the General Electric Co. for financial support. We also thank Fisons Instruments for carrying out the maldi-tof analyses.

REFERENCES

1 Fukuyama, J. M., Talley, J. J. and Cella, J. A. *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* 1989, **30**(2), 581
2 Mullins, M. J., Galvan, R., Bishop, M. T., Woo, E. P., Gorman, D. B. and Chamberlain, T. A. *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* 1991, **32**(2), 174
3 Calquhoun, H. M., Dudman, C. C., Thomas, M., O'Mahoney, C. A. and Williams, D. J. *J. Chem. Soc., Chem Commun.* 1990, 336
4 Mullins, M. J., Woo, E. P., Murray, D. J. and Bishop, M. T. *Chemtech* 1993 (August), 25
5 Xie, D. and Gibson, H. W. *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* 1994, **35**(1), 401
6 Brunelle, d. J., Boden, E. P. and Shannon, T. G. *J. Am. Chem. Soc.* 1990, **112**, 2399
7 Chan, K. P., Wang, Y. and Hay, A. S. *Macromolecules* 1995, **25**, 1877
8 Gao, C. and Hay, A. S. *Macromolecules* 1994, **27**, 6708
9 Gao, C. and Hay, A. S. *Synth. Commun.* in press
10 Singh, R. and Hay, A. S. *Macromolecules* 1992, **25**, 1017
11 Cella, J. A., Fukuyama, J. M and Guggenheim, T. L. *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* 1989, **30**(2), 142