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Novel macrocyclic aryl ether oligomers containing a diphenylacetylene moiety: synthesis, characterization and ring-opening polymerization

Yi-Feng Wang, Martino Paventi and Allan S. Hay*
Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6
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An efficient synthetic route to a range of macrocyclic aryl ether ketone and sulfone oligomers containing a cross-linkable diphenylacetylene moiety in the backbone is described. This new class of macrocyclic oligomers, obtained in excellent yield, is prepared by an aromatic nucleophilic substitution reaction from the potassium salt of bis(3-hydroxyphenyl)acetylene and activated difluoro-monomers. Detailed structural characterization of these novel oligomers by the combination of n.m.r. and matrix assisted laser desorption and ionization-time of flight-mass spectroscopy (MALDI-TOF-MS) confirms their cyclic nature; and the compositions of these macrocyclic oligomers are provided by g.p.c. and reverse-phase gradient h.p.l.c. analyses. MALDI-TOF-MS is a unique tool for the determination and the proof of the cyclic nature of random co-cyclic oligomers, and also provides answers to the possible combinations of monomer units in the cyclic olgiomeric components for the random co-cyclic oligomers. All macrocyclic oligomers are semicrystalline with T_m varying from 267 to 370°C and when the oligomers are heated an exothermic reaction, resulting from reaction of the acetylene units, occurs in the range of 340–470°C and the macrocyclics undergo a cross-linking reaction. Polymerization of the lower melting macrocyclic oligomers at 280–300°C, in the presence of a nucleophilic initiator, led to the formation of high molecular weight insoluble materials with limited cross-linking reactions taking place. The resulting polymers can be further cross-linked at 340°C with a T_g increase up to 100°C or complete disappearance of T_gs. Copyright © 1996 Elsevier Science Ltd.

(Keywords: high dilution; macrocyclic aryl ether oligomers; diphenylacetylene)

INTRODUCTION

High performance aromatic thermoplastic polymers, such as poly(aryl ether sulfone) and poly(aryl ether-ketone), are gaining importance as high performance polymers due to their inherent thermo-oxidative stability and toughness[1]. However, these high-performance polymers are generally very difficult to process due to their high softening temperatures and high melt viscosities. In recent years, in an effort to address the problem of high melt viscosities, development of low molecular weight macrocyclic aryl ether oligomers as intermediates for the preparation of high performance thermoplastics has attracted considerable attention[2–17]. The macrocyclic oligomers offer a unique combination of low melt viscosity and the possibility of undergoing controlled polymerization in the melt without the liberation of volatile byproducts. The *in situ* transformation of macrocyclic oligomers such as carbonates[2], esters[3], aryl ethers[4–7], aramids[8] and imides[9] via an anionic ring-opening polymerization route to high molecular weight linear polymers opens up the possibility of melt processing of aromatic thermoplastics in applications which are currently not accessible to the corresponding high molecular weight polymers due to their inherent high melt viscosities. In particular, the low viscosity of macrocyclic oligomers permits applications of high performance thermoplastics in the fabrication of long or continuous fibre reinforced thermoplastic composites via processing methods such as compression moulding, reaction injection moulding, and melt-pultrusion.

We recently reported the preparation[10–12], polymerization[13,14] and rheology studies[13,15] of macrocyclic aryl ether ketone oligomers containing the 1,2-dibenzoylbenzene moiety. One of the properties which is desirable for the application of the macrocyclic aryl ether oligomers as matrix resins for thermoplastic composites is an increase in solvent resistance of the final polymer. As a route to improving the solvent resistance, the incorporation of reactive groups, which would be stable during the ring-opening polymerization, into the backbone of macrocyclic aryl ether oligomers is desirable. After the ring-opening polymerization, by heating at high temperatures, such reactive groups should undergo controlled thermal reactions and result in cross-linking of the final polymers. The incorporation of reactive groups such as acetylene units into the backbone of linear high molecular weight poly(aryl ether)s has been

* To whom correspondence should be addressed

investigated[18,19]. When heated to elevated temperatures, the acetylene units undergo an exothermic reaction which results in cross-linking of the polymer without the evolution of volatile materials. This paper reports the synthesis, characterization, ring-opening polymerization and cross-linking studies of novel macrocyclic aryl ether oligomers containing acetylene groups in the backbone.

EXPERIMENTAL

General instruments and procedures

Nuclear magnetic resonance spectra were recorded on a Varian Unity-500 n.m.r. spectrometer. ^1H–^1H COSY correlation experiments and ^1H–^{13}C HMQC correlation experiments were performed to allow proton and carbon chemical shifts assignment. Proton spectra were referenced to internal tetramethylsiliane, while ^{13}C n.m.r. spectra were referenced to the $CDCl_3$ middle line at 77.00 ppm. The g.p.c. analysis of macrocyclic oligomers was carried out on a Waters 510 h.p.l.c. using four phenogel 5 μ columns in series (each 300 mm × 7.8 mm i.d., one linear and three 500 Å). Chloroform was used as the eluent with a flow rate of 1.0 ml min^{-1}, the u.v. detector was at 254 nm, and polystyrene standards were used for the calibration. Thermal analyses of macrocyclic oligomers were carried out on Seiko 220 d.s.c. and 220 t.g.a./d.t.a. instruments.

MALDI-TOF mass spectroscopy

Matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectra were recorded on a Kratos Kompact MALDI-III TOF instrument with a maximum laser output of 6 mW at a wavelength of 337 nm (N_2 laser light, 3 ns pulse width, 100 μm diameter spot). The MALDI instrument was operated in a positive reflection mode. The ions produced from each laser shot were accelerated to 20 keV into a 1 m drift region. An external calibration using bovine insulin and angiotensin was used, this provides mass accuracy within 0.02% for this instrument. The matrix used for all experiments was 1,8,9-anthracenetriol (dithranol) (Aldrich). Samples were prepared by dissolving the cyclic oligomers in chloroform at a concentration of 5.0 mg ml^{-1}. A 20 μl of the sample solution was added to 200 μl of a 10 mg ml^{-1} solution of the matrix dissolved in chloroform. This final solution was shaken briefly, and 0.5 μl was applied to a stainless steel sample slide and air dried prior to analysis.

Reverse-phase gradient h.p.l.c. analysis

The HPLC analyses were performed on a Milton Roy CM4000 pump equipped with a reverse phase column (Primesphere 5 μ C8, 256 × 4.6 mm i.d.) and a u.v. detector at 300 nm; THF/water gradient was used as the eluent at a flow rate of 1.0 ml min^{-1}. The reverse-phase gradient program was: step 1, 70–85% THF over 25 min at exponent −2; step 2, 85–100% THF over 1 min at exponent 1; step 3, 100% THF for 2 min; step 4, 100–70% THF over 2 min (recycle). The gradient h.p.l.c. analyses were also performed with detection at 254 and 300 nm on a Perkin–Elmer h.p.l.c. system comprising a Model 410 pump, ISS-100 autoinjector, and LC-235 diode array detector. The diode array detector was used for the generation of u.v. spectra and the dual detection system was used for the generation of composition of individual macrocycles at two different wavelengths (254 and 300 nm). THF/water gradient was used as the eluent with a flow rate of 2.0 ml min^{-1} for the election of product on a reverse phase column (Primesphere 5 μ C8, 256 × 4.6 mm i.d.). The gradient program was as follows: step 1, 60–84% THF over 17 min at exponent −2; step 2, 84–100% THF over 1 min at exponent 1; step 3, 100% THF for 6 min; step 4, 100–60% THF over 2 min (recycle).

Materials

Reagent-grade solvents dimethylformamide (DMF) and toluene were used without further purification. Bis(4-fluorophenyl)sulfone was purchased from Lancaster and recrystallized twice from toluene and finally from cyclohexane. 4,4′-Difluorobenzophenone was purchased from Aldrich and was used without further purification. 1,2-Bis(4-fluorobenzoyl)benzene and 1,2-bis(4-fluorobenzoyl)-3,6-diphenylbenzene were prepared according to the procedure reported previously[20]. Bis(3-hydroxyphenyl)acetylene was prepared according to the procedure reported previously[21]. It was purified by recrystallization from acetic acid, m.p. 175–176°C.

General procedure for synthesis of macrocyclic oligomers from bis(3-hydroxyphenyl)acetylene

The synthesis of macrocyclic oligomers **3a** is used as an example. The cyclization was conducted in a 1 l three-neck round-bottom flask which was equipped with a Dean–Stark trap and condenser, a thermometer and a nitrogen inlet. The reaction vessel was charged with DMF (700 ml), toluene (100 ml) and anhydrous potassium carbonate (8.706 g, 63.00 mmol). The mixture was magnetically stirred and heated under reflux under nitrogen. The refluxing temperature was kept at 145°C. Then, a solution of bis(3-hydroxyphenyl)acetylene **1** (6.6245 g, 31.50 mmol) and 4,4′-difluorobenzophenone **2a** (6.8730 g, 31.50 mmol) in DMF (45 ml) was added over an 8 h period via a syringe pump. After the addition, the resulting solution was kept at 145–8°C for another 8 h. The reaction mixture was cooled and filtered to remove salts. The filtrate was then concentrated to 100 ml under reduced pressure and added dropwise into vigorously stirring distilled water (700 ml) containing 10 ml of concentrated hydrochloric acid. The desired oligomers precipitated as a white solid, which were collected by filtration and washed with distilled water until acid-free (checked with pH paper). Then, the solid was stirred in 200 ml methanol for 30 min, filtered and dried in a vacuum over at 160°C for 24 h to give white powder (12.0 g, 94% yield). A similar procedure was applied for the preparation of other macrocyclic oligomers **3b–d**. Yields of the products are listed in *Table 1*.

Ring-opening polymerization reaction and cross-linking studies

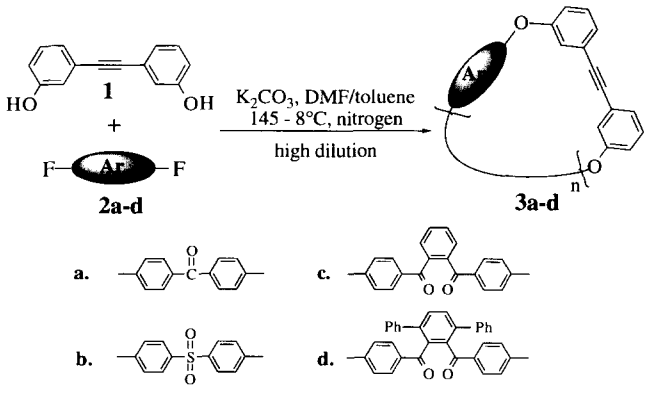
The macrocyclic oligomers **3a**, or **3c** or **4** (0.5 g of dried powder) were dissolved into a minimum amount of chloroform, and the required amount of potassium 4,4′-biphenoxide solution in methanol (10 mg ml^{-1}) was added to give a concentration of 1.0 mol% 4,4′-biphenoxide of the cyclic oligomers. The clear solution was evaporated, and the powder formed was further dried at 140°C under high vacuum overnight. The dried powder

was placed in a dry test tube, and after sweeping with nitrogen for a few minutes the test tube was sealed with a septum which was equipped with a nitrogen inlet and outlet. For **3a** and **3c**, the powder was heated at 300°C for 30 min under nitrogen, after which a tough, flexible and insoluble material resulted. Further cross-linking of the material was induced by heating a small fraction of the material at 340°C under nitrogen for the designated period of time. After cooling, the materials were analysed by d.s.c. For the co-cyclic oligomers **4**, the powder was heated at 280°C for 30 min under nitrogen. After cooling, the product was dissolved in chloroform and the soluble fraction was analysed by g.p.c.

RESULTS AND DISCUSSION

Preparation of macrocyclic aryl ether oligomers based on bis(3-hydroxyphenyl)acetylene

Macrocyclic oligomers containing the diphenylacetylene moiety were prepared by an aromatic nucleophilic substitution reaction from the potassium salt of bis(3-hydroxyphenyl)acetylene **1** and difluoro-monomers **2a–d** (*Scheme 1*). The reactions were conducted in DMF in the presence of anhydrous potassium carbonate under high-dilution conditions, according to the procedures reported previously[10]. Synthesis of macrocyclic oligomers are very often complicated by the formation of linear oligomers and high molecular weight polymers via competing polycondensation reaction. The selective formation of macrocyclic oligomers was achieved by creation of an environment in which the concentration of unreacted functional groups was kept at minimum and, therefore, the formation of high molecular weight linear polymers via an intermolecular polycondensation reaction was completely suppressed or at least minimized. Such an environment was created by slow addition of reactants into the reaction vessel at such a rate that a steady low concentration of unreacted end-groups was maintained and, hence, favouring the formation of cyclic oligomers even with a very high product concentration build-up. Thus, a concentrated solution (0.70 M) of reactants (monomer **1** and difluoro-monomer) in DMF was continuously added (via a syringe) pump to a mixture of DMF and anhydrous potassium carbonate at 145°C under nitrogen over 8 h which led to a final concentration of products as high as 45.0 mM. A small amount of toluene was used for continuous azeotropic removal of water generated during the formation of potassium phenoxide salt. The reaction mixture was kept under reflux for another 8 h in the temperature range of 145–8°C under nitrogen.



Scheme 1

Cyclic nature of the oligomers

The cyclization reaction led to essentially quantitative yield of a mixture of low molecular weight oligomers (*Table 1*). G.p.c. analysis indicates that the average degree of polymerization is 2–3. ^1H, ^{13}C and ^{19}F n.m.r. spectroscopy gives no indication of the presence of any fluoro or phenolic end groups, which suggests that the low molecular weight oligomers are macrocycles. Direct confirmation of the cyclic nature of these oligomers was provided by employing matrix-assisted laser desorption/ionization-time of flight-mass spectrometry (MALDI-TOF-MS).

Table 1 Yields and physical properties of macrocyclic aryl ether oligomers **3a–d** and the co-cyclic oligomer **4**

Cyclic oligomer	**3a**	**3b**	**3c**	**3d**	**4**
Isolated yield (%)	94	96	95	94	96
M_n^a	1400	900	800	1400	1100
M_w^a	4300	1600	1600	4400	3100
T_g(°C)[b]	138	151	145	187	147
T_m(°C)[b]	305[c]	306[c]	281[c]	371[c]	267[c]
	(242–314)[d]	(220-319)[d]	(253–290)[d]	(361–379)[d]	(240–280)[d]
ΔH_m (kJ mol^{-1})[e]	15.3	13.8	6.4	3.2	7.0
T_{ex}(°C)[f]	408[f]	412[f]	417[f]	431[f]	430[f]
	(340–458)[g]	(340–466)[g]	(350–467)[g]	(379–478)[g]	(350–430)[g]
ΔH_{ex} (kJ mol^{-1})[h]	89.3	93.4	95.6	96.1	91.5
$T_{-5\%}$(°C)[j]	559	520	519	545	539

[a] Measured by g.p.c. and calibrated against polystyrene standards
[b] Measured by d.s.c. under nitrogen (a flow rate of 100 ml min^{-1}) at heating rate of 20°C min^{-1}
[c] Peak temperature of melting endotherm
[d] On-set and off-set temperatures of melting endotherm
[e] Enthalpy change of the melting endotherm, measured by d.s.c. and calibrated against indium
[f] Peak temperature of exothermic peak of the reaction of acetylene units
[g] On-set and off-set temperatures of exothermic peak of the reaction of acetylene units
[h] Exothermic enthalpy change of the reaction of acetylene units, measured by d.s.c. and calibrated against indium
[j] 5% weight loss temperature, measured by t.g.a. under nitrogen (a flow rate of 200 ml min^{-1}) with a heating rate of 20°C min^{-1}

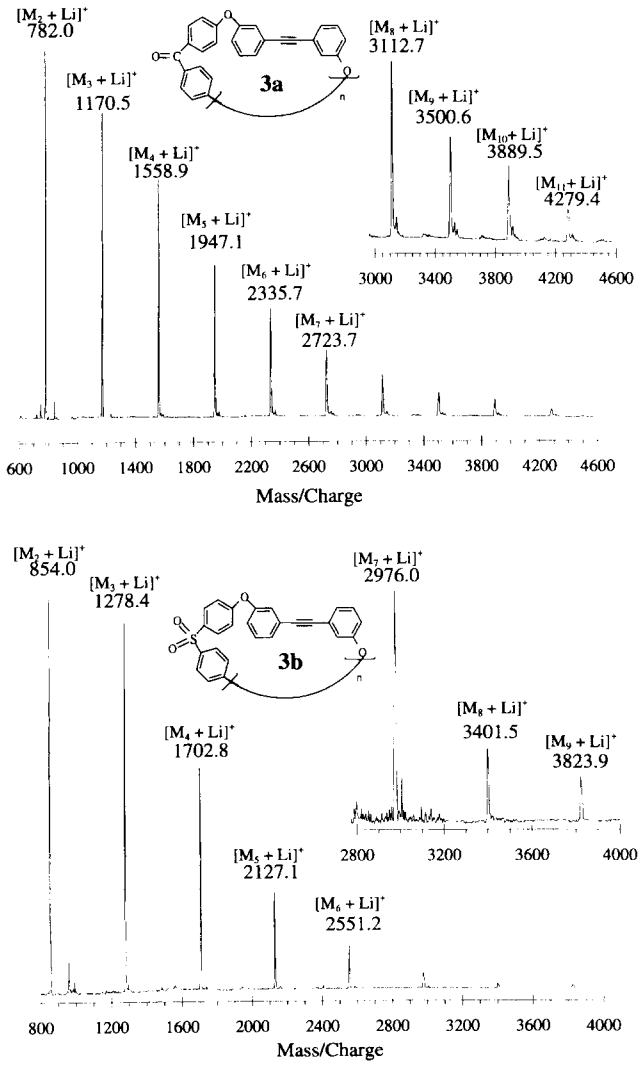


Figure 1 Positive ion MALDI-TOF mass spectra of cyclic oligomers **3a** and **3b**. The data were acquired in the reflection mode using dithranol as the matrix (dithranol/cyclics = 20/1 by weight)

The MALDI-TOF-MS technique is being widely used as a powerful method for the determination of molecular weight for biopolymers such as proteins[22], oligonucleotides[23], and polysaccharides[24]. The application of this technique for the determination of the absolute molecular weight distribution, sequence of the repeating units, impurities, and structural information about the end groups of synthetic polymers is also gaining attention[25]. Preliminary application of this technique for poly(acrylamide)[26], poly(hydroxyalkanoates)[27], polystyrene and poly(ethylene glycol)s[24] and poly(methyl methacrylate)[28] has been reported. For the MALDI analysis, the sample to be analysed is mixed uniformly with a matrix. In an environment in which large excess of the matrix is present, the sample molecules are surrounded by the matrix molecules in crystalline or amorphous states. The matrix which has resonance absorption at the laser wavelength used (337 nm), absorbs the laser energy and causes rapid heating of the matrix for the samples to be vaporized. The key to the successful application of this technique for synthetic polymeric materials is the dispersion of the polymer chains in the matrix at the molecular level and prevention of the entanglements between individual molecular chains. MALDI-TOF-MS is an ideal tool for the analysis of macrocyclic oligomers since there are no entanglements among the macrocyclic molecules. In the previous publications[10–12,16], we have demonstrated that MALDI-TOF-MS is a very simple and powerful technique for the detection and identification of macrocyclic oligomers. This technique is particularly useful for the analysis of co-macrocyclic oligomers[16].

The macrocyclic oligomers **3a–d** samples were analysed by MALDI-TOF spectrometry using 1,8,9-anthracenetriol (dithranol) as matrix. The positive ion MALDI-TOF mass spectra of macrocyclic oligomers *3a–d*, obtained in the reflection mode, give the correct molecular ion signals for lithium adducts $[M_n + Li]^+$ of the desired macrocyclic oligomers with excellent signal to noise ratio (*Figures 1* and *2*). The typical positive ion MALDI-TOF mass spectra presented in *Figure 1* clearly show that macrocyclic oligomers **3a** consist of macrocycles from dimer to undecamer ($n = 2–11$), and **3b** consist of macrocycles from dimer to nonamer ($n = 2–9$). The MALDI-TOF mass spectra in *Figure 2* shows that macrocyclic oligomers **3c** and **3d** consist of macrocycles from monomer to decamer ($n = 1–10$). In the mass range (m/z up to 6500), there is no indication of the presence of linear oligomers and there is no fragmentation of the macrocyclic oligomers detected. Although MALDI-TOF mass spectrum of **3b** only shows that the macrocyclic oligomers from dimer to nonamer, *EI* mass spectroscopy analysis shows that the cyclic oligomers **3b** also contain mono macrocycle ($n = 1$, 425 m/z). We have observed that in mass range of 1–500 m/z, the MALDI-TOF spectra are very often complicated by the matrix, therefore it is difficult to analyse molecules which have mass below 500. Based on ^1H n.m.r. analysis, it was estimated that the macrocyclic oligomers **3b** contain 40% cyclic monomer. The 19-member mono macrocycle of **3b** has been isolated. The isolation and structural characterization of the mono macrocycle and dimer of **3b** will be reported in a subsequent communication[29].

Composition of the macrocyclic oligomer

Using one linear and three 500 Å phenogel columns (arranged in series) as the g.p.c. columns with u.v. detector at 254 nm, g.p.c. analyses of the macrocyclic oligomer samples provided a good separation of individual macrocyclic oligomers up to pentamer (*Figure 3*). Based on the integration of the peak area, g.p.c. analysis indicates that macrocyclic oligomers **3a** contain 33.6% cyclic dimer, 13.4% cyclic trimer, 7.4% cyclic tetramer, 5.1% cyclic pentamer, 3.5% cyclic hexamer and 37.1% higher homologues. Macrocyclic oligomers **3b** contain 22.8% cyclic monomer, 25.8% cyclic dimer, 12.0% cyclic trimer, 7.3% cyclic tetramer, 5.1% cyclic pentamer, 4.0% cyclic hexamer and 22.9% higher homologues. Macrocyclic oligomers **3c** contain 32.9% cyclic monomer, 29.1% cyclic dimer, 11.6% cyclic trimer, 6.0% cyclic tetramer, 3.7% cyclic pentamer and 16.7% higher homologues. Macrocyclic oligomers **3d** contain 12.9% cyclic monomer, 29.7% cyclic dimer, 13.5% cyclic trimer, 6.9% cyclic tetramer, 4.5% cyclic pentamer, 3.3% cyclic hexamer and 28.8% higher homologues.

Reverse phase gradient h.p.l.c. analyses of macrocyclic oligomers show much better separation of the individual

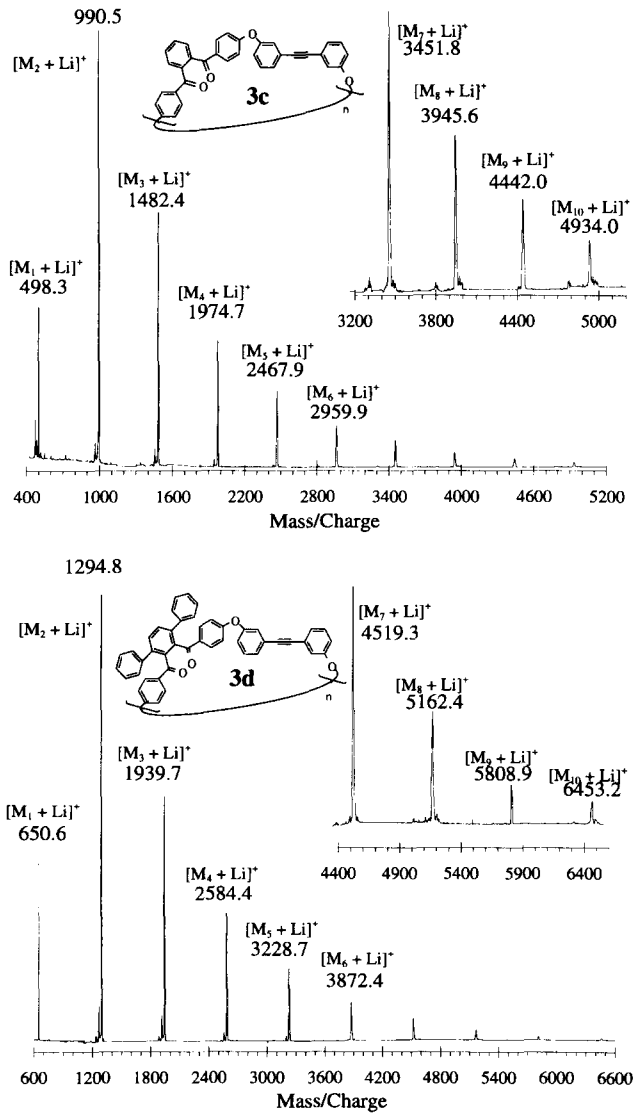


Figure 2 Positive ion MALDI-TOF mass spectra of cyclic oligomers **3c** and **3d**. The data were acquired in the reflection mode using dithranol as the matrix (dithranol/cyclics = 20/1 by weight)

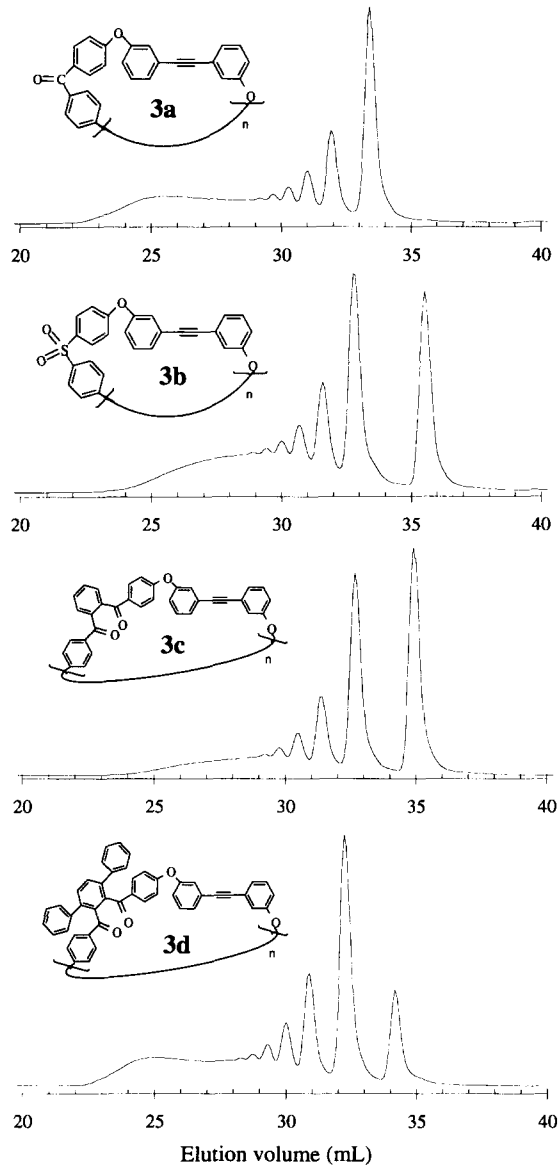


Figure 3 G.p.c. trace of cyclic oligomers **3a–d**. Detection was 254 nm

macrocycles of the macrocyclic mixtures. Using tetrahydrofuran (THF) as the (thermodynamically) good solvent and water as the (thermodynamically) poor solvent, at a flow rate of 1.0 ml min^{-1}, gradual increase of the volume fraction of THF (from 70 to 85% over 25 min) in an exponential (−2) mode led to a good separation of the oligomers with repeating units up to 15. Typical reverse-phase gradient h.p.l.c. traces of **3a** and **3d**, obtained from h.p.l.c. analyses with detection at 300 nm, are shown in *Figure 4*. The composition of macrocyclic oligomers **3a–d** obtained from reverse-phase gradient h.p.l.c. analyses with dual detection at 255 and 300 nm are shown in *Table 2*. It should be pointed out that the composition of macrocyclic oligomers determined by g.p.c. and h.p.l.c. analyses with the same detection wavelength are different. In general the compositions of macrocyclic oligomers obtained from h.p.l.c. analyses should be more accurate as it gives a much better separation of individual oligomers with a flat baseline. However, the data obtained from h.p.l.c. cannot be taken as the absolute value for the composition of individual macrocylces in a mixture of oligomers because there is a change in solvent composition as the separation of individual macrocycle proceeds which causes differences in absorptivity, and also the individual macrocycles have somewhat different extinction coefficients at a given wavelength. Typical u.v. spectra of cyclic monomer ($n = 1$), dimer ($n = 2$) and trimer ($n = 3$) or **3b** and **3d** are presented in *Figure 5*. The u.v. absorption of the dimer and trimer of **3b** and **3d** are very similar, but are different from that of monomer. This is particularly evident for cyclic monomer of **3b**. Quantitative interpretation of the u.v. spectra of the cyclic monomer and dimer of **3b** will be present in a subsequent communication[29].

Thermal analysis of macrocyclic oligomer

D.s.c. analyses show that the macrocyclic oligomers are semicrystalline. The thermal properties of macrocyclic oligomers are tabulated in *Table 1*. The endothermic and exothermic enthalpy change was measured using indium as the standard. In general, the macrocyclic

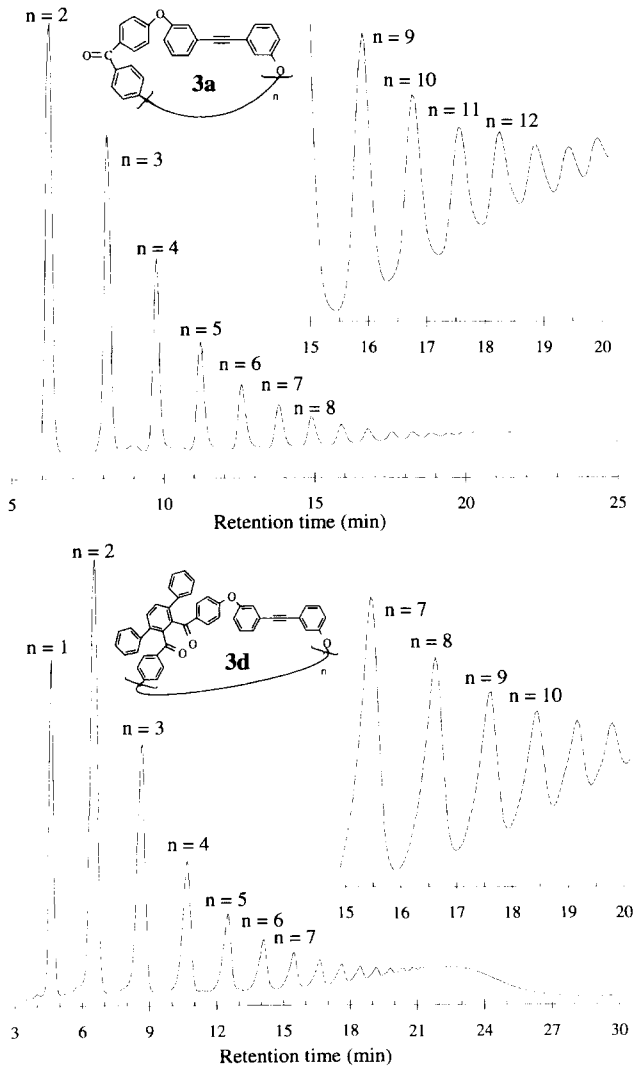


Figure 4 Reverse-phase gradient h.p.l.c. traces of cyclic oligomers **3a** and **3d**. Detection was at 300 nm

oligomers show a moderate T_g and a melting endotherm followed by an intensive exothermic peak due to the reaction of the acetylene units. Based on the measurement of the exothermic enthalpy change (ΔH_{ex}) of the reaction of acetylene units (see *Table 1*), one can suggest that the reactivity of the acetylene units in macrocyclic oligomers **3a–d** remains essentially the same. In particular, by d.s.c. macrocyclic oligomers **3a** shows a T_g at 142°C, a melting endotherm at 305°C with an on-set temperature of 242°C and off-set temperature of 314°C, followed by an exothermic peak which begins at 348°C, has a maximum at 408°C and is complete at 458°C. The d.s.c. trace of macrocyclic oligomers **3b** shows a T_g at 151°C, a melting endotherm at 306°C with an on-set temperature of 220°C and off-set temperature of 319°C, followed by an exothermic peak which begins at 340°C, has a maximum at 412°C and is complete at 466°C. The d.s.c. trace of macrocyclic oligomers **3c** shows a T_g at 145°C, a melting endotherm at 281°C with an on-set temperature of 253°C and off-set temperature of 290°C, followed by an exothermic peak which begins at 350°C, has a maximum at 417°C and is complete at 467°C. On the other hand, macrocyclic oligomers **3d** shows a T_g of 187°C, a melting endotherm peaked at 371°C with an on-set temperature of 361°C and off-set temperature of 379°C, followed immediately with an exothermic peak centered at 431°C. The corresponding linear high molecular polymers[30] are amorphous and generally have T_gs 10–20°C higher than the macrocyclic oligomers. The detection of T_m in the macrocyclic oligomers is due to the fact that a high percentage of cyclic monomer and dimer is present in the oligomeric mixture, and these monomers and dimers crystallize readily. The fact that the off-set melting temperatures of **3a–c** are lower than on-set temperatures of the exothermic reaction of the acetylene units provides a processing temperature window (from 20 to 60°C) which should allow the fabrication and ring-opening polymerization of the macrocyclic oligomers to be complete before significant cross-linking takes place.

Table 2 The compositions of macrocyclic aryl ether oligomers **3a–d** measured by reverse-phase gradient h.p.l.c. at detection of 255 nm and 300 nm

Cyclic oligomers	**3a** (255 nm)[a]	**3a** (300 nm)[b]	**3b** (255 nm)	**3b** (300 nm)	**3c** (255 nm)	**3c** (300 nm)	**3d** (255 nm)	**3d** (300 nm)
Monomer	–	–	30.6	41.7	37.0	30.4	15.4	13.5
Dimer	46.5	46.8	31.9	26.8	32.7	35.9	41.1	36.7
Trimer	21.0	22.7	14.7	12.1	12.4	14.4	17.2	19.1
Tetramer	10.5	11.2	7.4	6.2	6.0	7.0	9.1	10.3
Pentamer	5.9	6.5	4.4	3.6	3.5	4.2	5.4	6.1
Hexamer	3.4	3.9	3.5	3.0	2.2	2.7	3.6	4.1
Heptamer	2.1	2.3	2.6	2.2	1.6	1.9	2..4	2.8
Octamer	1.2	1.9	2.1	1.7	1.3	1.4	1.7	2.0
Nonamer	0.9	1.3	1.0	0.8	1.1	0.9	1.2	1.4
Decamer	0.6	1.0	0.8	0.5	0.8	0.5	0.9	1.1
Undecamer	0.4	0.7	0.5	0.3	0.7	0.3	0.7	0.8
Dodecamer	0.3	0.5	0.3	0.2	0.6	0.2	0.5	0.6
Tridecamer	0.2	0.4	–		0.2	0.1	0.3	0.4
Tetradecamer	0.1	0.3	–		–	–	0.2	0.3
Pentadecamer	0.1	0.1	–				0.1	0.2

[a]Detected at 255 nm
[b]Detected at 300 nm

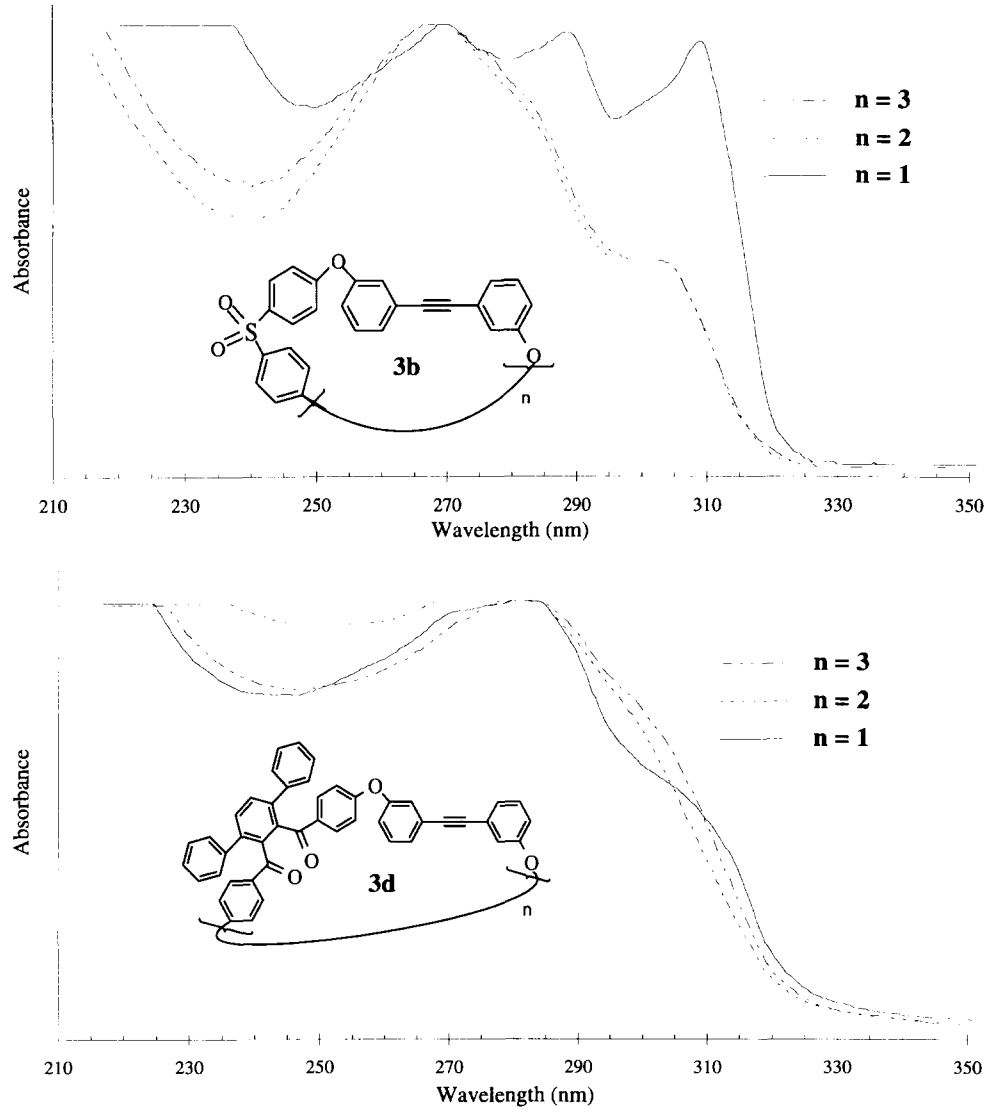


Figure 5 U.v.-visible absorption spectra of the monomer, dimer and trimer of cyclic oligomers **3a** and **3d**

Synthesis of random co-macrocyclic oligomers

The high melting temperature of macrocyclic oligomers such as **3d** is undesirable, since any processing advantage that might be realized by the low melt viscosity of these macrocyclic oligomers is offset by the high melting temperatures of these intermediates. Moreover, at such a high temperature which is very close to the on-set temperature of the cross-linking reaction of the acetylene units, significant cross-linking reaction takes place concurrent with the ring-opening polymerization. One way to overcome these shortcomings is to prepare random co-macrocyclic oligomers. The chemical structure of the co-macrocyclics is irregular which minimizes the crystallinity and lowers the melting temperatures of the macrocyclics. Co-macrocyclic oligomers **4** were therefore prepared to demonstrate this concept, using the same synthetic conditions as in the preparation of the homo-macrocyclic oligomers, by condensing monomer **1** with a mixture (50/50 molar ratio) of difluoro-monomers **2a** and **2b**. The yield and physical properties of co-macrocyclic oligomers **4** are presented in *Table 1*.

Characterization of co-macrocyclic oligomers

G.p.c. analysis show that random co-macrocyclic oligomers **4** are low molecular weight oligomers with an average degree of polymerization of about 3. The g.p.c. trace of co-macrocyclics **4** is shown in *Figure 6a*. ^{1}H, ^{13}C and ^{19}F n.m.r. spectroscopy also gives no indication of the presence of any fluoro or phenolic end groups, which suggests that the low molecular weight oligomers and macrocycles. Although the reverse-phase gradient h.p.l.c. analysis (see *Figure 6b*) shows a much better separation of the individual cyclic oligomers, only very few of early members (monomer and dimer) of co-macrocyclic oligomers **4** can be identified by comparing with h.p.l.c. traces of macrocyclic oligomers **3a** and **3b**. The co-macrocyclics larger than dimer are too complex to be analysed because of the large numbers of possible arrangements, considering there are $n+1$ types of n-mers! For instance, there are four different types of trimers and five different types of tetramers. MALDI-TOF-MS analysis provides a simple and powerful method for the (partial) analysis of co-macrocyclic oligomers. MALDI-TOF-MS spectra of co-macrocyclic

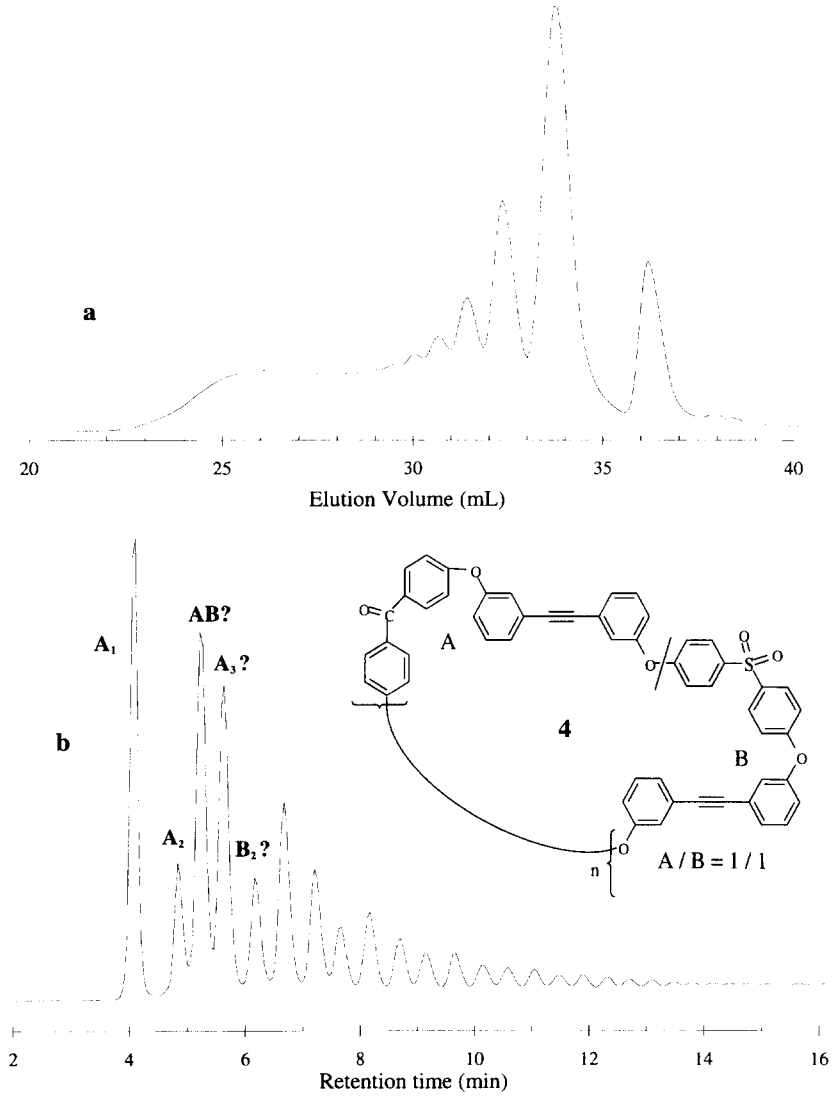
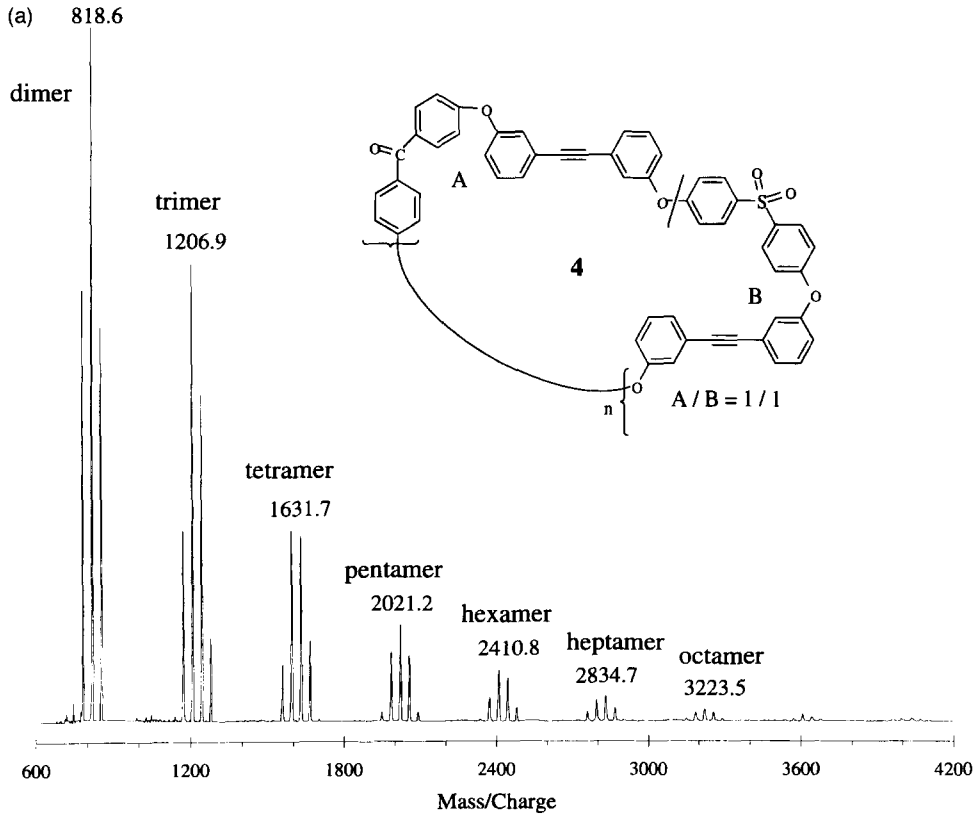
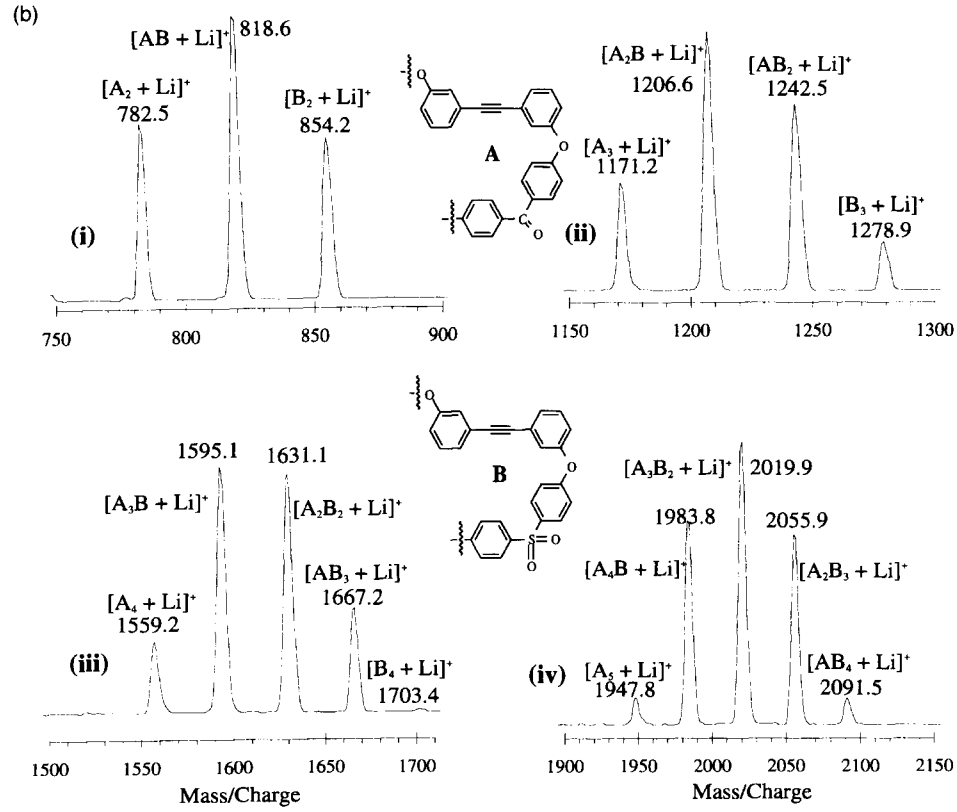


Figure 6 (a) G.p.c. trace (detected at 254 nm) and (b) reverse-phase gradient h.p.l.c. trace (detected at 300 nm) of co-cyclic oligomers **4**

oligomers, using dithranol as the matrix, give the correct molecular ion peaks for the desired macrocyclic oligomers, up to octamer, with excellent signal to noise ratio.

A typical positive ion MALDI-TOF mass spectrum of co-macrocyclic oligomers **4** is shown in *Figure 7a*. The expanded MALDI-TOF mass spectra of cyclic dimers, trimers, tetramers, pentamers, hexamers, heptamers and octamers of **4** are shown in *Figure 7b* and *Figure 7c*. The trace **i** in *Figure 7b* shows peaks only at *m/z* 782.5, 818.6 and 854.2, corresponding to the molecular ion signals for lithium adducts $[\mathbf{A}_2 + \mathrm{Li}]^+$, $[\mathbf{AB} + \mathrm{Li}]^+$ and $[\mathbf{B}_2 + \mathrm{Li}]^+$ of the desired cyclic dimers of $\mathbf{A}_2$, **AB** and $\mathbf{B}_2$, respectively. For the trace **ii** in *Figure 7b*, there are four peaks at *m/z* 1171.2, 1206.6, 1242.5, and 1278.9, corresponding to the molecular ion signals for lithium adducts $[\mathbf{A}_3 + \mathrm{Li}]^+$, $[\mathbf{A}_2\mathbf{B} + \mathrm{Li}]^+$, $[\mathbf{AB}_2 + \mathrm{Li}]^+$ and $[\mathbf{B}_3 + \mathrm{Li}]^+$ of the cyclic trimers of $\mathbf{A}_3$, $\mathbf{A}_2\mathbf{B}$, $\mathbf{AB}_2$ and $\mathbf{B}_3$, respectively. There are five peaks, in trace **iii** of *Figure 7b*, only at *m/z* 1559.2, 1595.1, 1631.1, 1667.2 and 1703.4, corresponding to the molecular ion signals for lithium adducts $[\mathbf{A}_4 + \mathrm{Li}]^+$, $[\mathbf{A}_3\mathbf{B} + \mathrm{Li}]^+$, $[\mathbf{A}_2\mathbf{B}_2 + \mathrm{Li}]^+$, $[\mathbf{AB}_3 + \mathrm{Li}]^+$ and $[\mathbf{B}_4 + \mathrm{Li}]^+$ of the cyclic trimers of $\mathbf{A}_4$, $\mathbf{A}_3\mathbf{B}$, $\mathbf{A}_2\mathbf{B}_2$, $\mathbf{AB}_3$ and $\mathbf{B}_4$, respectively. However, it has to be pointed out that the intensity of the signal corresponding to tetramer $\mathbf{B}_4$ is very weak which implies that the probability for the formation of homocyclic tetramer $\mathbf{B}_4$ is very small compared with that of $\mathbf{A}_4$. Five peaks corresponding to the molecular ion signals for lithium adducts of cyclic pentamers of $\mathbf{A}_5$, $\mathbf{A}_4\mathbf{B}$, $\mathbf{A}_3\mathbf{B}_2$, $\mathbf{A}_2\mathbf{B}_3$, and $\mathbf{AB}_4$ can also be assigned (trace **iv** in *Figure 7b*). The trace **i** in *Figure 7c* shows four main peaks at *m/z* 2372.9, 2407.8 and 2443.8 and 2480.3, corresponding to the molecular ion signals for lithium adducts $[\mathbf{A}_5\mathbf{B} + \mathrm{Li}]^+$, $[\mathbf{A}_4\mathbf{B}_2 + \mathrm{Li}]^+$, $[\mathbf{A}_3\mathbf{B}_3 + \mathrm{Li}]^+$ and $[\mathbf{A}_2\mathbf{B}_4 + \mathrm{Li}]^+$ of the cyclic hexamers of $\mathbf{A}_5\mathbf{B}$, $\mathbf{A}_4\mathbf{B}_2$, $\mathbf{A}_3\mathbf{B}_3$, and $\mathbf{A}_2\mathbf{B}_2$, respectively. The trace **ii** in *Figure 7c* shows four main peaks at 2763.9, 2798.8, 2834.7 and 2870.0 corresponding to the molecular ion signals for lithium adducts $[\mathbf{A}_6\mathbf{B} + \mathrm{Li}]^+$, $[\mathbf{A}_5\mathbf{B}_2 + \mathrm{Li}]^+$, $[\mathbf{A}_4\mathbf{B}_3 + \mathrm{Li}]^+$ and $[\mathbf{A}_3\mathbf{B}_4 + \mathrm{Li}]^+$ of cyclic heptamers of $\mathbf{A}_6\mathbf{B}$, $\mathbf{A}_5\mathbf{B}_2$, $\mathbf{A}_4\mathbf{B}_3$ and $\mathbf{A}_3\mathbf{B}_4$. The expanded MALDI-TOF mass spectra, in the range of 3100–3350 *m/z* (trace **iii** in *Figure 7c*) and 3550–3770 *m/z* (trace **iv** in *Figure 7c*), shows five signals and four signals respectively with reasonable signal to noise ratio. In trace **iii** of *Figure 7c*, the signal at 3152.9 Da corresponds to the molecular ion signal for lithium adduct $[\mathbf{A}_7\mathbf{B} + \mathrm{Li}]^+$ of cyclic octamer $\mathbf{A}_7\mathbf{B}$, signal at 3187.7 Da corresponds to the molecular ion signal for lithium adduct $[\mathbf{A}_6\mathbf{B}_2 + \mathrm{Li}]^+$ of cyclic


(a)
818.6
dimer
trimer
1206.9
tetramer
1631.7
pentamer
2021.2
hexamer
2410.8
heptamer
2834.7
octamer
3223.5
A
B
4
A / B = 1 / 1
600
1200
1800
2400
3000
3600
4200
Mass/Charge


(b)
[AB + Li]+ 818.6
[A2 + Li]+ 782.5
[B2 + Li]+ 854.2
(i)
750
800
850
900
A
[A2B + Li]+ 1206.6
[AB2 + Li]+ 1242.5
[A3 + Li]+ 1171.2
[B3 + Li]+ 1278.9
(ii)
1150
1200
1250
1300
1595.1
1631.1
[A3B + Li]+
[A2B2 + Li]+
[AB3 + Li]+ 1667.2
[A4 + Li]+ 1559.2
[B4 + Li]+ 1703.4
(iii)
1500
1550
1600
1650
1700
Mass/Charge
B
[A3B2 + Li]+ 2019.9
1983.8
2055.9
[A4B + Li]+
[A2B3 + Li]+
[AB4 + Li]+ 2091.5
[A5 + Li]+ 1947.8
(iv)
1900
1950
2000
2050
2100
2150
Mass/Charge

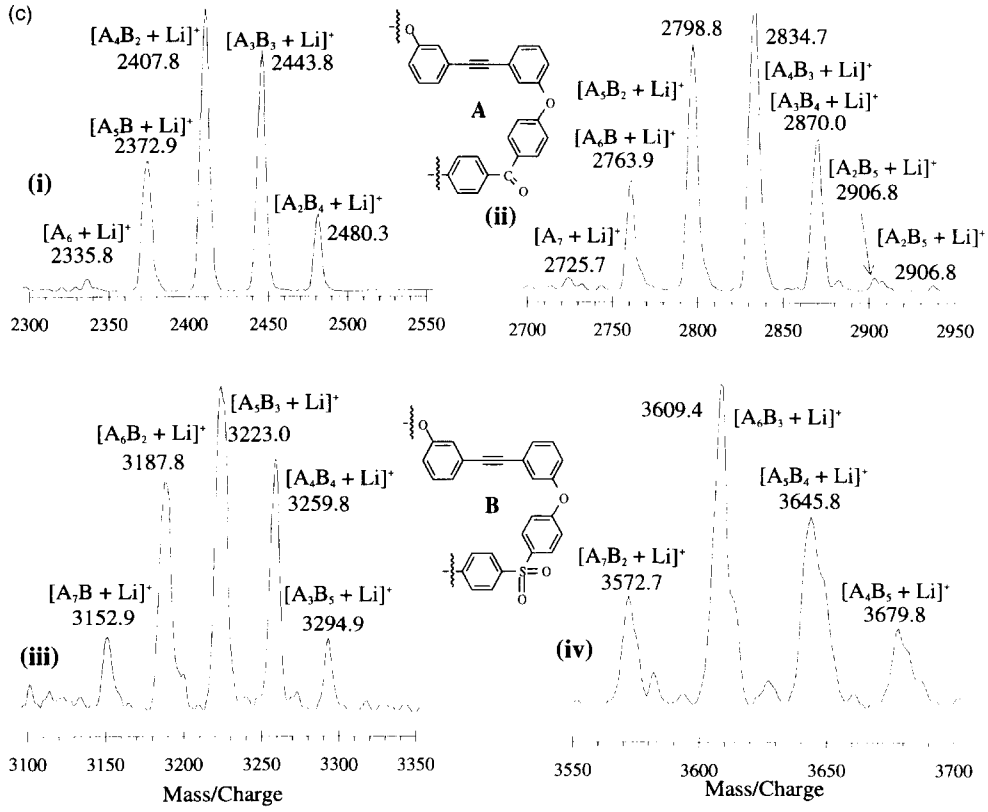


Figure 7 (a) Positive ion MALDI-TOF mass spectrum of co-cyclic oligomers **4**. The data were acquired in the reflection mode using dithranol as the matrix (dithranol/cyclics = 20/1 by weight). (b) Expanded scale of the positive ion MALDI-TOF mass spectra of co-cyclic oligomers **4**: (i) dimer, (ii) trimer, (iii) tetramer and (iv) pentamer. (c) Expanded scale of the positive ion MALDI-TOF mass spectra of co-cyclic oligomers **4**: (i) hexamer, (ii) heptamer, (iii) octamer and (iv) nonamer

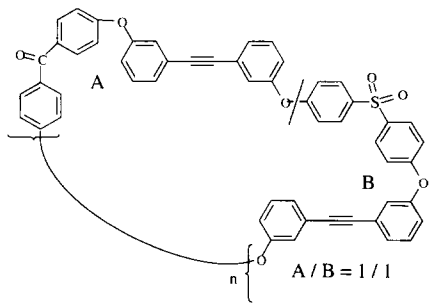
octamer $\mathbf{A_6B_2}$, signal at 3223.0 Da corresponds to the molecular ion signal for lithium adduct $[\mathbf{A_5B_3} + Li]^+$ of cyclic octamer $\mathbf{A_5B_3}$, signal at 3259.8 Da corresponds to the molecular ion signal signal for lithium adduct $[\mathbf{A_4B_4} + Li]^+$ of cyclic octamer $\mathbf{A_4B_4}$, and signal at 3294.9 Da corresponds to the molecular ion signal for lithium adduct $[\mathbf{A_3B_5} + Li]^+$ of cyclic octamer $\mathbf{A_3B_5}$. In trace **iv** of *Figure 7c*, signal at 3572.7 Da corresponds to the molecular ion signal for lithium adduct of cyclic nonamer $\mathbf{A_7B_2}$, signal at 3609.4 Da corresponds to the molecular ion signal for lithium adduct $[\mathbf{A_6B_3} + Li]^+$ of cyclic nonamer $\mathbf{A_6B_3}$, signal at 3645.8 Da corresponds to the molecular ion signal for lithium adduct $[\mathbf{A_5B_4} + Li]^+$ of cyclic nonamer $\mathbf{A_5B_4}$, and signal at 3679.8 Da corresponds to the molecular ion signal for lithium adduct $[\mathbf{A_4B_5} + Li]^+$ of cyclic nonamer $\mathbf{A_4B_5}$. In the mass range up to 4000, there is no indication of the presence of linear oligomers.

From d.s.c. cyclic oligomer **4** (*Table 1*) shows a T_g at 147°C, a moderate melting endotherm at 267°C with an on-set temperature of 240°C and off-set temperature of 280°C, followed by an intense exothermic peak which begins at 350°C, has a maximum at 430°C and is complete at 475°C. Although the co-macrocyclic oligomers **4** are still semicrystalline material, the melting temperature is depressed considerably.

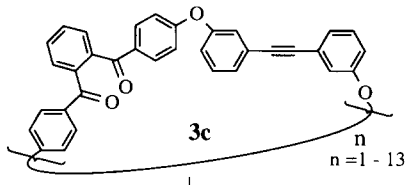
Ring-opening polymerization and cross-linking studies of the macrocyclic oligomers **3a**, **3c** *and* **4** *in the melt*

With the cyclic oligomers available, polymerization reactions and cross-linking reactions of the resulting polymers were next investigated. It was anticipated that the ring-opening polymerization of macrocyclic aryl ether oligomers could be initiated through an ether exchange reaction in the presence of a nucleophilic initiator. Since the aryl ether linkage is activated by an electron-withdrawing group, it undergoes an ether exchange reaction readily[4–7,10,13,14]. The effective nucleophilic initiators include cesium fluoride[4–7,10], alkali phenoxides[13,14] and alkali benzoates[14], among which potassium 4,4′-biphenoxide (KOPhPhOK) has been shown to be most effective for the ring-opening polymerization of macrocyclic aryl ether ketone oligomers containing the 1,2-dibenzoylbenzene moiety[13,14]. Macrocyclic aryl ether oligomers **3a–d** and **4** should also undergo ring-opening polymerization via the transetherification reaction, in the presence of a nucleophilic initiator, to form high molecular weight polymers. As macrocyclic oligomers **3a**, **3c** and **4** have melting temperatures which are substantially lower than the on-set temperature of the cross-linking reaction of acetylene units (see *Table 1*), polymerization of these macrocyclic oligomers at temperatures below 300°C should lead to formation of high molecular weight polymers with limited cross-linking reactions taking place.

In the presence of 1.0 mol% potassium 4,4′-biphenoxide, polymerization of macrocyclic oligomers **3c** at 300°C for 30 min under nitrogen led to the formation of a tough material **5** (*Scheme 2*). The material **5** is not soluble in most organic solvents such as chloroform, although the linear high molecular weight analogue of **3c** is very



4



1.0 mol% KOPhPhOK | 300°C, nitrogen 30 min

5

Scheme 2

Table 3 Thermal properties of polymers resulting from cyclic oligomers **3c**

Material	Curing conditions	T_g (°C)[a]	ΔH_{ex} (J g^{-1})[b]
3c	None	145	194
3c	300°C for 30 min	149	180
5	None	162	143
5	340°C for 15 min	195	76
5	340°C for 30 min	227	44
5	340°C for 45 min	241	26

[a]Measured by d.s.c. under nitrogen (a flow rate of 100 ml min^{-1}) at a heating rate of 20°C min^{-1}

[b]Exothermic enthalpy change of the reaction of acetylene units, measured by d.s.c. calibrated against indium

soluble in chloroform[30]. Due to the insolubility of **5** molecular characterization such as g.p.c. analysis cannot be performed, however, d.s.c. analysis of the material should provide information about the changes of T_g of the material before and after polymerization. The increase of T_g would result from either the formation of high molecular weight linear polymers and/or partial cross-linking of the materials (cyclics and linear polymers). Furthermore, measurements of the exothermic enthalpy changes (ΔH_{ex}) of the cross-linking reaction of acetylene units would also provide semi-quantitative information about the extent of cross-linking which occurred during polymerization. A d.s.c. scan of **5** at a heating rate of 20°C (trace **c** in *Figure 8*) shows that the material has a T_g of 162°C which is 17°C higher than that of macrocyclic oligomers **3c**, followed by an intense exothermic peak due to the reaction of acetylene units. The thermal properties of the material **5** are presented in *Table 3*. ΔH_{ex} of **5** is 143 J g^{-1} which is 26% lower than that of **3c**. This implies that a certain degree of cross-linking of the acetylene units took place during polymerization at 300°C which probably involved about 26% of the acetylene units. Heating cyclic oligomers **3c** under the same conditions, in the absence of initiator KOPhPhOK, also led to formation of an insoluble material which has a T_g of 149°C (4°C higher than that of **3c**) (see *Table 3*) with ΔH_{ex} of 180 J g^{-1} (7% lower than that of **3c**). This indicates that, at 300°C, a certain number of acetylene units in **3c** underwent a cross-linking reaction to form cross-linked macrocyclics. The large increase (17°C compared with 4°C) of T_g in the presence of nucleophilic initiator does, however, indicate that substantial ring-opening polymerization takes place with a limited amount of simultaneous cross-linking of the macrocycles. The larger decrease (26%) of ΔH_{ex} from **3c** to **5**, compared with 7% of **3c** cured at 300°C for 30 min without catalyst, might suggest that the acetylene units in linear polymers are more reactive towards cross-linking than those in the cyclic rings. Further cross-linking of polymer **5** can be induced by heating the material at higher temperatures. Heating **5** at 340°C for 15–45 min resulted in tough materials with T_gs which are significantly higher than that of **5**. D.s.c. traces of these materials are shown in *Figure 8* and their thermal properties are listed in *Table 3*. As shown in *Figure 9*, the T_g of the resulting material increases monotonically as the curing time increases, and the exothermic enthalpy change of the reaction of acetylene units decreases monotonically as the curing time increases. For example, heating **5** at 340°C for 15 min led to formation of a tough material with a T_g of 195°C which is 33°C higher that of **5**, and the ΔH_{ex} of 76 J g^{-1} which is only 39% of that of macrocyclic oligomers **3c**. When **5** was cured at 340°C for 45 min, the resulting material had a T_g of 241°C which is 79°C higher than that of **5**, and the ΔH_{ex} of the reaction of acetylene units is only 13% of that of **3c**.

Polymerization of cyclic oligomers **3a** at 300°C for 30 min under nitrogen, in the presence of 1.0 mol% KOPhPhOK, also led to formation of a tough insoluble material **6** (*Scheme 3*). The material **6** had a T_g of 165°C which is 23°C higher than that of the macrocyclic oligomers **3a**, and the exothermic enthalpy change was 201 J g^{-1} which is about 13% lower than that of cyclic oligomers **3a** (see *Table 4*). This implies that a certain amount of cross-linking of acetylene units took place during polymerization which probably involved 13% of acetylene units. Further cross-linking of **6** can be induced by heating the material at higher temperatures. For example, heating the material **6** at 340°C under nitrogen for 5 and 10 min resulted in materials having T_g of 202 and 252°C respectively (see *Table 4*). A thermosetting material resulted from curing the material at 340°C for 15 min under nitrogen.

As discussed above, polymerization of **3a** and **3c** at 300°C resulted in materials which are no longer soluble in common organic solvents, and based on the measurement of ΔH_{ex} of the reaction of acetylene units, some of the cross-linking reaction took place during polymerization. Although considerable increase of T_g resulted from heating the macrocyclic oligomers at 300°C in the presence of a nucleophilic initiator, it is difficult to verify if the ring-opening polymerization actually took place. To obtain soluble materials, ring-opening polymerization of macrocyclic oligomers should be conducted at relatively lower temperatures in order to avoid cross-linking reaction of the acetylene units. Therefore, polymerization of the co-macrocyclic oligomers **4** was conducted at 280°C. Heating **4** at 280°C for 30 min under

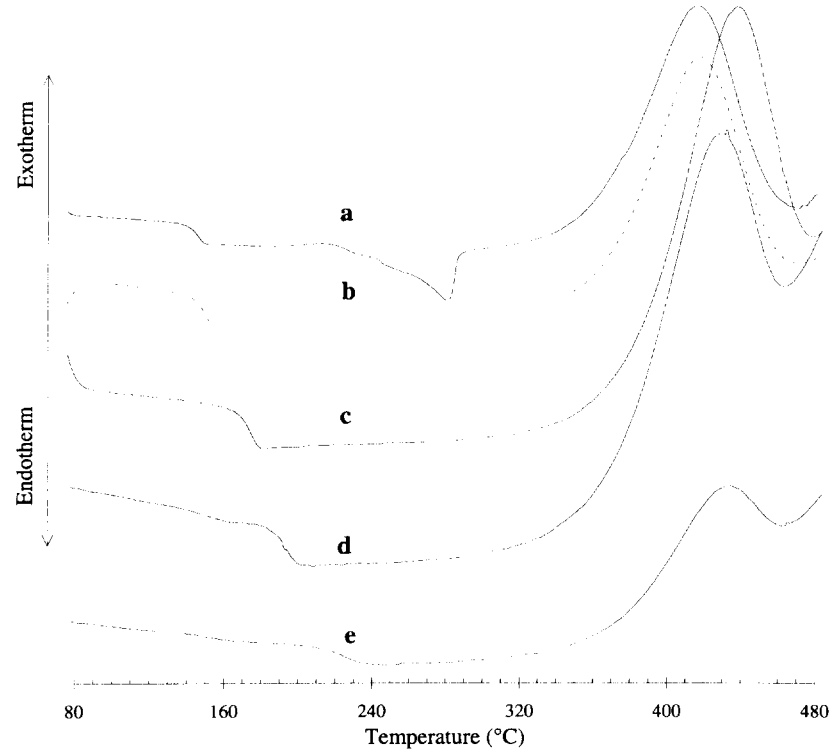


Figure 8 D.s.c. traces of (a) cyclic oligomers **3c**, (b) cyclic oligomers **3c** cured at 300°C under nitrogen for 30 min, (c) polymer **5** resulting from **3c**, (d) **5** cured at 340°C for 15 min under nitrogen, and (e) **5** cured at 340°C for 30 min under nitrogen (the first scan with a heating rate of 20°C min^{-1})

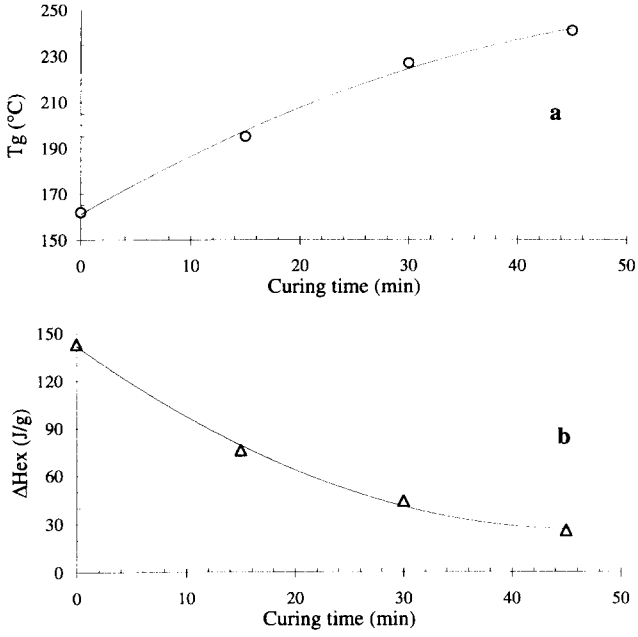
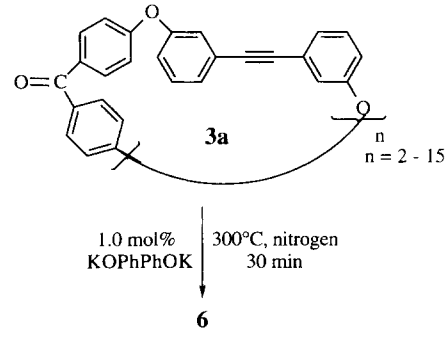


Figure 9 Plots of (a) T_g–curing time and (b) ΔH_{ex}–curing time for polymer **5**



Scheme 3

nitrogen, in the absence of a nucleophilic initiator, resulted in material which was still completely soluble in chloroform. G.p.c., h.p.l.c. and MALDI-TOF-MS analyses showed that the cyclic oligomers **4** were still intact. However, in the presence of 1.0 mol% KOPhPhOK, heating **4** at 280°C for 30 min under nitrogen resulted in a flexible and tough material which was partially soluble in chloroform. Only 46% of the resulting material was soluble in chloroform and 15% of the macrocyclic oligomers remained. A g.p.c. trace of the soluble fraction is presented in *Figure 10*, which clearly shows the formation of high molecular weight linear polymer. The high molecular weight fraction has an M_n of 15 600 and M_w of 194 000. Prolonging the polymerization time gave less amount of cyclic oligomers and the soluble fraction of high molecular weight materials was considerably reduced. The formation of soluble high molecular weight polymers clearly demonstrates that the ring-opening polymerization of the macrocyclic oligomers indeed takes place. Although there was still some of cross-linking of acetylene units during the ring-opening polymerization of **4** at 280°C, we speculate that the cross-linking reaction may take place predominantly in the linear polymers formed.

CONCLUSIONS

A synthetic route for the direct incorporation of cross-linkable diphenylacetylene functional units into the

Table 4 Thermal properties of polymers resulting from cyclic oligomers **3a**

Material	Curing conditions	T_g (°C)[a]	ΔH_{ex} (J g^{-1})[b]
3a	None	142	230
6	None	165	201
6	340°C for 5 min	202	100
6	340°C for 10 min	252	40
6	340°C for 15 min	Thermosetting	None

[a]Measured by d.s.c. under nitrogen (a flow rate of 100 ml min^{-1}) at a heating rate of 20°C min^{-1}

[b]Exothermic enthalpy change of the reaction of acetylene units, measured by d.s.c. and calibrated against indium

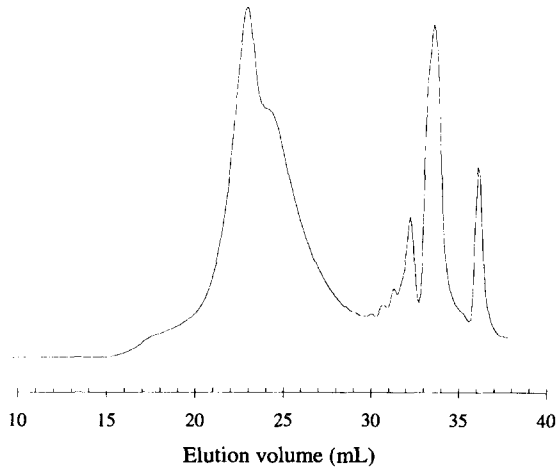


Figure 10 G.p.c. trace of the soluble fraction (in chloroform) of the material resulting from heating and co-cyclic oligomers **4** at 280°C for 30 min in the presence of 1.0 mol% potassium 4,4′-biphenoxide. Detection was at 254 nm

backbone of macrocyclic aryl ether oligomers has been developed. The macrocyclic aryl ether oligomers containing a diphenylacetylene moiety were prepared in high yield by reaction of bis(3-hydroxyphenyl)acetylene with a number of difluoro-monomers under high dilution conditions. The cyclic nature of the oligomers and composition of the cyclic oligomers were thoroughly studied by the combination of n.m.r., MALDI-TOF-MS, g.p.c. and reverse-phase gradient h.p.l.c. MALDI-TOF-MS, which enables the detection of oligomers with mass up to 6500 Da, is shown to be a remarkable tool for the analysis and proof of the cyclic nature of the oligomers. This technique is proven to be particularly useful for the analysis of co-cyclic oligomers. We were able to identify 37 individual macrocyclic species, with repeating units up to 9, for the co-cyclic **4**! Macrocyclic oligomers **3b–d** mainly consist of macrocycles from monomer to decamer. On the other hand, for **3a** there is no formation of macrocyclic monomer. Thermal analyses show that macrocyclic oligomers **3a–d** are semicrystalline with T_m varying from 280 to 370°C, the co-cyclic oligomers **4** are also semicrystalline with a moderate T_m of 267°C. Heating macrocyclic oligomers **3a** and **3c** at 300°C for 30 min, in the presence of an nucleophilic initiator, leads to the formation of tough and insoluble materials with T_gs which are significantly higher than that of the cyclic precursors. Measuring the exothermic enthalpy change (ΔH_{ex}) of reaction of the acetylene units in the resulting materials by d.s.c. analysis shows that some of cross-linking of the acetylene units takes place during the polymerization reaction at 300°C. Upon heating at 340°C, the resulting polymers can be thermally cross-linked further with an increase of T_g up to 100°C in a relatively short time. Polymerization of **4** at 280°C for 30 min, in the presence of 1.0 mol% KOPh-PhOK, led to the formation of a tough and flexible material. The resulting material is only partly soluble and g.p.c. analysis shows the formation of high molecular weight polymers which clearly shows that the cyclic oligomers indeed undergo ring-opening polymerization at 280°C or above in the presence of a nucleophilic initiator, although some of cross-linking reaction of the acetylene units takes place during the polymerization.

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