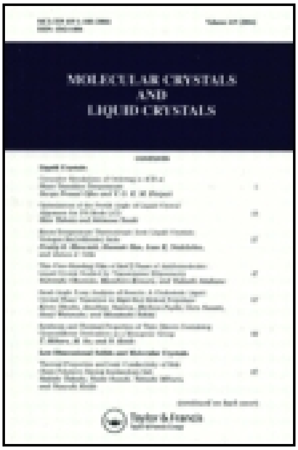

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At the Borderline between Glassy, Crystalline and Liquid Crystalline Macrocyclics[1a]

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At the Borderline between Glassy, Crystalline and Liquid Crystalline Macrocyclics[1a]

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The synthesis and characterization of the macrocyclic oligopolyethers based on the conformationally flexible 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) with 1,4-dibromobutane [TPB-(*c*)4(*z*), where *z* indicates the degree of oligomerization of the macrocyclic] and with 1,6-dibromohexane [TPB-(*c*)6(*z*)], respectively are described. These cyclic oligomers were synthesized by the phase transfer catalyzed polyetherification of TPB with 1,4-dibromobutane or 1,6-dibromohexane under high dilution conditions and the individual compounds were separated by column chromatography. Their cyclic structure was confirmed by 200 MHz ^{1}H-NMR spectroscopy. The mesomorphic behavior of TPB-(*c*)4(*z*) and TPB-(*c*)6(*z*) was characterized by differential scanning calorimetry (DSC) and optical polarized microscopy. The macrocyclic derivative with the shortest spacer based on TPB and α,ω-dibromoalkanes which displays a liquid crystalline mesophase is the tetramer obtained with 1,4-dibromobutane [TPB-(*c*)4(4)]. However its nematic mesophase is only monotropic and its isotropization transition temperature is lower than that of its corresponding high molecular weight linear polyether TPB-(1)4. The macrocyclic polyether with the shortest spacer based on TPB which displays a nematic phase with an isotropization temperature which is higher than its high molecular weight linear homologue is the tetramer based on 1,6-dibromohexane [i.e., TBP-(*c*)6(4)]. TPB-(*c*)6(3) exhibits an unidentified monotropic X phase. The enthaply changes associated with the isotropization temperatures of the macrocyclics are lower than those of the corresponding linear polymers.

Keywords: macrocyclic liquid crystals

INTRODUCTION

Soon after the discovery of liquid crystals [1b] it has been recognized that rigid linear and discotic molecules are the most suitable shapes which lead to molecular liquid crystals.[1c] 100 years later, the discussion on molecular structure-properties relationship in this field is still centered around the same two architectures and on few less conventional variants of them.[1d-k] Recently, we have predicted and demonstrated that low molar mass macrocyclic structures based on conventional rod-like mesogens should and indeed do display a higher ability to exhibit liquid crystalline

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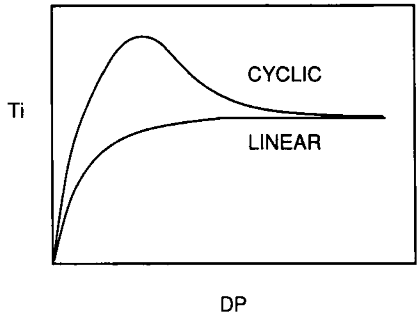


SCHEME 1 The dependence of the isotropization temperature (Ti) of cyclic and linear main chain liquid crystalline polymers on their degree of polymerization (DP). Both Ti and DP are in arbitrary units.

phases than their low molar mass linear and both linear and cyclic high molecular weight homologues (Scheme 1).[2b,c] The trend outlined in Scheme 1 is due to the fact that macrocyclics of a certain size are more rigid than the corresponding linear homologues and than both their high molecular weight linear and cyclic compounds. The particular examples reported so far are macrocyclic polyethers, i.e., the monomer, dimer, trimer, tetramer and pentamer of the conformationally flexible 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) with 1,5-dibromopentane,[2c] 1,7-dibromoheptane[2d] and 1,10-dibromodecane,[2b] respectively. The synthesis and thermal characterization of the linear high molecular weight polyethers based on TPB and flexible spacers containing from four to twenty methylenic units was also reported.[3] Characterization of these polymers by X-ray scattering experiments showed that they exhibit a conventional uniaxial nematic mesophase.[4]

This paper will describe the synthesis and characterization of the macrocyclic oligomers of TPB with 1,4-dibromobutane and with 1,6-dibromohexane respectively. The purpose of these experiments was to elucidate two problems. The first one was to determine the minimum length of the flexible spacer of the macrocyclic oligomer which provides the transition from a crystalline to a liquid crystalline macrocyclic. The second one was to determine the minimum length of the spacer which provides the first macrocyclic displaying a higher isotropization temperature than its high molecular weight linear homologue.

EXPERIMENTAL

Materials

Tetrabutylammonium hydrogen sulfate (TBAH) (97%, Aldrich) was used as received. 1,4-Dibromobutane (99%) and 1,6-dibromohexane (97%) (both from Aldrich) were purified by vacuum distillation. *o*-Dichlorobenzene was distilled under reduced pressure. 1-(4-Hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) (purity > 99% by HPLC) was synthesized according to the previously described procedure.[3] Silicagel plates with fluorescent indicator (Eastman Kodak) were used for thin-layer chromatography (TLC) analyses. All other chemical were commercially available and were used as received.

Syntheses of Linear Polyethers TPB-(1)4 and TPB-(1)6

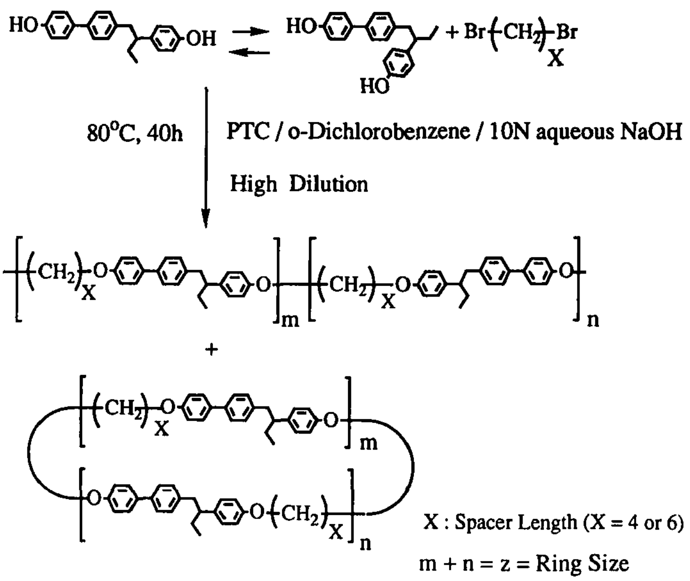
The linear polyether based on TPB and 1,4-dibromobutane [TPB-(1)4] (Mn = 14,700, Mw/Mn = 1.82), and the polyether based on TPB and 1,6-dibromohexane [TPB-(1)6] (Mn = 32,300, Mw/Mn = 2.10) were synthesized by a liquid two-phase [*o*-dichlorobenzene/NaOH aqueous solution (10 times excess to the phenol groups)] phase transfer catalyzed polymerization at high monomer concentration under nitrogen. Details of their syntheses, purification and characterization were presented elsewhere.[3]

Synthesis of Macrocyclic Polyethers TPB-(c)4(z) and TPB-(c)6(z) [Where z = 1 (Monomer, 2 (Dimer), 3 (Trimer), 4 (Tetramer)]

The macrocyclics of TPB with 1,4-dibromobutane and 1,6-dibromohexane were synthesized by polyetherification under high dilution conditions [monomer (mmol)/ solvent (ml) = 1/100] under nitrogen atmosphere at 80°C in an *o*-dichlorobenzene-10 N NaOH aqueous solution in the presence of TBAH as phase transfer catalyst. After a reaction time of 40 h the reaction mixture was separated into the individual cyclic oligomers and the high molecular weight part. A general procedure used for the preparation of cyclic polyethers TPB-(*c*)4(*z*) is described below.

To a 500 ml single-neck flask equipped with a condenser were successively added 0.318 g (1.00 mmol) of TPB, 100 ml of 10 N NaOH aqueous solution (1.0 mol), 100 ml of *o*-dichlorobenzene, 1,4-dibromobutane (0.216 g, 1.00 mmol), and 0.136 g (0.40 mmol, 20 mol% of phenol groups) of TBAH. A balloon filled with nitrogen was placed at the top of the condenser. The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80°C. After 40 h, the reaction mixture was diluted with water and chloroform. The organic layer was washed two times with water, with dilute hydrochloric acid, and three times with water. After the evaporation of the solvents, the product was dissolved in chloroform. To this solution silicagel was added and the chloroform was evaporated. The product adsorbed on silicagel was charged on the top of a column containing silicagel and was flushed with acetone to separate the mixture of cyclic oligomers. The remaining product at the top of the column was flushed with chloroform to separate the higher molecular weight part. The mixture of cyclic oligomers was separated into about 50 fractions by silica gel column chromatography with a mixture of acetone and hexanes (1:10 v/v). Each fraction was checked by TLC [developed by a mixture of acetone and hexanes (1:10 v/v) and detected with a UV lamp]. The fraction containing each cyclic oligomer was collected and the solvents were evaporated on a rotary evaporator to produce the separated cyclic oligomer. The cyclic oligomers were further purified by the filtration of their chloroform solution followed by precipitation in methanol.

The same procedure as that used in the case of TBP-(*c*)4(*z*) was used for the preparation and separation of TPB-(*c*)6(*z*) except that 1,6-dibromohexane (0.244 g, 1.00 mmol) was used instead of 1,4-dibromobutane. The ratio of acetone to hexanes used for column chromatographic experiments was 1:15 v/v. The column fractionation was repeated for the tetramer and pentamer with the same mixture of solvents.



SCHEME 2 Synthesis of cyclic polyethers based on TPB and α,ω-dibromoalkanes containing X methylenic units (X = 4 or 6).

Techniques

1-D ^{1}H-NMR (200 MHz) spectra were recorded on a Varian XL-200 NMR spectrometer. All spectra were acquired at room temperature with TMS as internal standard.

Relative molecular weights and purities were determined by gel permeation chromatography (GPC) and high pressure liquid chromatography (HPLC). GPC analyses were carried out with a Perkin-Elmer series 10 LC equipped with an LC-100 column oven, and a Nelson Analytical 900 series data station. The measurements were made by using the UV detector, chloroform as solvent (1 ml/min, 40°C), two PL gel columns of 5×10^2 and 10^4 Å, and a calibration plot constructed with polystyrene standards. HPLC analyses were performed with the same instrument with a PL gel column of 1×10^2 Å.

A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS data station Model 3600 was used to determine thermal transitions. Heating and cooling rates were 20°C/min in all cases. First-order transitions (crystalline-crystalline, crystalline-liquid crystalline, liquid crystalline-isotropic, etc.) were read at the maximum or minimum of the endothermic or exothermic peaks. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. All heating and cooling scans after the first heating scan produced perfectly reproducible data. We will report the transitions collected from first and second or subsequent heating scans and from first cooling scan.

A Carl Zeiss optical polarizing microscope (magnification 100×) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe thermal transitions and to analyze anisotropic textures.

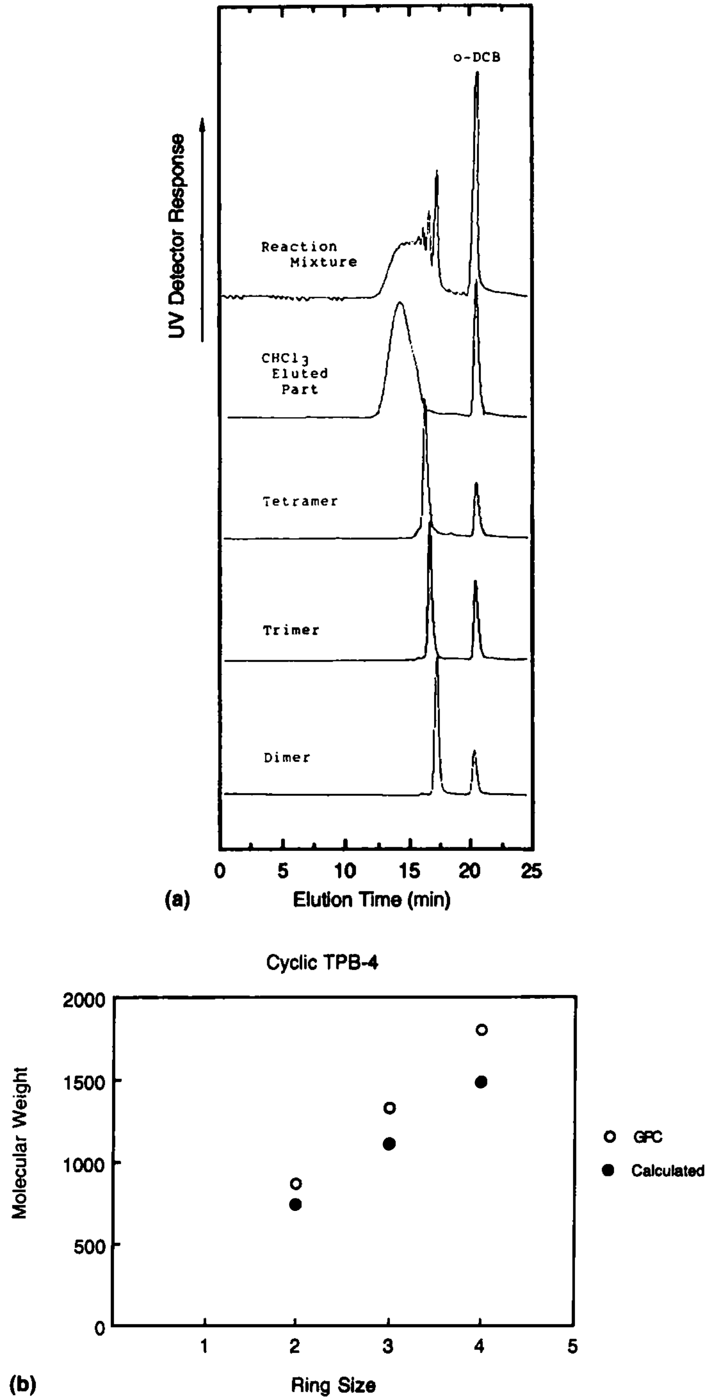


FIGURE 1 (a) GPC chromatograms of the cyclization mixture, of high molecular weight part, and of the separated cyclic oligomers [TPB-(*c*)4(*z*) series]; (b) the dependence of the peak molecular weight of cyclic oligomers (*c*)4(*z*) obtained by GPC (○), and calculated (●), versus ring size.

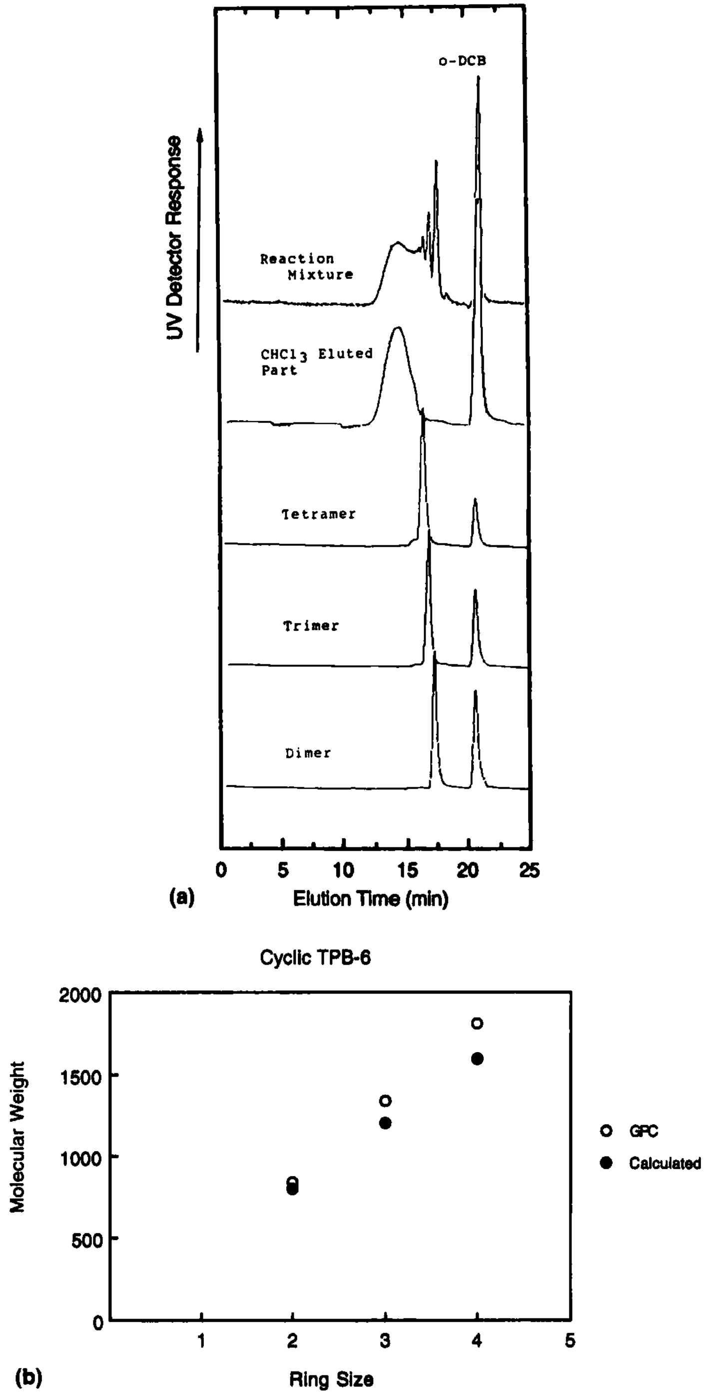


FIGURE 2 (a) GPC chromatograms of the cyclization mixture, of high molecular weight part, and of the separated cyclic oligomers [TPB-(*c*)6(*z*) series]; (b) the dependence of the peak molecular weight of cyclic oligomers TPB-(*c*)6(*z*) obtained by GPC (○), and calculated (●), versus ring size.

TABLE I

Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,4-dibromobutane

Ring size	Yield (%)	Purity by GPC (%)	Molecular weight by GPC at peak top		Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mru) in parentheses	
			Measured	Calculated	First heating Second heating	First cooling
2	9.9	98.7	877	745	k 181 (2.24) i	i 58 g
					g 62 i	
3	4.7	97.1	1336	1118	k 140 (2.12) k 152 (1.44) k 176 (1.36) i	i 64 g
					g 70 i	
4	3.2	95.8	1807	1490	g 59 k 123 (-1.85) k 188 (1.75) i	i 109 (0.31) n 55 g
					g 60 n 114 (0.23) i	
$CHCl_3$ Eluted Part	23.1	-	$M_n = 6.05 \times 10^3$		g 83 (-1.21) n 143 (1.64) i	i 138 (1.83) n 72 g
			$M_w/M_n = 1.57$		g 79 n 143 (1.71) i	
Linear	-	-	$M_n = 1.47 \times 10^4$		g 88 n 99 (-0.32) n 154 (2.04) i	i 142 (2.10) n 75 g
			$M_w/M_n = 1.82$		g 82 n 154 (2.04) i	

[a] Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan. [b] Overlapped peaks.

TABLE II

Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,6-dibromohexane

Ring size	Yield (%)	Purity by GPC (%)	Molecular weight by GPC at peak top		Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mru) in parentheses	
			Measured	Calculated	First heating Second heating	First cooling
2	6.9	>99	845	801	k 196 (8.94) i g 55 k 101 (-1.01) k 158 (-2.67) k 192 k 197 k 203 (8.34^b) i	i 105 (2.86) k 49 g
3	2.7	95.2	1344	1202	k 132 k 148 (3.46^b) i g 63 X 80 (0.35) i	i 74 (0.37) X 59 g
4	2.0	95.5	1812	1602	g 55 k 75 (0.13) n 148 (0.90) i g 61 n 149 (0.79) i	i 145 (0.85) n 54 g
$CHCl_3$ Eluted Part	21.8	-	$M_n = 7.24 \times 10^3$ $M_w/M_n = 1.60$		g 51 n (-0.44) n 131 (2.12) i g 62 n 130 (1.59) i	i 125 (2.07) n 57 g
Linear	-	-	$M_n = 3.23 \times 10^4$ $M_w/M_n = 2.10$		g 71 n 81 (-0.21) n 137 (2.21) i g 67 n 137 (2.16) i	i 122 (2.22) n 59 g

[a] Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan. [b] Overlapped peaks.

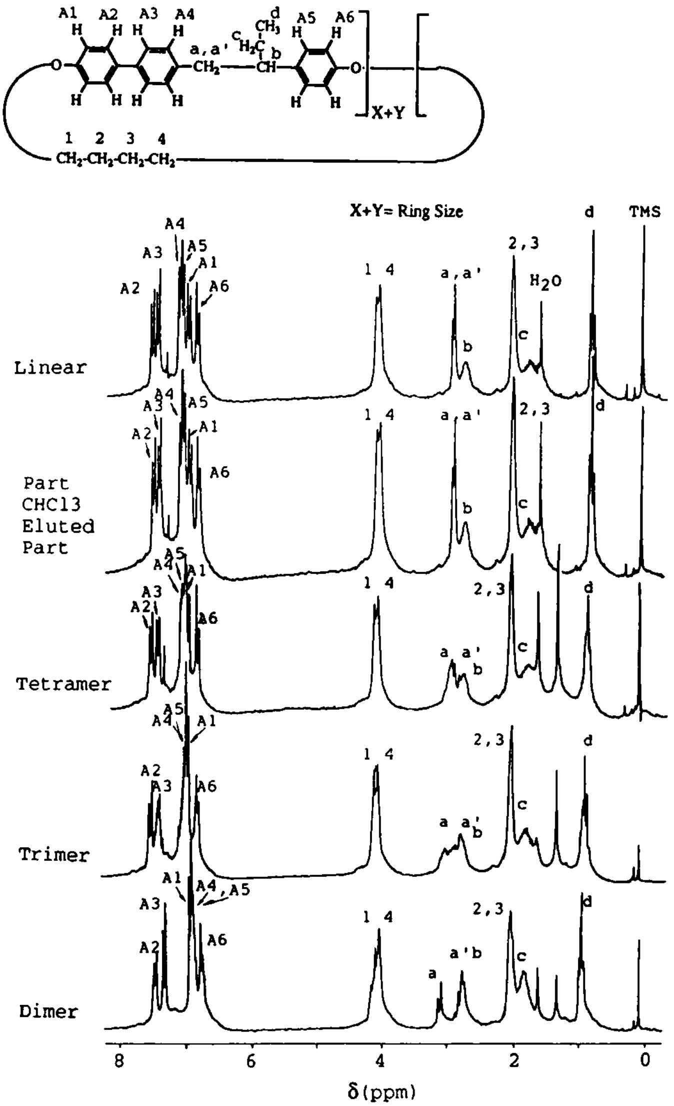


FIGURE 3 The 200 MHz ^{1}H-NMR spectra ($CDCl_3$, TMS) and the corresponding protonic assignments of the cyclic oligomers, of $CHCl_3$ eluted part [TPB-(*c*)4(*z*) series], and of the linear polymer TPB-(1)4.

RESULTS AND DISCUSSION

Scheme 2 outlines the synthesis of linear [TPB-(1)*X*] and cyclic [TPB-(*c*)4(*z*) and TPB-(*c*)6(*z*)] polyethers based on TPB and α,ω-dibromoalkane containing four and respectively six methylenic units. The influence of phase transfer catalyzed polyetherification conditions on the formation of cyclic and/or linear polyethers of TPB was discussed in a previous publication.[2a] Under high dilution conditions, i.e., 1 mmol TPB per 100 ml of polymerization solvent, mostly cyclic low and high molar

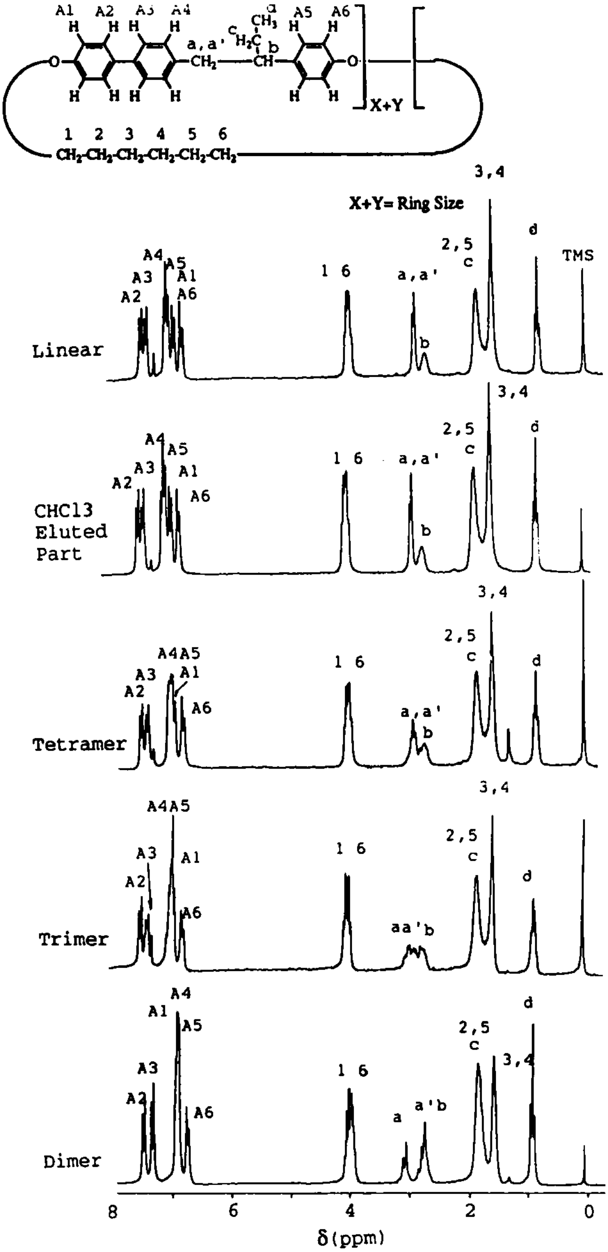


FIGURE 4 The 200 MHz ^{1}H-NMR spectra (CDCl$_3$, TMS) and the corresponding protonic assignments of the cyclic oligomers, of CHCl$_3$ eluted part [TPB-(c)6 series], and of the linear polymer TPB-(1)6.

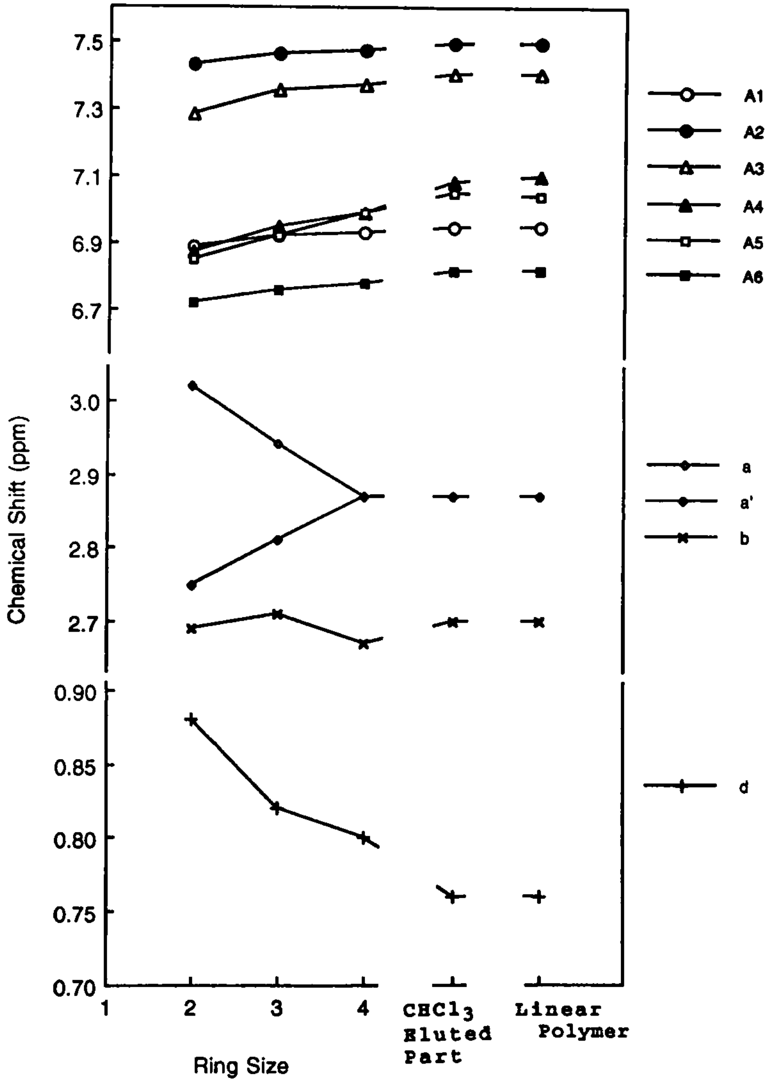


FIGURE 5 The dependence of the chemical shifts of the most representative protonic resonances of TPB-(*c*)4(*z*) cyclics as a function of ring size and their comparison with that of the linear polymer.

mass products were obtained. High molecular weight linear polymers were obtained when 2 ml of polymerization solvent were used for 1 mmol of TPB. The low molar mass cyclic oligomers were separated from the linear and cyclic polymers by eluting the product with acetone on a silicagel column. The high molecular weight part was collected by eluting with chloroform. The acetone eluted fraction was used to separate the individual cyclic compounds by using a mixture of acetone and hexanes. Additional details are presented in the experimental part. Figures 1(a) and 1(b) presents the GPC traces of the reaction mixture, of the high molecular weight fraction eluted with $CHCl_3$, and of the separated cyclic tetramer, trimer and dimer of TPB-(*c*)4(*z*), and the plots of the peak top molecular weight versus the ring size,

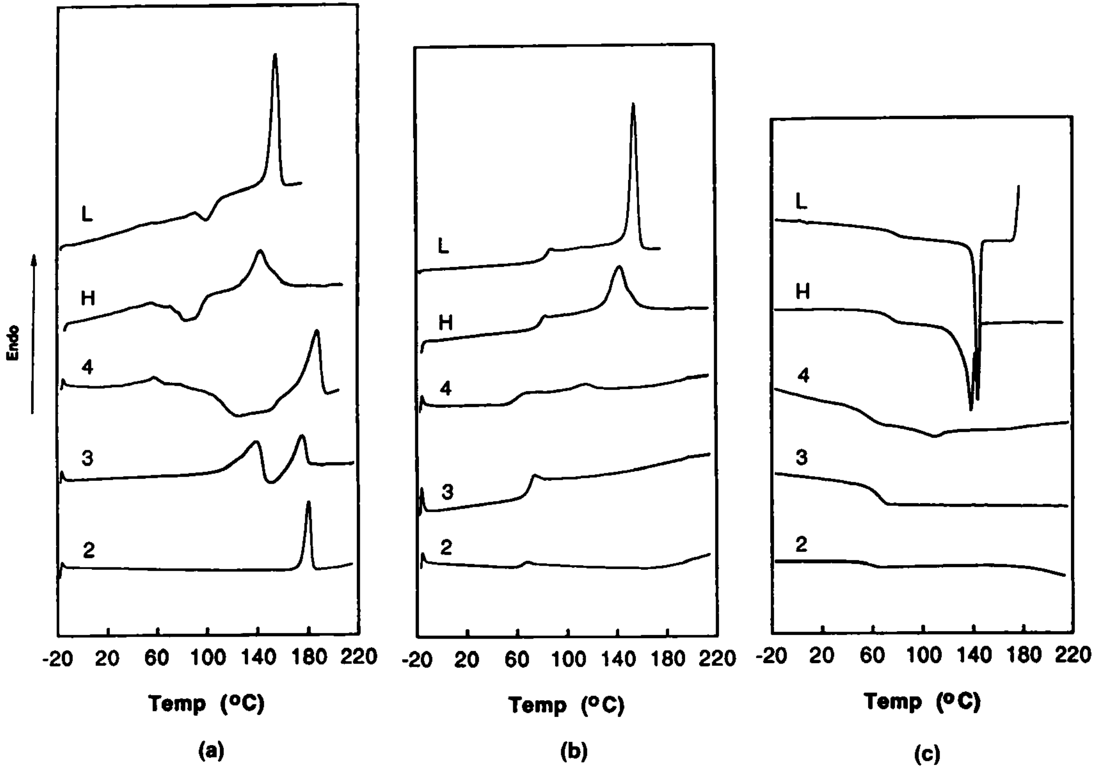


FIGURE 6 Representative DSC traces (20°C/min) of the first heating (a), second heating (b) and first cooling (c) scans of cyclic oligomers [TPB-(*c*)4(*z*), the numbers in the figure indicate the ring size (*z*)], of the $CHCl_3$ eluted part [TPB-(*c*)4, indicated as H], and of the linear polymer [TPB-(1)4, indicated as L].

respectively. Figures 2(a) and 2(b) presents the data for the TPB-(*c*)6(*z*) series. Due to the short length of the butane spacer no cyclic monomer TPB-(*c*)4(1) was obtained in the cyclization reaction with 1,4-dibromobutane. On the other hand, a very small amount of TPB-(*c*)6(1) was formed in the cyclization reaction with 1,6-dibromohexane. After column separation, cyclic oligomers from the dimer to tetramer with purities higher than 95% were obtained in both cases (Figures 1(a) and 2(a), Tables I and II). The linear dependence of the peak top molecular weight versus the ring size in both cases demonstrates the correct assignments of the ring size (Figures 1(b) and 2(b)).

The cyclic nature of these oligomers is demonstrated by 200 MHz 1-D ^{1}H-NMR spectroscopy. Figure 3 presents the assignments of the proton resonances of the linear polymer, of the high molecular weight part eluted with chloroform, and of the cyclic oligomers of TPB-(*c*)4(*z*) series while Figure 4 presents those of TPB-(*c*)6(*z*) series. These assignments agree with those of the cyclic TPB-(*c*)10(*z*) derivatives which were confirmed by extensive 2-D ^{1}H-NMR-COSY and NOESY

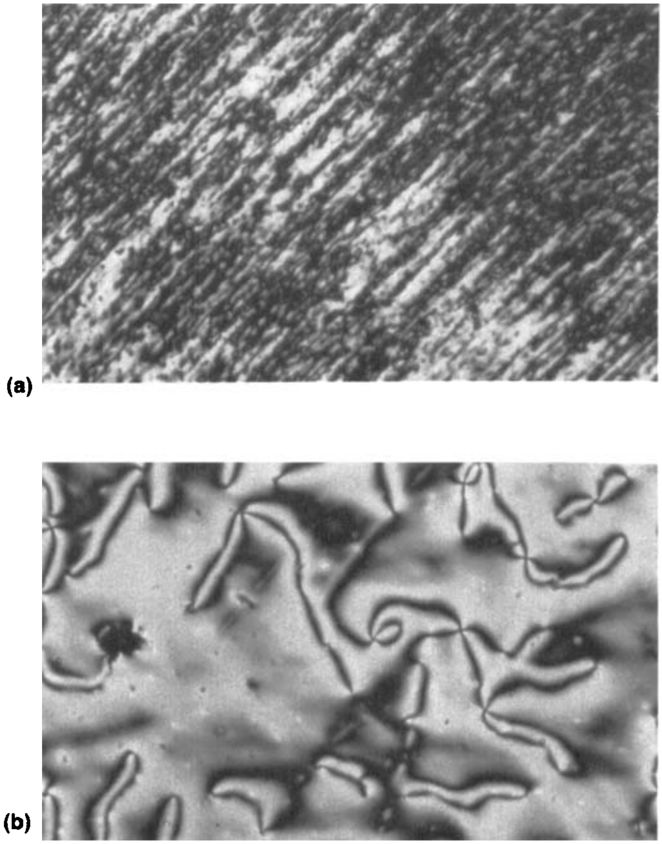
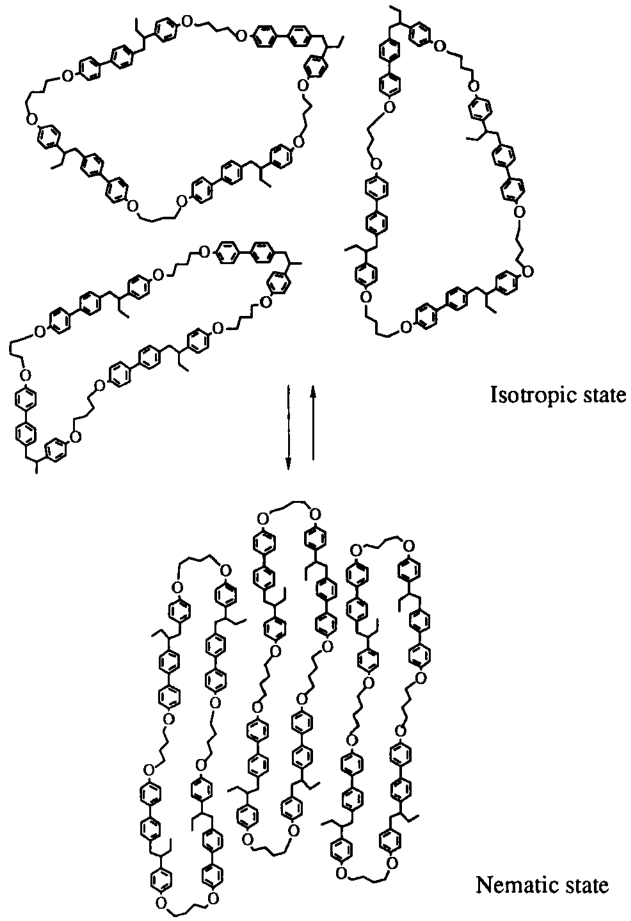


FIGURE 7 Representative optical polarized micrographs (× 100) of the nematic phase of (a) TPB-(*c*)4(4) (at 76°C after shearing); (b) TPB-(*c*)6(4) (after annealing at 128°C for 1 min).



SCHEME 3 Schematic representation of the isotropic-nematic transition of cyclic TPB-(*c*)4(4).

experiments.[2a] Two significant features of these spectra should be mentioned. First, these oligomers do not exhibit chain ends such as bromoalkane, phenol, olefin or alcohol.[2a] Secondly, the chemical shifts of methylene protons in the mesogenic unit (*a*, *a'*), methyl proton (*d*), and aromatic protons (A1 to A6) are strongly dependent on ring size as shown in Figure 5 for the case of TPB-(*c*)4(*z*) series. Linear oligomers do not exhibit such a dependence. This behavior is due to the change in the conformation of TPB unit as a function of the ring size which generates shielding and deshielding effects which were discussed in detail previously.[2a] Amplifications of the aliphatic region of the high molecular weight fractions separated from both cyclization experiments show the presence of $—CH_2—CH{=}CH_2$ (resonances at 5.0–5.2 ppm for $=C\underline{H}_2$) and $—C\underline{H}_2—OH$ (3.5–3.6 ppm) chain ends which are formed by elimination and respectively displacement of $—CH_2—Br$ by OH^-. Based on the integration results of these terminal groups versus the main chain groupsin the NMR spectra and the number average molecular weights obtained by GPC, it was calculated that about 68 mol% of the high molecular weight part separated from TPB-(*c*)4(*z*) series should represent macrocylclics. On the other hand, the

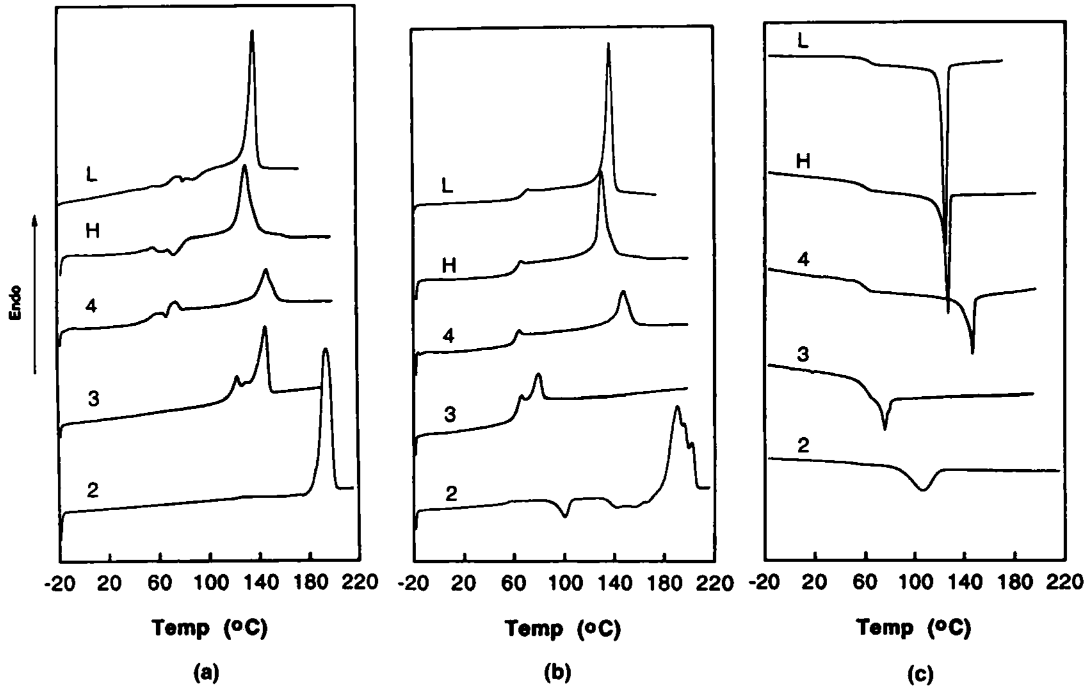


FIGURE 8 Representative DSC traces (20°C/min) of the first heating (a), second heating (b), and first cooling (c) scans of cyclic oligomers [TPB-(*c*)6(*z*), the numbers in the figure indicate the ring size (*z*)], of the $CHCl_3$ eluted part [TPB-(*c*)6, indicated as H], and of the linear polymer [TPB-(1)6, indicated as L].

high molecular weight part of TPB-(*c*)6(*z*) series contains about 63 mol% of macrocyclics. This is only an estimate since the molecular weights measured by GPC are relative to polystyrene standards.

DSC traces of the high molecular weight linear polyethers based on TPB and 1,4-dibromobutane TPB-(1)4 as well as of the high molecular weight fraction from the cyclization experiment TPB-(*c*)4(*z*) are presented in Figure 6. Both polymers display an enantiotropic nematic mesophase (Table I). The DSC traces of the cyclic dimer [TPB-(*c*)4(2)], trimer [TPB-(*c*)4(3)] and tetramer [TPB-(*c*)4(4)] are presented in the same figure. During the first heating scan all the cyclic oligomers are crystalline. During subsequent heating and cooling scans the dimer and trimer are glassy, while the tetramer displays a nematic mesophase. Figure 7(a) presents the representative nematic texture of TPB-(*z*)4(4). If the sample of the tetramer is annealed within its mesophase, it crystallizes. Therefore, TPB-(*c*)4(4) displays a monotropic nematic mesophase (Table I). Both the transition temperature and the enthalpy change associated with the nematic mesophase of this tetramer are lower than those of the corresponding high molecular weight cyclic and linear derivatives. Nevertheless TPB-(*c*)4(4) is the macrocyclic derivative with the shortest spacer from this series which displays a mesophase. Scheme 3 illustrates the nematic-isotropic transition of TPB-(*c*)4(4).

Figure 8 presents the DSC traces of the cyclic dimer, trimer and tetramer and of the high molecular weight fraction based on TPB and 1,6-dibromohexane. The high molecular weight linear and cyclic polymers display an enantiotropic nematic mesophase. TPB-(*c*)6(2) shows only melting and crystallization regardless of its thermal history. On the first heating scan TPB-(*c*)6(3) is only crystalline. However it displays an unidentified (*X*) mesophase on its subsequent heating and cooling scans. Upon annealing this trimer crystallizes again. Therefore, its *X* mesophase is monotropic (Table II). X-ray diffraction experiments could not yet identify exactly the nature of this metastable *X* phase. During the first heating scan the tetramer shows a melting transition which is followed by an enantiotropic nematic mesophase. As we can observe both from Figure 8 and from Table II, on subsequent heating and cooling scans TPB-(*c*)6(4) displays only the nematic mesophase. Its representative texture is presented in Figure 7(b). TPB-(*c*)6(4) is the first macrocyclic based on TPB and the shortest spacer investigated so far which displays a nematic mesophase whose isotropization transition temperature is higher than that of its high molecular weight linear and cyclic homologues.

A brief inspection of Tables I and II shows that the enthalpy changes (and the corresponding entropies) associated with the isotropization temperatures of macrocyclics are always lower than those of the corresponding linear high molecular weight polymers. This trend is most probably due to the fact that the difference between the entropies of macrocyclics in the isotropic and liquid crystalline phases is lower than the corresponding entropies of the linear polymers.

CONCLUSIONS

The macrocyclic derivative based on TPB and α,ω-dibromoalkanes with the shortest spacer length which displays a liquid crystalline mesophase is the tetramer obtained with 1,4-dibromobutane [TPB-(*c*)4(4)]. This is the only macrocyclic from this series which displays a mesophase. However its nematic mesophase is only monotropic and its isotropization transition temperature is lower than that of its corresponding high molecular weight linear polyether. The macrocyclic polyether with the shortest spacer based on TPB which displays a nematic phase with a higher isotropization temperature than its high molecular weight linear homologue is the tetramer based on 1,6-dibromohexane [i.e., TPB-(*c*)6(4)]. The only other macrocyclic from this series which exhibits a monotropic unidentified *X* phase is TPB-(*c*)6(3). The enthalpy and entropy changes associated with the isotropization transitions of macrocyclics are lower than those associated with the isotropization of the corresponding linear polymers.

Acknowledgments

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