Noncrystallizable Macrocyclics Exhibiting Enantiotropic Liquid-Crystalline Phases[1a]

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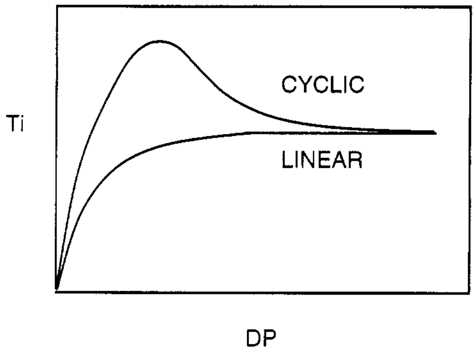
The synthesis and characterization of macrocyclics based on the conformationally flexible 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) with 1,8-dibromooctane [TPB-(c)8(*z*)] and of TPB with 1,9-dibromononane [TPB-(c)9(*z*)] (whose *z* defines the degree of oligomerization of the macrocyclic, i.e., $z = 2$ is dimer, $z = 3$ is trimer, etc.) are described. These cyclic oligomers were synthesized by the phase-transfer-catalyzed polyetherification of TPB with 1,8-dibromooctane and 1,9-dibromononane, respectively, under high-dilution conditions and were separated by column chromatography. Their cyclic structure was confirmed by 200-MHz ^{1}H NMR spectroscopy. Due to the conformational isomerism of the mesogenic unit, most of the chemical shifts of the protons are highly dependent on ring size. The mesomorphic behavior of TPB-(c)8(*z*) and of TPB-(c)9(*z*) was characterized by differential scanning calorimetry (DSC) and optical polarized microscopy. It was found that the TPB-(c)8(5) and TPB-(c)9(*z*) with z = 3, 4, and 5 are noncrystallizable macrocyclics with glass transitions above room temperature and a broad range of temperature of their nematic mesophases.

Introduction

Soon after the discovery of liquid crystals[1b] it was recognized that rigid linear and discotic molecules provide 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 a few less conventional variants of them.[1d-k] Recently, we have predicted and demonstrated that low molar mass macrocyclics based on conformationally flexible rodlike mesogens should and indeed do display a higher ability to exhibit liquid-crystalline phases than their low molar mass linear as well as both linear and cyclic high molecular weight homologues.[2] The trend outlined in Scheme I is due to the fact that macrocyclics of certain size are more rigid than the corresponding linear homologues as well as both high molecular weight linear and cyclic compounds. The particular examples reported so far are macrocyclic polyethers, i.e., monomer, dimer, trimer, tetramer, and pentamer of the conformationally flexible 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) with α,ω-dibromoalkanes containing four,[2d] five,[2b] seven,[2c] and ten[2a] methylenic units. The synthesis and thermal characterization of the linear high molecular weight polyethers based on TPB and flexible spacers containing from 4 to 20 methylenic units was also reported.[3] Characterization of these linear polymers by X-ray scattering experiments showed that they all exhibit a conventional uniaxial nematic mesophase with the exception of some of them with longer spacers which exhibit only a crystalline phase.[4]

Scheme I. Dependence of the Isotropization Transition Temperature (T_i) of Cyclic and Linear Main-Chain Liquid-Crystalline Polymers on Their Degree of Polymerization (DP) (Ti and DP in Arbitrary Units)



The previous publications on this novel class of molecular liquid crystals have addressed questions such as, what is the macrocyclic with the shortest spacer length based on TPB which displays a mesophase?[2d] What is the minimum size of the macrocyclic based on the same mesogenic group which displays a mesophase whose

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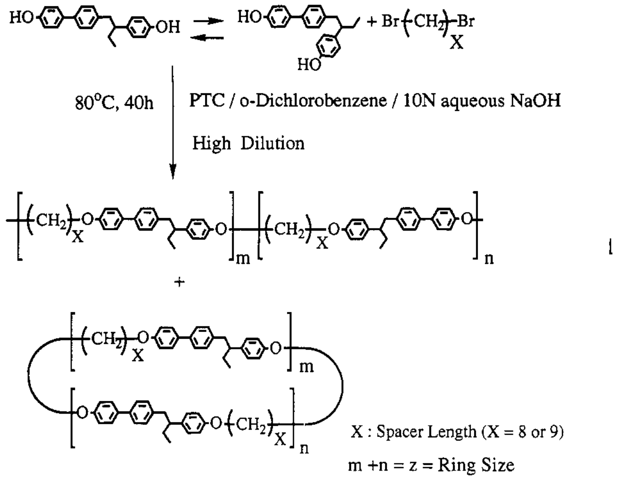
Scheme II. Synthesis of Cyclic Polyethers Based on TPB and α,ω-Dibromoalkanes Containing X Methylenic Units (*X* = 8 or 9)



isotropization temperature is higher than that of its linear high molecular mass homologue?[2a,d] What is the probability to transform kinetically prohibited[2b] and kinetically controlled[2c] mesophases of the linear polymer into enantiotropic mesophases via cyclization? Most of these macrocyclics have glass transition temperatures above room temperature and this property is of interest for various technological applications. There are only limited examples of molecular liquid crystals which exhibit a high glass transition temperature.[5] Noncrystallizable molecular liquid crystals with high glass transition temperature and broad range of temperature of their mesophase are of particular interest. Although few of the macrocyclics previously reported were noncrystallizable, none of them exhibited a large range of temperature of its mesophase.[2]

The goal of this paper is to report the synthesis and characterization of macrocyclics based on TPB with 1,8-dibromooctane [TPB-(c)8(*z*)], and of TPB with 1,9-dibromononane [TPB-(c)9(*z*)] (whose *z* defines the degree of oligomerization of the macrocyclic, i.e., *z* = 2 is dimer, *z* = 3 is trimer, etc.). These results will demonstrate that TPB-(c)8(5) and TPB-(c)9(*z*) with *z* = 3, 4, and 5 are noncrystallizable macrocyclics with glass transitions above room temperature and broad range of temperature of their mesophases.

Experimental Section

Materials. Tetrabutylammonium hydrogen sulfate (TBAH) (97%, Aldrich) was used as received. 1,8-Dibromooctane (98%) and 1,9-dibromononane (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] Silica gel plates with fluorescent indicator (Eastman Kodak) were used for thin-layer chromatography (TLC) analyses. All other chemicals were commercially available and were used as received.

Syntheses of Linear Polyethers TPB-(1)8 and TPB-(1)9. The linear polyether based on TPB and 1,8-dibromooctane [TPB-(1)8] (M_n = 30 300, M_w/M_n = 2.13), and the polyether based on TPB and 1,9-dibromononane [TPB-(1)9] (M_n = 39 300, M_w/M_n = 2.29) were synthesized by a liquid–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]

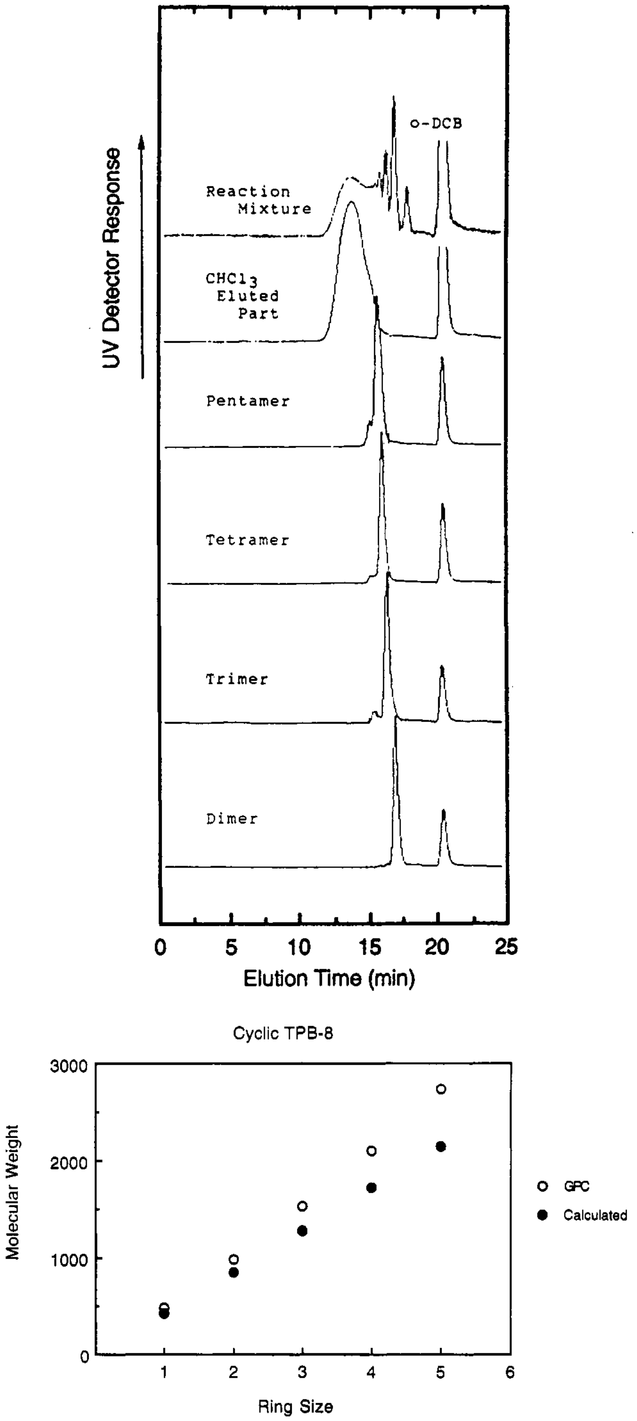


Figure 1. (a, top) GPC chromatograms of the cyclization mixture, of high molecular weight part, and of the separated cyclic oligomers [TPB-(c)8(*z*) series]; (b, bottom) dependence of the peak molecular weight of cyclic oligomers TPB-(c)8(*z*) obtained by GPC (○) and calculated (●), versus ring size.

Synthesis of Macrocyclic Polyethers TPB-(c)8(*z*) and TPB-(*c*)9(*z*) [Where *z* = 1 (Monomer), 2 (Dimer), 3 (Trimer), 4 (Tetramer), 5 (Pentamer)]. The macrocyclics of TPB with 1,8-dibromooctane or 1,9-dibromononane 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

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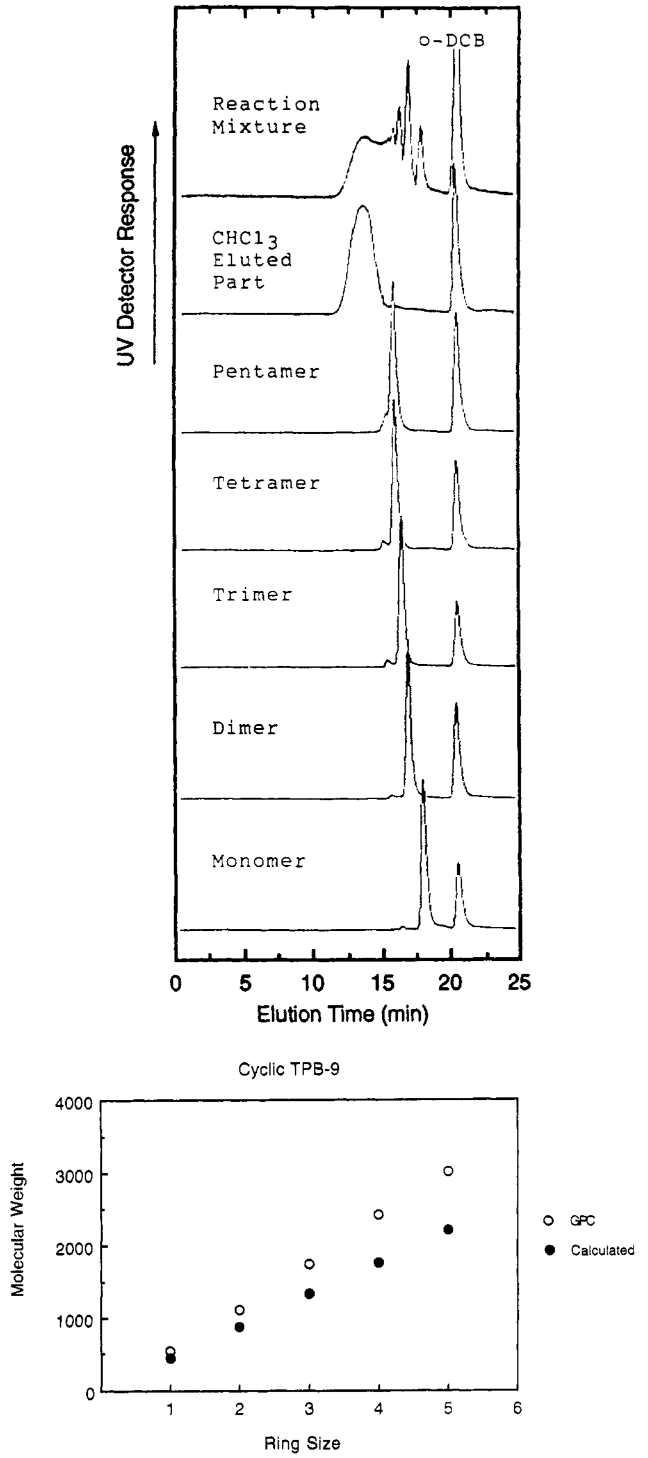

Figure 2. (a, top) GPC chromatograms of the cyclization mixture, of high molecular weight part, and of the separated cyclic oligomers [TPB-(c)9(*z*) series]; (b, bottom) the dependence of the peak molecular weight of cyclic oligomers TPB-(c)9(*z*) obtained by GPC (○), and calculated (●), versus ring size.

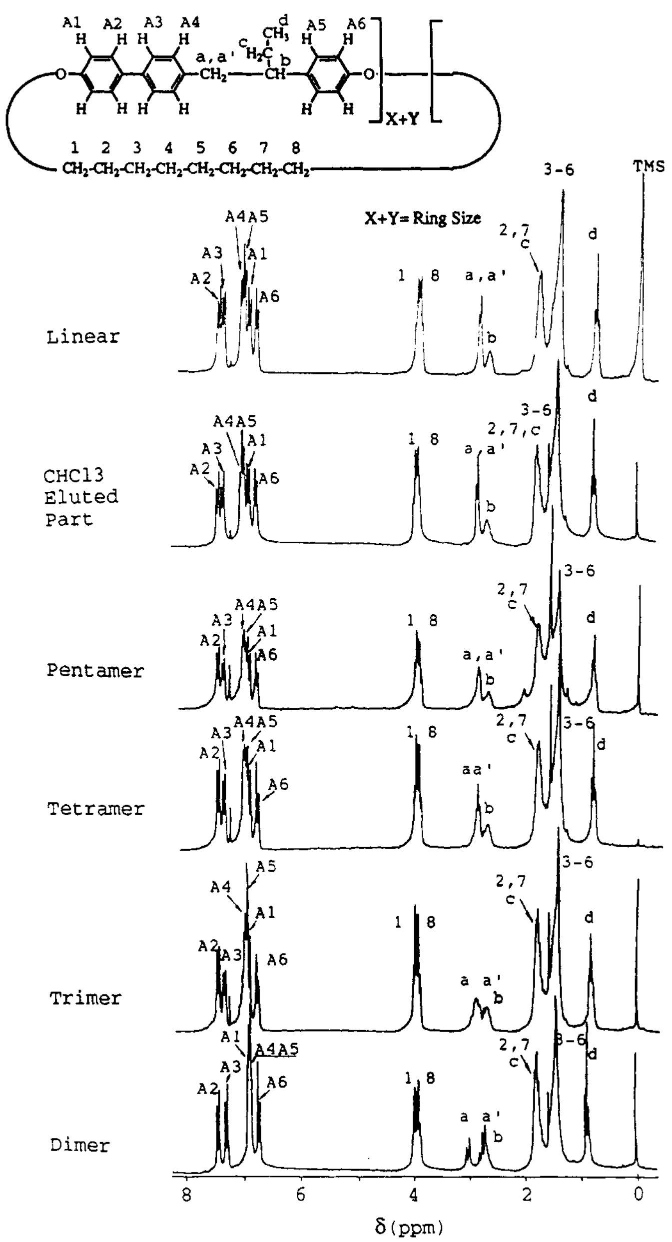

Figure 3. The 200-MHz ^{1}H NMR spectra ($CDCl_3$, TMS) and the corresponding protonic assignments of the cyclic oligomers, of the $CHCl_3$ eluted part [TPB-(c)8(*z*) series], and of the linear polymer TPB-(l)8.

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)8(*z*) is as follows.

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 solution91.0 mol), 100 mL of *o*-dichlorobenzene, 1,8-dibromooctane (0.272 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, once with dilute hydrochloric acid, and three times with water. After the evaporation of the solvents, the product was dissolved in chloroform. To this solution silica gel was added and the chloroform was evaporated. The product adsorbed on silica gel was charged on the top of a column containing silica gel 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 (1:15 v/v). Each fraction was checked by TLC [developed by a mixture of acetone and hexanes (1:15 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 give the separated cyclic oligomers. The cyclic oligomers were further purified by the filtration of their chloroform solution followed by precipitation in methanol.

The same procedure as for TPB-(c)8(*z*) was used for the synthesis of TPB-(c)9(*z*) except that 1,9-dibromononane (0.286 g, 1.00 mmol) was used. The ratio of acetone to hexanes for the column chromatographic separation was 1:20 v/v.

Table I. Characterization of Cyclic Oligomers and Corresponding Linear Polymer Based on TPB and 1,8-Dibromooctane

			mol wt by GPC at peak top		thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
ring size	yield (%)	purity by GPC (%)	measd	calcd	first heating second heating	first cooling
1	6.6	84.0	479	429		
2	8.8	98.5	983	857	k 127 k 139 k 145 (6.30[b]) i g 37 i 90 k 121 (−4.58) k 142 k 147 (4.41) i	i 31 g
3	1.5	91.9	1523	1286	g 43 s 69 (0.15) n 83 (0.08) i g 43 s 69 (0.15) n 83 (0.08) i	i 79 (0.07) n 66 (0.15) s 37 g
4	2.7	95.4	2106	1715	g 18 k 75 (0.41) n 132 (1.06) i g 36 n 141 (0.95) i	i 133 (0.84) n 31 g
5	0.9	76.5	2736	2143	g 42 n 123 (1.01) i g 38 n 128 (1.00) i	i 126 (0.65) n 33 g
$CHCl_3$ eluted part	32.8		$M_n = 8.73 \times 10^3$ $M_w/M_n = 1.62$		g 42 n 61 (−0.26) n 115 (2.18) i g 47 n 114 (2.12) i	i 109 (2.23) n 42 g
linear			$M_n = 3.03 \times 10^4$ $M_w/M_n = 2.13$		g 46 n 124 (2.39) i g 52 n 123 (2.43) i	i 107 (2.45) n 43

[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 1.9-Dibromononane

			mol wt by GPC at peak top		thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
ring size	yield (%)	purity by GPC (%)	measd	calcd	first heating second heating	first cooling
1	4.8	98.2	549	443		
2	13.7	97.8	1121	885	g 42 k 134 (4.61) i k 97 (−0.54) k 117 k 121 (2.17) k 134 (1.62) i	i 80 (2.75) k
3	3.4	95.2	1743	1328	g 43 n 96 (0.19) i g 40 n 96 (0.19) i	i 92 (0.18) n 36 g
4	2.7	93.9	2429	1771	g 41 n 121 (0.47) i g 40 n 121 (0.48) i	i 118 (0.42) n 37 g
5	0.8	90.9	3025	2213	g 46 n 110 (0.32) i g 44 n 110 (0.35) i	i 107 (0.52) n 42 g
$CHCl_3$ eluted part	23.4		$M_n = 1.04 \times 10^4$ $M_w/M_n = 1.62$		g 48 n 74 (0.54) i g 46 n 73 (0.78) i	i 67 (0.70) n 40 g
linear			$M_n = 3.93 \times 10^4$ $M_w/M_n = 2.29$		g 43 k 52 n 74 (1.16[b]) i g 47 n 74 (0.78) i	i 62 (0.77) n 39 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.

Techniques. 1-D ^1H 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.

Results and Discussion

Scheme II outlines the synthesis of linear [TPB-(1)X] and cyclic [TPB-(c)X(*z*)] polyethers based on TPB and α,ω-dibromoalkane containing *X* methylenic units (*X* = 8 or 9). The optimization of the reaction conditions for the predominant synthesis of macrocyclics or of linear polymers was described previously.[2a] Individual macrocyclics were separated by column chromatography using silica gel as a stationary phase with a mixture of acetone and hexanes as eluent, and were characterized by a combination of techniques consisting of 200-MHz ^1H NMR spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermal optical polarized microscopy. Figure 1, parts a and b, presents the GPC traces of the reaction mixture, of the high molecular weight fraction eluted with $CHCl_3$, and of the separated cyclic pentamer, tetramer, trimer, and dimer of TPB-(c)8(*z*) series, and the plot of the peak top molecular weight versus the ring size, respectively. Figure 2 presents similar data for the TPB-(c)9(*z*) series. After the column separation, cyclic oligomers with purities higher than 90% were obtained in both cases except TPB-(c)8-(5), whose purity was 76% (Figure 1a and 2a, Tables I and II). The linear dependences of the peak top molecular weights versus ring size indicates in both cases the correct assignments of the ring size (Figures 1b and 2b).

Figures 3 and 4 present the 200-MHz ^1H NMR spectra of the macrocyclic compounds and of the linear polymers. Cyclic compounds do not exhibit resonances characteristic for the chain ends expected for linear oligomers (i.e., $-CH_2$-Br, $-CH=CH_2$, $-CH_2OH$, and phenol) and their chemical shifts are strongly dependent on ring size (Figure 5). A detailed discussion on the interpretation of these NMR spectra by a combination of 1-D ^1H and 2-D ^1H NMR

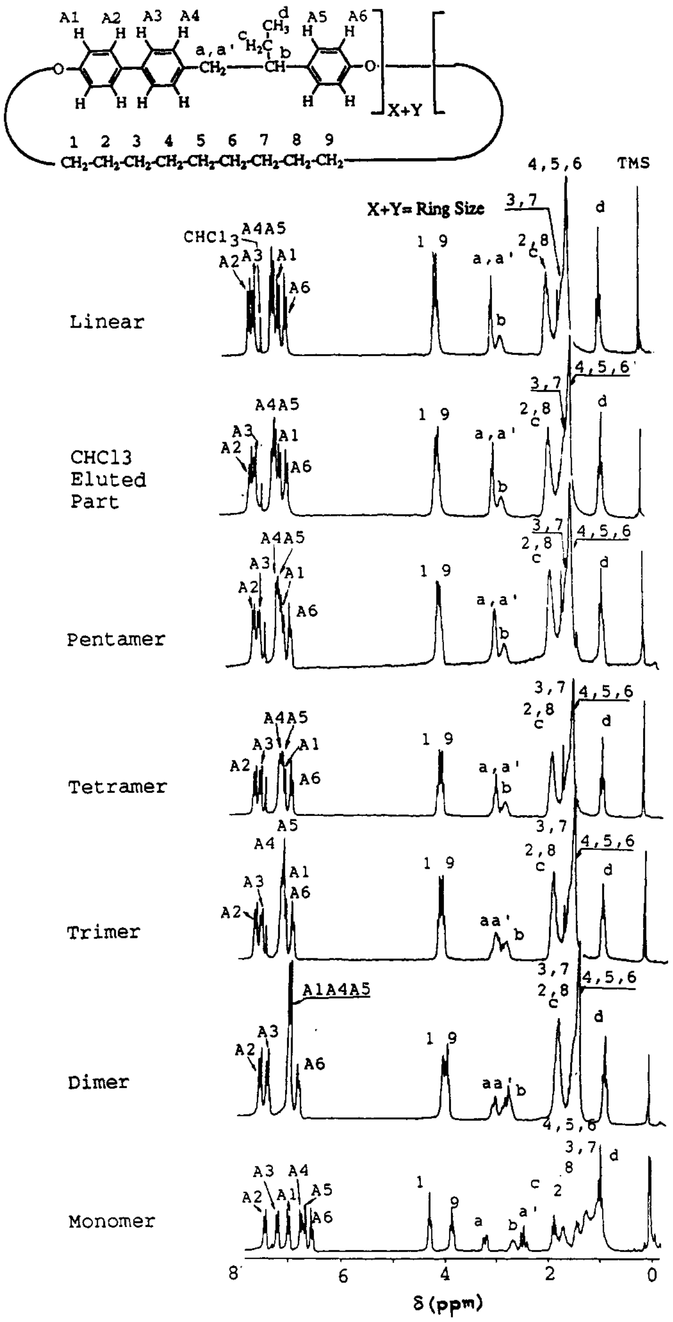

Figure 4. The 200-MHz ^1H NMR spectra ($CDCl_3$, TMS) and the corresponding protonic assignments of the cyclic oligomers, of the $CHCl_3$ eluted part [TPB-(c)9(*z*) series] and of the linear polymer TPB-(l)9.

spectroscopies was presented elsewhere.[2a] All these structural particularities demonstrate the cyclic structure of these oligomers. The high molecular weight fractions separated from both cyclization experiments exhibit only minor peaks in the amplified spectra. These minor peaks correspond to $—CH_2CH=CH_2$ (resonances at 5.0 ppm for $=CH_2$) and $—CH_2OH$ (3.6 ppm) chain ends which are formed by elimination and respectively displacement of $—CH_2Br$ by OH^-. On the basis of the integration results of these terminal groups versus the main-chain groups from the NMR spectra and the number average molecular weights obtained by GPC, it was calculated that about 44 mol % of the high molecular weight part separated from TPB-(c)8(*z*) series should represent macrocyclics. On the other hand, the high molecular weight part of TPB-(c)9(*z*) series contains about 41 mol % of macrocyclics. This

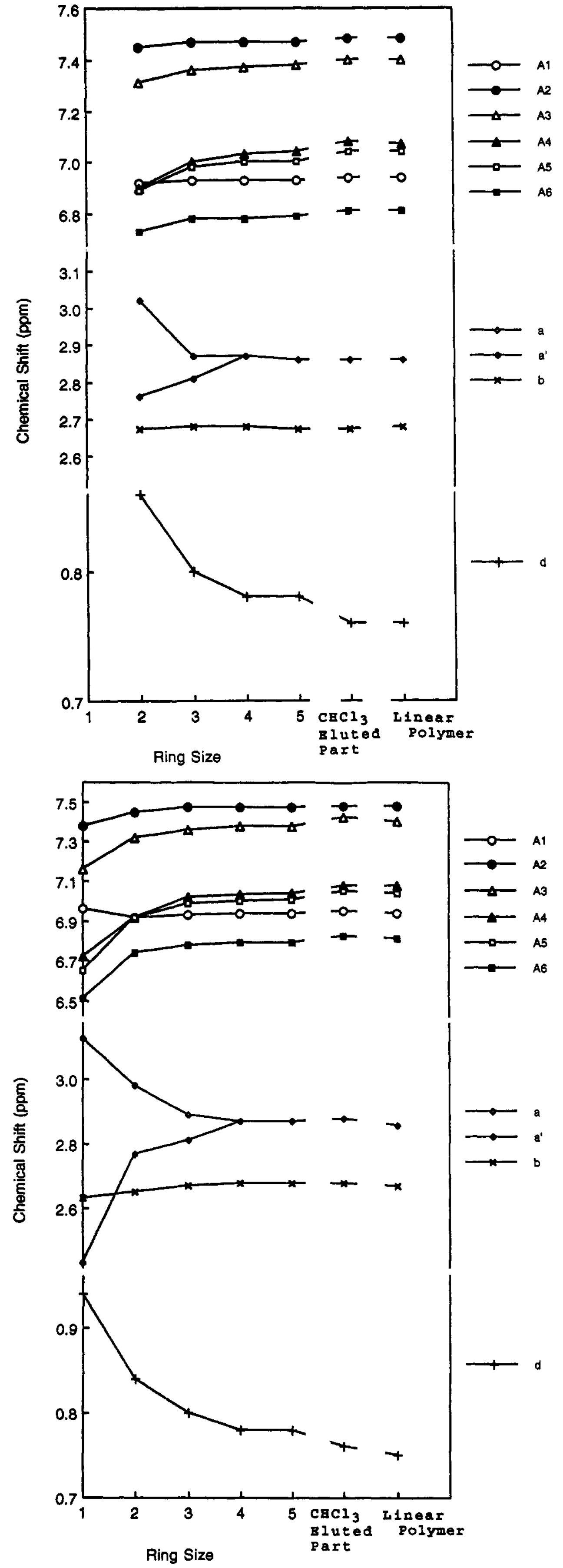

Figure 5. Dependence of the chemical shifts of the most representative protonic resonances of TPB-(c)8(*z*) cyclics (a, top) and TPB-(c)9(*z*) cyclics (b, bottom) as a function of ring size and their comparison with those of the linear polymer.

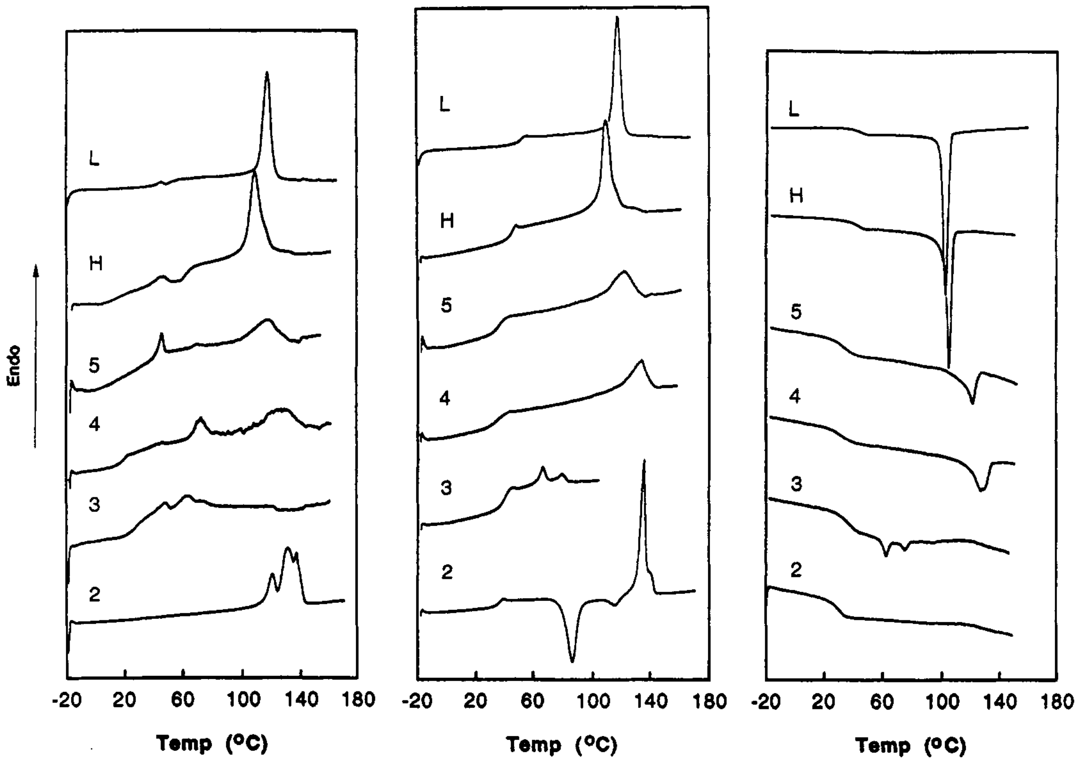

Figure 6. Representative DSC traces (20 °C/min) of the first heating (a, left), second heating (b, middle), and first cooling (c, right) scans of cyclic oligomers [TPB-(c)8(*z*), the numbers in the figure indicate the ring size (*z*)], of the CHCl$_3$ eluted part [TPB-(c)8(*z*), indicated as H], and of the linear polymer [TPB-(1)8, indicated as L].

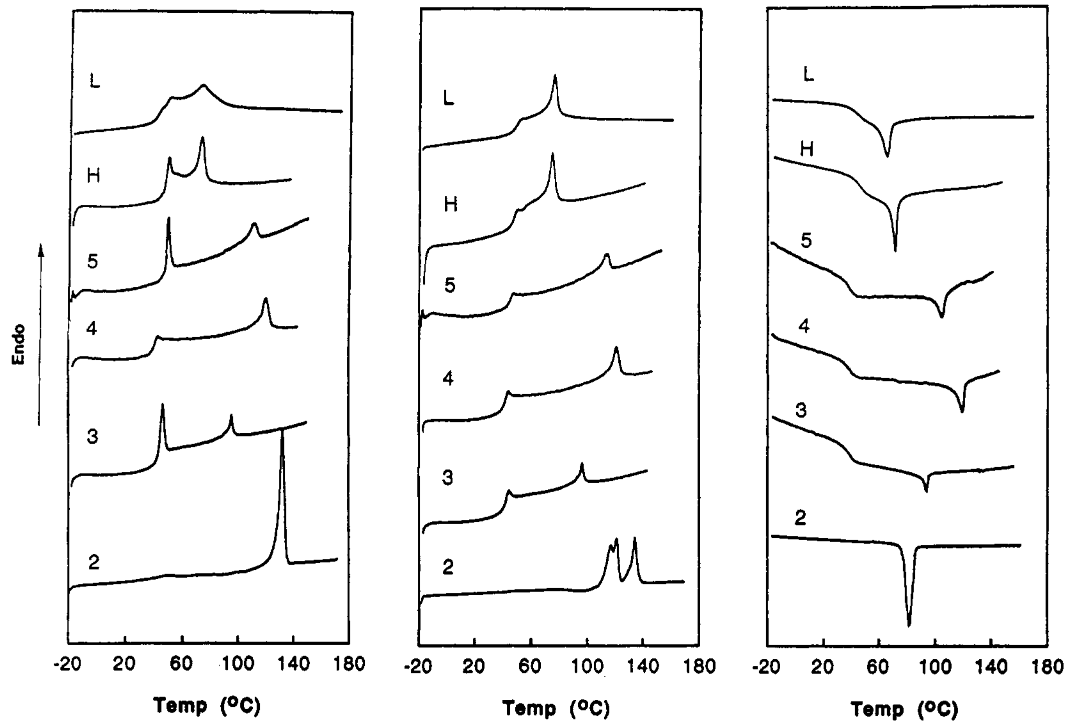

Figure 7. Representative DSC traces (20 °C/min) of the first heating (a, left), second heating (b, middle), and first cooling (c, right) scans of cyclic oligomers [TPB-(c)9(X), the numbers in the figure indicate the ring size (X)], of the CHCl$_3$ eluted part [TPB-(c)9, indicated as H], and of the linear polymer [TPB-(1)9, indicated as L].

is only an estimate since the molecular weights measured by GPC are relative to polystyrene standards.

The DSC traces of TPB-(c)8(*z*) and TPB-(1)8 are presented in Figure 6 and summarized in Table I, while those of TPB-(c)9(*z*) and TPB-(1)9 in Figure 7 and summarized in Table II.

TPB-(c)8(2) is crystalline, and upon cooling from the isotropic melt it shows only a glass transition. However, it crystallizes on heating (Figure 6, Table I). Also TPB-(c)8(4) displays a crystalline phase which during the first heating scan melts into a nematic mesophase. On subsequent heating and cooling scans it displays only an enantiotropic nematic mesophase. TPB-(c)8(3) displays two enantiotropic mesophases. The high-temperature mesophase is nematic. The low-temperature phase is most probably smectic. Its complete characterization by X-ray

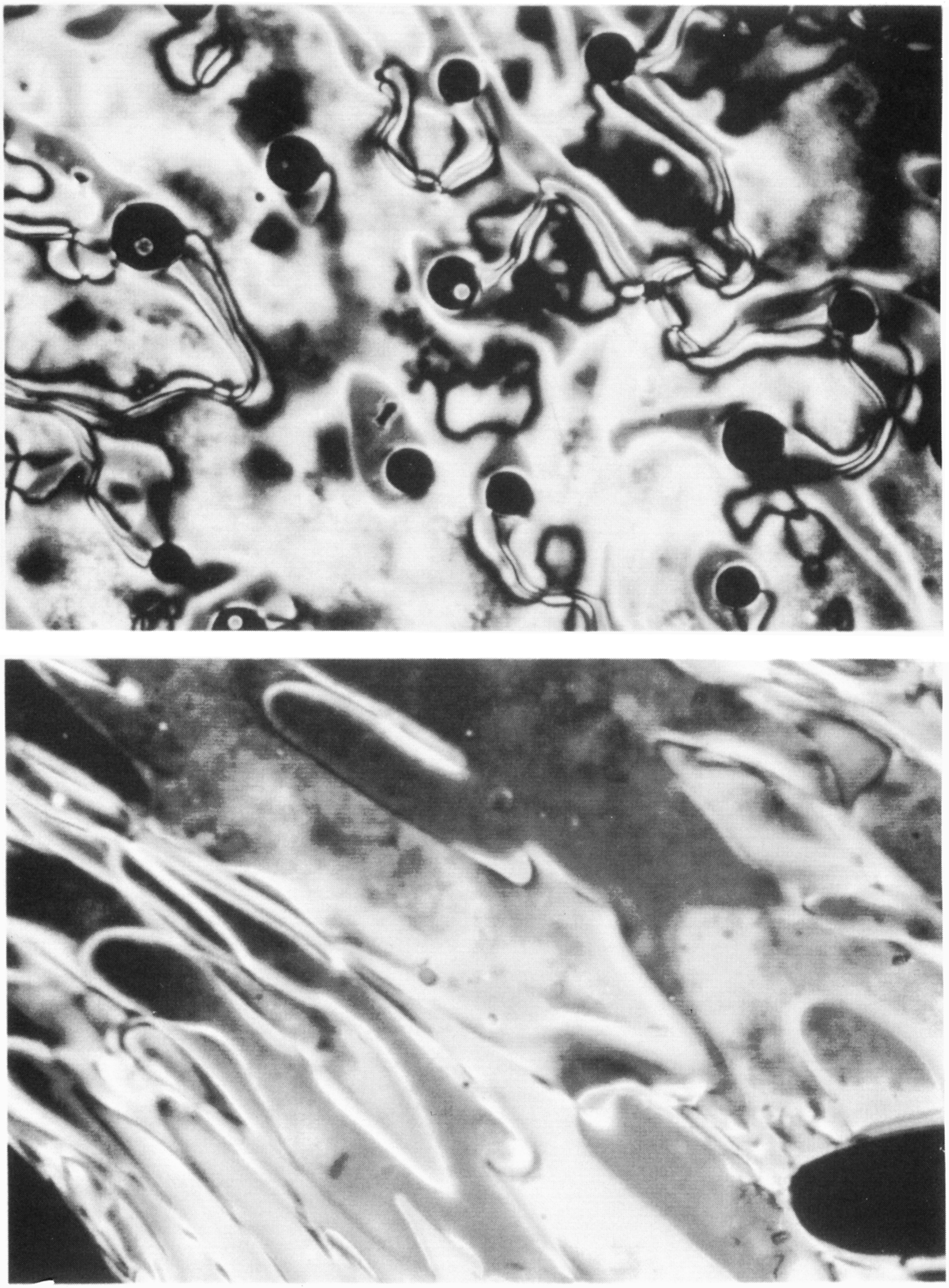

Figure 8. Representative optical polarized micrographs (×100) of the nematic phase of (a, top) TPB-(c)8(4) (after annealing at 102 °C for 2 min) (b, bottom) TPB-(c)9(4) (after annealing at 119 °C for 2 min).

scattering experiments will be described in a subsequent publication.[6] Regardless of its thermal history TPB-(c)8-(5) displays only a noncrystallizable conventional nematic mesophase (Figure 6, Table I). A comparison of the phase behavior of the nematic mesophases of TPB-(c)8(4) and TPB-(c)8(5) with that of the corresponding linear polymer TPB-(1)8 (Figure 6, Table I) shows that the isotropization transition temperatures of the macrocyclics are higher than those of their linear high molecular weight homologue. However, the enthalpy changes associated with the nematic–isotropic transition of these macrocyclics are much lower than those of the corresponding linear polymer. The high molecular weight fraction of TPB-(c)8(*z*) displays similar phase behavior to that of the linear polymer TPB-(l)8 except that the transition temperature is slighly lower and the transition peak associated with the nematic–isotropic transition is broader.

Figure 7 presents the DSC traces of TPB-(c)9(*z*) and of TPB-(1)9. Only TPB-(c)9(2) is crystallizable and does not show a mesophase regardless of its thermal history.

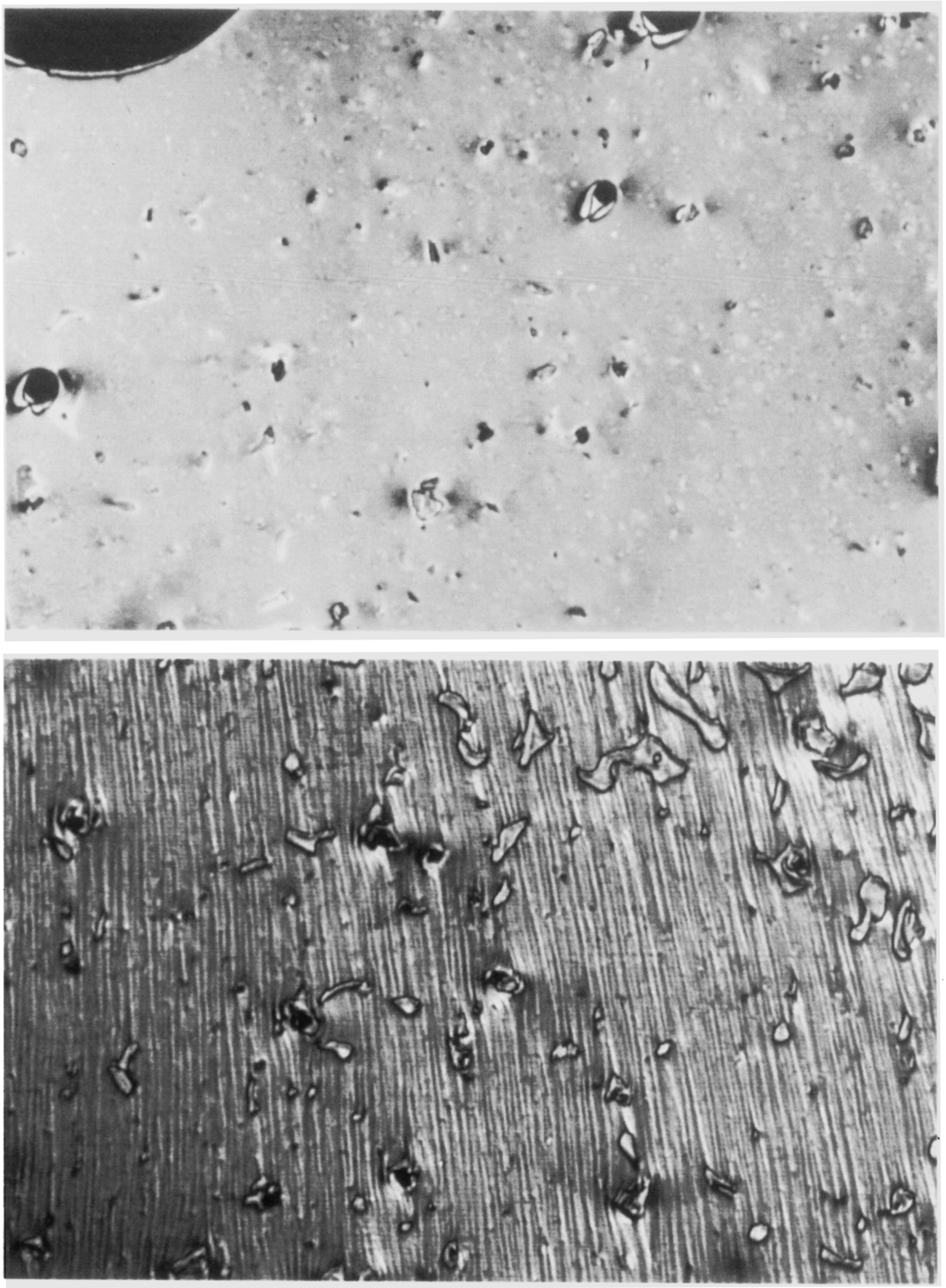

Figure 9. Representative optical polarized micrographs (×100) of TPB-(c)8(3) (a, top) nematic phase (after annealing at 74 °C for 11 min) and (b, bottom) second phase (after annealing at 62 °C for 5 min).

All other macrocyclics exhibit a noncrystallizable enantiotropic nematic mesophase. As both Figure 7 and Table II show, TPB-(c)9(*z*) macrocyclics with $z = 3$, 4, and 5 display higher isotropization transition temperatures with lower enthalpy changes than those of their linear high molecular weight homologues. Again the high molecular weight fraction of TPB-(c)9(*z*) displays a quite similar phase behavior to that of the linear polymer TPB-(1)8. Figure 8 presents representative textures exhibited by the nematic mesophase of the cyclic oligomers. While these textures are characteristic for a nematic mesophase, the texture of the probably smectic low temperature phase of TPB-(c)8(3) (Figure 9) is not sufficiently representative to make a definitive assignment without performing X-ray investigations. Finally, Figure 10 provides a schematic representation of the nematic mesophase displayed by these macrocyclics. The higher transition temperatures of the macrocyclics are due to the lack of chain ends and

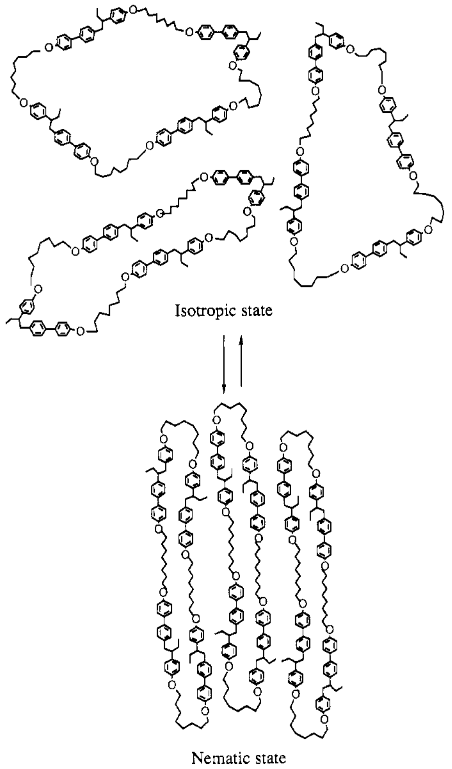

Figure 10. Schematic representation of the isotropic–nematic transition of cyclic TPB-(c)8(4).

higher rigidity of the cyclic structure (lower entropy of the cyclic structure) versus that of their linear counterpart. The lower difference between the enthalpy and entropy changes of the nematic–isotropic transitions of the macrocyclics are attributed to the lower difference between the configurational and conformational entropies of the macrocyclics of their isotropic and liquid crystalline phases versus those of the corresponding linear oligomers and polymers in the same phases.

Conclusions

Although the dimers TPB-(c)8(2) and TPB-(c)9(2) are crystalline, the other macrocyclics based on TPB with 1,8-dibromooctane and 1,9-dibromononane respectively do not crystallize after the first heating scan and exhibit enantiotropic nematic mesophases. Especially, TPB-(c)8(5) and TPB-(c)9(*z*) with $z = 3$, 4, and 5 do not exhibit a melting transition even during their first scan and therefore are noncrystallizable macrocyclics with glass transitions above room temperature and broad range of temperature of their mesophases. TPB-(c)8(*z*) with $z = 4$, 5 and TPB-(c)9(*z*) with $z = 3$, 4, 5 exhibit higher transition temperatures and lower enthalpy changes compared to those of their linear homologues. Only TPB-(c)8(3) exhibits a second phase which is most probably smectic.

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