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Transformation of a kinetically controlled nematic phase of a linear polymer into one which is thermodynamically controlled via cyclization [1]

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The synthesis and characterization of cyclic main chain liquid-crystalline oligomers based on 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) with 1,7-dibromoheptane (TPB-7(c)] are described. These oligomers were synthesized by the phase transfer catalysed polyetherification of TPB with 1,7-dibromoheptane under high dilution conditions and separated by column chromatography. Their cyclic structure was confirmed by 200 MHz ^{1}H NMR spectroscopy. The mesomorphic behaviour of TPB-7(c) was characterized by differential scanning calorimetry and polarized optical microscopy. The cyclic dimer is only crystalline, while the cyclic trimer, tetramer and pentamer exhibit an enantiotropic nematic mesophase. The high molecular weight linear homologue TPB-7(l) exhibits a nematic mesophase which has an isotropization transition temperature located in the very close proximity of its glass transition temperature. Therefore, this nematic phase is kinetically controlled. Due to the higher rigidity of cyclics versus linear structures the cyclic trimer, tetramer and pentamer exhibit higher isotropization transition temperatures than their linear homologue. Subsequently, the kinetically controlled nematic mesophase of the linear homologue is transformed into a thermodynamically controlled phase via cyclization.

1. Introduction

Cyclic oligomers and polymers are important natural compounds (i.e. ionophores [2], α- and β-cyclodextrins [2], DNA and peptides [3], etc.) and are also generated during both step condensation and ring opening polymerization reactions [3]. To date only few cyclic oligomers and polymers, i.e. polystyrene, [3, 4], polysiloxanes [3, 5], poly(2-vinylpyridine) [6], polycarbonate and a few other condensation polymers [7], polyethylene [3, 8], and side chain liquid-crystalline polysiloxanes [9], have been synthesized and characterized. The first cyclic main chain liquid-crystalline polyethers were recently reported from our laboratory [10, 11]. They were synthesized by phase transfer catalysed polyetherification of 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) with 1,5-dibromopentane [TPB-5(c)] [10] and 1,10-dibromodecane [TPB-10(c)] [11], respectively. Due to the higher rigidity of cyclics versus linear structures low molar mass macrocyclics [9] display a higher ability to exhibit liquid-crystalline phases than their linear low and high molecular weight homologues [TPB-X(l)] [12] (where X is the number of methylenic groups in the flexible spacer). Figure 1 outlines the dependence of the isotropization transition temperatures (T_i) of cyclic and linear main chain liquid-crystalline polymers on their degree of polymerization (*DP*).

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Both trends can be predicted by some thermodynamic schemes which were described previously and discussed in detail with experimental examples for the case of linear main chain and side chain liquid-crystalline polymers [13]. Since the entropy of the macrocyclics first decreases and then increases, by increasing their molecular weight their isotropization temperature should [13] and does [10, 11] follow the trend outlined in figure 1. TPB-5(l) is glassy since its glass transition temperature is higher that the isotropization transition temperature [10, 11]. Therefore, TPB-5(l) does not exhibit a liquid-crystalline phase since this phase is kinetically prohibited by its own glass transition temperature. The cyclic tetramer and pentamer of TPB-5(c) were shown to exhibit higher isotropization transition temperatures than their linear homologue [10]. Therefore, the kinetically prohibited mesophase of TPB-5(l) was transformed into an enantiotropic one via cyclization. The high molecular weight linear TPB-7(l) exhibits a nematic mesophase whose isotropization transition temperature is in the very close proximity of its glass transition temperature [12]. Therefore, this nematic phase is kinetically controlled. The goal of this paper is to demonstrate that the cyclic trimer, tetramer and pentamer of TPB-7(c) exhibit higher transition temperatures than the linear TPB-7(l) homologue. Subsequently, the kinetically controlled nematic mesophase of TPB-7(l) is transformed into a thermodynamically controlled phase via cyclization.

2. Experimental

2.1. *Materials*

Tetrabutylammonium hydrogen sulphate (TBAH) (97 per cent, Aldrich) was used as received. 1,7-Dibromoheptane (97 per cent, Aldrich) and *o*-dichlorobenzene were purified by vacuum distillation. TPB (purity, >99 per cent by HPLC) was synthesized as previously described [12]. Silica gel plates with fluorescent indicator (Eastman Kodak) were used for thin layer chromatography analyses.

2.2. *Synthesis of cyclic oligomers TPB-7(c)*

The polyetherification of TPB with 1,7-dibromoheptane was carried out 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 40 h of reaction time the reaction mixture was

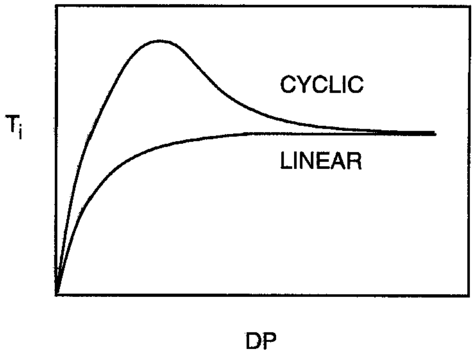


Figure 1. The dependence of the isotropization temperature (T_i) of cyclic and linear main chain liquid-crystalline polymers on their degree of polymerization (*DP*). Both T_i and *DP* are in arbitrary units.

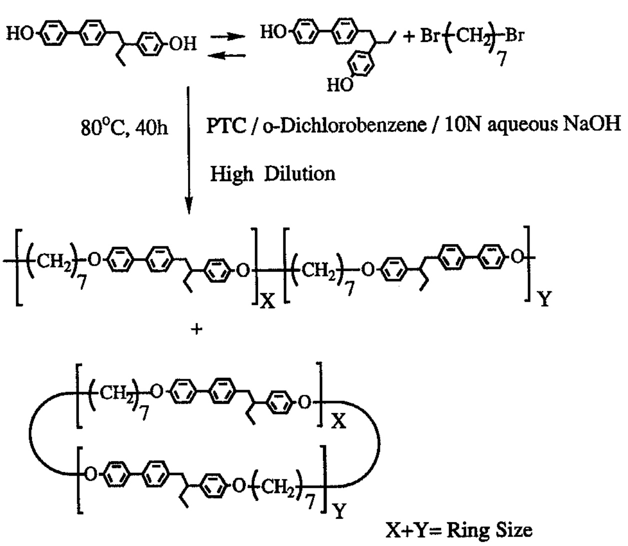
separated into the individual cyclic oligomers and the high molecular weight part. A general procedure used for the preparation of cyclic polyethers is as follows. To a 500 ml single-neck flask equipped with a condenser were successively added 0·318 g (1·00 mmol) of TPB, 100 ml of 10 N NaOH aqueous solution (1·0 mol), 100 ml of *o*-dichlorobenzene, 0·258 g (1·00 mmol) of 1,7-dibromoheptane, 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 condensor. 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 twice with water, then with dilute hydrochloric acid, and again 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 absorbed on silica gel was charged on the top of a column containing silica gel and was flushed with acetone to elute the mixture of low molar mass cyclic oligomers. The product remaining at the top of the column was flushed with chloroform to elute 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 thin layer chromatography (developed by a mixture of acetone and hexanes (1 : 15 v/v) and detected with a UV lamp). The fraction containing each cyclic was collected and the solvent was evaporated on a rotary evaporator to give the separated cyclic oligomer.

2.3. *Techniques*

One dimensional ^{1}H NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. TMS was used as an internal standard. Relative molecular weights and purities were determined by gel permeation chromatography (GPC). 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^{-1}, 40°C), two PL gel columns of 5×10^2 and 10^4 Å, and a calibration plot constructed with polystyrene standards. The molecular weights of cyclics were read at the peak top. The purities were estimated by the HPLC program of a Nelson Analytical 900 series data station. A Perkin–Elmer DSC-4 differential scanning calorimeter equipped with a TADS data station Model 3600 was used to determine the thermal transitions. Heating and cooling rates were 20°C min^{-1} in all cases. First order transitions (crystal–crystal, crystal–liquid crystal, liquid crystal–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. 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 the thermal transitions and to analyse the anisotropic textures.

3. Results and discussion

Scheme 1 outlines the synthesis of linear [TPB-7(l)] and cyclic [TPB-7(c)] polyethers based on TPB and 1,7-dibromoheptane. The influence of phase transfer catalysed polyetherification conditions on the formation of cyclic [11] and/or linear [12] polyethers of TPB was discussed in previous publications. Under high dilution conditions, i.e. 1 mmol TPB per 100 ml of polymerization solvent, mostly cyclic low and high molar mass products are obtained. High molecular weight linear polymers are



Scheme 1. Synthesis of linear [TPB-7(l)] and cyclic [TPB-7(c)] polyethers based on TPB and 1,7-dibromoheptane.

obtained when 2 ml of polymerization solvent are used for 1 mmol of TPB. The low molar mass cyclic oligomers of TPB-7 were separated from the linear and cyclic polymers by eluting the product with acetone on a silica gel 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 (1/15, v/v). Additional details are presented in the Experimental. Figure 2 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-7(c). Due to the short length of the heptane spacer only a very small amount of cyclic monomer was formed in this cyclization reaction. The cyclic monomer was not isolated. Figure 3 plots the dependence of the theoretical and experimental values (GPC with polystyrene standards) of the molecular weight versus ring size. The linear dependence observed demonstrates the correct assignment of the ring size.

The cyclic nature of these oligomers is demonstrated by 200 MHz one dimensional ^1H NMR spectroscopy. Figure 4 presents the assignments of the proton resonances of linear polymer, of $CHCl_3$ eluted fraction and of cyclic oligomers. These assignments agree with those of the cyclic TPB-10(c) derivatives which were confirmed by extensive two dimensional ^1H COSY and NOESY experiments, [11] and of TPB-5(c) derivatives [10]. Two significant features of these spectra should be mentioned. First, these oligomers do not exhibit chain ends such as bromoalkane, phenol, olefin or alcohol. Second, the chemical shifts of protons a, a′, b, d and A1 to A6 are strongly dependent on ring size (see figure 5). Linear oligomers do not exhibit such a dependence. This behaviour is due to the change in the conformation of the TPB unit as a function of ring size which generates shielding and deshielding effects which were discussed in detail previously [11]. As we can see from figures 4 and 5 the cyclic pentamer already approaches the chemical shifts of the linear polymer. An amplification of the aliphatic region of the $CHCl_3$ eluted fraction shows the presence of $-CH_2-CH{=}CH_2$ (resonances at 5·74 ppm for $-C\underline{H}{=}$ and 4·94 ppm for $=C\underline{H}_2$) and$-C\underline{H}_2-OH$ (3·58 ppm) chain ends which are formed by elimination and displacement of $-CH_2-Br$ by OH^-, respectively.

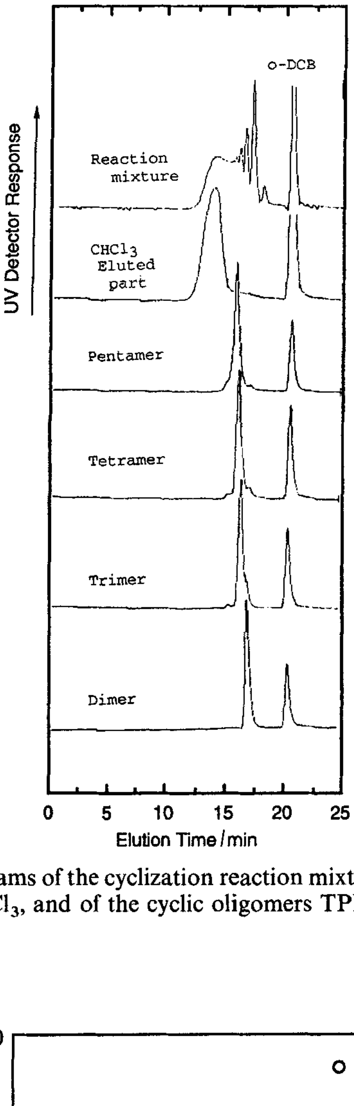


Figure 2. GPC chromatograms of the cyclization reaction mixture, of the polymer eluted with $CHCl_3$, and of the cyclic oligomers TPB-7(c).

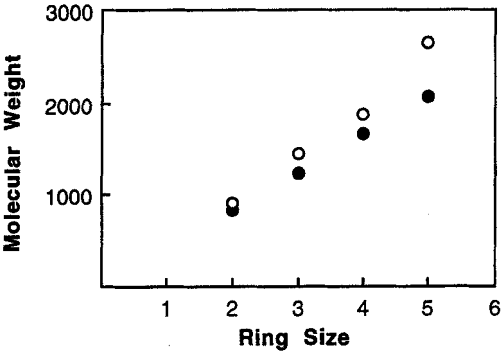


Figure 3. The dependence of the peak molecular weight of cyclic oligomers (TPB-7(c) obtained by GPC (○) and calculated (●) versus ring size.

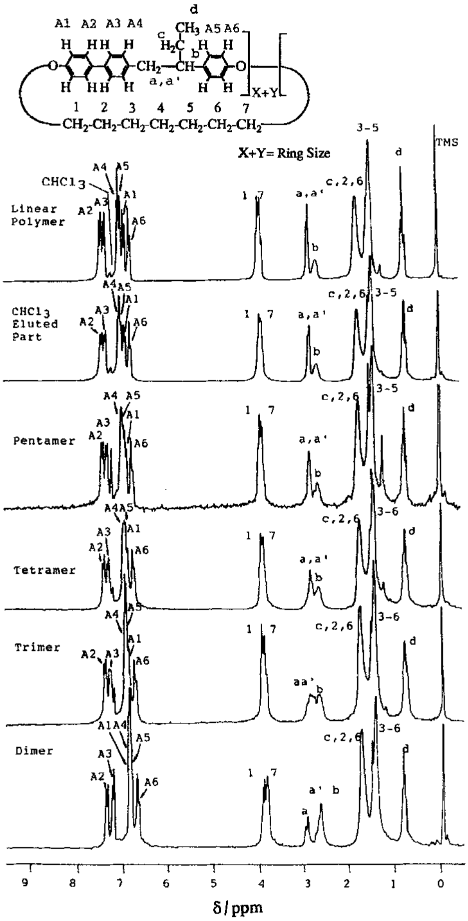


Figure 4. The 200 MHz ^1H NMR spectra ($CDCl_3$, TMS) and the corresponding protonic assignments of the cyclic oligomers, of $CHCl_3$ eluted part, and of the linear polymer.

The concentration of the chain ends containing double bonds is $5{\cdot}7 \times 10^{-5}\,\mathrm{mol\,g^{-1}}$ while that of chain ends containing alcohols is $8{\cdot}8 \times 10^{-5}\,\mathrm{mol\,g^{-1}}$. The total concentration of chain ends corresponding to $\bar{M}_n = 10100$ (GPC) should be $19{\cdot}8 \times 10^{-5}\,\mathrm{mol\,g^{-1}}$. Therefore, about 27 mol% of the $CHCl_3$ eluted fraction should be macrocyclic. This is only an estimate since its molecular weight is relative to polystyrene standards.

Figures 6 (*a*) and (*b*) present representative DSC traces exhibited during second and subsequent heating and first and subsequent cooling scans. As we can observe from these figures, the cyclic dimer is crystalline, while the cyclic trimer, tetramer and pentamer exhibit an enantiotropic nematic phase whose isotropization transition temperatures are higher than that of the linear molecular weight TPB-7(1) polymer. The peaks of the nematic phase of the linear TPB-7(1) polymer and of the chloroform eluted fraction are located in the close proximity of their glass transition temperature. Therefore, their nematic phase is formed with difficulty since it is kinetically controlled due to the close proximity of the glass transition. In fact, the nematic isotropic transition peak cannot be observed on the cooling DSC scan (see figure 6 (*b*)). However, this nematic phase can be seen on the optical microscope. In the case of the cyclic

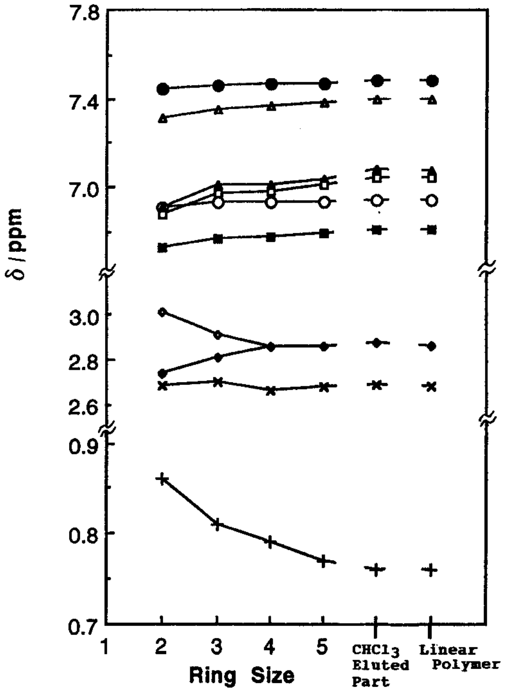
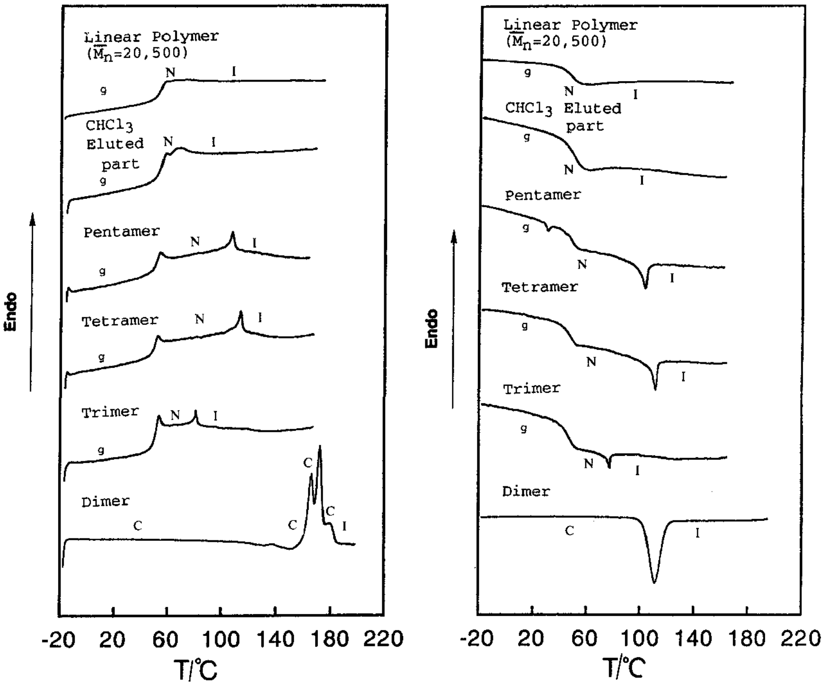
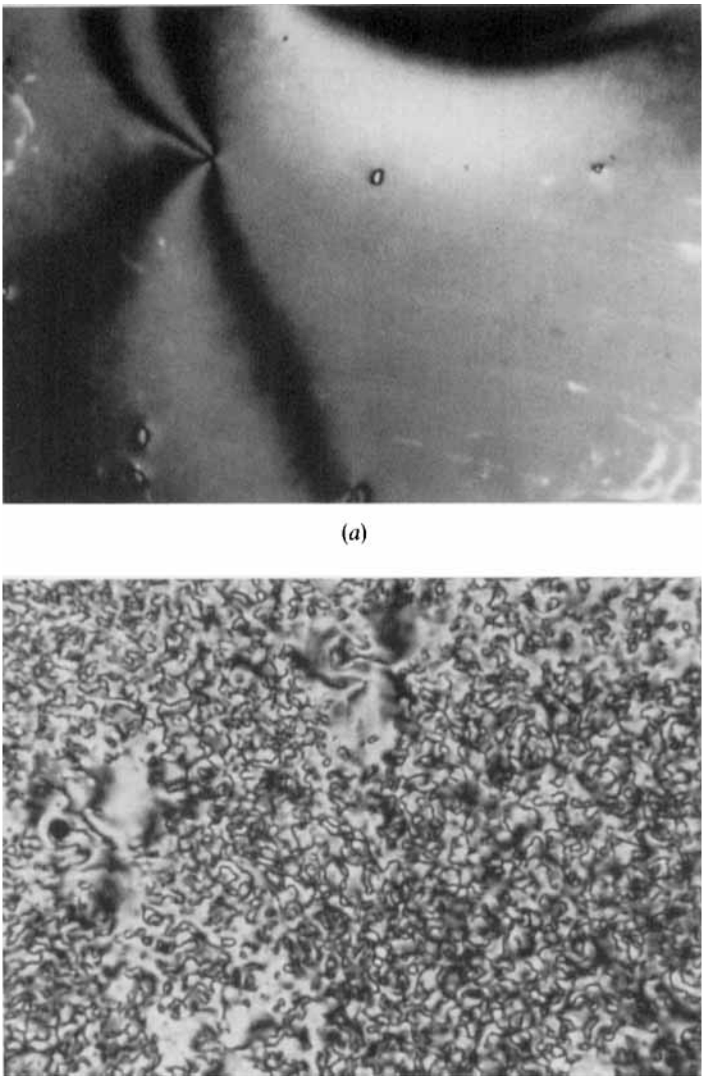


Figure 5. The dependence of the chemical shifts of the most representative protonic resonances of TPB-7(c) cyclics as a function of molecular weight and their comparison with those of the linear polymer. Protonic resonances: ○, A1; ●, A2; △, A3; ▲, A4; □, A5; ■, A6; ◇, a; ◆, a′; ×, b; +, d.



(*a*) (*b*)

Figure 6. Representative DSC traces (20°C min^{-1}) of the second heating (*a*) and first cooling (*b*) scans of cyclic oligomers, of the $CHCl_3$ eluted part, and of the linear polymer.


(a)

(b)

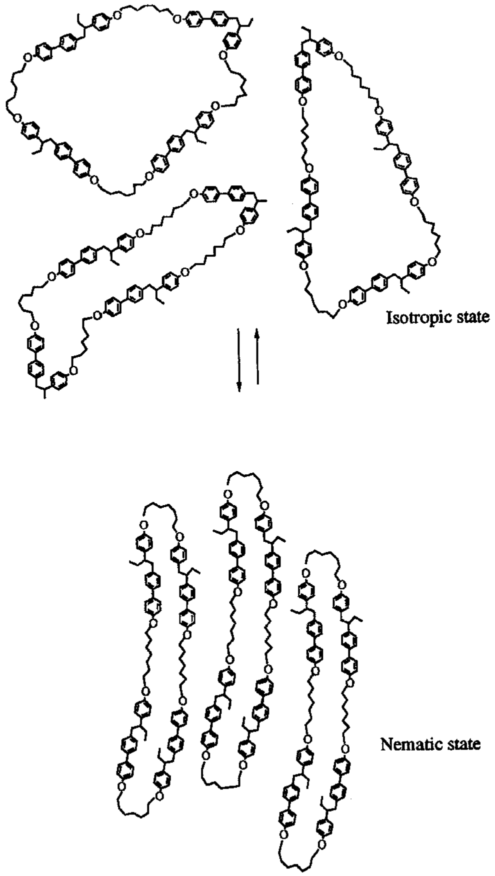
Figure 7. Representative optical polarized micrographs (× 100) of the nematic phase of TPB-7(c): (a) tetramer (after annealing at 90·3°C for 4 min); (b) trimer (after annealing at 78·4°C for 6 min).

trimer, tetramer and pentamer the nematic mesophase becomes thermodynamically controlled since its isotropization temperature is located further away from the glass transition temperature. This mesophase was confirmed by optical polarized microscopy. Representative textures of the nematic phase of the cyclic tetramer and trimer are presented in figures 7(a) and (b), respectively. The table summarizes all data available for cyclic oligomers, $CHCl_3$ eluted fraction and linear polymer. As we can observe from the table the cyclic tetramer exhibits a melting transition located in the close proximity of the glass transition only during the first heating scan. Due to this proximity the tetramer crystallizes from solution but not from the melt phase. Scheme 2 suggests the conformations of the TPB-7(c) tetramer in the isotropic and nematic

Characterization of cyclic oligomers and corresponding linear polymer based on TPB and 1,7-dibromoheptane.

Ring size	Yield	Purity by HPLC	$\overline{M_W}$ by GPC at the peak top		Thermal transitions (°C) and corresponding enthalpy changes ($J\,mru^{-1}$) in parenthesis†	
			Measured	Calculated	Heating	Cooling
2	5·9	>99	901	829	C 171 C 180 (28·6‡) I C 150 (−4·14) C 166 C 172 C 180 (23·1‡) I	I 111 (16·8) C
3	4·5	92	1453	1244	g 52 N 81 (0·29) I g 49 N 81 (0·34) I	I 77 (0·29) N 46 g
4	1·9	93	1884	1658	g 52 C 64 (0·50) N 115 (1·17) I g 50 N 114 (1·42) I	I 111 (1·21) N 46 g
5	2·1	89	2650	2073	g 47 N 108 (1·21) I g 51 N 107 (1·51) I	I 103 (1·13) N 48 g
$CHCl_3$ eluted part			$\bar{M}_n = 10{,}100$	$\bar{M}_w/\bar{M}_n = 1{\cdot}40$	g 53 N 69 (1·09) I g 53 N 67 (0·42) I	I 62 (0·63) N 48 g
Linear polymer			$\bar{M}_n = 20{,}500$	$\bar{M}_w/\bar{M}_n = 2{\cdot}07$	g 47 N 74 (3·47‡) I g 53 N 72 (0·21) I	I 60 (0·42) N 48 g

† Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan.
‡ Overlapped peaks.



Scheme 2. Representation of the nematic–isotropic transition of the cyclic tetramer TPB-7(c).

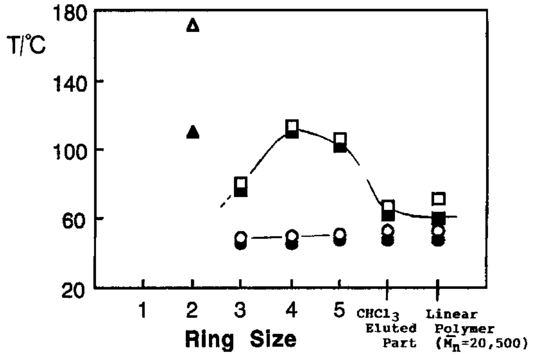


Figure 8. The dependence of the glass transition (○, second heating; ●, cooling), nematic–isotropic transition (□, second heating; ■, cooling) melting (△) and crystallization (▲) temperatures on molecular weight for cyclics and their comparison with those of the linear polymer.

phases. The transitional motion available in conventional linear nematic liquid crystals, most probably, becomes a jump reptation motion analogous to that known from cyclic paraffins [8]. During this motion both the conformation of the methylenic groups of the flexible spacer and of the mesogenic group change when they pass through the fold. Figure 8 plots the dependence of glass transition and isotropization transition temperatures of cyclic and linear TPB-7 as a function of molecular weight. This plot demonstrates the trend predicted in figure 1.

In conclusion, we have demonstrated that cyclization can transform a kinetically controlled mesophase of a linear compound into one which is thermodynamically controlled. This is due the fact that certain low molar mass cyclic compounds are more rigid than their linear homologues and therefore, exhibit higher isotropization transition temperatures. These cyclic compounds represent a novel class of liquid crystals which do not have chain ends. Since many technological applications of conventional rod-like low molar mass liquid crystals are determined by their ability to attain alignment via their chain ends, this new family of liquid crystals opens up a series of very fundamental questions and investigations.

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