Macrocyclization Overrides the *Polymer Effect* in the Stabilization of Liquid Crystalline (LC) Phases with a Novel Odd−Even Alternation. A Demonstration with LC Crown Ethers

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ABSTRACT: The synthesis and characterization of a novel series of crown ethers based on triethylene glycol (3EO) and the conformationally flexible 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane (TPB), *i.e.* TPB-(c)3EO(*z*) (where c stands for cyclic and $z = 1-10$ is the degree of polymerization (DP) of the cyclic compound), and of the corresponding linear polymer, TPB-(l)3EO (where l stands for linear), are described. The cyclic monomer, the cyclic trimer, the mixture of high molecular weight cyclics, and the linear polymer are amorphous. The cyclic tetramer to decamer display an enantiotropic nematic phase. The isotropization temperatures and the associated entropy and enthalpy changes of these cyclics increase in an odd−even dependence with DP. This unprecedented odd−even effect is determined by the *anti* and, respectively, *gauche* conformations of TPB in the supramolecular quasi-rigid rods obtained from collapsed macrocyclics in their nematic phase and contrasts with the continuous increase of the same parameters as a function of DP in linear main-chain LC polymers. These results demonstrate that macrocyclization overrides the well-established *polymer effect* in the formation and stabilization of liquid crystalline (LC) phases. Therefore, contrary to what has been considered for over 100 years, the cyclic and not the linear architecture is the most powerful in the design of molecular and macromolecular LCs.

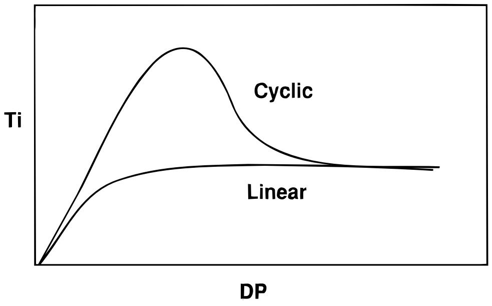
Introduction

Almost simultaneously with the discovery of thermotropic liquid crystals[1] (LC), it was realized that linear rodlike molecules represent the most suitable architecture which produces LC phases.[2] More than 100 years later, the activity on the molecular structure−properties dependence in the field of molecular,[3] macromolecular,[4] and, more recently, supramolecular[5] LCs is still focused on the same architecture and on very few less conventional variants.[6]

The conversion of monomers into side-chain[7a−c] and main-chain[7d,e] liquid crystalline polymers (LCPs) shifts the LC to isotropic phase transition to higher temperatures (Scheme 1). The stabilization of LC phases via polymerization, known as the *polymer effect*, received various theoretical explanations[4a,7a,8] and represented for a long time the most powerful synthetic strategy for the stabilization of LC phases.

Contrary to what has been considered for over 100 years, in 1992 we predicted and demonstrated that certain sizes of low-molar-mass cyclic homologues of main-chain LCPs based on conformationally flexible rodlike mesogens should, and do, exhibit more stable LC phases than their low-molar-mass linear and their high-molar-mass linear and cyclic homologues (Scheme 1).[9] The trend from Scheme 1 can be understood if we consider that a certain cyclic size which contains a minimum ring strain and a suitable combination of spacer and mesogen lengths which can generate a LC phase should have a lower entropy and higher rigidity and, therefore, must exhibit higher isotropization temperatures than the corresponding high-molar-mass cyclic and linear homologues. Subsequent research in our[10] and other laboratories[7e,11,12] has definitively confirmed our original hypothesis and first experimental results[9] and started to elucidate the structure−property relationship in this new class of LCs. The prediction[9] that macrocyclics are more rigid than their linear homologues was demonstrated experimentally.[13] New physical properties which are not encountered in their linear partners such as a biaxial nematic phase were also discovered in cyclic LCs.[14] The elaboration of new synthetic methods which allow the preparation of macrocyclic LCs on a large scale[15] produced the first entry in the synthesis of more complex systems such as main-chain and side-chain LCPs containing macrocyclic mesogens.[16]

Scheme 1. Predicted Dependence of the Isotropization Temperature of Cyclic and the Predicted and Experimental Dependence of Linear Main-Chain LC Polymers on DP (T_i and DP Are in Arbitrary Units)



Most of the previous research was carried out on cyclics ranging in size from monomer to pentamer.[10g,17] The use of these compounds in the design and synthesis of more complex systems demands a detailed elucidation of the trend illustrated in Scheme 1. This requires the synthesis and characterization of a series of cyclics covering a larger range of degrees of polymerization (DP). A brief inspection of the available data on the phase behavior and the structure of cyclic LCs in various phases[17] raised the hypothesis that the odd- and even-

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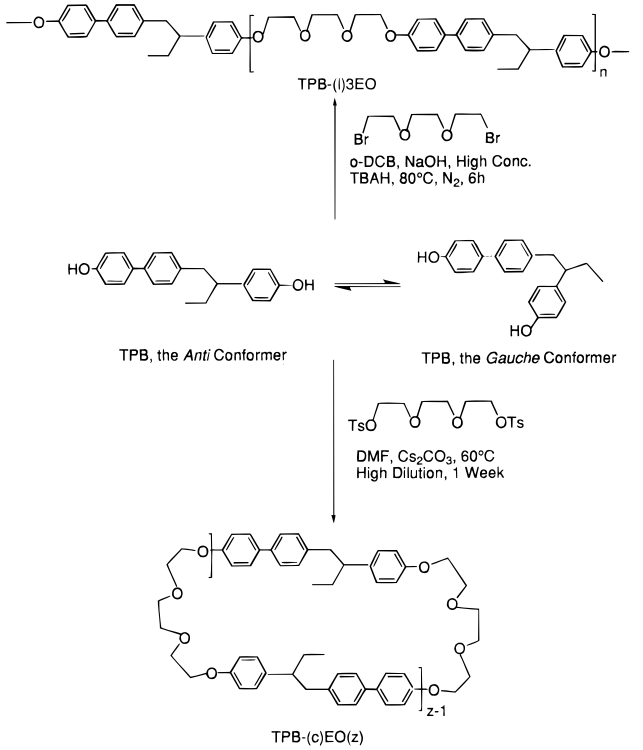
Scheme 2. Synthesis of Macrocyclics Based on TPB and Triethylene Glycol (TPB-(c)3EO(*z*)) and of the Corresponding Linear Polymer (TPB-(l)3EO)



size series of cyclics may not show a single continuous dependence of their isotropization temperature on DP, as is the case for linear polymers (Scheme 1). In order to verify this hypothesis and also to provide the first series of cyclics exhibiting both a nematic phase and cation binding properties, we decided to investigate the phase behavior of a homologous series of cyclic and linear polyethers containing various oligooxyethylene spacers and conformationally flexible mesogens.

The goal of this publication is to report the synthesis and characterization of the first series of LC crown ethers based on 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane (TPB) and triethylene glycol (3EO), *i.e.* TPB-(c)3EO(*z*) (where c stands for cyclic and $z = 1-10$ is the DP of the macrocyclic) and of the linear polymer, TPB(l)3EO. This series of experiments will elucidate the influence of DP on the phase behavior of linear and cyclic main-chain LCPs.

Results and Discussion

Synthesis and Structural Characterization. Scheme 2 presents the synthesis of the linear TPB-(l)-3EO and cyclic TPB-(c)3EO(z) polyethers. The linear polymer was synthesized by a conventional two phase (organic solvent−aqueous NaOH) phase transfer catalyzed[7e,9] polyetherification of 1,8-dibromo-3,6-dioxaoctane with TPB at high concentration. The cyclization reaction of TPB with 1,8-bis((*p*-tolylsulfonyl)oxy)-3,6-dioxaoctane was performed in DMF under high dilution using Cs_2CO_3 as base and template.[18] In solution and in the isotropic melt state, TPB exists as a dynamic equilibrium between the *anti* and *gauche* conformers. The elongated, *anti* conformer favors the formation of the linear polymer, while the bent, *gauche* conformer favors cyclization. When the polyetherification is carried out at high concentration, the linear polymer TPB-(l)3EO accompanied by a very small amount of macrocyclic compounds forms. The cyclic compounds were separated from the linear polymer by the precipitation of the polymer from its $CHCl_3$ solution into acetone followed by filtration. When this polyetherification is performed under high dilution, mostly cyclic compounds form.

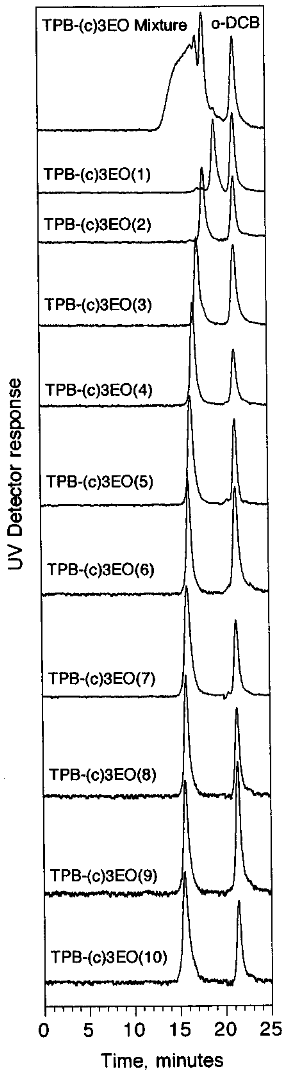


Figure 1. GPC traces of the TPB-(c)3EO(*z*) cyclization mixture and of the isolated cyclic oligomers with $z = 1-10$.

The individual cyclic compounds with $z = 1-10$ were separated by a combination of column chromatography and preparative TLC (see Experimental Section). The GPC traces of the reaction mixture and of TPB-(c)3EO-(z) ($z = 1-10$) obtained under high dilution are presented in Figure 1. Due to the short length of the 3EO spacer, the *gauche* conformation of TPB is accommodated with difficulty in the cyclic monomer and, therefore, TPB-(c)3EO(1) is formed in a very small amount. The dominant cyclic species produced in this cyclization reaction is the dimer, whereas the yields of the larger cyclics decrease with the increase in *z*.

Figure 2 plots the dependence of the calculated and experimental molecular weights (determined by GPC) of TPB-(c)3EO(z) vs ring size, *z*. The hydrodynamic volume of TPB-(c)3EO(z) cyclics is smaller than that of their linear homologues of identical DP. However, due to the presence of the rigid TPB units in their chain, the hydrodynamic volume of TPB-(c)3EO(*z*) with *z* larger than 2 is higher than that of the more flexible linear polystyrene with identical DP. Therefore, for

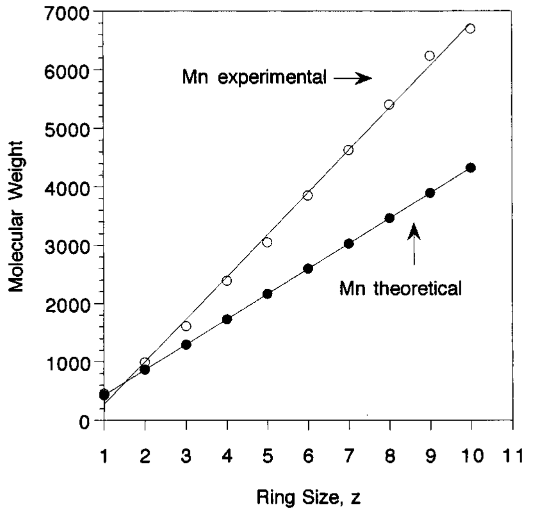


Figure 2. Dependence of the calculated ($M_{n,theor}$ = ●) and experimental (obtained by GPC) ($M_{n,exp}$ = ○) molecular weight on DP.

cyclics with $z > 2$, the molecular weights of TPB-(c)-3EO(z) measured by GPC calibrated with polystyrene standards are overestimated. The correct size assignment of these cyclics demands a linear dependence between the experimental molecular weight and DP. Therefore, the plot from Figure 2 demonstrates the correct ring size assignment for this series of cyclic compounds. The same plot can also be used for an absolute calibration of the GPC for this series of cyclic compounds.

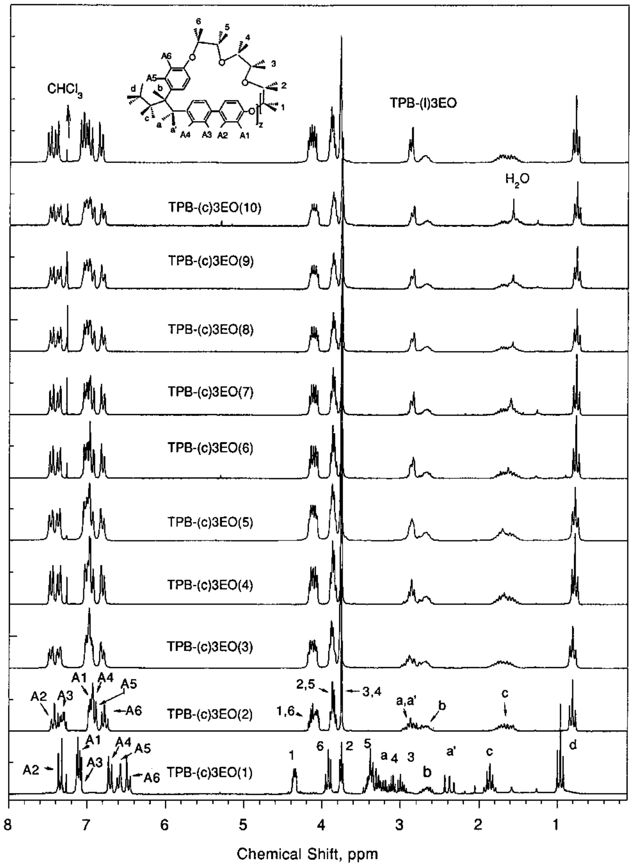


Figure 3. ^{1}H-NMR spectra of the TPB-(c)3EO(z) series, of the mixture of higher molecular weight cyclics, and of the linear polymer.

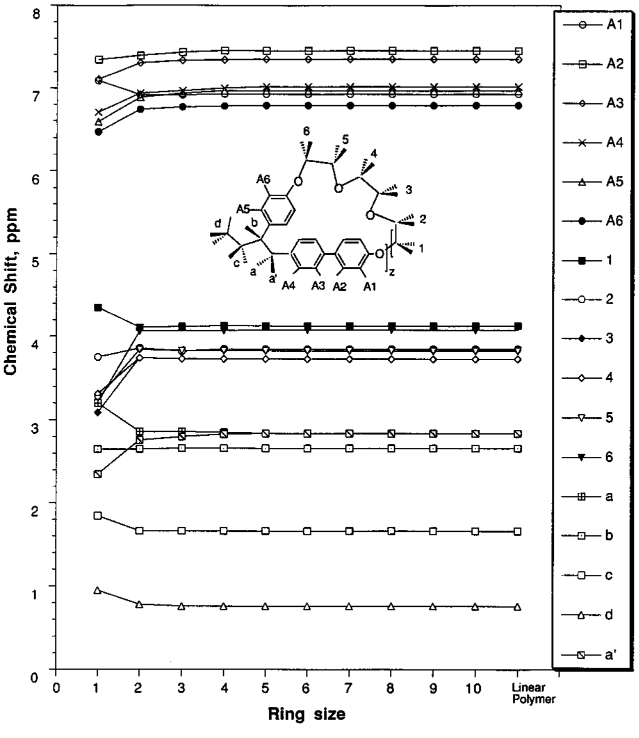
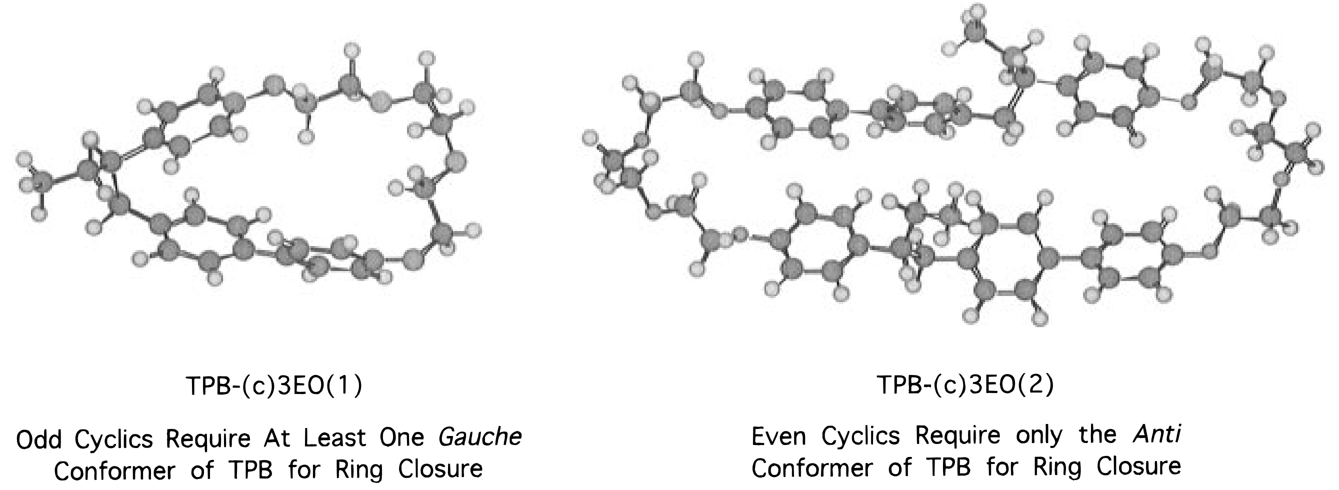


Figure 4. Dependence of the ^{1}H-NMR chemical shifts of the TPB-(c)3EO(z) series, of the mixture of higher molecular weight cyclics, and of the linear polymer on DP.

Figure 3 presents the ^{1}H-NMR spectra of TPB-(l)3EO and of TPB-(c)3EO(z) (z = 1−10). The asignment of the chemical shifts was made as reported previously.[9] The dependence of the ^{1}H chemical shifts on z is plotted in Figure 4. The ^{13}C-NMR spectra of the same compounds are presented in Figure 5, while Figure 6 plots the dependence of the ^{13}C chemical shifts on z. Two significant features of these spectra are used to ascertain the cyclic nature of the TPB-(c)3EO(z) oligomers. First, resonances corresponding to possible chain ends such as $-CH_2OTs$, $-CH{=}CH_2$ or PhOH are absent. Second, both ^{1}H and ^{13}C spectra are strongly dependent on ring size, especially for small values of z. This behavior is not encountered in the corresponding linear structures of TPB-(l)3EO and in other similar systems.[7e] This effect is due to the dependence of the conformation of TPB and of the triethylene oxide (3EO) groups on z. Particularly, the different conformations of TPB generate shielding and deshielding effects that determine the chemical shifts of the aromatic and aliphatic resonances. The most restricted, *gauche* conformation of TPB is encountered in the cyclic monomer, TPB-(c)3EO(1). Its structure is shown in Scheme 3. Due to the *gauche* conformation of TPB, the monophenyl ring and the phenyl ring of the biphenyl *ipso* to $-CH_2CH(Et)-$ are brought into close proximity and therefore, they are shielding each other. This shielding effect shifts almost all aromatic resonances in both the ^{1}H- and ^{13}C-NMR spectra upfield in TPB-(c)3EO(1). Exceptions are A1 and the corresponding C2, which are shifted downfield. C3 and C4 also shift downfield, but to a smaller extent. The second phenyl ring of the biphenyl unit shields the spacer fragment connected to the monophenyl unit. Consequently, especially for the cyclic monomer, the corresponding resonances 6, 5, 4, 3, 2 (^{1}H-NMR) and f, e, d (^{13}C-NMR) are shifted upfield, while the resonances 1 (^{1}H-NMR) and a, c (^{13}C-NMR) that belong to the spacer segment directly connected to the biphenylyloxy shift downfield. Each of the carbons of the spacer provides a signal in the ^{13}C-NMR spectra of TPB-(c)-3EO(1) and, accordingly, the corresponding methylene

Scheme 3. Minimized Molecular Conformations of TPB-(c)3EO(1) and TPB-(c)3EO(2)



TPB-(c)3EO(1)

Odd Cyclics Require At Least One *Gauche* Conformer of TPB for Ring Closure

TPB-(c)3EO(2)

Even Cyclics Require only the *Anti* Conformer of TPB for Ring Closure

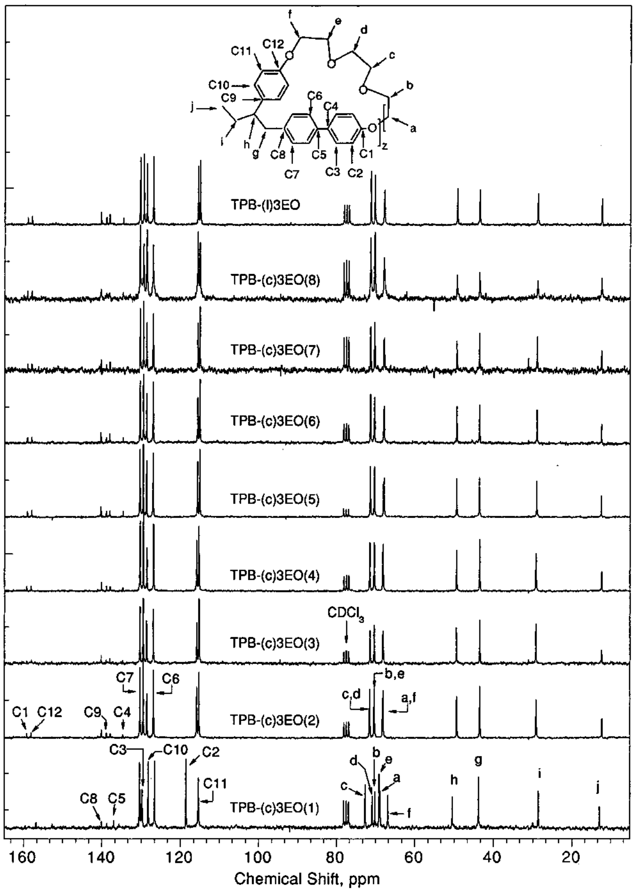


Figure 5. ^{13}C-NMR spectra of the TPB-(c)3EO(z) series, of the mixture of higher molecular weight cyclics, and of the linear polymer.

units give a complex pattern in the ^{1}H-NMR spectra. With increasing ring size, at $z > 5$ all these resonances converge to those of the linear polymer. The ^{1}H (a, b, c, d) and ^{13}C (h, g, i, j) resonances of the internal $-CH_2-CH(Et)-$ unit move to higher field with increasing ring size, since the *anti* conformation of TPB places them in the shielding region of the aromatic rings. Positioned next to a chiral center, protons a and a′ are diastereotopic and thus have a different chemical shift. As the ring size increases, these two resonances converge into a doublet. When the ring size gets larger, the population of *anti* conformers increases at the expense of their *gauche* counterparts. At the same time, the shielding/deshielding effects weaken. Thus, for $z > 5$, both ^{1}H- and ^{13}C-NMR resonances reach a plateau.

Thermal Characterization. Figure 7 presents the second heating and cooling DSC traces of TPB-(c)3EO-(z) ($z = 1-10$), of the mixture of higher cyclics, and of the linear polymer, TPB-(l)3EO. The transition temperatures and their associated enthalpy changes are reported in Table 1 together with the corresponding data of TPB-(c)8(z)[10g] and TPB-(l)8[19] (where 8 represents the number of methylene units in the alkane spacer). The phase behavior of TPB-(c)3EO(z) is both interesting and complex. The transition temperatures of TPB-(c)3EO-(z) are plotted as a function of z in Figure 8. As seen from Figures 7 and 8, the cyclic monomer exhibits only a glass transition (T_g). The cyclic dimer, by contrast, is crystalline. The cyclic trimer exhibits a T_g followed by a nematic phase. The isotropization temperature of this nematic phase overlaps T_g (Figure 8). The cyclic tetramer, TPB-(c)3EO(4), is the first compound with an even degree of oligomerization from this series which exhibits an enantiotropic nematic mesophase. However, its isotropization temperature is the highest in the entire series. The cyclic pentamer, TPB-(c)3EO(5), is the smallest cyclic compound with an odd degree of oligomerization which shows an enantiotropic nematic phase. Nonetheless, its isotropization temperature is the lowest from the entire series. All other cyclics with $z = 6-10$ exhibit an enantiotropic nematic phase. In the series of even values of z, the isotropization temperature decreases from $z = 4$ to $z = 10$. In the series of odd values of z, the isotropization temperature increases up to $z = 7$ and then decreases. The mixture of cyclics with $z > 10$ and the linear polymer TPB-(l)-3EO are amorphous. In the nematic phase, the X-ray diffractograms of these compounds display only a diffuse ring at wide angles, typical for a calamitic nematic phase.

The phase behavior of this series of compounds reveals two remarkable trends which were never observed before in the field of molecular and macromolecular LCs.[3a,4,19−23] First, on increasing z, the cyclic compounds TPB-(c)3EO(z) evolve from amorphous to liquid crystal, then back to amorphous. Second, an odd−even dependence of the isotropization temperature *as a function of ring size* (*i.e.* DP or molecular weight) is observed.

In molecular,[3a,20,21] main-chain[4,7d,e,20−23] and side-chain[4,7a−c] macromolecular LCs, the transition temperatures follow an odd−even dependence *on spacer length*

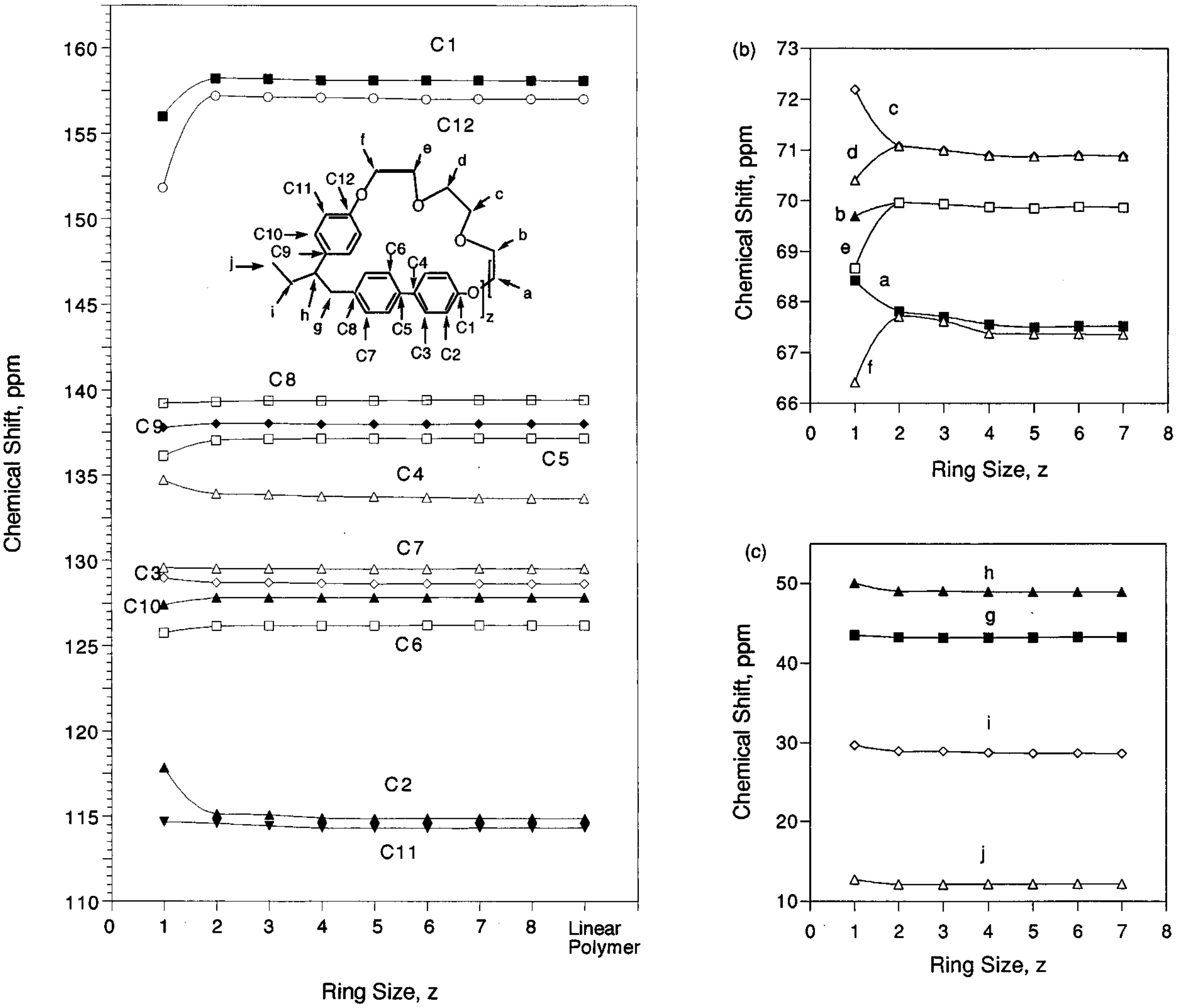


Figure 6. Dependence of the ^{13}C-NMR chemical shifts of the TPB-(c)3EO(*z*) series, of the mixture of higher molecular weight cyclics, and of the linear polymer on DP.

Table 1. Characterization of TPB-(c)3EO(*z*) (*z* = 1−10), TPB-(l)3EO, TPB-(c)8(*z*) (*z* = 1−5) and TPB-(l)8

		mol wt		transition temperatures and corresponding enthalpy changes (kcal/mru) in parentheses	
compound	yield (%)	theor	exp (GPC)	second heating	first cooling
TPB-(c)3EO(1)	0.8	454	432	g 8 i	i 0 g
TPB-(c)8(1)	6.6	429	479	i	i
TPB-(c)3EO(2)	19.3	989	864	k 204 (8.24) i	i 162 (8.13) k
TPB-(c)8(2)	8.8	857	983	g 37 k 90 k 121 (−4.58) k 142 (4.41) i	i 31 g
TPB-(c)3EO(3)	3.6	1607	1296	g 33 i	i 26 g
TPB-(c)8(3)	1.5	1286	1523	g 43 s 69 (0.15) n 83 (0.08) i	i 79 (0.07) n 66 (0.15) s 37 g
TPB-(c)3EO(4)	3.2	2385	1728	g 41 n 112 (1.10) i	i 105 (1.03) n 34 g
TPB-(c)8(4)	2.7	1715	2106	g 36 n 141 (0.95) i	i 133 (0.84) n 31 g
TPB-(c)3EO(5)	1.6	3045	2160	g 38 n 57 (0.13) i	i 51 (0.11) n 32 g
TPB-(c)8(5)	0.9	2143	2736	g 38 n 128 (1.00) i	i 126 (0.65) n 33 g
TPB-(c)3EO(6)	1.2	3852	2592	g 43 n 92 (1.08) i	i 81 (1.07) n 35 g
TPB-(c)3EO(7)	0.8	4624	3024	g 38 n 68 (0.49) i	i 62 (0.47) n 31 g
TPB-(c)3EO(8)	0.4	5406	3456	g 41 n 82 (1.18) i	i 67 (1.15) n 34 g
TPB-(c)3EO(9)	0.3	6239	3988	g 37 n 66 (0.71) i	i 56 (0.65) n 31 g
TPB-(c)3EO(10)	0.2	6704	4320	g 40 n 74 (0.84)i	i 57 (0.77) n 29 g
higher cyclics	30		8000	g 30 i	i 22 g
TPB-(l)3EO			18000	g 38 i	i 31 g
TPB-(l)8			30000	g 52 n 123 (2.43) i	i 107 (2.45) n 43 g

but not on DP. In all cases, the spacers containing an even number of methylene groups yield higher transition temperatures than the one containing an odd number. Also, in the present case, the even-size cyclics display broader and higher isotropization temperatures than those of the odd-size cyclis. The odd−even alternation of the isotropization temperature is as high as 55 °C for *z* = 4, 5 and decreases to 9 °C for *z* = 9, 10. A weak odd−even dependence of the glass transition temperature on *z* is also observed in Figure 8.

The thermodynamic parameters associated with the isotropization temperatures of these macrocyclics can be calculated per mole and, respectively, per mole of repeat units (mru). The plots of these two sets of data

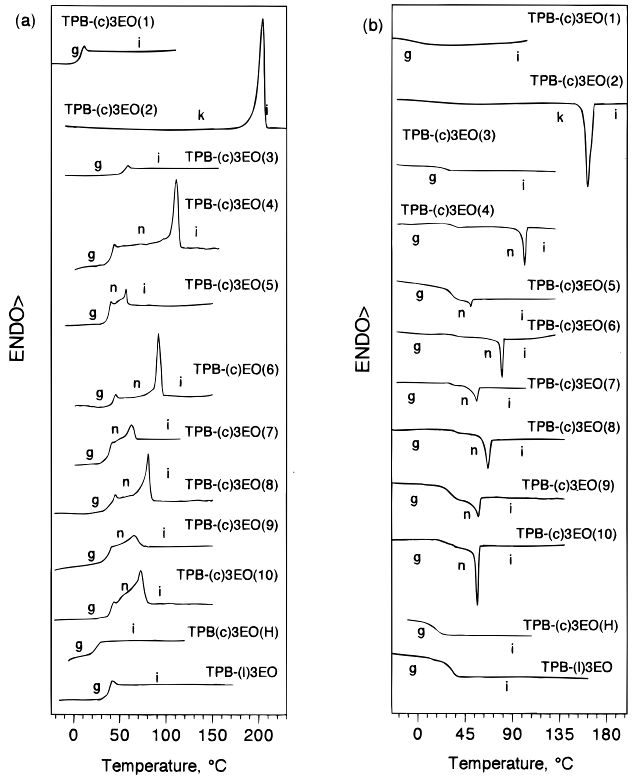


Figure 7. DSC traces of the TPB-(c)3EO(*z*) series, of the mixture of higher molecular weight cyclics, and of the linear polymer (TPB-(l)3EO): (a) second heating scan; (b) first cooling scan.

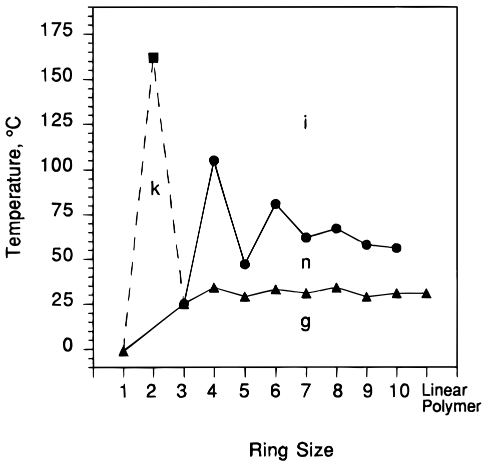


Figure 8. Dependence of the transition temperatures of the TPB-(c)3EO(*z*) series, of the mixture of higher molecular weight cyclics, and of the linear polymer (TPB-(l)3EO) on DP. Data from the first cooling scan (T_{in} = ●, T_g = ▲, T_{ik} = ■).

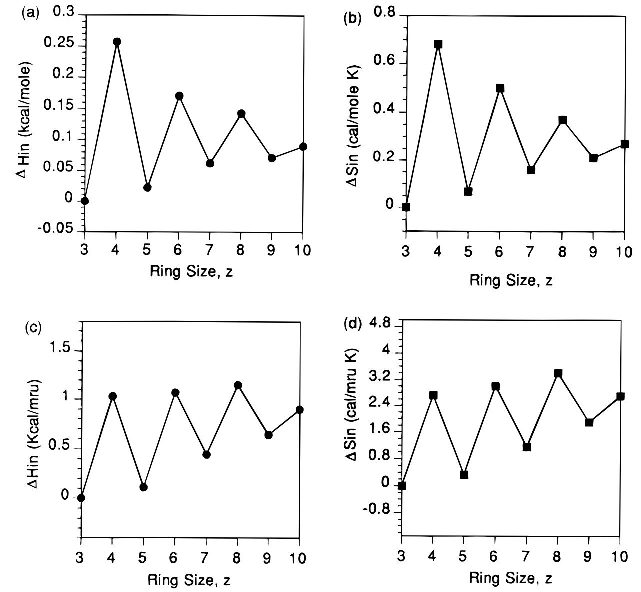


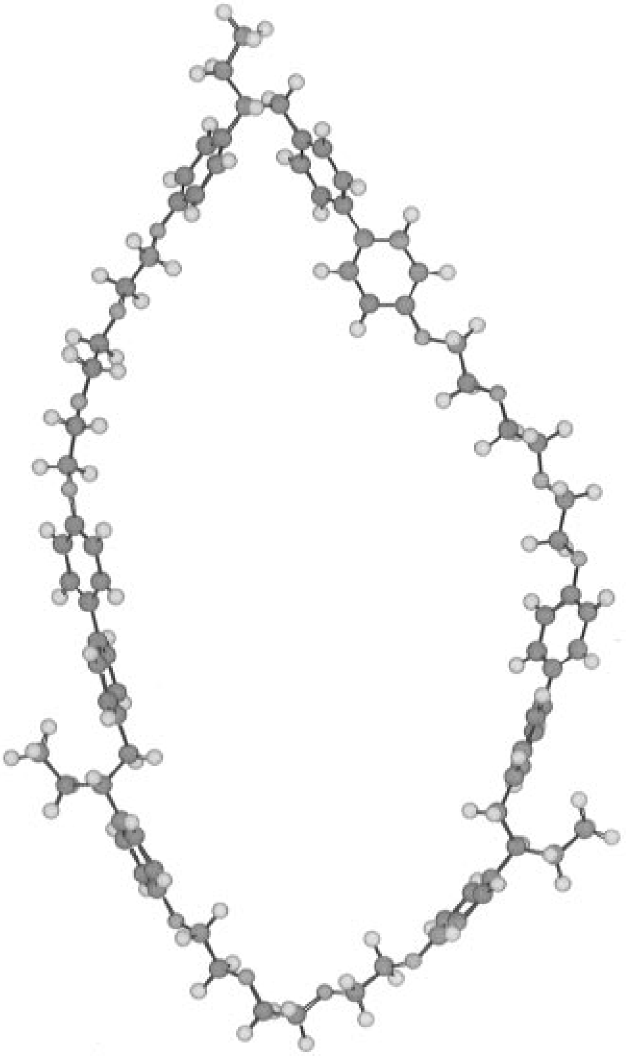
Figure 9. Dependence of the enthalpy (ΔH = ●) and entropy (ΔS = ■) associated with the isotropic to nematic transition of TPB-(c)3EO(*z*) (*z* = 4−10). (a) and (b) values reported per mole; (c) and (d) values reported per mole of repeat units (mru).

provide different information. When plotted per mole they give information on the overall macrocyclic, while when plotted per mru they provide information on the repeat unit of the macrocyclic. The dependences of the enthalpy and entropy changes associated with the isotropization on *z*, reported per mole, are plotted in Figure 9 a,b. The trend from Figure 9a,b provides information about the difference between the overall order in the nematic and respectively isotropic phases displayed by these macrocyclics. Both thermodynamic parameters follow an odd-even alternation as a function of *z* which resembles that of the corresponding isotropization temperatures. At high *z* values the difference between odd and even sizes vanishes. The continuous decrease of ΔH and ΔS vs *z* for the even series of cyclics is due to the decrease of the rigidity of the cyclic with increasing size. Simultaneously, the rigidity of the odd series of macrocyclics increases from $z = 3$ to $z = 9$. These plots demonstrate that in the even series of these macrocyclics the lowest members have the highest tendency to form LC phases. Simultaneously, in the odd series, the trend is reversed.

Figure 9c,d plots the enthaply and entropy changes reported per mru as a function of *z*. These plots provide information about the order of the repeat unit (*i.e.* one TPB mesogen connected to one 3EO spacer) as a function of macrocyclic size. The results from Figure 9c,d demonstrate an increase in the degree of order of the repeat unit which parallels the increase in ring size for both odd and even *z* values. This increase follows an odd−even alternation on *z*.

Mechanism of the New Odd−Even Effect. What is the explanation for this new and extremely interesting behavior? Let us first inspect Scheme 5 which outlines the conformations of these cyclics in their LC phase. X-ray scattering experiments carried out in the smectic A phase of various macrocyclics demonstrated that they exhibit a collapsed, highly stretched conformation,[10g,h,17] which generates a supramolecular rod, *i.e.* a conformationally flexible, quasi-rigid rodlike mesogen. The architecture of this supramolecular rod is determined by the relationship between the length of the *anti* conformer of the mesogen (L_m), that of the fully extended, all-trans spacer (L_s), and the parity and value of the DP or *z*.[10g,17] The spacer length affects only the architecture of the odd size cyclics. When $L_s < L_m$ the collapsed architecture of odd-size macrocyclics is distorted since one of the TPB units in its *gauche* conformation is required to be part of one fold. The other fold contains a sharp turn based on at least two *gauche* conformers of the spacer methylene units. For $L_s > L_m$, an ideal collapsed supramolecular conformation is obtained for odd cyclics with both folds containing only spacers. The collapsed conformations for the odd series of cyclics are presented for comparison in Scheme 5 for both $L_m < L_s$ and $L_m > L_s$. The conformation of even cyclics is not affected by spacer length since they always require only *anti* TPB conformers which are arranged

Scheme 4. Minimized Molecular Conformation of TPB-(c)3EO(3)



TPB-(c)3EO(3)

symmetrically, facing each other from the opposite sides of the collapsed ring. At a particular degree of polymerization, an increase in spacer length increases the axial ratio[21] (L/d, where L = length and d = diameter) of the collapsed macrocyclic. Therefore, DP expresses itself in the overall shape and size of these cyclics and in their mesogenic ability. The length of the shortest fully extended spacer that can accommodate an ideal collapsed cyclic trimer containing only *anti* TPB conformers was estimated[10g] from eq 1 (Scheme 5) to be at least 21 Å. This corresponds to a spacer containing 15

$$2L_m + L_s = 2(L_s - 2.5) + L_m \qquad (1)$$

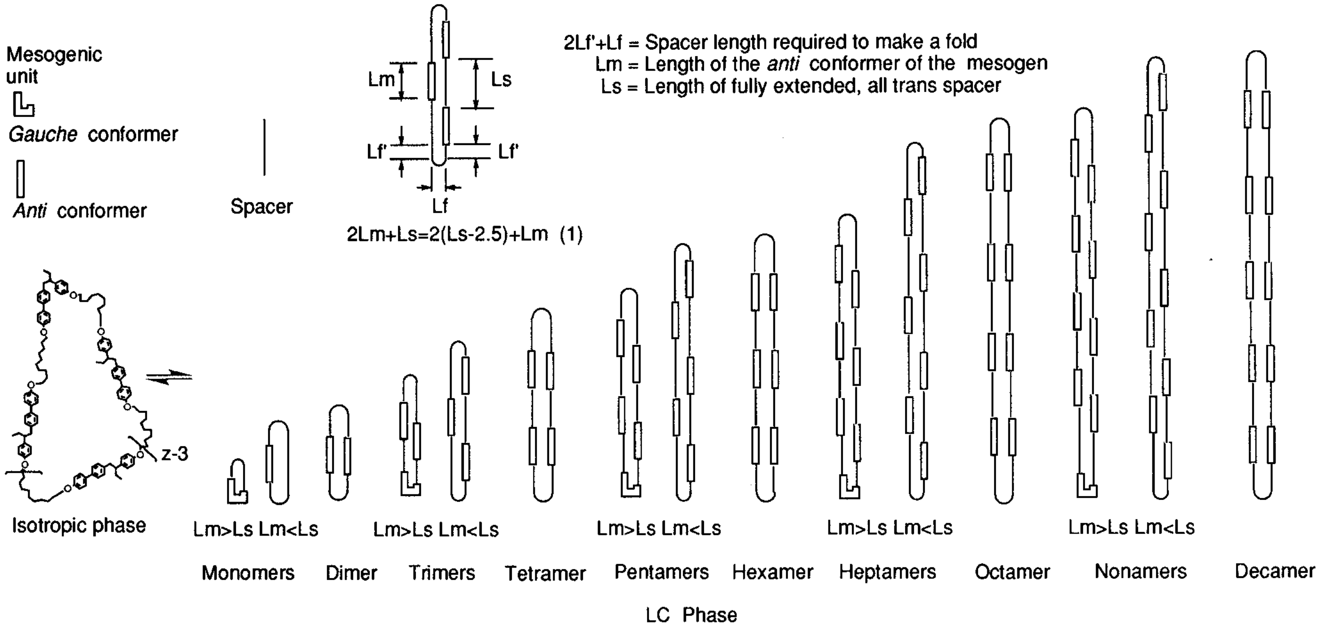
methylenic units. Equation 1 assumes that the length of the sum of two mesogens and one extended spacer should be equal to the sum of the lengths of one mesogen and the remaining parts which do not contribute to the fold of the other two spacers. The minimum number of methylene groups in the 180° turn is two or more, *i.e.* 2.5 Å or more. In the present case, molecular modeling gives L_s = 11.1 Å for the 3EO spacer and L_m = 16.1 Å for the TPB unit, *i.e.* $L_s < L_m$. This dependence is the key to the odd−even effect in terms of ring size.

As observed in Scheme 3, the cyclic monomer can accommodate only the *gauche* TPB conformer. The overall shape of TPB-(c)3EO(1) is distorted and cannot generate a supramolecular rodlike mesogen. Therefore, a LC phase is not generated and the cyclic monomer is amorphous. The symmetric cyclic dimer contains two *anti* TPB conformers. Its structure (Scheme 3) allows a good packing and TPB-(c)3EO(2) forms a crystalline phase. Most probably, its axial ratio is too small to generate a stable enantiotropic nematic phase. The cyclic trimer contains one *gauche* and two *anti* TPB units. Although more elongated than the monomer, its molecular conformation (Scheme 4) is still distorted and its axial ratio is not sufficient to produce a thermodynamically stable LC phase. An ideal collapsed structure incorporating only *anti* TPB conformers is achieved in the cyclic tetramer. The axial ratio and the rigidity of TPB-(c)3EO(4) are optimum and, therefore, it displays the most stable nematic mesophase from the entire series. The cyclic pentamer is based on one *gauche* and four *anti* TPB blocks. Its conformation is still distorted, however less than that of the trimer, and its axial ratio has increased. Therefore, it exhibits a narrow nematic phase. For $z > 5$, the even series decreases while the odd series increases its isotropization temperature. The plot of chemical shifts vs z from Figure 4 shows that at $z = 4$, the macrocyclic still contains some ring strain which, however, can accomodate the collapsed rodlike supramolecular shape. On increasing the even z values, both the axial ratio and the flexibility of the supramolecular rod increase. Subsequently, the stability of the nematic phase decreases. In the odd series, with the increase in z the stability of the nematic phase increases.

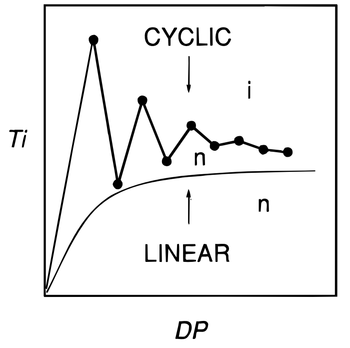
The main difference between the odd and even series is that in the odd series there is permanently one TPB mesogen in the fold, and this provides both a lower axial ratio and a lower rigidity. The presence of the TPB unit in the fold is responsible for the odd−even effect vs z observed in cyclics. This effect is not encountered in linear liquid crystal polymers.[4,7,8] On increasing z for the odd series, the molar fraction of *gauche* TPB conformers present in the fold decreases and, therefore, the architecture of the odd macrocyclics approaches that of the even ones. Therefore, in the odd series, an increase in the isotropization temperature with z is observed. At a certain value of z, the isotropization temperatures of the odd and even series should converge to the same value. At even higher values of z, these macrocyclics should behave as their linear homologues, therefore losing their nematic mesophase. This most probably will take place at the value of z for which the isotropization temperature overlaps T_g. This assumption is supported by the phase behavior of the mixture of larger cyclics which are amorphous.

At this point, let us compare the phase behavior of TPB-(c)3EO(z) with that of TPB-(c)8(z)[10g,17] (Table 1). TPB-(c)8(3) exhibits enantiotropic smectic A and nematic mesophases while TPB-(c)3EO(3) is amorphous. The isotropization of TPB-(c)8(3) is 50 °C higher than the T_g of TPB-(c)3EO(3). TPB-(c)8(z) with z = 4 and 5 exhibit enantiotropic mesophases. Their stability is 29 °C and respectively 71 °C higher than that of the corresponding TPB-(c)3EO(z). Both series of cyclics display an odd−even dependence on z. Therefore, as expected, the more flexible oligooxyethylene spacer destabilizes the LC phase by comparison with its alkane analogue. The effect is seen also in the linear polymers; *i.e.* TPB-(l)3EO is amorphous, while TPB-(l)8 exhibits an enantiotropic nematic phase which undergoes isotro-

Scheme 5. Molecular Conformations of TPB-(c)3EO(z) (z = 1−10) in the LC Phase and Their Dependence on Spacer Length



Scheme 6. Experimental Dependence of the Isotropization Temperature (T_i) of Cyclic ($L_s < L_m$) and Linear LC Polymers on DP (T_i and DP Are in Arbitrary Units)



pization at 123 °C, *i.e.* 85 °C above the T_g of TPB-(l)-3EO. TPB-(c)8(z) contains an alkane spacer which is more rigid than 3EO and, therefore, displays broader and more ordered LC phases than TPB-(c)3EO(z).

The classic odd−even effect, well established in the field of linear LCs, produces an alternation of the isotropization temperatures and of their associated thermodynamic parameters via the parity of the number of atoms in the spacer.[19−23] This trend was explained by the different orientational order of the mesogen, generated via the extended spacer containing an odd or even number of atoms. The even spacers produce a higher orientational order of the mesogen, and this translates into a higher order in the nematic phase and, subsequently, in a higher isotropization temperature. The transition from monomer to polymer produces an additional, continuous increase of the isotropization temperature.

In the case of cyclic compounds discussed in this paper, the conformation of one of the TPB-derived repeat units is determined by the odd or even DP of the cyclic. In addition, in the odd series of cyclic sizes, the molar concentration of the *gauche* TPB repeat unit is determined by DP. The odd−even influence of ring size on the shape of these supramolecular rodlike macrocyclics explains also the odd−even dependence of T_g on z. The value of T_g is determined by the free volume of the polymer. Therefore, the larger free volume associated with the odd cyclics in their nematic phase explains the lower T_g of the odd cyclics. Consequently, the difference between the architecture of the odd and even cyclics in their LC phase dictates their free volume and through it, the odd−even dependence of T_g on ring size.

Scheme 6 outlines the experimentally observed dependence of the isotropization temperature of cyclic and linear LCs which could not be predicted quantitatively at the initiation of these series of investigations.[9] Thus, this novel odd−even effect is different from the classic one and provides unusual opportunities for the design of nematic crown ethers with a predetermined placement and binding capabilities of their oligooxyethylene groups. An oligooxyethylene group placed in the fold of an odd cyclic binds independently, while one between two TPB units in an even cyclic should bind in a cooperative way (Scheme 5). Therefore, we foresee that in the nematic phase, the binding properties of these crown ethers can be manipulated by this odd−even effect. This combination of effects determines the difference between the diameter, length, and symmetry and, therefore, the molecular geometry and axial ratio of the supramolecular rodlike mesogen generated from the odd or the even sizes of these cyclics.

On the optical polarized microscope, the nematic phase of all macrocyclics with an even DP exhibits a schlieren texture. The cyclics with odd DP display a nematic threaded texture. This difference between the textures of the nematic phase of odd and even cyclics persists over the entire range of DPs. The dissimilarity between the textures of these two nematic phases is in agreement with the different structures of these two series of compounds.

Research along these lines and on the synthesis of cyclic crown ethers based on TPB and oligooxyethylene spacers longer than TPB is in progress. We foresee (Scheme 5) that cyclic compounds based on TPB and longer oligooxyethylene spacers than TPB will provide a different phase behavior, which most probably will resemble that of the linear polymers.

Experimental Section

Materials. 1,8-Bis((*p*-tolylsulfonyl)oxy)-3,6-dioxaoctane,[24] 1,8-dibromo-3,6-dioxaoctane,[25] and 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane (TPB)[19] were synthesized according to literature procedures. *N*,*N*-Dimethylformamide (DMF) was dried over CaH_2 and was freshly distilled before use. Silica gel fluorescent thin-layer chromatographic (TLC) plates (Kodak), preparative chromatographic plates (Whatman), and all other chemicals were commercially available and were used as received.

Techniques. A Varian Gemini 200 NMR spectrometer was used to record the ^{1}H-NMR (200 MHz) and ^{13}C-NMR (50 MHz) spectra at 20 °C. TMS was used as the internal standard. Relative molecular weights and purities were determined on a Perkin-Elmer Series 10-LC GPC/HPLC instrument, equipped with a LC-100 column oven, a Nelson Analytical 900 Series data station, and a UV detector. The measurements were done using THF as solvent (1 mL/min, 40 °C) and two PL gel columns of 5×10^2 and 10^4 Å. A calibration plot constructed with polystyrene standards was used for the determination of the relative molecular weights. The purity of the compounds was also supported by TLC. Elemental analysis was performed by Galbraith Laboratories. A Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) equipped with a TAC7/DX thermal analysis controller was used to record the first-order thermal transitions, which were read at the maximum or minimum of the endothermic or exothermic peaks. Glass transitions were measured as the middle of the change in heat capacity. The instrument was calibrated with In and Zn standards. Scanning rates were 20 °C/min in all cases. All heating and cooling scans were perfectly reproducible after the first heating scan. The first heating scan could be reobtained after proper annealing. An Olympus BX40 optical polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to analyze the anisotropic textures. X-ray scattering patterns were recorded by using either a helium-filled, flate-plate, wide-angle (WAXS) camera or a pinhole-collimated small-angle (SAXS) and an image plate area detector (MAR Research) with a graphite-monochromatized pinhole-collimated beam and a helium tent. The samples, in glass capillaries, were held in a temperature-controlled cell (±0.1 °C). Molecular modeling was performed on a Silicon Graphics Indy workstation using the MacroModel software (version 5, from Columbia University) with the MM3 force field for energy minimization.

Synthesis of the Linear Polymer, TPB-(l)3EO. Conventional liquid−liquid two-phase (organic solvent−aqueous NaOH) phase transfer catalyzed polyetherification conditions were employed in the synthesis of the linear polymer.[19] To a 25 mL one-neck flask equipped with a condenser and N_2 inlet−outlet were successively added TPB (0.191 g, 0.60 mmol), *o*-dichlorobenzene (*o*-DCB) (1.2 mL), 1,8-dibromo-3,6-dioxaoctane (0.166 g, 0.60 mmol), NaOH (10 N, 1.2 mL), and TBAH (0.082 g, 0.24 mmol), and the reaction mixture was stirred at 80 °C. After 6 h, the organic and aqueous layers were diluted with $CHCl_3$ and respectively H_2O. The organic phase was washed with H_2O, dilute HCl, and H_2O. The polymer solution was filtered, concentrated, and precipitated into MeOH, and the precipitate was filtered and dried to yield 0.22 g (92%). The polymer was further purified by precipitation first from $CHCl_3$ into acetone and then from $CHCl_3$ into MeOH.

Synthesis of the Macrocyclics, TPB-(c)3EO(*z*) (*z* = 1−10). A one-step cyclization reaction was carried out under high-dilution conditions as follows. To a 5 L three-neck flask equipped with a mechanical stirrer, containing DMF (4 L), TPB (2.55 g, 8 mmol), and Cs_2CO_3 (15.12 g , 48 mmol), a solution of 1,8-bis((*p*-tolylsulfonyl)oxy)-3,6-dioxaoctane (3.66 g, 8 mmol) in DMF (100 mL) was added dropwise over an 8 h period via a syringe pump. The reaction mixture was stirred under N_2 at 60 °C for 7 days. DMF was then distilled, H_2O (200 mL) and CH_2Cl_2 (200 mL) were added, and the organic phase was washed with H_2O, dilute HCl, and H_2O and dried over $MgSO_4$. The solvent was evaporated, and the mixture of low molecular weight cyclics was separated by column chromatography (SiO_2, CH_2Cl_2:Et_2O:NEt_3 = 20:1:0.01). The mixture of higher oligomers was eluted with CH_2Cl_2:MeOH = 1:1, the solvent was evaporated, and the product was precipitated into CH_3OH, filtered, and dried. **1,4,7,10-Tetraoxa-24-ethyl-[10.0.2]paracyclophane** (*i.e.* cyclic monomer, TPB-(c)-3EO(1)), **1,4,7,10,29,32,35,38-octaoxa-24,52-diethyl[10.0.2.10.0.2]-paracyclophane** (*i.e.* cyclic dimer, TPB-(c)3EO(2)), **1,4,7,10,-29,32,35,38,57,60,63,66-dodecaoxa-24,52,80-triethyl-[10.0.2.10.0.2.10.0.2]paracyclophane** (*i.e.* cyclic trimer, (TPB-(c)3EO(3)), and **1,4,7,10,29,32,35,38,57,60,63,66,85,88,-91,94-hexadecaoxa-24,52,80,108-tetraethyl[10.0.2.10.-0.2.10.0.2.10.0.2]paracyclophane** (*i.e.* cyclic tetramer, TPB-(c)3EO(4)) were separated by repeated column chromatography (SiO_2, CH_2Cl_2:Et_2O = 20:1). Anal. Calcd for TPB-(c)3EO(2), $C_{56}H_{64}O_8$: C, 77.75; H, 7.46. Found: C, 77.73; H, 7.59. Anal. Calcd for TPB-(c)3EO(3), $C_{84}H_{96}O_{12}$: C, 77.75; H, 7.46. Found: C, 77.54; H, 7.64. Anal. Calcd for TPB-(c)3EO(4), $C_{112}H_{128}O_{16}$: C, 77.75; H, 7.46. Found: C, 77.57; H, 7.37.

1,4,7,10,29,32,35,38,57,60,63,66,85,88,91,94,113,116,119,-122-Eicosaoxa-24,52,80,108,136-pentaethyl[10.0.2.-10.0.2.10.0.2.10.0.2.10.0.2]paracyclophane (*i.e.* cyclic pentamer, TPB-(c)3EO(5)), **1, 4, 7, 10, 29, 32, 35, 38, 57, 60, 63, 66, 85, 88, 91, 94, 113, 116, 119, 122, 141, 144, 147, 150-tetracosaoxa-24, 52, 80, 108, 136, 164-hexaethyl[10.0.2.10.-0.2.10.0.2.10.0.2.10.0.2.10.0.2]paracyclophane** (*i..e.*cyclic hexamer, TPB-(c)3EO(6)), **1, 4, 7, 10, 29, 32, 35, 38, 57, 60, 63, 66, 85, 88, 91, 94, 113, 116, 119, 122, 141, 144, 147, 150, 169, 172, 175, 178-octacosaoxa-24, 52, 80, 108, 136, 164, 192-heptaethyl[10.0.2.10.0.2.10.0.2.10.0.2.10.0.2.10.0.2.10.0.2]-paracyclophane** (*i.e.* cyclic heptamer, TPB-(c)3EO(7)), **1,4,7,-10,29,32,35,38,57,60,63,66,85,88,91,94,113,116,119,122,-141,144,147,150,169,172,175,178,197,200,203,206-dotriacontaoxa-24,52,80,108,136,164,192,220-octaethyl[10.0.-2.10.0.2.10.0.2.10.0.2.10.0.2.10.0.2.10.0.2.10.0.2]paracyclophane** (*i.e.* cyclic octamer, TPB-(c)3EO(8)), **1,4,7,10,29,32,35,38,-57,60,63,66,85,88,91,94,113,116,119,122,141,144,147,150,-169,172,175,178,197,200,203,206,225,228,231,234-hexatriacontaoxa-24,52,80,108,136,164,192,220,248-nonaethyl-[10.0.2.10.0.2.10.0.2.10.0.2.10.0.2.10.0.2.10.0.2.10.0.2.-10.0.2]paracyclophane** (*i.e.* cyclic nonamer, TPB-(c)3EO(9)), and **1,4,7,10,29,32,35,38,57,60,63,66,85,88,91,94,113,116,-119,122,141,144,147,150,169,172,175,178,197,200,203,206,-225,228,231,234,253,256,259,262-tetracontaoxa-24,52,80,-108,136,164,192,220,248,276-decaethyl[10.0.2.10.0.2.10.-0.2.10.0.2.10.0.2.10.0.2.10.0.2.10.0.2.10.0.2.10.0.2]paracyclophane** (*i.e.* cyclic decamer, TPB-(c)3EO(10)) were isolated by preparative TLC (SiO_2, toluene:Et_2O = 1:1). The CH_2Cl_2 solution of each cyclic was filtered and was precipitated into MeOH. The resulting product was filtered and was dried under vacuum. Anal. Calcd for TPB-(c)3EO(5), $C_{140}H_{160}O_{20}$: C, 77.75; H, 7.46. Found: C, 77.59; H, 7.34. Anal. Calcd for TPB-(c)3EO(6), $C_{168}H_{192}O_{24}$: C, 77.75; H, 7.46. Found: C, 77.78; H, 7.58. Anal. Calcd for TPB-(c)3EO(7), $C_{224}H_{256}O_{32}$: C, 77.75; H, 7.46. Found: C, 77.47; H, 7.61.

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