Macromolecules **1990,** *23,* 3509–3520

Liquid Crystalline Polyethers Based on Conformational Isomerism. 10. Synthesis and Determination of the Virtual Mesophases of Polyethers Based on 1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane and α,ω-Dibromoalkanes Containing from 17 to 20 Methylene Units[†,‡]

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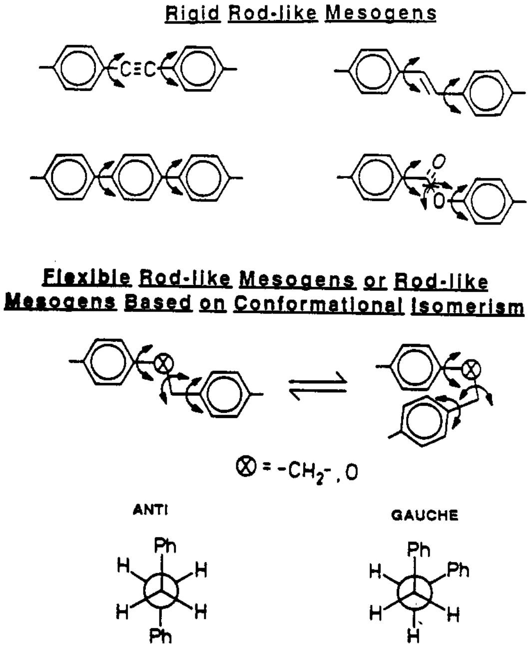
Received December 15, 1989; Revised Manuscript Received February 5, 1990

ABSTRACT: The synthesis and characterization of the polyethers based on the flexible mesogen 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) and α,ω-dibromoalkanes containing 17, 18, 19, and 20 methylene units (MBPE-17, MBPE-18, MBPE-198 and MBPE-20) are described. All polymers present a virtual nematic mesophase. The virtual isotropic–nematic transition tempertures and thermodynamic parameters were determined from copolymerization experiments. Both virtual isotropic–nematic transition temperatures and thermodynamic parameters of the entire set of polyethers MBPE-X (X = number of methylene units in the flexible spacer) with X = 4–20 were plotted and lead to the following conclusions. Virtual isotropic–nematic thermal transition temperatures and their associated enthalpy and entropy changes follow an odd–even dependence on X. At large X, the odd–even dependence tends to vanish. Extrapolation of the virtual isotropic–nematic temperatures to X values approaching infinity suggests the presence of a virtual mesophase in polyethylene. Previously, this mesophase was only theoretically predicted.[22] The conformational entropic contribution per CH_2 unit at the isotropic–nematic transition agrees very well for both the even and odd series with the data reported for thermotropic polyesters based on rigid rodlike mesogens and flexible spacers.[4] The entropic contribution per MBPE unit is, however, larger than the one reported for the rigid rodlike mesogenic group 4,4′-dihydroxy-2,2′-dimethylazoxybenzene.[4] This difference was explained by considering that in the case of the flexible MBPE this entropic factor represents a combination of orientational and conformational contributions, while in the case of the rigid rodlike mesogens this factor contains only an orientational contribution. Consequently, the entropy changes associated with the isotropization temperatures of polyethers based on flexible rodlike mesogens are higher than those of polyesters based on rigid rodlike mesogens most probably due to the lower entropy of the former in the isotropic phase and not due to a higher degree of order in the mesomorphic phase.

Introduction

The traditional synthetic procedure employed in the preparation of main-chain and side-chain liquid crystalline polymers is based on the use of the concept of rigid rodlike mesogenic units.[1–8] Additional classes of mesogenic groups were recently reviewed.[9] Rigid rodlike mesogenic units exhibit an anisotropic elongated or rodlike conformation due to the conformational rigidity or semirigidity of the molecule (Scheme I).

Scheme I
Comparison of Rigid and Flexible Mesogens or Rodlike Mesogens Based on Conformational Isomerism



In some previous publications from our laboratory, we have advanced the concept of rodlike mesogenic units based on conformational isomerism or of flexible rodlike mesogenic units (Scheme I).[10–18] In the case of flexible rodlike mesogenic units, the elongated or rodlike conformation of the mesogen is accomplished by thermodynamics. That is, when the lowest free energy conformer exhibits a molecular structure similar to that of a rigid rodlike mesogen, it may display a mesomorphic phase. In the isotropic phase the lowest free energy conformer is in dynamic equilibrium with a series of different conformers (Scheme I). The thermodynamic stability of the mesophase exhibited by such a compound is expected to be lower than of the corresponding rigid rodlike homologue. Therefore, on the basis of thermodynamic reasons that were presented in a previous publications,[19] polymers based on flexible mesogenic units and flexible spacers are expected to display mostly virtual or monotropic

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[†] Part 9: ref 18.

[‡] Dedicated to Professor C. I. Simionescu in honor of his 70th birthday.

0024-9297/90/2223-3509$02.50/0

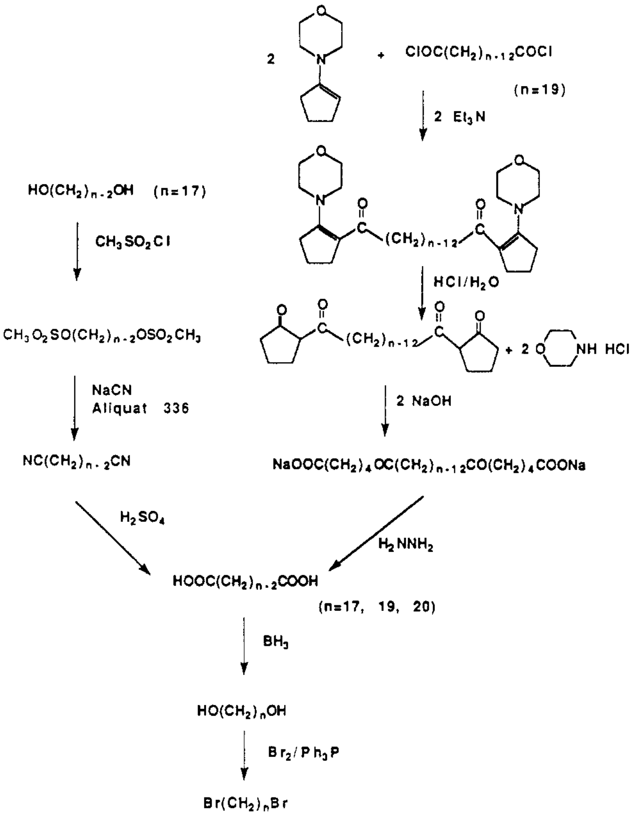
mesophases.

The goal of this series of publications is to provide a comprehensive understanding of our ability to tailor-make liquid crystalline polymers that do not contain any rigid rodlike mesogenic units. These polymers exhibit much faster dynamics than the corresponding polymers based on rigid rodlike mesogens. Our present investigations are directed toward the molecular design and understanding of liquid crystal polyethers based on flexible mesogens and flexible spacers[11-18] and of flexible liquid crystal polyethers without flexible spacers.[10] One of the previous publications in this series explained our reasons for performing these experiments with liquid crystal polyethers.[15]

The first examples of liquid crystal polyethers based on flexible mesogens and flexible spacers are using 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) as a mesogenic unit and α,ω-dibromoalkane-derived flexible spacers.[11-18] Most of these polymers display only virtual mesophases. Exceptions are the polyethers based on MBPE and 1,5-dibromopentane (MBPE-5) and MBPE and 1,9-dibromononane (MBPE-9), which display two monotropic (a nematic and an unidentified) mesophases;[11,12,15] the polyethers based on MBPE and 1,11-dibromoundecane (MBPE-11), which exhibit a monotropic nematic mesophase;[11,12,15] and the polyether based on MBPE and 1,8-dibromooctane (MBPE-8), which diplays a very narrow enantiotropic nematic mesophase.[13] The virtual mesophases of the MBPE-*X* polyethers with up to 16 methylene units in the flexible spacer were determined from copolymerization experiments.[11-18] The other polyethers based on MBPE and flexible spacers containing an odd number of methylene units display two virtual (a nematic and an unidentified) mesophases, while those based on MBPE and flexible spacers containing an even number of methylene units display only a virtual nematic mesophase. The mesophase exhibited by MBPE-*X* containing an even number of methylene units in their flexible spacer and the high-temperature mesophase of the polymers containing an odd number of methylene units are uniaxial nematic (Nu) phases.[20,21] No definitive assignment on the nature of the second mesophase exhibited by the polymers containing an odd number of methylene units is yet available. Simultaneous X-ray and DSC experiments could not yet definitively identify this mesophase.[20]

The first goal of this paper is to present the synthesis and characterization of the polyethers based on MBPE and α,ω-dibromoalkanes containing between 17 and 20 methylene units. Their virtual mesophases will be determined from copolymerization experiments of MBPE with the corresponding α,ω-dibromoalkane and 1,8-dibromooctane. The second goal of this paper is to summarize and discuss the phase behavior of the polyethers based on MBPE and α,ω-dibromoalkanes containing between 5 and 20 methylene units. The dependence between the virtual mesomorphic phase transition temperatures, their thermodynamic parameters, and the number of methylene units in the flexible spacer will be critically discussed. The experimental determination of the virtual mesophase displayed by a polyether based on MBPE and a flexible spacer containing a number of methylene units that approaches infinity would correspond to the virtual mesophase displayed by polyethylene. Although a virtual nematic mesophase was theoretically predicted and calculated for polyethylene,[22] to our knowledge the first attempt to experimentally estimate this value will be presented in this paper.

Scheme II
Synthesis of α,ω-Dibromoalkanes



Experimental Section

Materials. 1,8-Dibromooctane (98%, Aldrich), 1,15-pentadecanediol (98%, Wiley Organics), 1,18-dibromooctadecane (K and K Laboratories), azelaoyl chloride, 4-(1-cyclopenten-1-yl)morpholine, BH_3·THF complex (1 M), triphenylphosphine (99%), *o*-dichlorobenzene (99%), tetrabutylammonium hydrogen sulfate (TBAH, 97%, all from Aldrich), 1,20-eicosanedioic acid (95%, Tokyo Kasei), and the other commercially available chemicals were used as received.

Synthesis of 1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE). This compound was synthesized as previously reported.[11] It purity was >99.9% (HPLC); mp (DSC, 20 °C/min) 148 °C.

The synthesis of α,ω-dibromoalkanes used in this paper is outlined in Scheme II.

Synthesis of 1,15-Bis(methylsulfonyl)pentadecane. A solution of 11.3 g (0.098 mol) of methanesulfonyl chloride in 50 mL of dried pyridine was added dropwise to an ice-cooled solution containing 8 g (0.033 mol) of 1,15-pentadecanediol in 250 mL of dried pyridine. The reaction mixture was stirred for 2 h. A white precipitate formed. The reaction mixture was kept in a refrigerator for 1 day, after which it was poured into 700 mL of water. The resulting white precipitate was filtered, dried, and recrystallized from methanol to yield 10.8 g (83%) of white crystals: mp 77–78 °C; ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 1.26 [m, 22 H, $(CH_2)_{11}$], 1.75 (quintet, 4 H, $CH_3SO_3CH_2CH_2$), 3.01 (s, 6 H, $CH_3SO_3CH_2$), 4.23 (t, 4 H, $CH_3SO_3CH_2CH_2$).

Synthesis of 1,17-Heptadecanedinitrile. 1,15-Bis(methylsulfonyl)pentadecane (10 g, 0.025 mol) and 0.20 g (0.0005 mol) of Aliquat-336 (tricaprylmethylammonium chloride) were added to a solution of 7.35 g (0.75 mol) of NaCN in 70 mL water. The reaction mixture was stirred at 100 °C for 2 h, cooled to room temperature, and poured into water. The resulting precipitate was filtered and recrystallized from methanol to yield 6.22 g (95%) of white crystals: mp 44 °C; ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 1.26 [m, 22 H, $(CH_2)_{11}$], 1.66 (quintet, 4 H, $NCCH_2CH_2$), 2.34 (t, 4 H, $NCCH_2CH_2$).

Synthesis of 1,17-Heptadecanedioic Acid. A mixture of 6.0 g (0.03 mol) of 1,17-heptadecanedinitrile and 100 mL of 50% H_2SO_4 was refluxed for 2 h. The reaction mixture was poured into 500 mL of water, and the resulting precipitate was filtered and recrystallized from a 1/1 (v/v) mixture of ethanol and water to yield 5.95 g (86%) of white crystals: mp 116–117 °C (lit.[23] mp 116–117 °C); ^1H NMR (DMSO-d_6, TMS, δ, ppm) 1.25 [m, 22 H, $(CH_2)^{11}$], 1.49 (m, 4 H, $HOOCCH_2CH_2$), 2.78 (t, 4 H, $HOOCCH_2CH_2$).

Synthesis of 1,17-Heptadecanediol. 1,17-Heptadecanedioic acid (5.5 g, 0.018 mol) was dispersed in 100 mL of $LiAlH_4$-dried THF, and the mixture was cooled with ice to 0–5 °C. To this mixture was added dropwise 69 mL (0.069 mol) of $BF_3 \cdot THF$ complex (1 M, Aldrich). After addition, the reaction temperature was raised to 40–50 °C and maintained overnight. The reaction mixture was poured into 2 L of water, and the white precipitate was filtered and then washed with water followed by $NaHCO_3$ and water. After drying, the product was recrystallized from benzene to yield 4.2 g (84%) of white crystals: mp 93–94 °C (lit.[24] mp 96–96.5 °C); ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.26 [m, 26 H, $(CH_2)_{13}$], 1.57 (m, 4 H, $HOCH_2CH_2$), 3.64 (t, 4 H, $HOCH_2CH_2$).

Synthesis of 1,17-Dibromoheptadecane. Bromine (5.0 g, 0.031 mol) was added dropwise under nitrogen to an ice-cooled solution of 8.1 g (0.031 mol) of PPh_3 in 120 mL of dried DMF. To the resulting $Ph_3P \cdot Br_2$ complex was added dropwise a dispersion of 4.0 g (0.015 mol) of 1,17-pentadecanediol in 120 mL of dried DMF. The reaction mixture was stirred at 50 °C overnight and then poured over 1 L of water. The white precipitate formed was filtered, washed with water, and dried. The white product was extracted twice with 200 mL of hexane, and the remaining insoluble white product (Ph_3PO) was filtered. The hexane was evaporated and the residue was recrystallized from methanol to yield 4.2 g (72%) of white crystals: mp 37–38 °C (lit.[24] mp 38–38.4 °C); ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.26 [m, 26 H, $(CH_2)_{13}$], 1.85 (quintet, 4 H, $BrCH_2CH_2$), 3.41 (t, 4 H, $BrCH_2CH_2$).

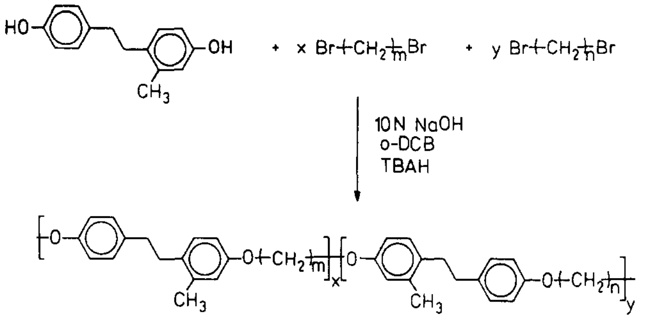
Synthesis of 1,19-nonadecanedicarboxylic acid was performed by a method discussed in the synthesis of docosanedioic acid.[25]

Synthesis of 2,2′-Azelaoyldicyclopentanone. 4-(1-Cyclopenten-1-yl)morpholine (20.4 g, 0.133 mol) and a solution of 13.5 g (0.133 mol) of KOH-dried triethylamine in 100 mL of CaH_2-dried chloroform were added to a 500-mL three-neck flask. The reaction mixture was maintained at 35 °C under stirring while a solution of 15 g (0.067 mol) of azelaoyl chloride in 50 mL of dry chloroform was added within ca. 30 min. The reaction was stirred at 35 °C for 3 h. During this time a solid started to precipitate from the orange-red solution. HCl (100 mL of a 20% aqueous solution) was added, and the mixture was refluxed for 17 h. After the solution cooled to room temperature, the chloroform layer was separated and extracted three times with water. The combined aqueous layers were adjusted to pH = 5–6 and then extracted with chloroform. The combined chloroform layers were evaporated, and the remaining dark red oil residue consisting of 2,2′-azelaoyldicyclopentanone was used in the next reaction step without further purification.

Synthesis of Disodium 6,14-Diketononadecanedioate. The crude 2,2′-azelaoyldicyclopentanone was dissolved in 50 mL of ethanol and added to a solution of 16 g (0.4 mol) of NaOH in 100 mL of ethanol. The reaction mixture was refluxed for 1 h. The resulting precipitate was filtered, washed with ethanol, and dried to yield 19.4 g (73% from azelaoyl chloride) of disodium 6,14-diketononadecanedioate.

Synthesis of 1,19-Nonadecanedicarboxylic Acid. The crude disodium 6,14-diketononadecanedioate (19.4 g) was added to 150 mL of triethanolamine and refluxed until the salt dissolved (ca. 20 min). The solution was cooled to 130 °C, 66 g of 99% hydrazine hydrate was added, and the reaction mixture was refluxed for 4 h. A solution of 22 g (0.40 mol) of KOH in 60 mL of triethanolamine (obtained by refluxing the corresponding mixture) was added to the reaction mixture under strong stirring. The open reaction mixture was boiled under strong stirring in order to drive off the water and the excess of hydrazine hydrate. After ca. 2 h, the reaction mixture reached ca. 140 °C and the decomposition of bishydrazone began with evolution of nitrogen and considerable foaming. Within ca. 2 h the temperature of the reaction mixture was increased to 195 °C and was held at this temperature for 6 h. The reaction mixture was cooled, poured into 1 L of water, and acidified to pH = 2–3 with concentrated hydrochloric acid. The resulting precipitate was filtered, washed with water, and recrystallized from ethanol to yield 8.0 g (37% based on azelaoyl chloride) of 1,19-nonadecanedioic acid: mp 116 °C (lit.[23] mp 119 °C); ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.26 [m, 30 H, $(CH_2)_{15}$), 1.57 (m, 4 H, $HOCH_2CH_2$), 3.64 (t, 4 H, $HOCH_2CH_2$).

Scheme III
Synthesis of Polyethers and Copolyethers Based on 1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane and α,ω-Dibromoalkanes



Synthesis of 1,19-Nonadecanediol. 1,19-Nonadecanediol was synthesized by the reduction of 1,19-nonadecanedioic acid with $BH_3 \cdot THF$. The synthetic procedure used was similar to that described for the preparation of 1,17-heptadecanediol. A total of 5.1 g (80%) of 1,19-nonadecanediol was obtained by starting from 7.0 g (0.021 mol) of 1,19-nonadecanedioic acid and 80 mL (0.80 mol) of 1 M $BH_3 \cdot THF$: mp 99–100 °C (benzene) (lit.[24] mp 101 °C); ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.26 [m, 30 H, $(CH_2)_{15}$], 1.57 (m, 4 H, $HOCH_2CH_2$), 3.64 (t, 4 H, $HOCH_2CH_2$).

Synthesis of 1,19-Dibromononadecane. 1,19-Dibromononadecane was synthesized in 75% yield (5.4 g) by the bromination of 5.0 g (0.077 mol) of 1,19-nonadecanediol with the $PPh_3 \cdot Br_2$ complex prepared from 5.6 g (0.035 mol) of bromine and 9.2 g (0.035 mol) of PPh_3 in dry DMF. The general procedure is similar to that described in the synthesis of 1,17-dibromoheptadecane: mp 49.5 °C (methanol) (lit.[24] mp 46.2–46.5 °C); ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.26 [m, 30 H, $(CH_2)_{15}$), 1.86 (quintet, 4 H, $BrCH_2CH_2$), 3.41 (t, 4 H, $BrCH_2CH_2$).

Synthesis of 1,20-Eicosanediol. 1,20-Eicosanediol (12.4 g, 90%) was prepared by the reduction of 1,20-eicosanedioic acid (15 g, 0.044 mol) with $BH_3 \cdot THF$ (164 mL, 0.164 mol, 1 M) by using a procedure similar to that described for the synthesis of 1,17-heptadecanediol: mp 100–101 °C (benzene) (lit.[24] mp 103 °C); ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.26 [m, 32 H, $(CH_2)_{16}$], 1.57 (m, 4 H, $HOCH_2CH_2$), 3.64 (t, 4 H, $HOCH_2CH_2$).

Synthesis of 1,20-Dibromoeicosane. 1,20-Dibromoeicosane (12 g, 72%) was synthesized by the bromination of 12 g (0.038 mol) of 1,20-eicosanediol with $PPh_3 \cdot Br_2$ complex [prepared from 21.1 g (0.080 mol) of PPh_3 and 12.9 g (0.080 mol) of Br_2] in DMF. The synthetic procedure used was identical with that described in the preparation of 1,17-dibromoheptadecane: mp 69 °C (methanol) (lit.[24] mp 67.4–68 °C); ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.26 [m, 32 H, $(CH_2)_{16}$], 1.86 (quintet, 4 H, $BrCH_2CH_2$), 3.41 (t, 4 H, $BrCH_2CH_2$).

Synthesis of Polyethers and Copolyethers. The synthesis of polyethers and copolyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane and α,ω-dibromoalkanes is outlined in Scheme III. Conventional liquid–liquid two-phase (organic solvent–aqueous NaOH solution) phase-transfer-catalyzed polyetherification conditions were used for the preparation of polyethers and copolyethers.[11] The polyetherifications were carried out under a nitrogen atmosphere at 80 °C in an o-dichlorobenzene–10 N NaOH water solution (10-fold molar excess of NaOH versus phenol groups) in the presence of TBAH (15 mol % of phenol groups) as phase-transfer catalyst. The molar ratio of nucleophilic to electrophilic monomers was in every case 1.0/1.0.

An example of copolyetherification is as follows. To a 25-mL single-neck flask equipped with condenser and nitrogen inlet–outlet were successively added 0.187 g (0.8213 mmol) of 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane, 1.65 mL

Table I
Characterization of Polyether Based on MBPE and 1,8-Dibromooctane (MBPE-8), Polyether Based on MBPE and 1,17-Dibromoheptadecane (MBPE-17), and the Corresponding Copolyethers [MBPE-8/17(*A*/*B*)]

copolymer MBPE-8/17(*A*/*B*) 8/17 mole ratio	$(M_n)_{GPC}$	$(M_w/M_n)_{GPC}$	thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
			heating	cooling
100/0	29400	2.05	k 122 n 132 (3.81^a) i	i 119 (4.55^b) n 116 k
90/10	16200	2.02	g −3 k 110 n 124 (3.33) i	i 113 (2.38) n 97 (1.13) k −7 g
80/20	13300	1.81	g −1 k 112 n 115 (3.81) i	i 107 (2.53) n 80 (0.77) k −5 g
70/30	13000	1.89	g 3 k 103 n 108 (4.13^a) i	i 100 (2.47) n 56 (0.64) k −5 g
60/40	13500	2.13	g 6 k 70 (0.16) k 93 n 104 (3.96^a) i	i 96 (2.66) n 45 (1.22) k 0 g
50/50	10500	1.53	g 5 k 71 (0.62) k 81 k 88 n 92 (3.86^a) i	i 85 (2.49) n 53 (1.84) k 3 g
40/60	15500	2.39	g 11 k 86 k 98 (4.56^a) i	i 88 (2.78) n 64 (1.70) k 2 g
30/70	21400	2.98	g 11 k 89 (4.63) i	i 81 (4.72^a) n 73 k −1 g
20/80	22900	1.73	g 12 k 92 k 98 (5.89^a) i	i 79 (5.89) k 0 g
10/90	16800	2.01	g 10 k 93 (4.96) k 101 (1.75) i	i 79 (7.08^a) k 75 k −6 g
0/100	7300	1.85	k 73 k 89 k 98 (8.88^a) i	i 80 (7.97^a) k 66 k 57 k

[a] Overlapping transition. [b] Overlapping transition; however, the value used in calculation is the virtual value of 2.33 from ref 13.

Table II
Characterization of Polyether Based on MBPE and 1,8-Dibromooctane (MBPE-8), Polyether Based on MBPE and 1,18-Dibromooctadecane (MBPE-18), and the Corresponding Copolyethers [MBPE-8/18(*A*/*B*)]

copolymer MBPE-8/18(*A*/*B*) 8/18 mole ratio	$(M_n)_{GPC}$	$(M_w/M_n)_{GPC}$	thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
			heating	cooling
100/0	29400	2.05	k 122 n 132 (3.81^a) i	i 119 (4.55^b) n 116 k
90/10	43200	2.13	g −3 k 112 n 127 (3.18^a) i	i 113 (2.45) n 95 (0.78) k −9 g
80/20	50800	2.11	g −1 k 107 n 118 (2.99^a) i	i 107 (2.54) n 73 (0.43) k −6 g
70/30	37200	2.12	g 1 k 105 n 112 (4.09^a) i	i 103 (2.71) n 65 (1.23) k −3 g
60/40	45500	1.84	g 4 k 97 n 109 (4.33^a) i	i 99 (3.01) n 74 (1.71) k 1 g
50/50	36200	2.08	g 5 k 100 k 109 (5.08^a) i	i 97 (3.20) n 83 (2.08) k −1 g
40/60	17200	2.32	g 11 k 97 k 101 (4.73^a) i	i 78 (3.92) k 2 g
30/70	39000	1.56	g 7 k 109 (6.86) i	i 89 (6.18) k 2 g
0/100	7300	2.86	k 106 k 110 (8.91^a) i	i 90 (9.21) k 57 (0.49) k

[a] Overlapping transition. [b] Overlapping transition; however, the value used in calculation is the virtual value of 2.33 from ref 13.

of 10 N NaOH, 0.0894 (0.3285 mol) of 1,8-dibromooctane, 0.1963 g (0.4928 mol) of 1,17-dibromoheptadecane, 1.5 mL of *o*-dichlorobenzene, and 0.0837 g (0.2465 mmol) of TBAH. The ratio between the volume of *o*-dichlorobenzene and the total moles of monomers was maintained constant during the synthesis of the entire species of MBPE-*X* with *X* = 4–20. The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80 °C under nitrogen. After 12 h of reaction, the organic and aqueous layers were diluted with chloroform and water, respectively, and the aqueous layer was removed. The organic layer was washed several times with water, followed by dilute hydrochloric acid, and finally with water again. The polymer was separated by precipitation of the polymer solution into methanol to obtain 0.321 g (94%) of white fibrous precipitate. The polymer was further purified by two successive precipitations from chloroform solution, first into acetone and then into methanol. It is important to notice that the synthesis of polyethers containing flexible spacers equal to or shorter than 1,16-dibromohexadecane were performed by using only 10 mol % of TBAH versus the phenol groups and 6 h of reaction time.[11–18]

In this entire paper the polyethers will be designated MBPE-*X*, where *X* is the number of methylene units in the spacer. Similarly, copolyethers will be designated MBPE-*X*/*Y*(*A*/*B*), where *X* is the number of methylene units in one of the spacers, *Y* is the number of methylene units in the other, and *A*/*B* refers to the molar ratio of the two spacers. Therefore, for example, MBPE-*X*/*Y*(100/0) represents MBPE-*X*.

Techniques. ^{1}H NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer.

Molecular weights were determined by gel permeation chromatography (GPC). High-pressure liquid chromatography (HPLC) and GPC analyses were carried out with a Perkin-Elmer Series 10LC equipped with an LC-100 column oven, an LC600 autosampler, 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), a set of PL gel columns of 10^2, 5×10^2, 10^3, 10^4, and 10^5 Å, and a calibration plot constructed with polystyrene standards.

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 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. A detailed discussion on the influence of the thermal history of the sample on phase transitions was presented in a previous publication.[12] The transitions reported were taken from the second or third heating or cooling scans.

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 observed the thermal transitions and to analyze the textures.[26]

Results and Discussion

Tables I–IV summarize the results on the characterization of MBPE-17, MBPE-18, MBPE-19, MBPE-20, and the copolymers with 1,8-dibromooctane. All polymers and copolymers were obtained with yields >95%. Therefore, we can assume that their conversions are close to 100% and subsequently, copolymer compositions are identical with monomer feed compositions. Most of the number-average molecular weights of these polymers and copolymers are above values that are influencing phase transition temperatures (i.e., M_n = 12 000).[27,28] Therefore, phase transition temperatures and their corresponding thermodynamic parameters can be quantitatively compared.[11–17] In order to obtain polymers with high molecular weights, we increased the concentration of the phase-transfer catalyst from 10 mol % versus the phenol groups to 15 mol % and the reaction time from 6 to

Table III
Characterization of Polyether Based on MBPE and 1,8-Dibromooctane (MBPE-8), Polyether Based on MBPE and 1,19-Dibromononadecane (MBPE-19), and the Corresponding Copolyethers [MBPE-8/19(*A*/*B*)]

copolymer MBPE-8/19(*A*/*B*) 8/19 mole ratio	$(M_n)_{GPC}$	$(M_w/M_n)_{GPC}$	thermal transition (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
			heating	cooling
100/0	29400	2.05	k 122 n 132 (3.81[a]) i	i 119 (4.55[b]) n 116 k
90/10	26200	2.35	g 6 k 100 n 112 (3.47[a]) i	i 96 (1.98) n 65 (0.77) k -4 g
80/20	27400	2.16	g -1 k 95 (0.07) k 103 n 115 (3.31[a]) i	i 104 (2.67) n 76 (0.46) k -4 g
70/30	17600	2.57	g 5 k 99 n 109 (3.39[a]) i	i 95 (2.62) n 42 (0.83) k -2 g
60/40	42400	1.95	g 8 k 72 k 83 k 90 n 102 (3.26[a]) i	i 91 (2.95) n 49 (1.18) k -2 g
50/50	43200	2.07	g 10 k 99 (3.84) i	i 86 (2.93) n 55 (1.16) k 3 g
40/60	39100	1.71	g 12 k 90 k 96 (4.88[a]) i	i 84 (3.05) n 70 (1.46) k 3 g
30/70	52700	1.69	g 13 k 94 (5.67) i	i 82 (3.28) n 75 (1.67) k 7 g
0/100	36800	1.85	g 8 k 95 (7.15) i	i 75 (6.94) k -9 g

[a] Overlapping transition. [b] Overlapping transition; however, the value used in calculation is the virtual value of 2.33 from ref 13.

Table IV
Characterization of Polyether Based on MBPE and 1,8-Dibromooctane (MBPE-8), Polyether Based on MBPE and 1,20-Dibromoeicosane (MBPE-20), and the Corresponding Copolyethers [MBPE-8/20(*A*/*B*)]

copolymer MBPE-8/20(*A*/*B*) 8/20 mole ratio	$(M_n)_{GPC}$	$(M_w/M_n)_{GPC}$	thermal transitions (°C), and corresponding enthalpy changes (kcal/mru) in parentheses	
			heating	cooling
100/0	29400	2.05	k 122 n 132 (3.81[a]) i	i 119 (4.55[b]) n 116 k
90/10	11800	2.55	g -2 k 104 n 113 (4.10[a]) i	i 101 (2.20) n 86 (1.33) k -5 g
80/20	39000	1.70	g -2 k 91 k 109 n 113 (3.48[a]) i	i 103 (2.60) n 71 (0.76) k -5 g
70/30	31500	2.30	g 1 k 96 k 106 n 109 (4.71[a]) i	i 99 (2.75) n 76 (1.23) k -5 g
60/40	27100	2.22	g 6 k 97 n 105 (4.91[a]) i	i 92 (2.84) n 78 (1.98) -1 g
50/50	42000	2.02	g 5 k 106 (5.72) i	i 91 (3.34) n 85 (2.27) -9 g
40/60	13900	1.89	g 6 k 100 (6.87) i	i 82 (5.61) k 0 g
0/100	31900	2.05	g 5 k 111 (8.61) i	i 90 (6.63) k 71 (0.24) k 2 g

[a] Overlapping transition. [b] Overlapping transition; however, the value used in calculation is the virtual value of 2.33 from ref 13.

12 h. The previous reaction conditions have always provided high molecular weights for polymers based on spacer lengths equal to or shorter than 1,16-dibromohexadecane.[11-18] An enlargement of the spacer length above this value decreases (for the same ratio between the volume of polymerization solvent and the moles of monomers) the overall molar concentration of the dibromoalkane electrophile in the reaction mixture to the extent that longer reaction times and higher phase-transfer catalyst concentrations are required to reach both high polymer conversions and molecular weights.

Figure 1 presents second DSC heating scans and first DSC cooling scans of the polyethers MBPE-*X* with *X* = 4–20. MBPE-5 and MBPE-9 display two monotropic mesophases,[10,11] while MBPE-11 displays a monotropic mesophase.[10,11] MBPE-8 exhibits a very narrow enantiotropic mesophase.[14] Characterization of these mesophases by optical polarized microscopy coupled with DSC,[11-14] simultaneous X-ray diffraction and DSC,[20] X-ray diffraction, and kinetic DSC[21] experiments have demonstrated that the isotropic–nematic transitions of these polymers provide a uniaxial nematic mesophase. The second mesophase displayed by MBPE-5 and MBPE-9 was initially assumed to be due to a nematic–smectic phase transition.[12-15] However, simultaneous X-ray/DSC experiments could not yet add support for a smectic mesophase.[20] Therefore, it could be that this mesophase represents a second nematic phase.[20] The existence of a second nematic phase in main-chain liquid crystalline polymers containing flexible spacers and mesogenic groups has been theoretically suggested.[29] Research is in progress to elucidate the nature of this second mesophase. For the sake of simplicity within this paper we will label these two mesophases as n_1 and n_2.

All the other polyethers are only crystalline although they exhibit multiple melting transitions. A brief inspection of Figure 1 demonstrates an odd–even dependence of both melting and crystallization transitions on the number of methylene units in the flexible spacer. This odd–even dependence decreases with the increase of the spacer length. Figure 2 plots the melting and crystallization temperatures as a function of the number of methylene units of the flexible spacer, *X*. The same phase transitions temperatures were plotted as a function of $1/X$ in Figure 3. The phase transition temperatures of MBPE-4 to MBPE-16 were collected from our previous publications.[11-18]

All polyethers from MBPE-4 to MBPE-16 exhibit virtual mesophases.[11-18] These virtual mesophases were determined from copolymerization experiments. The strategy behind these experiments is as follows. Copolymers based on MBPE and two flexible spacers are synthesized over the entire range of comonomer compositions. The structural units of these copolymers are not always isomorphic within their crystalline phase but are always isomorphic within some of their mesophases. The melting and crystallization transition temperatures of the copolymers are lower than their weight-averaged values. This effect may represent a combination of kinetic and thermodynamic effects. That is, the copolymer structure combined with a lower rate of crystallization may decrease the perfection of the crystal phase and lower the nonequilibrium melting transition temperatures of the copolymers whose structural units are isomorphic within their crystalline phase.[12] However, the structural units of these copolymers are isomorphic within the nematic phase which appears below the isotropization temperature. This is the case for copolymers prepared from pairs of flexible spacers containing odd–odd,[11,12] even–even,[13] and odd–even[14-18] numbers of methylene units in the flexible spacer. Both mesomorphic phase transition temperatures and the corresponding thermodynamic parameters of these copolymers obey a linear dependence of copolymer composition. The virtual transition temperatures and the corresponding thermodynamic parameters of the homopolymers and of various copolymers were determined by the

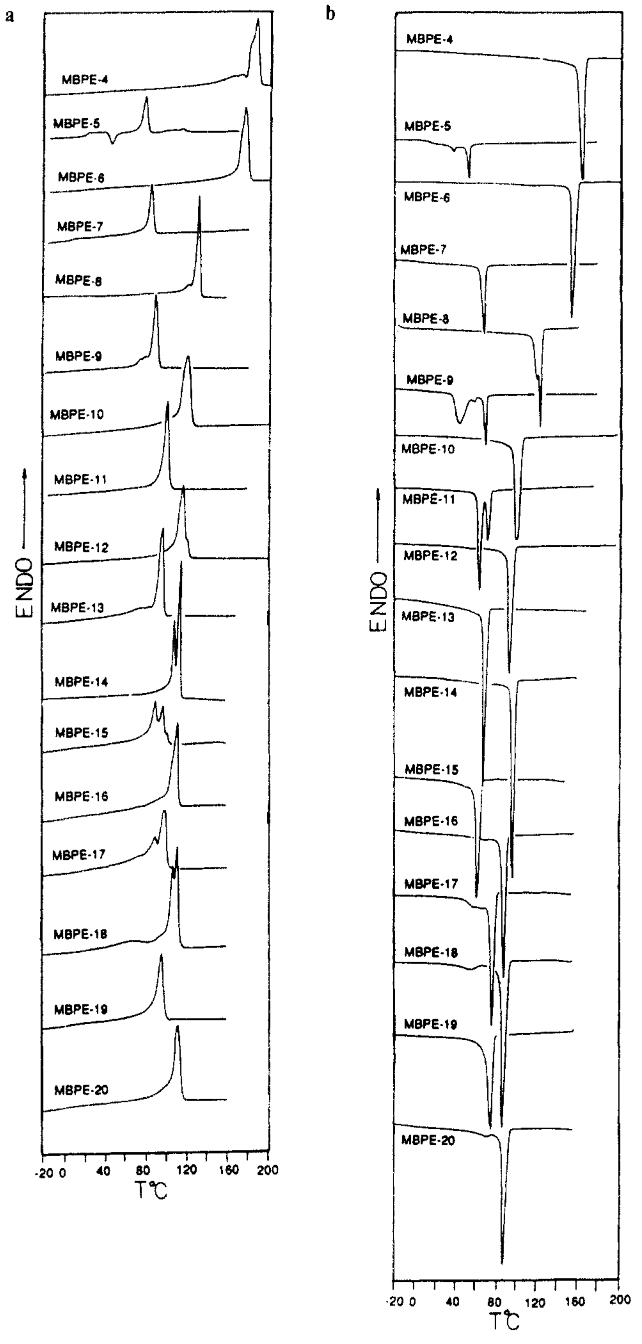


Figure 1. Heating (a) and cooling (b) DSC thermograms (20 °C/min) of polyethers based on MBPE and α,ω-dibromoalkanes (MBPE-X).

extrapolation of these linear dependences. The parameters of the second mesophase which is observable as a monotropic mesophase in MBPE-5 and MBPE-9 display a linear dependence on composition only for copolymers based on odd–odd pairs of flexible spacers.[11,12,14] Therefore, this virtual mesophase (n_2) can be determined only from copolymers based on odd–odd pairs of flexible spacers,[14] while the nematic mesophase from the proximity of the isotropic phase (n_1) can be determined from copolymers based on any combination of flexible spacers, i.e., odd–odd, even–even, or odd–even.[11-18]

In this paper we will be concerned with the determination of the highest temperature nematic mesophase (n_1). The most accurate copolymerization experiment that can be used for the determination of virtual mesophases is based on a pair of spacers from which one leads to a homopolymer that displays an enantiotropic mesophase. MBPE-8 does this.[13] On this account, the determination of the virtual mesophases of the homopolymers MBPE-17 to MBPE-20 will be performed by synthesizing copolymers based on MBPE and 1,8-dibromooctane with 1,17-dibromoheptadecane, 1,18-dibromooctadecane, 1,19-dibromononadecane, and 1,20-dibromomododecane.

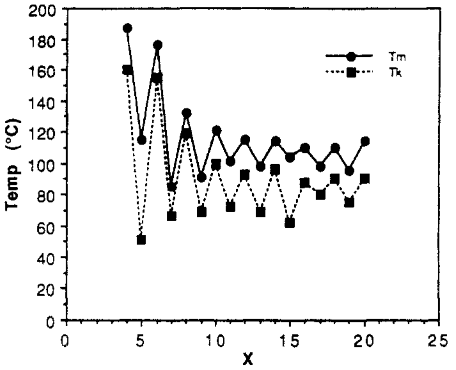


Figure 2. Dependence of melting (T_m (●)) and crystallization (T_k (■)) temperatures of MBPE-X on the number of methylene units in their flexible spacer, X.

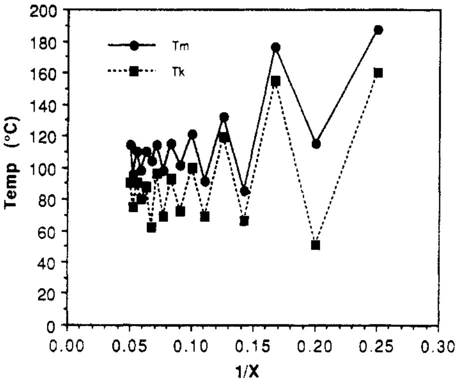


Figure 3. Dependence of melting (T_m (●)) and crystallization (T_k (■)) temperatures of MBPE-X on the inverse of the number of methylene units in their flexible spacer, $1/X$.

We will discuss in some detail the synthesis and characterization of the copolymer system based on MBPE, 1,8-dibromooctane, and 1,17-dibromoheptadecane [MBPE-8/17(A/B)]. Table I summarizes the characterization of MBPE-8/17(A/B) copolymers. Thermal transition temperatures and enthalpy changes were determined from the DSC traces presented in Figure 4. Let us first discuss the DSC curves obtained on the cooling scans (Figure 4b). MBPE-8 presents an isotropic–nematic transition at 119 °C followed by a nematic–crystalline transition at 116 °C. MBPE-17 presents several crystallization peaks. Upon copolymerization, the two transition peaks of MBPE-8 become better separated, while the crystallization peak of MBPE-17 gets split into two peaks. The isotropic–nematic transition temperature displays a linear dependence of copolymer composition while the crystalline peaks show a eutectic point for the copolymer MBPE-8/17(60/40). On the heating DSC scans, MBPE-8 to MBPE-8/17(50/50) polymers display a melting into a nematic mesophase, followed by isotropization (Figure 4a, Table I). These two transition temperatures are not well enough separated to be useful for quantitative calculations. The isotropic–nematic (T_{in}) transition temperatures and their corresponding enthalpy changes (ΔH_{in}) were plotted as a function of MBPE-8/17(A/B) copolymer composition in Figure 5. The virtual enthalpy change associated with the isotropic–nematic transition equal to 2.33 kcal/mru[13] was used for MBPE-8. The extrapolation of these two plots leads to the determination of the

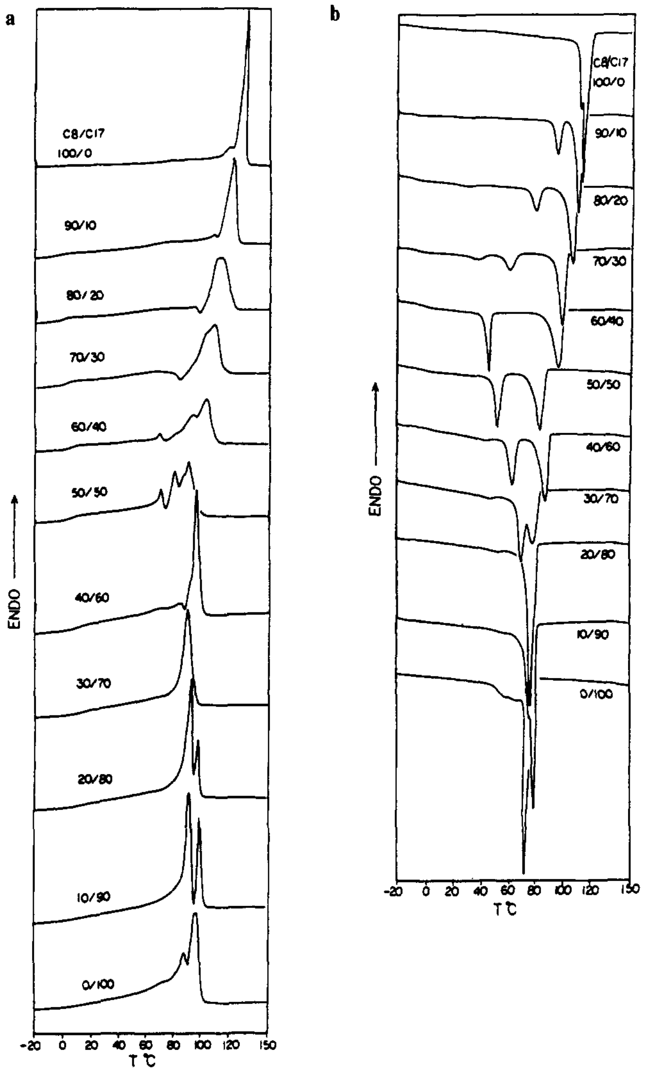


Figure 4. Heating (a) and cooling (b) DSC thermograms (20 °C/min) of polyether based on MBPE and 1,8-dibromononane (MBPE-8), polyether based on MBPE and 1,17-dibromoheptadecane (MBPE-17), and corresponding copolyethers [MBPE-8/17(*A*/*B*)].

virtual parameters of MBPE-17, i.e., T_{in} = 63 °C and ΔH_{in} = 2.94 kcal/mru.

The analysis of the experimental data of the copolymers MBPE-8/18(*A*/*B*), MBPE-8/19(*A*/*B*), and MBPE-8/20(*A*/*B*) was performed in a similar way. Tables II-IV summarize the characterization of all these copolymers. The virtual phase transition temperatures and thermodynamic parameters of MBPE-17 to MBPE-20 are presented in Table V. The mesophases of copolymers MBPE-8/17, MBPE-8/18, MBPE-8/19, and MBPE-8/20 display typical schlieren textures.[26]

As we have mentioned previously, these series of experiments do not allow us to estimate whether MBPE-17 and MBPE-19 display a second mesomorphic phase (n_2), since this would require the synthesis and characterization of copolymers based on MBPE and 1,17-dibromoheptadecane and MBPE and 1,19-dibromononadecane, respectively, with a second spacer based on an odd number of methylene units.

Table V summarizes the phase transition temperatures and the thermodynamic parameters of the system MBPE-*X* with *X* = 4–20. These results provide the most complete collection of data available to date on the dependence of phase transition parameters versus spacer length for main-chain liquid crystalline polymers containing flexible spacers. The most complete set of data available

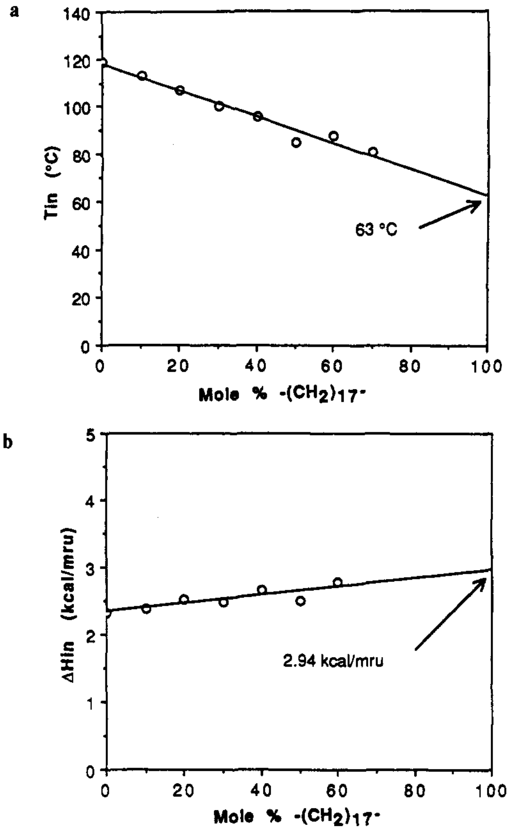


Figure 5. Isotropic–nematic transition temperatures (a) and enthalpy changes (b) of homopolymer MBPE-8 and of copolymers MBPE-8/17(*A*/*B*). Arrows point to virtual thermal transition and enthalpy change of MBPE-17.

prior to these results were on the polyesters based on 4,4′-dihydroxy-2,2′-dimethylazoxybenzene and α,ω-alkanedioic acids containing from five to sixteen and respectively eighteen methylene units in the flexible spacer.[4,30–32] We will try to discuss our results by comparison with data reported on the polyesters based on 4,4′-dihydroxy-2,2′-dimethylazoxybenzene and α,ω-alkanedioic acids,[4,30–32] several other series of polyesters containing flexible spacers of different length,[33–35] and a few series of model compounds containing two mesogenic groups interconnected by a flexible spacer of variable length.[36–41]

We will begin our discussion by considering the dependence between the isotropic–anisotropic (T_{in}) phase transition temperature and the number of methylene units in the flexible spacer (*X*). The dependence T_{in} versus *X* is plotted in Figure 6a. This dependence presents an odd–even effect similar to that displayed by polymers based on flexible spacers and rigid rodlike mesogens[30–35] and by model compounds containing two rigid rodlike mesogenic groups interconnected by a flexible spacer of variable length.[36–41] T_{in} of the MBPE-*X* containing an even number of methylene units in the flexible spacer decreases with increasing spacer length (Figure 6a). T_{in} of the MBPE-*X* containing an odd number of methylene units first increases with increasing spacer length, reaching a maximum for *X* = 9, and then starts to decrease (Figure 6a). The odd–even dependence decreases with increasing spacer length. Some dimeric model compounds[38–41] and polymers[35] display a trend identical with that exhibited by MBPE-*X*.

These results are in agreement with the theoretical model, which assumes that mesophases of polymers containing flexible spacers and rigid rodlike mesogenic units are determined by both the orientational contribution

Table V
Characterization of Virtual Liquid Transitions and Thermodynamic Parameters (in Square Brackets) for Polyethers MBPE-*X*

MBPE-*X*	thermal transitions (°C) and the corresponding enthalpy changes (kcal/mru) in parentheses		ref
	heating	cooling	
MBPE-4	k 171 k 187 (5.53[a])	i 160 (4.90) k [159 ± 8 (2.23 ± 0.4)] n	
averaged from			
MBPE-4/12		i 160 (4.90) k [160 (1.85)] n	13
MBPE-4/11		i 160 (4.90) k [151 (2.49)] n	14
MBPE-4/9		i 160 (4.90) k [166 (2.35)] n	14
MBPE-5	g 20 n_2 [44 ± 2 (0.14 ± 0.02)] n_1 [60 ± 4 (0.43 ± 0.10)] k 79 (1.44) k 115 (0.33) i	i 51 (0.57) n_1 37 (0.10) n_2 13 g	11
averaged from			
MBPE-5/7	g 20 s [46 (0.16)] n [61 (0.55)] k 79 (1.44) k 115 (0.33) i	i 51 (0.57) n_1 37 (0.10) n_2 13 g	11
MBPE-5/9	g 20 s [44 (0.14)] n [56 (0.45)] k 79 (1.44) k 115 (0.33) i	i 51 (0.57) n_1 37 (0.10) n_2 13 g	11
MBPE-5/11	g 20 s [48 (0.13)] n [63 (0.31)] k 79 (1.44) k 115 (0.33) i	i 51 (0.57) n_1 37 (0.10) n_2 13 g	11
MBPE-6	k 176 (5.30) i	i 155 (4.85) k [136 ± 2 (2.59 ± 0.49)[b]] n	this paper
averaged from			
MBPE-6/12		i 155 (4.85) k [138 (2.30)] n	13
MBPE-6/11		i 155 (4.85) k [135 (2.39)] n	14
MBPE-6/9		i 155 (4.85) k [135 (3.08)] n	14
MBPE-7	g 7 s [64 ± 4 (0.15 ± 0.04)] n [76 ± 4 (0.59 ± 0.12)] k 85 (2.18) i	i 66 (2.01) k [65 ± 1 (0.76 ± 0.04)] n_1 [57 ± 2 (0.16 ± 0.05)] n_2 0 g	11
MBPE-5/7	g 7 s [64 (0.13)] n [75 (0.66)] k 85 (2.18) i	i 66 (2.01) k [64 (0.72)] n_1 [55 (0.17)] n_2 0 g	11
MBPE-7/9	g 7 s [60 (0.14)] n [73 (0.64)] k 85 (2.18) i	i 66 (2.01) k [66 (0.77)] n_1 [58 (0.19)] n_2 0 g	11
MBPE-7/11	g 7 s [68 (0.19)] n [80 (0.47)] k 85 (2.18) i	i 66 (2.01) k [66 (0.78)] n_1 [58 (0.11)] n_2 0 g	11
MBPE-8	k 122 n 132 (3.81[a]) i	i 119 [2.33 ± 0.15] n 116 k	13
averaged from			
MBPE-8/12		i 119 [2.22] n 116 k	13
MBPE-8/10		i 119 [2.49] n 116 k	13
MBPE-5/8		i 119 [2.28] n 116 k	13
MBPE-9	g 6 s [71 ± 1 (0.14)] n [80 ± 7 (0.99 ± 0.10)] k 75 k 80 k 91 (2.67) i	i 69 (1.05) n_1 58 (0.06) n_2 48 (2.13) k 0 g	11
averaged from			
MBPE-5/9	g 6 s [71 (0.14)] k 75 k 80 n [85 (0.88)] k 91 (2.67) i		11
MBPE-7/9	g 6 s [70 (0.14)] k 75 k 80 n [81 (1.09)] k 91 (2.67) i		11
MBPE-9/11	g 6 n [73] k 75 k 80 k 91 (2.67) i		11
MBPE-10	n [113] k 121 (7.20) i	i [103 ± 3 (2.45 ± 0.11)] n 100 (6.26) k	13, 14
averaged from			
MBPE-10/12		i [103 (2.40)] n 100 (6.26) k	13
MBPE-8/10	n [113] k 121 (7.20) i	i [101 (2.56)] n 100 (6.26) k	13
MBPE-5/10		i [106 (2.39)] n 100 (6.26) k	14
MBPE-11	g 5 n_2 [72 ± 3 (0.05 ± 0.01)] n_1 [84 ± 5 (1.39 ± 0.04)] k 101 (4.49) i	i 72 (1.09) n_1 [66 ± 3 (1.09 ± 0.03)] n_2 64 (2.66) k	11
averaged from			
MBPE-5/11	g 5 n_2 [76 (0.05)] n_1 [85 (1.35)] k 101 (4.49) i	i 72 (1.09) n_1 [69 (0.08)] n_2 64 (2.66) k	11
MBPE-7/11	g 5 n_2 [69 (0.04)] n_1 [79 (1.42)] k 101 (4.40) i	i 72 (1.09) n_1 64 (2.66) k [64 (0.14)] n_2	11
MBPE-9/11	g 5 n [89] k 101 (4.49) i	i 72 (1.09) n_1 [66 (0.11)] n_2 64 (2.66) k	11
MBPE-12	g 3 n [107] k 115 (6.83) i	i 93 (6.42) k [93 ± 6 (2.85 ± 0.18)] n	13, 14
averaged from			
MBPE-10/12		i 93 (6.42) k [92 (3.03)] n	13
MBPE-8/12	g 3 n [107] k 115 (6.83) i	i 93 (6.42) k [96 (2.85)] n	13
MBPE-6/12		i 93 (6.42) k [87 (2.85)] n	13
MBPE-5/12		i 93 (6.42) k [98 (2.68)] n	14
MBPE-13	k 77 k 85 k 98 (4.26[a]) i	i [70 ± 3 (1.63 ± 0.24)] n_1 69 (5.24) k [60 ± 6 (0.03 ± 0.02)] n_2	16
averaged from			
MBPE-5/13		i [71 (1.60)] n_1 69 (5.24) k [59 (0.02)] n_2	16
MBPE-7/13		i 69 (5.24) k [68 (1.54)] n_1 [58 (0.03)] n_2	16
MBPE-9/13		i [73 (1.67)] n_1 69 (5.24) k [66 (0.04)] n_2	16
MBPE-11/13		i 69 (5.24) k [69 (1.87)] n_1 [55 (0.01)] n_2	16
MBPE-14	k 108 k 114 (7.38[a]) i	i 96 (6.59) k [87 ± 7 (2.77 ± 0.21)] n	17
averaged from			
MBPE-5/14		i 96 (6.59) k [94 (2.56)] n	17
MBPE-8/14		i 96 (6.59) k [82 (2.83)] n	17
MBPE-9/14		i 96 (6.59) k [85 (2.92)] n	17
MBPE-15	k 89 k 97 k 104 (5.62[a]) i	i [62 (2.58)] n 62 (5.55) k	18[c]
determined from MBPE-8/15			
MBPE-16	g 1 k 110 (5.21) i	i 88 (5.74) k [73 (3.15)] n 0 g	18[c]
determined from MBPE-8/16			
MBPE-17	k 73 k 89 k 98 (8.88[a]) i	i 80 (7.97[a]) k [63 (2.94)] n 66 k 57 k	this paper
determined from MBPE-8/17			
MBPE-18	k 106 k 110 (8.91[a]) i	i 90 (9.21) k [73 (4.16)] n 57 (0.49) k	this paper
determined from MBPE-8/18			
MBPE-19	g 8 k 95 (7.15) i	i 75 (6.94) k [66 (3.90)] n −9 g	this paper
determined from MBPE-8/19			
MBPE-20	g 5 k 111 (8.61) i	i 90 (6.63) k 71 (0.24) k [64 (4.51)] n 2 g	this paper
determined from MBPE-8/20			

[a] Overlapping transition. [b] ΔH value was recalculated by using the experimental data from refs 13 and 14. [c] Experimental data from ref 18; ΔH values were recalculated by taking into account also the virtual ΔH_{in} = 2.33 kcal/mru from ref 13.

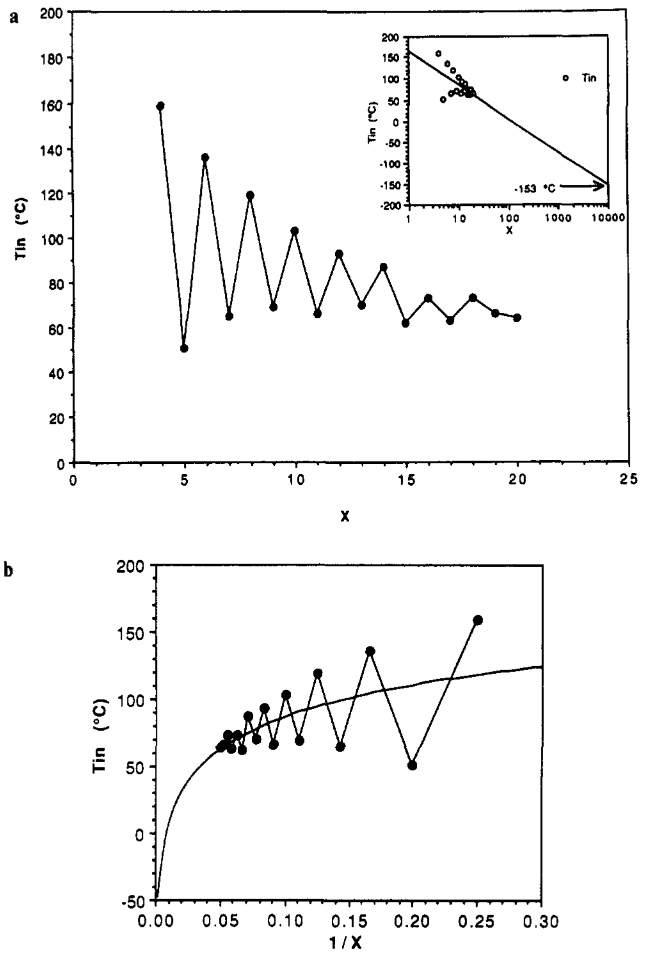


Figure 6. (a) Dependence of the virtual isotropic–nematic (T_{in}) phase transition temperature of MBPE-X homopolymers on the number of methylene units in the flexible spacer (X). Upper right side corner presents the logarithmic plot of this dependence. (b) Dependence of the virtual isotropic–nematic (T_{in}) phase transition temperature of MBPE-X homopolymers on the inverse of the number of methylene units in the flexible spacer ($1/X$). The logarithmic dependence is presented with a continuous line.

of the mesogen and the conformational contribution of the flexible spacer.[22,42–45] The dependence between T_{in} and the number of methylene units in the flexible spacer, X, can be fitted by a logarithmic plot, which is presented in the right corner of Figure 6a. If this dependence is correct, MBPE-X containing X = 10 000 displays a virtual isotropic–anisotropic transition at −153 °C. The structure of MBPE-10000 is certainly very close to that of polyethylene. The theoretically calculated value of the virtual anisotropic phase of polyethylene (−198 °C)[22] is within the same range of temperature as our experimental result. Certainly, the plot from Figure 6a requires additional experimental data in order to confirm the accuracy of this extrapolation. Normal paraffins and therefore polyethylene were considered for a long time to fulfill the requirement of geometric anisotropy for the formation of a liquid crystal mesophase. However, they do not exhibit an enantiotropic liquid crystalline mesophase for the simple reason that the attractive forces operating between the paraffinic molecules are insufficiently strong to maintain a parallel arrangement of the molecules after the crystal lattice has melted.[46] Our present results suggest that polyethylene does exhibit a liquid crystalline mesophage, which, however, is thermodynamically unstable with respect to its crystalline phase. A slight increase of its rigidity through insertion of comonomeric structural units can, as theoretically predicted,[19] reverse this situation and provide a monotropic or even an enantiotropic mesophase. Figure 6b presents the plot of T_{in} versus $1/X$ together with the logarithmic dependence that best fits these data. Again we can see that these results clearly suggest the existence of a virtual mesophase in polyethylene. A similar dependence of T_{in} versus both X and $1/X$ to that displayed by MBPE-X was observed for a few other series of polyethers containing flexible spacers. These data will be reported in due time.

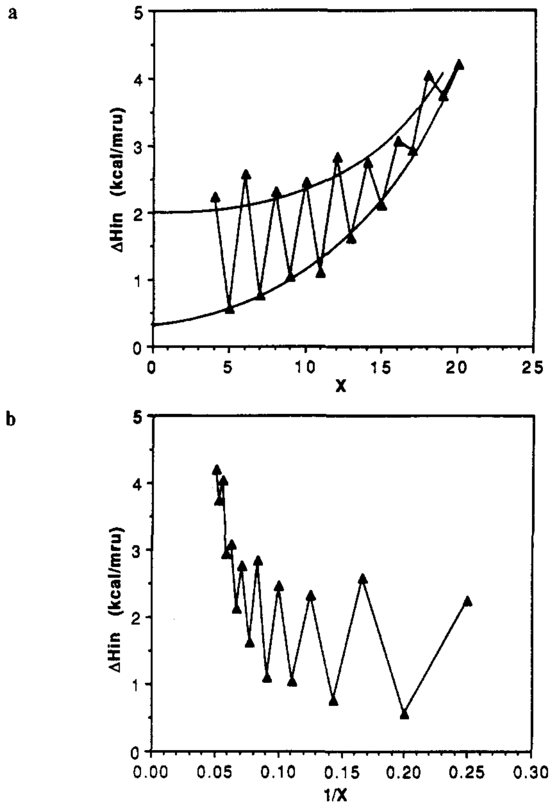


Figure 7. (a) Dependence of the enthalpy change associated with the isotropic–nematic phase transition temperatures (ΔH_{in}) of MBPE-X and the number of methylene units in the flexible spacer (X). (b) Same dependence on the inverse of the number of methylene units in the flexible spacer ($1/X$).

The enthalpy changes associated with the isotropic–nematic phase transition temperature (ΔH_{in}) were plotted as a function of the number of methylene units in the flexible spacer, X, in Figure 7a and as a function of $1/X$ in Figure 7b. Both plots demonstrate an odd–even dependence of ΔH_{in} versus spacer length. This dependence tends to vanish for very long flexible spacers. This odd–even dependence agrees with the experimental data reported for other polymer systems[4,30,34,35] and with the data obtained on model compounds.[37–41] However, it is the first time that the disappearance of the odd–even dependence for long spacer lengths was observed experimentally. The dependences of ΔH_{in} versus X were extrapolated to X = 0 for the series of flexible spacers containing both even and odd numbers of methylene units. The results are $(\Delta H_{in})_{even}$ = 2.0 kcal/(mol of mesogen) and $(\Delta H_{in})_{odd}$ = 0.3 kcal/(mol of mesogen). For rigid rodlike mesogens these enthalpy changes refer to the order contribution of the mesogenic unit which is orientational in nature. For a series of polyesters based on 4,4′-dihydroxy-2,2′-dimethylazoxybenzene and α,ω-alkanedioic acids, Blumstein et al. obtained $(\Delta H_{in})_{even}$ = 1.12 kcal/(mol of mesogen) and $(\Delta H_{in})_{odd}$ = 0.22 kcal/(mol of mesogen).[4] The slopes of the ΔH_{in}–X dependences from Figure 7a

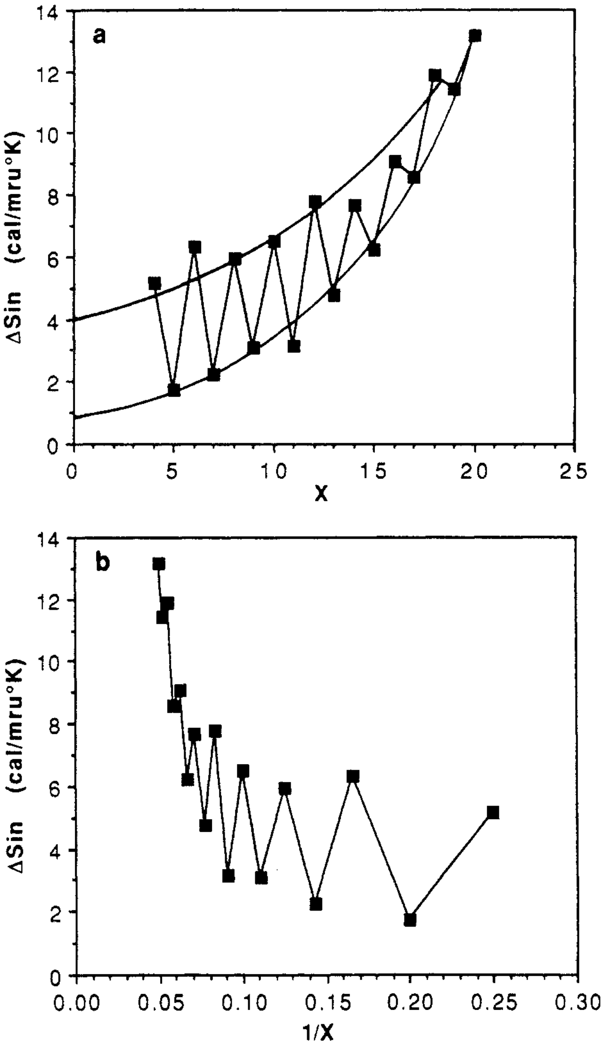


Figure 8. (a) Dependence of the entropy change associated with the isotropic–nematic phase transition temperatures (ΔS_{in}) of MBPE-X and the number of methylene units in the flexible spacer (X). (b) Same dependence on the inverse of the number of methylene units in the flexible spacer ($1/X$).

lead to the determination of the conformational order contribution per mole of methylene unit. These values are $[\Delta(\Delta H_{\mathrm{in}})/\Delta n]_{\mathrm{even}} = 0.14$ kcal/(mol of methylene) and $[\Delta(\Delta H_{\mathrm{in}})/\Delta n]_{\mathrm{odd}} = 0.24$ kcal/(mol of methylene). The corresponding values obtained for the series of polyesters described above are $[\Delta(\Delta H_{\mathrm{in}})/\Delta n]_{\mathrm{even}} = 0.038$ kcal/(mol of methylene) and $[\Delta(\Delta H_{\mathrm{in}}/\Delta n]_{\mathrm{odd}} = 0.045$ kcal/(mol of methylene).[4]

Finally, Figure 8a plots the dependence of the entropy change associated with the isotropic–nematic phase transition temperature (ΔS_{in}) versus X. Figure 8b plots the dependence of ΔS_{in} versus $1/X$. Again we observe an odd–even dependence versus spacer length. This dependence compares favorably with experimental data reported in the literature on polymers[30,31,35] and on model compounds.[37–41] However, we can compare our results only from MBPE-X with $X = 4$ to a maximum of 16 with data available in the literature. No data from $X = 16$ to $X = 20$ were available in the literature. The dependence between the entropy change of isotropization and number of methylene units in the flexible spacer for model compounds based on two mesogenic units separated through a flexible spacer follow several different trends. In the case of α,ω-bis(4-(4-cyanophenyl)phenoxy)alkanes with X from 2 to 12, ΔS_{in} increases for odd-X numbers and decreases for even numbers.[38,39] The odd–even dependence decreases with the spacer length. The entropy changes versus X dependence presents a negative slope for the even series and a positive slope for the odd series. An identical dependence was observed for the other two series of similar compounds.[37] A series of α,ω-(4-((2,4-dimethylphenyl)imino)phenoxy)alkanes with $X = 4$–12 presents a continuous increase of ΔS_{in} versus X for both the odd and even series. The slopes of these dependences are almost similar. This last dependence resembles most of the results reported on several series of polymers except that the positive slopes of the odd and even series are different.[30–32,34,35] The reliability of the data on polymers, with the exception of those reported by Blumstein et al.[30–33] and by us on MBPE-X, is questionable since their molecular weights are not known. It is well-known that entropy changes are molecular weight dependent.[4,27,28,31] The dependences ΔS_{in} for even and odd spaces of MBPE-X were extrapolated to $X = 0$. This extrapolation leads to $(\Delta S_{\mathrm{in}})_{\mathrm{even}} = 4.02$ cal/(mol of mesogen K) for the series of polymers containing an even number of methylene units in the flexible spacer and to $(\Delta S_{\mathrm{in}})_{\mathrm{oddS}} = 0.85$ cal/(mol of mesogen K) for the series of polymers containing an odd number of methylene units in the flexible spacer. These values represent the entropic contribution of the mesogenic group at the isotropic–nematic transition. Since the entropic contribution of the mesogen is orientational in nature, these results demonstrate that the degree of alignment of the mesogen in the series of polymers based on even spacers is higher than that in the series of polymers based on odd spacers. This is an expected result and agrees with the data reported by Blumstein et al. on its series of polyesters.[4,30–32] In the even series of polymers the mesogenic group can adopt a parallel arrangement while in the odd series they are inclined. The ratio between $(\Delta S_{\mathrm{in}})_{\mathrm{even}}/(\Delta S_{\mathrm{in}})_{\mathrm{odd}}$ for MBPE-X is 4.73 while the same ratio for the series of polyesters based on 4,4′-dihydroxy-2,2′-dimethylazoxybenzene and α,ω-alkanedioic acids is 5.35.[4,30–32] We think this represents very good agreement. However, the intrinsic values are different. For the polyesters investigated by Blumsten et al.[4,30–32] $(\Delta S_{\mathrm{in}})_{\mathrm{even}} = 1.80$ cal/(mol of mesogen K) while $(\Delta S_{\mathrm{in}})_{\mathrm{odd}} = 0.34$ cal/(mol of mesogen K). This means that the entropic contribution of MBPE is about 2 times higher than that of 4,4′-dihydroxy-2,2′-dimethylazoxybenzene. However, we have to consider that the first mesogen is flexible while the second one is rigid. The entropic contributions per methylene group from the even and odd spacers indicate the conformational order. They are the slopes of the plots ΔS_{in} vs X which are presented in Figure 8a. $[\Delta(\Delta S_{\mathrm{in}})/\Delta n]_{\mathrm{even}} = 0.30$ cal/K and $[\Delta(\Delta S_{\mathrm{in}})/\Delta n]_{\mathrm{odd}} = 0.20$ cal/K. The corresponding results obtained by Blumstein et al.[4,30–32] are $[\Delta(\Delta S_{\mathrm{in}})\Delta n]_{\mathrm{even}} = 0.21$ cal/K and $[\Delta(\Delta S_{\mathrm{in}})/\Delta n]_{\mathrm{odd}} = 0.14$ cal/K. We think these two series of results are in very good agreement.

The thermodynamic parameters corresponding to the orientational and conformational order contributions for MBPE-X and for the polyesters based on 4,4′-dihydroxy-2,2′-dimethylazoxybenzene and α,ω-alkanedioic acids (DMAB)[4] are summarized in Table VI.

As we mentioned previously, we think that the entropic contribution to the conformational order per mole of methylene unit obtained for MBPE-X, although slightly higher, is in good agreement with the values obtained for DMAB-X. We believe the entropic contribution to the conformational order should be determined only by the structure of the flexible spacer (i.e., linear or branched, paraffinic, oligooxyethylenic, etc.) and therefore be less dependent on the nature of the mesogenic unit. The agree-

Table VI
Thermodynamic Parameters Corresponding to the Orientational and Conformational Order Contributions in MBPE-*X* and of the Polyesters Based on 4,4′-Dihydroxy-2,2′-dimethylazoxybenzene and α,ω-Alkanedioic Acids (DMAB-*X*; Data from Ref 4)

	$(\Delta H_{in})_{even}$, kcal/mol		$(\Delta H_{in})_{odd}$, kcal/mol		$(\Delta S_{in})_{even}$, cal/(mol K)		$(\Delta S_{in})_{odd}$, cal/(mol K)	
nature of order	MBPE-*X*	DMAB-*X*	MBPE-*X*	DMAB-*X*	MBPE-*X*	DMAB-*X*	MBPE-*X*	DMAB-*X*
orientational/mol of mesogen	2.00	1.12	0.30	0.22	4.02	1.80	0.85	0.34
conformational/mol of CH_2	0.14	0.038	0.24	0.045	0.30	0.21	0.20	0.14

ment between our results and Blumstein's[4] data confirms this assumption.

The entropic contribution to the orientational order per mole of mesogenic unit is higher for MBPE-*X* than for DMAB-*X*. This difference can be accounted for if we consider the difference between the two mesogenic units. 4,4′-Dihydroxy-2,2′-dimethylazoxybenzene is a rigid rodlike trisubstituted mesogen which theoretically would provide a lower degree of orientational order than the corresponding di-, mono-, or unsubstituted mesogen. MBPE is monosubstituted but at the same time is flexible (Scheme I). At the present time we have no information on the dynamic equilibrium between the anti and gauche conformers of the MBPE mesogen within mesomorphic and isotropic phases. However, we may assume that in the mesomorphic phase this mesogen adopts only an anti conformation while in the isotropic phase it displays both the anti and gauche conformers which are in dynamic equilibrium.[10,11] If so, the entropic contribution of MBPE is not only orientational in nature but represents a combination of orientational and conformational order of the mesogen. In this way we easily can understand why the entropic contribution per mole of mesogen is higher for MBPE than for DMAB. This entropic contribution is higher for MBPE, first, for pure orientational reasons since the two mesogens have different degrees of substitution and, second, because the flexible mesogen presents both orientational and conformational contributions within the same parameter. That is, MBPE presents a higher degree of disorder in the isotropic phase than DMAB, since MBPE has both orientational and conformational disorder, while DMAB has only orientational disorder.

The most unexpected experimental trend observed so far refers to the dependence of the enthalpy and entropy changes associated with the isotropization temperature for high values of *X*. Additional results are required to fully understand this trend.

Conclusions

This paper and the previous publication in this series have definitively demonstrated that the synthesis of liquid crystalline polymers does not require rigid rodlike mesogenic units. Rodlike mesogenic units can be obtained from flexible structural units when their lowest free energy conformer displays an anisotropic rodlike conformation. This concept was applied to the synthesis of polyethers without[10] and with flexible spacers. All these polymers display classic nematic and smectic mesophases.[20,21] However, the thermodynamic stability of these mesophases is lower than that of the corresponding polymers based on rigid rodlike mesogens although their isotropization enthalpies and entropies are higher. Therefore many of these polymers may display only monotropic or virtual mesophases. Both monotropic and enantiotropic mesophases of these polymers can be transformed into enantiotropic mesophases by copolymerization. Virtual mesophases can be determined by copolymerization experiments which were detailed in this and in the previous publications.[11-18] The phase behavior of copolymers based on a single mesogenic unit and combinations of two,[11-14,16-18] three,[15] and more than three[46] flexible spacers is determined by the difference between the isomorphism of their structural units within different phases. The phase behavior of the MBPE-*X* with *X* = 4–20 was determined. Virtual phase transition temperatures and their corresponding thermodynamic parameters display an odd–even dependence on *X* as theoretically predicted[22,42-45] and experimentally observed[4,31] for liquid crystal polymers based on flexible spacers and rigid rodlike mesogens. The extrapolation of the virtual isotropic–nematic transition temperatures of MBPE-*X* to infinity demonstrates that the odd–even dependence vanishes at long spacers and leads to the assumption that polyethylene should display a virtual mesophase as was theoretically predicted.[22] Additional experiments with both longer spacers and different mesogens are required to support the accuracy of the extrapolation from MBPE-*X*. These experiments are in progress in our laboratory. The conformational entropic contribution per CH_2 unit and the orientational entropic contribution per MBPE unit at the isotropic–nematic transition were determined for both even and odd series of MBPE-*X*. Both sets of values are higher for the even series. The conformational entropic contributions per CH_2 unit of MBPE-*X* agree very well with those reported in the literature for polyesters based on rigid rodlike mesogens and containing both even and odd flexible spacers.[4] The entropic contributions per MBPE unit are, however, larger than the data based on rigid rodlike mesogens.[4] This difference was explained by considering that in the case of MBPE this entropic factor represents a combination of orientational and conformational contributions, while in the case of the rigid rodlike mesogens this factor contains only an orientational contribution. We can consider that the entropy of the isotropic phase of the polymers based on flexible mesogens is lower than that of the polymers based on rigid mesogens, and this can account for the larger entropy change of isotropization displayed by the former. So far, the main differences observed between the polymers based on flexible and rigid mesogens consist in the lower thermodynamic stability of the mesophase displayed by the former with respect to their crystalline phase and in the very fast dynamics of the flexible polymers. All polymers and copolymers based on MBPE and other flexible mesogens display very sharp mesomorphic phase transition peaks in their DSC traces.[11-18] This behavior is still unexplained. The examples of polyethers based on flexible mesogens synthesized so far can be considered as the flexible homologues of phenyl benzoate type mesogens since they were based on either diphenylethane or methylene ether units (Scheme I). The next generation of flexible mesogens does not contain structural units that resemble conventional rigid rodlike mesogens and will be reported soon.

Acknowledgment. Financial support by the National Science Foundation, Polymers Program (DMR-86-19724), is gratefully acknowledged.

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Carbon-13 Nuclear Magnetic Resonance Measurements of Local Segmental Dynamics of Polyisoprene in Dilute Solution: Nonlinear Viscosity Dependence

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Received November 21, 1989; Revised Manuscript Received February 6, 1990

ABSTRACT: The local segmental dynamics of polyisoprene in dilute solution have been studied with natural-abundance ^{13}C NMR spectroscopy. Ten solvents covering a factor of 70 in viscosity were utilized. Correlation times (τ_c) extracted from T_1 measurements were determined as a function of temperature in all solvents. Contrary to the predictions of Kramers' theory in the high friction limit, it was found that $\tau_c \propto \eta^{0.41\pm0.02}$ at constant temperature. The potential barrier height for local dynamics extracted from these measurements is 13 ± 2 kJ/mol. The use of Kramers' theory to extract this barrier height leads to serious errors and nonphysical results. The results are discussed in terms of Grote–Hynes theory in which the friction opposing conformational transitions is frequency dependent. Ratios of nT_1 values for methine and methylene carbons are independent of solvent and not equal to unity.

Introduction

The local segmental dynamics of polymer chains have an important influence on the macroscopic properties of polymeric systems. In polymer solutions where local dynamics occur on picosecond and nanosecond time scales, this influence is mainly through the larger distance scale motions, which dominate ordinary viscoelastic properties under these conditions. Dynamics on the length scale of a few monomer units depend strongly on the details of the monomer structure. Hence information about local segmental dynamics provides an important intermediate link between molecular structure and larger motions. In a polymer melt near T_g, the time scales for local conformational transitions slow significantly. Dynamics on the scale of a few monomer units are intimately connected with the main glass transition in many polymers.

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0024-9297/90/2223-3520$02.50/0