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Synthesis and Characterization of Thermotropic Polyethers Based on 4,4′-dihydroxy-α-methylstilbene and Flexible Spacers Containing Even Numbers of Methylene Units and Copolyethers Based on Pairs of Flexible Spacers Containing Even and Odd-Even Numbers of Methylene Units

V. Percec [a], K. Asami [a], D. Tomazos [a], J. L. Feijoo [b], G. Ungar [b] & A. Keller [b]

[a] Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH, 44106, U.S.A.

[b] H. H. Willis Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol, BS8 1TL, U.K.

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Synthesis and Characterization of Thermotropic Polyethers Based on 4,4′-dihydroxy-α-methylstilbene and Flexible Spacers Containing Even Numbers of Methylene Units and Copolyethers Based on Pairs of Flexible Spacers Containing Even and Odd-Even Numbers of Methylene Units

V. PERCEC, K. ASAMI and D. TOMAZOS

Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, U.S.A.

and

J. L. FEIJOO, G. UNGAR and A. KELLER

H. H. Willis Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, U.K.

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This paper describes the synthesis and characterization of thermotropic polyethers based on 4,4′-dihydroxy-α-methylstilbene (HMS) and flexible spacers containing an even number of methylene units and copolyethers based on 4,4′-dihydroxy-α-methylstilbene (HMS) and flexible spacers containing even-even and even-odd numbers of methylene units [i.e., HMS-X/Y(A/B), where X and Y refer to the number of methylene units in the first and second spacer, and A/B refers to the molar ratio between the two spacers]. The following polyethers and copolyethers were synthesized and characterized: HMS-6, HMS-8, HMS-10, HMS-12, HMS-6/8(A/B), HMS-6/10(A/B), HMS-6/12(A/B), HMS-8/10(A/B), HMS-8/12(A/B), HMS-10/12(A/B), HMS-6/7(A/B), HMS-6/9(A/B), HMS-7/10(A/B), HMS-8/11(A/B), HMS-7/12(A/B), and HMS-9/12(A/B). Due to their low solubility, both homopolymers and copolymers based on even-even combinations of flexible spacers were obtained with low molecular weights. High molecular weight copolymers were obtained only when odd-even combinations of flexible spacers were used. The thermal transition temperatures of homopolymers "corrected" for high molecular weights were determined from copolymerization experiments. Both the crystalline and the liquid crystalline phases of homopolymers and copolymers are kinetically controlled. However, the liquid crystalline phase transitions of the homopolymers based on even spacers are less affected by kinetics than those of the homopolymers based on odd spacers. Both quasi-equilibrium values of the liquid crystalline-isotropic thermal transition temperatures and of their associated thermodynamic parameters exhibit an odd-even dependence versus the number of methylene units in the spacer. The orientational contribution of the HMS mesogen and the conformational contribution of the methylene unit from the flexible spacer at the nematic-isotropic phase transition were determined for both the odd and the even series of spacers and were discussed by comparison with other similar data available in the literature.

TABLE I

Characterization of polyethers and copolyethers based on HMS, 1,6-dibromohexane and 1,8-dibromooctane [HMS-6/8(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line

HMS-6/8(A/B)	M_n	M_w/M_n	Thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	2300	1.50	k 196 n 213(0.03*) i g 16 k 193 n [200(-)] i	i 173(0.36) n 147 k 12 g
8/2	2100	1.85	k 177 n 215(1.98) i g 20 k 174 n 206(1.01*) i	i 181(1.50) n 129 k 14 g
6/4	2400	1.80	k 161 n 202(2.22) i g 18 k 160 n 197(1.40) i	i 184(1.84) n 122 k 9 g
5/5	5800	1.60	k 151 n 210(2.40) i g 17 k 150 n 204(2.17) i	i 185(2.08) n 117 k 11 g
4/6	3600	2.01	k 156 n 208(1.97) i g 25 k 147 n 204(1.03) i	i 174(1.97) n 106 k 24 g
2/8	3700	2.06	k 165 n 190(1.79) i g 18 k 162 n 185(0.49*) i	i 164(1.30) n 119 k 16 g
0/10	3900	2.12	k 183 n 196(0.14*) i g 15 k 187 n 196(0.03*) i	i 170(0.15*) n 154 k 17 g

*Overlapped transitions; [ ] virtual transitions.

INTRODUCTION

In the preceding paper[1] we have described the synthesis and qualitative data on the thermal characterization of polyethers and copolyethers based on 4,4′-dihydroxy-α-methylstilbene (HMS) and α,ω-dibromoalkanes containing an odd number of methylene units (i.e., from five to thirteen). These experiments have confirmed the existence of nonequilibrium states in the mesomorphic and isotropic[3,4] phases of these liquid crystalline polymers. Actually, one of the most important conclusions derived from the previous series of experiments refers to the recognition that thermal characterization results obtained from the first DSC heating scans are the closest to equilibrium. The goal of this paper is to continue these investigations on HMS polyethers by extending the previous studies to polyethers based on HMS and α,ω-dibromoalkanes containing an even number of methylene units in the flexible spacer and to copolyethers based on HMS and pairs of spacers containing an even or a combination of odd and even numbers of methylene units.

TABLE II

Characterization of polyethers and copolyethers based on HMS, 1,6-dibromohexane and 1,10-dibromodecane [HMS-6/10(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line

HMS-6/10(A/B)	M_n	M_w/M_n	Thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	2300	1.50	k 196 n 213(0.03*) i g 16 k 193 n [200(-)] i	i 173(0.36) n 147 k 12 g
8/2	3600	2.90	k 180 n 206(1.35*) i g 21 k 174 n 196(0.69*) i	i 176(1.36) n 128 k 16 g
6/4	8700	2.30	k 160 n 203(1.25) i g 21 k 152 n 193(2.09*) i	i 169(1.12) n 96 k 17 g
5/5	5000	2.20	k 162 n 193(1.60) i g 15 k 155 n 188(0.52*) i	i 162(1.42) n 87 k 10 g
4/6	6900	2.17	k 149 n 188(0.77*) i g 16 k 142 n 181(0.42) i	i 157(1.18) n 90 k 12 g
2/8	2600	1.62	k 160 n 178(0.63*) i g 5 k 157 n 170(0.04*) i	i 152(0.44*) n 112 k 3 g
0/10	2400	1.68	k 177 n [177(-)] i g 6 k 167 n [167(-)] i	i [146(-)] n 146 k 1 g

*Overlapped transitions; [ ] virtual transitions.

EXPERIMENTAL

Materials

1,6-Dibromohexane (97%), 1,8-dibromooctane (98%), 1,10-dibromodecane (97%) (all from Aldrich) and 1,12-dibromododecane (98%) (from Lancaster Synthesis) were used as received. 4,4′-Dihydroxy-α-methylstilbene (HMS) was synthesized as described in the previous publication.[1]

Synthesis and Characterization of Polyethers and Copolyethers

Both polyethers and copolyethers were synthesized and characterized as described in the previous paper for the series of polyethers and copolyethers based on HMS and α,ω-dibromoalkanes containing an odd number of methylene units in the flexible spacer.[1]

Techniques

The instrumentation and the characterization techniques used were identical to those described previously.[1]

TABLE III

Characterization of polyethers and copolyethers based on HMS, 1,6-dibromohexane and 1,12-dibromododecane [HMS-6/12(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line

HMS-6/12(A/B)	M_n	M_w/M_n	Thermal transitions (oC) and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	2300	1.50	k 196 n 213(0.03*) i g 16 k 193 n [200(-)] i	i 173(0.36) n 147 k 12 g
8/2	4800	2.50	k 183 n 204(0.89*) i g 16 k 177 n 196(0.13*) i	i 171(1.30) n 134 k 12 g
6/4	3400	2.40	k 163 n 192(1.56*) i g 13 k 158 n 187(0.86*) i	i 163(1.91) n 101 k 7 g
5/5	5700	2.60	k 161 n 188(1.05) i g 20 k 136 n 166(0.01*) i	i 155(0.68) n 74 k 14 g
4/6	7100	2.70	k 156 n 188(1.22) i g 12 k 147 n 174(0.37*) i	i 163(1.14) n 107 k 10 g
2/8	7100	1.71	k 160 n 172(0.11*) i g 5 k 157 n 170(0.04*) i	i 160(0.89) n 128 k 1 g
0/10	8200	2.00	k 161 n [164(-)] i g 9 k 153 n [160(-)] i	i [146(-)] n 143 k 2 g

* Overlapped transitions; [ ] virtual transitions.

Notations

Polyethers based on HMS are labeled as HMS-X where X refers to the number of methylene units in the flexible spacer. Copolyethers based on HMS and pairs of α,ω-dibromoalkanes are labeled as HMS-X/Y(A/B), where X and Y refer to the number of methylene units in the first and second spacer, while A/B refers to the molar ratio between the two spacers. The x phase from all tables refers to an unidentified liquid crystalline or crystalline phase. See Reference 1 for more details.

RESULTS AND DISCUSSION

Polyethers and Copolyethers Based on Pairs of Flexible Spacers Containing Even Numbers of Methylene Units

The following series of polyethers and copolyethers based on HMS and pairs of α,ω-dibromoalkanes containing even numbers of methylene units were synthesized and characterized: HMS-6/8, HMS-6/10, HMS-6/12, HMS-8/10, HMS-8/12, and

TABLE IV

Characterization of polyethers and copolyethers based on HMS, 1,8-dibromooctane and 1,10-dibromodecane [HMS-8/10(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line

HMS-8/10(A/B)	M_n	M_w/M_n	Thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	3900	2.12	k 183 n 196(0.14*) i g 15 k 181 n 196(0.03*) i	i 170(0.15*) n 154 k 17 g
8/2	3400	1.74	k 173 n 198(0.89) i g 20 k 174 n 193(0.29*) i	i 166(0.40) n 136 k 11 g
6/4	5200	1.75	k 150 n 196(1.27) i g 24 k 143 n 173(0.27*) i	i 162(1.00) n 106 k 18 g
5/5	3400	1.80	k 154 n 182(1.86) i g 17 k 145 n 174(0.61*) i	i 153(1.22) n 107 k 11 g
4/6	3400	1.40	k 157 n 185(1.59) i g 18 k 152 n 179(0.72*) i	i 155(0.93) n 121 k 11 g
2/8	2500	1.40	k 161 n 170(-*) i g 3 k 159 i	i 144(-*) n 127 k
0/10	2400	1.68	k 177 n [177(-)] i g 6 k 167 n [167(-)] i	i [146(-)] n 146 k 1 g

* Overlapped transitions; [ ] virtual transitions.

HMS-10/12. Their molecular weights and phase transition temperatures are summarized in Tables I to VI. A brief inspection of the molecular weights of these polymers and copolymers reveals our inability to synthesize polymers with high molecular weights. The number average molecular weights of the system HMS-6/8 is within the range from M_n = 2,000 to M_n = 4,000. By increasing the length of the pair of flexible spacer the molecular weights of the copolymer tend to increase. For the copolymer system HMS-10/12 the number average molecular weights are between 2,000 to 10,000. The molecular weights of these copolymers are limited by the low solubility of the polyethers and copolyethers based on HMS and flexible spacers containing an even number of methylene units in the flexible spacer, in the polymerization solvent.

HMS-6 displays an enantiotropic mesophase both in the first and second or subsequent DSC scans (Tables I–III). The peak of this enantiotropic nematic mesophase overlaps the melting and crystallization transitions. HMS-8 presents an enantiotropic nematic mesophase only in the first heating scan. In the second heating scan these polymers show only a monotropic nematic mesophase (Tables I, IV and V). Both HMS-10 and HMS-12 are only crystalline (Tables II to VI).

TABLE V

Characterization of polyethers and copolyethers based on HMS, 1,8-dibromooctane and 1,12-dibromododecane [HMS-8/12(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line

HMS-8/12(A/B)	M_n	M_w/M_n	Thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	3900	2.12	k 183 n 196(0.14*) i g 15 k 181 n 196(0.03*) i	i 170(0.15*) n 154 k 17 g
8/2	4300	1.73	k 164 n 181(1.11) i g 10 k 161 i	i 153(0.57) n 117 k 5 g
6/4	6300	1.49	k 157 n 187(1.57) i g 16 k 149 n 181(0.89*) i	i 154(1.52) n 96 k 8 g
5/5	6100	1.57	k 146 n 181(1.33) i g 15 k 137 n 175(1.09*) i	i 150(1.46) n 93 k 8 g
4/6	6300	2.08	k 146 n 180(0.88) i g 10 k 143 n 181(1.22*) i	i 173(1.60) n 96 k 4 g
2/8	-	-	k 161 n 168(-*) i g 8 k 157 i	i 151(0.34*) n 127 k 7 g
0/10	8200	2.00	k 161 n [164(-)] i g 9 k 153 n [160(-)] i	i [146(-)] n 143 k 2 g

* Overlapped transitions; [ ] virtual transitions.

Let us discuss in more detail the thermal behavior of the copolymers HMS-6/8 and HMS-10/12. The DSC traces of HMS-6/8 obtained from the first heating scan are presented in Figure 1a. Figure 1b presents the second DSC heating scans of HMS-6/8. Cooling DSC scans for the same system are presented in Figure 1c. An inspection of Figure 1a shows that the isotropization peaks of HMS-6 and HMS-8 overlap the melting peaks. However, the isotropization and melting peaks of HMS-6/8(8/2) to HMS-6/8(2/8) copolymers are well separated. This behavior is due to both a slight increase of the molecular weights of copolymers versus those of the parent homopolymers (Table I), but mostly due to a decrease of the melting temperatures of the copolymers. The DSC traces obtained from the second heating scans (Figure 1b) display isotropization temperatures which are only a few degrees lower than those determined from the first heating scans (Figure 1a). The nematic-isotropic peak width is only slightly broader in the second heating scan. As a consequence, on the second DSC scan HMS-6 displays only a monotropic nematic mesophase. The largest difference between the isotropization temperature determined from the first and second heating scan is 10°C (Table I). Most frequently this difference is only a few degrees. This difference is much lower than that

TABLE VI

Characterization of polyethers and copolyethers based on HMS, 1,10-dibromodecane and 1,12-dibromododecane [HMS-10/12(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line

HMS-10/12(A/B)	M_n	M_w/M_n	Thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	2400	1.70	k 177 n [177(-)] i g 6 k 167 n [167(-)] i	i [146(-)] n 146 k 1 g
8/2	4900	1.58	k 161 n 177(0.23*) i g 4 k 164 n 178(0.27*) i	i 169(1.24) n 139 k 4 g
6/4	7300	1.73	k 150 n 173(0.46) i g 23 k 145 n 172(0.65) i	i 164(1.30) n 117 k 10 g
5/5	2400	1.75	k 150 n 166(0.64*) i g 13 k 150 n 166(0.68*) i	i 160(1.26) n 127 k
4/6	4100	1.99	k 149 i g 4 k 150 i	i 147(0.24*) n 126 k
2/8	10000	2.43	k 149 n 171(0.39*) i g 18 k 141 n 158(0.04) i	i 145(0.65*) n 108 k 9 g
0/10	8200	2.00	k 161 n [164(-)] i g 9 k 153 n [160(-)] i	i [146(-)] n 143 k 2 g

* Overlapped transitions; [ ] virtual transitions.

reported for polyethers and copolyethers based on HMS and flexible spacers containing an odd number of methylene units in the spacer which usually is between 20 and 30°C.[1] Therefore, polyethers based on HMS and flexible spacers containing an even number of methylene units in the flexible spacer display a nematic mesophase which is almost thermodynamically controlled. This statement is supported by the plots of thermal transition temperatures collected from first and second heating scans and from cooling scans (Figure 2). As we can observe from this figure, the dependences of the isotropization transition temperatures determined from the first and second heating scans versus copolymer composition are located on the same straight line. Figure 3 presents the plot of the enthalpy changes associated with the isotropization temperature as a function of copolymer composition. The accuracy of these data is not very high since some of the isotropization peaks overlap the melting transition peaks in the first DSC scans and most of them also do in the second heating scans (Figures 1a, b). Nevertheless, even so, it seems that these enthalpy changes are located on a straight line which upon extrapolation leads to the determination of the ΔH_i values of homopolymers. the ΔH_i values of homopolymers as determined directly from their DSC traces do not have quantitative meaning since their peaks are overlapping the melting peaks.

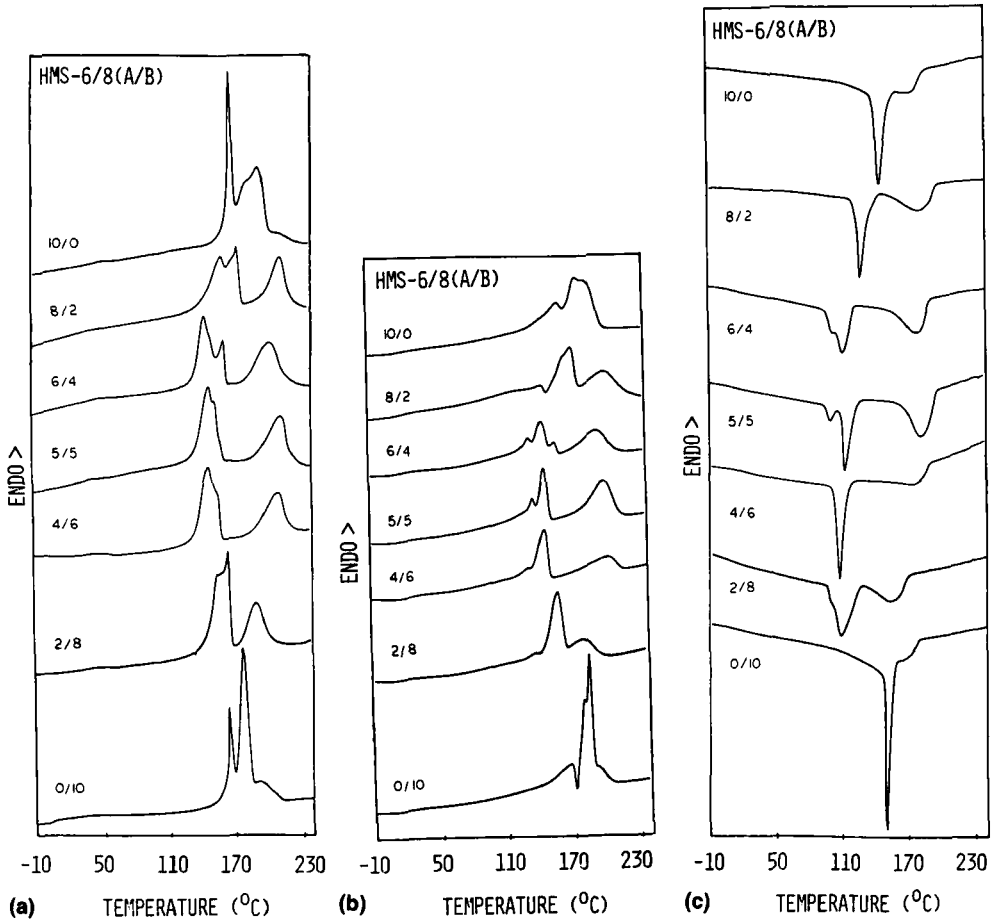

FIGURE 1 a) First DSC heating scans (20°C/min) of HMS-6/8(A/B); b) Second DSC heating scans (20°C/min) of HMS-6/8(A/B); c) First DSC cooling scans (20°C/min) of HMS-6/8(A/B).

The second example of copolymers which will be discussed in more detail is HMS-10/12. These copolymers are based on the parent homopolymers HMS-10 and HMS-12 which do not display any mesophase on their heating and cooling DSC scans. The first heating DSC scans of this system are presented in Figure 4a. While HMS-10 and HMS-12 display only melting transitions, with the exception of HMS-10/12(4/6) all copolymers display a nematic mesophase both on first and second heating scans, as well as on their cooling scans (Figures 4a, b, c). HMS-10/12(4/6) exhibits an isotropic-nematic transition on the cooling scan and therefore is monotropic. We can certainly assume that both HMS-10 and HMS-12 display a thermodynamically unstable (in respect to the crystalline phase) virtual mesophase. However, upon copolymerization the melting transition temperature was suppressed and as a consequence, the virtual mesophase displayed by homopolymers becomes enantiotropic in copolymers (Figures 4a and c). Second heating scans present isotropization transition temperatures which are only slightly lower than

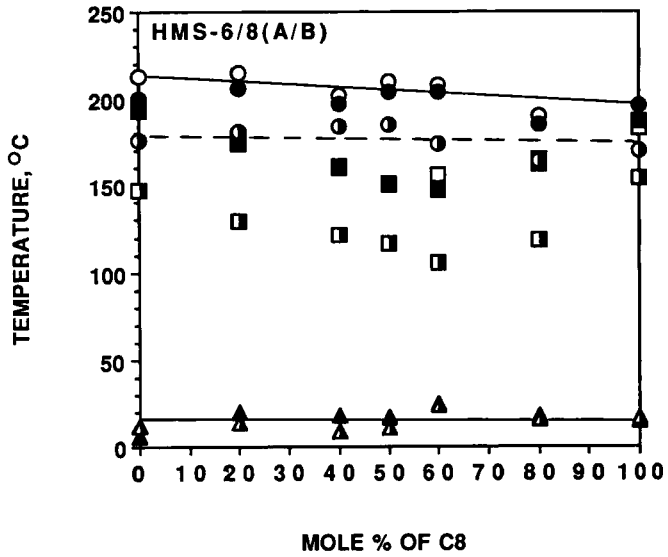

FIGURE 2 The dependence between thermal transition temperatures obtained from first and second heating and first cooling scans of HMS-6/8(A/B) copolymers. T_g (▲ second heating scan, ▲ first cooling scan), T_m (□ first heating scan, ■ second heating scan), T_{n-k} (◨ first cooling scan), T_{n-i} (○ first heating scan, ● second heating scan), T_{i-n} (◑ first cooling scan).

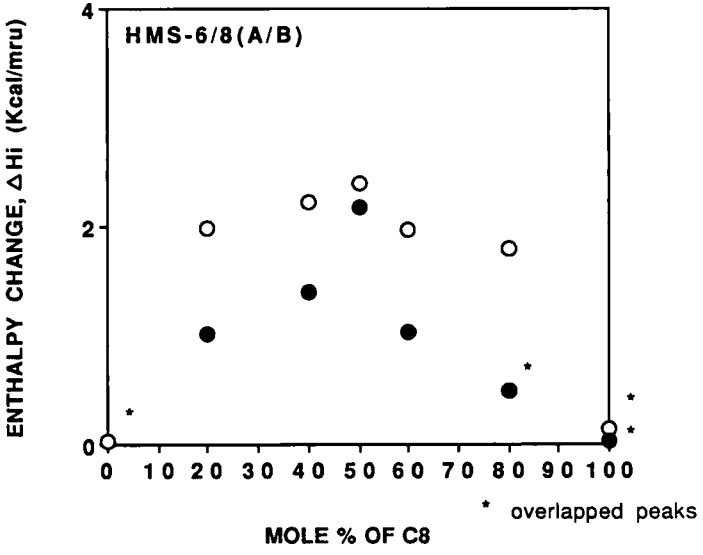

FIGURE 3 The dependence between the enthalpy change associated with the isotropization transition (ΔH_i) and HMS-6/8(A/B) copolymer composition. ○ first heating scan, ● second heating scan.

those determined from the first heating scans (Figure 4b and Table VI). This conclusion is supported by plotting the thermal transition temperatures determined from different DSC scans (Figure 5). The nematic-isotropization transition temperatures are situated on the same straight line suggesting that this transition is

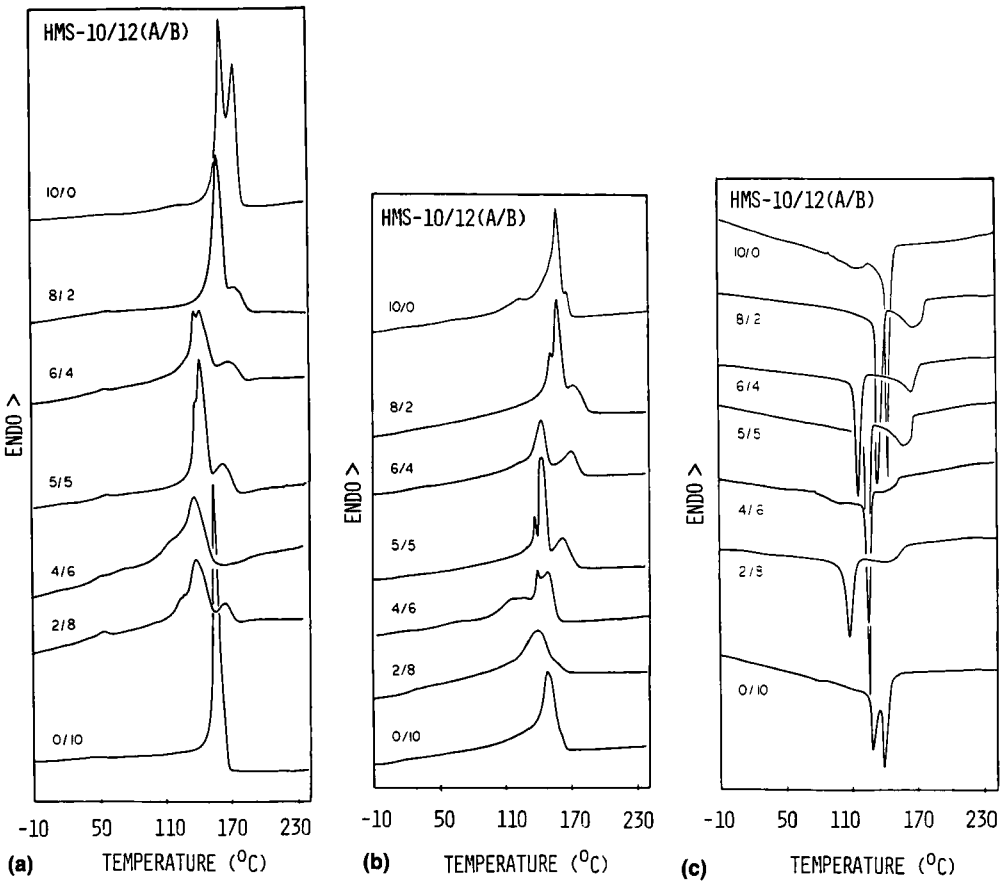

FIGURE 4 a) First DSC heating scans (20°C/min) of HMS-10/12(A/B); b) second DSC heating scans (20°C/min) of HMS-10/12(A/B); c) first DSC cooling scans (20°C/min) of HMS-10/12(A/B).

under very little kinetic control. The extrapolation of this linear dependence allowed the virtual nematic-isotropic and isotropic-nematic transition temperatures of HMS-10 and HMS-12 to be determined (Table VI). The enthalpy changes associated with the isotropization temperature determined from this set of copolymers have little significance since they all were determined from overlapped peaks.

A more detailed discussion on the determination of virtual mesomorphic transition temperatures and of their thermodynamic parameters was presented for the copolyethers based on the flexible mesogen 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane.[5-9]

The series of copolymers HMS-6/10, HMS-6/12, HMS-8/10, HMS-8/12 present an intermediary behavior between that of the copolymers HMS-6/8 and MS-10/12. That is, all these copolymers are based on one homopolymer which displays an enantiotropic nematic mesophase (HMS-6 or HMS-8) and one which displays a virtual nematic mesophase (HMS-10 or HMS-12).

Their phase behavior was treated as in the previous two examples and their phase

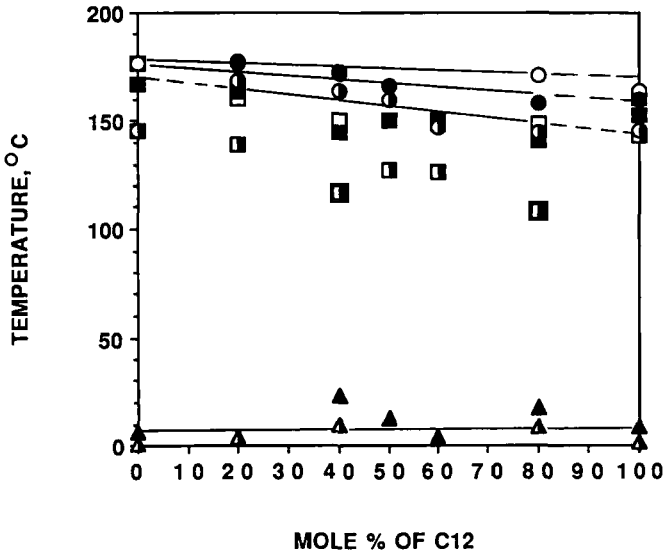

FIGURE 5 The dependence between thermal transition temperatures obtained from first and second heating and first cooling scans of HMS-10/12(A/B) copolymers. T_g (▲ second heating scan, ▵ first cooling scan), T_m (□ first heating scan, ■ second heating scan), T_{n-k} (◨ first cooling scan), T_{n-i} (○ first heating scan, ● second heating scan), T_{i-n} (◑ first cooling scan).

transitions and thermodynamic parameters are summarized in Tables II to V. Although from all these series of copolymers we could determine the transition temperatures of the virtual nematic mesophase displayed by HMS-10 and HMS-12, these data are still molecular weight dependent. This is because the number average molecular weight of all polyethers and copolyethers based on HMS and flexible spacers containing an even number of methylene units in the spacer are below 12,000–14,000.

Copolyethers Based on Pairs of Flexible Spacers Containing Odd and Even Numbers of Methylene Units

These copolymers were synthesized and characterized for two different purposes. All polyethers based on HMS and flexible spacers containing an odd number of methylene units display an enantiotropic mesophase which is strongly dependent on the thermal history of the sample.[1] Both polyethers and copolyethers could be synthesized with higher molecular weights than the limit under which phase transitions are molecular weight dependent. Polyethers and copolyethers based on HMS and flexible spacers containing an even number of methylene units are less soluble and therefore could only be synthesized with molecular weights which are below this limit. Their nematic phases are however only very little dependent on the thermal history of the sample. Although we could determine the transition temperatures of the virtual nematic mesophases of HMS-10 and HMS-12 they are still molecular weight dependent. It is of obvious interest to determine the influence of thermal history of the sample on the mesophase displayed by copolymers based on HMS and combinations of flexible spacers containing odd and even numbers

TABLE VII

Characterization of polyethers and copolyethers based on HMS, 1,6-dibromohexane and 1,7-dibromoheptane [HMS-6/7(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line

HMS-6/7(A/B)	M_n	M_w/M_n	Thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
0/10	17200	2.56	g 29 k 145 n 178(0.55) i g 26 k 125 n 163(0.34) i	i 157(0.50) n 86 x 60 k 19 g
1/9	41200	2.40	g 27 k 135 n 180(0.86) i g 24 k 116 n 176(0.64) i	i 147(0.47) n 68 k 18 g
2/8	52500	2.18	g 27 k 118 n 183(0.93) i g 26 k 114 n 185(0.87) i	i 152(0.67) n 61 k 21 g
3/7	60000	2.60	g 28 k 114 n 180(0.90) i g 24 k 176(0.88) i	i 147(0.64) n 22 g
3.5/6.5	-	-	g 20 k 125 n 204(1.00) i g 23 k 127 n 187(0.42) i	i 171(0.58) n 19 g
4/6	48300	2.00	g 24 k 162 n 205(0.87) i g 23 k 136 n 176(0.28*) i	i 173(0.70) n 21 g

* Overlapped transitions.

of methylene units. It is also of interest to see whether these copolymers can be synthesized with higher molecular weights than the copolymers based on pairs of spacers containing only even numbers of methylene units. If so, these experiments could be useful to calculate, by extrapolation, the thermal transition temperatures corresponding to the high molecular weights of the homopolymers based on HMS and flexible spacers containing even number of methylene units.

The following series of copolymers were synthesized and characterized: HMS-6/7, HMS-6/9, HMS-7/10, HMS-8/11, HMS-7/12, and HMS-9/12. Their characterization is summarized in Tables VII and XII. The composition of the synthesized copolymers was determined by the solubility limit which allowed the synthesis of copolymers with number average molecular weights higher than 15,000.

We will discuss in more detail only the copolymer system HMS-8/11. Characterization data of this copolymer are summarized in Table X. Figure 6a plots thermal transition temperatures obtained from first and second heating scans as a function of copolymer composition. Most of the experimental data for this copolymer and for the other copolymers based on HMS and pairs of flexible spacers containing combinations of odd and even numbers of methylene units are within the range of high contents of odd spacers. Therefore, in this region the influence of thermal history of the sample on the mesomorphic phase transition is proportional to the content of odd spacers, and is high. On decreasing the content of odd spacers this

TABLE VIII

Characterization of polyethers and copolyethers based on HMS, 1,6-dibromohexane and 1,9-dibromononane [HMS-6/9(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line

HMS-6/9(A/B)	M_n	M_w/M_n	Thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
0/10	23500	2.75	g 26 k 135 n 167(0.53) i g 21 k 128 n 169(0.49) i	i 151(0.66) n 89 x 51 k 18 g
1/9	44100	2.07	g 29 k 125 n 179(1.03) i g 24 k 95 n 172(0.81) i	i 143(0.75) n 77 x 34 k 16 g
2/8	23400	2.42	g 18 k 118 n 177(0.88) i g 21 k 90 n 174(0.88) i	i 145(0.84) n 62 x 28 k 13 g
3/7	36900	2.47	g 24 k 113 n 186(1.08) i g 23 k 114 n 181(1.07) i	i 153(1.07) n 28 k 17 g
4/6	25600	2.81	g 26 k 131 n 181(0.91) i g 21 k 124 n 178(0.81) i	i 152(0.83) n 14 g

influence decreases. This trend can be observed from the dependence of the difference between the isotropization temperatures determined from first and second heating scans as a function of copolymer composition (Figure 6a). Taking into account this discussion, we have extrapolated the virtual temperatures of isotropization from first and second heating scans (Figure 6a) and from cooling scans (Figure 6b) for HMS-8. Certainly, the most reliable values are those determined from the first heating scans since they provide the closest values to equilibrium. The determination of the enthalpy changes associated with these virtual mesophases was done by using the technique described for the other copolymers.

Table XIII summarizes the thermal transition temperatures of the enantiotropic mesophases of HMS polyethers of high molecular weight, i.e., based on odd flexible spacers which were determined in the previous publication,[1] and the virtual mesophases of polymers based on even spacers. The virtual transition temperatures of HMS homopolymers containing even spacers corresponding to high molecular weight data are, as expected, higher than those determined directly, or by the extrapolation of low molecular weight HMS copolymers based on even pairs of spacers (Tables I to VI).

The dependence between the nematic-isotropic transition temperatures determined from the first heating scans and spacer length is plotted in Figure 7a, while the dependence between their corresponding enthalpy changes and spacer length are plotted in Figure 7b. Both plots display the well known odd-even effect.[9,13-15] Figure 7c presents the dependence between the entropy changes associated with the nematic-isotropic transition temperatures of HMS homopolymers. The dependence of ΔH_i and ΔS_i from Figures 7b and 7c for the series of even and odd

TABLE IX

Characterization of polyethers and copolyethers based on HMS, 1,7-dibromoheptane and 1,10-dibromodecane [HMS-10/12(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line

HMS-7/10(A/B)	M_n	M_w/M_n	Thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	17200	2.56	g 29 k 145 n 178(0.55) i g 26 k 125 n 163(0.34) i	i 157(0.50) n 86 x 60 k 19 g
9/1	38200	2.57	g 36 k 136 n 174(0.78) i g 31 k 111 n 157(0.43) i	i 130(0.46) n 24 g
8/2	26800	2.82	g 27 k 116 n 174(0.66) i g 26 k 106 n 154(0.44) i	i 139(0.41) n 20 g
7/3	41300	2.38	g 27 k 107 n 175(0.78) i g 24 k 100 n 151(0.63) i	i 137(0.66) n 17 g
6/4	15400	2.19	g 20 k 136 n 179(0.83) i g 20 k 134 n 169(0.66) i	i 149(0.72) n 56 k 10 g
5.5/4.5	48100	2.33	g 26 k 146 n 176(0.64) i g 26 k 127 n 154 i	i 138(0.64) n 45 k 16 g

spacers of HMS-X were extrapolated to X = 0. These values represent the enthalpic and entropic contribution of the mesogenic group at the nematic-isotropic transition. The resulting values are presented in Table XIV. Since the entropic contribution of the mesogen is orientational in nature, these results demonstrate that the degree of alignment of the mesogen in this series of polymers based on even spacers is higher than that in the series of polymers based on odd spacers. These data show the same trend with the results of Blumstein *et al.*[15] obtained on polyesters based on 4,4′-dihydroxy-2,2′-dimethylazoxybenzene and α,ω-alkanedioic acids (DMAB-X) which are also summarized in Table XIV. The enthalpic and entropic contributions of HMS are larger than those of DMAB since the first mesogen has one substituent while the second one has three substituents. Consequently, the HMS based polymers can get better organized than DMAB based polymers. Both the orientational enthalpic and entropic contributions of the HMS and DMAB rigid rod-like mesogens are lower than those of 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE)[9] and 1-(4-hydroxyphenyl)-2-(2-chloro-4-hydroxyphenyl)ethane (ClBPE).[16] As explained in a previous paper[9] this result is expected since the MBPE and ClBPE flexible mesogens' values contain both an orientational and conformational contribution in their orientational term.

The slope of the ΔH_{ni} and ΔS_{ni} versus X dependences from Figures 7b and 7c were determined for both the even and odd series of spacers. These slopes provide information about the conformational order contribution per mole of methylene unit at the nematic-isotropic transition and are also summarized in Table XIV. As

TABLE X

Characterization of polyethers and copolyethers based on HMS, 1,8-dibromooctane and 1,11-dibromoundecane [HMS-8/11(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line

HMS-8/11(A/B)	M_n	M_w/M_n	Thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
0/10	18900	2.04	g 23 k 126 n 153(0.84) i g 15 k 122 n 143(0.35) i	i 124(0.44) n 94 k 9 g
1/9	42900	1.86	g 15 k 122 n 164(0.81) i g 15 k 119 n 147(0.49) i	i 138(0.58) n 96 k 7 g
2/8	38700	1.96	g 26 k 111 n 171(0.94) i g 22 k 104 n 157(0.72) i	i 139(0.47) n 52 k 10 g
3/7	17000	1.93	g 26 k 123 n 177(1.10) i g 25 k 90 n 164(0.71) i	i 137(0.64) n 40 k 15 g
4/6	33400	2.04	g 22 k 128 n 179(1.01) i g 23 k 119 n 175(0.97) i	i 145(0.72) n 45 k 11 g
4.5/5.5	47300	2.70	g 35 k 134 n 177(1.07) i g 23 k 119 n 165(0.96) i	i 142(0.83) n 43 k 15 g

TABLE XI

Characterization of polyethers and copolyethers based on HMS, 1,7-dibromoheptane and 1,12-dibromododecane [HMS-7/12(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line

HMS-7/12(A/B)	M_n	M_w/M_n	Thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	17200	2.56	g 29 k 145 n 178(0.55) i g 26 k 125 n 163(0.34) i	i 157(0.50) n 86 x 60 k 19 g
9/1	26800	2.39	g 26 k 137 n 175(0.65) i g 24 k 120 n 168(0.48) i	i 143(0.58) n 62 k 17 g
8/2	30500	2.23	g 23 k 129 n 172(0.67) i g 21 k 109 n 159(0.67) i	i 152(0.64) n 17 g
7/3	17500	2.40	g 19 k 109 n 162(0.67) i g 18 k 107 n 140(0.30) i	i 130(0.59) n 15 g
6/4	58900	2.18	g 37 k 118 n 164(0.69) i g 21 k 110 n 151(0.51) i	i 132(0.68) n 44 k 13 g
5.5/4.5	26200	2.46	g 17 k 142 n 165(0.68) i g 19 k 141 n 158(-) i	i 132(0.70) n 74 k 13 g

TABLE XII

Characterization of polyethers and copolyethers based on HMS, 1,9-dibromononane and 1,12-dibromododecane [HMS-9/12(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line

HMS-9/12(A/B)	M_n	M_w/M_n	Thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	23500	2.57.	g 26 k 135 n 167(0.53) i g 21 k 129 n 159(0.47) i	i 151(0.66) n 89 x 51 k 18 g
9/1	28700	2.10	g 22 k 121 n 166(0.79) i g 20 k 103 n 153(0.62) i	i 145(0.67) n 70 x 35 k
8/2	31200	2.10	g 37 k 115 n 164(0.89) i g 20 k 95 n 154(0.85) i	i 127(0.85) n 32 k 14 g
7/3	45300	2.20	g 25 k 110 n 156(0.72) i g 20 k 102 n 149(0.68) i	i 122(0.69) n 37 k 13 g
6/4	28900	2.20	k 118 n 155(-*) i g 16 k 114 n 143(-*) i	i 131(0.73) n 59 k 14 g
5/5	37800	2.15	g 25 k 123 n 158(-*) i g 17 k 116 n 142(-*) i	i 129(0.66*) n 69 k 14 g
4/6	22500	2.30	g 34 k 144 n 156(-*) i g 16 k 133 i	i 126(0.64*) n 87 k 18 g

* Overlapped transitions.

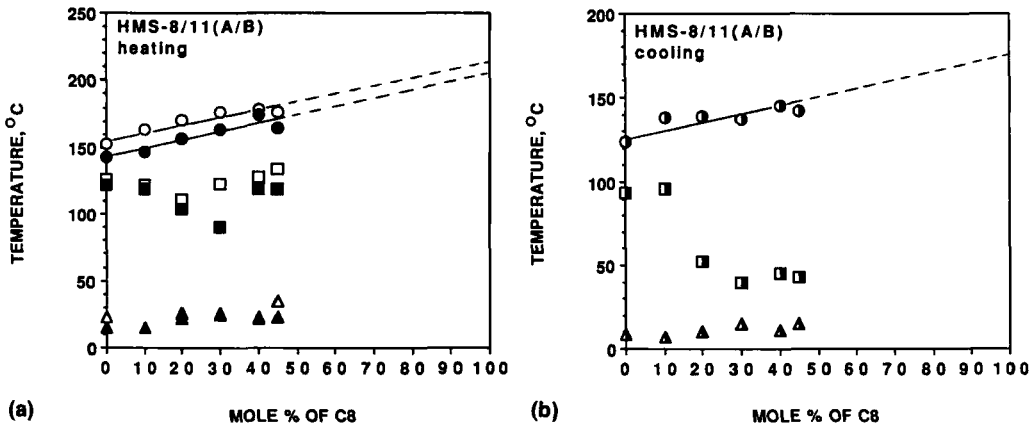

FIGURE 6 a) The dependence between thermal transition temperatures obtained from first and second heating scans of HMS-8/11(A/B) copolymers. T_g (△ first scan, ▲ second scan), T_m (□ first scan, ■ second scan), T_{n-i} (○ first scan, ● second scan); b) The dependence between thermal transition temperatures obtained from first cooling scans of HMS-8/11(A/B) copolymers. T_g (◭), T_{n-k} (◨), T_{i-n} (◑).

TABLE XIII

Averaged and virtual [ ] liquid crystalline transitions and the corresponding enthalpy changes of HMS-X as determined from binary copolymers. For polymers containing even spacers the tabulated data correspond to high molecular weights. Data for odd spacers are from Reference 1. Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scans.

Polymer	Thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
	Heating	Cooling
HMS-5	n 179(0.45±0.05) i n 149±5(0.27) i	i 135(0.13±0.03) n 95 x
HMS-6	n [245±1(1.60)] i n [240±2(1.60)] i	i [218±10(1.34)] n
HMS-7	n 180(0.61±0.01)] i n 165(0.56) i	i 157(0.50) n 80 x
HMS-8	n [220(1.65) i n [194(1.55)] i	i [179(1.34) n
HMS-9	n 166(0.74±0.08) i n 159(0.54) i	i 146+5(0.52±0.08) n 89 x
HMS-10	n [185(1.70)] i n [177(1.16)] i	i [168(1.50)] n
HMS-11	n 159±4(0.86±0.04) i n 144(0.50) i	i 127±3(0.56) n
HMS-12	n [165±3(1.75)] i n [153±7(-)] i	i [110±5(-)] n
HMS-13	n 148(0.82) i n [138(0.620] i	i 127(0.50) n

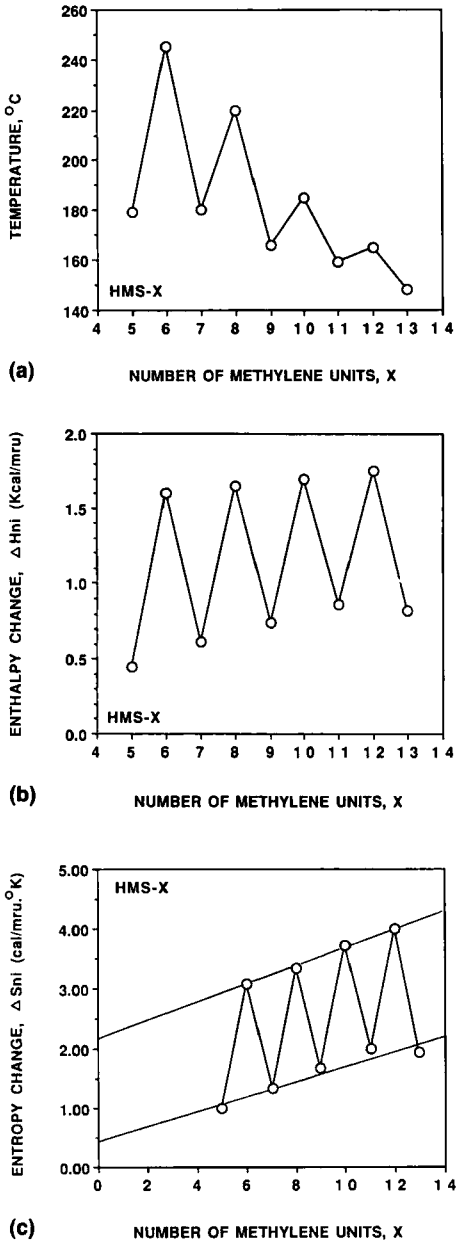

FIGURE 7 a) The dependence between the isotropization temperature (T_{n-i}) and the number of methylene units in the spacer for HMS-based homopolymers; b) The dependence between the enthalpy change (ΔH_i) associated with the nematic-isotropic transition temperatures and the number of methylene units in the spacer for HMS-based homopolymers; c) The dependence between the entropy change (ΔS_{n-i}) associated with the nematic-isotropic transition temperatures and the number of methylene units in the spacer for HMS-based homopolymers.

TABLE XIV

Thermodynamic parameters corresponding to the orientational and conformational order contributions in polyethers based on 4,4′-dihydroxy-α-methylstilbene and α,ω-dibromoalkanes (HMS-X), polyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane and α,ω-dibromoalkanes (MBPE-X),[9] polyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane and α,ω-dibromoalkanes (ClBPE-X),[16] and polyesters based on 4,4′-dihydroxy-2-2′-dimethylazoxybenzene and α,ω-alkanedioic acids (DMAB-X).[15] Data for HMS-X refer to ΔHni and ΔSni collected from the first heating scans, while data for MBPE-X, ClBPE-X and DMAB-X are from cooling scans

Nature of Order	(ΔHin)even (kcal/mru)				(ΔHin)odd(kcal/mru)			
	HMS-X	MBPE-X	ClBPE-X	DMAB-X	HMS-X	MBPE-X	ClBPE-X	DMAB-X
Orientational/ mole of mesogen	1.45	2.00	1.63	1.12	0.34	0.30	0.20	0.22
Conformational/ mole of -CH_2-	0.03	0.01	0.03	0.38	0.04	0.03	0.04	0.045
Nature of Order	(ΔSin)even(cal/mol°K)				(ΔSin)odd(cal/mol°K)			
	HMS-X	MBPE-X	ClBPE-X	DMAB-X	HMS-X	MBPE-X	ClBPE-X	DMAB-X
Orientational/ mole of mesogen	2.15	4.02	3.60	1.80	0.45	0.85	0.62	0.34
Conformational/ mole of -CH_2-	0.15	0.17	0.12	0.21	0.13	0.11	0.07	0.14

[a]Data from Reference 9; the conformational contribution values reported in Reference 9 were incorrect; they were corrected in this Table.
[b]Data from Reference 16.
[c]Data from Reference 15.

expected, within experimental error these data are equal to those obtained for the polymers MBPE-X, ClBPE-X and DMAB-X. That is, the conformational contribution per methylenic unit is not dependent on the rigid or flexible nature of the rod-like mesogen.

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References

1. V. Percec, K. Asami, D. Tomazos, A. Keller, J. L. Feijoo and G. Ungar, *Mol. Cryst. Liq. Cryst.*, previous paper in this issue.
2. J. L. Feijoo, G. Ungar, A. J. Owen, A. Keller and V. Percec, *Mol. Cryst. Liq. Cryst.*, **155**, 487 (1988).
3. J. L. Feijoo, G. Ungar, A. Keller and V. Percec, *Polymer*, **31**, 2019 (1990).
4. J. L. Feijoo, G. Ungar, A. Keller, J. A. Odel, A. J. Owen and V. Percec, *Mol. Cryst. Liq. Cryst.*, in press.
5. V. Percec and R. Yourd, *Macromolecules*, **22**, 524 (1989).
6. V. Percec and R. Yourd, *Macromolecules*, **22**, 3229 (1989).
7. V. Percec and R. Yourd, *Makromol. Chem.*, **191**, 25 (1990).

8. V. Percec and R. Yourd, *Makromol. Chem.*, **191**, 49 (1990).
9. V. Percec and Y. Tsuda, *Macromolecules*, **23**, 3509 (1990).
10. V. Percec, *Mol. Cryst. Liq. Cryst.*, **155**, 1 (1988).
11. V. Percec and H. Nava, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 405 (1987).
12. V. Percec, H. Nava and H. Jonsson, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 1943 (1987).
13. A. Blumstein and O. Thomas, *Macromolecules*, **15**, 1264 (1982).
14. A. Blumstein, *Polym. J.*, **17**, 277 (1985).
15. R. B. Blumstein and A. Blumstein, *Mol. Cryst. Liq. Cryst.*, **165**, 361 (1988).
16. V. Percec and M. Zuber, to be published.