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Liquid crystalline polyethers based on conformational isomerism

9. Synthesis and determination of the virtual mesophases of polyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl) ethane with 1,15-dibromopentadecane and 1,16-dibromohexadecane

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SUMMARY

This paper describes the synthesis and characterization of the polyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl) ethane (MBPE) and 1,15-dibromopentadecane (MBPE-15), MBPE and 1,16-dibromohexadecane, and of the copolyethers based on MBPE and 1,8-dibromooctane with 1,15-dibromopentadecane (MBPE-8/15), and with 1,16-dibromohexadecane (MBPE-8/16). MBPE-15 and MBPE-16 are only crystalline while MBPE-8/15 and MBPE-8/16 display a monotropic or even an enantiotropic nematic mesophase. The virtual isotropic-nematic transition temperature of MBPE-15 determined from these copolymers is 62°C ($\Delta H = 2.58$ kcal/mru), while the virtual isotropic-nematic transition temperature of MBPE-16 is 73 °C ($\Delta H = 3.15$ kcal/mru).

INTRODUCTION

In the previous papers from this series we have advanced the concept of flexible mesogenic units or rod-like mesogenic units based on conformational isomerism (Scheme 1) (1-8). This concept was applied to the synthesis of liquid crystalline polyethers without flexible spacers (1), and of liquid crystalline polyethers with flexible spacers (2-8). These polymers represent the first examples of main chain liquid crystalline polymers which do not contain rigid rod-like mesogenic units (9-15). Presently we are investigating the phase behavior of polyethers (MBPE-n) based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl) ethane (MBPE) and α,ω-dibromoalkanes (2-8). Most of these polymers display only virtual mesophases (2-8, 16, 17). The virtual mesophases displayed by the polyethers containing up to fourteen carbon atoms in their flexible spacers were determined from copolymerization experiments which were detailed in previous publications (2-8), and were recently explained theoretically (18). The experimental determination of the virtual nematic mesophase displayed by a polyether based on MBPE and flexible spacers containing an infinite number of carbon atoms would correspond to the virtual nematic mesophase of polyethylene. Although a virtual nematic mesophase was theoretically predicted for polyethylene (19) it was not yet experimentally determined. On this account we are extending our experiments to polyethers containing spacer lengths which upon extrapolation may lead to the determination of the experimental parameters of the nematic virtual mesophase of polyethylene.

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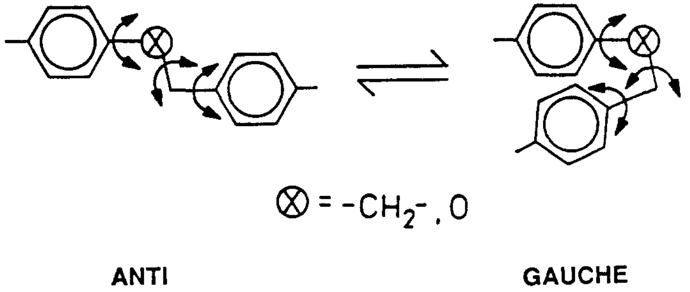
Flexible Rod-like Mesogens or Mesogens Based on Conformational Isomerism



Scheme 1

The goal of this paper is to describe the synthesis and determine the phase behavior of polyethers based on MBPE and 1,15-dibromopentadecane (MBPE-15), and MBPE and 1,16-dibromohexadecane (MBPE-16).

EXPERIMENTAL

Materials

1,15-Pentadecanediol (98% from Wiley Organics), 1,8-dibromooctane (98% from Aldrich), 1,16-dibromohexadecane (mp. 56-57 °C, from Pfaltz & Bauer Research Chemicals) as well as the other chemicals were used as received.

1,15-Dibromopentadecane It was synthesized by the bromination of the corresponding diol, by two different methods. The best yield was obtained by using Method 1.

Method 1 Bromine (6.9 g, 0.043 mol) was added dropwise under nitrogen to an ice cooled (0-10 °C) solution of 11.3 g (0.043 mol) of triphenylphosphine in 100 ml of dried DMF. To the resulting orange solution was added dropwise a solution of 5.0 g (0.021 mol) of 1,15-pentadecanediol in 100 ml of dried DMF, and the reaction mixture was stirred at 50 °C overnight. The reaction mixture was poured into 1 l of water and the white precipitate was filtered, washed with water and dried. Then it was extracted twice with 200 ml of hexane and the white insoluble solid (Ph_3PO) was filtered. Hexane was removed in a rotary evaporator and the residue was recrystallized from methanol to yield 4.9 g (65%) of white crystals. mp = 28 °C (lit 21, mp = 27.2-27.5 °C). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.26 (m, 20H, -($C\underline{H}_2$)$_{10}$-), 1.85 (quintet, 4H, $BrCH_2C\underline{H}_2$-), 3.41 (t, 4H, $BrC\underline{H}_2CH_2$-). -CH_2OH group could not be detected by NMR analysis.

Method 2 To a solution of 5 g (0.02 mol) of 1,15-pentadecanediol in 300 ml of sodium dried toluene were added at 80 °C 6.1 g (0.09 mol) of imidazole and 11.7 g (0.05 mol) of Ph_2PCl (20). The reaction mixture was cooled to room temperature and a solution of 4.3 g (0.05 mol) of Br_2 in 20 ml of dried toluene was added dropwise under stirring. After 2 hr, the reaction mixture was poured into a separatory funnel containing an equal volume of NaOH (10%). Iodine was added until the toluene phase remained colored. The toluene layer was separated, washed with water, dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (Silicagel, chloroform as eluent). The obtained white product was recrystallized from methanol to yield 2.8 g (37%) of white crystals. Analytical data were identical as above.

1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) (100% purity by HPLC) was synthesized as previously reported (2).

Techniques.

The analytical techniques used were described previously (2-6).

Synthesis of Polyethers and Copolyethers.

Both polyethers and copolyethers were synthesized and purified as described in previous publications (2-6). The molecular weight of MBPE-8 synthesized previously (4, 5) was only Mn = 10,400. Mn increases (Mn ≈ 30,000) when a longer reaction time was used, i. e, 9 hrs instead of 6 hrs. Therefore, MBPE-8 used in all present calculations is based on the new sample.

RESULTS AND DISCUSSION

As has been briefly mentioned in the introduction, most of the polyethers based on MBPE and α,ω-dibromoalkanes display only virtual mesophases (2-8, 16, 17). Exceptions are the polymers based on 1,5-dibromopentane (MBPE-5), 1,9-dibromononane (MBPE-9) and 1,11-dibromoundecane (MBPE-11) which exhibit two monotropic nematic mesophases (2, 16, 17), and the polymer based on 1,8-dibromooctane (MBPE-8) which displays an enantiotropic nematic mesophase (4, 5, 16). All polyethers based on odd flexible spacers display two virtual nematic mesophases while the polymers based on even spacers present one virtual nematic mesophase. The nematic mesophase displayed by the polymers containing even spacers and the high temperature nematic mesophase of the polymers based on odd spacers is a Nu (16,17). No final assignment on the nature of the second nematic mesophase displayed by polyethers containing odd spacers is yet available (16).

The virtual mesophases of crystalline homopolymers can be determined by copolymerization experiments (2-8). When two dissimilar spacer lengths are inserted into the structural units of a copolymer, crystalline phase transitions are suppressed. Simultaneously, liquid crystalline mesophases belonging to isomorphic copolymeric structural units display a linear dependence of their phase transition parameters on copolymer composition. This behavior is the result of the fact that the structural units of the copolymers are not isomorphic in the crystalline phase while they are isomorphic in some of their liquid crystalline phases. Any combination of odd-odd, even-even and odd-even spacers lead to structural units which are isomorphic in the Nu phase (2-6). However, the parameters of the second nematic mesophase display a linear dependence on composition only for copolymers based on odd-odd pairs of flexible spacers (2,4). Therefore, this last mesophase can be determined only from copolymers based on odd-odd pairs of flexible spacers. Simultaneously, the Nu mesophase can be determined from copolymers based on any combination of flexible spacers ie, odd-odd, even-even and odd-even (2-8).

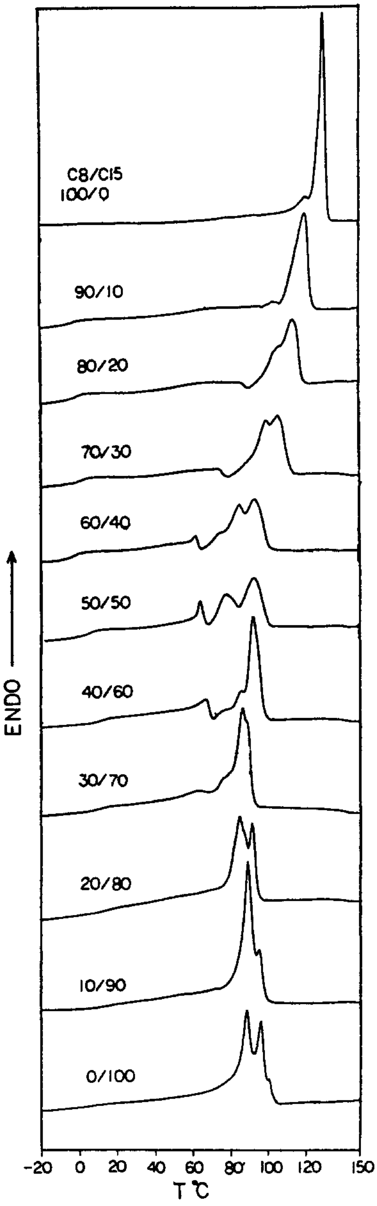


Figure 1a: Second heating DSC traces (20 °C/min) of MBPE-8/15 (A/B)

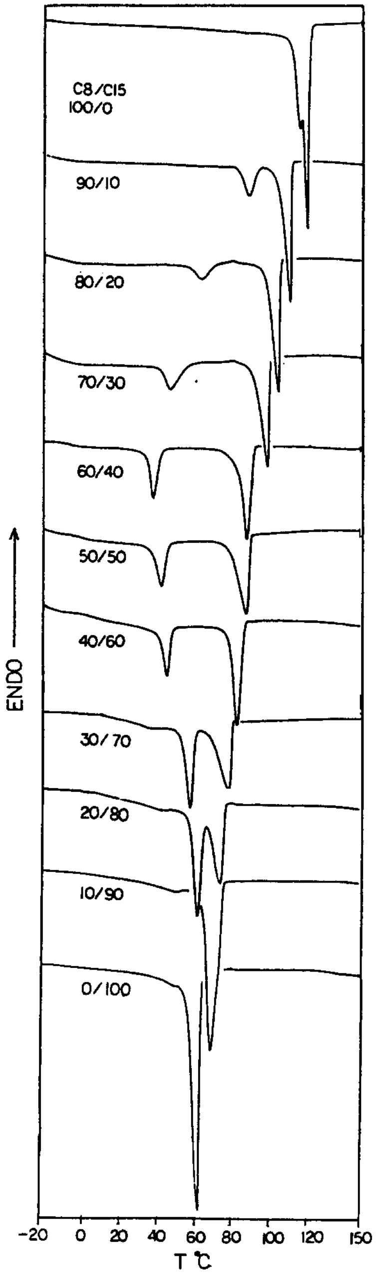


Figure 1b: Cooling DSC traces (20 °C/min) of MBPE-8/15 (A/B)

Table I Characterization of Polyethers based on MBPE and 1,8-dibromooctane (MBPE-8), MBPE and 1,15-dibromotetradecane (MBPE-15) and of Corresponding Copolyethers [MBPE-8/15 (A/B)]

Copolymer MBPE-8/15 (A/B)	Mw	Mw/Mn	Thermal transitions (° C), and corresponding enthalpy changes (Kcal/mru) in parentheses	
8/15 Mole Ratio	GPC		heating	cooling
100/0	29,400	2.05	k 122 n 132(3.81*)i	i 119(3.53*) n 116 k
90/10	29,900	1.97	g -2 k 106 n 121(3.05*) i	i 109(2.23) n 88 k -7 g
80/20	41,400	1.73	g 0 k 107 n 114(3.26) i	i 103(2.45) n 64(0.50) k -8 g
70/30	22,000	1.92	g 3 k 100 n 107(3.63) i	i 97(2.34) n 47(0.83) -6 g
60/40	15,300	1.81	g -1 k 63(0.18) k 76 k 86 n 95(3.69*) i	i 89(2.15) n 39(0.97) k -7 g
50/50	16,300	2.04	g 6 k 65(0.56) k 79 n 95(3.34*) i	i 88(2.22) n 43(1.05) k 4 g
40/60	32,100	2.24	g 12 k 67(0.56) k 87 k (3.05*) i	i 84(2.23) n 46(1.02) k 3 g
30/70	11,500	2.16	g 12 k 64 k 77 k 87 k 90(4.50*) i	i 77(2.13) n 57(1.81) k 4 g
20/80	22,700	2.64	g 12 k 86 k 93(4.44*) i	i 75(2.22) n 63(2.29) k 5 g
10/90	29,400	2.19	g 13 k 90 k 96(5.28*) i	i 71(5.08) k 5 g
0/100	21,300	2.17	k 89 k 97 k104(5.62*) i	i 62(5.55) k

* overlapping transition

The most accurate copolymerization experiment useful in the determination of virtual mesophases is based on a pair of spacers, from which, one leads to a homopolymer displaying an enantiotropic mesophase. MBPE-8 does this (4-8). On this account, the determination of the virtual mesophases of the homopolymer MBPE-15 and MBPE-16 will be performed by synthesizing copolymers based on MBPE with 1,8-dibromooctane and 1,15-dibromopentadecane [MBPE-8/15 (A/B)] and respectively based on MBPE with 1,8-dibromooctane and 1,16-dibromohexadecane [MBPE-8/16 (A/B)].

Figure 1a presents the second DSC heating scans of the copolymers MBPE-8/15 (A/B). A/B refers to the molar ratio between the two spacers. The corresponding cooling DSC scans are presented in Figure 1b. Table I summarizes the characterization of MBPE-8, MBPE-15 and the series of copolymers MBPE-8/15. Number average molecular weights of all polymers and copolymers are above 15000. Consequently, their phase transition temperatures are molecular weight independent (Table I). MBPE-8 displays a very narrow enantiotropic nematic mesophase (Figure 1a, b). MBPE-15 displays several melting peaks on the heating scan, and a single crystallization peak on cooling, and therefore, is only crystalline (Figure 1a, b). Upon copolymerization, the isotropic-nematic and nematic-crystalline peaks of MBPE-8 get a better separation (Figure 1b). This is because the isotropic nematic peaks display a linear dependence of copolymer composition, while the nematic-crystalline peaks are suppressed upon copolymerization. The isotropic-nematic peak can be observed from MBPE-8 to MBPE-8/15 (20/80) (Figure 1b, Table I). On the heating scan, an enantiotropic nematic mesophase can be detected from MBPE-8 to MBPE-8/15 (50/50) (Figure 1a, Table I).

The thermal transition temperatures associated with the isotropic-nematic transitions were plotted in Figure 2a, while their corresponding enthalpy changes in Figure 2b. Upon extrapolation to the composition of MBPE-15, both the virtual isotropic-nematic transition temperature and its corresponding enthalpy change were determined.

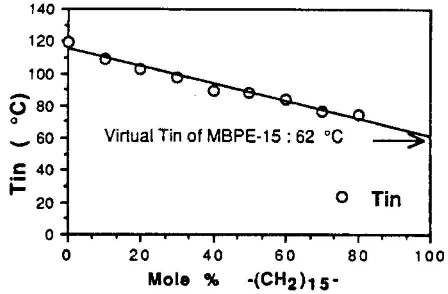


Figure 2a: The dependence between isotropic-nematic transition temperature of MBPE-8/15 (A/B) and copolymer composition

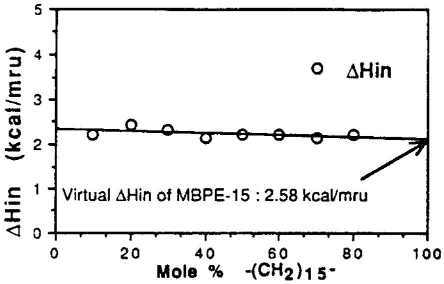


Figure 2b: The dependence between the enthalpy changes associated with the isotropic-nematic transition of MBPE-8/15 (A/B) and copolymer composition

As described above, this experiment does not allow to estimate whether MBPE-15 displays a second nematic mesophase. This would require the synthesis of copolymers based on MBPE, 1,15-dibromopentadecane and a second spacer based on an odd number of methylene units.

Table II Characterization of Polyethers based on MBPE and 1,8-dibromooctane (MBPE-8), MBPE and 1,16-dibromohexadecane (MBPE-16) and of Corresponding Copolyethers [MBPE-8/16 (A/B)]

Copolymer MBPE-8/16 (A/B)	Mw	Mw/Mn	Thermal transitions (° C), and corresponding enthalpy changes (Kcal/mru) in parentheses	
8/16 Mole Ratio	GPC		heating	cooling
100/0	29,400	2.05	k 122 n 132(3.81*)i	i 119(3.53*) n 116 k
90/10	18,400	1.93	g -5 k 102 n 118(2.67*) i	i 108(2.26) n 87(1.07) k -7 g
80/20	24,700	1.99	g -3 k 87(0.26) k106 n 113(3.85*) i	i 105(2.45) n 65(0.91) k -7 g
70/30	25,400	1.89	g -1 k 75(0.10) 97 n 110(3.88*) i	i 100(2.39) n 44(0.97) k -6 g
60/40	28,100	2.63	g 1 k 98 n 104(3.40*) i	i 95(2.54) n 56(0.95) k -9 g
50/50	17,300	1.88	g 0 k 90(0.08) k 100(3.47) i	i 93(2.72) n 73(2.00) k -3 g
40/60	25,900	1.88	g 1 k 102(4.15) i	i 91(2.75) n 78(1.80) k -1 g
30/70	34,600	1.87	g 2 k 104(5.13) i	i 88(4.88*) n 85 k 0 g
20/80	26,200	1.66	g 2 k 100 k 105(5.46*) i	i 86(5.08) k 5 g
10/90	28,000	1.88	g -2 k 108(6.08) i	i 87(5.44) k 1 g
0/100	32,300	2.06	g 1 k 110(5.21) i	i 88(5.74) k 0 g

* overlapping transition

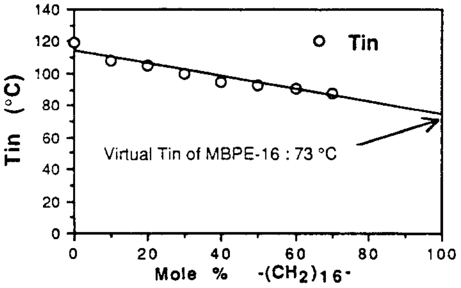


Figure 4a: The dependence between isotropic-nematic transition temperature of MBPE-8/16 (A/B) and copolymer composition

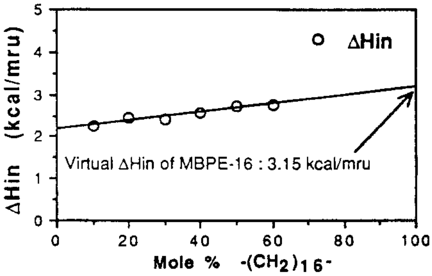


Figure 4b: The dependence between the enthalpy changes associated with the isotropic-nematic transition of MBPE-8/16 (A/B) and copolymer composition

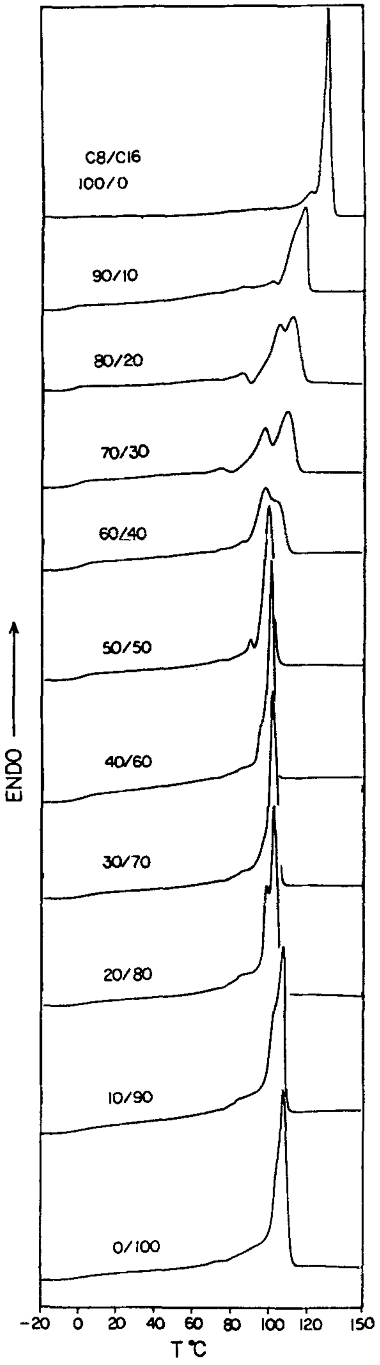


Figure 3a: Second heating DSC traces (20 °C/min) of MBPE-8/16 (A/B)

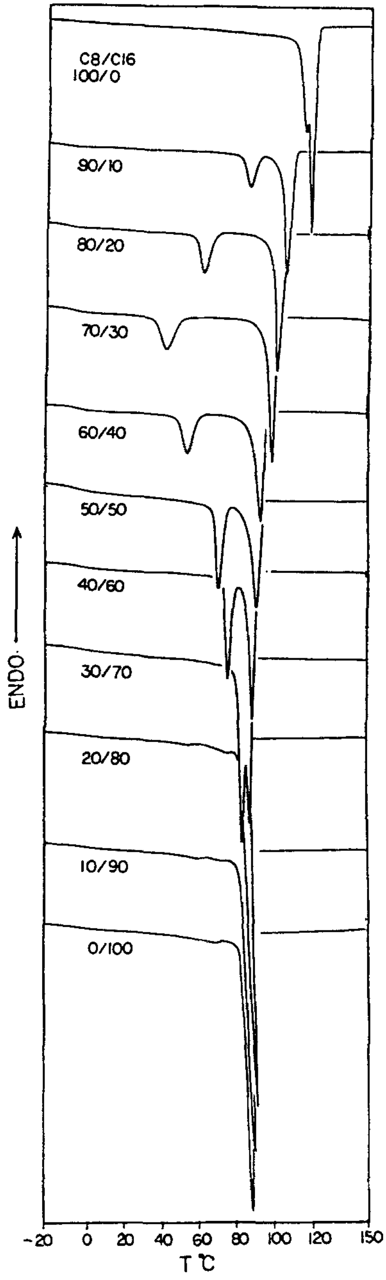


Figure 3b: Cooling DSC traces (20 °C/min) of MBPE-8/16 (A/B)

Figure 3a displays the second heating DSC scans of the copolymers MBPE-8/16 (A/B). The corresponding cooling DSC scans of these copolymers are presented in Figure 3b. Table II summarizes the characterization of MBPE-8/16 (A/B) copolymers. MBPE-16 is only crystalline (Figure 3a,b). Copolymers from MBPE-8 to MBPE-8/16 (20/80) display an isotropic-nematic and a nematic-crystalline transition (Figure 3b). On the heating scan an enantiotropic mesophase can be observed from MBPE-8 to MBPE-8/16 (60/40). Isotropic-nematic transition temperatures of MBPE-8/16 (A/B) are plotted in Figure 4a. The corresponding enthalpy changes are plotted in Figure 4b. The virtual isotropic-nematic transition temperature of MBPE-16 and its corresponding enthalpy change were determined by extrapolation. These values are presented in Figure 4a and b.

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