

Liquid-crystalline polyethers based on conformational isomerism: 12. Molecular engineering of phase transitions in copolyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane and multiple combinations of flexible spacers

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This paper describes the synthesis and characterization of copolyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) and various combinations of from three to eight α,ω -dibromoalkanes. Copolymers containing spacers with an odd number of methylene units display a uniaxial nematic mesophase and a second unidentified mesophase. Copolymers containing spacers with odd and even or only even numbers of methylene units display a uniaxial nematic mesophase. The parameters of the mesomorphic phase transitions of all copolymers represent weight-averaged values of the corresponding parameters of the parent homopolymers. This proves that the structural units of these copolymers are isomorphic within their mesophase. These results also demonstrate that the parameters of the mesomorphic phases can be engineered by copolymerization. All MBPE copolymers are crystallizable. Their crystallizability decreases by increasing the number of flexible spacers and decreasing their length, and by using an odd rather than an even number of methylenic units in the spacer.

(Keywords: liquid-crystalline copolyethers; conformational isomerism; mesomorphic phase transitions)

INTRODUCTION

The traditional methods employed in the molecular design of main-chain and side-chain liquid-crystalline polymers are based on the use of the concept of rigid rodlike mesogenic unit¹⁻⁸. Alternative classes of mesogenic groups were recently reviewed⁹. Rigid rodlike mesogenic units exhibit an anisotropic elongated or rodlike conformation due to the conformational rigidity or semirigidity of the molecule (*Figure 1*).

In the previous publications from this series we have advanced the concept of rodlike mesogenic unit based on conformational isomerism or of flexible rodlike mesogenic unit (*Figure 1*)¹⁰⁻²⁰. 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 (*Figure 1*). The thermodynamic stability of the mesophase exhibited by such a compound is expected to be lower than that of the corresponding rigid rodlike homologue²¹. Therefore, most of the homopolyethers based on the flexible mesogenic unit 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) and flexible spacers display only virtual or monotropic

mesophases¹¹⁻²⁰. The virtual transition temperatures and thermodynamic parameters of the polyethers based on MBPE and α,ω -dibromoalkanes containing 4-20 methylenic units were determined by copolymerization experiments¹¹⁻¹⁹ and were summarized in a previous publication¹⁹. The strategy behind these experiments is as follows. Copolymers based on MBPE and two^{11-14,16-19} or three¹⁵ flexible spacers were synthesized to cover 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 behaviour is determined by a combination of kinetic and thermodynamic effects²¹. That is, the copolymer structure combined with a lower rate of crystallization decrease the perfection of the crystal phase and lower the non-equilibrium or equilibrium melting transition temperatures of the copolymers. At the same time, the temperature transitions and enthalpy changes associated with the mesomorphic phase transitions of the copolymers whose structural units are isomorphic within their mesophase display weight-averaged dependences on copolymer composition. The virtual transition temperatures and the corresponding thermodynamic parameters of the homopolymers and of various copolymers are determined by the extrapolation of their linear dependences on copolymer composition¹¹⁻¹⁹. Alternatively, if two homopolymers displaying virtual mesophases are

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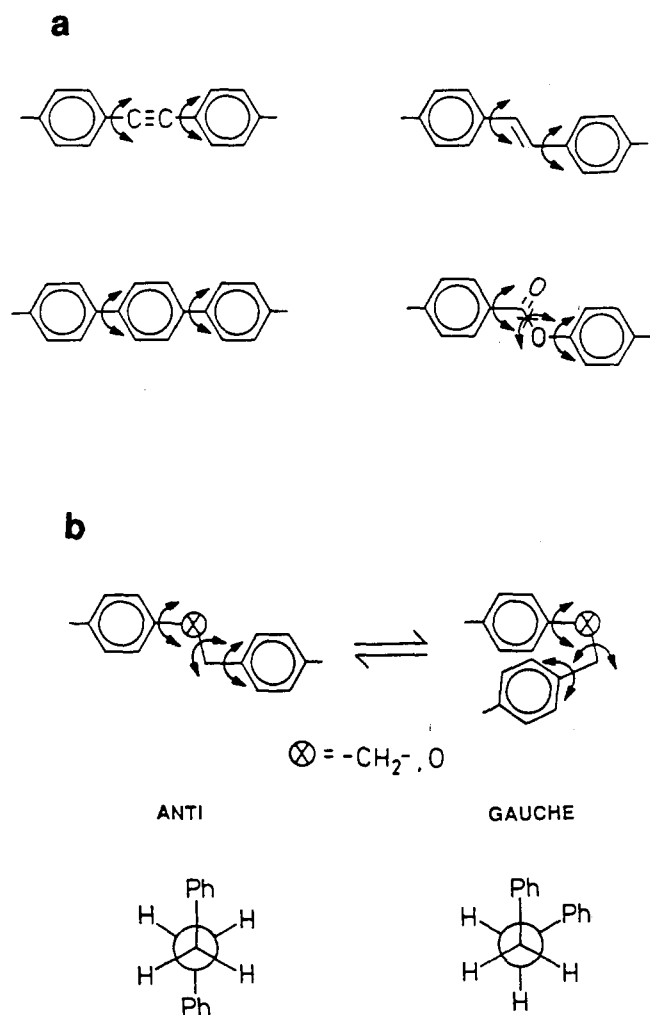


Figure 1 (a) Rigid rodlike mesogens and (b) flexible rodlike mesogens or rodlike mesogens based on conformational isomerism

isomorphic within their mesophase, the phase diagrams of their blends can be used to determine the virtual parameters of their parent homopolymers²⁰.

So far it has been demonstrated that copolymerization of a mesogenic unit with two or three dissimilar flexible spacers provides the most reliable analytical method to determine virtual mesomorphic parameters. This is because very few homopolymer chains were found to be isomorphic even when they displayed an identical mesophase²⁰. There is, however, an additional preparative reason for which copolymerization could become very important. If copolymers based on a mesogenic unit and more than three flexible spacers would still display a weight-averaged dependence of their mesomorphic phase transitions and thermodynamic parameters on composition, they could be useful to design at will both the phase transition temperature and the degree of order of the mesophase.

The goal of this paper is to summarize our results on the dependence of the phase transition temperatures and thermodynamic parameters of the copolyethers based on MBPE and from three to eight different combinations of α,ω -dibromoalkanes. These experiments will complete our series of investigations on flexible liquid-crystal copolyethers based on one mesogenic unit and combinations of two or more flexible spacers.

EXPERIMENTAL

Materials

1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) was synthesized as reported previously¹¹; purity (h.p.l.c.) 99.9%; m.p. (d.s.c., 20°C min⁻¹) 148°C. The α,ω -dibromoalkanes used in the synthesis of copolyethers were of commercial origin or were synthesized in our laboratory. The source, purification and purity of these compounds are available in the papers describing the synthesis of polyethers and copolyethers based on MBPE and α,ω -dibromoalkanes. Polyethers based on MBPE and odd spacers containing 5–11 methylene units are described in ref. 11, those based on even spacers containing 4–12 methylene units in ref. 13 and those based on odd and even spacers containing 4–12 methylene units in ref. 14. The polyethers and copolyethers based on MBPE and longer flexible spacers are described in the following publications: 1,13-dibromotridecane in ref. 16, 1,14-dibromotetradecane in ref. 17, 1,15-dibromopentadecane and 1,16-dibromohexadecane in ref. 18, and from 1,17-dibromoheptadecane to 1,20-dibromoeicosane in ref. 19.

Synthesis of copolyethers based on MBPE and various combinations of α,ω -dibromoalkanes

All copolyethers were synthesized by phase transfer catalysed polyetherification according to two procedures, which were described in detail in previous publications. The difference between these two procedures consists of the amount of phase transfer catalyst used and the duration of the reaction. This difference is dictated by the spacer length. Copolyethers based on spacer lengths that are each shorter than 1,17-dibromoheptadecane were synthesized according to the method described in ref. 11. The copolyethers containing at least one spacer equal to or longer than 1,17-dibromoheptadecane were synthesized according to the procedure described in ref. 19.

In this entire paper, copolyethers will be designated MBPE-*X/Y/Z*/...(*A/B/C*...) where *X* is the number of methylene units in the first spacer, *Y* in the second spacer, *Z* in the third spacer, etc., and *A/B/C*/... refers to the molar ratio of the corresponding spacers.

Techniques

Molecular weights were determined by gel permeation chromatography (g.p.c.). G.p.c. analyses were carried out with a Perkin-Elmer Series 10LC equipped with an LC-100 column oven, LC 600 autosampler and a Nelson Analytical 900 series data station. The measurements were made by using the u.v. detector, chloroform as solvent (1 ml min⁻¹, 40°C), a set of PL gel columns of 10², 5 × 10², 10³, 10⁴ and 10⁵ 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⁻¹ 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. First heating scans differ from second heating scans. This

difference will be discussed later. A discussion of the influence of the thermal history of the sample on phase transitions was reported previously¹².

A Carl Zeiss optical polarizing microscope (magnification 100×) equipped with a Mettler FP-82 hot stage and a Mettler 800 central processor were used to observe the thermal transitions and to analyse the textures²².

RESULTS AND DISCUSSION

We will first recapitulate briefly the phase behaviour of polyethers and binary copolyethers based on MBPE and flexible spacers. A detailed discussion on this subject is presented in a previous publication¹⁹.

All polyethers and binary copolyethers based on MBPE and flexible spacers containing an even number of methylene units display a uniaxial nematic mesophase and two crystalline phases^{19,23}. This uniaxial nematic mesophase will be labelled with n_1 . The low-temperature crystalline phase corresponds to an 'intermeshed' arrangement of the flexible spacers and mesogens, while the high-temperature crystalline phase corresponds to a 'layered' arrangement of the spacers and mesogenic groups^{23,24}. Upon copolymerization of MBPE with two dissimilar spacers, the rate of formation of the high-temperature crystalline phase is reduced to the extent that many copolymers do not crystallize during the second cooling and/or heating d.s.c. scans. Special annealing is required to re-form this crystalline phase. In many instances, particularly in the case of homopolymers, the melting of the high-temperature crystalline phase overlaps the isotropization temperature, and subsequently these polymers display only a monotropic or even virtual nematic mesophase. Upon copolymerization of MBPE with two different spacers, the rate of crystallization of the high-temperature phase is lowered, and therefore most copolymers display a monotropic or even enantiotropic nematic mesophase. However, under equilibrium conditions, the melting temperatures of many of these binary copolymers are increased, overlapping again the isotropization temperature. Therefore, most of the binary copolymers display only a pseudo-enantiotropic nematic mesophase¹². This behaviour was discussed in detail in a previous publication for several series of binary copolymers¹². The rate of crystallization of the low-temperature crystalline phase is less affected by copolymerization¹².

All polyethers and binary copolyethers based on MBPE and flexible spacers containing an odd number of methylene units display a uniaxial nematic mesophase, a second mesophase and two crystalline phases^{19,23}. The uniaxial nematic mesophase will be labelled with n_1 . The second mesophase has not yet been definitively assigned^{19,23} but presents the symptoms of a second nematic phase, and so will be labelled with n_2 . The n_2 phase appears only in copolymers based on MBPE and both binary^{11,12} and ternary¹⁵ combinations of flexible spacers containing an odd number of methylene units¹⁹. Copolymers based on MBPE and binary combinations of odd and even flexible spacers display only the n_1 mesophase^{13,19}. The kinetically controlled crystallization process influences the temperature range of the mesophase displayed by the copolymers based on MBPE and combinations of odd-odd or even-even spacers, according to the pattern described for copolymers based on

MBPE and pairs of spacers containing even numbers of methylene units.

The purpose of the experiments described in this paper is first to learn how many flexible spacers can be accommodated into the crystalline and liquid-crystalline phases displayed by a copolymer containing a single mesogenic group. Secondly, we would like to elucidate at least in a qualitative way the mechanism by which various combinations of flexible spacers affect the phase behaviour of various phases of the resulting copolymers.

The number-average molecular weights of all copolymers discussed in this paper are above 25 000, and their polydispersities are about 2.00. Since these molecular weights are above values that influence phase transition temperatures, they will not be tabulated.

Let us first discuss some selected examples of ternary copolymers. As we observe from *Figure 2*, when we consider the constitutional isomerism of the MBPE-derived structural unit, ternary copolymers consist of more than three structural units. Nevertheless, for the sake of simplicity, over this entire paper we will consider all copolymers only according to their number of flexible spacers.

Figure 3 presents various heating and cooling d.s.c. scans of a ternary copolymer containing three different spacers each with an odd number of methylene units, i.e. MBPE-5/7/9(33/33/33). The phase behaviour of MBPE-5/7/9(A/B/C) copolymers obtained from second heating and cooling scans was discussed over the entire range of compositions in a previous publication¹⁵. On the second heating scan and on any cooling scans, the MBPE-5/7/9(33/33/33) copolymer displays enantiotropic n_1 and n_2 mesophases. Under these characterization conditions, this copolymer does not crystallize. The experimental values of the $T_{n_2-n_1}$, $\Delta H_{n_2-n_1}$, T_{n_1-i} and ΔH_{n_1-i} are summarized in *Tables 1* and *2* and agree very well with the corresponding calculated values. The calculated values represent the weight-averaged values of the corresponding parameters of the parent homopolymers¹⁹:

$$T = \sum_{i=1}^n X_n T(n) \quad \text{and} \quad \Delta H = \sum_{i=1}^n X_n \Delta H(n)$$

where X_n is the mole fraction of the structural unit n from copolymer, and T and ΔH are the transition temperature and the corresponding enthalpy change associated with the same phase transition of the parent homopolymer based on an identical structural unit. This copolymer presents a very low tendency towards crystallization. After one week of annealing at room temperature, the first heating scan (curve b in *Figure 3*) still does not exhibit any crystalline melting. Only after about 40 days of annealing at room temperature can we observe a small melting endotherm on the heating d.s.c. scan (curve d in *Figure 3*). One year later the enthalpy change associated with this melting endotherm increases (curve d, *Figure 3*). However, the copolymer still presents both n_2 and n_1 enantiotropic mesophases. In most cases the first d.s.c. heating scan of the copolymers described in this paper resemble the first d.s.c. scan obtained after annealing at room temperature for about one week. Therefore, these data will be discussed only if they show a different behaviour.

The insertion of longer flexible spacers in the structure of a ternary copolymer based on MBPE and three

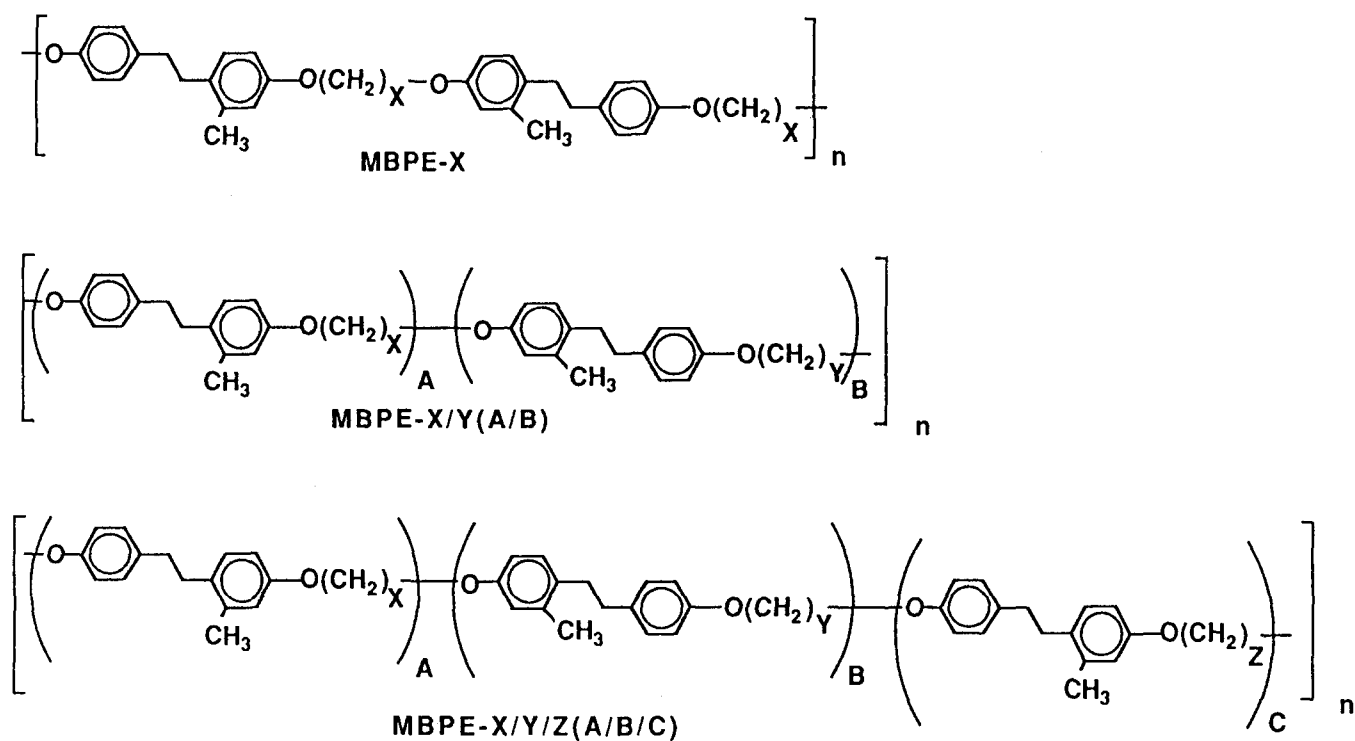

Figure 2 Structures of polyethers and copolyethers based on MBPE and flexible spacers (α,ω -dibromoalkanes)

Table 1 Characterization of copolyethers based on MBPE and α,ω -dibromoalkanes

Copolymers	Thermal transitions ($^{\circ}\text{C}$) and corresponding enthalpy changes (kcal/mru) in parentheses	
<i>Odd-odd spacers</i>		
MBPE-5/7/9(33/33/33)	Second heating	g 11 n ₂ 59(0.16) n ₁ 70(0.75) i
	RTA ^b , 1 week	g 10 n ₂ 58(0.34) n ₁ 69(0.91) i
	RTA, 40 days	g 11 k 44 n ₂ 59 n ₁ 70(1.45 ^a) i
	RTA, 1 year	g 10 k 47 k 51 n ₂ 58 n ₁ 69(1.81 ^a) i
	Cooling	i 63(0.72) n ₁ 54(0.16) n ₂ 6 g
MBPE-5/7/9/11(25/25/25/25)	Second heating	g 9 n ₂ 62(0.48) n ₁ 73(0.88) i
	RTA, 1 week	g 8 k 40(0.19) n ₂ 63(0.39) n ₁ 73(1.03) i
	Cooling	i 65(1.06) n ₁ 56(0.33) n ₂ 3 g
MBPE-5/7/9/11/13(20/20/20/20/20)	Second heating	g 6 n ₂ 58(0.34) n ₁ 70(1.19) i
	RTA, 1 week	g 7 k 43 n ₂ 61 n ₁ 72(2.36 ^a) i
	Cooling	i 66(1.19) n ₁ 56(0.40) n ₂ 3 g
MBPE-5/11/19(33/33/33)	Second heating	g 9 k 71 n ₁ 74(3.51 ^a) i
	RTA, 1 week	g 9 k 42 k 72 n ₁ 74(4.20 ^a) i
	Cooling	i 67(1.83) n ₁ 56(2.28) k 7 g
<i>Even-even spacers</i>		
MBPE-8/10/12(33/33/33)	Second heating	g -6 k 71(0.32) k 85(0.83) n ₁ 109(2.43) i
	RTA, 1 week	g -7 k 43 k 71(0.99 ^a) k 85(0.83) n ₁ 110(2.50) i
	Cooling	i 101(2.51) n ₁ 53(1.19) g
<i>Odd-even spacers</i>		
MBPE-7/8/9(33/33/33)	Second heating	g -2 k 80 n ₁ 87(1.83 ^a) i
	RTA, 1 week	g 0 k 38(0.04) k 79 n 87(1.81 ^a) i
	Cooling	i 79(1.34) n ₁ 34(0.40) k -5 g
MBPE-8/9/10(33/33/33)	Second heating	g -2 k 56(0.23) k 74(0.55) n ₁ 102(1.82) i
	RTA, 1 week	g -2 k 39(0.13) k 73(0.51) n 102(1.69) i
	Cooling	i 94(1.95) n ₁ 21(0.78) k -5 g

Table 1 (continued)

Copolymers	Thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
MBPE-5/8/10(33/33/33)	Second heating	g -2 k 54(0.05) k 73(0.55) n ₁ 100(1.80) i
	RTA, 1 week	g -1 k 43 k 55(0.58 ^a) 74(0.71) n ₁ 100(1.89) i
	Cooling	i 92(1.76) n ₁ -8 g
MBPE-7/8/9/10(25/25/25/25)	Second heating	g -5 n ₁ 94(1.63) i
	RTA, 1 week	g 0 k 43 k 55(0.76 ^a) n ₁ 94(1.58) i
	Cooling	i 83(1.78) n ₁ -5 g
<i>Odd-even containing 5/7/9</i>		
MBPE-4/5/7/9(25/25/25/25)	Second heating	g 12 k 90 n ₁ 101(1.42 ^a) i
	RTA, 2 weeks	g 12 k 43(0.10) k 88 n ₁ 99(1.53 ^a) i
	Cooling	i 86(1.15) n ₁ 6 g
MBPE-5/6/7/9(25/25/25/25)	Second heating	g 9 k 87 n ₁ 98(1.93 ^a) i
	RTA, 2 weeks	g 10 k 44(0.13) k 89 n ₁ 98(1.78 ^a) i
	Cooling	i 79(1.19) n ₁ 56(0.63) k 5 g
MBPE-5/7/8/9(25/25/25/25)	Second heating	g -1 n ₁ 78(1.24) i
	RTA, 2 weeks	g 0 k 41 k 54 n ₁ 80(2.02 ^a) i
	Cooling	i 71(1.25) n ₁ -4 g
MBPE-5/7/9/10(25/25/25/25)	Second heating	g -1 n ₁ 77(1.28) i
	RTA, 1 week	g 0 k 40 k 49 k 61 n ₁ 74(2.17 ^a) i
	Cooling	i 70(1.37) n ₁ -3 g
MBPE-5/7/9/16(25/25/25/25)	Second heating	g 7 k 82(3.02) i
	RTA, 1 week	g 8 k 40(0.21) k 80(2.64) i
	Cooling	i 70(1.42) n ₁ 44(0.64) k 3 g
MBPE-5/7/9/18(25/25/25/25)	Second heating	g 3 k 72 k 77(3.42 ^a) i
	RTA, 1 week	g 3 k 40(0.13) k 70(3.22) i
	Cooling	i 64(1.61) n ₁ 51(1.54) k -9 g
MBPE-5/7/9/20(25/25/25/25)	Second heating	g 8 k 85(3.76) i
	Cooling	i 70(1.68) n ₁ 66(1.50) k 5 g
MBPE-5/7/8/9/10(10/10/35/10/35)	Second heating	g 0 k 62 k 77(0.66 ^a) n ₁ 107(1.97) i
	RTA, 1 week	g 0 43(0.31) k 76(0.35) n ₁ 106(2.02) i
	Cooling	i 99(2.09) n ₁ 37(0.42) k -6 g
MBPE-5/7/8/9/10/11/12/13(12.5 each)	Second heating	g 6 n 87(1.69) i
	RTA, 12 h	g 5 k 42(0.46) n ₁ 87(1.61) i
	RTA, 1 week	g 5 k 42(0.59) n ₁ 87(1.66) i
	Cooling	i 79(1.68) n ₁ -1 g

^aOverlapping transition^bRTA = room-temperature annealingTable 2 Experimental and calculated values of mesomorphic transition temperatures and corresponding enthalpy changes of copolymers based on MBPE and α,ω -dibromoalkanes. Data on first line refer to T_{n_1-i} and ΔH_{n_1-i} and the reversed parameters. Data on second line refer to $T_{n_2-n_1}$ and $\Delta H_{n_2-n_1}$ and the reversed parameters

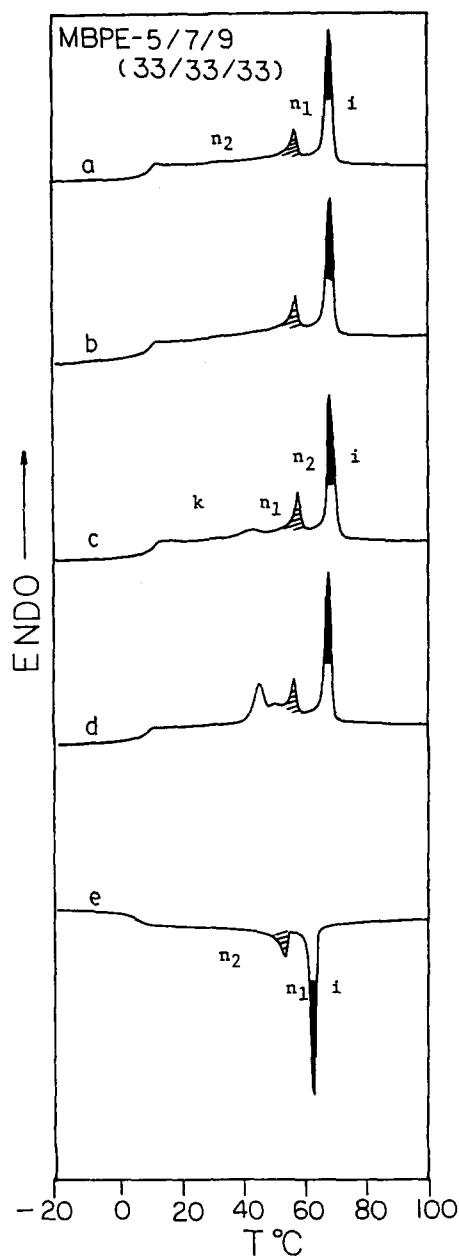
Copolymers	T_{n_1-i}	T_{n_1-i}	Dev.	ΔH_{n_1-i}	ΔH_{n_1-i}	Dev.	T_{i-n_1}	T_{i-n_1}	Dev.	ΔH_{i-n_1}	ΔH_{i-n_1}	Dev.
	$T_{n_2-n_1}$ (obs.)	$T_{n_2-n_1}$ (calc.)		$\Delta H_{n_2-n_1}$ (obs.)	$\Delta H_{n_2-n_1}$ (calc.)		$T_{n_1-n_2}$ (obs.)	$T_{n_1-n_2}$ (calc.)		$\Delta H_{n_1-n_2}$ (obs.)	$\Delta H_{n_1-n_2}$ (calc.)	
<i>Odd-odd spacers</i>												
MBPE-5/7/9(33/33/33)	70	72	-2	0.75	0.67	0.08	63	62	2	0.72	0.79	-0.07
	59	60	1	0.16	0.14	0.02 ^a	54	51	3	0.16	0.11	0.05 ^a
MBPE-5/7/9/11(25/25/25/25)	73	75	-2	0.88	0.85	0.03	65	65	0	1.06	0.87	0.19
	62	63	-1	0.48	0.12	0.36 ^a	56	55	1	0.30	0.11	0.19 ^a
MBPE-5/7/9/11/13(20/20/20/20/20)							66	64	2	1.19	1.02	0.17
							56	56	0	0.40	0.09	0.31 ^a
MBPE-5/11/19(33/33/33)							67	63	4	1.83	1.85	-0.02 ^a
<i>Even-even spacers</i>												
MBPE-8/10/12	109	117	-8				101	105	-4	2.51	2.54	-0.03

Table 2 (continued)

Copolymers	T_{n_1-i}	T_{n_1-i}	Dev.	ΔH_{n_1-i}	ΔH_{n_1-i}	Dev.	T_{i-n_1}	T_{i-n_1}	Dev.	ΔH_{i-n_1}	ΔH_{i-n_1}	Dev.
	$T_{n_2-n_1}$	$T_{n_2-n_1}$		$\Delta H_{n_2-n_1}$	$\Delta H_{n_2-n_1}$		$T_{n_1-n_2}$	$T_{n_1-n_2}$		$\Delta H_{n_1-n_2}$	$\Delta H_{n_1-n_2}$	
	(obs.)	(calc.)		(obs.)	(calc.)		(obs.)	(calc.)		(obs.)	(calc.)	
<i>Odd-even spacers</i>												
MBPE-7/8/9(33/33/33)	87	96	-9				79	84	-5	1.34	1.38	-0.04
MBPE-8/9/10(33/33/33)	102	109	-7				94	97	-3	1.95	1.94	0.01
MBPE-5/8/10(33/33/33)	100	102	-2				92	91	1	1.76	1.78	-0.02
MBPE-7/8/9/10(25/25/25/25)	94	100	-6				83	89	-6	1.78	1.65	0.13
<i>Odd-even containing 5/7/9</i>												
MBPE-4/5/7/9(25/25/25/25)							81	86	-5	1.11	1.15	-0.04
MBPE-5/7/6/9(25/25/25/25)							79	80	-1	1.19	1.27	-0.08
MBPE-5/7/8/9(25/25/25/25)	78	87	-9				71	76	-5	1.25	1.18	0.07
MBPE-5/7/9/10(25/25/25/25)	77	82	-5				70	72	-2	1.37	1.21	0.16
MBPE-5/7/9/16(25/25/25/25)							69	65	4	1.42	1.38	0.04
MBPE-5/7/9/18(25/25/25/25)							64	65	-1	1.61	1.64	-0.03
MBPE-5/7/9/20(25/25/25/25)							70	62	8	1.68	1.72	-0.04
MBPE-5/7/8/9/10(10/10/35/10/35)	107	107	0				96	96	0	2.09	1.91	0.18
MBPE-5/7/8/9/10/11/12/13(12.5 each)							79	79	0	1.68	1.59	0.09

obs = observed; calc = calculated; dev = deviation, i.e. $dev = T(\Delta H)_{obs} - T(\Delta H)_{calc}$

^aThe deviation for $\Delta H_{n_2-n_1}$ and $\Delta H_{n_1-n_2}$ are large due to a combination of very low intrinsic values of $\Delta H_{n_2-n_1}$ and $\Delta H_{n_1-n_2}$ and of overlapped peaks



different flexible spacers containing odd numbers of methylene units enhances the tendency towards crystallization. Figure 4 displays representative d.s.c. traces of MBPE-5/11/19(33/33/33). On the heating scan this copolymer displays a melting transition which overlaps the $n_1 - i$ transition. On the cooling scan T_{n_1-k} overlaps the $T_{n_1-n_2}$ transition and, therefore, under non-equilibrium conditions, this copolymer displays only a very narrow enantiotropic n_1 phase (curves b, c and d, Figure 4). Under quasi-equilibrium conditions, it presents only a monotropic n_1 phase (curves a and d, Figure 4).

The multiple copolymers MBPE-5/7/9/11(25/25/25/25) and MBPE-5/7/9/11/13(20/20/20/20/20) each behave in a similar way to copolymer MBPE-5/7/9(33/33/33). That is, all of them display enantiotropic n_1 and n_2 mesophases. In both cases, crystallization represents a very slow process (Table 1). The experimental and calculated parameters associated with their mesomorphic phase transitions agree very well.

Figure 5 displays some representative d.s.c. traces exhibited by two ternary copolymers based on flexible spacers containing either only an even number of methylenic units (MBPE-8/10/12(33/33/33)) or a combination of both even and odd number of methylenic units (MBPE-5/8/10(33/33/33)). Both copolymers display an enantiotropic n_1 mesophase. MBPE-8/10/12(33/33/33) presents crystallization and melting transitions on each of the cooling and heating d.s.c. scans (Figure 5, Table 1). MBPE-5/8/10(33/33/33) does not crystallize on the cooling d.s.c. scans (curve g, Figure 5); however, it both crystallizes and melts on its heating d.s.c. scan (curve e, Figure 5). After annealing at room temperature, the perfection of the crystalline phase increases in both copolymers. The phase behaviour of copolymers MBPE-7/8/9(33/33/33) and MBPE-8/9/10

Figure 3 Representative d.s.c. traces of MBPE-5/7/9(33/33/33): (a) second heating scan; (b) first heating scan after 1 week annealing at room temperature; (c) first heating scan after 40 days annealing at room temperature; (d) first heating scan after 1 year annealing at room temperature; (e) cooling scan

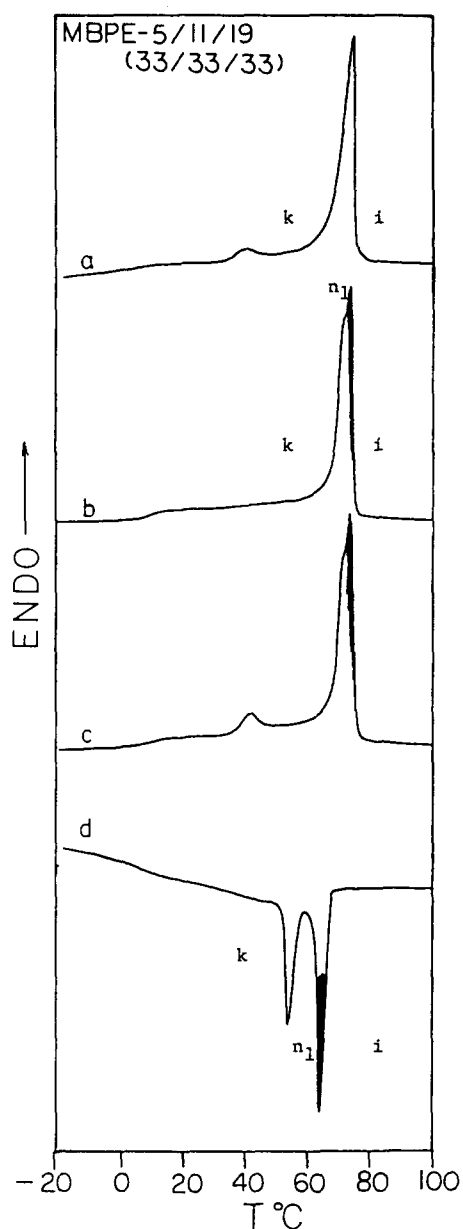


Figure 4 Representative d.s.c. scans of MBPE-5/11/19(33/33/33): (a) first heating scan; (b) second heating scan; (c) first heating scan after 1 week annealing at room temperature; (d) cooling scan

(33/33/33) is similar to that of copolymer MBPE-8/10/12(33/33/33) (Tables 1 and 2).

Copolymers based on MBPE and four different spacers based on combinations of even and odd numbers of methylene units all shorter than 10 display lower crystallization tendency than the corresponding ternary copolymers. Figure 6 presents some heating and cooling d.s.c. traces of MBPE-5/7/8/9(25/25/25/25) and MBPE-4/5/7/9(25/25/25/25) respectively. MBPE-5/7/8/9(25/25/25/25) does not crystallize on the cooling or second heating d.s.c. scans (Figure 6, curves d and b); however, it crystallizes after one week annealing at room temperature (curve c, Figure 6). The copolymers MBPE-7/8/9/10(25/25/25/25) and MBPE-5/7/9/10(25/25/25/25) display identical behaviour with that of MBPE-5/7/8/9(25/25/25/25) (Tables 1 and 2). MBPE-4/5/7/9(25/25/25/25) does not crystallize on cooling (curve h, Figure 6); however, it crystallizes on the heating scans (curve f, Figure 6). MBPE-5/6/7/9(25/25/25/25) crystallizes both on heating and cooling (Tables 1 and 2). MBPE-7/8/9/10

(25/25/25/25), MBPE-5/7/8/9(25/25/25/25), MBPE-5/6/7/9(25/25/25/25), MBPE-4/5/7/9(25/25/25/25) and MBPE-5/7/9/10(25/25/25/25) display an enantiotropic n_1 mesophase.

Increasing the length of at least one of the spacers of the ternary MBPE copolymers transforms the enantiotropic n_1 mesophase into a monotropic mesophase. Representative examples are provided by the copolymers MBPE-5/7/9/16(25/25/25/25), MBPE-5/7/9/18(25/25/25/25) and MBPE-5/7/9/20(25/25/25/25) (Tables 1 and 2).

MBPE copolymers based on more than four flexible spacers still display a high ability towards crystallization. Some representative d.s.c. traces of MBPE-5/7/8/9/10(10/10/35/10/35) are presented in Figure 7. Regardless of the thermal history of the sample, this copolymer displays an enantiotropic n_1 mesophase and one or more

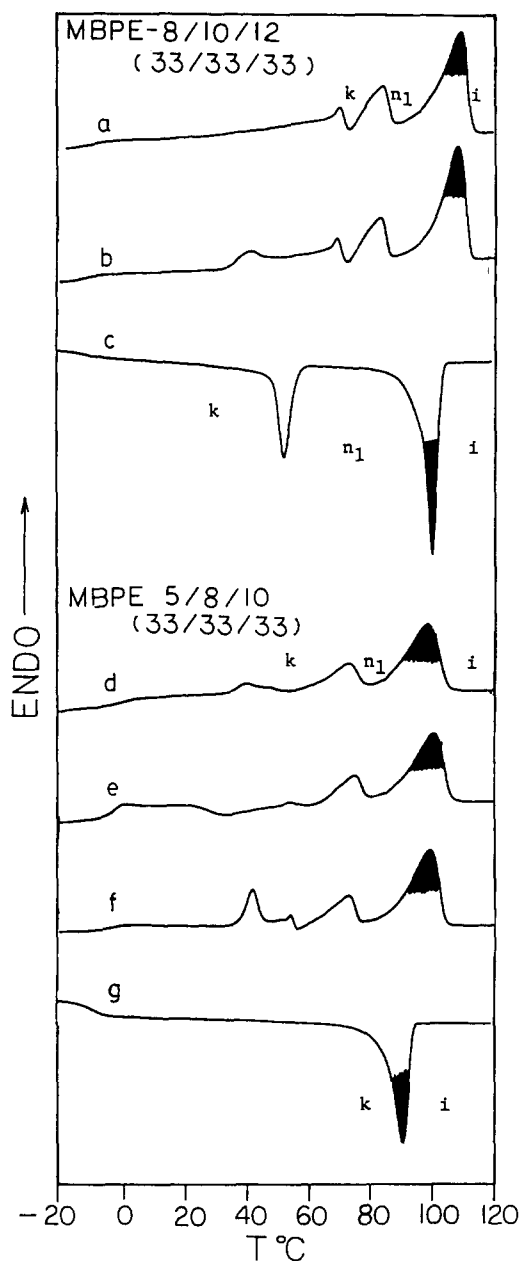


Figure 5 Representative d.s.c. scans of MBPE-8/10/12(33/33/33): (a) second heating scan; (b) first heating scan after 1 week annealing at room temperature; (c) cooling scan; and of MBPE-5/8/10(33/33/33): (d) first heating scan; (e) second heating scan; (f) first heating scan after 1 week annealing at room temperature; (g) cooling scan

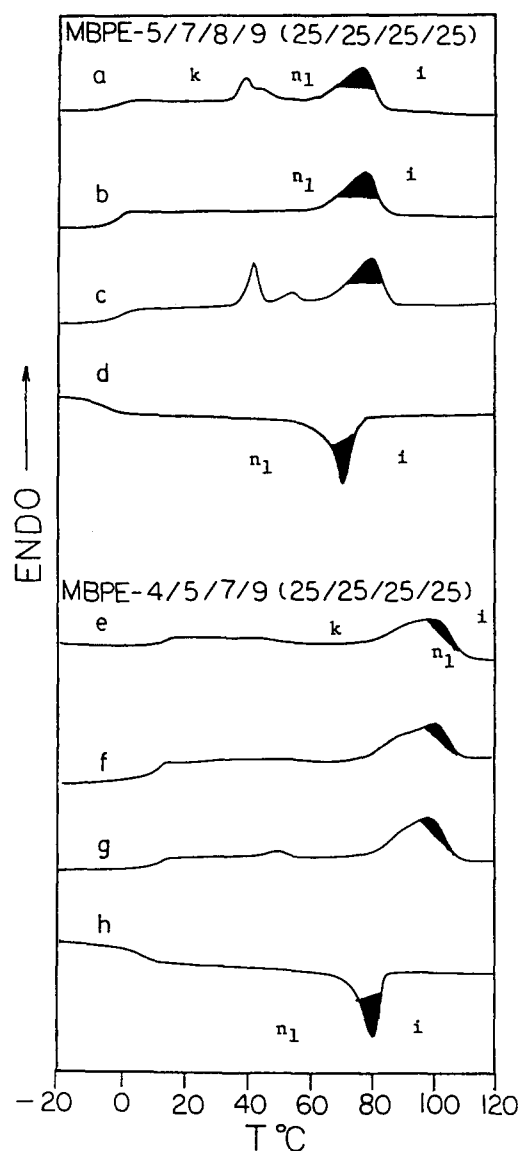


Figure 6 Representative d.s.c. scans of MBPE-5/7/8/9(25/25/25/25): (a) first heating scan; (b) second heating scan; (c) first heating scan after 1 week annealing at room temperature; (d) cooling scan; and of MBPE-4/5/7/9(25/25/25/25): (e) first heating scan; (f) second heating scan; (g) first heating scan after 2 weeks annealing at room temperature; (h) cooling scan

crystallization and melting transitions (Figure 7, Tables 1 and 2). Even a copolymer based on MBPE and as many as eight different flexible spacers can crystallize. Figure 7 (curves e to i) presents representative heating and cooling d.s.c. scans of MBPE-5/7/8/9/10/11/12/13 (12.5/12.5/12.5/12.5/12.5/12.5/12.5/12.5). In the first cooling and second heating scans this copolymer does not present any crystalline transition. However, it requires only 12 h of annealing at room temperature to crystallize (curve g, Figure 7). The calculated and experimental parameters of the enantiotropic n_1 mesophase of MBPE copolymers based on five and eight flexible spacers agree very well (Tables 1 and 2).

The n_1 mesophase of these copolymers displays a threaded nematic texture which is similar to that observed previously for other copolymers based on MBPE¹¹. The n_2 mesophase exhibits a texture which resembles a smectic mesophase¹¹. However, X-ray experiments could not yet support a smectic phase²³.

These experiments have provided the following conclu-

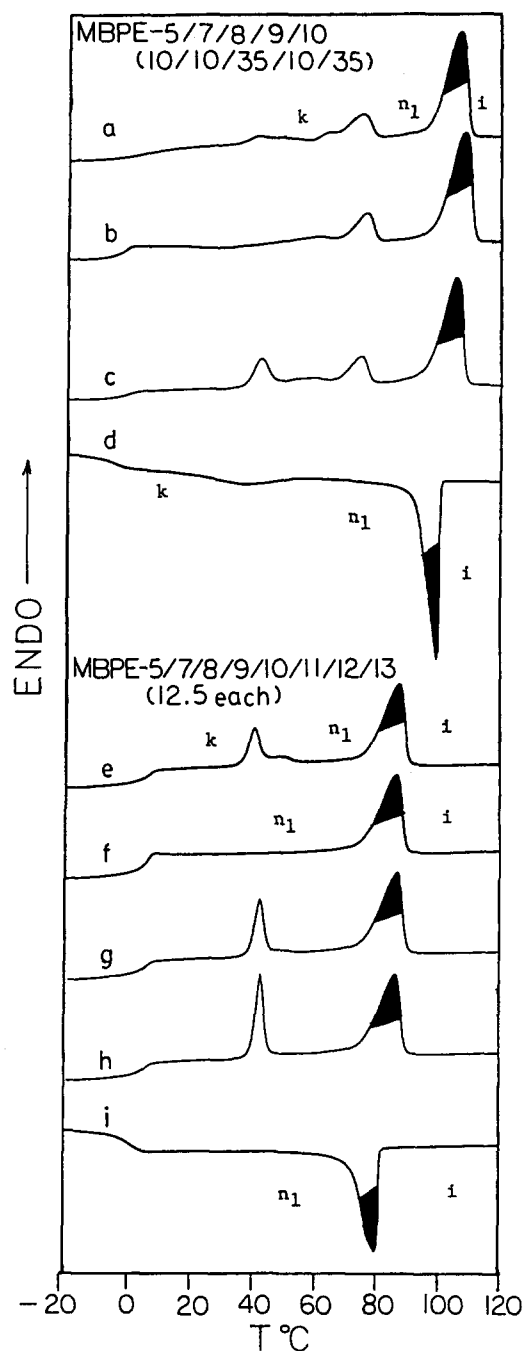


Figure 7 Representative d.s.c. scans of MBPE-5/7/8/9/10(10/10/35/10/35): (a) first heating scan; (b) second heating scan; (c) first heating scan after annealing 1 week at room temperature; (d) cooling scan; and of MBPE-5/7/8/9/10/11/12/13(12.5/12.5/12.5/12.5/12.5/12.5/12.5/12.5): (e) first heating scan; (f) second heating scan; (g) first heating scan after 12 h annealing at room temperature; (h) first heating scan after annealing 1 week at room temperature; (i) cooling scan

sions. All copolymers based on MBPE and multiple combinations of odd-odd, even-even and odd-even spacers display an n_1 mesophase and at least one crystalline phase. Both the experimental temperature transitions and the thermodynamic parameters associated with their n_1 mesophase represent weight-averaged values of the corresponding parameters of the parent homopolymers. This demonstrates that the structural units of these multiple copolymers are isomorphic within their n_1 mesophase. Copolymers based on MBPE and various combinations of spacers containing an odd

number of methylenic units display both n_2 and n_1 mesophases. The parameters of these mesophases behave in a similar way to those of the n_1 mesophase exhibited by the other copolymers. The crystallization tendency of these copolymers decreases with the increase of the number of flexible spacers in the copolymer and increases with the increase of the spacer lengths. Copolymers based on MBPE and spacers containing an even number of methylene units exhibit a higher tendency towards crystallization. Therefore, the lowest rate of crystallization is displayed by the copolymers based on multiple combinations of short flexible spacers all containing only an odd number of methylene units. It is our belief that no combination based on MBPE and multiple flexible spacers can lead to non-crystallizable copolymers. This behaviour can be understood if we consider that both the 'intermeshed' and the 'layered' crystalline phases can easily accommodate an infinite number of flexible spacers²⁴. These two crystalline morphologies should be more sensitive to multiple combinations of mesogens rather than multiple combinations of spacers.

These experiments have demonstrated that both the temperature transitions and the degree of order of the mesophase displayed by multiple copolymers based on MBPE and flexible spacers can be designed in advance. Last but not least, we can consider that a simple data point copolymerization experiment is sufficient to determine the virtual transition temperature and the enthalpy change of a homopolymer. This statement is supported by the good agreement between the experimental and calculated data, which are summarized in *Table 2*.

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