Liquid-crystalline polyethers based on conformational isomerism: 11. Isomorphism in liquid-crystal polyethers and copolyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane and α,ω-dibromoalkanes

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The isomorphism of polyether chains based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) and α,ω-dibromoalkanes (MBPE-X, MBPE-$X/Y(A/B)$ and MBPE-$X/Y/Z(A/B/C)$, where X, Y, Z are the number of methylene units in the spacer and $A/B/C$ the molar ratio between each spacer), most of which display virtual mesophases, was investigated in their crystalline and liquid-crystalline phases. Binary mixtures of polyethers with even–even, even–odd and odd–odd spacers, binary copolyethers and polyethers, binary copolyethers and copolyethers, ternary copolyethers and polyethers, and ternary mixtures of polyethers were all investigated. Out of 20 mixtures studied, only eight were isomorphic either within both their crystalline and liquid-crystalline phases or within only their liquid-crystalline or crystalline phases. The mixtures displaying isomorphism are: MBPE-7/MBPE-9, MBPE-8/MBPE-10, MBPE-5/13(50/50)/MBPE-9/11(50/50), MBPE-5(33)/MBPE-7(33)/MBPE-9(33), MBPE-5/7/9(33/33/33)/MBPE-5, MBPE-5/7/9(33/33/33)/MBPE-7, MBPE-8/10(50/50)/MBPE-8/16(50/50) and MBPE-5/7/9(33/33/33)/MBPE-9. In the case of mixtures of homopolymers, the tendency towards isomorphism increases with the decrease of the difference between the spacer length and parity. In the case of mixtures of copolymers with copolymers and of copolymers with homopolymers the tendency towards isomorphism increases by increasing the number of flexible spacers from the copolymer. By analogy with copolymers containing structural units that are isomorphous within mesomorphic phases, mixtures of polymer chains that display virtual mesophases and are isomorphic in their mesophase can be used to determine virtual mesomorphic phase transition temperatures and thermodynamic parameters of the parent homopolymers.

(Keywords: liquid crystal; polyethers; copolyethers; conformational isomerism; polymer chains; copolymer isomorphism; virtual mesophase)

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 unit[1–6]. Rigid rodlike mesogenic units exhibit an anisotropic elongated or rodlike conformation due to the conformational rigidity or semirigidity of the molecule (*Figure 1*).

In some previous publications from our laboratory, we have advanced the concept of rodlike mesogenic unit based on conformational isomerism or of flexible rodlike mesogenic unit (*Figure 1*)[7–16]. In the case of flexible rodlike mesogenic units, the elongated or rodlike conformation of the mesogen is accomplished and maintained by thermodynamics. Liquid-crystalline polyethers both without[7] and with[8–16] flexible spacers were designed based on this concept. These experiments have demonstrated that the synthesis of main-chain liquid-crystalline polymers does not require rigid rodlike mesogenic units.

Mesomorphic behaviour can be obtained for polymers containing flexible structural units that exhibit conformational isomerism when their most stable conformer adopts an extended linear conformation.

The examples of liquid-crystalline polyethers based on flexible mesogens and flexible spacers reported so far have used 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) as a mesogenic unit and α,ω-dibromoalkane-derived flexible spacers[8–16]. Based on thermodynamic reasons, which were detailed elsewhere[17], most of these polymers display virtual mesophases. The virtual mesophases of these polymers were determined by copolymerization experiments[8–16]. These experiments have used the isomorphism of the monomeric structural units of the copolymers in the liquid-crystalline phase as an avenue towards determination of the virtual mesophases displayed by the parent homopolymers. In principle, a similar technique can be developed by using the isomorphism of the homopolymer chains in their liquid-crystalline phase.

The goal of this paper is to determine and discuss the isomorphism of different pairs of polyethers and copoly-

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ethers based on MBPE and different α,ω-dibromoalkanes (MBPE-X and MBPE-$X/Y/Z(A/B/C)$ where X, Y, Z represent the number of methylene units in the spacer and $A/B/C$ refer to the molar ratio between the spacers). Most of these polymers display only virtual mesophases. The isomorphism of polymer chains within liquid-crystalline phases will be discussed by comparison with the isomorphism of monomeric structural units of copolymers based on similar combinations of flexible spacers. In order to avoid confusion, our discussion will

be preceded by a brief recapitulation of the concept of macromolecular isomorphism in crystalline polymers and of isomorphism in low-molar-mass liquid crystals. By analogy with macromolecular isomorphism in liquid-crystalline polymers, this discussion will recommend the use of a uniform nomenclature concerning macromolecular isomorphism in crystalline and liquid-crystalline polymers.

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

EXPERIMENTAL

Synthesis of polyethers and copolyethers

Polyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) and α,ω-dibromo-alkanes (MBPE-X, where X is the number of methylene units in the flexible spacer), binary copolyethers based on MBPE and two flexible spacers containing different numbers of methylene units (MBPE-$X/Y(A/B)$, where Y is the number of methylene units in the second flexible spacer and A/B is the molar ratio between the two spacers) and ternary copolyethers based on MBPE and three different flexible spacers (MBPE-$X/Y/Z(A/B/C)$, where X, Y, Z are the number of methylene units in each flexible spacer and $A/B/C$ the molar ratio between each flexible spacer) were synthesized and characterized by procedures reported in our previous publications[8-16]. *Figure 2* outlines the structure of the polymers and copolymers based on MBPE and α,ω-dibromoalkanes. *Table 1* summarizes their molar masses and phase transitions, and the literature in which the synthesis and the characterization of the corresponding polymer was presented in detail.

Preparation of polymer blends

The blends of the polyethers and copolyethers described in this paper were prepared by mixing the chloroform solutions of the polymers followed by precipitation into methanol. The precipitated polymers were filtered and dried in vacuum to constant weight.
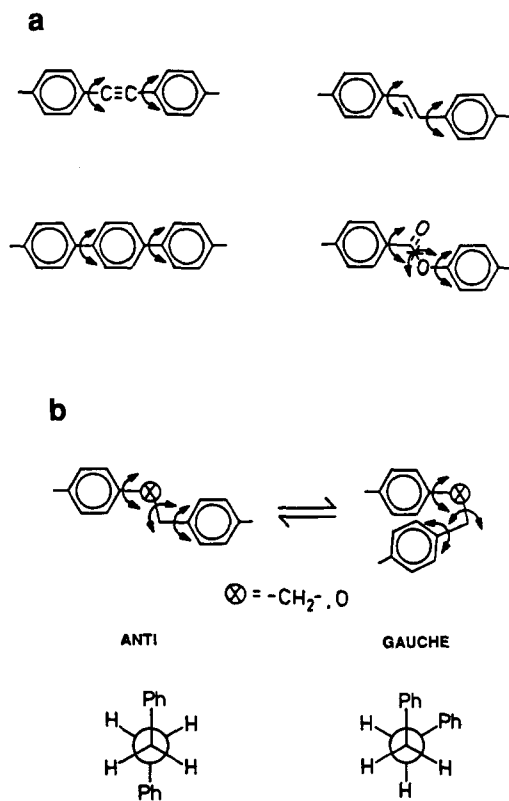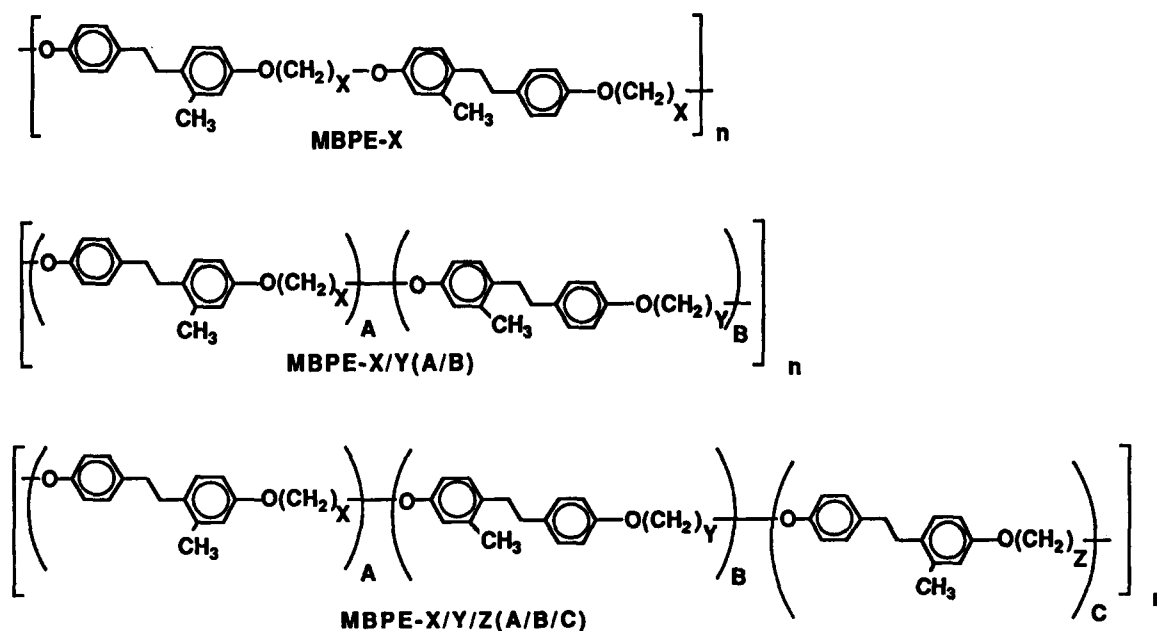

Figure 2 The structures of the polyethers and copolyethers based on MBPE and flexible spacers (α,ω-dibromoalkanes)

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

Polymer	G.p.c.		Thermal transitions (°C), and the corresponding enthalpy changes (kcal/mru^d) in parentheses		Ref.
	M_n	M_w/M_n	Heating	Cooling	
MBPE-5	19 000	1.90	g 20 n$_2$ [44 ± 2(0.14 ± 0.02)]^b 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	8
MBPE-7	27 700	1.82	g 9 k 85(2.41) i	i 68(2.27^a) n 65 k 7 g	This paper^c
MBPE-8	29 400	1.70	k 122 n 132(3.81^a) i	i 119(2.33 ± 0.15) n 116 k	14
MBPE-9	20 600	1.38	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	8
MBPE-10	14 100	2.27	n [113] k 121(7.20) i	i [103 ± 3(2.45 ± 0.11)] n 106(6.26) k	10, 11
MBPE-12	29 900	2.62	g 3 n [107] k 115(6.83) i	i 93(6.42) k [93 ± 6(2.85 ± 0.18)] n	10, 11
MBPE-14	17 900	1.66	k 108 k 114(7.38^a) i	i 96(6.59) k [87 ± 7(2.77 ± 0.21)] n	14
MBPE-5/8(50/50)	25 900	1.92	g 7 n 99(1.55) i	i 86(1.49) n – 1 g	11
MBPE-5/13(50/50)	20 400	1.70	g 9 k 54 k 59 k 65(2.13^a) k 74(0.18) i	i 59(1.03) n$_1$ 45(0.05) n$_2$ 31(0.44) k 3 g	13
MBPE-8/10(50/50)	31 600	1.92	g –4 k 88(1.21) k 99(1.06) n 122(2.48) i	i 109(2.57) n 70(1.77) k	10
MBPE-8/16(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	15
MBPE-9/11(50/50)	26 800	1.86	g 12 k 47(0.62) k 65 n$_2$ 71 n$_2$ 75 n$_1$ 82(1.08) i	i 71(1.17) n$_1$ 64(0.08) n$_2$ 22(0.24) k 4 g	8
MBPE-5/7/9(33/33/33)	18 300	1.38	g 11 n$_2$ 59(0.16) n$_1$ 70(0.75) i	i 63(0.72) n$_1$ 54(0.16) n$_2$ 6 g	12

^{a} Overlapping transition
^{b}[ ] virtual liquid-crystalline transition and thermodynamic parameters
^{c} MBPE-7 newly synthesized for this study shows a very narrow monotropic nematic phase. Previous data from ref. 8 was changed to present data
^{d} mru = mol repeat unit

Techniques

Molar masses were determined by gel permeation chromatography (g.p.c.). G.p.c. analyses were carried out with a Perkin–Elmer Series 10LC equipped with a LC100 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 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^{-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. All heating and cooling scans after the first heating scan produced perfectly reproducible data. A detailed discussion on the effect of the thermal history of the sample on phase transitions was presented in a previous publication[9]. The transitions reported in this manuscript 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 80 central processor was used to observe the thermal transitions and to analyse the textures[18].

RESULTS AND DISCUSSION

Macromolecular isomorphism and isomorphism in liquid crystals

Recently, the Commission on Macromolecular Nomenclature of the Macromolecular Division of the International Union of Pure and Applied Chemistry made the following recommendation concerning the definition of isomorphism in crystalline polymers[19]. Macromolecular isomorphism represents the statistical co-crystallization of different constitutional repeat units, which may either belong to the same copolymer chains (copolymer isomorphism) or originate from different homopolymer chains (homopolymer isomorphism). The isomorphism in crystalline polymers was discussed in

Table 2 Macromolecular isomorphism

1 Isomorphism of monomer structural units (copolymer isomorphism)
   1.1 Isomorphous units with different chemical constitution. The parent polymers are:
      1.1.1 Both crystalline, and display similar crystal structures
      1.1.2 Both crystalline, and display different crystal structures
      1.1.3 One crystalline and the other amorphous
   1.2 Isomorphous units with identical chemical constitution, but different configuration
      1.2.1 Opposite geometrical isomerism, i.e. atactic vinyl polymers
      1.2.2 Head-to-head and head-to-tail enchainment
   1.3 Isomorphous units with identical chemical constitution, but different conformations
      1.3.1 Different cis and trans contents

2 Isomorphism of chains (homopolymer isomorphism)
   2.1 Isomorphism of macromolecules with different chemical constitution
   2.2 Isomorphism of macromolecules having the same chemical and geometrical structure, but randomly different orientations in the crystalline lattice

several representative publications and reviews[20–24]. *Table 2* presents a classification of the macromolecular isomorphism in crystalline polymers, which is based on a detailed discussion available in the literature[23].

The most important conditions to be fulfilled in order to have isomorphism in a macromolecular system are: (a) the different types of monomer units must approximately have the same shape and occupy the same volume, and (b) the same chain conformation must be compatible with either of them. The physical properties of isomorphic homopolymers and of monomer structural units display a continuous dependence on composition, which for an ideal situation can be linear. There are many examples where the melting temperatures and other physical parameters of copolymers based on isomorphic structural units and of isomorphous pairs of homopolymers display a linear dependence on composition[22,23].

In the field of low-molar-mass liquid crystals, Arnold, Sackmann and Demus have developed the miscibility rules[25–28], which can be summarized as follows. If two liquid-crystalline phases are miscible, they are isomorphic, and therefore belong to the same type of mesophase. However, if two liquid-crystalline phases are immiscible, they are not isomorphic, but still may belong

to the same type of phase. Most identical mesophases displayed by low-molar-mass liquid crystals are isomorphous and therefore are miscible, regardless of their chemical structure. Consequently, these rules were extensively used to assign mesophases of low-molar-mass liquid crystals. The second application of these rules is derived from the fact that the phase transition temperatures of isomorphic or miscible liquid crystals display a continuous and, for ideal situations, a linear dependence on composition. Subsequently, isomorphic mixtures of low-molar-mass liquid crystals were used to determine virtual mesomorphic phase transitions of low-molar-mass liquid crystals[29,30].

More recently, these miscibility rules were applied to the identification of mesophases displayed by both main-chain and side-chain liquid-crystal polymers[31,32]. In this last case it is quite frequently encountered that identical mesophases of low-molar-mass liquid crystals and of polymers are not miscible and therefore are not isomorphous[31-39].

By analogy with the macromolecular isomorphism discussed for the case of crystalline polymers and summarized in *Table 2*, we suggest a classification of the isomorphism in liquid crystals, which should however consider both low-molar-mass liquid crystals and liquid-crystalline polymers. In the case of liquid crystals, besides the types of isomorphism similar to that described in points 1 and 2 in *Table 2*, we should consider two additional types, i.e. isomorphism of polymer chains with low-molar-mass liquid crystals and isomorphism of low-molar-mass liquid crystals. A detailed classification based on these assumptions is made in *Table 3*. We think that the isomorphism of chains should include not only homopolymer chains but also copolymers, as explained in points 2.1.1, 2.1.2 and 2.1.3. Eventually this modification should be considered also in *Table 2*. The most important condition to be fulfilled in order to have isomorphism in a liquid-crystal system is that the different types of monomer units should exhibit the same type of mesophase, similar chemical structures and chain conformations.

Since most low-molar-mass and macromolecular liquid crystals display both liquid-crystalline and crystal-line phases, their isomorphism should be considered independently in their crystalline (*Table 2*) and liquid-crystalline (*Table 3*) phases.

The isomorphism of low-molar-mass liquid crystals (no. 4 in *Table 3*) is well established and used, as described previously, to identify unknown mesophases[24-27] and determine virtual mesophases[29,30]. The isomorphism of liquid-crystal polymers with low-molar-mass liquid crystals (no. 3 in *Table 3*) was also investigated, and has been used mostly to assign mesophases in polymers[31-40]. There are very few examples where the isomorphism of polymer chains or the homopolymer isomorphism was investigated. We will cite two representative publications, which demonstrated that the nematic phases displayed by several different pairs of main-chain liquid-crystal polymers were miscible and therefore the nematic mesophases of these polymers were isomorphic[41,42]. In both cases investigated, the binary polymer mixtures were based on homopolymers containing either even or odd flexible spacers with small difference of their spacer lengths[41,42]. Mixtures of side-chain liquid-crystalline polymers were also investigated. Although in several cases identical mesophases displayed by two different polymers were miscible and therefore isomorphic, there are many examples in which blends of homopolymers revealed immiscibility and were non-isomorphic even in the cases where the two mesogenic groups were chemically similar[43,44].

From the category of isomorphism of monomer structural units or of copolymer isomorphism (no. 1 in *Table 3*) we will mention briefly several examples that are relevant to the present paper. It has been shown that main-chain liquid-crystalline copolymers based on one mesogenic unit and two flexible spacers display a single type of mesophase, which is identical to that of the parent homopolymers. Both the transition temperatures and thermodynamic parameters of this mesophase exhibit a weight-averaged, i.e. a linear, dependence on copolymer composition[41,45-50]. Therefore, the structural units of these copolymers are isomorphous. The isomorphism of the monomeric structural units of copolymers was used by us to develop a method for the determination of the virtual mesophases and thermodynamic parameters displayed by the polyethers based on MBPE and α,ω-dibromoalkanes[8-16]. This method is based on the following principles. Binary copolymers based on MBPE and two different flexible spacers are prepared to cover the entire range of composition. In most cases the structural units of these copolymers are isomorphous both within their crystalline and their identical liquid-crystalline phases. However, crystalline transition temperatures are suppressed upon copolymerization while liquid-crystalline transitions are not. Consequently, virtual liquid-crystalline transitions of homopolymers became monotropic or even enantiotropic upon copolymerization, and display a linear dependence of their parameters on copolymer composition. These linear dependences are extrapolated to the composition of each homopolymer in part, and the virtual thermal transition temperatures and thermodynamic parameters of these homopolymers are calculated. The following rule was established. If the thermal transition temperatures and thermodynamic parameters of a liquid-crystalline phase displayed by a copolymer exhibit a continuous, or under ideal conditions a linear, dependence on copolymer composition, then the structural units of the copolymer

Table 3 Isomorphism in liquid crystals

1   *Isomorphism of monomer structural units (copolymer isomorphism)*
    1.1   Isomorphous units with different chemical constitution. The parent polymers are:
        1.1.1   Both LC, and display identical LC phases
        1.1.2   Both LC, and display different LC phases
        1.1.3   One LC and the other LC or amorphous
    1.2   Isomorphous units with identical chemical constitution, but different configuration
        1.2.1   Opposite geometrical isomerism, i.e. atactic vinyl polymers
        1.2.2   Head-to-head and head-to-tail enchainment
    1.3   Isomorphous units with identical chemical constitution, but different conformations

2   *Isomorphism of chains (polymer isomorphism)*
    2.1   Isomorphism of macromolecules with different chemical constitution, but identical mesophases
        2.1.1   Isomorphism of homopolymers
        2.1.2   Isomorphism of homopolymers with copolymers
        2.1.3   Isomorphism of copolymers

3   *Isomorphism of polymers and low-molar-mass liquid crystals*

4   *Isomorphism of low-molar-mass liquid crystals*

are isomorphic within the corresponding liquid-crystalline phase. It has been demonstrated that this rule is obeyed also by ternary copolymers[12]. This class of isomorphisms refers to no. 1.1.1 in *Table 3*. So far, it has very important analytical and preparative implications, since it can be used both to determine virtual phase transition parameters and to tailor-make phase transitions in liquid-crystalline polymers.

The previous paper in this series reported the dependence of the virtual phase transition temperatures and thermodynamic parameters of the polyethers based on MBPE and α,ω-dibromoalkanes containing from 4 to 20 methylene units in the flexible spacers[16]. These virtual parameters were determined by copolymerization.

However, copolymerization does not provide us with information on the isomorphism of the parent homopolymer chains from which the copolymer structural units were derived.

Examples of isomorphous monomer structural units corresponding to nos. 1.1.2, 1.1.3, 1.2 and 1.3 from *Table 3* can easily be selected from the experimental data available in the literature. They are not relevant for the purpose of this paper, and therefore will be described at the proper time in further publications from our laboratory.

Isomorphism of MBPE polyethers

By analogy with our interest in the isomorphism of the monomer structural units, the interest in isomorphism of polymer chains is determined by two different reasons. First, the isomorphism of two different polymer chains in a certain liquid-crystalline phase can be used to tailor-make phase transition temperatures and polymer properties. Secondly, if two polymer chains are isomorphous within a virtual mesophase, we assume, by analogy with our experiments performed on copolymers, that their virtual mesophases can be determined and calculated by plotting the phase diagrams of the corresponding polymer mixtures.

In order to establish the capabilities of isomorphous polymer chains *versus* those of the isomorphous monomer structural units, we will investigate the isomorphism of binary and ternary mixtures of polymer chains based on MBPE and α,ω-dibromoalkanes. This class of isomorphism corresponds to no. 2 in *Table 3*. The systems investigated in this paper can be divided into five classes: binary mixtures of MBPE-X polyethers containing combinations of odd–odd, even–even and odd–even numbers of methylene units in their flexible spacers; binary mixtures containing a MBPE-$X/Y(A/B)$ copolyether and a MBPE-X polyether; binary mixtures of MBPE-$X/Y(A/B)$ copolyethers; ternary mixtures of MBPE-X homopolymers; and binary mixtures of MBPE-$X/Y/Z(A/B/C)$ ternary copolymers with MBPE-X polyethers.

As previously reported, all MBPE-X with X representing an even number of methylene units display a virtual nematic mesophase[8–16,51]. Only MBPE-8 displays a very narrow enantiotropic nematic mesophase[10,11,16]. Polyethers MBPE-X with X representing an odd number of methylene units display two virtual mesophases. The one at high temperature is a uniaxial nematic mesophase, while the one at lower temperature is a mesophase that has not yet been definitively identified. Since simultaneous d.s.c. and X-ray diffraction experiments[51] could not show any evidence for a smectic mesophase, we will

label the latter with n_2 and the first mesophase with n_1. MBPE-5 and MBPE-9 exhibit monotropic n_1 and n_2 mesophases, while MBPE-7 and MBPE-11 show a monotropic n_1 mesophase. *Table 1* summarizes the phase behaviour of all polyethers and copolyethers investigated in this paper. The monomer structural units of MBPE-$X/Y(A/B)$ copolymers containing any combination of even–even, odd–odd and odd–even flexible spacers are isomorphous within the n_1 mesophase. Only the monomer structural units of MBPE-$X/Y(A/B)$ copolymers containing odd–odd pairs of flexible spacers are isomorphous within their n_2 mesophase. The isomorphism of different pairs of polymer chains will be determined by miscibility studies using d.s.c. to establish the miscibility or the immiscibility of different polymer phases.

Binary pairs of MBPE-X polyethers with X = odd

Three pairs of mixtures of polyethers were investigated: MBPE-5 with MBPE-7, MBPE-5 with MBPE-9, and MBPE-7 with MBPE-9.

We will discuss the isomorphism of MBPE-5 with MBPE-7 based on the miscibility of the different phases as determined by d.s.c. experiments. *Figure 3a* displays representative d.s.c. cooling scans of different mixtures of MBPE-5/MBPE-7. MBPE-5 presents the isotropic–n_1 transition at 53°C and the n_1–n_2 transition at 38°C. MBPE-7 presents two overlapped peaks at 67 and 65°C. The first one is due to the onset of the isotropic–n_1 phase while the second is due to n_1–crystalline transition. Blends of different compositions show the presence of both the isotropic–n_1 peaks characteristic for both MBPE-5 and MBPE-7 and a crystallization peak. The n_1 phase from MBPE-5 is not miscible with the n_1 phase from MBPE-7, and therefore these two polymers are not isomorphous within their n_1 phase. *Figure 3b* presents the phase diagram resulting from the data collected from *Figure 3a*. The enthalpy changes of the transitions associated with the n_1 phases of MBPE-5 and MBPE-7 could not be calculated since the corresponding peaks are overlapped. However, we can observe at least qualitatively that the areas of these peaks are proportional to the amount of the corresponding sample in the polymer mixture.

Figure 4a presents representative d.s.c. cooling curves exhibited by different mixtures of MBPE-5 with MBPE-9. Both MBPE-9 and MBPE-5 display monotropic n_1 and n_2 mesophases. The investigation of the d.s.c curves from *Figure 4a* demonstrates that the n_1 phase of MBPE-5 is not miscible with the n_1 phase of MBPE-9, and the n_2 phase of MBPE-5 is not miscible with the n_2 phase of MBPE-9. Therefore MBPE-5 is not isomorphous with MBPE-9 in any of their phases. *Figure 4b* presents the corresponding phase diagram of the MBPE-5/MBPE-9 mixtures.

Finally, *Figure 5a* presents the d.s.c. cooling scans of MBPE-7/MBPE-9 mixtures. This figure demonstrates very clearly that these two polymers are isomorphous within their n_1, n_2 and crystalline phases. However, while the crystallization temperatures are decreased by comparison to those of the parent polymers, the n_1 and n_2 transition temperatures and the corresponding associated enthalpy changes display a linear dependence on blend composition. The phase diagram describing the thermal transition temperatures of these mixtures is presented in *Figure 5b* while the diagram presenting the thermo-
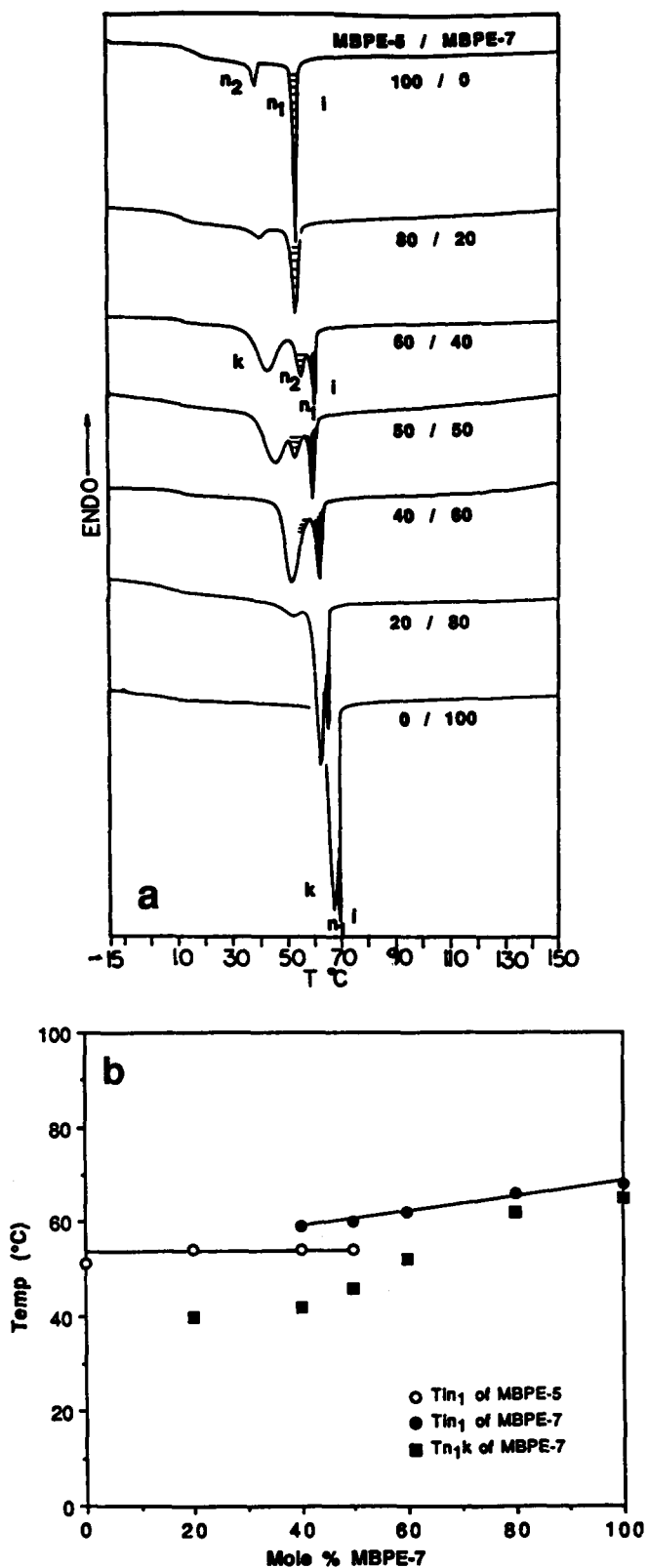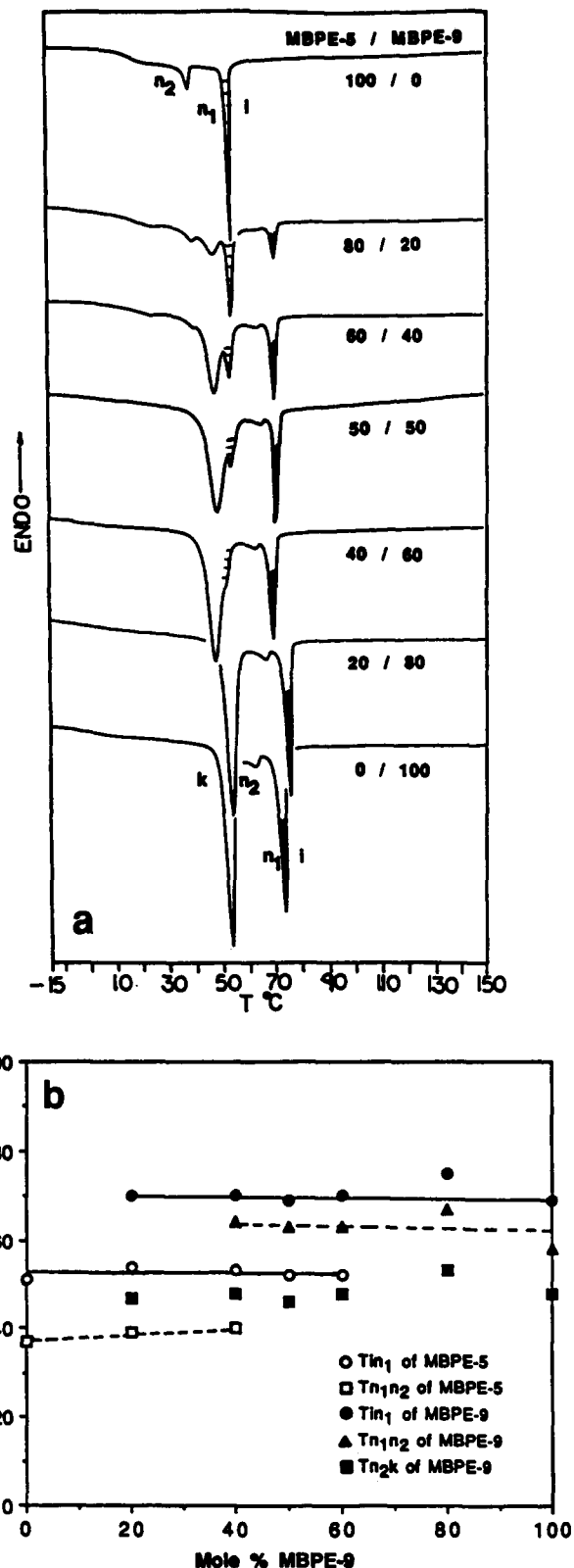
Figure 3 (a) Representative d.s.c. cooling scans of MBPE-5/MBPE-7 mixtures and (b) phase diagram of the mixtures of MBPE-5 with MBPE-7 as determined from these d.s.c. cooling curves

dynamic parameters is shown in *Figure 5c*. The extrapolations of the thermal transition temperatures from *Figure 5b* and of the thermodynamic parameters from *Figure 5c* lead to the determination of the virtual phase transitions and thermodynamic parameters of MBPE-7, which are: i [68(1.04)] n_1 67 k 65 k [59] $_2$. These results agree very well with the data obtained by copolymerization experiments which are reported in *Table 1*.

Binary pairs of MBPE-X polyethers with X = even

The following polymer mixtures were investigated: MBPE-8 with MBPE-10, MBPE-8 with MBPE-12, MBPE-8 with MBPE-14, and MBPE-10 with MBPE-12. D.s.c. cooling curves for MBPE-8/MBPE-10 mixtures are presented in *Figure 6a*. MBPE-10 is crystalline. The

Figure 4 (a) Representative d.s.c. cooling scans of MBPE-5/MBPE-9 mixtures and (b) phase diagram of the mixtures of MBPE-5 with MBPE-9 as determined from these d.s.c. cooling curves
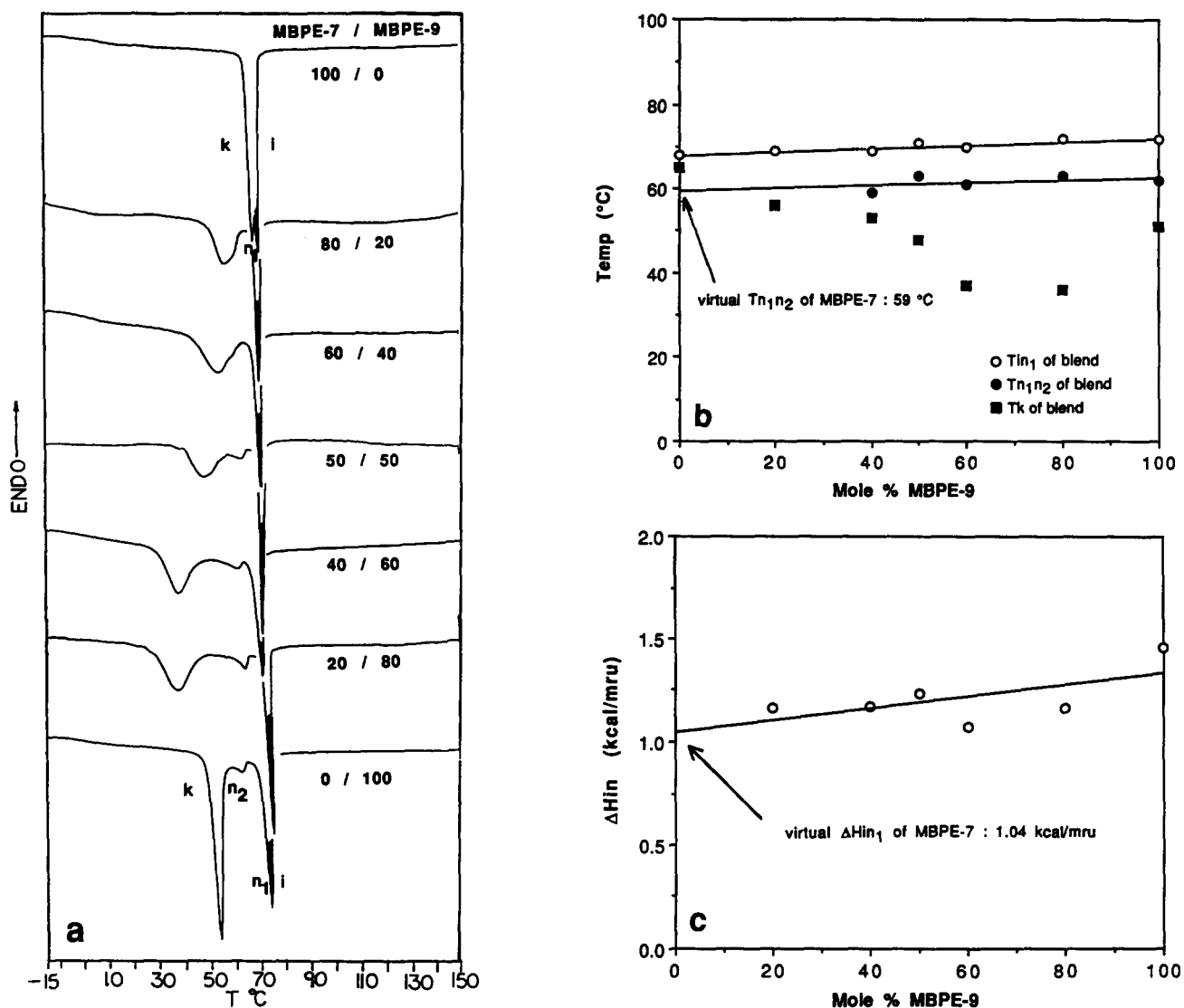
Figure 5 (a) Representative d.s.c. cooling scans of MBPE-7/MBPE-9 mixtures and (b) phase diagrams of MBPE-7/MBPE-9 mixtures as determined from these d.s.c. cooling curves; (c) enthalpy changes associated with the isotropic–n_1 phase

crystallization peak of MBPE-10 is at 106°C. MBPE-8 displays a very narrow enantiotropic mesophase, which overlaps the crystallization peak. The isotropic–nematic transition of MBPE-8 is at 119°C, while the nematic–crystalline transition is at 116°C. Upon blending MBPE-10 with MBPE-8, the crystallization peak of MBPE-10 splits into an isotropic–nematic peak and a nematic–crystalline peak. Approaching compositions close to pure MBPE-8, we can observe that the nematic phases displayed by the two polymers are miscible, while the crystalline phases are not. Blends with compositions of MBPE-8/MBPE-10 from 80/20 to 50/50 display a single peak due to the isotropic–nematic transition and two crystallization peaks; one of these is due to the crystallization of MBPE-8 and the other is due to the crystallization of MBPE-10. Therefore, MBPE-8 and MBPE-10 are isomorphous within their nematic phase but not within their crystalline phase. The phase diagrams from *Figures 6b* and *6c* allowed the determination of the virtual isotropic–nematic phase transition temperature of MBPE-10, i.e. i [104] n 106(6.26) k. This value agrees well with that determined by copolymerization experiments, which is presented in *Table 1*.

MBPE-8/MBPE-12, MBPE-8/MBPE-14 and MBPE-

10/MBPE-12 pairs are immiscible in both their crystalline and liquid-crystalline phases and therefore are not isomorphic in any of these phases. *Figures 7a* and *7b* present some representative examples of cooling d.s.c. traces for the systems MBPE-8/MBPE-12 (*Figure 7a*) and MBPE-8/MBPE-14 (*Figure 7b*).

Binary pairs of MPBE-X polyethers based on odd and even spacers

The following mixtures were investigated: MBPE-8/MBPE-9, MBPE-7/MBPE-8, MBPE-5/MBPE-8 and MBPE-7/MBPE-10. None of these mixtures are isomorphic in their liquid-crystalline or crystalline phases. Representative examples of d.s.c. cooling scans for the system MBPE-8/MBPE-9 are presented in *Figure 8*. These d.s.c. traces demonstrate that none of the liquid-crystalline or crystalline phases of these polymers are miscible. Only a better separation of the nematic and crystalline phases displayed by MBPE-8 is obtained upon blending.

Binary pairs of binary MBPE-X/Y(A/B) copolymers with MBPE-X polymers

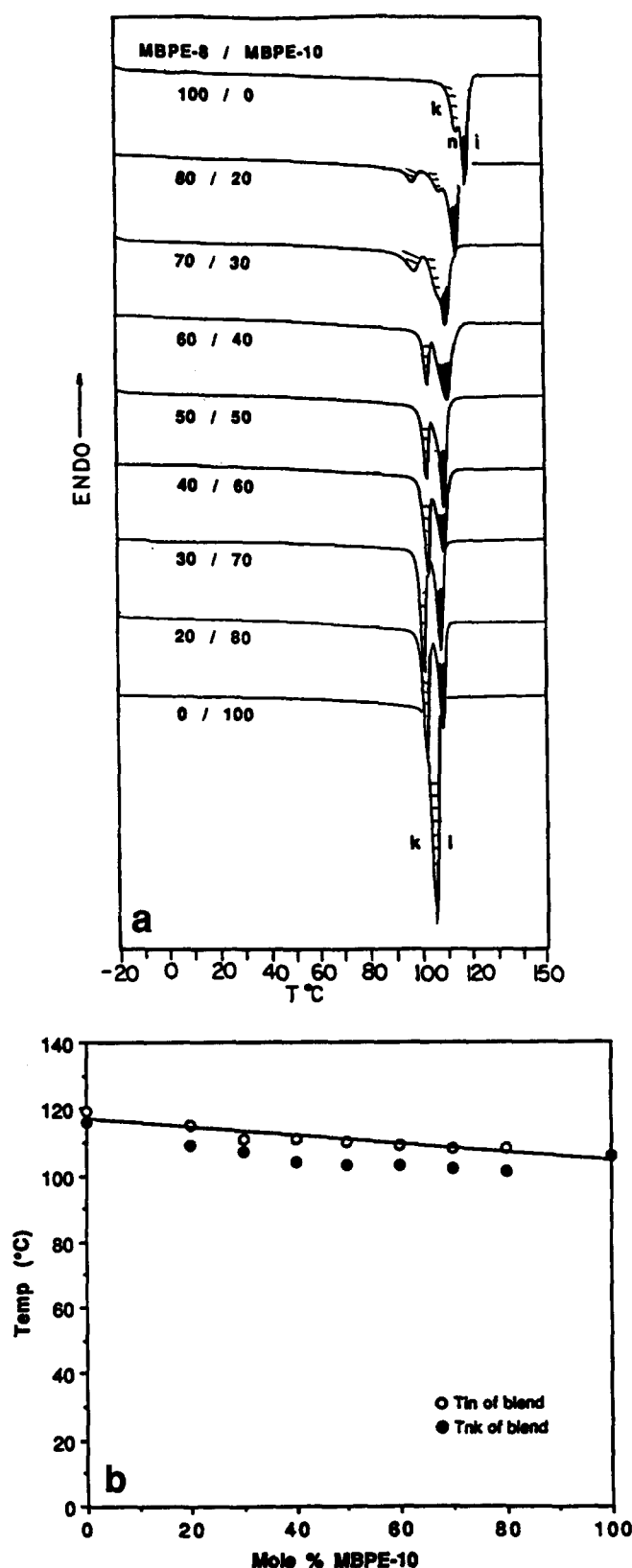The following two systems were investigated: binary

Figure 6 (a) Representative d.s.c. cooling scans of MBPE-8/MBPE-10 mixtures and (b) phase diagram of MBPE-8/MBPE-10 mixtures

mixtures of MBPE-5/8(50/50) with MBPE-5 and with MBPE-8. MBPE-5/8(50/50) displays an enantiotropic mesophase[11], MBPE-5[8] a monotropic n_1 and a monotropic n_2 while MBPE-8[10,11] an enantiotropic n_1 mesophase. *Figure 9a* presents representative d.s.c. cooling scans of MBPE-5/8(50/50)/MBPE-5 mixtures. The isotropic–n_1 transition of MBPE-5/8(50/50) appears

at 86°C and is almost independent of the blend composition. The isotropic–n_1 transition of MBPE-5 is at 53°C. The n_1–n_2 transition of MBPE-5 is at 38°C. Both are almost independent of the blend composition. Therefore, this pair of polymers does not show isomorphism in any of their phases. *Figure 9b* presents representative d.s.c. cooling scans of MBPE-5/8(50/50)/ MBPE-8 blends. The n_1 phase of MBPE-8 is immiscible with the n_1 phase of MBPE-5/8(50/50) and therefore the two polymers are not isomorphic within their n_1 phase.

Binary pairs of binary MBPE-X/Y(A/B) copolymers

The following pairs of mixtures of copolymers were investigated: MBPE-5/13(50/50)/MBPE-9/11(50/50), MBPE-8/16(50/50)/MBPE-9/11(50/50) and MBPE-8/10(50/50)/MBPE-8/16(50/50). The phase behaviours of these copolymers are summarized in *Table 1*.

The polymer mixture MBPE-5/13(50/50)/MBPE-9/11(50/50) is isomorphic within both the n_1 and n_2 mesophases. MBPE-8/16/(50/50)/MBPE-9/11(50/50) is not miscible in any of their crystalline or liquid-crystalline phases.

The polymer blend based on MBPE-8/10(50/50) with MBPE-8/16(50/50) displays an unexpected behaviour. Representative d.s.c. cooling scans of these blends are presented in *Figure 10*. Both copolymers present an n_1 and a crystalline phase. The nematic phase of MBPE-8/10(50/50) is not miscible with the nematic phase of MBPE-8/16(50/50). However, the crystalline phases are. Therefore, these two copolymers are not isomorphic within their nematic phase but are isomorphic within their crystalline phase.

Ternary mixtures of MBPE-X polymers and binary mixtures of MBPE-X/Y/Z(A/B/C) ternary copolymers with MBPE-X polymers

The following systems were studied: a ternary mixture of MBPE-5 with MBPE-7 and MBPE-9 (33/33/33 wt% ratio), and binary mixtures of MBPE-5/7/9(33/33/33) with MBPE-5, MBPE-7 and MBPE-9 (all in 50/50 wt% ratios). Their d.s.c. cooling traces are presented in *Figure 11*. It is interesting to observe that MBPE-5/MBPE-7 and MBPE-5/MBPE-9 mixtures were not miscible in their mesomorphic phases. Only MBPE-7/MBPE-9 blends were isomorphic in both their crystalline and liquid-crystalline phases. However, the ternary mixture MBPE-5(33)/MBPE-7(33)/MBPE-9(33) is miscible within both n_1 and n_2 and in their crystalline phases. In fact, the d.s.c. trace of their mixture resembles the one displayed by the MBPE-5/7/9(33/33/33) copolymer. The suppression of the crystallization peak by blending is less pronounced than that obtained by copolymerization (*Figure 11*). Therefore, while some binary mixtures of polymers are not isomorphous, their ternary mixtures are isomorphous in both their two different liquid-crystalline phases and their crystalline phase. At the same time, the ternary copolyether MBPE-5/7/9(33/33/33) is isomorphous in both its mesomorphic phases with each of its parent homopolymers, i.e. MBPE-5, MBPE-7 and MBPE-9 (*Figure 11*).

The isomorphism displayed by all MBPE polymer chains investigated in this paper is summarized in *Table 4*.

CONCLUSIONS

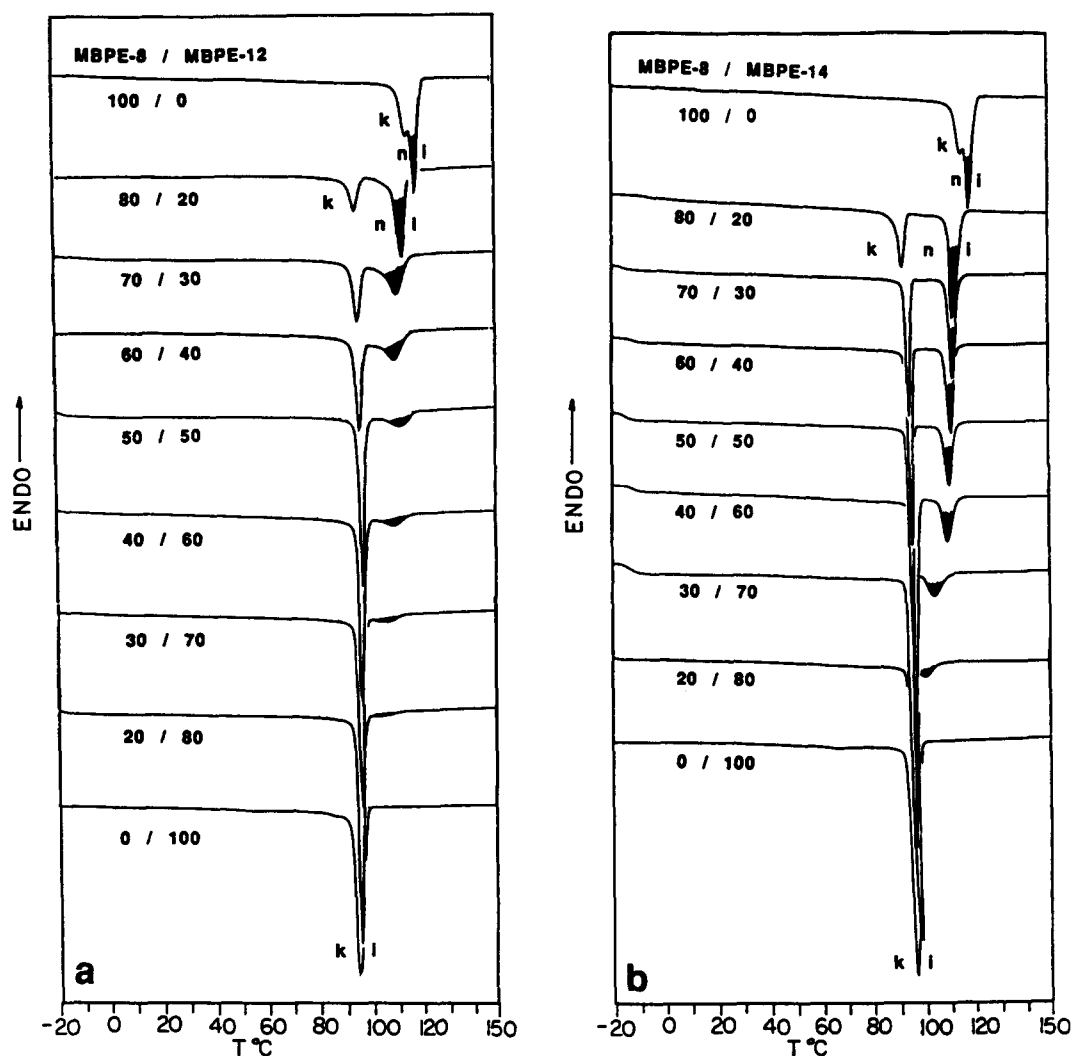Unlike similar mesophases of low-molar-mass liquid

Figure 7 Representative d.s.c. cooling scans of (a) MBPE-8/MBPE-12 mixtures and (b) MBPE-8/MBPE-14 mixtures

Table 4 Isomorphism of MBPE-based polyether and copolyether chains in different liquid-crystalline and crystalline phases (+ = isomorphic, − = non-isomorphic)

Polymer mixture	Isomorphism in phase		
	n_1	n_2	K
MBPE-5/MBPE-7	−	−	−
MBPE-5/MBPE-9	−	−	−
MBPE-7/MBPE-9	+	+	+
MBPE-8/MBPE-10	+		−
MBPE-8/MBPE-12	−		−
MBPE-8/MBPE-14	−		−
MBPE-10/MBPE-12	−		−
MBPE-8/MBPE-9	−	−	−
MBPE-7/MBPE-8	−	−	−
MBPE-5/MBPE-8	−	−	−
MBPE-7/MBPE-10	−	−	−
MBPE-5/8(50/50)/MBPE-5	−	−	−
MBPE-5/8(50/50)/MBPE-8	−	−	−
MBPE-5/13(50/50)/MBPE-9/11(50/50)	+	+	ND
MBPE/16(50/50)/MBPE-9/11(50/50)	−	−	−
MBPE-8/10(50/50)/MBPE-8/16(50/50)	−		+
MBPE-5(33)/MBPE-7(33)/MBPE-9(33)	+	+	+
MBPE-5/7/9(33/33/33)/MBPE-5	+	+	+
MBPE-5/7/9(33/33/33)/MBPE-7	+	+	+
MBPE-5/7/9(33/33/33)/MBPE-9	+	+	+

ND = Could not be determined

crystals, which are isomorphous regardless of their chemical structure, polymer chains of MBPE-based polyethers and copolyethers are isomorphous in very few similar mesophases. Out of 20 mixtures of polymers investigated, only the MBPE-7/MBPE-9 mixtures are isomorphic in both mesophases displayed by the two polymers. MBPE-8/MBPE-10 mixtures are isomorphic in their liquid-crystalline nematic phase and non-isomorphic in their crystalline phase. None of the mixtures of MBPE-X polymers containing even and odd flexible spacers of almost similar lengths were isomorphous. This may represent the result of the different conformational coupling between the spacer and mesogen in the odd and even series[16,52]. The binary mixtures of MBPE-5/13(50/50)/MBPE-9/11(50/50) are isomorphous in both of their mesomorphic phases. The ternary mixture of MBPE-5(33)/MBPE-7(33)/MBPE-9(33) and the binary mixtures MBPE-5/7/9(33/33/33) with MBPE-5, MBPE-7 and MBPE-9 are isomorphous in their two liquid-crystalline phases and in the crystalline phase. The binary mixture of MBPE-8/10(50/50)/MBPE-8/16(50/50) is not isomorphous in the nematic phase but is isomorphous in the crystalline phase. Therefore, the isomorphism of liquid-crystal polymer chains should be considered independently for the crystalline and liquid-crystalline phases. By analogy with
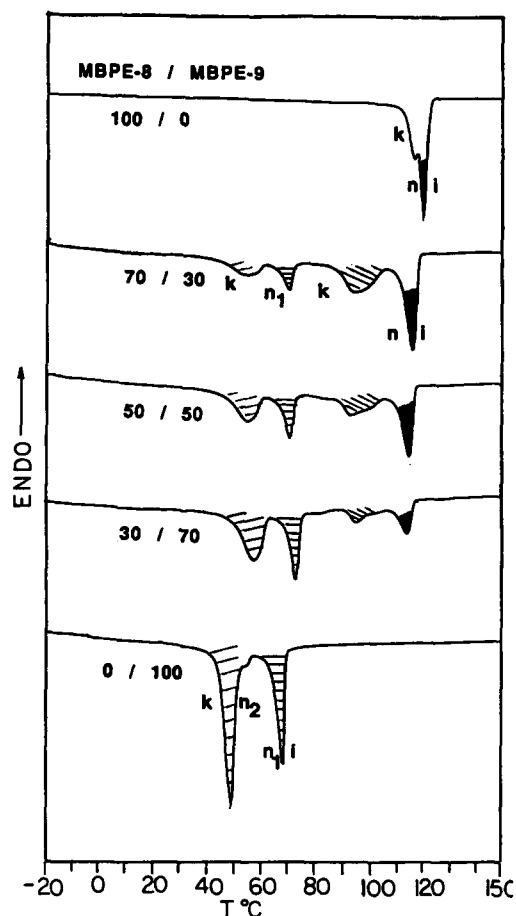
Figure 8 Representative d.s.c. cooling scans of MBPE-8/MBPE-9 mixtures

MBPE-$X/Y(A/B)$ copolymers displaying isomorphic structural units in selected mesophases, when polymer chains based on MBPE are isomorphous in a certain mesophase they can be used to determine the virtual mesophases displayed by the parent homopolymers. Upon blending isomorphic polymer pairs, their virtual mesophases can be transformed into monotropic or even enantiotropic mesophases. The thermal transition temperatures and thermodynamic parameters associated with isomorphic mesophases show a linear dependence on polymer mixture composition. The crystallization temperatures of the isomorphous polymer chains are decreased *versus* those of the parent homopolymers. This decrease is lower than in the corresponding copolymers. For binary mixtures based on homopolymers containing either odd or even number of methylene units in their flexible spacer, the tendency towards isomorphism increases with the decrease of the difference between the spacer lengths. Isomorphous polymer chains were not observed for pairs of polymers containing even and odd spacer lengths. Ternary mixtures of homopolymers and binary mixtures of ternary copolymers with homopolymers show higher tendency towards isomorphism than their binary mixtures of homopolymers or of binary mixtures containing copolymers and homopolymers. Although mixtures of isomorphic polymer chains can be used to determine virtual mesophases of parent polymers and to tailor-make their phase transition temperatures, they are much less powerful than the corresponding copolymers displaying isomorphous monomeric structural units.
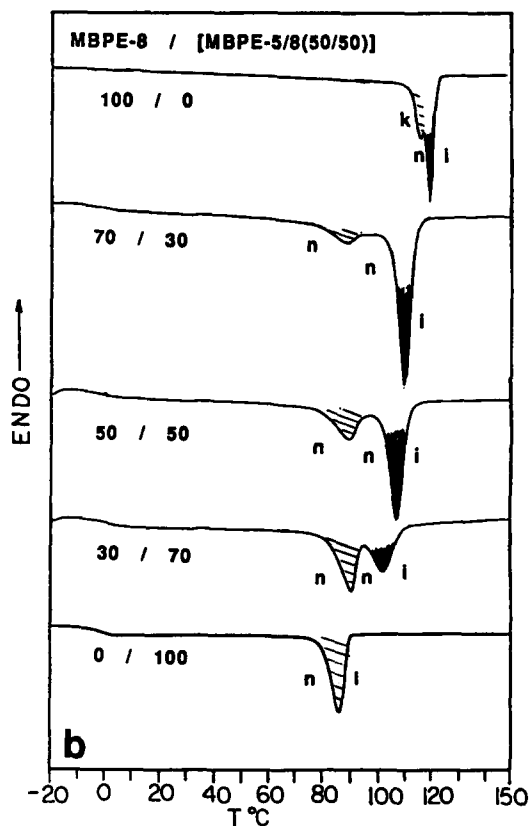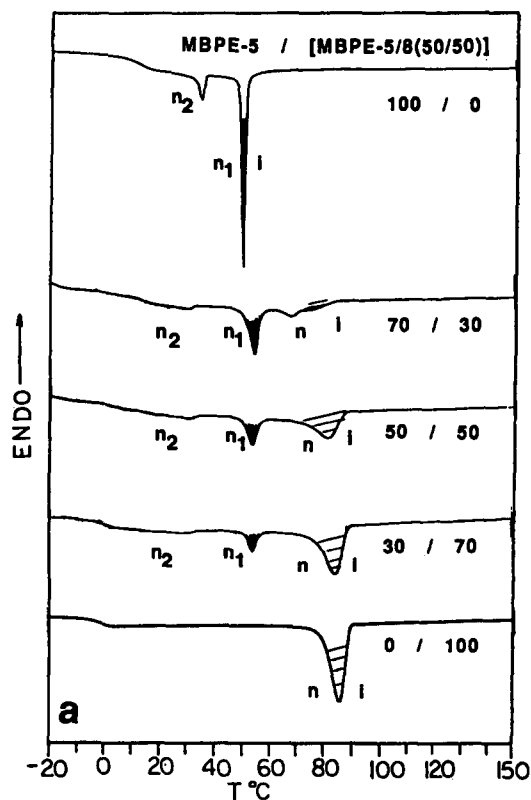

Figure 9 Representative d.s.c. cooling scans of (a) MBPE-5/8(50/50)/MBPE-5 mixtures and (b) MBPE-5/8(50/50)/MBPE-8 mixtures
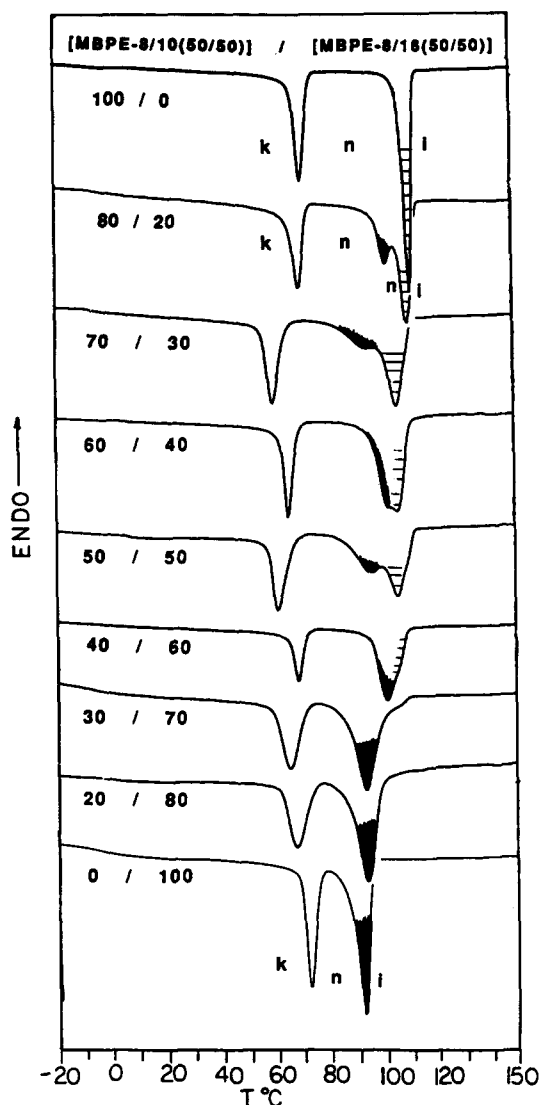
Figure 10 Representative d.s.c. cooling scans of MBPE-8/10(50/50)/MBPE-8/16(50/50) mixtures
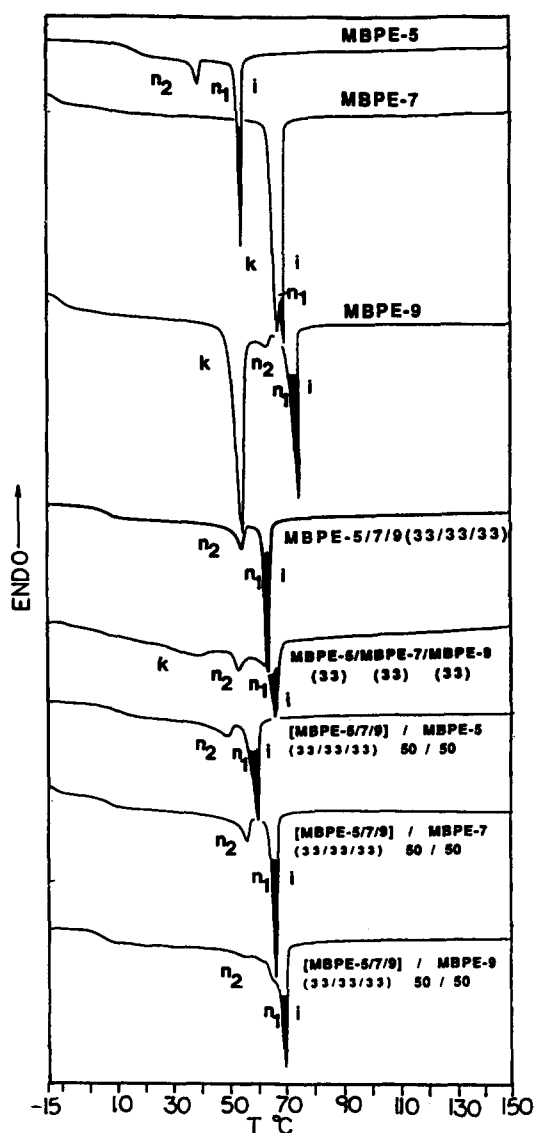

Figure 11 D.s.c. cooling traces of MBPE-5, MBPE-7 and MBPE-9 polymers, MBPE-5/7/9(33/33/33) copolymer, MBPE-5(33)/MBPE-7(33)/MBPE-9(33) ternary mixture, and MBPE-5/7/9(33/33/33)/MBPE-5 (50/50 mixture), MBPE-5/7/9(33/33/33)/MBPE-7 (50/50 mixture) and MBPE-5/7/9(33/33/33)/MBPE-9 (50/50 mixture) binary mixtures

ACKNOWLEDGEMENT

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