Liquid Crystalline Polyethers Based on Conformational Isomerism. 20.[†] Nematic–Nematic Transition in Polyethers and Copolyethers Based on 1-(4-Hydroxyphenyl)-2-(2-R-4-hydroxyphenyl)ethane with R = Fluoro, Chloro, and Methyl and Flexible Spacers Containing an Odd Number of Methylene Units

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ABSTRACT: A new type of thermotropic phase transition occurring between two uniaxial nematic phases in a class of main-chain liquid crystalline polyethers and copolyethers is reported. The polymers exhibiting this phase transition are based on 1-(4-hydroxyphenyl)-2-(2-R-4-hydroxyphenyl)ethane where R = F, Cl, and CH_3 and flexible spacers containing an odd number of methylene units (RBPE-X where X is the number of methylene units in the flexible spacer). In homopolymers and copolymers based on a single mesogenic unit and three spacers containing 5, 7, and 9 methylene units in the molar ratio 33/33/33, the low-temperature nematic phase is monotropic. In copolymers based on two and three different mesogens (in the molar ratio $A/B/C$) and three different spacers containing 5, 7, and 9 methylenic units in the molar ratio 33/33/33 [i.e., FBPE/ClBPE/MBPE($A/B/C$)-5/7/9(33/33/33)] this mesophase is enantiotropic. The possible relationship between the two presently observed nematic phases and those theoretically predicted by Vasilenko et al.[11] is briefly considered.

Introduction

This paper deals with the unidentified sharp first-order thermal transition that has consistently been observed approximately 12–15 °C below the isotropic–nematic transition temperature, T_i, in a family of main-chain polyethers and copolyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) and flexible spacers containing an odd number of methylene units (MBPE-X, where X is the number of carbons in the spacer).[1] Recently the same phase transition was observed in the polyethers based on 1-(4-hydroxyphenyl)-2-(2-chloro-4-hydroxyphenyl)ethane (ClBPE) and flexible spacers containing an odd number of methylenic groups.[2] Originally this transition was tentatively labeled as nematic to smectic,[1a–c] but subsequent work had cast doubt on this assignment[3a,b] and this low-temperature phase was denoted with x or n_2.[1d–f] Studies of this unidentified phase transition have been hampered in the MBPE-X homopolymers and in copolymers based on MBPE and combinations of 2,[1a,b,d] 3,[1c] and more than 3[1f] flexible spacers by the fact that in most cases both the nematic and the x phases are only metastable (monotropic) with respect to the crystalline phase and, therefore, are relatively short-lived. However, fast time-resolved experiments by simultaneous synchrotron X-ray diffraction and differential scanning calorimetry (XDDSC)[3a,4] indicated that neither crystallization nor smectic or any other positional ordering occurred on cooling through the sharp n–x phase transition. Only unoriented samples have been studied by XDDSC, since any effort at producing oriented fibers resulted in polymer crystallization. Similarly, the development of characteristic optical textures was preempted by crystal formation.

As further progress on identification of phase x depended on the ability to additionally depress the crystal melting point, T_m, an attempt was made to produce copolymers whose structural units contain not only different spacer lengths but also different RBPE mesogenic units. This synthetic route has proved successful in reducing the melting transition, T_m, well below the n–x temperature or even below the glass transition temperature, thus enabling the present and future studies of the x and n phases at equilibrium. This paper reports the first results, foremost of which is the confirmation that the x phase is a second uniaxial nematic phase.

Experimental Section

Materials. 1,5-Dibromopentane (97%), 1,7-dibromoheptane (97%), 1,9-dibromononane (97%), tetrabutylammonium hydrogen sulfate (TBAH, 97%), and *o*-dichlorobenzene (97%) (all from Aldrich) were used as received. 1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE),[1a] 1-(4-hydroxyphenyl)-2-(2-chloro-4-hydroxyphenyl)ethane (ClBPE),[5] and 1-(4-hydroxyphenyl)-2-(2-fluoro-4-hydroxyphenyl)ethane (FBPE)[5] all of higher purity than 99.9% (HPLC) were synthesized as reported previously.

Synthesis of Copolyethers. The synthesis of copolyethers based on a 33/33/33 molar ratio of 1,5-dibromopentane, 1,7-dibromoheptane, and 1,9-dibromononane and various combinations of FBPE, ClBPE, and MBPE in the $A/B/C$ molar ratio [FBPE/ClBPE/MBPE($A/B/C$)-5/7/9(33/33/33)] is outlined in Scheme I. All copolymers were synthesized by liquid–liquid phase-transfer-catalyzed polymerization reactions. The polyetherifications were carried out under nitrogen atmosphere at 80 °C in an *o*-dichlorobenzene/10 N aqueous NaOH mixture (10-fold molar excess of NaOH versus phenol groups) in the presence of TBAH (20 mol % of the phenol groups) as the phase-transfer catalyst. The molar ratio of nucleophilic to electrophilic monomers was in every case 1.0/1.0. After 12 h of reaction, the organic and aqueous layers were diluted with chloroform and water, respec-

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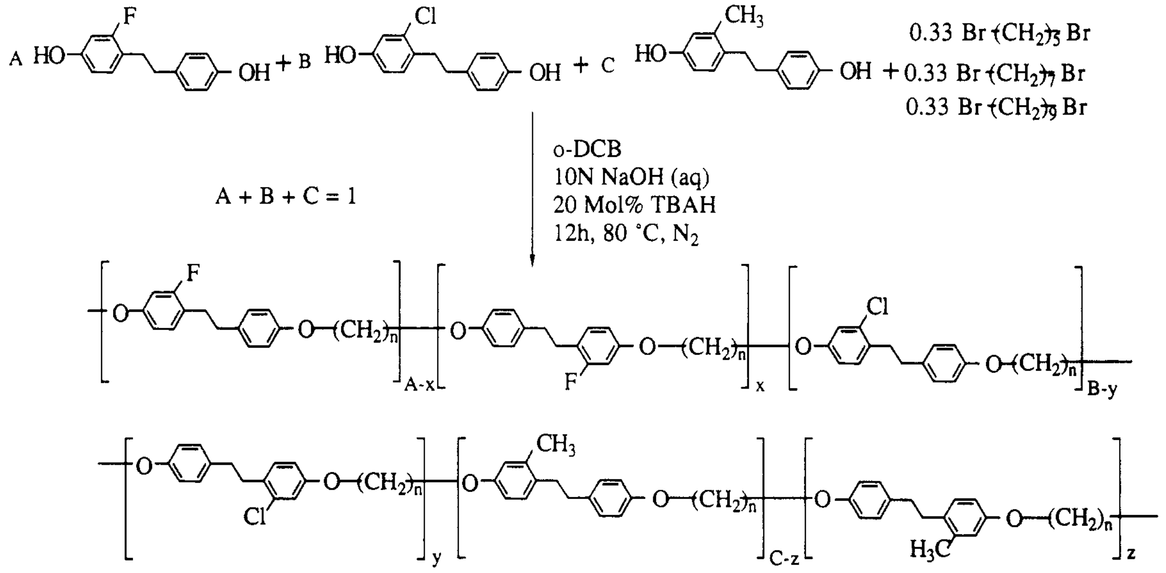
Scheme I
Copolymerization of FBPE, ClBPE, and MBPE (in an *A/B/C* Molar Ratio) with a 33/33/33 Molar Ratio of 1,5-Dibromopentane, 1,7-Dibromoheptane, and 1,9-Dibromononane



tively. The organic layer was separated and washed several times with water, dilute HCl, and finally with water. The polymer was separated by precipitation into methanol. The yields were always higher than 90%. The polymer was purified by successive precipitation from chloroform solution into acetone, from tetrahydrofuran solution into water, and finally from chloroform solution into methanol to yield a white fibrous precipitate. The noncrystallizable polymers separated as a viscous gum.

Techniques. Relative molecular weights were determined by gel permeation chromatography (GPC). GPC analyses were carried out with a Perkin-Elmer Series 10LC instrument equipped with an LC-100 column oven, LC-600 autosampler, and a Nelson Analytical 900 Series data station. Measurements were made by using a UV detector, chloroform as solvent (1 mL/min, 40 °C), a set of PL gel columns of 500 and 10^5 Å, and a calibration plot constructed with polystyrene standards (Supelco).

A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine the thermal transitions. Heating and cooling rates were 20 °C/min in all cases. First-order transitions (crystalline–crystalline, crystalline–liquid crystalline, liquid crystalline–isotropic, etc.) were read at the maximum or minimum of the endothermic or exothermic peaks. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. For all other copolymers with the exception of FBPE/ClBPE/MBPE(33/33/33)-5/7/9(33/33/33) first heating scans differ from the second heating scans. This difference will be discussed.

A Carl Zeiss optical polarizing microscope (magnification 100×) equipped with a Mettler FP-82 hot stage and a Mettler 800 central processor was used to observe the thermal transitions and to analyze the polymer textures.[6]

Fibers for the X-ray scattering experiments were produced by heating the polymer into the isotropic phase and then cooling through the nematic range to 10–20 °C and drawing. A flat-plate camera with a temperature-controlled cell (±0.1 °C) and Ni-filtered Cu Kα radiation was used to record the patterns. For unoriented samples a Philips diffractometer equipped with an evacuated temperature cell and a crystal monochromator was used.

Results and Discussion

Previous experiments have demonstrated that the x phase of MBPE-*X* can be transformed from monotropic into enantiotropic by synthesizing MBPE copolymers containing 1,5-dibromopentane, 1,7-dibromoheptane, and 1,9-dibromononane in a molar ratio of 33/33/33.[1c] However, upon annealing MBPE-5/7/9(33/33/33) crystallizes and the crystalline melting is close to the x phase. Increasing the number of flexible spacers in the MBPE copolymers does not decrease their ability toward crystallization.[1f] Therefore, the next series of experiments required the use of various combinations of RBPE mesogenic groups and the same combination of flexible spacers. ClBPE-*X* polymers containing an odd number of carbons in the flexible spacer exhibit the same x phase[2] as MBPE-*X* polymers.[1d] Figure 1 presents the first and second heating and the first cooling DSC scans of the FBPE/ClBPE/MBPE(A/B/C)-/5/7/9(33/33/33) copolymers. All heating and cooling scans following the first heating scan are identical. After annealing the first heating can be reestablished. Therefore, the first heating scan corresponds to a quasi-equilibrium situation.

Let us discuss very briefly the DSC traces of the copolymers from Figure 1. The corresponding phase transition temperatures are summarized in Table I. FBPE/ClBPE/MBPE(100/0/0)-5/7/9(33/33/33) exhibits only the high-temperature nematic mesophase (n_1). FBPE/ClBPE/MBPE(0/100/0)-5/7/9(33/33/33) behaves almost similarly to FBPE/ClBPE/MBPE(0/0/100)-5/7/9(33/33/33).[1c] That is in the first heating scan it exhibits a crystalline phase followed by the high-temperature nematic (n_1) phase. Subsequent heating and cooling scans exhibit only the two n_1 and n_2 mesophases and a glass transition temperature. Upon annealing above its glass transition temperature the copolymer crystallizes. Both FBPE/ClBPE/MBPE(50/50/0)-5/7/9(33/33/33) and FBPE/ClBPE/MBPE(50/0/50)-5/7/9(33/33/33) display enantiotropic n_1 and n_2 mesophases and a low-temperature crystalline phase. FBPE/ClBPE/MBPE(0/50/50)-5/7/9(33/33/33) shows a lower tendency toward crystallization. Finally, regardless of the thermal history of the sample FBPE/ClBPE/MBPE(33/33/33)-5/7/9(33/33/33) does not crystallize and exhibits thermodynamically stable n_1 and n_2 phases. In all cases the n_1 and n_2 phases are separated by a highly reversible first-order transition. The temperatures, enthalpy, and entropy changes of these phases are summarized in Table I.

X-ray scattering patterns of FBPE/ClBPE/MBPE(33/33/33)-5/7/9(33/33/33) and FBPE/ClBPE/MBPE(0/50/50)-5/7/9(33/33/33) fibers were recorded both before and after annealing below T_{in}. It was established that annealing had no effect on the pattern of FBPE/ClBPE/

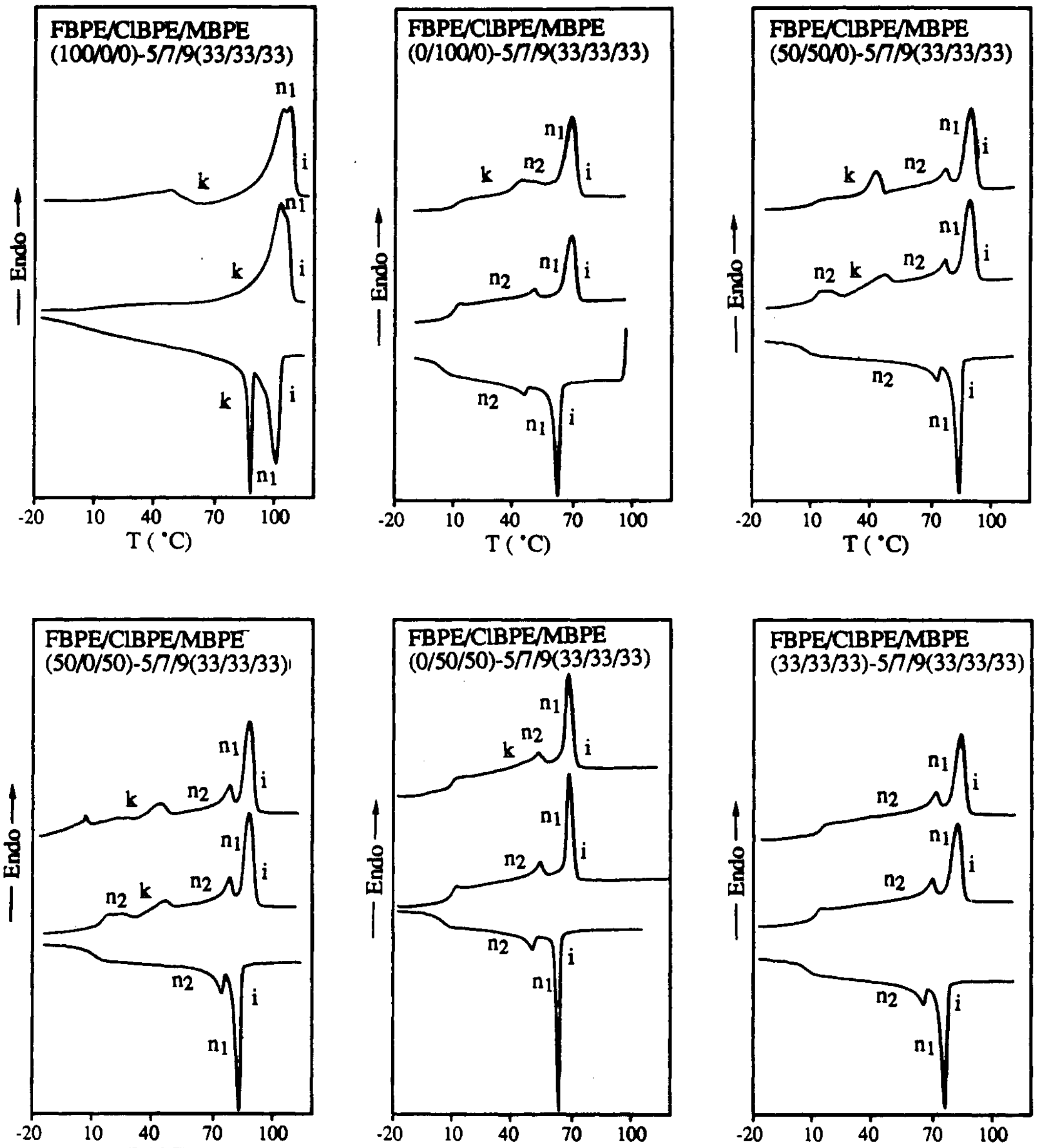


Figure 1. First heating (top curve in each figure), second heating (second curve in each figure), and cooling (third curve in each figure) DSC traces of FBPE/ClBPE/MBPE(*A*/*B*/*C*)-5/7/9(33/33/33) copolymers. The composition of the copolymer is on the top part of each figure.

MBPE(33/33/33)-5/7/9(33/33/33), while prolonged annealing induces partial crystallization in the case of FBPE/ClBPE/MBPE(0/50/50)-5/7/9(33/33/33). Room-temperature scattering photographs of unannealed or briefly annealed FBPE/ClBPE/MBPE(0/50/50)-5/7/9(33/33/33) and FBPE/ClBPE/MBPE(33/33/33)-5/7/9(33/33/33) fibers are identical. Parts a and b of Figure 2 show, respectively, the patterns of unannealed FBPE/ClBPE/MBPE(0/50/50)-5/7/9(33/33/33) and of FBPE/ClBPE/MBPE(33/33/33)-5/7/9(33/33/33) annealed at 45° C for 2 h. Only a diffuse scattering can be seen.

The diffuse maxima in Figure 2a,b are not equatorial but are disposed in a characteristic four-point pattern, which indicates a staggered short-range packing of mesogens. From measured coordinates of the scattering maxima in reciprocal space and by applying simple Bragg's law, it can be crudely estimated that the average distance between chains is 4.8 Å and that the mesogens on neighboring chains are displaced by approximately 10 Å, or half the monomer repeat distance, along the fiber axis. Similar four-point patterns at wide scattering angles have also been observed in quenched fibers of certain MBPE copolymers.[7]

No trace of sharp reflections has been found either at wide or at low scattering angles in any fiber pattern of unannealed FBPE/ClBPE/MBPE(0/50/50)-5/7/9(33/33/33) or in either annealed or unannealed FBPE/ClBPE/MBPE(33/33/33)-5/7/9(33/33/33) polymers. A smectic fundamental is expected in the region of 20 Å: this is on the order of the monomer repeat and is in the range of smectic periodicities found in analogous polymers based on 1,2-bis(4-hydroxyphenyl)ethane (BPE) mesogen.[8] A 20-Å reflection would be well within the angular range covered by the patterns in Figure 2. Additional small-angle scattering patterns were also recorded, but no sign of larger periodicities were found either. In view of these findings, coupled with the established presence of optical birefringence in quiescent polymer at all temperatures below T_i, we can only conclude that phase x (i.e., n_2) is nematic.

Scattering patterns from unoriented samples of FBPE/ClBPE/MBPE(33/33/33)-5/7/9(33/33/33) could be recorded at close temperature intervals, since neither degradation (low T_i) nor crystallization could occur. The three experimental scattering curves in Figure 3a correspond to the three thermotropic phases of this polymer:

Table I
Characterization of Copolyethers Based on FBPE, ClBPE, and MBPE in an *A*/*B*/*C* Molar Ratio and 1,5-Dibromopentane, 1,7-Dibromoheptane, and 1,9-Dibromononane in a 33/33/33 Molar Ratio [FBPE/ClBPE/MBPE(*A*/*B*/*C*)-5/7/9(33/33/33)]

FBPE/ClBPE/MBPE(*A*/*B*/*C*)-5/7/9(33/33/33), (*A*/*B*/*C*) molar ratio	GPC		thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
	M_n	M_w/M_n		
100/0/0	21 000	2.01	1st heating	g 24 k 48 (0.08) k 102 n_1 106 (2.47[a]) i
			2nd heating	g 12 k 103 n_1 106 (2.76[a]) i
			cooling	i 99 (0.94) n_1 87 (1.55) k 1 g
0/100/0	18 600	1.98	1st heating	g 10 k 43 n_2 49 (0.20[a]) n_1 68 (1.10) i
			2nd heating	g 9 n_2 49 (0.14) n_1 68 (0.99) i
			cooling	i 60 (0.96) n_1 44 (0.18) n_2 3 g
50/50/0	20 300	1.85	1st heating	g 11 k 42 (0.29) n_2 76 (0.35) n_1 88 (1.15) i
			2nd heating	g 12 n_2 25 (0.14) k 46 (0.12) n_2 76 (0.25) n_1 88 (1.14) i
			cooling	i 82 (1.13) n_1 70 (0.41) n_2 6 g
50/0/50	24 200	1.92	1st heating	g 12 k 42 (0.24) n_2 77 (0.36) n_1 86 (1.10) i
			2nd heating	g 14 n_2 28 (0.07) k 44 (0.07) n_2 74 (0.39) n_1 86 (1.09) i
			cooling	i 81 (1.06) n_1 72 (0.36) n_2 8 g
0/50/50	17 400	2.32	1st heating	g 10 k 45 n_2 53 (0.27[a]) n_1 68 (1.00) i
			2nd heating	g 9 n_2 54 (0.27) n_1 68 (0.92) i
			cooling	i 62 (0.93) n_1 49 (0.22) n_2 4 g
33/33/33	28 000	2.34	1st heating	g 13 n_2 69 (0.34) n_1 82 (1.04) i
			2nd heating	g 11 n_2 69 (0.36) n_1 82 (1.04) i
			cooling	i 74 (1.09) n_1 63 (0.35) n_2 5 g

[a] Overlapping transition.

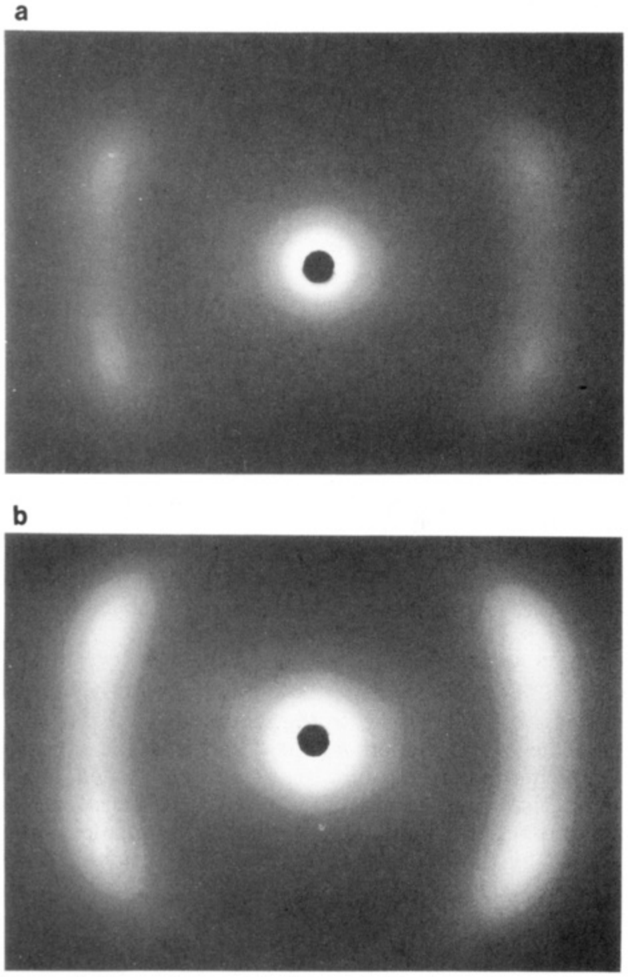


Figure 2. Room-temperature X-ray scattering patterns of unannealed FBPE/ClBPE/MBPE(0/50/50)-5/7/9(33/33/33) (a) and of FBPE/ClBPE/MBPE(33/33/33)-5/7/9(33/33/33) annealed at 45 °C for 2 h (b). The fiber axis is vertical.

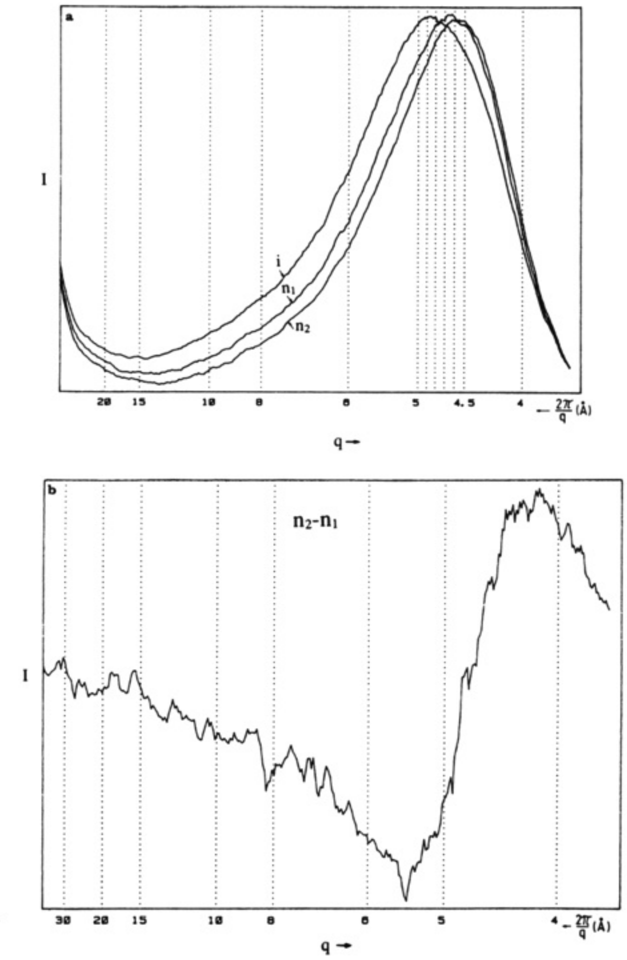


Figure 3. (a) Experimental powder scattering curves corresponding to the three thermotropic phases of polymer FBPE/ClBPE/MBPE(33/33/33)-5/7/9(33/33/33): isotropic (i) at 85 °C, high-temperature nematic (n_1) at 74 °C, and low-temperature nematic (n_2) at 63 °C. (b) Difference curve obtained by subtracting the diffractogram of phase n_1 from the diffractogram of phase n_2: I = uncorrected intensity, q = wavevector ($4\pi \sin \theta/\lambda$).

isotropic at 85 °C, high-temperature nematic at 74 °C, and low-temperature nematic at 63 °C. The high-temperature nematic phase will henceforth be referred to as n_1 and the low-temperature nematic as n_2. Only the diffuse maximum in the 4.5–5-Å range is seen, with no sharp diffraction peak in any of the phases. As expected, the

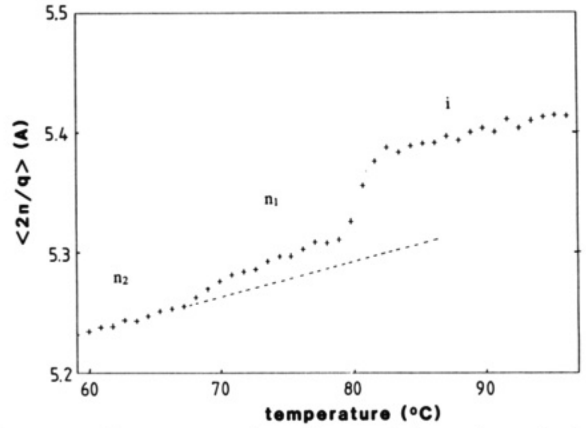


Figure 4. Temperature dependence of the reciprocal of the center of gravity of the diffuse scattering peak, $2\pi/\langle q\rangle$, where $\langle q\rangle$ is defined by eq 1. The polymer is FBPE/ClBPE/MBPE-(33/33/33)-5/7/9(33/33/33). The two discontinuous jumps in $2\pi/\langle q\rangle$ correspond, respectively, to the n_2–n_1 and n_1–isotropic transitions.

position of the maximum moves to larger wavevectors (smaller spacing) upon the isotropic–nematic transition, as closer packing is achieved through parallelization of mesogen directions. A further small shift of the diffuse maximum occurs upon the transition from the n_1 to n_2 phase.

The absence of additional diffraction features in phase n_2 relative to n_1 can be best seen from the difference curve in Figure 3b, obtained by subtracting the diffractogram of n_1 from that of n_2. The ordinate scale is greatly amplified compared to Figure 3a, but the only statistically significant feature is the smooth sinusoidal curvature caused by the small shift of the diffuse peak upon the n_1–n_2 transition.

The shifts in position of the diffuse peak can be quantified in a somewhat arbitrary way by plotting the temperature dependence of the reciprocal of the mean wavevector $\langle q\rangle$, where $\langle q\rangle$ is

$$\langle q\rangle = \frac{q\,i(q)\,\mathrm{d}q}{i(q)\,\mathrm{d}q} \qquad (1)$$

and $i(q)$ is the uncorrected scattered intensity. The experimental plot for copolymer FBPE/ClBPE/MBPE-(33/33/33)-5/7/9(33/33/33) is shown in Figure 4. In addition to a linear increase in $2\pi/\langle q\rangle$ with temperature, associated with thermal expansion, there are two discontinuous jumps: a larger one at T_i and a small one at $T_{n_1n_2}$. Their respective magnitudes are 0.051 and 0.015 Å.

The textures of n_1 and n_2 phases of FBPE/ClBPE/MBPE(33/33/33)-5/7/9(33/33/33) are identical. Figure 5 exhibits a representative optical micrograph of the n_2 phase obtained after annealing for 2 h at 67 °C.

To our knowledge this is the first documented case of a nematic–nematic transition in a polymer. The question of the possible existence of two nematic phases has, in the past, mainly revolved around the problem of uniaxial/biaxial nematic. It may also be mentioned that phase separation into two nematic phases of different compositions has been observed in some polymer solvent systems.[9] The biaxial nematic phase has been reported relatively recently in some lath-shaped low molar compounds with a highly anisometric cross-section normal to their long axis, such as hemiphasmids and other combinations of half-disk and rodlike molecules.[10] However, a biaxial nematic phase is highly unlikely in the present flexible polymers, having a conformationally mobile "mesogen" whose section normal to the long axis is only moderately anisometric.

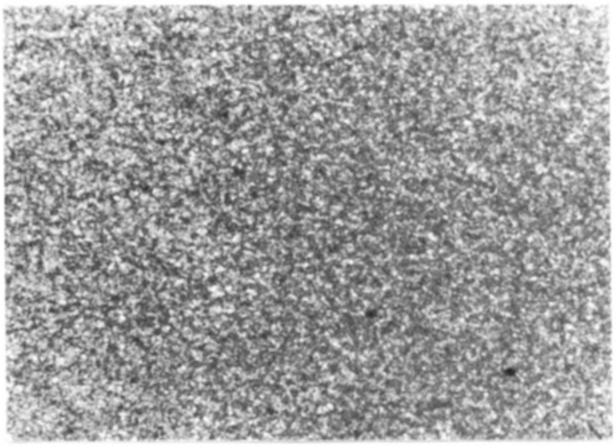


Figure 5. Optical polarized micrograph of the n_2 phase of FBPE/ClBPE/MBPE(33/33/33)-5/7/9(33/33/33) obtained after annealing at 67 °C for 2 h.

As already mentioned, a thermotropic nematic–nematic transition has not been previously observed in a polymer, whereas in low molar mass compounds it has been associated with a change in symmetry.[10] On the other hand, the lattice theory of main-chain polymer melts by Vasilenko et al.[11] actually allows for the existence of two nematic phases under certain conditions. Both phases have the same, i.e., uniaxial, symmetry but differ in the value of the order parameter. According to the theory, only the usual highly anisotropic nematic phase should occur for monomer units with a low flexibility parameter f_0. This nematic phase is replaced by the isotropic melt with increasing spacer length. However, for a higher f_0, i.e., for polymers with a more flexible spacer, a second nematic phase of weaker anisotropy is predicted to occur within a certain range of the ratio $a = x'/(x' + x'')$, where x' and x'' are the respective lengths of the flexible and the rigid part of the repeat unit. The region of the weakly anisotropic phase is bound at low a's by the highly anisotropic phase and at high a's by the isotropic melt.

The underlying cause of the existence of the two nematic phases in the theory of Vasilenko et al.[11] is the conflict between the stiffening and the diluent (plasticizer) roles of a flexible spacer linking the individual mesogens. While the stiffening effect is dominant in the highly anisotropic phase, the diluent effect prevails in the weakly anisotropic phase. Thus, the transition between the former to the latter phase can produce a considerable decrease in the order paramter S_s associated with the spacer.

The possible thermotropic transition between the two nematic phases has not been dealt with explicitly in Vasilenko's paper,[11] but such a transition could be envisaged in the framework of the theory, e.g., through the variation of f_0 with temperature.

While it is tempting to relate the currently observed n_1–n_2 transition to the theoretical predictions by Vasilenko et al.,[11] more experimental as well as theoretical work is required before firmer conclusions can be drawn. For example, it is of interest to mention that the width of the temperature range of the n_1 (high-temperature) phase (12–15 °C) is almost the same for all polymers and copolymers where the n_1–n_2 transition has been observed.[1,2] This feature is unlikely to be a mere coincidence. In contrast, from the theory one might expect a variation in the width of the n_1 interval with spacer length. It may also be noted that the n_1–n_2 transition entropy, $\Delta S_{n_1n_2}$, is also practically independent of the polymer.

The fact that the n_1–n_2 transition is only observed in polymers with odd-numbered spacers apparently also agrees with the qualitative concept of the theory. An even spacer allows better packing and easier alignment of the mesogens in the nematic phase, as verified, e.g., by higher T_i and ΔS_i of even spacer polymers[1d,2] as well as by their smaller interchain distance measured by X-ray scattering.[3a] Thus, the stiffening role of an even spacer is enhanced in comparison with that of an odd spacer, while the diluent effect is unaffected by the parity of the spacer. Hence, for even spacer $T_{n_1n_2}$ may shift to above T_i.

Finally, we recall again that the polymers being considered here are unique within the main-chain nematogenic macromolecules in that their mesogen can change conformation from straight to bent and can thus be regarded alternatively as consisting of two "rigid" mesogens entailing only one benzene ring each. These polyether macromolecules are certainly the most flexible known to exhibit a nematic phase. This feature may hold the key to the reason that the nematic–nematic transition has been observed in these but not in other liquid crystal polymers.

Further research on the characterization of these two nematic phases is in progress.

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Registry No. FBPE/Br$(CH_2)_5$Br/Br$(CH_2)_7$Br/Br$(CH_2)_9$Br (copolymer), 137436-38-5; ClBPE/Br$(CH_2)_5$Br/Br$(CH_2)_7$Br/Br$(CH_2)_9$Br (copolymer), 137436-39-6; FBPE/ClBPE/Br$(CH_2)_5$Br/Br$(CH_2)_7$Br/Br$(CH_2)_9$Br (copolymer), 137436-40-9; FBPE/MBPE/Br$(CH_2)_5$Br/Br$(CH_2)_7$Br/Br$(CH_2)_9$Br (copolymer), 137436-41-0; ClBPE/MBPE/Br$(CH_2)_5$Br/Br$(CH_2)_7$Br/Br$(CH_2)_9$Br (copolymer), 137464-60-9; FBPE/ClBPE/MBPE/Br$(CH_2)_5$Br/Br$(CH_2)_7$Br/Br$(CH_2)_9$Br (copolymer), 137436-42-1.