Macromolecules **1990**, *23*, 3411-3416 **3411**

(7) Takeda, T.; Yasuhara, S.; Watanabe, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2566.
(8) Gu, X. P.; Ikeda, S.; Okahara, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 397.
(9) Rokicki, G.; Kuran, W.; Marciniak, B. P. *Monatsh. Chem.* **1984**, *115*, 205.
(10) Baba, A.; Nozaki, T.; Matsuda, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1552.
(11) Nishikubo, T.; Iizawa, T.; Iida, M.; Isobe, N. *Tetrahedron Lett.* **1986**, *27*, 3741.
(12) Yu, Y.; Bell, J. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 247.
(13) For example: (a) Regen, S. L. *J. Am. Chem. Soc.* **1975**, *97*, 5956. (b) Regen, S. L. *Angew. Chem., Int. Ed. Engl.* **1981**, *46*, 2125.
(14) Montanari, F.; Landini, D.; Rolla, F. *Top. Curr. Chem.* **1982**, *101*, 147.
(15) Ford, W. T.; Tomoi, M. *Adv. Polym. Sci.* **1984**, *55*, 49.
(16) Tomoi, M.; Ford, W. T. *Syntheses and Separation Using Functional Polymers*; Sherrington, D. C., Hodge, P., Eds.; Wiley: New York, 1988; pp 181-207.
(17) (a) Nishikubo, T.; Shiina, A.; Isobe, N. *Chem. Lett.* **1988**, 1605. (b) Nishikubo, T.; Iizawa, T.; Shimojo, M.; Kato, T.; Shiina, A. *J. Org. Chem.*, in press.
(18) Miyaki, K.; Yamagishi, S. *J. Pharm. Soc. Jpn.* **1956**, *76*, 436.
(19) Landini, D.; Maia, A.; Montanari, F. *J. Am. Chem. Soc.* **1978**, *100*, 2796.
(20) Tomoi, M.; Ford, W. T. *J. Am. Chem. Soc.* **1981**, *103*, 3821.
(21) Asahara, T., Tokura, N., Okawara, M., Kumanotani, J., Seno, M., Eds. *Handbook of Solvents*; Kodansha: Tokyo, 1976.
(22) Landini, D.; Montanari, F. *Nouv. J. Chim.* **1979**, *3*, 575.
(23) Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: Weinheim, FRG, 1979; pp 270-272.

Registry No. 22a, 122-60-1; **22b**, 930-37-0; **22c**, 2426-08-6; **23a**, 934-87-2; **23b**, 884-09-3; **24a**, 120915-43-7; **24b**, 127333-32-8; **26a**, 84137-77-9; DMSO, 67-68-5; DMF, 68-12-2; diglyme, 111-96-6; chlorobenzene, 108-90-7; anisole, 100-66-3; toluene, 108-88-3.

Simultaneous X-ray/DSC Study of Mesomorphism in Polymers with a Semiflexible Mesogen

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ABSTRACT: In order to investigate the limits of macromolecular chain flexibility tolerated by the nematic state, a new group of polyethers has recently been synthesized, where not only the spacer but also the mesogen provide a degree of flexibility. This is achieved by introducing a rotationally mobile ethylene group linking the two phenyl rings in the 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE). These "mesogens" are separated by flexible $-O(CH_2)_nO-$ spacers, where n is either a single value (homopolymers) or has two different values (copolymers). Results of X-ray diffraction studies of MBPE polymers using the simultaneous X-ray diffraction and DSC technique (XDDSC) conclusively prove the existence of the nematic phase in most homopolymers and all copolymers. Depending on the polymer, the phase is either mono- or enantiotropic. While in a few cases the phase is thermodynamically stable, in most cases it is metastable. The weak first-order transition below the I-N transition temperature appears not to be the nematic-smectic transition as previously suspected, and its nature is still being investigated. Current X-ray evidence shows further that the molecular packing density in the nematic phase is considerably higher for polymers with even spacers than it is in polymers with odd spacers.

Introduction

The beneficial effect of liquid crystallinity in the processing of polymers with superior mechanical properties is now well established. However, in order to facilitate processing of main-chain nematogenic polymers, the introduction of flexible spacers into the chain has been experimented with extensively. In order to investigate still further the limits of flexibility tolerated by the nematic state, a new group of polyethers has recently been synthesized,[1-4] where not only the spacer but also the mesogen provide a degree of flexibility. This is achieved by introducing a rotationally mobile ethylene group linking the two phenyl rings in the 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE). Both homo- and copolymers were prepared, the latter containing spacers of two[1-3] or three[4] different lengths in a random sequence.

Original studies by DSC and optical microscopy suggested that the polymers exhibit liquid-crystal phases, presumed nematic and possibly also smectic. Presently we show results of X-ray diffraction studies of MBPE polymers using the simultaneous X-ray diffraction and DSC technique (XDDSC).[5] The results conclusively prove the existence of the nematic phase in most homopolymers and all copolymers. Depending on the polymer, the

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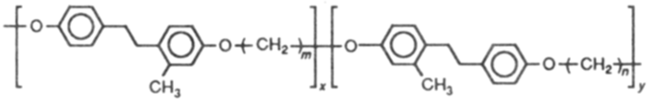
phase is either mono- or enantiotropic. While in a few cases the phase is thermodynamically stable, in most cases it is metastable. In addition, it will be shown that the nematic phase in polymers with even spacers is considerably more ordered than that in polymers with odd spacers.

Materials and Methods

MBPE homo- and copolyethers of the chemical formula



were synthesized as described in ref 1–3. Here $m \neq n$ denotes copolymers and $m = n$ homopolymers.

Thermotropic behavior was initially investigated by polarizing optical microscopy and by DSC (Perkin-Elmer DSC-7). Fiber X-ray diffraction patterns showed rich polymorphism in the crystalline state, as will be described separately.[6] The main technique used in the present work is simultaneous X-ray diffraction and differential scanning calorimetry (XDDSC).[5] In this method time-resolved powder diffractograms are collected during linear heating or cooling of the specimen, while at the same time the differential heat flow in or out of the specimen is recorded. Thus diffractograms can unambiguously be related to the features (peaks) in the thermogram, and transient metastable phases, as well as those existing in a narrow temperature range, can be easily identified. The powerful X-ray beam was provided by the synchrotron source at Daresbury, U.K. The technique has originally been introduced by Russell and Koberstein,[7] and the details of our improved version are given elsewhere.[5]

Results and Discussion

MBPE-9 Homopolymer. DSC heating and cooling thermograms of a typical MBPE homopolymer, MBPE-9, are shown in parts a–c of Figure 1. There is only one endotherm on heating, attributed to crystal melting directly into the isotropic phase (note that the small broad endotherm below the main melting peak in Figure 1a is due to the small fraction that crystallized on quenching subsequent to the annealing). On cooling, however, two exotherms appear if the cooling rate is low (Figure 1c). The phase between the two exotherms has been presumed monotropic nematic.[1,2] On faster cooling, the crystallization exotherm (the lower exotherm of Figure 1c) is further supercooled to expose yet another small exotherm at 60 °C (Figure 1b). This has been tentatively attributed to the nematic–smectic transition.[1,2]

Typical polarizing optical texture produced upon the first exothermic transition during cooling a MBPE polymer from the isotropic state is shown in Figure 2, MBPE-9 being the example. On the basis of such textures, it has been proposed previously[1] that the first anisotropic phase produced on cooling is nematic, although clear Schlieren-type nematic textures could not be created by annealing since crystallization would intervene. For the same reason the conjecture that the lower temperature phase, below the small sharp exotherm, is monotropic smectic could not be tested properly either. No apparent change in texture takes place upon this transition, and annealing again leads to crystallization. Conventional X-ray diffraction experiments were also limited by the transient nature of the presumed liquid crystal phases and, to some extent, by their narrow temperature interval. Thus, we resorted to the XDDSC technique, which appeared ideally suited to resolving problems of this kind.

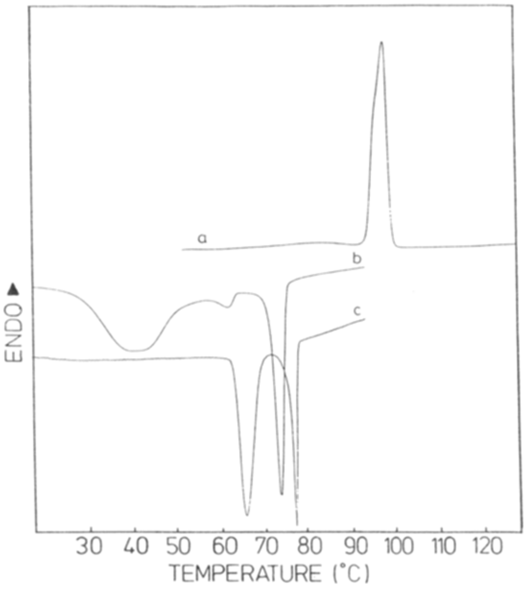


Figure 1. DSC thermograms of MBPE-9: (a) heating scan of the polymer previously annealed at 87 °C; (b) cooling scan, rate −20 °C/min; (c) cooling scan, rate −2 °C/min.

Figure 2. Optical micrograph of MBPE-9, taken through crossed polars at 70 °C immediately on cooling from the isotropic melt.

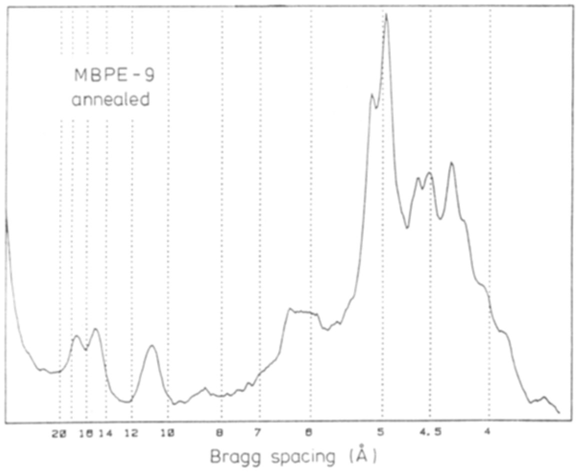


Figure 3. Room-temperature X-ray diffractogram of homopolymer MBPE-9, which had been annealed at 85 °C.

For reference, in Figure 3 we show the room-temperature X-ray diffractogram of the MBPE-9 homopolymer, which had been annealed at 85 °C. The material is clearly crystalline. For completeness, in Figure 4 the diffraction pattern is shown of a melt-drawn and annealed fiber of the same material. Crystal structures will be discussed elsewhere.[6]

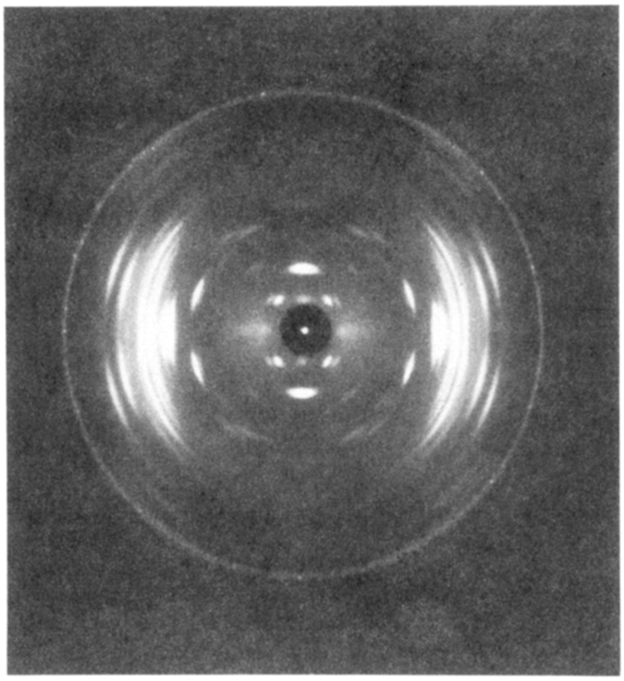


Figure 4. X-ray diffraction pattern of an annealed fiber of MBPE-9. Fiber axis vertical.

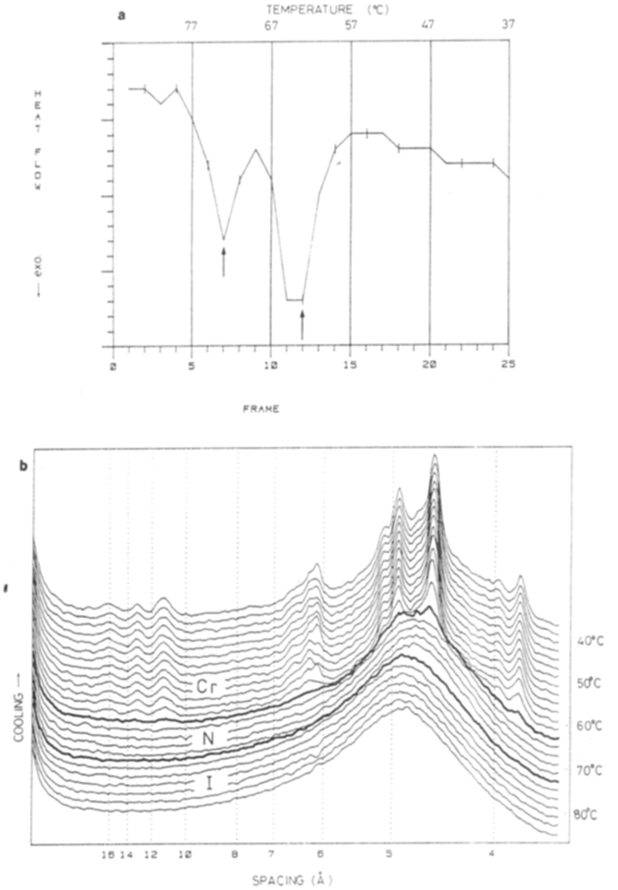


Figure 5. Simultaneous X-ray/DSC (XDDSC) cooling scan (−2 °C/min) for MBPE-9: (a) thermogram, (b) diffractograms (one every 2 °C). Bold diffractograms correspond to arrowed positions in the thermogram: Cr = crystal, N = nematic, I = isotropic.

The results of a cooling XDDSC scan of MBPE-9 homopolymer are shown in Figure 5. The cooling rate was 2 °C/min. The thermogram, which was recorded during the actual XDDSC run, is shown in Figure 5a. It features two exotherms, in agreement with the DSC-7 trace in Figure 1b. Diffractograms in this run were recorded as 30-s time frames, i.e., every degree Celsius. These are displayed in Figure 5b, after coadding consecutive pairs of frames; hence, each curve in Figure 5b covers a temperature interval of 2 °C. The two bold thermograms correspond to arrowed positions, i.e., to exothermic peaks, in the DSC trace (Figure 5a).

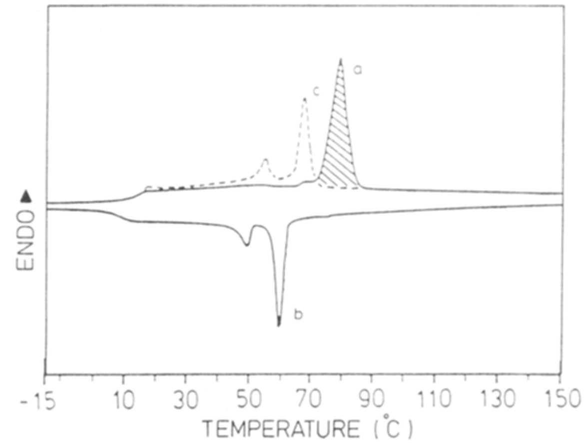


Figure 6. DSC thermograms of copolymer MBPE-5,7 (1:1 comonomer ratio): (a) heating scan of the sample previously annealed at 60 °C; (b) cooling scan; (c) reheating scan after cooling. Rate of heating and cooling: 20 °C/min.

The main point to note in Figure 5b is that the phase between the two exothermic transitions is indeed amorphous. Not only are there no wide-angle reflections present but there are no low-angle peaks either. Thus the phase is neither crystalline nor smectic, and since it is birefringent, it can be unambiguously identified as nematic. This confirms previous tentative conclusions about the liquid crystal forming ability of this material.[1-4] More generally, it clearly illustrates that rigid moieties are not necessarily required to render a polymer nematogenic. It is evident that semiflexible units, like diphenylethane, are also capable of lending liquid-crystal properties to a macromolecule, even where such units are themselves linked by fully flexible spacers. This conclusion will be further substantiated by additional examples below.

The lower temperature exotherm in Figure 5a clearly represents crystallization. However, note that the crystal form in Figure 5b is not the same as that in Figure 4. The present form is metastable and will transform into that of Figure 4 upon heat annealing. It may be mentioned that the diffraction patterns in Figures 3 and 4 in fact represent superposed patterns of two similar forms present in the annealed sample.[6] As in other segmented mesogenic polymers,[8,9] there is an abundance of crystal polymorphs in most homo- and copolymers studied.[6]

MBPE-5,7 Copolymer. Thermograms of MBPE-5,7, a typical representative of MBPE copolymers with odd-numbered spacers, are shown in Figure 6. In this polymer $-O(CH_2)_5O-$ and $-O(CH_2)_7O-$ spacers, in a 1:1 molar ratio, are randomly distributed along the chains, and crystallization is suppressed relative to either of the parent homopolymers.[1,2] A well-annealed specimen gives only one melting endotherm on heating (curve a; note that the small step in the base line at 65 °C results from the annealing at 60 °C and that its position varies with the annealing temperature; this effect is well documented for aromatic polymers; see, e.g., ref 12). On cooling two exotherms are seen (curve b), and on immediate reheating the two transitions reappear in reverse order (curve c). Such behavior is also typical of most other copolymers with odd-numbered spacers, such as MBPE-5,9, MBPE-

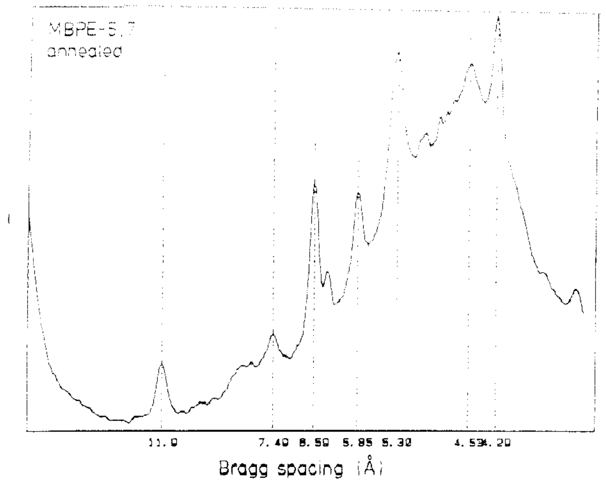


Figure 7. Room-temperature X-ray diffractogram of copolymer MBPE-5,7, which had been annealed at 65 °C.

7,11, and MBPE-9,11. Within the practicable range of cooling rates the two exotherms remain unchanged, unlike the situation in MBPE-9 parts b and c of Figure 1. The lower temperature peak in the copolymers is smaller in area than the higher one, and it is always sharp. The enthalpies of the upper and lower exotherm in MBPE-5,7 are, respectively, 0.7 and 0.17 kJ/mol repeat unit, while in MBPE-9 they are 1.1 and 2.5 kJ/mol repeat unit (for the present purpose the repeat unit of the 1:1 MBPE-5,7 copolymer is taken as the repeat unit of homopolymer MBPE-6).

The diffractogram in Figure 7 confirms that the annealed copolymer is crystalline at room temperature. The XDDSC heating run performed with such a sample indeed shows that the crystals melt at 78 °C (cf Figure 6a).

It is an interesting finding, revealed by the present experiments on MBPE-5,7, that on cooling from the isotropic melt all three phases that appear are amorphous; i.e., neither of them displays any wide- or small-angle diffraction peaks, apart from the broad amorphous halo. The low-temperature amorphous phase in MBPE-5,7, as well as in other copolymers such as MBPE-7,9 and MBPE-5,9, can be frozen at room temperature (glass transition temperature is around 15 °C). On reheating, such a nonequilibrium sample undergoes the reverse sequence of phase transitions. A reheating XDDSC scan is shown in Figure 8 for MBPE-5,7. Immediately prior to the scan, the specimen was cooled at 5 °C/min. As seen in Figure 8b, there is no noticeable change in the powder diffractogram on going through the two first-order transitions, apart from some change in position and width of the amorphous halo, which will be discussed further below. Optical studies have shown[1,2] that both low-temperature phases are birefringent, displaying fine grain texture. Unfortunately, attempts to develop coarser textures by annealing failed due to incipient crystallization. In view of the fact that both low-temperature phases show only amorphous scattering and that they are optically anisotropic, one would conclude that both phases are nematic, and the possibility of a new type of transition[13] may not be ruled out. A more detailed study of this unusual phase behavior is currently under way. For the present purpose we shall denote the lower temperature phase as phase X. It should be noted that the "nematic–X" transition is consistently occurring in most copolymers with odd spacers, as well as in some homopolymers (e.g., the middle exotherm in the fast cool thermogram of MBPE-9; Figure 1c).

As is clear from this example, the nematic phase in MBPE copolymers with odd spacers can be easily made enantiotropic, i.e., to appear both on cooling and reheating, even though it is metastable (cf. the discussion of metastable polymeric mesophases in ref 10).

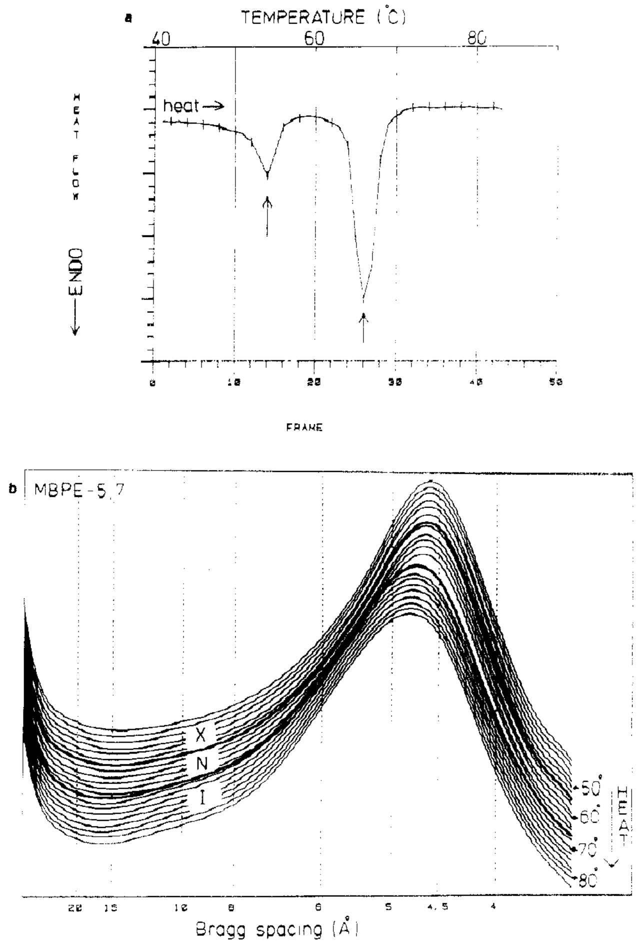


Figure 8. XDDSC heating scan (5 °C/min) for MBPE-5,7 previously cooled from the isotropic phase at −5 °C/min: (a) thermogram, (b) diffractograms (one every 2 °C). Bold diffractograms correspond to arrowed positions in the thermogram.

MBPE-8,10 Copolymer. MBPE polymers with an even number of carbon atoms in their flexible spacers have a somewhat different phase behavior than the odd MBPEs.[3] Both the crystal melting points and isotropization temperatures, where a suspected N–I transition occurs, are higher than in the odd members. Most homopolymers do not actually show mesophases, while in a number of copolymers, a thermodynamically stable nematic phase is suspected.[3] Here we show the example of MBPE-8,10 where two strong first-order transitions are observed on both heating and cooling (Figure 9a,b). The intermediate phase is birefringent and no amount of annealing will dispense of it; i.e., it is an equilibrium phase. A XDDSC heating scan is shown in Figure 10. It confirms the previously tentative assignment[3] of the phases as crystalline, nematic, and isotropic, in the order of ascending temperatures. No "N–X" transitions were observed with even-spacer polymers.

Packing Density in Nematic Polymers with Even and Odd Spacers. In all polymers studied in this work there is a significant shift in the position of the amorphous peak upon the I–N transition toward smaller spacings (larger angles). This is accompanied by some decrease in peak width. The reverse happens on the N–I transition, where such transition is observed (see Figure 8). This behavior indicates that, with respect to the isotropic phase, improved intermolecular contact and correla-

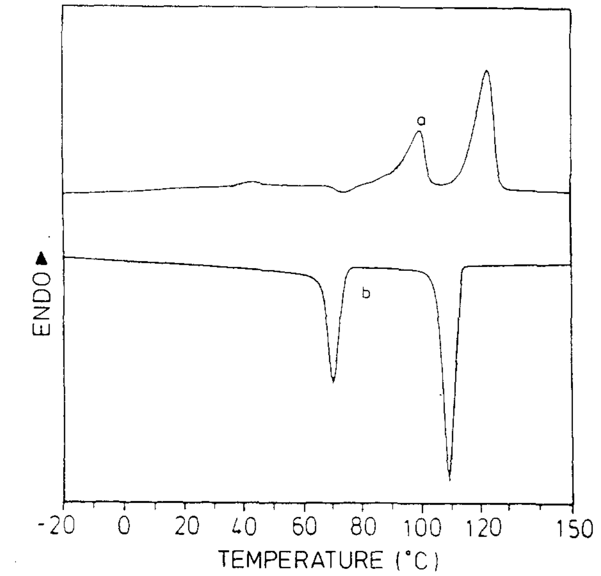


Figure 9. DSC thermograms of copolymer MBPE-8,10 (1:1 comonomer ratio): (a) heating scan; (b) cooling scan. Scan rate: 20 °C/min.

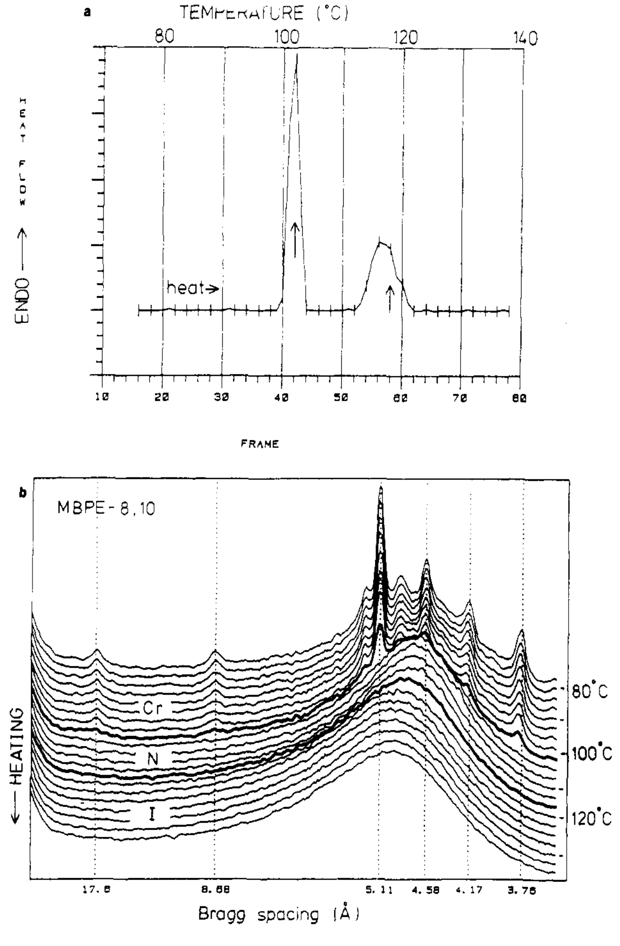


Figure 10. XDDSC heating scan (5 °C/min) for MBPE-8,10 previously cooled from the isotropic phase at -5 °C/min: (a) thermogram, (b) diffractograms (one every 3 °C). Bold diffractograms correspond to arrowed positions in the thermogram.

tion is found in the nematic phase. This is a general feature of the nematic state.

In order to illustrate these effects in a more quantitative way, the mean amorphous peak position, expressed as Bragg spacing in angstroms, was calculated as

$$\langle r \rangle = 1/\langle s \rangle \tag{1}$$

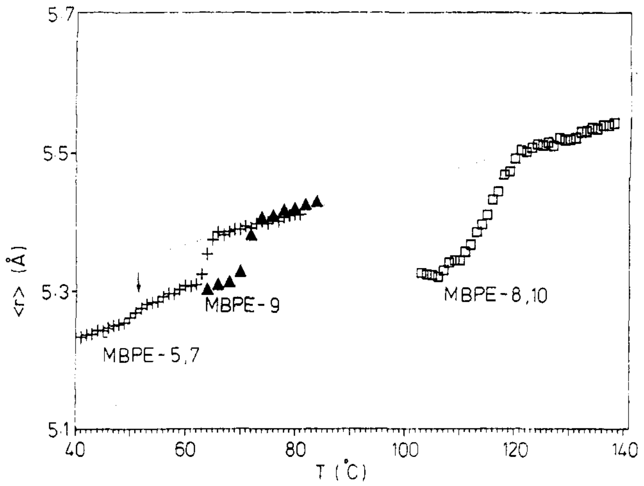


Figure 11. Mean amorphous scattering peak position $\langle r \rangle$ (see eqs 1 and 2) vs temperature for homopolymer MBPE-9 (▲) and copolymers MBPE-5,7 (+) and MBPE-8,10 (□). The main jump in $\langle r \rangle$ corresponds to the N–I transition, and the small jump in MBPE-5,7, marked by an arrow, corresponds to the "N–X" transition.

where the mean wavevector $\langle s \rangle$ is given by

$$\langle s \rangle = \frac{\int_{s_1}^{s_2} si \, ds}{\int_{s_1}^{s_2} i \, ds} \tag{2}$$

i is the uncorrected scattered intensity and s_1 and s_2 are appropriate integration limits. $\langle r \rangle$ can be viewed as an arbitrary empirical parameter of the radial distribution function, which, in turn, is determined by molecular correlations in the liquid. The temperature dependence of $\langle r \rangle$ is shown in Figure 11 for MBPE-9 (cooling), MBPE-5,7 (heating), and MBPE-8,10 (heating).

The jump in $\langle r \rangle$ upon the N–I transition is clearly seen in Figure 11 for all three polymers. An additional small jump of about 0.02 Å (marked by an arrow) is observed in MBPE-5,7 at the N–X transition temperature. As would be expected, the $\langle r \rangle$ values for the isotropic phase of all three polymers fall on the same line (dotted line in Figure 11), which is ascending with temperature due to thermal expansion. The isotropic melt can be taken as the reference state; its structure ought not to be significantly affected by the length of the flexible spacers as these should have a fairly random conformation anyway.[11] The notable distinction between the polymers in Figure 11 is in the amount by which $\langle r \rangle$ drops upon the transition into the nematic phase. This drop, $\Delta\langle r \rangle$, is significantly larger in MBPE-8,10 than in the two polymers with odd spacers, MBPE-9 and MBPE-5,7. $\Delta\langle r \rangle$ is 0.18 Å for MBPE-8,10, but only 0.10 Å for MBPE-9, and 0.08 Å for polymers MBPE-5,7 and MBPE-7,9 (the latter is not shown). We interpret this difference in $\Delta\langle r \rangle$ as indicating that molecular packing in the nematic phase is significantly denser for the polymer with even spacers (MBPE-8,10), compared with that in polymers with odd spacers.

The latter conclusion is also supported by the measured values of the entropy of the N–I transition. A selection of these values is listed in Table I for a number of MBPE polymers with even and odd spacers. The transition entropy for polymers with even spacers is seen to be consistently higher than those for odd-spacer polymers, by a factor of 2.5 on average. The higher packing density, and hence lower enthalpy, of the nematic phase is also reflected by T_i, which is by about 40 °C higher for even spacer polymers than that for their odd-spacer

Table I
Temperatures (T_i) and Entropies (ΔS_i) of N–I Transition and the Change in Mean Amorphous Scattering Peak Position, $\Delta\langle r\rangle$ for Odd- and Even-Spacer MBPE Polymers

	T_i, °C	ΔS_i, J/mol repeat unit/K	$\Delta\langle r\rangle$, Å
MBPE-8,10	120	27	0.18
MBPE-8,12	119	27	
MBPE-10,12	113	29	
average (even)	117	28	(0.18)
MBPE-5,7	70	8.5	0.08
MBPE-7,9	79	12	0.08
MBPE-9,11	81	13	
MBPE-9	74	13	0.10
average (odd)	76	11.6	0.09

counterparts. As has been proposed previously,[11] there is a rationale for a higher nematic order in polymers with even spacers: in such polymers the lowest energy all-trans conformation of the alkylene spacer would keep the attached mesogenic moieties parallel to each other, a favorable situation overall. On the other hand, for an odd number of carbon atoms within the spacer, the adjacent mesogens attached to the terminal atoms would be at a considerable angle to each other. This is unfavorable for chain packing; thus, from a purely energetic consideration, a compromise will need to be established between the opposing tendencies for parallel alignment of mesogens and for the minimum energy conformation of the spacer.

Conclusion

The main results of the present XDDSC study of the newly available polymers with semiflexible mesogens and flexible spacers are as follows:

1. It is conclusively proven that macromolecules as flexible as MBPE polyethers can exhibit the nematic phase, which is either monotropic or enantiotropic. Thus rigid linear mesogens are not essential ingredients of a nematic polymer; even when interchange between extended and bent conformations is allowed in both the spacer and the "mesogen", nematic state is still possible. The simultaneous DSC and X-ray technique employed proved to be very useful in studies of this kind, especially where transient metastable phases, or phases occurring in a narrow temperature range, are investigated.

2. The suggested existence of a metastable smectic phase in MBPE polymers[1,2] is not supported by present experiments: neither crystalline nor smectic reflections are found below the sharp first-order transition occurring in odd-spacer copolymers below the I–N transition. The possibility of it being a nematic–nematic transition[13] is currently being investigated.

3. It is shown that the nematic phase in polymers with even spacers is considerably more densely packed than that in polymers with odd spacers.

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References and Notes

(1) Percec, V.; Yourd, R. *Macromolecules* **1989**, *22*, 524.
(2) Percec, V.; Yourd, R. *Macromolecules* **1989**, *22*, 3229.
(3) Percec, V.; Yourd, R. *Macromolecules*, in press.
(4) Percec, V.; Tsuda, Y. *Macromolecules* **1990**, *23*, 5.
(5) Ungar, G.; Feijoo, J. L. *Mol. Cryst. Liq. Cryst.*, in press.
(6) Ungar, G.; Yourd, R.; Percec, V.; Keller, A., in preparation.
(7) Russell, T. P.; Koberstein, J. T. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1109.
(8) Petraccone, V.; Roviello, A.; Sirigu, A.; Tuzi, A.; Martuscelli, E.; Pracella, M. *Eur. Polym. J.* **1980**, *16*, 261.
(9) Ungar, G.; Keller, A. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 313.
(10) Keller, A.; Ungar, G. *J. Appl. Polym. Sci.*, in press.
(11) Yoon, D. Y.; Bruckner, S.; Volksen, W.; Scott, J. C. *Faraday Discuss. Chem. Soc.* **1985**, *79*, paper 4.
(12) Bassett, D. C.; Olley, R. H.; Al Raheil, I. A. M. *Polymer* **1987**, *29*, 1745.
(13) Vasilenko, S. V.; Khokhlov, A. R.; Shibaev, V. P. *Macromolecules* **1984**, *17*, 2270.