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Liquid-Crystalline Polyethers Based on Conformational Isomerism. 16.[†] Hexagonal Columnar Phase (Φ_h) in a Nondiscotic Copolyether Based on 1,2-Bis(4-hydroxyphenyl)ethane, 1,8-Dibromooctane, and 1,12-Dibromododecane and the Novel 2-Dimensional–3-Dimensional Φ_h–s_B Transition

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ABSTRACT: The copolyethers based on 1,2-bis(4-hydroxyphenyl)ethane (BPE) and a 1/1 molar ratio of 1,8-dibromooctane and 1,12-dibromododecane [BPE-8/12(1/1)] was characterized by a combination of techniques consisting of differential scanning calorimetry (DSC), simultaneous X-ray diffraction/DSC (XDDSC), and thermal optical polarized microscopy. On cooling from the isotropic phase, BPE-8/12(1/1) exhibits a hexagonal columnar (Φ_h) followed by a smectic-B (s_B) phase. Both mesophases are enantiotropic. To our knowledge this represents the first example of a flexible nondiscotic liquid-crystalline polymer that displays a hexagonal columnar mesophase. The new Φ_h–s_B transition represents an almost ideal case of a 2-dimensional–3-dimensional transition where longitudinal long-range order is established without significantly affecting the in-plane order. The Φ_h phase of BPE-8/12(1/1) [which can be viewed as a copolymer containing structural units derived from polyethylene and poly(*p*-xylylene)] bridges the gap between the columnar phases of polyethylene and of poly(*p*-xylylene). The present new addition to the list of columnar phases in flexible nondiscotic polymers is particularly significant as the phase occurs above the temperature range of a smectic phase. A further proof is thus provided that this class of "hexagonal" phases is liquid crystalline in nature.

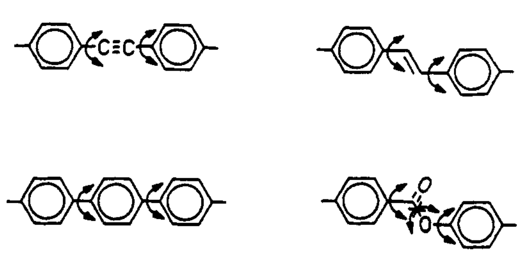
Introduction

Polymers with alternating rigid-rod-like mesogenic units and flexible spacers in the main chain have been studied extensively for their liquid-crystal properties.[1] Nematic and, in some cases smectic, phases were found. To investigate the limits of chain flexibility tolerated by liquid crystals, we have begun a study of main-chain polyethers containing a flexible rather than a rigid "mesogenic" unit.[2-15] The flexible mesogen is based on substituted 1,2-bis(4-hydroxyphenyl)ethane (BPE), where rotation around the 1,2-ethane bond allows both an extended (anti) or a bent (gauche) conformation of the "mesogen" (Scheme I). The study of polyethers containing the methyl-substituted BPE (MBPE) mesogenic unit showed the existence of a nematic phase provided the $-O(CH_2)_nO-$ spacers were made of unequal length to suppress crystallization. On the other hand, similar copolyethers containing unsubstituted BPE units and even spacers exhibit a smectic B phase (s_B).[16] Thus, the work performed so far has proven that conventional liquid-crystal phases can be obtained in polymers with considerable chain flexibility.

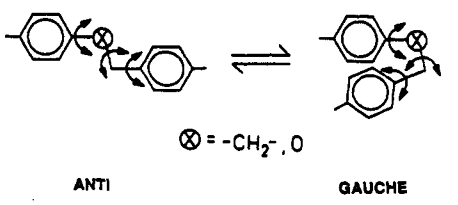
In this report we present results that show two interesting new features of the copolyether based on 1,4-bis-(4-hydroxyphenyl)ethane (BPE) and a 1/1 molar ratio of 1,8-dibromooctane and 1,12-dibromododecane [BPE-8/12(1/1)]. First, a two-dimensionally ordered hexagonal columnar phase is observed, with the columns extending in the chain direction and with no positional order along the columns. Second, lowering the temperature leads to

Scheme I
Comparison of Rigid and Flexible Rodlike Mesogens or Rodlike Mesogens Based on Conformational Isomerism

Rigid Rod-like Mesogens



Flexible Rod-like Mesogens or Rod-like Mesogens Based on Conformational Isomerism



[†] Part 15 in this series: ref 16.

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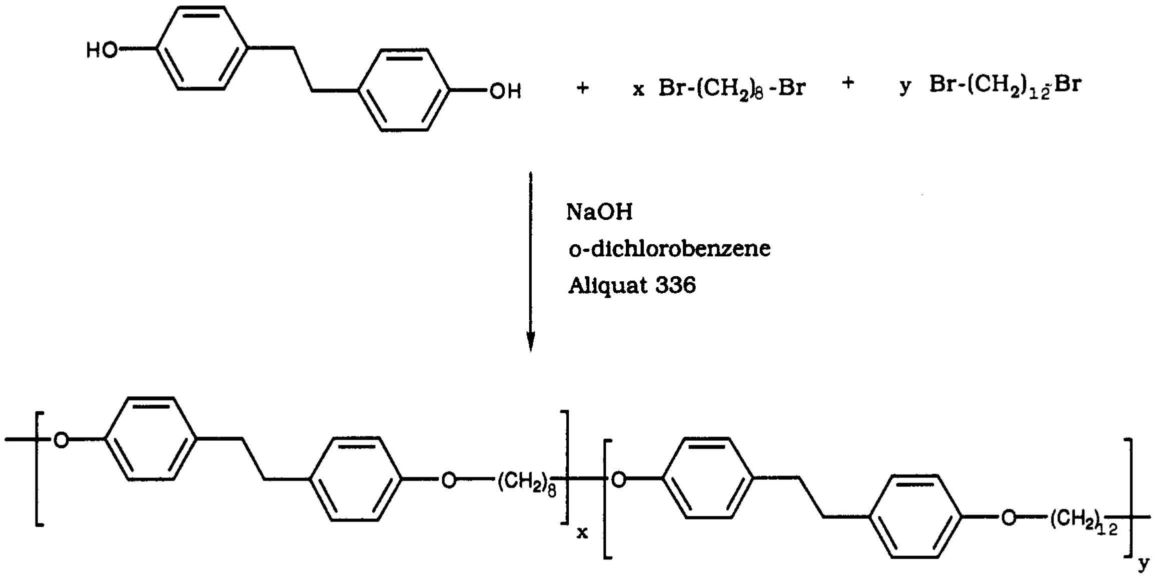
Scheme II

Synthesis of Copolyether Based on 1,2-Bis(4-hydroxyphenyl)ethane (BPE), 1,8-Dibromooctane, and 1,12-Dibromododecane (BPE-8/12(1/1))



the establishment of longitudinal order through a unique columnar–smectic B transition. The lateral hexagonal order remains practically unaffected by this transition.

The knowledge gained herewith could help tailor new polymers exhibiting the columnar phase and possibly other novel transitions.

Experimental Section

Materials. 1,8-Dibromooctane (98%, Aldrich) was used as received. 1,12-Dibromododecane (technical, Aldrich) was recrystallized once from methanol. The synthesis and characterization of 1,2-bis(4-hydroxyphenyl)ethane (BPE, purity = 100%) were performed as described in the previous paper from this series.[16] The other materials were used as received. The polyether based on BPE and a 1/1 molar ratio of 1,8-dibromooctane and 1,12-dibromododecane was synthesized by a liquid–liquid two-phase, phase-transfer-catalyzed polyetherification described in the previous publication (Scheme II);[16] $M_n = 23\,300$, $M_w/M_n = 2.4$ (GPC).[16]

Techniques. Conventional differential scanning calorimetry was performed on a Perkin-Elmer DSC-4 instrument equipped with a TADS Model 3600 data station. Heating and cooling rates were 20 °C/min. First-order transitions were recorded at the maximum of the endothermic or exothermic peaks. X-ray diffraction on unoriented samples was recorded simultaneously while recording the heat flow in and out of the specimen during a programmed heating or cooling cycle (XDDSC technique). The details of this combined XDDSC technique, using synchrotron radiation, were described previously.[17] Optical microscopy was performed on a Zeiss Ultraphot microscope equipped with a Mettler FP-82 hot stage and a Mettler 800 central processor. The other characterization techniques are similar to those conventionally used in our laboratories.[4-6,7]

Results and Discussion

The observations in this work were made on copolyether BPE-8/12(1/1) having a 1/1 molar ratio of octylene and dodecylene spacer groups. DSC thermograms of this copolymer are shown in Figure 1. Two endotherms are seen both on heating and on cooling. The enthalpy of the higher temperature transition is $\Delta H = 4.66$ kcal/mru (entropy, $\Delta S = 10.3$ cal/K mru, where the average repeat unit is taken as that of BPE-10 homopolymer). The enthalpy and entropy associated with the smaller low temperature peak are $\Delta H = 0.10$ kcal/mru and $\Delta S = 0.26$ cal/K mru.

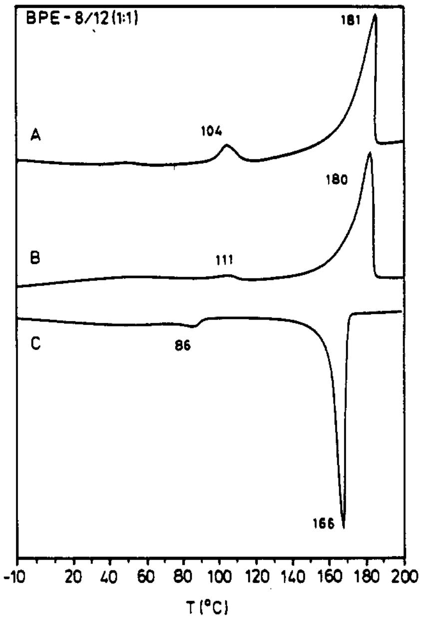


Figure 1. Representative heating and cooling DSC traces (20 °C/min) of BPE-8/12(1/1): (A) first heating scan; (B) second and subsequent heating scans; (C) first and subsequent cooling scan.

Polarized optical microscopy shows that above 180 °C transition the polymer is in the isotropic state, while below this temperature a broken-fan texture is observed. Figure 2 shows the time evolution of this texture a few degrees below the isotropization temperature. Batonnettes are seen at the early stage (Figure 2a), their impingement at the intermediate stage (Figure 2b), and finally fanning out (Figure 2c). We note the similarity of the texture in Figure 2c with that on the columnar phase in some low molecular mass disklike compounds (see, for example, ref 18). Apart from a change in light intensity, no difference in texture is observed upon cooling below the low-temperature transition.

The series of X-ray diffractograms recorded during a 5 °C/min cooling XDDSC scan of BPE-8/12(1/1) is shown in Figure 3a. The diffractogram recorded at 50 °C is shown in Figure 3b. Figure 3a is most revealing. In the observed Q range, i.e., from $Q = 0$ to $Q = 2\pi/3$ Å^{-1} (only the range

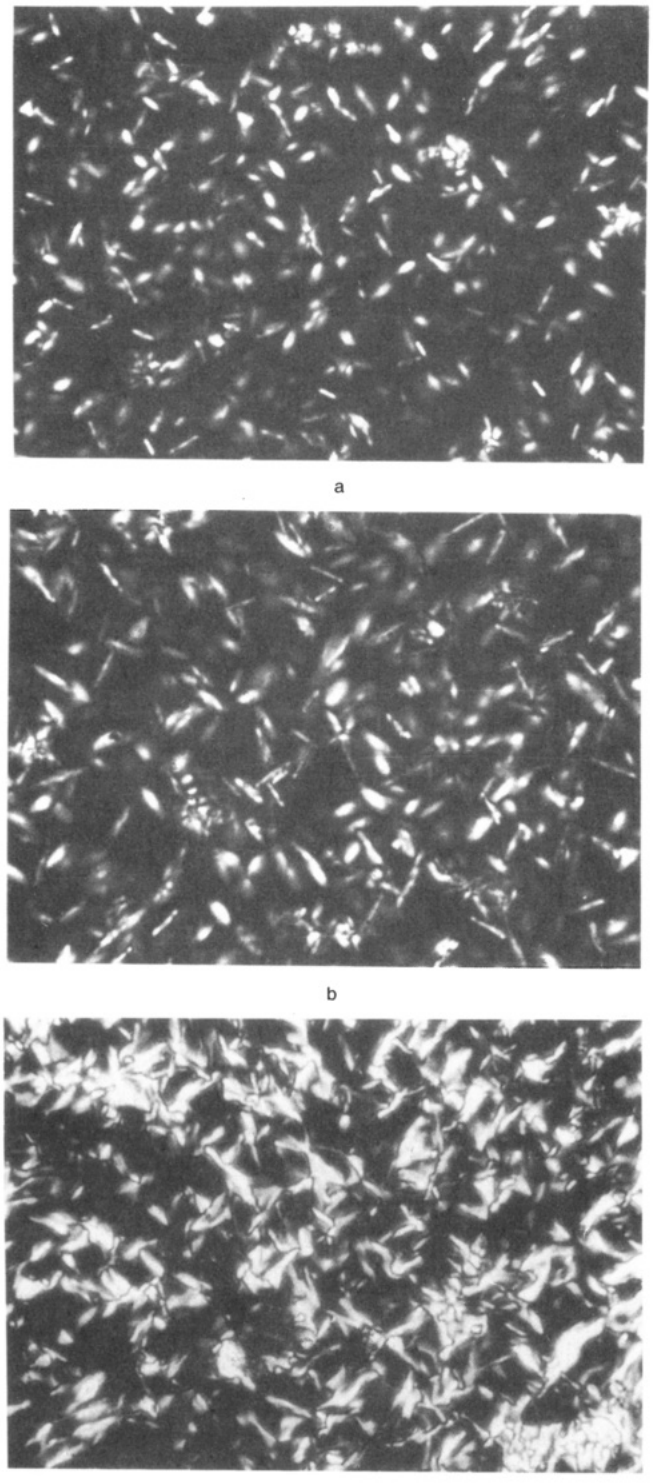


Figure 2. Optical polarized micrographs (100×) of the Φ_h phase of BPE-8/12(1/1) obtained on cooling from the isotropic phase: (a) batonnets formed after few seconds at 176 °C; (b) batonnets after 10 min of annealing at 176 °C; (c) fan-shaped texture at 167 °C.

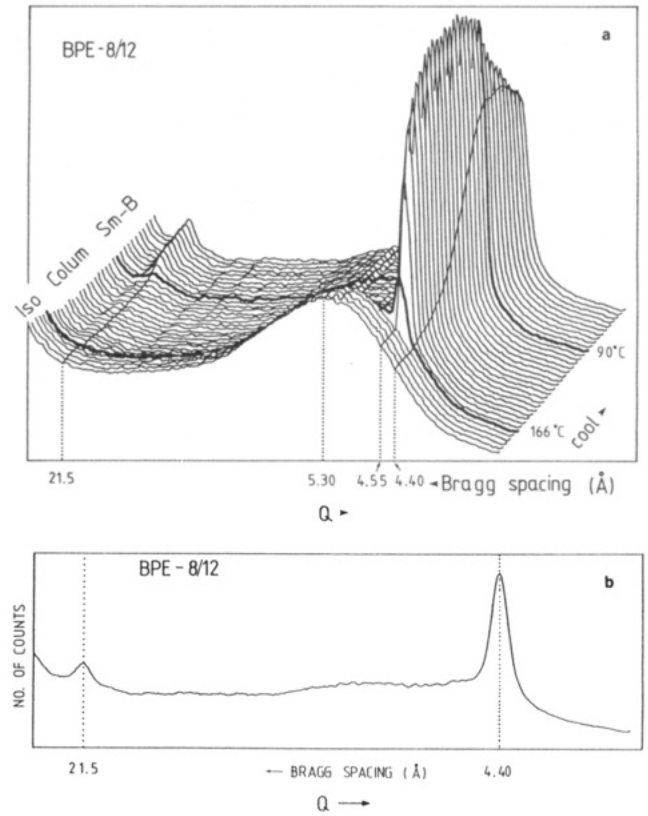


Figure 3. (a) Series of X-ray diffractograms of BPE-8/12(1/1) recorded during an XDDSC cooling scan (cooling rate −5 °C/min) spanning the isotropic, hexagonal columnar, and smectic B phases; (b) X-ray diffractogram of the smectic-B phase recorded at 50 °C.

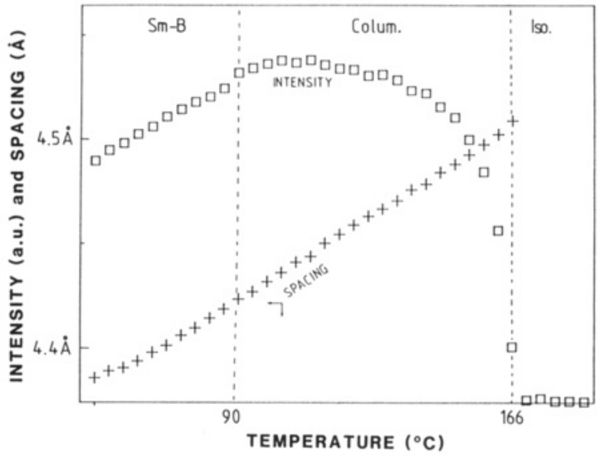


Figure 4. Temperature dependence of the hexagonal 100 spacing and of the integrated 100 diffraction peak intensity. Data from diffractograms in Figure 3a. Note the minimal change at the hexagonal columnar–smectic B transition at 90 °C.

0–$2\pi/4$ Å^{-1} is shown) only one Bragg reflection is observed in the high-temperature phase. The reflection is sharp and intense and corresponds to a Bragg spacing of 4.5 Å. The exact spacing, as a function of temperature, together with the relative intensity of the diffraction peak, is shown in Figure 4. Apart from the 4.5-Å peak, a weak diffuse scattering maximum is observed in the temperature region between 166 and 90 °C. This is centered around $2\pi/20$ Å^{-1} (note that the occasional additional weak ripples in the experimental curves stem from the imperfectly corrected unevenness in the detector response).

At the lower temperature transition (90 °C) the weak diffuse feature at $Q = 2\pi/20$ Å^{-1} intensifies and sharpens up to give a reflection corresponding to a Bragg spacing of 21.5 Å. At the same time the wide-angle region shows practically no change. The diffractogram retains the same features down to room temperature (Figure 3b) and is essentially the same as that for the liquid-crystal phase of the BPE-10/12(1/1) copolyether,[16] described as smectic B. The smectic layer spacing of 21.5 Å closely corresponds to the calculated repeat distance of 22.1 Å for a fully extended conformation of polymer chain.[16]

The single intense peak at about 4.5 Å is characteristic of a hexagonal packing of molecules within the smectic layers. The orientation of chain director perpendicular to the layers is supported by the close agreement between the calculated chain periodicity and the observed layer spacing, as well as by the absence of other reflections in the vicinity of the 4.5-Å peak. However, in the absence of a well-aligned and ideally monodomain specimen, the possibility of a tilted hexagonal smectic phase (s_G or s_J) cannot be completely ruled out. It is likely that the smectic phase has true three-dimensional positional order and is actually of the crystal B type.[19]

The high-temperature liquid-crystal phase, stable between 105 and 180 °C, is of primary interest in this work. It is distinguished from the low-temperature smectic phase only by the lack of layer periodicity, i.e., periodicity along the chain direction. The lateral hexagonal two-dimensional order is preserved, the order being most likely truly long range, as far as can be judged by the sharp resolution-limited 4.5-Å peak. The diffuse scattering around $Q = 2\pi/20$ Å^{-1} indicates the existence of only short-range intramolecular order in place of the long-range order of the smectic phase. Thus, by the current classification of liquid-crystal phases[19,20] the phase is hexagonal columnar.

The two observations of main interest are (1) the existence of the columnar liquid-crystal phase Φ_h in a nondiscotic polymer of considerable flexibility and (2) the appearance of a simple two-dimensional to three-dimensional transition Φ_h–s_B. We shall first discuss the significance of the former observation in the wider content of polymer mesomorphism.

Columnar phases in thermotropic systems have so far been recognized only in molecules containing disklike mesogens; hence they are often called discotic mesophases.[21,22] Occasionally other types of small molecules, e.g., phasmids,[23] were also found to form columnar phases, but even in these cases disklike entities, produced by combination of half-disk and rodlike molecules, are the building blocks. However, as recently argued by one of us,[24] there is a whole range of polymers exhibiting a hexagonal columnar phase, which has not been recognized as such. The polymers concerned include polyethylene (high-pressure phase, radiation-induced and stretch-induced phase), poly(1,4-*trans*-butadiene, poly(tetrafluoroethylene), and poly(*p*-xylylene) as well as certain substituted polysiloxanes, polyphosphazenes, and polysilanes. One characteristic of the hexagonal mesophase in all these systems is the existence of appreciable conformational disorder.[25] There has generally been a reluctance to consider such mesophases as liquid-crystalline since the polymers involved are mainly flexible and thus atypical of liquid-crystal-forming compounds. The findings reported in this work ought to help bridge the conceptual gap between the hexagonal mesophases in the listed flexible polymers and the more conventional liquid-crystalline phases. BPE-8/12(1/1) is the first polymer that exhibits both the hexagonal mesophase and a conventional liquid-crystalline, in this case smectic, phase. The similarity of natural optical textures in the present Φ_h phase and that in the s_B phase in BPE-10/12(1/1)[16] is rather striking. Moreover, we recall that it takes only a methyl group substituent on one of the phenylene rings to replace the columnar phase in BPE-8/12(1/1) by the nematic phase in MBPE-8/12(1/1).[5] Thus the BPE family of polyethers can be safely regarded as belonging to the liquid-crystal-forming types of compounds by traditional standards and the appearance of the columnar liquid-crystal phase should not be taken as particularly unusual.

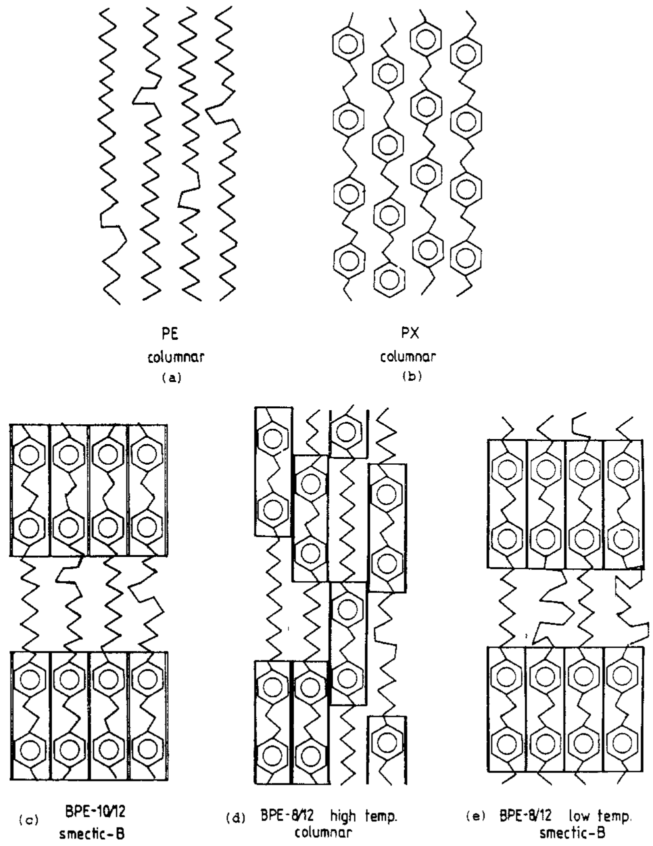


Figure 5. Schematic representation of the hexagonal columnar phases in polyethylene (a) and poly(*p*-xylylene) (b); of the smectic B phase in BPE-10/12(1/1) copolymer with similar spacing length (c); and of the high-temperature columnar (d) and low-temperature smectic-B phase (e) in BPE-8/12(1/1) copolymer with highly disimilar spacer lengths.

Next, the similarity in chemical structure between BPE-based polyethers and some other polymers showing hexagonal mesophases will be examined. It is instructive to regard BPE polyethers as having a structure intermediate between those of polyethylene and poly(*p*-xylylene). Poly(*p*-xylylene) containing only "mesogen" moieties and polyethylene containing only "spacers" both exhibit the hexagonal mesophase.[26,27] However, neither of them form an enantiotropic or monotropic smectic phase and instead at lower temperatures, they form regular crystals of low symmetry.

It is therefore not surprising to find the same mesophase in BPE-based polyethers. The fact that it is actually observed in BPE-8/12(1/1) appears to be due to the fact that in this copolymer both the crystalline and the smectic phases are sufficiently destabilized as to "uncover" the columnar phase. Homopolymers like BPE-8, BPE-10, and BPE-12 form stable crystals of low symmetry that melt directly into the isotropic liquid. In copolymers with spacers of similar lengths, such as BPE-8/10(1/1) and BPE-10/12(1/1), the crystal melting point is suppressed below the smectic–isotropic transition temperature.[16] With increasing disimilarity in spacer lengths even the smectic phase stability is suppressed sufficiently, and the columnar phase, with no longitudinal order, appears as the stable phase in BPE-8/12(1/1). The above ideas are schematically illustrated in Figure 5.

It is interesting to compare the thermodynamic parameters of the columnar–isotropic transition of polyethylene and poly(*p*-xylylene) with those of their "copolymer" BPE-8/12(1/1). The relevant data are presented in Table I. As expected, the transition temperature of

Table I
Temperature (T_i) and Entropies (ΔS_i) of the Hexagonal Columnar–Isotropic Transition of BPE-8/12 (1/1), Polyethylene (PE), and Poly(*p*-xylylene) (PX)

polymer	T_i, °C	ΔS_i cal/K g	ΔS_i cal/K mru[e]
PE	≃140[a]	0.072[b]	1.03[b]
		0.086[c]	1.17[c]
PX	430[d]	0.020[d]	2.10[d]
BPE-8/12 (1/1)	180	0.03	10.30

[a] From $T_{\text{columnar-isotropic}}$ for irradiated linear PE at atmospheric pressure, extrapolated to zero irradiation dose and inifinite lamellar thickness (from ref 28). [b] Measured on bulk linear PE irradiated with 1000 Mrad; uncorrected for degree of "crystallinity" (from ref 28). [c] Measured on constrained high-modulus gel-drawn polyethylene fibers; refers to 100% crystallinity (from ref 29). [d] Data for the "melting" transition of the β_2 phase, crystallinity 100% (from ref 27). [e] Mru = mole of repeating units.

BPE-8/12(1/1) is intermediate between those of polyethylene and poly(*p*-xylylene), as is the transition entropy per unit mass. A closer comparison of isotropization entropies can be made if the measured molar ΔS_i for BPE-8/12(1/1) is compared with that calculated as a linear combination of ΔS_i values for polyethylene (PE) and poly(*p*-xylylene) (PX) according to the number of flexible bonds. Thus ΔS_i for a mole of BPE-10 repeat units, representing BPE-8/12(1/1), is calculated as

$$(\Delta S_i)_{\text{BPE-10(calc)}} = (\Delta S_i)_{\text{PX}} + 12(\Delta S_i)_{\text{PE}} = 2.1 + 12 \times 1.17 = 14.80 \text{ cal/K mru}$$

Here we treat the two ether oxygens as methylene groups. The calculated value $(\Delta S_i)_{\text{BPE-10(calc)}}$ is in fair agreement with the measured value of 10.3 cal/K mru for BPE-8/12(1/1). The agreement is particularly good, considering that the degree of "crystallinity" of the latter polymer is less than 100%. The above crude comparison of T_i and ΔS_i values between BPE-8/12(1/1) on one hand and the polyethylene and poly(*p*-xylylene) on the other gives further indication of the similarity in nature of hexagonal columnar phases in these polymers.

As to the columnar–s_B transition in BPE-8/12(1/1), this is the first time such a transition is observed. Its absence in conventional discotics is understandable considering that disklike molecules, while forming columnar phases, do not form smectic phases. To our knowledge, there has been only one reported case of a smectic–columnar thermotropic transition, but this involved the s_A rather than the s_B phase. The transition was observed in a phasmidic low molar mass compound,[23] and a complex reorientation and association process occurred. The usual crystallization of discotic compounds from the columnar phase involves a larger reduction of symmetry than observed here, and accordingly, crystallization entropies are much larger than that of the Φ_h–s_B transition in BPE-8/12(1/1).[30] The latter appears to be the simplest possible case of a 2D–3D transformation: short-range longitudinal order becomes long range through a first-order transition, while the in-plane hexagonal order remains practically unaffected. The transition seems to be prototype one-dimensional crystallization of the columnar phase as originally envisaged by Helfrich.[20]

Conclusions

The present study has shown several novel features of considerable general interest: (a) A new class of polymers is added to the list of nondiscotic macromolecules exhibiting the hexagonal columnar mesophase. (b) A new type of transition, columnar–s_B, is observed; this presents an almost ideal case of a 2D–3D transition, where longitudinal long-range order is established without significantly affecting the in-plane order. (c) The Φ_h phase observed in BPE-8/12(1/1) bridges the gap between the columnar phases in polymers as diverse as polyethylene and poly(*p*-xylylene); comparison of the phase behavior of these three polymers, as well as comparisons within the BPE family of copolyethers, provides considerable improvement in our understanding of the interdependence of molecular structure and thermotropic mesomorphims in flexible and semiflexible polymers; future work will focus on further progress in this direction and on tailoring new polymers. (d) The existence of the hexagonal phase above the temperature range of the smectic phase further confirms it as liquid crystalline, rather than being a crystalline variant as sometimes claimed.

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Registry No. (BPE)(Br(CH$_2$)$_8$Br)(Br(CH$_2$)$_{12}$Br) (copolymer), 131236-56-1.