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Molecular Engineering of a Hexagonal Columnar (Φ_h) Mesophase Exhibited by Flexible Copolyethers Based on 1-(4-Hydroxyphenyl)-2-(2-R-4-hydroxyphenyl)ethane with R = H, F, and Flexible Spacers[1]

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Introduction

While most of the synthetic efforts in the area of main-chain liquid-crystalline polymers (LCP) are devoted to the preparation of systems exhibiting nematic (n) mesophases,[2] a brief survey of the literature on natural polymers and low molar mass compounds shows that the most frequently encountered mesophases are cholesteric and columnar hexagonal (Φ_h) in the case of polymers[3a] and lamellar and Φ_h in the case of low molar mass amphiphilic compounds.[3b] DNA,[3a,4] xanthan,[4] polypeptides,[3a] r-RNA,[3a] and various substituted polyglutamates,[5] to name just a few, all exhibit cholesteric and Φ_h mesophases. In reality, many flexible synthetic polymers which have not been designed to display liquid-crystalline phases exhibit a Φ_h mesophase. Various poly(dialkylsilylene)s,[6] poly(diethylsiloxane) and poly(di-*n*-propylsiloxane),[7] polyethylene,[8] poly(vinyltrimethylsilane),[9a,b] poly[bis(2,2,2-trifluoroethoxy)phosphazene],[9a,b] poly(*p*-xylylene),[9c] and many other conventional flexible polymers[10] exhibit a Φ_h liquid-crystalline phase.

The structural requirements for the synthesis of polymers exhibiting n mesophases are well established.[2,11] However, this is not yet the case for polymers exhibiting Φ_h mesophases. The main and well-established characteristic of the Φ_h phase in all polymers reported to date is the existence of appreciable conformational disorder.[12] Presently, we are investigating the structural requirements which lead to supramolecular polymers[13] and main-chain LCPs without side groups,[14] which display Φ_h mesophases. Although there are many flexible polymers which exhibit Φ_h mesophases, most of them contain side groups.[5–7,9,10] The two basic main-chain polymers which do not contain side groups are polyethylene (PE)[8] and poly(*p*-xylylene) (PX).[9c] However, PE displays a virtual Φ_h phase and PX an enantiotropic Φ_h phase at very high temperatures. We have generated the first tailor-made main-chain polymer exhibiting a Φ_h phase by inserting structural units of PE and PX within the structure of the same copolymer. This was accomplished by copolyetherification of 1,2-bis(4-hydroxyphenyl)ethane (BPE) with a 50/50 mole ratio of 1,8-dibromooctane to 1,12-dibromododecane.[14]

The goal of this paper is to report the first series of experiments which will provide access to the molecular engineering of polymers exhibiting Φ_h mesophases by copolymerization experiments. The use of copolymerization experiments in the molecular design of main-chain liquid-crystalline polymers exhibiting nematic mesophases is well established.[11] The particular examples described in this paper refer to copolyethers of 1-(4-hydroxyphenyl)-2-(2-fluoro-4-hydroxyphenyl)ethane (FBPE) with various ratios of 1,8-dibromooctane to 1,12-dibromododecane [FBPE-8/12(*X*/*Y*)] (where *X*/*Y* refers to the molar ratio between 1,8-dibromooctane and 1,12-dibromododecane) and copolyethers based on various ratios of 1,2-bis(4-hydroxyphenyl)ethane (BPE) to FBPE with a 50/50 (mol/mol) ratio of 1,8-dibromooctane to 1,12-dibromododecane [BPE/FBPE(*A*/*B*)-8/12(50/50)] (where *A*/*B* refers to the molar ratio between BPE and FBPE).

Experimental Section

Materials. 1,8-Dibromooctane (98%; Aldrich) was used as received. 1,12-Dibromododecane (technical; Aldrich) was recrystallized from methanol. 1,2-Bis(4-hydroxyphenyl)ethane[15] (BPE; purity = 100%) and 1-(4-hydroxyphenyl)-2-(2-fluoro-4-hydroxyphenyl)ethane[16] (FBPE; purity = 99.8%) were synthesized as described in previous publications from our laboratory. The other materials were used as received. All polyethers and copolyethers were synthesized by a liquid-liquid two-phase, phase-transfer-catalyzed polyetherification [*o*-dichlorobenzene as solvent, 10 N aqueous NaOH solution, tetrabutylammonium hydrogen sulfate (TBAH; 20 mol %) vs phenol groups as phase-transfer catalyst, 80 °C, 12 h reaction time] which was described previously.[11,16] After separation from the reaction mixture all polymers were purified by three successive precipitations from chloroform in acetone, from tetrahydrofuran in water, and from chloroform in methanol.

Techniques. Relative molecular weights were determined by gel permeation chromatography (GPC) using a Perkin-Elmer Series 10 LC equipped with a LC-100 column oven, an LC-600 autosampler, and a Nelson Analytical 900 Series data station. The measurements were made by using a UV detector with 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 were read at the maximum or minimum of the endothermic and exothermic peaks. Glass transition temperatures (T_g) were determined as the middle of the change in the heat capacity. All heating and cooling scans after the first heating scan produced perfectly reproducible data.

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

X-ray scattering patterns were recorded with either a flat-plate wide-angle (WAXS) vacuum camera (room temperature and elevated temperatures) or a pinhole collimated small-angle (SAXS) camera (room temperature). Ni-filtered Cu Kα radiation was used. The samples were in the form of bulk samples in Lindemann capillaries cooled from the melt or as-prepared polymers in the form of a free-standing powder. The temperature stability of the X-ray heating cell was ±0.1 °C.

Results and Discussion

The synthesis of FBPE-8/12(*X*/*Y*) and BPE/FBPE(*A*/*B*)-8/12(50/50) is outlined in Scheme I. The characterization of FBPE-8/12(*X*/*Y*) copolymers is summarized in Table I and that of BPE/FBPE(*A*/*B*)-8/12(50/50) copolymers in Table II.

Let us first discuss the DSC thermograms of FBPE-8/12(*X*/*Y*). Second and subsequent heating scans are perfectly reproducible. The DSC traces obtained from the first heating scan can be reproduced if the sample is annealed at room temperature or is dissolved, precipitated, dried, and subsequently rescanned. The main difference between the first and second heating DSC traces consists

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Scheme I
Synthesis of Polyethers and Copolyethers Based on BPE, FBPE, 1,8-Dibromooctane, and 1,12-Dibromododecane

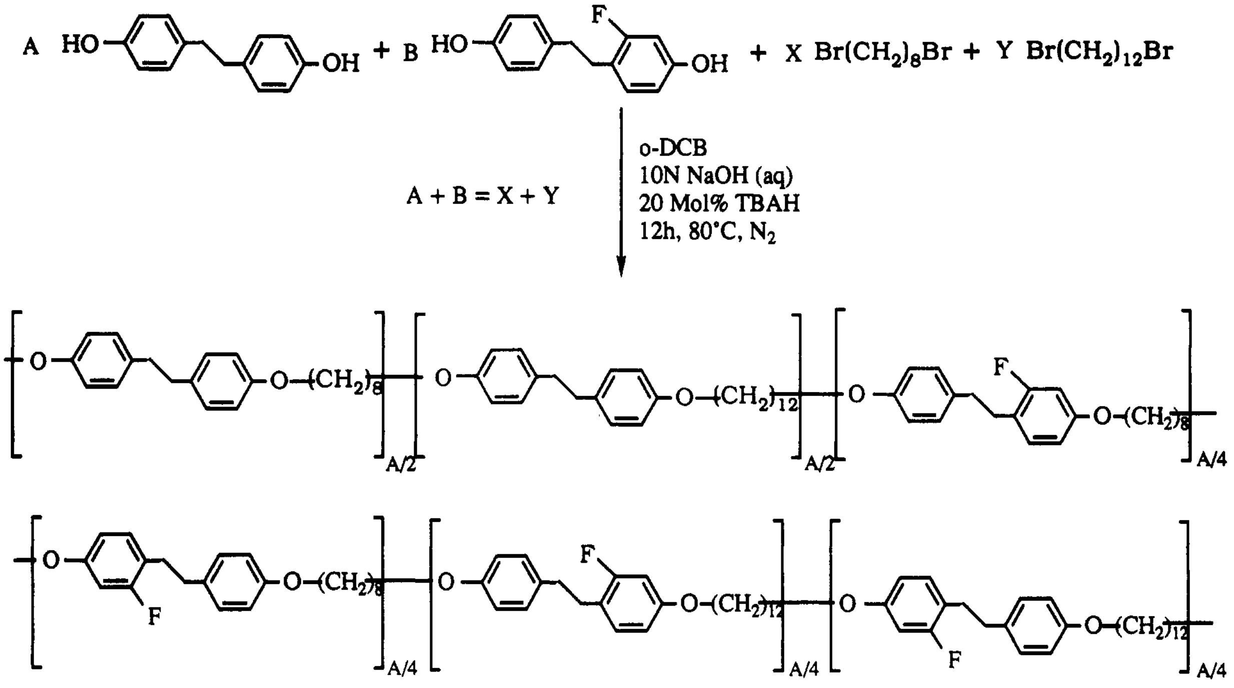

Table I
Characterization of Polyethers Based on FBPE and 1,8-Dibromooctane (FBPE-8) and 1,12-Dibromododecane (FBPE-12) and of the Corresponding Copolyethers [FBPE-8/12 (X,Y)]

			thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses[a]	
X/Y, mol ratio	M_n	M_w/M_n (GPC)	heating	cooling
100/0	17 600	2.54	k 34 (0.07) k 137 n 165 (6.38*) i k 62 (0.55) k 147 n 163 (4.80*) i	i 152 n 142 (4.66*) k 37 (0.59) k
80/20	26 300	2.01	k 49 (0.12) k 96 (0.18) k 114 Φ_h 127 n 146 (5.42*) i k 34 (0.04) k 125 Φ_h 146 (3.92*)i	i 141 (2.85) n 125 (0.27) Φ_h 109 (0.69) k 20 (0.07) k
60/40	20 400	2.46	k 48 (0.13) k 96 (0.15) Φ_h 142 (4.96) i k 91 (0.15) k 139 Φ_h 145 (4.02*) i	i 136 n 128 (3.48*) Φ_h 55 (0.49) k
50/50	16 200	1.97	k 48 (0.21) k 109 (0.97) Φ_h 136 (4.06) i k 109 (1.24) Φ_h 136 (3.21) i	i 130 (3.62) Φ_h 62 (0.57) k
40/60	15 800	1.87	k 47 (0.18) k 90 (0.2) k 104 k 121 Φ_h 132 (5.88*) i k 105 k 122 Φ_h 133 (5.18*) i	i 125 (3.09) Φ_h 104 (0.26) s 89 (1.62) k
20/80	16 700	2.29	k 44 (0.17) k 135 (5.96) i k 122 Φ_h 134 (5.31*) i	i 126 (3.49) Φ_h 103 (1.83) k
0/100	34 000	2.28	k 49 (0.15) k 137 (6.87) i k 136 (6.64) i	i 122 Φ_h 116 k (6.41*) k

[a] Data from first and second DSC heating scans are on the first and second lines respectively. Asterisks indicate overlapping transitions.

of a small endothermic peak which appears at low temperatures only on the first heating scans and is associated with a melting process. Only in the case of FBPE-8/12(80/20) the first melting endotherm from the second and subsequent heating scans appears at a lower temperature than the one observed in the first heating scan. The transition temperatures collected from first and second heating and from cooling scans are summarized in Table I. According to thermal polarized optical microscopy analysis, FBPE-8/12(100/0), i.e., FBPE-8, exhibits an enantiotropic nematic mesophase.[16] In the first heating scan FBPE-8/12(80/20) and FBPE-8/12(60/40) exhibit only an enantiotropic Φ_h and a monotropic nematic mesophase. In the second heating scan these two copolymers display enantiotropic nematic and Φ_h mesophases. Regardless of the thermal history of the sample, FBPE-8/12(50/50) and FBPE-8/12(40/60) form an enantiotropic Φ_h mesophase. FBPE-8/12(20/80) exhibits a monotropic Φ_h phase in the first heating scan and an enantiotropic Φ_h phase in the second heating scan. Regardless of the thermal history of the sample, FBPE-8/12(0/100) shows only a monotropic Φ_h phase. The Φ_h mesophase of FBPE-8/12(50/50) was identified also by X-ray scattering experiments and will be discussed later.

Therefore, by analogy with BPE-8/12(50/50),[14] FBPE-8/12(50/50) exhibits an enantiotropic Φ_h mesophase. Consequently, by using the structural units derived from BPE-8/12(50/50) and FBPE-8/12(50/50) we can perform a set of copolymerization experiments which will clarify if the temperatures and thermodynamic parameters associated with i–Φ_h phase transition follow the same rules as that of the i–n and i–s phase transitions. That is, if the structural units of the new copolymer are isomorphic with those of the parent homopolymers or copolymers within a certain phase, the corresponding transition temperatures and associated thermodynamic parameters follow a continuous dependence of copolymer composition. This dependence was demonstrated to be valid both for the case of nematic mesophases of main-chain liquid-crystalline copolymers[11] and of the n, s_A, and s_C* mesophases

Table II
Characterization of Copolyethers Based on a 1/1 Molar Ratio of 1,8-Dibromooctane and 1,12-Dibromododecane and BPE and FBPE [BPE/FBPE(*A*/*B*)-8/12(50/50)]

BPE/FBPE(*A*/*B*)-8/12(50/50)			thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses[a]	
A/*B*, mol ratio	M_n	M_w/M_n (GPC)	heating	cooling
100/0	20 300	2.20	k 43 (0.18) s_B 104 (1.7) Φ_h 174 (4.65) i s_B 102 (0.33) Φ_h 175 (4.69) i	i 165 (4.57) Φ_h 81 (0.42) s_B
80/20	18 100	2.37	k 46 (0.20) s_E 101 (0.43) Φ_h 164 (3.91) i s_E 97 (0.52) Φ_h 164 (3.92)i	i 154 (4.16) Φ_h 74 (0.73) s_E
60/40	26 100	2.51	k 47 (0.16) s_E 98 (0.21) Φ_h 159 (3.94) i s_E 96 (0.15) Φ_h 159 (4.28) i	i 150 (4.12) Φ_h 69 (0.41) s_E
50/50	19 300	2.67	k 46 (0.22) s_E 96 (0.63) Φ_h 157 (4.16) i s_E 93 (0.32) Φ_h 157 (3.88) i	i 148 (3.98) Φ_h 67 (0.52) s_E
40/60	17 200	2.70	k 48 (0.23) s_E 109 (1.17) Φ_h 152 (4.11) i s_E 103 (0.52) Φ_h 151 (4.02) i	i 143 (3.95) Φ_h 66 (0.52) s_E
20/80	20 300	2.65	k 47 (0.17) s_E 105 (1.12) Φ_h 148 (3.98) i s_E 98 (0.48) Φ_h 147 (4.03) i	i 137 (3.94) Φ_h 58 (0.46) s_E
0/100	16 200	1.97	k 48 (0.21) k 109 (0.97) Φ_h 136 (4.06) i k 109 (1.24) Φ_h 136 (3.21) i	i 130 (3.62) Φ_h 62 (0.57) k

[a] Data from first and second DSC heating scans are on the first and second lines, respectively.

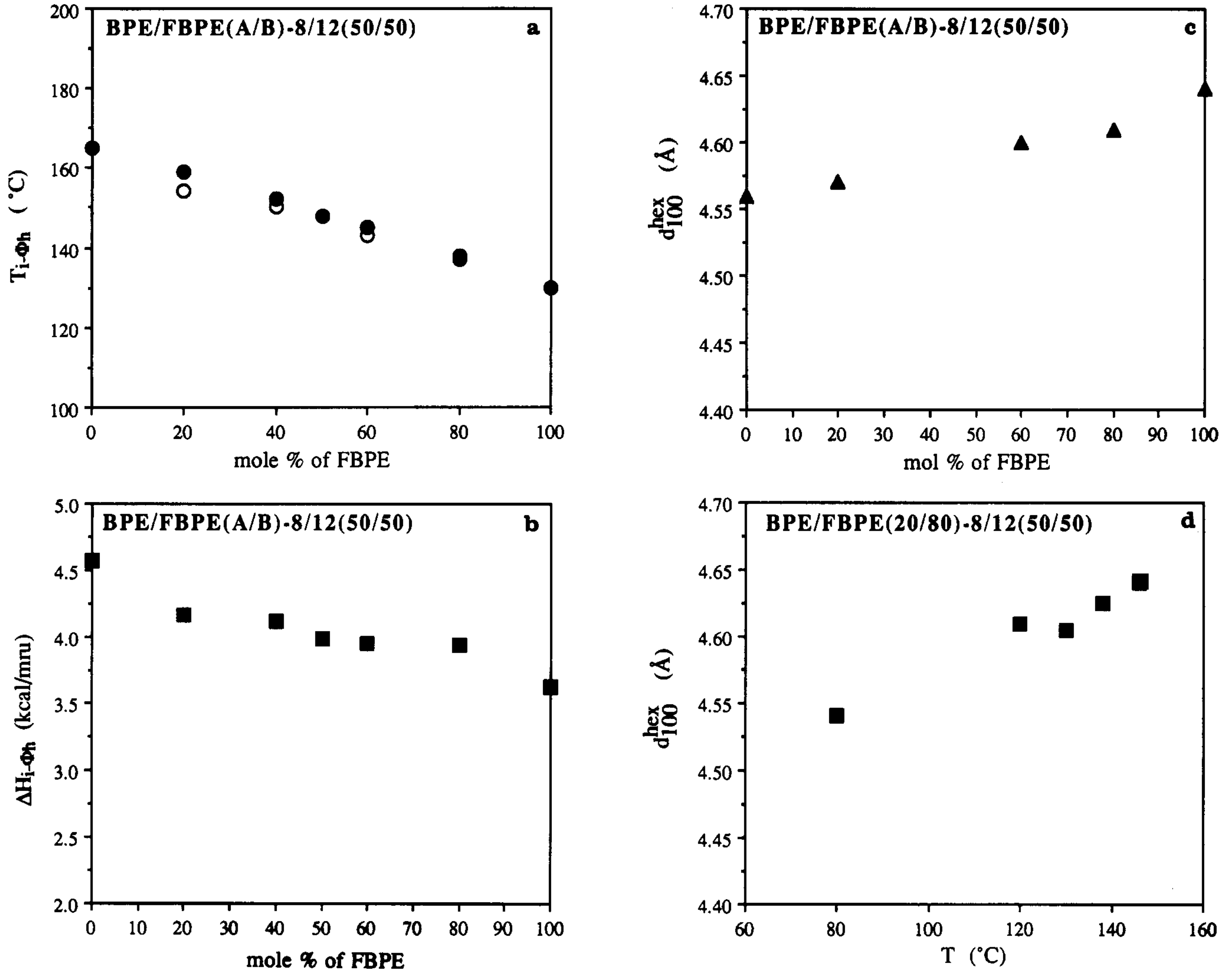

Figure 1. (a) Dependence of the i–Φ_h transition temperature of BPE/FBPE(*A*/*B*)-8/12(50/50) (○, experimental; ●, predicted by the Schroeder–Van Laar equation) versus composition. (b) Dependence of $\Delta H_{i-\Phi_h}$ of BPE/FBPE(*A*/*B*)-8/12(50/50) copolymers on composition. (c) Dependence of d_{100}^{hex} (determined at 120 °C) of the copolyethers BPE/FBPE(*A*/*B*)-8/12(50/50) on composition. (d) Dependence of d_{100}^{hex} of copolyether BPE/FBPE(20/80)-8/12(50/50) on temperature.

of side-chain liquid-crystalline copolymers.[17] Since isomorphic structural units of a copolymer behave like an ideal solution of these structural units, the phase behavior of this copolymer can also be predicted by the Schroeder–Van Laar equations.[18,19]

Table II summarizes the characterization of BPE/FBPE(*A*/*B*)-8/12(50/50) copolymers. The only difference between the first heating and the second heating DSC traces of these copolymers consists of a small endotherm which is available on the first scan at low temperatures. This endotherm is associated with a melting transition (Table II). In the second heating and cooling scans all BPE/FBPE(*A*/*B*)-8/12(50/50) copolymers exhibit two phase transitions which were identified by X-ray scattering

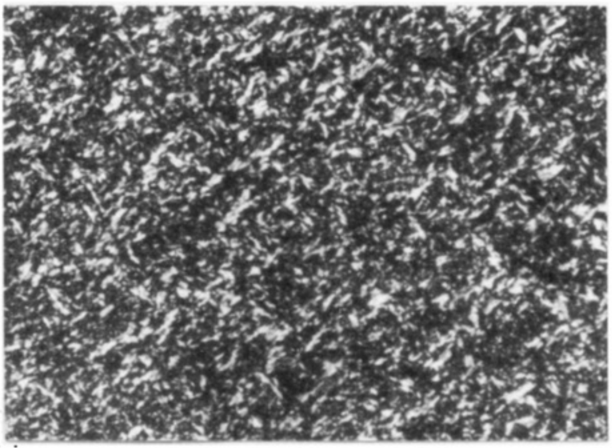

Figure 2. Representative polarized optical micrograph of the broken fan-shaped texture of the Φ_h mesophase of BPE/FBPE-(60/40)-8/12(50/50) obtained after annealing for 10 h at 157 °C.

experiments. The phase from low temperature is dependent on copolymer composition (Table II). BPE-8/12(50/50) exhibits a s_B phase which was characterized previously.[14,15] FBPE-8/12(50/50) displays a crystalline phase.[20] All other BPE/FBPE(*A*/*B*)-8/12(50/50) copolymers exhibit a s_E mesophase.[21] The s_E phase of all these copolymers exhibits two reflections at wide angles. Within instrumental error these reflections are independent of copolymer composition; i.e., $d_{200} = 3.90$ Å and $d_{110} = 4.46$ Å. The s_E phase has a rectangular projection as opposed to the hexagonal projection of the s_B phase. The cross-sectional area per chain of BPE/FBPE(*A*/*B*)-8/12(50/50) in the s_E phase is $ab/2 = 21.2$ Å^2. The cross-sectional area per chain of BPE-8/12(50/50) in the s_B phase is 22.7 Å^2. This result suggests that the presence of the F substituent even in a small proportion breaks the symmetry and subsequently changes the hexagonal packing into the orthorombic one (s_E). At high temperatures, all BPE/FBPE(*A*/*B*)-8/12-(50/50) copolymers exhibit an enantiotropic Φ_h mesophase. The Φ_h mesophase exhibits one intense and sharp reflection in the wide angle which corresponds to the d_{100}^{hex} spacing. There is no reflection at low angles. Therefore, this phase cannot be a s_B mesophase. The transition from the s_B to Φ_h phase is reversible. The temperature associated with the i–Φ_h transition and its enthalpy change exhibit continuous, linear dependences of copolymer composition. Figure 1a presents the dependence of the $T_{i-\Phi_h}$ versus copolymer composition together with the theoretical dependence predicted by the Schroeder–Van Laar equations.[18,19] The dependence of $\Delta H_{i-\Phi_h}$ versus copolymer composition is plotted in Figure 1b.

On the basis of these results, we can safely state that the structural units of the BPE/FBPE(*A*/*B*)-8/12(50/50) copolymers are isomorphic within the Φ_h phase and, accordingly, behave similar to an ideal solution. The d_{100}^{hex} of the Φ_h phase of BPE/FBPE(*A*/*B*)-8/12(50/50) copolymers increases linearly with the increase of the FBPE content of the BPE/FBPE(*A*/*B*)-8/12(50/50) copolymer. This dependence is presented in Figure 1c. Figure 1d presents the dependence of the d_{100}^{hex} of BPE/FBPE(20/80)-8/12-(50/50) copolymer as a function of temperature.

Finally, we have some comments on the texture of the Φ_h mesophase exhibited by these copolymers. As described previously,[14] the Φ_h phase of BPE-8/12(50/50) is very viscous and displays a fan-shaped texture. By contrast to BPE-8/12(50/50), FBPE-8/12(50/50) exhibits a very fluid Φ_h mesophase which displays a broken fan-shaped texture. The viscosity of the Φ_h phase of the BPE/FBPE(*A*/*B*)-8/12(50/50) copolymers decreases with an increase of the d_{100}^{hex} spacing which is directly proportional to the amount of FBPE units in the copolymer. The Φ_h phase of these copolymers exhibits a broken fan-shaped texture. A representative example of this broken fan-shaped texture is presented in Figure 2.

In conclusion, the experiments described in this paper have demonstrated that copolymerization can be used to molecularly engineer both the temperature transition and the degree of order (i.e., interchain distance and subsequently enthalpy change associated with this transition) of the Φ_h mesophase exhibited by main-chain liquid-crystalline polymers. The viscosity of the Φ_h phase decreases with an increase of the interchain distance and simultaneously both the viscosity and the texture of the Φ_h mesophase start to resemble the behavior of conventional liquid-crystalline phases. Since the Φ_h mesophase exhibits a lower concentration of hairpin defect than that of nematic phase, it provides an interesting alternative for the generation of crystalline phases exhibiting extended-chain conformations from flexible polymers.

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References and Notes

(1) (a) This paper represents part 21 in the series Liquid Crystalline Polyethers Based on Conformational Isomerism. (b) Part 20: Ungar, G.; Percec, V.; Zuber, M. *Macromolecules*, in press.

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(19) Achard, M. F.; Mauzac, M.; Richard, M.; Sigaud, M.; Hardouin, F. *Eur. Polym. J.* **1989**, *25*, 593.

(20) The crystalline phase of FBPE-8/12(50/50) shows the following *d* spacings: 19.7 Å (s), 5.12 Å (s), 4.63 Å (m), 4.07 Å (m), 3.81 Å (s), 3.18 Å (w). This crystalline phase is isomorphic with that of MBPE-10/12(50/50) [where, MBPE = 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane] which exhibits the following *d* spacings: 17.6 Å (m), 8.68 Å (w), 5.11 Å (s), 4.58 Å (m), 4.17 Å (m), 3.76 Å (s).

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