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Molecular Engineering of Liquid Crystal Polymers by Living Polymerization. 23. Synthesis and Characterization of AB Block Copolymers Based on [(4-Cyano-4'-biphenyl)oxy]alkyl Vinyl Ether with 1H, 1H, 2H, 2H-Perfluorodecyl Vinyl Ether, and of 2-(4-Biphenyloxy)alkyl Vinyl Ether with 1H, 1H, 2H, 2H-Perfluorodecyl Vinyl Ether with 1H, 1H, 2H, 2H- Perfluorodecyl Vinyl Ether

Virgil Percec and Myongsoo Lee
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106-2699

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This paper describes the synthesis and characterization of AB block copolymers based on w-[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether (6-n) with alkyl being ethyl (6-2), propyl (6-3), nonyl (6-9) and undecanyl (6-11) with 1H, 1H, 2H, 2H-perfluorodecyl vinyl ether (CF8), poly[(6-n)-b-CF8]X/Y (where X/Y refers to the weight ratio of the two segments), and of 2-(4-biphenyloxy)ethyl vinyl ether (BEVE) with 1H, 1H, 2H,2H-perfluoeodecyl vinyl ether, poly[BEVE-b-CF8]X/Y. They were prepared by living cationic polymerization and exhibit a narrow molecular weight distribution. All block copolymers display a microphase separated morphology when the A segment is in the liquid crystalline phase. Block copolymers based on 6-2, 6-3 and BEVE with CF8 exhibit a microphase separated morphology also in the melt phase of A and B block.

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22a NAME OF RESPONSIBLE INDIVIDUAL
Virgil Percec

22b TELEPHONE (Include Area Code)
(216) 368-4242

22c. OFFICE SYMBOL

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Virgil Percec* and Myongsoo Lee
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH. 44106

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* To whom correspondence should be addressed.

SYNOPSIS

This paper describes the synthesis and characterization of AB block copolymers based on ω-[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether (6-n) with alkyl being ethyl (6-2), propyl (6-3), nonyl (6-9) and undecanyl (6-11) with 1H,1H,2H,2H-perfluorodecyl vinyl ether (CF8), poly[(6-n)-b-CF8]X/Y (where X/Y refers to the weight ratio of the two segments), and of 2-(4-biphenyloxy)ethyl vinyl ether (BEVE) with 1H,1H,2H,2H-perfluorodecyl vinyl ether, poly[BEVE-b-CF8]X/Y. They were prepared by living cationic polymerization and exhibit a narrow molecular weight distribution. All block copolymers display a microphase separated morphology when the A segment is in the liquid crystalline phase. Block copolymers based on 6-2, 6-3 and BEVE with CF8 exhibit a microphase separated morphology also in the melt phase of A and B blocks.

INTRODUCTION

Since the first examples of mesogenic vinyl ethers and poly(vinyl ether)s were reported from our laboratory,[1] several other research groups have become actively engaged in the cationic polymerization of mesogenic vinyl ethers because they can be performed under living conditions.[2-4]

Recently, we have demonstrated that mesogenic vinyl ethers containing various functional groups can be polymerized by a living mechanism and these polymerizations allowed systematic investigations of the molecular weight effect on the phase transitions of the resulting polymers.[5,6,8] Binary copolymerization experiments were performed to investigate the influence of copolymer composition on the phase behavior of the copolymers with constant molecular weight. These results were used to tailor make polymers exhibiting nematic, smectic A, reentrant nematic, chiral smectic C, and cholesteric mesophases.[7,8a,b] In addition, we have demonstrated that a quantitative functionalization of a polymer chain end is possible and can be used to produce side chain liquid crystalline macromonomers.[9]

There are only few reports on the synthesis of AB block copolymers containing an amorphous A-block and a side chain liquid crystalline B-block.[11,12] They were prepared by polymer homologous reactions of poly(styrene-b-butadiene) A-B block copolymer,[11] and respectively by succesive living polymerization of methyl methacrylate and a mesogenic methacrylate by group transfer polymerization.[12] The theoretical interest on AB block copolymers containing liquid crystalline and amorphous segments was discussed in detail by Adams and Gronski.[11a]

Presently, we are investigating the synthesis and characterization of block copolymers containing side chain liquid crystalline segments in one block and fluorocarbon segments in the second block by living cationic polymerization. It is well known that the miscibility of fluorocarbon and hydrocarbon molecules is very poor. As a consequence, fluorocarbon-hydrocarbon compounds are surface active systems and can assemble into aggregates both in nonaqueous solutions and in melt.[10] Therefore, block copolymerization of mesogenic vinyl ethers with fluorocarbon-substituted vinyl ethers should allow the preparation of polymer materials with new microphase separated morphologies at very low degrees of polymerization of the hydrocarbon and fluorocarbon blocks.

The goal of this paper is to describe the synthesis and thermal characterization of AB block copolymers based on ω-[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether (6-n) with alkyl being ethyl (6-2), propyl (6-3), nonyl (6-9) and undecanyl (6-11), with 1H,1H,2H,2H-perfluorodecyl vinyl ether (CF8) poly[(6-n)-b-CF8]X/Y (where X/Y refers to the weight ratio of the two segments), and of 2-(4-biphenyloxy)ethyl vinyl ether (BEVE) with 1H,1H,2H,2H-perfluorodecyl vinyl ether poly[BEVE-b-CF8]X/Y.

EXPERIMENTAL

Materials

Methyl sulfide (anhydrous, 99%, Aldrich) was refluxed over 9-borabicyclo[3.3.1]nonane (crystalline, 98%, Aldrich) and then distilled under argon.

Dichloromethane (99.6%, Aldrich) used as polymerization solvent was first washed with concentrated sulfuric acid, then with water, dried over magnesium sulfate, refluxed over calcium hydride and freshly distilled under argon before each use. Trifluoromethane sulfonic acid (triflic acid, 98%, Aldrich) was distilled under vacuum. 1H,1H,2H,2H-Perfluorodecan-1-ol (Strem Chemicals, mp; 40-43 °C) was used as received.

Techniques

^{1}H-NMR spectra were recorded on Varian XL-300 and Varian XL-200 spectrometers. TMS was used as internal standard. A Perkin Elmer DSC-4 differential scanning calorimeter, equipped with a TADS data station was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic or exothermic peaks respectively. In all cases, heating and cooling rates were 20°C/min unless otherwise specified. Glass transition temperatures (Tg) were read at the middle of the change in the heat capacity. First heating scans differ from second and subsequent heating scans. However, second and subsequent heating scans are identical. A Carl-Zeiss optical polarized microscope (magnification: 100x) 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 anisotropic textures[13,14]. Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin Elmer series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler and a Nelson analytical 900 series integrator data station. The measurements were made at 40°C using the UV detector. A set of Perkin Elmer PL gel columns of 10^4 and 500 Å with $CHCl_3$ as solvent (1ml/min) and a calibration plot constructed with polystyrene standards was used to determine the molecular weights. High pressure liquid chromatography (HPLC) experiments were performed with the same instrument.

Synthesis of Monomers

2-[(4-Cyano-4'-biphenyl)oxy]ethyl vinyl ether (6-2),[5b] 3-[(4-cyano-4'-biphenyl)oxy]propyl vinyl ether (6-3),[5b] 9-[(4-cyano-4'-biphenyl)oxy]nonyl vinyl ether

(6-9),[5d] 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11),[5a] 2-(4-biphenyloxy)ethyl vinyl ether (BEVE)[5f] and 1H,1H,2H,2H-perfluorodecyl vinyl ether (CF8)[6f] were synthesized as described previously. Additional details for the synthesis of CF8 are presented below.

Synthesis of 1H,1H,2H,2H-Perfluorodecanyl vinyl ether (CF8).

1H,1H,2H,2H-Perfluorodecan-1-ol (14 g, 0.03 mol) was added to a mixture of 100 ml of n-butyl vinyl ether, 100 ml of chloroform, and 1,10-phenanthroline palladium(II) diacetate[5a] (0.8 g, 2 mmol) and kept under argon. The yellow mixture slowly turned green while it was refluxed for 12h. After filtration, the solvent was removed in a rotary evaporator. The crude product was purified by column chromatography (silica gel, CH_2Cl_2 eluent) and then extracted with MeOH to remove residual n-butyl vinyl ether. The obtained product (yield 12 g, 74 %)was then dried over CaH_2 and freshly distilled under vacuum before each use. Purity: >99% (GC); bp: 71 ^{o}C (3 mm); 200MHz ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 2.51 (2 *protons*, $-CF_2-C\underline{H}_2-$, m), 4.00 (2 protons, $-C\underline{H}_2O-$, t), 4.10 (1 proton, $OCH=C\underline{H}_2$ trans, d), 4.23 (1 proton, $OCH=C\underline{H}_2$ cis, d), 6.47 (1 proton, $CH_2=C\underline{H}O-$, q).

Synthesis of block copolymers

The syntheis of block colymers was carried out in glass flasks equipped with teflon stopcocks and rubber septa under argon atmosphere at $0^{o}C$ by sequentially polymerizing first the mesogenic vinyl ether and then CF8. All glassware was dried overnight at $130^{o}C$. The monomer was further dried under vacuum overnight in the polymerization flask. Then the flask was filled with argon, cooled to $0^{o}C$ and the methylene chloride, dimethyl sulfide and triflic acid were added via a syringe. The first monomer concentration was about 10 wt% of the solvent volume and the dimethyl sulfide concentration was 20 times larger than that of the initiator. After 40 min of reaction time, when the polymerization of the first monomer had reached about 100% conversion, freshly distilled CF8 was injected into the polymerization solution. After two more hours, the polymerization was quenched with ammoniacal methanol. The reaction mixture was then precipitated into methanol. The filtered polymers were dried and precipitated from methylene chloride solutions into methanol (two or three times) until GPC traces showed no traces of unreacted monomer. Tables I summarizes the polymerization results.

RESULTS AND DISCUSSION

The mesogenic vinyl ethers, 6-n and BEVE were polymerized by initiation with $CF_3SO_3H/S(CH_3)_2$ in methylene chloride at 0°C.[15] After 40 min, CF8 was injected into the polymerization solution as a second monomer. The synthesis of block copolymers is outlined in Scheme I. Figure 1 shows typical GPC traces of poly(6-2) and of the resulting block copolymer. The polymerization of mesogenic vinyl ether had reached almost quantitative conversion in 40 min to produce the homopolymer with controlled molecular weight and narrow molecular weight distribution (Table I, Figure 1b). Subsequent sequential addition of CF8, led to block copolymers with a monomodal, narrow molecular weight distribution which however, was slightly broader than that of the parent mesomorphic homopolymers (Table I, Figure 1a). This sequence of polymerization was selected since poly(CF8) is insoluble in conventional solvents.[6f] However, its insertion into a block copolymer leads to soluble block copolymers and demonstrates that CF8 can be polymerized by a living mechanism.

The structure and composition of the block copolymers were determined by 300 MHz ^1H-NMR spectroscopy. Figure 2 presents a typical 300 MHz ^1H-NMR spectrum of poly[(6-2)-b-CF8]5/5. This spectrum exhibits the aromatic protons of the (6-2) repeating units at 6.9-7.7 ppm and the methylene protons of the CF8 repeating units at 2.31 ppm . In addition, the resonances of the acetal and methoxy protons which are formed after quenching the living carbocationic polymerization with methanol are observed at 4.70 and 3.31 ppm, respectively. No other signals indicative of side reactions are observed. The composition of block copolymers was determined from the ratio of the aromatic protons (o to alkoxy, signal d in Figure 2) to the methylene protons (-$\underline{H}$ CH_2CF_2-, signal m in Figure 2). The composition of block copolymers determined from their NMR spectra and presented in weight ratio in Table I is in good agreement with the feed weight ratio of the two monomers.

The mesomorphic behavior of all block copolymers was characterized by DSC and optical polarized microscopy and compared to that of the homopolymers with similar degrees of polymerization of the A block.

Let us discuss first the thermal behavior of poly[(6-2)-b-CF8]5/5 and poly[BEVE-b-CF8]5/5. Both block copolymers are synthesized from the mesogenic monomers whose parent homopolymers exhibit a glassy phase when it is determined from second DSC heating scan[5b] (Table II, Figures 3 and 4), and fluorinated monomer whose parent homopolymer displays a crystalline melting.[6f] In the first heating scan, poly[(6-2)-b-CF8]5/5 exhibits a crystalline melting which corresponds to the CF8 block followed by an X phase of the mesogenic segment. The transition temperature of each phase in the block copolymer is very close to that of poly(6-2) (Table II) and poly(CF8).[6f] Second heating and cooling DSC scans of poly[(6-2)-b-CF8]5/5 display the same behavior except that the X phase does not appear since this mesophase is located in close proximity to the glass transition temperature of the mesogenic segment and therefore, it is strongly kinetically controlled (Figure 3). The DSC traces of the first heating, second heating and cooling scans of poly[BEVE-b-CF8]5/5 are presented in Figure 4. Thermal behavior of poly[BEVE-b-CF8]5/5 is similar to that of poly[(6-2)-b-CF8]5/5 except that the melting transition of the mesogenic segment is absent in the first DSC heating scan.

One of the unique feature of these block copolymers is the persistence of mesomorphic behavior above the isotropization temperatures of the corresponding mesogenic homopolymers (Table II, Figures 3,4). This is most probably due to a microphase separated morphology in the melt state. Since the refractive indices of these two segments are highly dissimilar, they exhibit an anisotropic texture on the optical polarized microscope. A characteristic example of the mesomorphic texture obtained for poly[(6-2)-b-CF8]5/5 at 190 °C is presented in Figure 5.

Poly[(6-3)-b-CF8]5/5 is based on the mesogenic monomer (6-3) whose parent homopolymer poly(6-3)[5b] exhibits a nematic mesophase. This block copolymer exhibits a crystalline melting of the fluorinated segment, the X and nematic phases of the mesogenic segment, and the newly generated mesophase indicative of microphase separated morphology above the isotropization temperature (Table II, Figure 6). Both the mesomorphic-mesomorphic transition temperature and the enthalpy change associated with the mesophase of poly[(6-3)-b-CF8]5/5 decreases in comparison to that of the parent homopolymers (Table II). This trend agrees well with previous results available in the literature[11] and is predicted by theory.[16,17] The following speculative explanation about this phenomenon is possible. The decrease of enthalpy change may be caused by a disordering of the mesogens at the interphase. Although the phase boundary is sharp on a local scale, the interphase may be of very irregular structure which could oppose the ordering of the mesogens at the interphase.

The observation of textures of poly[(6-3)-b-CF8]5/5 by optical polarized microscopy reveals significant difference in comparison to the behavior of their respective homopolymers. Figure 7 shows the schlieren texture of both poly(6-3) and poly[(6-3)-b-CF8]5/5 which is characteristic of a nematic mesophase. However the domain size of the schlieren texture in block copolymer is much smaller than that of the parent homopolymer even after overnight annealing.

DSC traces of poly[(6-9)-b-CF8]7/3 and poly[(6-11)-b-CF8]7/3 are presented in Figures 8 and 9 respectively. Both block copolymers are synthesized from mesogenic monomers whose parent homopolymers exhibit a s_A phase as their highest temperature mesophase. In the case of the first heating DSC scan of poly[(6-9)-b-CF8]7/3, this block copolymer exhibits the melting of the fluorinated segment and the s_A phase of the mesogenic segment which is indicative of a microphase separated morphology. The first order transition at 41.3°C (Table II, Figure 8) may result from different crystalline size of the fluorinated segment. In second and first cooling scans this first order transition does not appear, and there are only transitions which correspond to those of each homopolymer. Both the transition temperature from s_A to the isotropic state and the enthalpy change associated with this mesophase decrease when they are compared to those of the corresponding mesogenic homopolymers poly(6-9)[5d] and poly(6-11)[5a] (Table II).

Figure 9 displays representative optical polarized micographs of the s_A phase of poly(6-9) (a) and of poly[(6-9)-b-CF8]7/3 (b). The s_A phase of poly(6-9) displays a typical focal conic texture. The s_A phase of poly[(6-9)-b-CF8]7/3, on the other hand, exhibits striations on the focal conic texture which is clearly different from that of the parent homopolymer. It is believed that these striations are manifestations of microphase separation of the fluorinated block within the s_A phase.

Figure 10 presents first and second heating, and first cooling DSC scans of poly[(6-11)-b-CF8]7/3. The thermal behavior of this block copolymer is similar to that of poly[(6-9)-b-CF8]7/3 except that there is a melting transition of the mesogenic segment in the case of first heating scan.

Distinct from the behavior of the block copolymers based on mesogenic monomers with two and three methylene units in the spacer, the optical micrographs of poly[(6-9)-b-CF8]7/3 and poly[(6-11)-b-CF8]7/3 display a lack of mesomorphic behavior in melt state. This phenomenon illustrates the role of longer length spacer in decreasing the immiscibility between the mesogenic segment and fluorinated segment, and/or its influence on the difference between the refractive indices of the two segments.

In conclusion, block copolymers containing side chain liquid crystalline segments in one block and fluorocarbon segments in the second block can be synthesized by living cationic polymerization. The resulting block copolymers exhibit narrow molecular weight distribution and the weight ratio composition of block copolymers is in good agreement with the feed weight ratio of the each monomer. The thermal behavior of all block copolymers synthesized in this paper was determined by DSC and optical polarized micoscopy and shows a microphase separated morphology, although the degrees of polymerization of the mesogenic and fluorocarbon blocks are very low. For mesogenic monomers with short spacer lengths the microphase separated morphology is also maintained in the melt phase up to a temperature where the fluorinated and mesogenic segments become miscible.

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FIGURES AND SCHEME CAPTION

Scheme I.	Synthesis of block copolymers
Figure 1.	GPC traces of poly[(6-2)-b-CF8]5/5 (a) and of poly(6-2) (DP=12) (b)
Figure 2.	300 MHz ^{1}H-NMR spectrum of poly[(6-2)-b-CF8]5/5
Figure 3.	DSC traces displayed by the first heating (a), second heating (b) and the first cooling scans (c) of poly[(6-2)-b-CF8]5/5
Figure 4.	DSC traces displayed by the first heating (a), second heating (b) and the first cooling scans (c) of poly[BEVE-b-CF8]5/5
Figure 5.	Representative optical polarized micrograph (100x) of the mesophase displayed by poly[(6-2)-b-CF8]5/5 at 190 °C after annealing 1 day.
Figure 6.	DSC traces displayed by the first heating (a), second heating (b) and the first cooling scans (c) of poly[(6-3)-b-CF8]5/5
Figure 7.	Representative optical polarized micrographs (100x) of the mesophase displayed by poly(6-3) (DP=16) at 90 °C (a) and poly[(6-3)-b-CF8]5/5 (b) at 90 °C after annealing overnight.
Figure 8.	DSC traces displayed by the first heating (a), second heating (b) and the first cooling scans (c) of poly[(6-9)-b-CF8]7/3
Figure 9.	Representative optical polarized micrographs (100x) of the mesophase displayed by poly(6-9) (DP=16) (a) and poly[(6-9)-b-CF8]7/3 (b) at 130 °C.
Figure 10.	DSC traces displayed by the first heating (a), second heating (b) and the first cooling scans (c) of poly[(6-11)-b-CF8]7/3

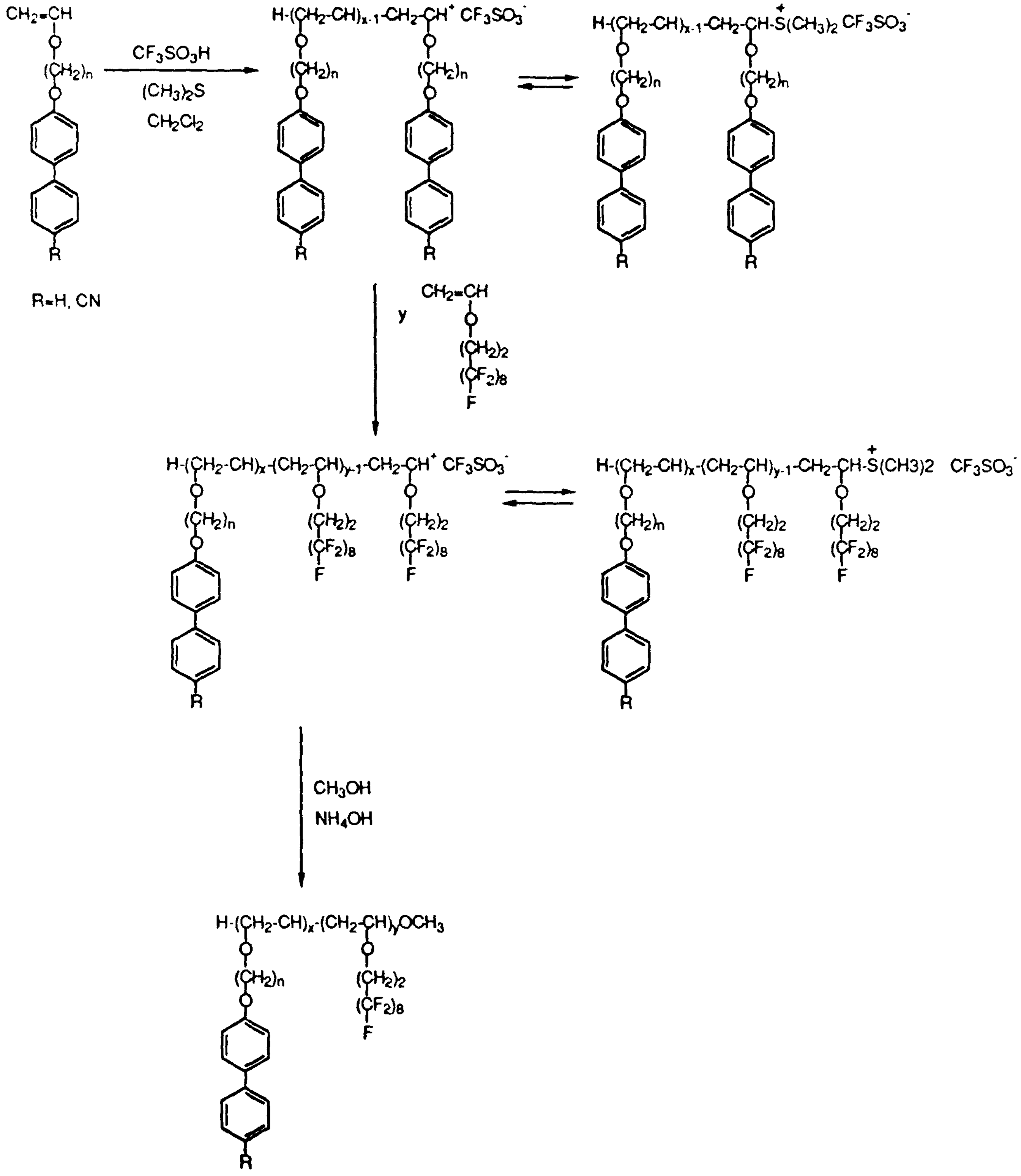
Table I; Block Copolymers of Mesogenic Vinyl Ethers (M) and CF8 via Sequential Living Polymerization by $CF_3SO_3H/(CH_3)_2S$. ($[M]_0/[I]_0=15$, $[(CH_3)_2S]_0/[I]_0=20$)

No.	Block copolymer	$M_n \times 10^{-3}$ (A)	Mw/Mn (A)	$M_n \times 10^{-3}$ (AB)	Mw/Mn (AB)	DP_A/DP_B	DP_A/DP_B	w_A/w_B	w_A/w_B	yield
		GPC		GPC		(theo)	(GPC)	(theo)	(NMR)	(%)
1	poly[(6-2)-b-CF8]5/5	3.7	1.12	7.5	1.26	15/8	14/7	5:5	5.5/4.5	87
2	poly[BEVE-b-CF8]5/5	3.2	1.08	5.9	1.15	15/8	13/6	5:5	5.6/4.4	80
3	poly[(6-3)-b-CF8]5/5	4.0	1.13	8.2	1.24	15/8	15/8	5:5	4.6/5.4	89
4	poly[(6-9)-b-CF8]7/3	5.6	1.08	7.8	1.18	15/4	16/4	7:3	6.8/3.2	81
5	poly[(6-11)-b-CF8]7/3	5.5	1.14	7.8	1.20	15/5	14/4	7:3	6.9/3.1	80

A=mesogenic segment; B=fluorinated segment; AB=block copolymer; DP_A, DP_B=degree of polymerization of segment A and B respectively; w_A and w_B=weight fractions of segment A and B in block copolymer respectively

Table II. Thermal characterization of the AB block copolymers and of the parent homopolymers. Data on first line are from first heating and cooling scans. Data on second line
are from second heating scan

sample no.	polymer	phase transitions (°C) and corresponding enthalpy changes (kcal/mru) heating	cooling
1	poly(6-2)	g 78.5 X 86.0 (0.18) i g 72.8 i	i 63.8 g
2	poly[(6-2)-b-CF8]	k -4.6 (-0.12) k 21.5 (0.30) g 75.1 X 83.1 (0.11) mes[a] 250 dec[b] k -0.9 (-0.11) k 20.1 (0.32) g 78.4 mes 250 dec	250 mes[a] 69.0 g -12.8 (0.18) k
3	poly(BEVE)	g 58.9 k 70.1 (1.04) i g 52.1 i	i 45.7 g
4	poly[(BEVE)-b-CF8]	k 30.2 (0.013) k 65.7 (0.82) mes 250 dec k 25.4 (0.010) g 50.0 mes 250 dec	250 mes 42.8 g 8.2 (0.011) k
5	poly(6-3)	g 59.5 X 64.5 (0.26) n 97.8 (0.094) i g 56.4 n 95.9 (0.07) i	i 90.8 (0.078) n 50.3 g
6	poly[(6-3)-b-CF8]	k -11.6 (-0.14) k 15.1 (0.37) g 60.0 X 64.0 (0.050) n 96.6 (0.04) mes[a] 250 dec[b] k -4.84 (-0.07) k 14.1 (0.35) g 59.0 n 95.2 (0.047) mes[a] 250 dec[b]	250 mes[a] 90.1 (0.042) n 52.0 g -14.5 (0.17) k
7	poly(6-9)	g 13.3 s_A 141.5 (0.62) i g 12.5 s_A 141.0 (0.60) i	i 136.7 (0.61) s_A 7.5 g
8	poly[(6-9)-b-CF8]	k -6.91 (0.054) g 12.3 k 22.6 (0.17) s_X 41.3 (0.03) s_A 140.1 (0.50) i g 10.2 k 22.1 (0.25) s_A 139.2 (0.47) i	i 134.5 (0.41) s_A 4.7 g -6.5 (0.11) k
9	poly(6-11)	g 17.0 k 66.3 (3.29) s_A 155.2 (0.82) i g 14.7 s_A 150.1 (0.77) i	i 143.4 (0.78) s_A 8.3 g
10	poly[(6-11)-b-CF8]	g 9.5 k 54.4 (-) k 64.4 (3.20)[c] s_A 146.2 (0.78) i g 8.4 k 20.5 (0.30) s_A 146.3 (0.72) i	i 140.0 (0.71) s_A 4.2 g -5.74 (0.09) k



Scheme I

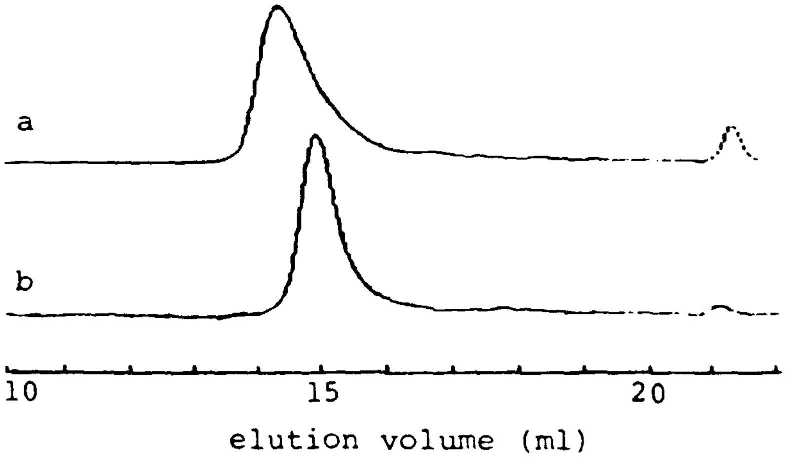


Figure 1

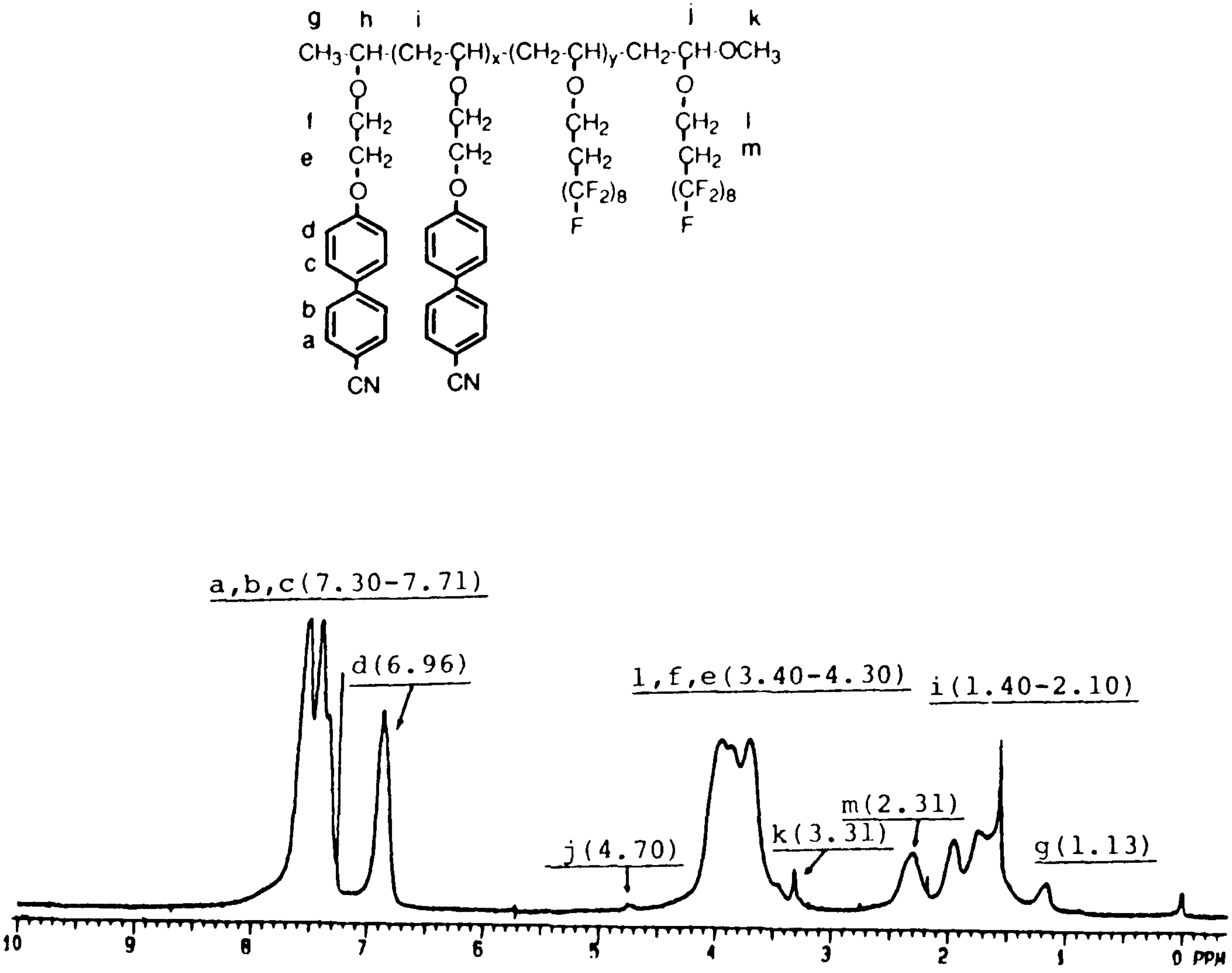

g h i j k
CH3·CH·(CH2·CH)x·(CH2·CH)y·CH2·CH·OCH3
f e d c b a
l m
CN
(CF2)8
F
a,b,c(7.30-7.71)
d(6.96)
j(4.70)
l,f,e(3.40-4.30)
k(3.31)
m(2.31)
i(1.40-2.10)
g(1.13)
10
9
8
7
6
5
4
3
2
1
0 PPM

Figure 2

Poly[(6-2)-b-CF8]5/5

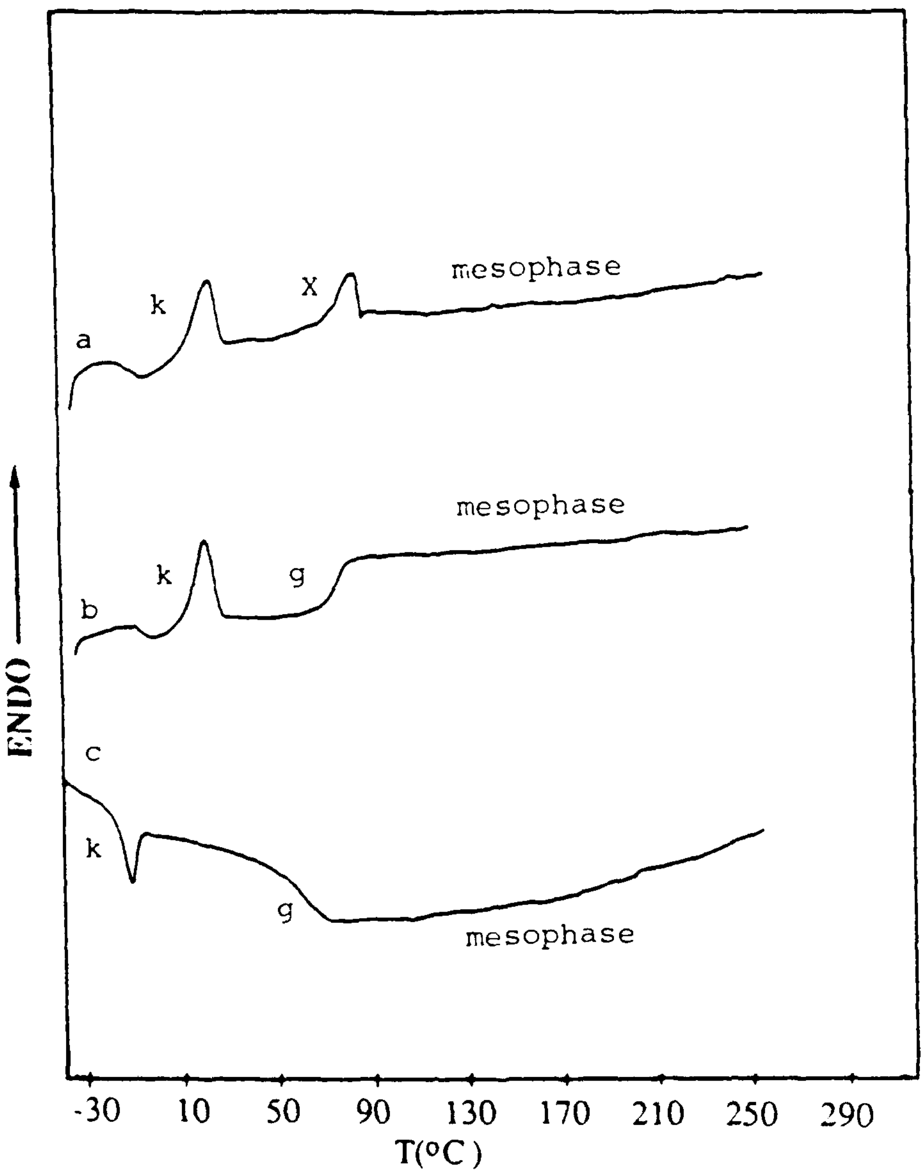


Figure 3

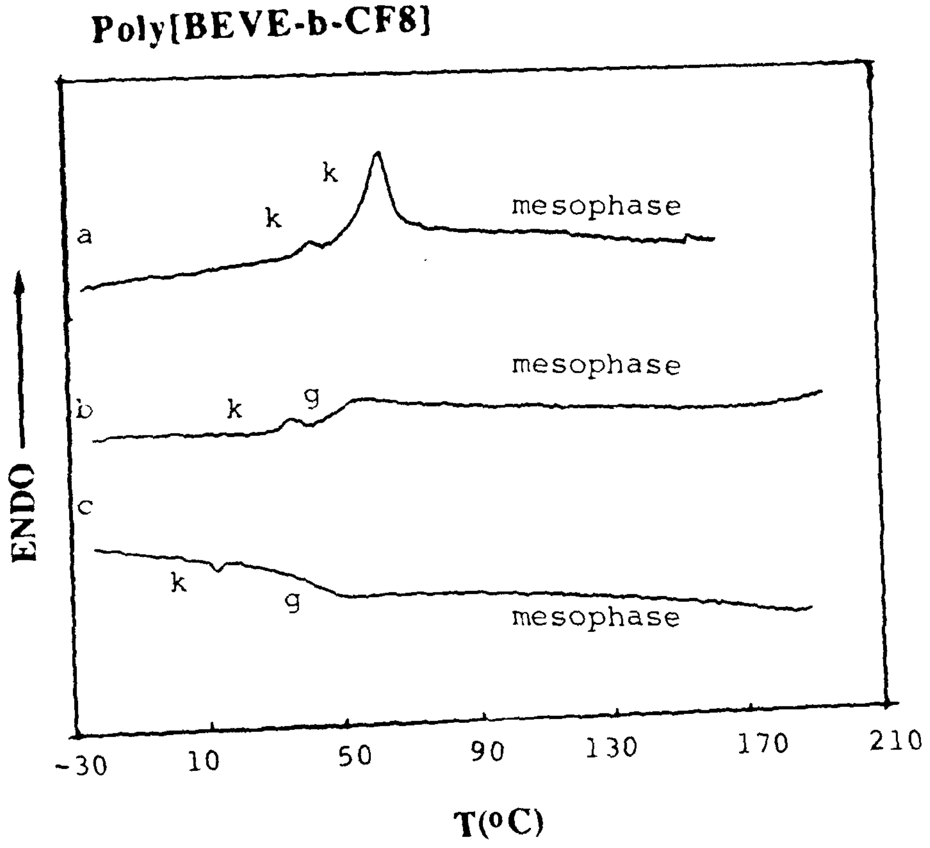

Poly[BEVE-b-CF8]
ENDO
a
k
k
mesophase
b
k
g
mesophase
c
k
g
mesophase
-30
10
50
90
130
170
210
T(°C)

Figure 4

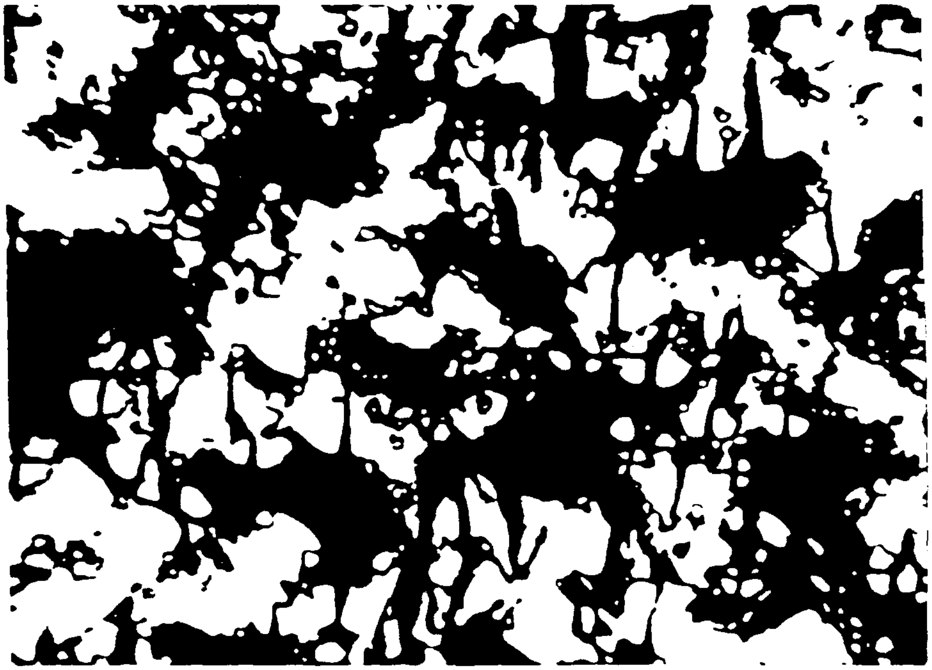
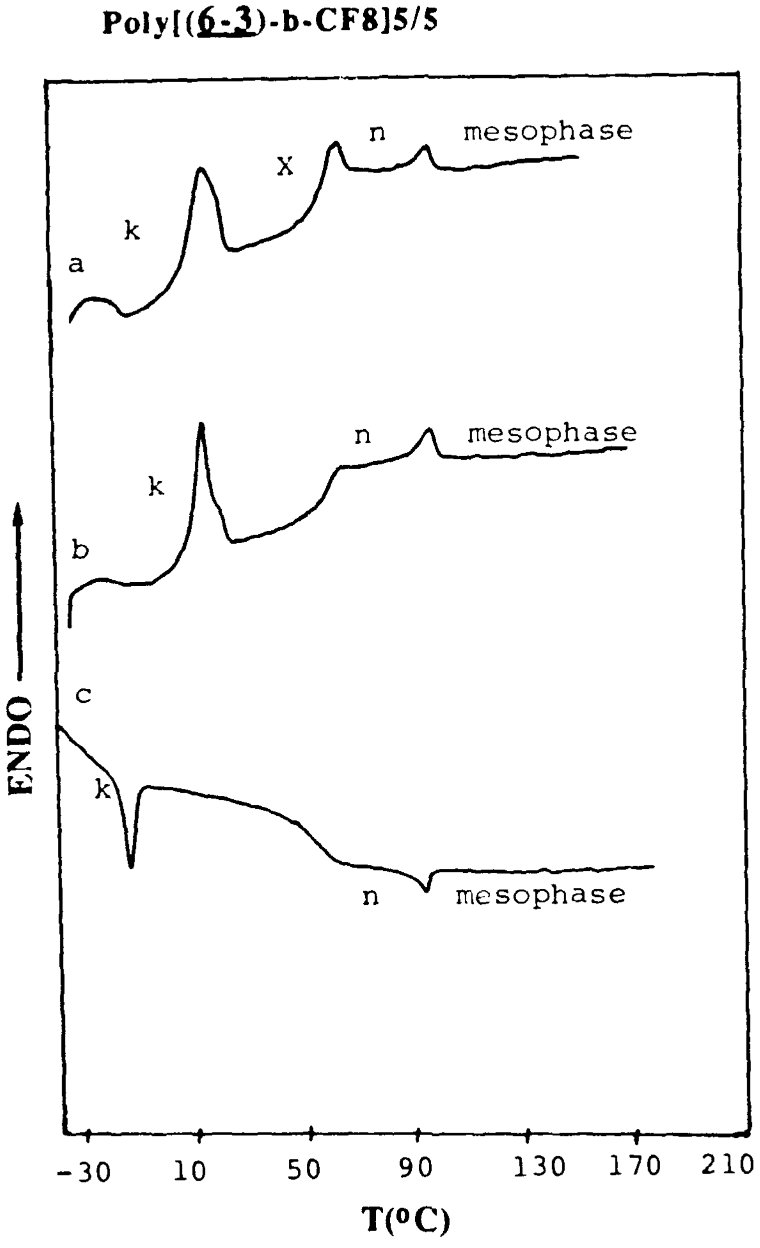


Figure 5



Poly[(6-3)-b-CF8]5/5
a
k
X
n
mesophase
b
k
n
mesophase
c
k
n
mesophase
ENDO
-30
10
50
90
130
170
210
T(°C)

Figure 6

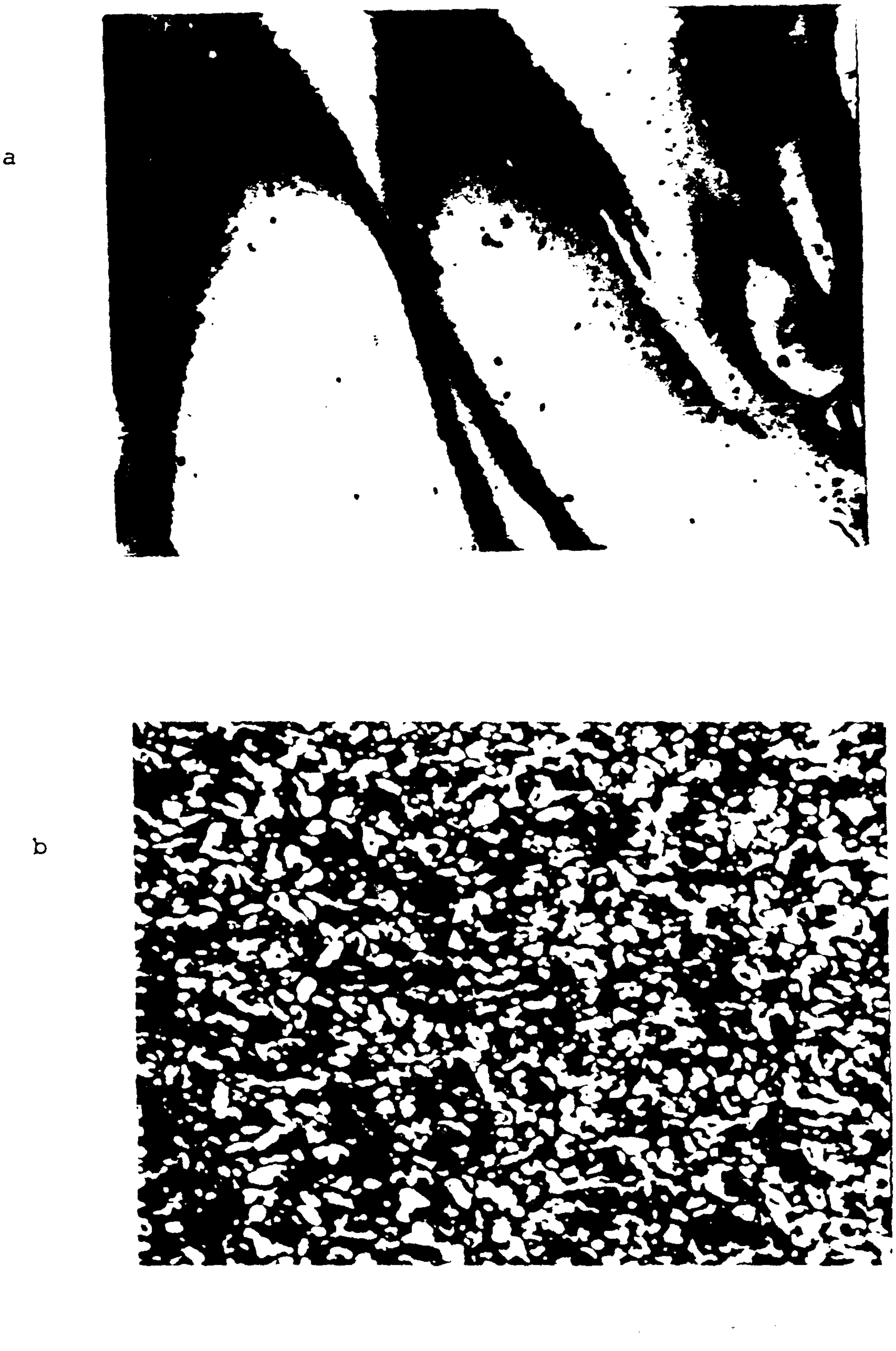
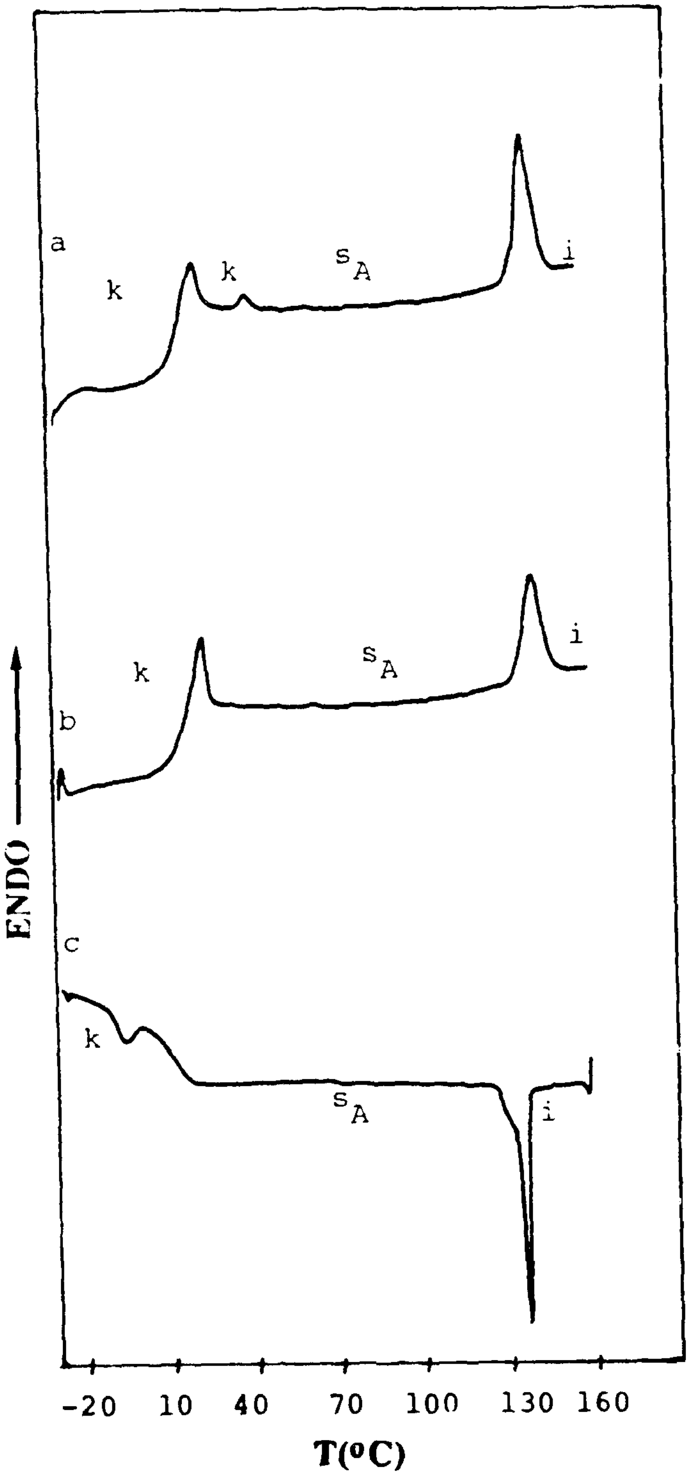


Figure 7



Poly[(6-9)-b-CF8]7/3

Figure 8

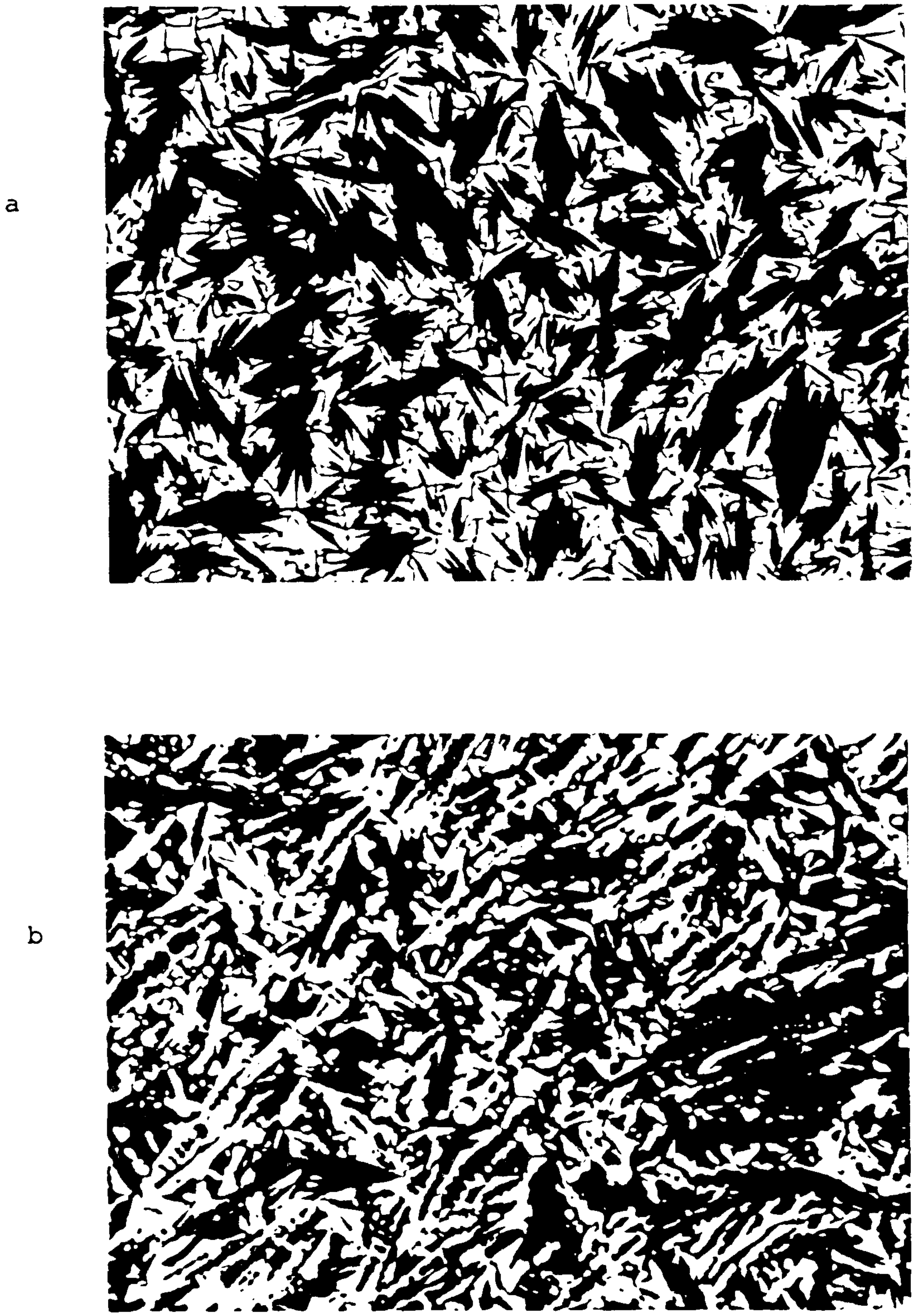


Figure 9

Poly[(6-11)-b-CF8]7/3

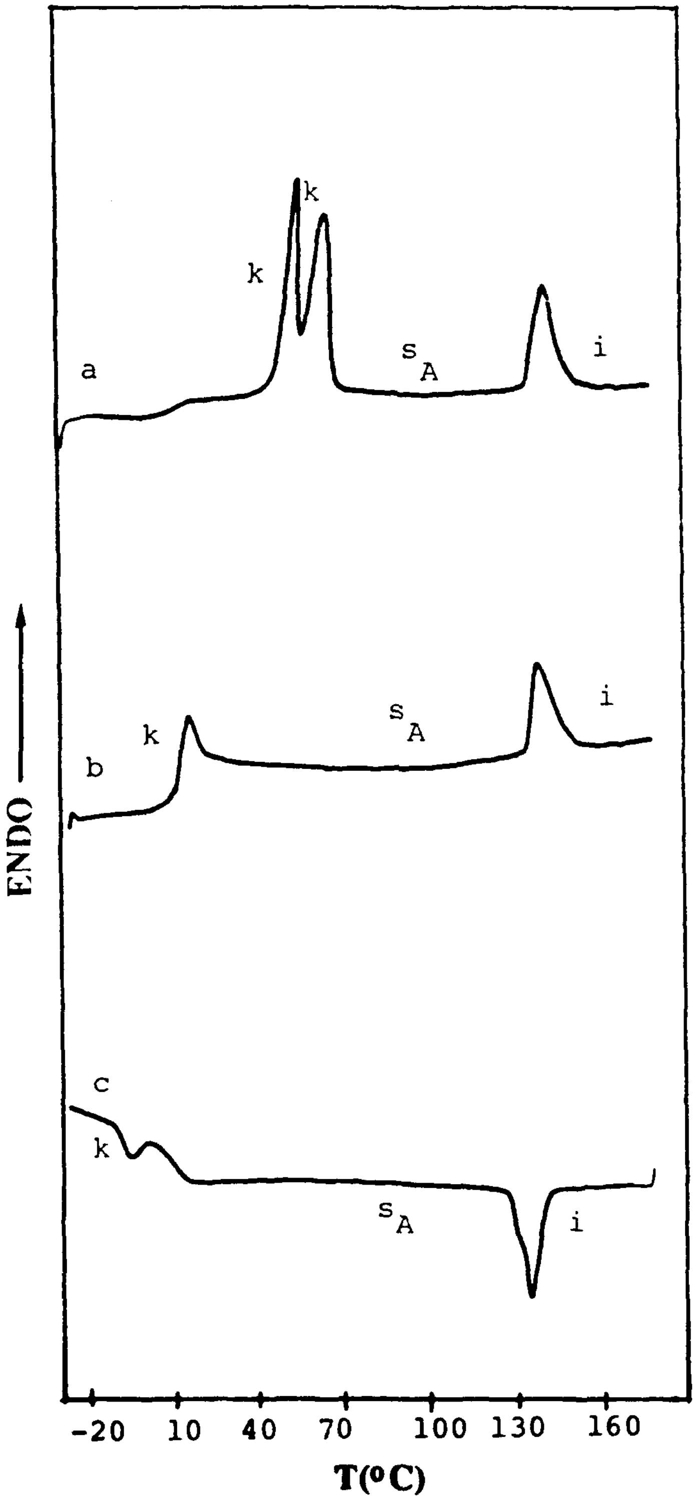


Figure 10