

## **CHIRAL LIQUID-CRYSTALLINE BLOCK COPOLYMERS BASED ON POLYETHER AND MESOGENIC POLYACRYLATE BLOCKS**

**EMO CHIELLINI, GIANCARLO GALLI**

Dipartimento di Chimica e Chimica Industriale, Università di Pisa,  
56126 Pisa, Italy

**ERSIN I. SERHATLI, YUSUF YAGCI**

Department of Chemistry, Istanbul Technical University,  
80626 Istanbul, Turkey

**MICHELE LAUS, ANNINO SANTE ANGELONI**

Dipartimento di Chimica Industriale e dei Materiali, Università di  
Bologna, 40136 Bologna, Italy

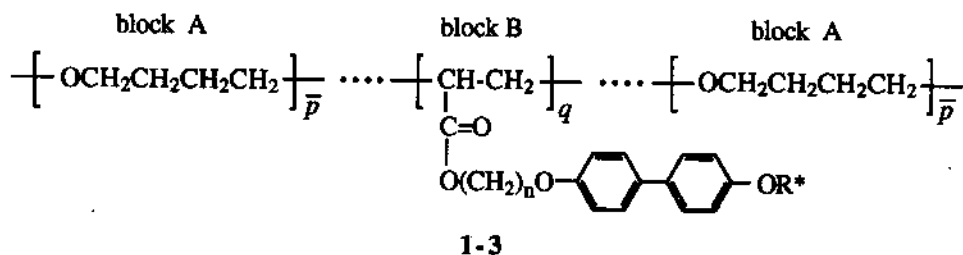
**Abstract** New liquid-crystalline ABA triblock copolymers containing crystalline polytetrahydrofuran (A) and chiral side-chain liquid-crystalline (B) blocks were prepared, and their phase behavior was studied. Block B was one of different polyacrylates containing the biphenyl mesogen variously spaced from the backbone and substituted with chiral groups, that are known to exhibit an electroclinic response in the chiral smectic A phase of the relevant homopolymers. The copolymers appeared to be phase-separated and formed mesophases characterized by lower transition temperature and enthalpy than those of the corresponding polyacrylate homopolymers.

### **INTRODUCTION**

Liquid crystals and block copolymers are two most prominent examples of materials exhibiting non-crystalline ordered structures. We are interested<sup>1-3</sup> in developing novel liquid-crystalline molecular architectures combining in one single polymer structure the orientational order at the molecular level typical of liquid crystals and the compositional supramolecular order typical of block copolymers. In fact, block copolymers that are comprised of two normally incompatible segments interconnected by covalent bonds will tend to phase-separate producing microheterogeneous structures.<sup>4</sup> The type of morphology obtained in phase-separated block copolymers depends upon a

variety of factors, but basically the major component will usually exist as the continuous phase, with the minor component present as discrete domains (Fig. 1). The latter assume spherical shapes at low volume fractions, and rod-like shapes at somewhat higher fractions. When the two phases are present with nearly equal compositions, they can exist as two continuous phases with lamellar structures. Obviously, these morphological variations can exert a major influence on physical properties that are strongly dependent on the nature of the continuous phase.

In this paper we report on some preliminary results about the synthesis and some properties of a new class of ABA triblock copolymers 1-3, whose simplified structure is schematically represented as follows:



- 1 :  $n = 11$ ;  $\text{R}^* = \text{OCCH}^*(\text{Cl})i.\text{C}_3\text{H}_7$   
 2 :  $n = 11$ ;  $\text{R}^* = \text{OCCH}^*(\text{Cl})\text{CH}^*(\text{CH}_3)\text{C}_2\text{H}_5$   
 3 :  $n = 10$ ;  $\text{R}^* = \text{CH}_2\text{CH}^*(\text{CH}_3)\text{C}_2\text{H}_5$

Block copolymers with liquid-crystalline blocks could give rise to microseparated phases, such as those sketched in Fig. 1, and their study may be of fundamental importance in elucidating the mesophase transitions of liquid crystals in confined geometries.<sup>5</sup> On the other hand, the ordering field of the thermotropic mesophase could exert significant effects on the structure

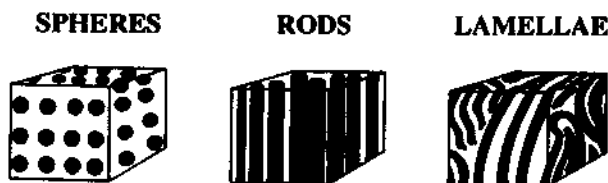
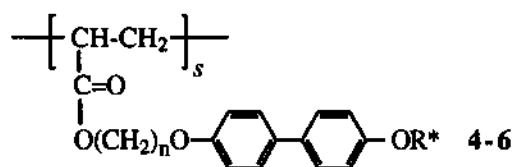


FIGURE 1. Schematic representation of different morphologies in block copolymers.

and morphology of the separated phase.<sup>6</sup> Furthermore, new practical opportunities of liquid-crystalline block copolymers can be envisioned, especially for their use as new materials with tailored properties for electrooptical applications.

Copolymers 1-3 are constituted by one central chiral liquid-crystalline polyacrylate block (block B) and two lateral polytetrahydrofuran (poly(THF)) blocks (blocks A). The former was derived from acrylate monomers containing the biphenyl mesogenic unit variously substituted which gave rise to chiral smectic mesophases in the relevant homopolymers characterized by an electroclinic response in the chiral smectic A phase.<sup>7</sup>

The phase behavior of the block copolymers 1-3 is described and compared with those of polytetrahydrofuran and polyacrylates 4-6 obtained by homopolymerization of the corresponding mesogenic monomers:



- 4 :  $n = 11$ ;  $\text{R}^* = \text{OCCH}^*(\text{Cl})i.\text{C}_3\text{H}_7$   
 5 :  $n = 11$ ;  $\text{R}^* = \text{OCCH}^*(\text{Cl})\text{CH}^*(\text{CH}_3)\text{C}_2\text{H}_5$   
 6 :  $n = 10$ ;  $\text{R}^* = \text{CH}_2\text{CH}^*(\text{CH}_3)\text{C}_2\text{H}_5$

## EXPERIMENTAL PART

**Materials:** Tetrahydrofuran (THF) was freshly distilled from potassium/benzophenone.  $\text{AgPF}_6$  (Fluka) was used as received. 4,4'-Azobis(4-cyanopentanoyl chloride) (**7**) was prepared from 4,4'-azobis(4-cyanopentanoic acid) (Fluka) according to a previous procedure.<sup>8</sup> Acrylate monomers **11-13** containing the biphenyl mesogen substituted with various chiral groups were synthesized and polymerized to the corresponding polyacrylates **4-6** as already described.<sup>9,10</sup>

**Synthesis of macroinitiator 9:** In a typical polymerization reaction, 1.42 g (4.5 mmol) of **7** and 2.50 g (9.9 mmol) of  $\text{AgPF}_6$  were dissolved in 100 ml of THF at room temperature under dry nitrogen. After reacting for two min at the same temperature, the reaction mixture was filtered and polymer **9** was recovered by precipitation into cold water. The polymer was dissolved in diethyl ether and the ether solution was washed with water and then dried over  $\text{Na}_2\text{SO}_4$ .

After removing the solvent, the polymer sample was dried under high vacuum. Reaction yields typically ranged from 45 to 60%.

*Synthesis of block copolymers:* In a typical copolymerization reaction, 1.1 g (2.1 mmol) of monomer **11** and 0.4 g (18.6  $\mu\text{mol}$  corresponding to 5.5 mmol of THF r.u.) of macroinitiator **9** were dissolved in 20 ml of THF. The reaction mixture was introduced into a Pyrex glass ampoule, thoroughly freeze-thaw degassed and then sealed under vacuum. After reacting for 48 h at 70°C, the copolymer was precipitated by addition of a ten-fold excess of methanol, filtered and purified from polytetrahydrofuran by extraction with boiling ethanol in a Kumagawa extractor. Conversion of **11** was 10%.

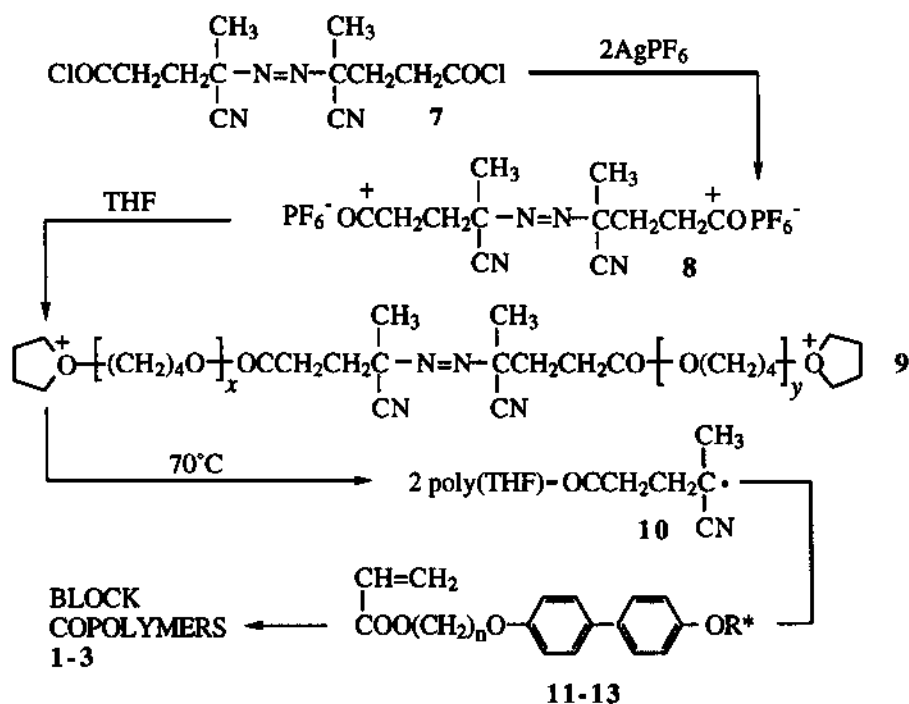
*Physicochemical characterization:* The  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were recorded on a Varian Gemini 200 spectrometer. Average molecular weights were determined by size exclusion chromatography (SEC) of THF solutions with a 590 Waters chromatograph equipped with refractive index and ultraviolet detectors, using a Shodex KF-804 column calibrated with polystyrene standard samples. The thermal and liquid-crystalline properties of the polymers were studied by a combination of differential scanning calorimetry (Mettler TA3000 at a scanning rate of 10  $\text{Kmin}^{-1}$ ) and hot stage polarized light microscopy (Reichert Polyvar microscope equipped with a programmable Mettler FP52 heating stage at a scanning rate of 10  $\text{Kmin}^{-1}$ ). Dynamic-mechanical (DMA) measurements were performed with a Perkin Elmer DMTA-7 apparatus at a scanning rate of 4  $\text{Kmin}^{-1}$  at 1 Hz frequency. Samples were compression molded in the mesophase at various temperatures for 15 min to form ~1 mm thick sheets and the three point bending geometry was used.

## RESULTS AND DISCUSSION

The block copolymers **1-3** were synthesized via a two-step procedure recently developed by us for the preparation of liquid-crystalline block copolymers<sup>1-3</sup>, as illustrated in Scheme 1.

It consisted of two successive cationic and free-radical initiation processes starting from a bifunctional low molar mass initiator containing one azo group and two acyl chloride end groups. The 4,4'-azobis(4-cyanopentanoyl chloride) (**7**) is highly efficient in initiating the free-radical polymerization of a variety of monomers, very much like the most typical initiator AIBN<sup>11</sup>, even if incorporated into a polymer chain.<sup>12,13</sup>

SCHEME 1. Synthetic pathway for the preparation of block copolymer 1-3.



When reacted with a silver salt constituted by a low nucleophilic counterion in THF, **7** produces the diacyl cation **8** which is then able to polymerize THF at both ends by an addition mechanism.<sup>8</sup> Accordingly, in this reaction stage the macroinitiator **9** was obtained based on poly(THF) and possessing one reactive azo group in the main chain. Subsequently, macroinitiator **9** was used to generate poly(THF) macroradicals **10** through the thermal decomposition of the azo group at 70°C, which in turn initiated the free-radical polymerization of the acrylate monomers **11-13**. Low conversions of the monomers were achieved (7-30%). Copolymers **3a** and **3b** were obtained with different molecular weights by using different monomeric ratios in the feed mixture and reaction times. All copolymers were precipitated several times from chloroform solution into methanol to eliminate unreacted monomers and were purified by extraction in ethanol where poly(THF) homopolymer is soluble. Residual traces of polyacrylate homopolymer could still be present but were not detectable by SEC or NMR.

It is well established that the free-radical polymerization of acrylate monomers terminates almost exclusively by a combination process<sup>11</sup>, which in the present polymerization system resulted in the formation of ABA block copolymers 1-3 comprised of two polytetrahydrofuran blocks (blocks A) and one polyacrylate block (block B). However, any preference for a disproportionation termination mechanism would eventually yield minor amounts of an AB diblock structure, as schematically outlined in Fig.2.

The structure of the copolymers was characterized by <sup>13</sup>C NMR and <sup>1</sup>H NMR spectroscopy, while the copolymer composition was evaluated from the <sup>1</sup>H NMR spectra and confirmed by elemental analysis. Assignment of the various signals was made by combined chemical shift calculations and comparison of the spectra with those of monomers and low molar mass intermediate compounds. The content of the poly(THF) blocks ranged from 3 to 13 wt.-% by NMR.

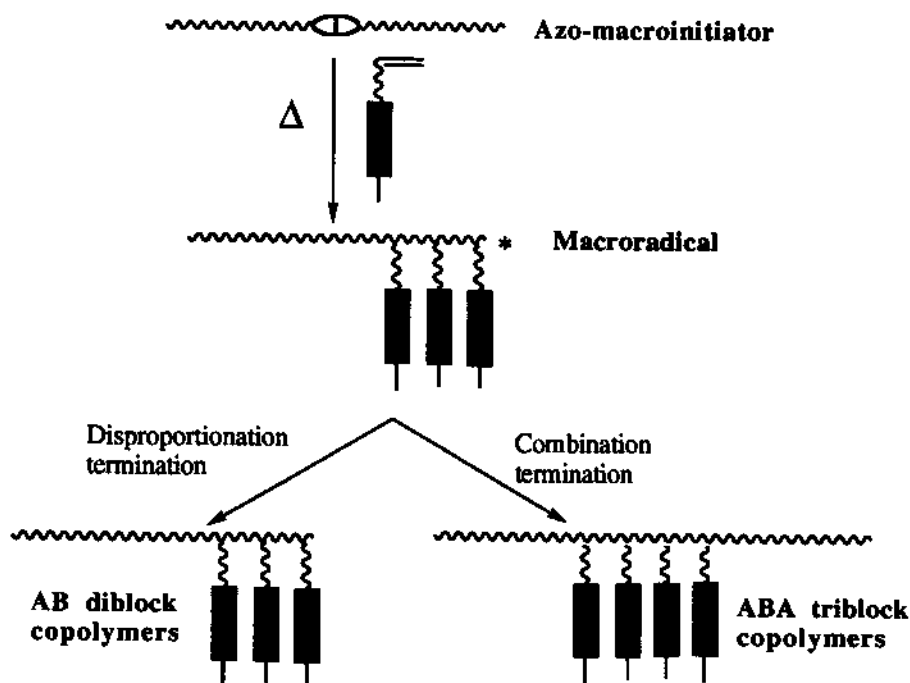


FIGURE 2. Schematic representation of the synthetic procedure adopted for the preparation of liquid-crystalline block copolymers.

A clear proof of the block copolymer formation was obtained by SEC with dual detection by refractive index and ultraviolet recordings. The wavelength of 360 nm at which poly(THF) is transparent was used for the ultraviolet detector. In each case, the SEC traces obtained using both detectors were superposable in terms of shape and peak position, thus indicating the formation of copolymers in which both polyacrylate and poly(THF) blocks of different lengths were uniformly distributed over the whole macromolecular species determining the molecular weight dispersion curve. A number average molecular weight ( $M_n$ ) of 21,500, corresponding to an average degree of polymerization ( $2\bar{p} = x+y$ ) of 300, was determined by SEC for the macroinitiator **9**. The  $M_n$  value of the ABA block copolymers was estimated from the molecular weight of the macroinitiator **9** taking into account the stoichiometry of the reaction and the weight ratio of the A and B blocks. Therefore, the  $M_n$  values in Tab.I are upper limits.

TABLE I. Physicochemical characteristics of block copolymers 1-3 and macroinitiator **9**.

sample	poly(THF) <sup>a)</sup> (wt.-%)	$[\alpha]_{25D}^{25}$ <sup>b)</sup> (deg)	$M_n$ <sup>c)</sup>	$\bar{p}$ <sup>c)</sup>	$q$ <sup>c)</sup>
<b>1</b>	3	+1.0	720,000	150	1360
<b>2</b>	9	+1.1	240,000	150	440
<b>3a</b>	3	+7.0	720,000	150	1550
<b>3b</b>	13	+6.3	170,000	150	360
<b>9</b>	100	--	21,500	300 <sup>d)</sup>	--

a)By  $^1\text{H}$  NMR.

b)In chloroform solution.

c)By  $^1\text{H}$  NMR;  $\bar{p} = (x+y)/2$ .

d) $2\bar{p} = x+y$ ; by SEC.

The average degree of polymerization of the poly(THF) block of copolymers ( $\bar{p} = (x+y)/2$ ) was 150, while the average degree of polymerization of the polyacrylate block ( $q$ ) was in the range 300-1500. Therefore, the different blocks had comparable (**2** and **3b**) or otherwise very different lengths (**1** and **3a**). All copolymers were optically active, and their optical rotatory power ( $[\alpha]_{25D}^{25}$ ) was consistent with the value expected on the basis of

their composition and optical rotation of the corresponding optically active homopolymer.

The glass and sub-glass transitions of the polymers were studied by DMA in the linear viscoelastic range at 1 Hz frequency. Fig.3 illustrates the trend of the dynamic storage modulus ( $G'$ ) as a function of temperature for polymers 1, 4, and 9, as typical examples. In all samples,  $G'$  was in the range  $1\text{-}2\cdot 10^9$  Pa at 150 K and then decreased with increasing temperature reflecting a number of relaxation processes. 9 and 4 were characterized by a significant drop in  $G'$  at their glass transition temperature ( $T_g$ ) at 350 and 208 K respectively, whereas two glass transitions were seen in 1 at 335 and 200 K. In the copolymer, an intermediate relaxation process at about 305 K was associated with the softening of the poly(THF) blocks, that was barely visible in the DSC scans. The dual glass transition behavior of block copolymers clearly suggests that the blocks are phase-separated in the glassy state; however, comparison with the homopolymers reveals that in copolymers 1-3 the glass transitions extended over a broader range at lower temperatures possibly due to the existence of a rather diffuse interphase. The phase transition temperatures and enthalpies, as measured by DSC, of block

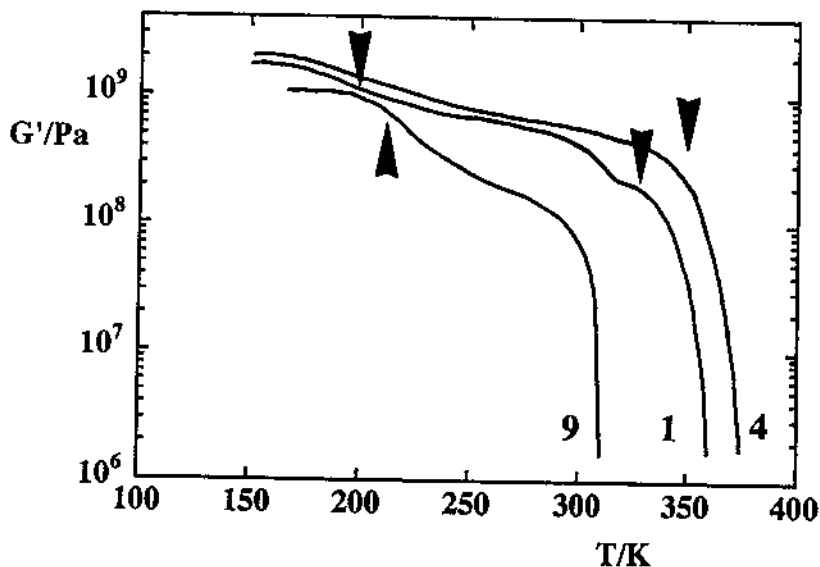


FIGURE 3. Trend of the dynamic storage modulus ( $G'$ ) as a function of temperature for block copolymer 1, macroinitiator 9 and homopolymer 4 (arrows indicate the glass transitions).



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copolymers 1-3 are collected in Tabs.II and III. The liquid-crystalline behavior of polyacrylates 4-6 has already been described.<sup>10</sup> Each of them formed a smectic A phase, an additional monotropic smectic C phase being present in polyacrylate 6. Their phase transition parameters are also collected in Tabs.II and III for comparison. The block copolymers exhibited the same general mesophase behavior, including the same phase sequences (Fig.4), as that of the corresponding polyacrylates 4-6.

TABLE II. Liquid-crystalline properties of block copolymers 1-2, relevant homopolymers 4-5, and macroinitiator 9.

sample	poly(THF) (wt.-%)	T <sub>m</sub> <sup>a)</sup> (K)	T <sub>X-A</sub> <sup>b)</sup> (K)	T <sub>A-i</sub> <sup>b)</sup> (K)	ΔH <sub>m</sub> <sup>a)</sup> (J/g)	ΔH <sub>A-i</sub> <sup>b)</sup> (J/g)
1	9	297	370	387	nd	7.9
2	3	nd	360	369	nd	≈8 <sup>c)</sup>
4	0	--	371	407	--	9.1
5	0	--	345	382	--	9.3
9	100	302	--	--	72.5	--

a) Polytetrahydrofuran block (block A).

b) Polyacrylate block (block B). X: semicrystalline or ordered smectic; A: smectic A; i: isotropic.

c) DSC peaks not well resolved.

TABLE III. Liquid-crystalline properties of block copolymers 3, relevant homopolymer 6, and macroinitiator 9.

sample	poly(THF) (wt.-%)	T <sub>m</sub> <sup>a)</sup> (K)	T <sub>X-C</sub> <sup>b)</sup> (K)	T <sub>C-A</sub> <sup>b)</sup> (K)	T <sub>A-i</sub> <sup>b)</sup> (K)	ΔH <sub>m</sub> <sup>a)</sup> (J/g)	ΔH <sub>A-i</sub> <sup>b)</sup> (J/g)
3a	3	nd	356	365	380	nd	8.7
3b	13	300	362	369	387	8.6	8.4
6	0	--	376	(375) <sup>c)</sup>	399	--	13.1
9	100	302	--	--	--	72.5	--

a) Polytetrahydrofuran block (block A).

b) Polyacrylate block (block B). X: semicrystalline or ordered smectic; C: smectic C; A: smectic A; i: isotropic.

c) Monotropic transition.

Thus, while 1 and 2 formed a smectic A phase (Tab.II), 3a and 3b presented smectic C and A phases (Tab.III). In any case at lower temperatures, for instance below 361 K for 1, there was either a semicrystalline phase characterized by a very low degree of crystallinity, or an ordered smectic mesophase that could not be clearly identified by X-ray diffraction measurements. The structuring of the phase transition in multiple components in the 345-470 K range for polymers 1 and 4 supports the occurrence of a semicrystalline phase in these samples (Fig.4). Therefore, the different blocks were phase-separated and underwent their individual mesophase transitions as dictated by the liquid-crystalline polyacrylate block. However, the smectic C-smectic A ( $T_{C-A}$ ) and smectic A-isotropic ( $T_{A-i}$ ) transition temperatures of block copolymers were much lower than those of the corresponding polyacrylate homopolymers.

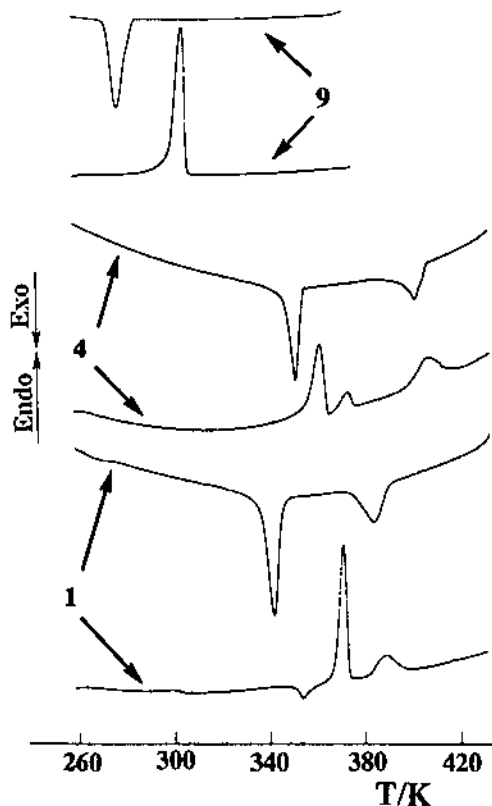


FIGURE 4. DSC heating and cooling curves of block copolymer 1, macroinitiator 9, and homopolymer 4.

As a consequence, the enantiotropic smectic C phase of copolymers **3a** and **3b** extended over a relatively narrow temperature range ( $\sim 10$  K), whereas it was monotropic in polyacrylate **6**. This will enable us to investigate the electrooptic properties of these copolymers in the smectic C phase too, which in contrast was not possible with homopolymer **6**. In addition, the smectic A-isotropic transition enthalpy ( $\Delta H_{A-i}$ ) in copolymers was typically smaller than that of the relevant homopolymer, even after normalization for their wt.-% composition. This was more evident for copolymer **3b** that incorporated a significant amount of poly(THF) blocks, for which the experimental value of  $\Delta H_{A-i} = 8.4$  J/g was in a striking contrast to the expected value of 11.4 J/g. Therefore, block copolymers **1-3** show a diminished propensity to mesomorphism than do homopolymers **4-6**. This finding cannot be accounted for by the different molecular weight dependences of the phase transition parameters ( $T$ ,  $\Delta H$ ) of the samples. The values of  $q$  evaluated for the copolymers were, in fact, very high and such as to guarantee that the mesophase behavior of the copolymers should not be affected by molecular weight to any appreciable extent. In the phase-separated morphology of liquid-crystalline block copolymers,<sup>6,14,15</sup> an interphase region will exist with either a relatively sharp or rather diffuse boundary among the liquid-crystalline microphases. In the latter case an overall less stable and ordered mesophase may result with respect to the bulk mesophase of homopolymers.<sup>6,14</sup> This should also be favored by the molecular weight polydispersity of the blocks in the present block copolymers. Finally, we note that the crystallization tendency of the crystallizable blocks was strongly depressed in the copolymers **1-3** and there was no detectable crystallization process in block copolymers containing low, although significant, contents of poly(THF) blocks. This can be due to the dilution of the short poly(THF) blocks or to a morphological effect. Crystallization of one component in block copolymers should provide another strong driving force for phase separation even when the blocks are low in molecular weight.

## CONCLUSION

We have prepared new liquid-crystalline block copolymers containing chiral side-chain liquid-crystalline blocks of different nature. While the blocks appear to be phase-separated in the glassy and melt states, the thermodynamic parameters of the various phase transitions were

significantly lower than those of the relevant homopolymer. The block copolymers exhibited a variety of chiral mesophases, each copolymer exhibiting at least a smectic A phase.

Our current investigation of the electrooptic response in these chiral smectic A phases reveals the occurrence of an electroclinic effect, with a field induced tilt of several degrees and a response time in the microsecond range. A full report will be given in the due course.

### ACKNOWLEDGMENTS

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