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Synthesis of hybrid liquid crystalline block copolymers by combination of cationic or promoted cationic and free-radical polymerizations

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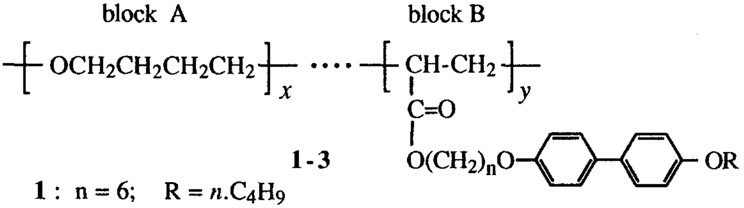
Summary

The synthesis of two new classes of liquid crystalline block copolymers (**1-5**) by a two-step combination of cationic and free-radical polymerizations is described. An azo-macroinitiator was prepared first by cationic polymerization of tetrahydrofuran or promoted cationic polymerization of cyclohexene oxide, which was then used to initiate the free-radical polymerization of an acrylate monomer containing a variously substituted biphenyl mesogenic group. The semicrystalline and liquid crystalline blocks were essentially microphase-separated and gave rise to different thermotropic mesophases.

Introduction

Liquid crystalline (LC) block copolymers have been introduced very recently and have only been sparingly investigated by a few research groups[1]. However, they appear to be able to provide an opportunity for a new breakthrough in the area of polymeric materials for advanced technology, especially in engineering and processing. Most examples of LC block copolymers deal with amorphous-LC copolymers[1], but very little is known on the synthesis and phase behavior of semicrystalline-LC copolymers[2,3].

In this paper we present the synthesis of two new classes of LC block copolymers comprising a semicrystalline block, either polytetrahydrofuran (poly(THF)) (samples **1-3**) or poly(cyclohexene oxide) (poly(CHO)) (samples **4, 5**), and an LC block of different structures (Fig.1). The ABA triblock copolymers were prepared by a two-step combination of different polymerization reactions, that is the cationic polymerization of THF or CHO (monomer A) and the free-radical polymerization of an LC acrylate (monomer B). The mesophase properties of the block copolymers are also briefly discussed.



1-3

1 : n = 6; R = $n.C_4H_9$
2 : n = 11; R = $n.C_4H_9$
3 : n = 11; R = (S)-OCCH*(Cl)$i.C_3H_7$

Figure 1A. Simplified structure of block copolymers **1-3**.

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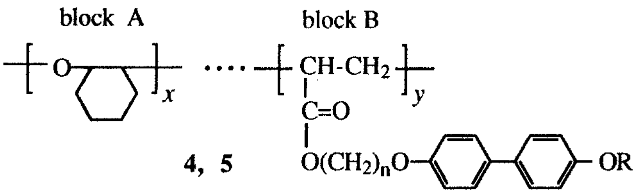


4, 5

4 : n = 11; R = (*S*)-OCCH*(Cl)*i*.C_3H_7
5 : n = 10; R = (*S*)-$CH_2CH^*(CH_3)C_2H_5$

Figure 1B. Simplified structure of block copolymers **4, 5**.

Experimental

Initiators. α,α'-[Azobis(4-cyanopentanoyl chloride)] (**6**) and α,α'-[azobis(4-cyano-1-oxo-1,4-pentanediyl)oxymethylene]bis(benzoin)dimethyl ether (**7**) were prepared as previously described[4,5]. 1-Ethoxy-2-methylpyridinium hexafluorophosphate (**8**) was synthesized according to literature[6].

Monomers. THF and CHO were purified by distillation immediately prior to use. The mesogenic acrylates **9-12** consisting of different spacer segments (n = 6, 10, 11) and substituents (R = *n*.C_4H_9, (*S*)-$CH_2CH^*(CH_3)C_2H_5$, (*S*)-OCCH*(Cl)*i*.C_3H_7) were synthesized by starting from 4,4'-biphenol as previously described[7]. They were purified by repeated crystallizations.

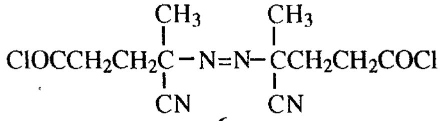
Azo-macroinitiators. Macroinitiator **14** was prepared from THF using **6** as an initiator, as previously reported[2]. Macroinitiator **18** was prepared from CHO by using a combination of **7** and **8** as an initiating system. Prior to irradiation on a Rayonet merry-go-round photoreactor equipped with lamps emitting light at nominally 350 nm, nitrogen was bubbled through the solution of CHO (1.45 g, 14.8 mmol) in dichloromethane (1 ml) containing **7** (11.0 mg, 23.7 μmol) and **8** (4.5 mg, 32.6 μmol). A phenanthrene solution (10^{-2} M) in *n*.hexane was used as a filter throughout the work in order to prevent direct absorption by the pyridinium salt. After 3 h irradiation at 20°C, the polymer was precipitated in methanol, filtered, and purified by several precipitations from dichloromethane solutions into methanol.

Block copolymers. Block copolymers **1-3** were prepared by following the general procedure previously described[2,3]. The copolymers were purified by selective extraction with boiling ethanol in a Kumagawa extractor. Block copolymers **4, 5** were prepared by reaction of **18** (110 mg, 1.1 mmol CHO r.u.) with the acrylate monomer **9-12** of choice (200 mg, ≈ 0.4 mmol) in THF (5 ml) solution, after freeze-thaw degassing. The solution was heated at 70°C for 48 h, and finally the polymer formed was precipitated into methanol. It was further purified by selective extraction with boiling *n*.hexane in a Kumagawa extractor.

Physicochemical characterization. ^1H and ^{13}C 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 DSC (Mettler TA4000, at a scanning rate of 10 $K \cdot min^{-1}$) and polarized light microscopy (Reichert Polyvar microscope equipped with a programmable Mettler FP52 stage at a scanning rate of 10 $K \cdot min^{-1}$).

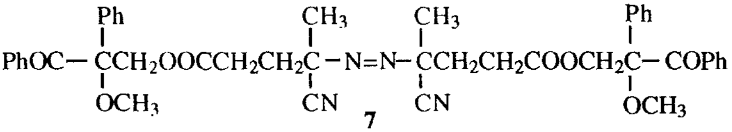
Results and discussion

Polyfunctional initiators are widely used in the synthesis of block copolymers[8]. Due to



$$ClOCCH_2CH_2\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}CH_2CH_2COCl$$

6



$$PhOC-\underset{OCH_3}{\overset{Ph}{C}}CH_2OOCCH_2CH_2\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}CH_2CH_2COOCH_2\underset{OCH_3}{\overset{Ph}{C}}-COPh$$

7

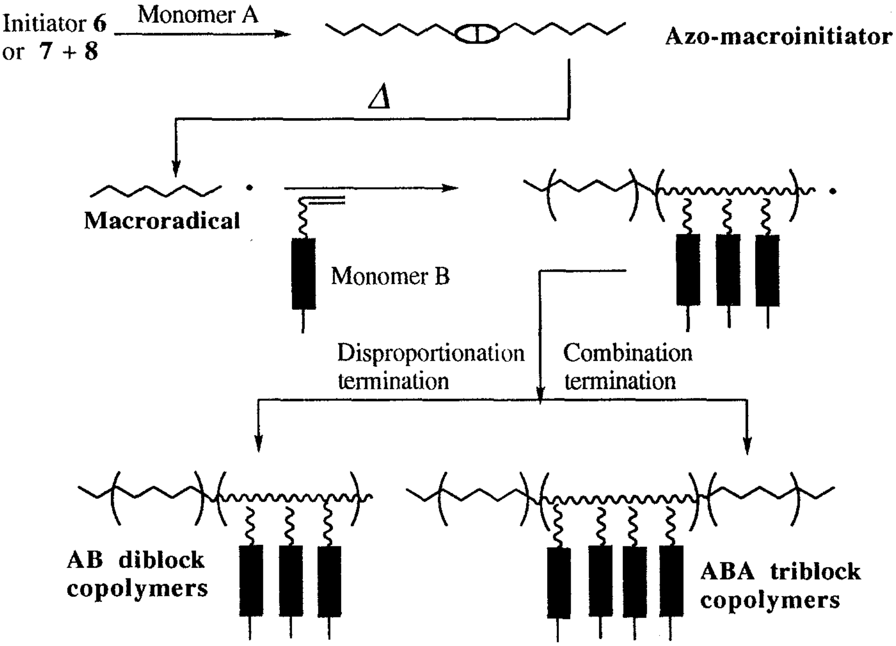


Figure 2. Schematic representation of the synthetic procedure adopted for the preparation of LC block copolymers.

their functional nature, initiators like **6** and **7** are in fact incorporated into a diversity of azo-macroinitiators, that afterwards can be used to initiate the free-radical polymerization of mesogenic vinyl monomers via the formation of primary macroradicals, leading to various architectures of LC block copolymers (Fig.2). Both **6** and **7** are highly efficient free-radical initiators, like the most widely used AIBN[9], even when inserted in a macromolecular chain[10,11].

When reacted with a silver salt constituted by a low nucleophilic counterion in THF, initiator **6** produces the diacyl cation **13** which is then able to polymerize THF at both ends by an addition mechanism[4] (Fig.3). Accordingly, in this reaction stage the macroinitiator **14** was obtained based on poly(THF) and possessing one reactive azo group in the main chain. Subsequently, **14** was used to generate poly(THF) macroradicals **15** through the thermal decomposition of the azo group at 70°C, which in turn initiated the free-radical polymerization of the mesogenic acrylates **9-11**. In each experiment, an azomacroinitiator **14**

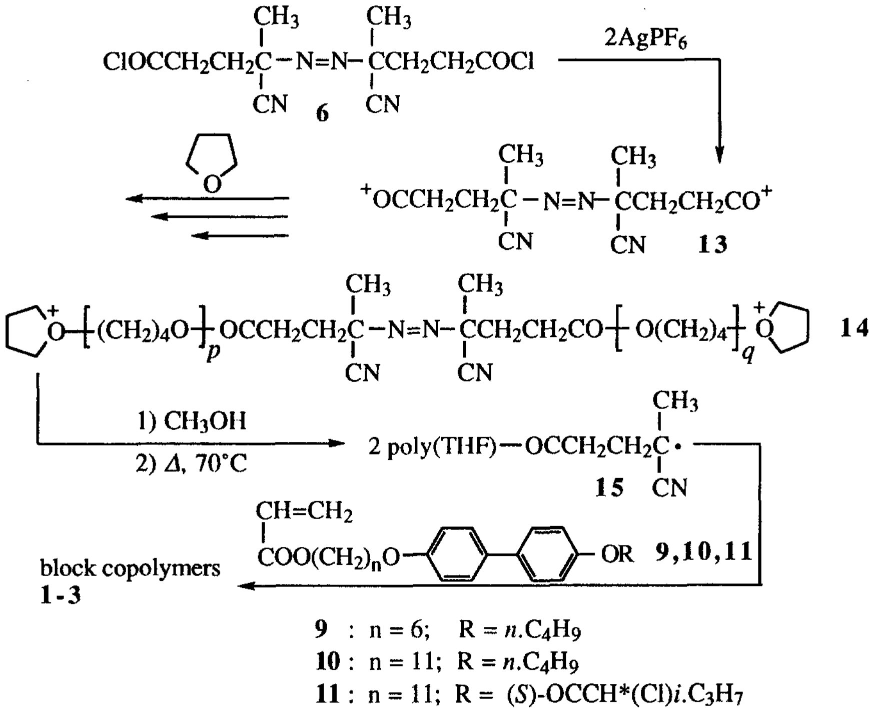
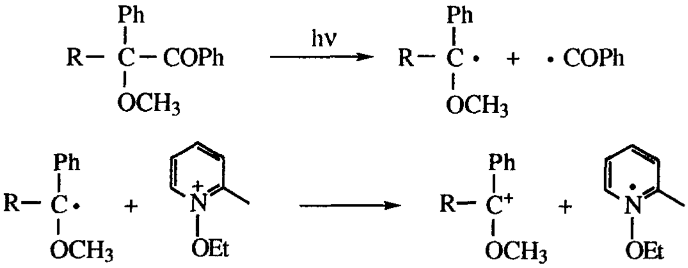


Figure 3. Reaction scheme for the preparation of LC block copolymers **1-3**.

with M_n = 21500 and M_w/M_n = 2.3 was used. Low conversions of the monomers were generally achieved (5-50 %). Copolymers **1a** and **1b** were obtained with different compositions and molecular weights by using different monomer ratios in the feed mixture. All copolymers were purified by extraction with boiling ethanol where poly(THF) homopolymer is soluble. Residual traces of polyacrylate homopolymer could still be present but were not detected by SEC analysis.

Initiators like **7** possess two chromophoric groups, namely the azo and the benzoin moieties, that differ significantly in thermal activity and photoactivity. UV-light irradiation of the benzoin group provides free radicals, and the oxidation of the electron donor radical to the corresponding carbocation may be conveniently employed to promote the cationic polymerization of epoxides, cyclic ethers, and vinyl ethers[12]:



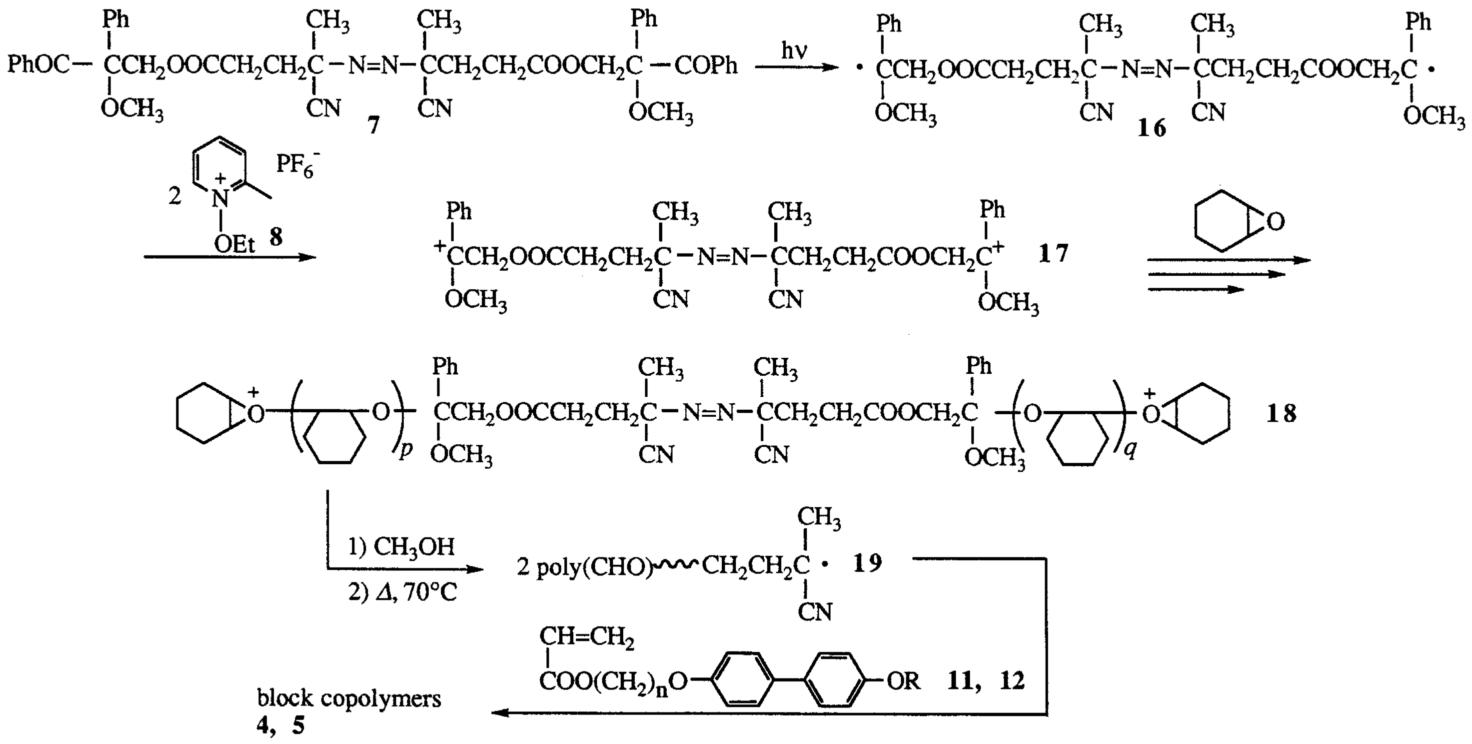
In accord with this scheme, block copolymers **4, 5** were synthesized by a two-step procedure (Fig.4). Photoinitiated polymerization of CHO using **7** in conjunction with **8** yielded poly(CHO) **18** incorporating one azo group per polymer chain. At the irradiation wavelength (λ = 350 nm) most of the emitted light is absorbed by benzoin chromophores ($\varepsilon \approx$ 225 $M^{-1}cm^{-1}$), as the azo groups have a much weaker absorption ($\varepsilon \approx$ 20 $M^{-1}cm^{-1}$). **18** was then used as a source of macroradicals at 70°C to polymerize acrylates **11, 12**. In both experiments, an azomacroinitiator **18** with M_n = 3500 and M_w/M_n = 1.9 was used. Relatively low conversions of the monomer (30-35 %) were obtained. The copolymers were purified by extraction of residual poly(CHO) homopolymer with boiling *n*.hexane.

The structure of the copolymers was characterized by ^{13}C NMR and ^1H NMR spectroscopy, while the copolymer composition was evaluated from the ^1H NMR spectra and confirmed by elemental analysis. 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) and poly(CHO) are transparent was used for the ultraviolet detector. In each case, the SEC traces obtained by using both detectors were superposable in terms of shape and peak position, thus indicating the formation of copolymers in which the blocks of different lengths were uniformly distributed over the whole macromolecular species determining the molecular weight dispersion curve. The molecular weights of the block copolymers were evaluated by SEC and ^1H NMR, by taking into consideration their composition and the stoichiometry of the polymerization. Polystyrene was used for SEC calibration, and the reported values of M_n are approximate. The degrees of polymerization of the poly(THF) and poly(CHO) segments in **14** and **18** are expected to be slightly different ($p \neq q$), but only an average value ($x = (p + q)/2$) of the block length in the copolymers can be evaluated. The average degrees of polymerization determined were $x \approx$ 150 and y = 200 to 1300 for **1-3** (Tab.1) and $x \approx$ 17 and y = 12 to 14 for **4, 5** that were therefore oligomeric products (Tab.2). While the mechanistic aspects of the polymerization were not investigated here, it is well known[9] that the free-radical polymerization of acrylate monomers terminates almost quantitatively by a combination mechanism. This gives rise in copolymers **1-5** to an ABA triblock structure, the THF or CHO block being the A component and the LC block being the B component (Fig.2).

Table 1. Physicochemical properties of macroinitiator **14**, block copolymers **1-3**, and relevant homopolymers **20-22**.

sample	M_n[a]	$[\alpha]^{25}_D$[b]	block A		block B		
		(deg)	content (wt. %)	T_m[c] (°C)	T_m[d] (°C)	$T_{SX\text{-}SA}$[d] (°C)	$T_{SA\text{-}i}$[d] (°C)
14	21500	--	100	29	--	--	--
1a	432000	--	5	nd[e]	124	129	145
1b	110000	--	20	27	127	131	151
2	215000	--	10	27	123	128	146
3	720000	+1.0	3	nd[e]	97	--	114
20	14000	--	0	--	129	136	162
21	10000	--	0	--	128	132	158
22	17000	+1.1	0	--	88	--	134

[a] Average molecular weight by SEC and ^1H NMR. [b] Optical rotatory power, in chloroform. [c] Melting (m) temperature of the poly(THF) block. [d] Melting (m), smectic-to-smectic (S_X-S_A), and smectic-to-isotropic (S_A-i) temperatures of the LC block. [e] Not detectable by DSC.



11 : n = 11; R = (*S*)-OCCH*(Cl)*i*.C_3H_7
12 : n = 10; R = (*S*)-$CH_2CH^*(CH_3)C_2H_5$

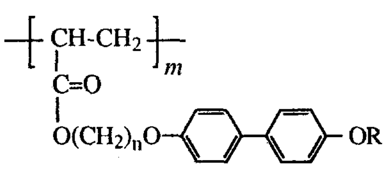
Figure 4. Reaction scheme for the preparation of LC block copolymers **4, 5**.

Table 2. Physicochemical properties of macroinitiator **18**, block copolymers **4**, **5**, and relevant homopolymers **22**, **23**.

sample	M_n[a]	$[\alpha]^{25}_D$[b] (deg)	block A content (wt. %)	block A T_m[c] (°C)	block B T_m[d] (°C)	block B $T_{SX\text{-}SA}$[d] (°C)	block B $T_{SA\text{-}i}$[d] (°C)
18	3500	--	100	67	--	--	--
4	10000	+0.5	35	nd[e]	88	--	102
5	10000	+4.1	35	nd[e]	83	90	103
22	17000	+1.1	0	--	88	--	134
23	19000	+7.5	0	--	103	(102)[f]	126

[a] Average molecular weight by SEC and ^{1}H NMR. [b] Optical rotatory power, in chloroform. [c] Melting (m) temperature of the poly(CHO) block. [d] Melting (m), smectic-to-smectic (S_X-S_A), and smectic-to-isotropic (S_A-i) temperatures of the LC block. [e] Not detectable by DSC. [f] Monotropic transition.

The block copolymers formed different mesophases, depending upon the length (n) of the spacer segment and the nature of the substituent (R) on the biphenyl unit in the side chains. Their mesophase behavior is compared to that of the corresponding LC polyacrylate homopolymers **20-23**.



20-23

20 : n = 6; R = $n.C_4H_9$
21 : n = 11; R = $n.C_4H_9$
22 : n = 11; R = (S)-OCCH*(Cl)$i.C_3H_7$
23 : n = 10; R = (S)-$CH_2CH^*(CH_3)C_2H_5$

Copolymers **1**, **2**, and **5** gave rise to two phases in the thermal range between the melting temperature (T_m) and the isotropization temperature ($T_{SA\text{-}i}$) with an intermediate phase transition at a temperature $T_{SX\text{-}SA}$, while copolymers **3** and **4** presented one mesophase (Tabs.1 and 2). The mesophase above $T_{SX\text{-}SA}$ of **1** and **2** was smectic A, whereas the underlying phase was an unidentified ordered or semicrystalline one, analogous to homopolymers **20** and **21** (Tab.1). **5** exhibited smectic C and A phases similar to **23**, but the C phase was enantiotropic in the copolymers and monotropic or metastable in the homopolymer (Tab.2). **3** and **4** formed one smectic A phase in agreement with **22** (Tabs.1 and 2). Thus, block copolymers **1-5** are essentially microphase-separated, with minor effects of the semicrystalline block, either poly(THF) or poly(CHO), on the overall mesophase behavior. However, in each copolymer sample the mesophase transition temperatures were significantly lower than those of the corresponding LC homopolymer, particularly in copolymers consisting of poly(CHO) segments. As an example, $T_{SA\text{-}i}$ of **1** and **2** was 114 and 102°C respectively, as compared to 134°C for **22**. Furthermore, the isotropization transition extended over a wider temperature range, and the isotropic and smectic phases coexisted over a broad thermal range. This suggests that some compatibility between the blocks may exist, especially in **4**, **5** comprising the rather short segments of the LC monomer units. As a result, a morphological effect may depress the crystallization tendency of the poly(THF) block in **1**-**3**, which in contrast appears to be completely inhibited for the poly(CHO) blocks of **4**, **5**. No crystalline melting transition was, in fact, detected for these samples incorporating as much as 35 wt. % of poly(CHO) blocks. A critical dependence of the transition temperatures on the molecular weight must also operate in the latter copolymers, as is well documented for side-chain LC polymers[13]. This influence might be substantial for the short LC segments.

Conclusions

LC block copolymers consisting of semicrystalline-LC blocks can be prepared by a two-step combination of cationic and free-radical polymerizations. In the synthetic scheme adopted, a macroinitiator is obtained in the first step by cationic or promoted cationic polymerization. The macroinitiator incorporates one central labile azo group per polymer chain. This generates macroradicals that then polymerize a mesogenic acrylate monomer by a free-radical mechanism leading to block copolymers. They are essentially microphase-separated systems and form smectic mesophases, analogous to the corresponding LC homopolymers. The chiral smectic A phase of the homopolymers, e.g. **22**, is known to exhibit an electroclinic effect when an electric field is applied[14], and an investigation of the electrooptical response of the block copolymers is in progress.

Acknowledgments

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