

# Synthesis of Liquid Crystalline–Amorphous Block Copolymers by Combination of CFRP and ATRP Mechanisms

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**ABSTRACT:** Block copolymers of liquid crystalline 6-(4-cyanobiphenyl-4'-oxy) hexyl acrylate (LC6) and styrene (St) were obtained by the combination of two different free-radical polymerization mechanisms namely conventional free-radical polymerization (CFRP) and atom transfer radical polymerization (ATRP). In the first part, thermosensitive azo alkyl halide, difunctional initiator (AI), was prepared and then used for CFRP of LC6 monomer. The obtained bromine-ended difunctional liquid crystalline polymers (PLC6) were used as initiators in ATRP of St, in bulk in conjunction with CuBr/*N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) as catalyst. In the second part, AI was firstly polymerized by CFRP in the presence of St and then the obtained difunctional bromine ended polystyrenes (PSt) were used as initiators in ATRP of LC6 in diphenyl

ether solvent in conjunction with CuBr/PMDETA. The spectral, thermal, and optical measurements confirmed a fully controlled living polymerization, which results in formation of ABA-type block copolymers with very narrow polydispersities. In both cases, blocks of the different chemical composition were segregated in the solid and melt phases. The mesophase transition temperatures of the liquid crystalline block were found to be very similar to those of the corresponding homopolymers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3187–3194, 2006

**Key words:** atom transfer radical polymerization; conventional free radical polymerization; block copolymer; liquid crystal; amorphous

## INTRODUCTION

Block copolymers often have so many useful and unique properties, either in the solid state or in solution, because of the thermodynamic incompatibility of the constituent blocks. The superiority of the block copolymers in advanced materials technology attracts attention both academically and industrially.<sup>1–6</sup> Therefore, the synthesis of block copolymers is also popular area that has being developed continuously. There are so many routes to synthesize block copolymers, including living polymerizations (e.g., ionic, controlled/living radical) and end-group transformations.<sup>7–11</sup>

The transformation polymerization, which allows to combine various polymerization mechanisms, is one of the major methods to obtain well-defined block copolymers.<sup>12–14</sup> The studies on block copolymer synthesis certainly show a variety of transformation routes, wherein a variety of monomers are utilized.

Free-radical polymerization has distinct advantages over other polymerization methods, such as tolerance to trace impurities and less stringent conditions, and is also able to polymerize a wide range of monomers.<sup>15</sup> On the other hand, the presence of irreversible termination and transfer reactions, which lead to the poor control of macromolecular structures, including degrees of polymerization, polydispersities, end functionalities, chain architectures, and compositions, are significant.

Controlled radical polymerization such as atom transfer radical polymerization (ATRP),<sup>16–18</sup> radical addition fragmentation (RAFT),<sup>19–24</sup> stable radical-mediated radical polymerization (SFRP)<sup>25–29</sup> provides the preparation of many novel polymeric materials that could not be earlier achieved via conventional radical polymerization. These materials termed well-defined polymers have low polydispersities, also controlled end functionalities and compositions. Similarly, bifunctional initiators were used for the preparation of block copolymers of styrene with various vinyl monomers, using conventional radical polymerization and ATRP.<sup>30–34</sup> Paik and Matyjaszewski used difunctional initiators to copolymerize styrene with vinyl acetate.<sup>35</sup>

In spite of the extensive number of studies on ATRP–living/controlled radical polymerization for the different monomers, its application to special poly-

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mers, such as liquid crystalline polymers, has been very rare. Recently, Gomes and Laus reported liquid crystalline and amorphous block copolymers by living/controlled radical polymerization.<sup>36–42</sup>

Block copolymers with liquid crystalline blocks could give rise to microseparated phases. Liquid crystalline (LC) block copolymers have been given much attention lately because of their potential use as polymeric materials for advanced technology, especially in engineering and processing. It is desirable to combine the properties of liquid crystalline and isotropic (I) polymers by forming an LC/I block copolymer.<sup>43–48</sup> This kind of a system is expected to show a microphase-separated structure with coexisting isotropic and anisotropic phases. However, the microphase separation in LC/I block copolymers is important; in order to study the microphase separation in LC/I block copolymers, it is also necessary to synthesize polymeric materials with well-defined structure and narrow molecular weight distribution.

In this paper, we report a novel method for the synthesis of ABA-type liquid crystalline amorphous block copolymers using CFRP and ATRP methods. The presence of an activated alkyl halide at a polymer chain end enables to synthesize diblock copolymers by ATRP. Block copolymers can be generated from a macroinitiator synthesized by either ATRP or a different mechanism altogether.

## EXPERIMENTAL

### Materials

Liquid crystalline monomer LC6 was prepared according to the procedure in the literature.<sup>49</sup> 4,4'-Azobis(4-cyano pentanol) (ACP) was synthesized by Bamford's method.<sup>50</sup> Tetrahydrofuran (THF) (J.T. Baker) was dried over potassium hydroxide, and finally distilled over CaH<sub>2</sub>. Dimethyl sulfoxide (DMSO) (Merck) was refluxed over CaH<sub>2</sub> and then distilled under reduced pressure (76°C/12 mmHg). Benzene (Merck) was purified by shaking with concentrated H<sub>2</sub>SO<sub>4</sub>, then with water, dilute NaOH and water, followed by drying on CaCl<sub>2</sub>, and distilled over sodium wire (80°C/760 mmHg). *N,N*-Dimethyl formamide (DMF) was dried over MgSO<sub>4</sub>, then distilled under reduced pressure. Chloroform (J.T. Baker) was shaken with several portions of concentrated H<sub>2</sub>SO<sub>4</sub> washed thoroughly with water and dried over CaCl<sub>2</sub> before filtering and distilling (61°C/760 mmHg). Styrene (St) was purified by conventional methods, and distilled *in vacuo* from CaH<sub>2</sub> just before use. *N,N,N',N',N''*-Pentamethyldiethylenetriamine (PMDETA), acryloyl chloride (Aldrich), and triethylamine (J.T. Baker) were dried and distilled over CaH<sub>2</sub>. Acryloyl chloride (Aldrich) was distilled over P<sub>2</sub>O<sub>5</sub> (72°C/760 mmHg). Other chemicals were used as-received.

### Synthesis of 4-((*e*)-2-{4-[(2-bromopropanoyl)oxy]-1-cyano-1-methylbutyl}-1-diazenyl)-4-cyanopentyl 2-bromopropanoate (AI)

AI was prepared according to the modified method of Paik *et al.*<sup>35</sup> About 1.78 mL (16.91 mmol) of 2-bromopropionyl bromide was added dropwise, under nitrogen, to a mixture of 1.7 g (6.74 mmol) 4,4'-azobis(4-cyano pentanol) (ACP) and 2.34 mL (16.91 mmol) triethylamine that had been stirred in 150 mL of CHCl<sub>3</sub> in an ice bath for 1 h. After complete addition of the acid bromide, the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was washed with water (3 × 150 mL) and then dried over MgSO<sub>4</sub>, evaporation of CHCl<sub>3</sub> gave a greasy product. It was dissolved in CHCl<sub>3</sub> again and precipitated in cold hexane, then filtered and dried under vacuum (yield 49%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) = 1.6–1.8 (s, 6H, —CCN(CH<sub>2</sub>)CH<sub>3</sub>), 1.8–2.0 (d, 6H, —CH(Br)CH<sub>3</sub>), 2.0–2.3 (m, 8H, —CH<sub>2</sub>CH<sub>2</sub>), 4.1–4.3 (q, 2H, —CH—Br), 4.3–4.5 (m, 4H, —OCH<sub>2</sub>).

### General polymerization procedure for CFRP of LC6 and St

In a typical polymerization reaction, the required amounts of monomer LC6 or St and macroinitiator AI were dissolved in solvent. The reaction mixture was introduced in a Pyrex glass ampoule, thoroughly freeze-thaw degassed and sealed under vacuum. After reacting for variable time periods at 80°C or 110°C, the polymer was precipitated by addition of a 10-fold excess of methanol, filtered, and purified by reprecipitation into methanol. The polymer was then dried *in vacuo* for 18 h. The amounts of monomer LC6 or St and initiator AI, reaction times, and conversions for the different preparations of macroinitiators MI-1–3 and MI-4 are given in Table I.

### General copolymerization procedure for ATRP of St and LC6

To a schlenk tube equipped with magnetic stirrer, vacuum and dry nitrogen was applied three or four times, then certain amounts of styrene or LC6, solvent, ligand (PMDETA), CuBr, and macroinitiator were added in the order mentioned under nitrogen. Diphenyl ether, solvent, was only used with LC6 monomer. The reaction solution was bubbled with nitrogen to remove dissolved gases and then the tube was immersed in an oil bath and held by a thermostat at 110°C, with rigorous stirring. The copolymerization was performed for a determined time and was terminated by cooling to room temperature. The reaction mixture was dissolved in large excess of THF. The THF solution was passed through a short alumina column to remove copper complex and then concentrated by evaporation. The polymer was precipitated

TABLE I  
CFRP of LC6 and St by Using AI

	[AI] (mol/L)	Solvent	Temp. (°C)	Time (h)	Conv. (%)	$M_n^a$	$M_w/M_n^a$
MI-1 <sup>b</sup>	$7.7 \times 10^{-4}$	Benzene	80	100	75	11,100	1.63
MI-2 <sup>b</sup>	$7.7 \times 10^{-4}$	DMF	110	100	94	5,200	1.32
MI-3 <sup>b</sup>	$2.6 \times 10^{-3}$	Benzene	80	100	88	7,850	1.92
MI-4 <sup>c</sup>	$6.4 \times 10^{-2}$	Benzene	80	1	47	7,300	1.55

<sup>a</sup> Determined from GPC, based on PSt standards.

<sup>b</sup> [LC6] =  $3.5 \times 10^{-1}$  mol/L.

<sup>c</sup> [St] = 4.4 mol/L.

into excess methanol and filtered. The polymer was dried under vacuum. The conversion was determined by gravimetrically. Copolymerization conditions are given in Table II.

### Analysis of polymers

<sup>1</sup>H NMR spectra were recorded on a Bruker 250-MHz spectrometer, with CDCl<sub>3</sub> as solvent and tetramethylsilane as the internal standard. GPC analyses were carried out with a set up consisting of the Agilent pump and refractive-index detector (Model 1100) and three Waters Styragel columns (HR 4, HR 3, and HR 2). THF was used as the eluent at a flow rate of 0.3 mL/min. Molecular weight of the polymers was calculated with the aid of polystyrene standards. The thermal and liquid crystalline properties of the polymers were studied using Perkin-Elmer DSC 6 at a scanning rate of 5°C/min and 10°C/min, and optical polarized light microscopy Leitz DMRP, equipped with a Linkam-System TMS, THMS 600 stage at a scanning rate of 10°C/min.

## RESULTS AND DISCUSSION

In this work, ABA-type amorphous-liquid crystalline block copolymers were synthesized via two-step procedure involving CFRP and ATRP methods. This successive CFRP and ATRP initiation processes started from a difunctional azo alkyl halide, a low molar mass

initiator containing one azo group and two bromine end groups. AI is highly efficient in initiating the CFRP and ATRP for the suitable monomers (Scheme 1).

AI was prepared by esterification of the hydroxyl-azo compound with the acid halides and then polymerized in the presence of liquid crystalline or styrene monomer by the thermal decomposition of the azo moiety at 80°C or 110°C. Initiation of styrene and LC6 polymerization by means of radical initiator AI is expected to yield two reactive bromine end group because of the radical-radical combination-type termination. Consequently, PLC6 or PSt homopolymers possessing two reactive bromine end groups in the main chain was obtained.

These macroinitiators PLC6 or PSt having bromine end groups were then isolated and subsequently used to initiate ATRP of the second monomer in the presence of copper catalyst.

In this system, the type of block copolymer formed depends greatly on the kinetic behavior of the particular monomer involved. Initiation of St or LC6 polymerization by means of Br-difunctional macroinitiators expected to yield ABA-type block copolymers because termination occurs by radical-radical combination.

### Preparation of PSt-*b*-PLC6-*b*-PSt copolymers by CFRP and ATRP

In the first synthetic route, AI was first used for the polymerization of LC6 by CFRP as shown in Scheme 2.

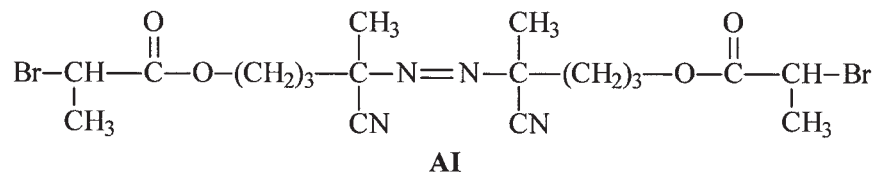
TABLE II  
ATRP of St and LC6 Initiated by Bromine-Terminated MI<sup>a</sup>

Initiator no	[MI] (mol/L)	Solvent	$[I_0]^b/[Cu^+]/[PMDTA]/[M_0]^c$	Time (h)
MI-I-B1	$3.7 \times 10^{-3}$	Bulk	1/21/42/2589	9
MI-2-B1	$8.7 \times 10^{-3}$	Bulk	1/21/42/2589	9
MI-3-B1	$3.7 \times 10^{-3}$	Bulk	1/21/42/2589	16
MI-3-B2	$1.7 \times 10^{-3}$	Benzene	1/21/42/2589	11
MI-4-B1	$9.2 \times 10^{-4}$	Diphenyl ether	1/64/128/500	96
MI-4-B2	$3.7 \times 10^{-4}$	Diphenyl ether	1/64/128/500	96

<sup>a</sup> Temperature = 110°C.

<sup>b</sup>  $[I_0]$  = initial [MI].

<sup>c</sup>  $[M_0]$  = initial [St] or [LC6].



Scheme 1

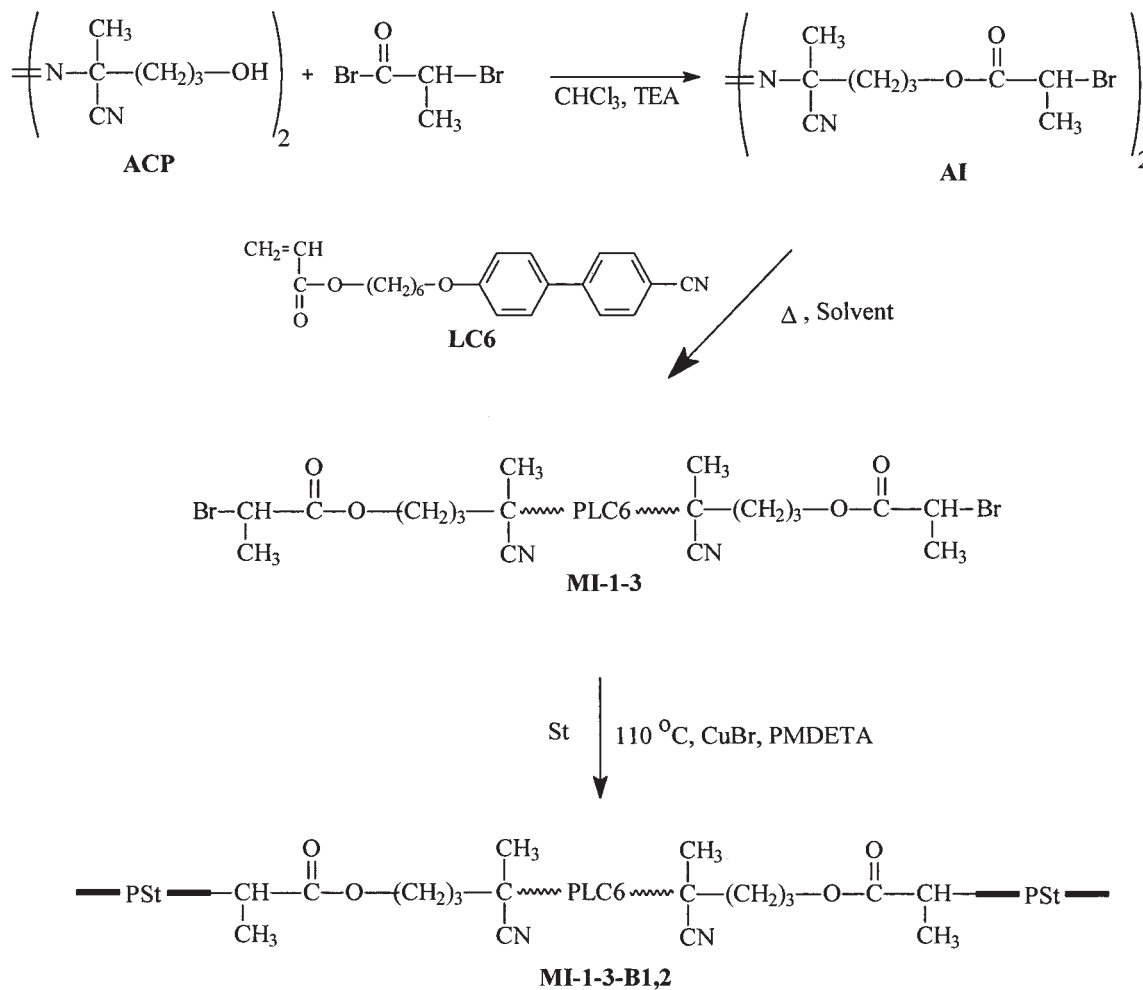
Polymerization conditions and results are given in Table I. Acrylic liquid crystalline segment, which was obtained via this initiation method, contained liquid crystalline macromolecular chain of the block copolymers. Since termination occurred predominantly by coupling, the macroinitiators MI-1-3 would have two functional bromine end groups for the ATRP process (Scheme 2).

<sup>1</sup>H NMR spectra prove the expected structure of the macroinitiator MI-1. As may be seen in the spectrum (Fig. 1), the signals originating from the esterificated Br end group of MI-1 were discerned at 1.8–2.0 ppm,

(—CH(Br)CH<sub>3</sub>), 2.0–2.3 (—CH<sub>2</sub>—CH<sub>2</sub>), and 3.9–4.2 ppm (—OCH<sub>2</sub>), (—CH—Br).

Macroinitiators were isolated and subsequently used to initiate ATRP of styrene in the presence of a copper catalyst at the different reaction conditions (Table II). The results of ATRP of styrene are presented in Table III.

Block copolymerization reached low conversions even yielding high molecular weight. On the other hand, the experimental molecular weights were in agreement with the theoretical expectations, and polydispersities of the corresponding block copolymers (MI-3-B2) decreased



Scheme 2

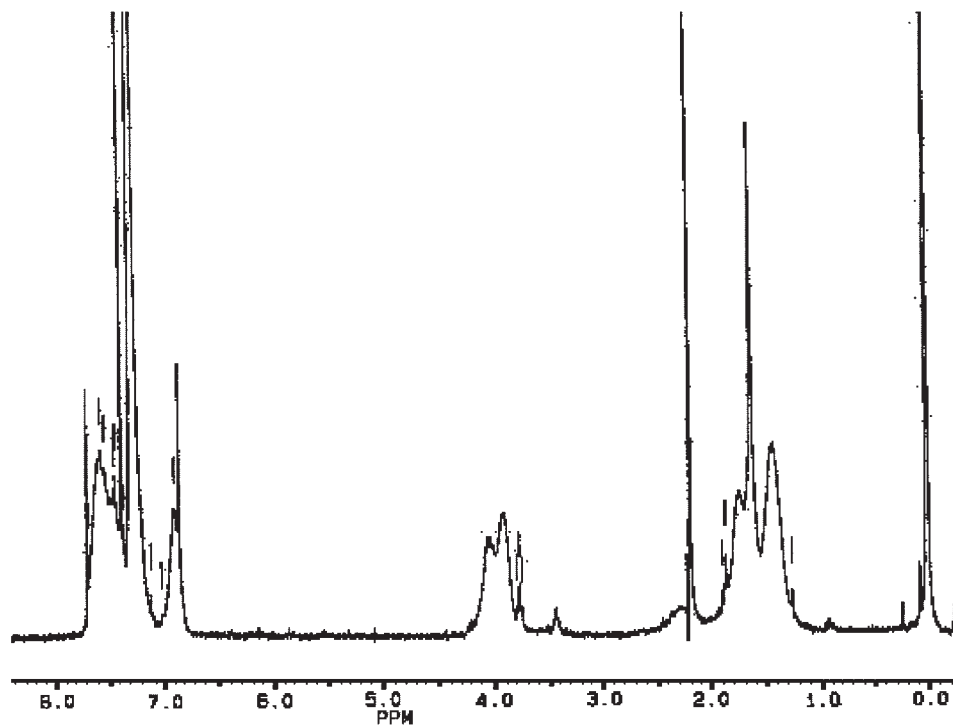


Figure 1  $^1\text{H}$  NMR spectrum of MI-1 in  $\text{CDCl}_3$ .

very sharply from 1.9 to 1.1 (Table III). These copolymers were purified by extraction with boiling cyclohexane, which is selective solvent for PSt.

Block copolymer composition was determined by  $^1\text{H}$  NMR and GPC measurements. The NMR spectrum of MI-1-B1 (Fig. 2) displays signals at 1.2–2.1 ppm ( $-\text{CH}-\text{CH}_2$  (PSt) and  $-\text{CH}-\text{CH}_2$ ,  $(-\text{CH}_2)_4$  (PLC6)), 3.6–4.0 ppm ( $-\text{OCH}_2$  (PLC6)), and 6.2–7.5 ppm (aromatic protons of PSt and PLC6).

The structure of the block copolymers was established by  $^1\text{H}$  NMR spectroscopy. Integration of the signals in  $^1\text{H}$  NMR spectrum of MI-1-B1 displays signals of aromatic protons of St at 6.5 and  $-\text{OCH}_2$  groups of PLC6 at 3.9–4.0 ppm.

A clear indication of block copolymer formation was obtained by GPC, using refractive index record-

ing. The GPC traces of the samples MI-1-B1, MI-3-B1, and MI-3-B2 obtained using refractive index (RI) and ultraviolet (UV) recordings at the 270 nm wavelength are shown in Figures 3 and 4.

GPC analysis of the purified samples indicated no signal of residual macroinitiators and monomers in the elution traces. Thus, the blocks of different lengths are uniformly distributed over the whole macromolecular species determining the molecular weight dispersion curve.

The number-average molecular weight ( $M_n$ ) for the MI-1-B1 sample, obtained by GPC and theoretical calculation, were 79,000 and 72,000 g/mol, respectively. Almost the same  $M_n$  values were obtained from  $^1\text{H}$  NMR analyses. Polydispersity of the corresponding copolymer sample decreased from 1.63 to 1.20. Con-

TABLE III  
Results of ATRP of St and LC6 Initiated by Bromine-Terminated MI

	Conv. (%)	$M_n^a$	$M_{n(\text{Theor})}^b$	$M_n$ (NMR) <sup>c</sup>	$M_w/M_n^a$	% LC6 in copolymer <sup>c</sup>
MI-1-B1	22	79,000	72,000	82,000	1.20	14
MI-2-B1	19	15,500	25,200	24,000	1.11	22
MI-3-B1	39	99,200	112,500	113,000	1.12	7
MI-3-B2	15	76,500	49,000	56,000	1.10	14
MI-4-B1	2	39,500	60,200	70,000	1.39	36
MI-4-B2	9	61,000	88,000	80,000	1.29	45

<sup>a</sup> Determined from GPC, based on PSt standards.

<sup>b</sup> Calculated by  $[M_0]/[I_0] \times \text{Conv.} \times \text{MW}_{\text{monomer}} + M_{n(\text{macroinitiator})}$ .

<sup>c</sup> Calculated by  $^1\text{H}$  NMR.

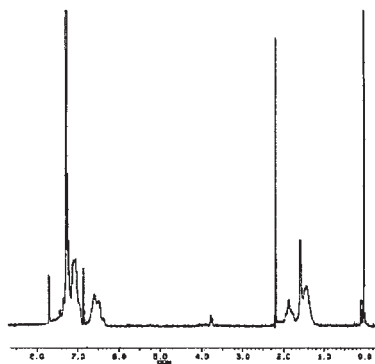


Figure 2  $^1\text{H}$  NMR spectrum of MI-1-B1 in  $\text{CDCl}_3$ .

version of the styrene monomer ranged from 15% to 39%. The narrow molecular weight distributions were also obtained for MI-3-B1, MI-3-B2 block copolymer samples (Fig. 4).

The phase behaviors of the homopolymers and triblock copolymers were characterized by combination techniques consisting of the differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The transition temperatures of all samples were obtained from the second heating and the first cooling scans. The phase transition temperatures are given in Table IV.

Copolymers MI-1-B1, MI-2-B1, MI-3-B1, and MI-3-B2 gave rise to two phases in the thermal range between the glass transition temperature ( $T_g$ ) and the isotropization temperature ( $T_{N-I}$ ) (Table IV). Their mesophase behavior is compared with that of the corresponding LC6 homopolymers.<sup>51</sup> For each copolymer sample, the mesophase transition temperatures were relatively same as the corresponding LC6 homopolymer. Block copolymer samples show glass transition temperatures of liquid crystalline block at 36–38°C

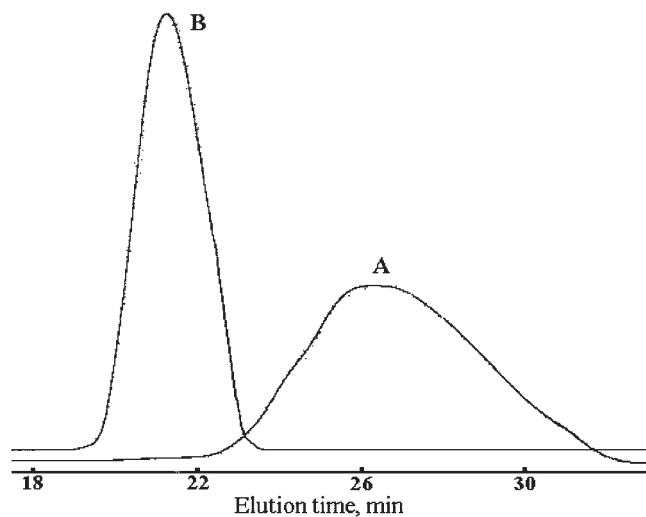


Figure 3 GPC traces of MI-1 (A) and MI-1-B1 (B).

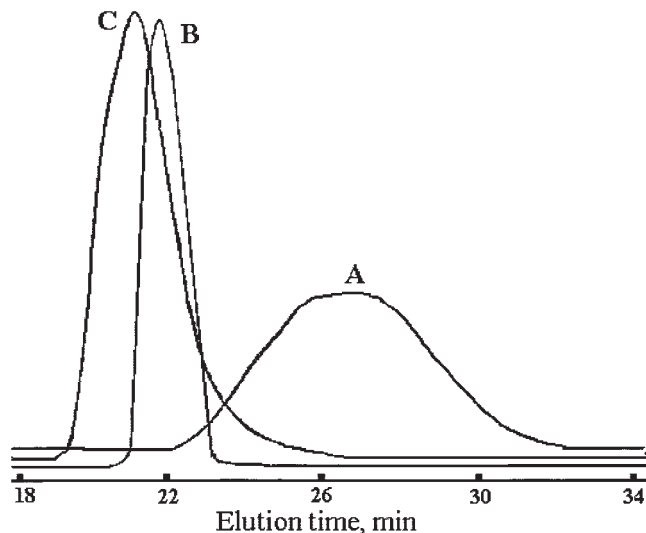


Figure 4 GPC traces of MI-3 (A), MI-3-B2 (B), and MI-3-B1 (C).

and polystyrene block at 102–105°C, depending on block compositions. Nematic–isotropic transition temperatures were also observed between 117°C and 123°C under optical microscopy at different heating rates. POM observations of all samples were consistent with the DSC results.

#### Synthesis of PLC6-*b*-PSt-*b*-PLC6 block copolymers by CFRP and ATRP

The different sequence of the same procedure may be employed as an alternative way to incorporate liquid crystalline segment into a block copolymer. In this approach, styrene monomer was firstly polymerized by CFRP and then copolymerized by ATRP in the presence of liquid crystalline monomer (Scheme 3).

TABLE IV  
Thermal and Liquid Crystalline Properties of Macroinitiators and Block Copolymers

	$T_g^{a,b}$ (°C)	$T_g^{a,c}$ (°C)	$T_{N-I}^{a,d}$ (°C)
MI-1	39	—	120
MI-2	37	—	117
MI-3	38	—	123
MI-4	—	97	—
MI-1-B1	38	105	120
MI-2-B1	39	102	122
MI-3-B1	36	105	121
MI-3-B2	36	103	122
MI-4-B1	36	nd <sup>e</sup>	119
MI-4-B2	36	nd <sup>e</sup>	119

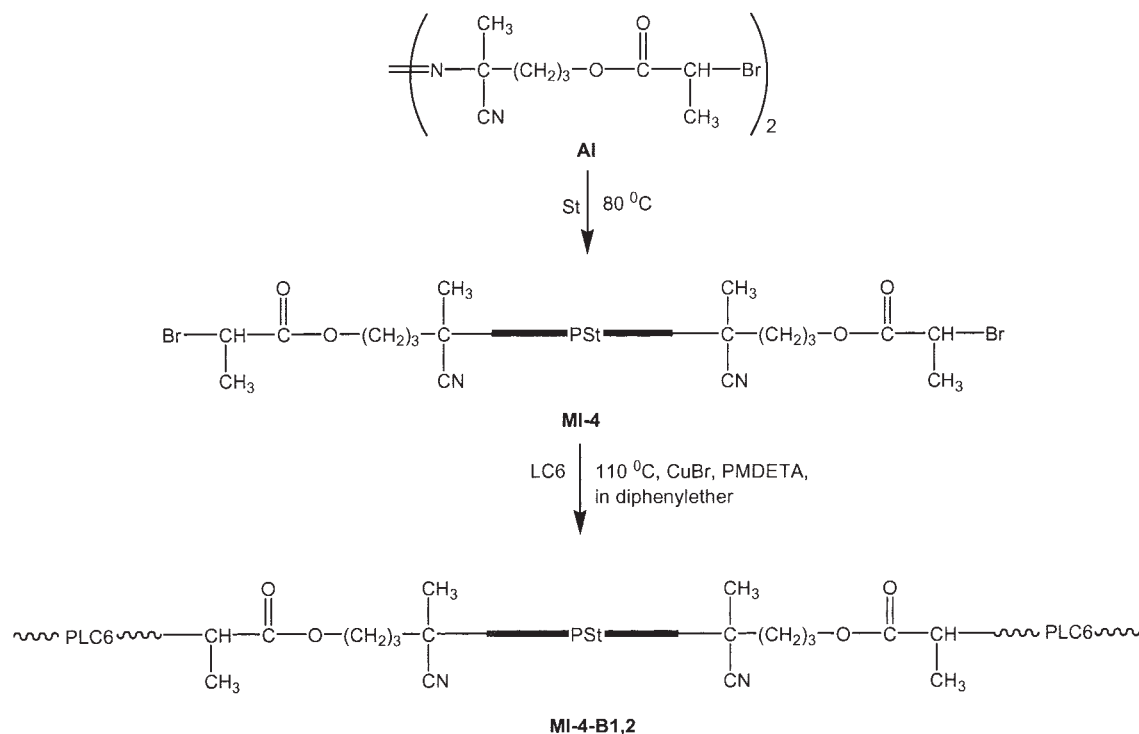
<sup>a</sup> Detected by DSC.

<sup>b</sup> Referred to PLC6 segment of polymer.

<sup>c</sup> Referred to PSt segment of polymer.

<sup>d</sup> Observed by polarizing microscopy.

<sup>e</sup> Not detected.



Scheme 3

The conditions and results of polymerization of styrene by CFRP are presented in Table I. Unfortunately, the preparation of block copolymers using ATRP mechanism was not successful with liquid crystalline acrylate monomer. Although all ATRP processes utilize similar conditions and catalyst, one set of conditions cannot be applied to every set of monomers because of the specific values of propagation and exchange rate constants. LC6 was the first monomer example of using ATRP, starting from a macroinitiator initiating system. These values can also be attributed to the formation of the residual homo liquid crystalline polymer as result of the high temperature condition. Additionally, these copolymers were not purified enough by extraction with a suitable solvent that is selective solvent for only PLC6. The conditions and the results of ATRP of LC6 are given in Tables II and III.

The copolymerization was achieved only with low conversions and yielded low molecular weight polymers as determined GPC analyses. Polydispersity of the corresponding copolymers (MI-4-B1,2) remained roughly the same with the precursor polymers (Table III).

The observed molecular weights were found to be higher than that of the GPC values for the polymerization of LC6. This could be explained with the differences obtained by GPC when comparing the PLC6 to linear polystyrene standards and remaining homopolymer.

ATRP of the liquid crystalline monomer require additional adjustments to the reaction conditions. Es-

pecially, the free-radical polymerization difficulties for bulky LC6 monomer can be minimized by choosing specific ligand and copper catalyst concentration values in ATRP.

Thermal behavior of the MI-4-B1 and MI-4-B2 was observed to be quite similar to the transition temperatures of the related homopolymers and copolymers (Table IV).

In conclusion, the synthesis of liquid crystalline-amorphous block copolymers by using sequential CFRP and ATRP was achieved. Resulting copolymers may provide an opportunity for a new breakthrough in the area of polymeric materials for advanced technology by obtaining with the lower polydispersities. Our work can be regarded as a new attempt to prepare liquid crystalline block copolymers by CFRP-ATRP combination in living/controlled radical polymerization.

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