

# New Synthetic Approach For the Synthesis of Liquid Crystalline Block and Graft Copolymers

Yeşim HEPUZER, İ. Ersin SERHATLI, & Yusuf YAĞCI  
*İstanbul Technical University, Department of Chemistry,  
80626 Maslak, İstanbul-TURKEY*

Received 27.10.1997

Liquid crystalline block and graft copolymers were synthesized according to the macroinitiator and macroinimer concept. For this purpose, side chain block copolymers (polytetrahydrofuran-*b*-polymethylmethacrylate) having liquid crystalline 4,4'-cyanobiphenyl blocks were prepared and characterized. Unlike the liquid-crystalline homopolymer with mesogenic units in the side chain, all block and graft copolymers showed a smectic A mesophase. The transition temperatures are hardly affected by the composition and molecular weight of the block copolymers.

## Introduction

Liquid crystalline (LC) block and graft 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 straightforward to combine the properties of liquid crystalline and isotropic (I) polymers by forming an LC/I block copolymer. Such a system is expected to show a microphase-separated structure with coexisting isotropic and anisotropic phases. In order to study the microphase separation in LC/I block copolymers it is necessary to synthesize macromolecules with well-defined structure and narrow molecular weight distribution. For the LC block, the rigid-rod or disk-like mesogenic groups can be either situated in the polymer main chain (main-chain LC polymer) or attached to a flexible polymer as pendant groups (side-chain LC polymer). In order for a polymer containing mesogenic side groups attached without a flexible space to form a mesophase, the polymer backbone must be significantly distorted from its normal random-coil conformation. At the same time, the backbone sterically hinders the packing of the mesogens.

Because of this, most polymers with the mesogenic groups directly attached to the backbone are amorphous. However, when the side chain ordering is sufficiently strong to overcome the normal barriers associated with the random coil conformation of the backbone, the polymer should exhibit liquid crystalline mesomorphism<sup>1</sup>. Main-chain LC polymers used in the synthesis of segmented polymers and AB-type block copolymers have been reported<sup>2-4</sup>. However because of the polycondensation reactions that are applied to build up the main chain LC block, the resulting polymers exhibit fairly large polydispersities. because of the broad distribution of the different segments no regular morphology is observed<sup>2,3</sup>. In contrast, the polymerization techniques used for side chain LC polymers allow the synthesis of macromolecules with regular structure. There are two principal approaches to building AB-type structures. The first involves the

sequential living or “quasi living” polymerization of the two monomers A and B; the other utilizes reactive sites on macromolecules to build the AB structure in a two-step process. The synthesis of AB-type structures can be also achieved by free radical polymerization using azo macroinitiators. The synthesis of isotropic AB blockcopolymers using azo macroinitiators is well known<sup>5</sup> and its use with LC monomers has been extensively studied by our group<sup>4,6–10</sup>. In this study, we present the synthesis of a new class of block and graft copolymers possessing LC segments. Polytetrahydrofuran macroinitiators and macroinimers possessing the appropriate thermal and photochemical functionality were used as precursors for the subsequently blocking and grafting reactions.

## Experimental

### Materials

Tetrahydrofuran (THF) was dried over potassium hydroxide, distilled over sodium wire and finally distilled over sodium benzophenone ketyl prior to use. Methacryloyl chloride (MAC) and acryloyl chloride (AC) were distilled over phosphorus pentoxide. Methylmethacrylate (MMA) was distilled in vacuo. 4'-hydroxy-4-biphenylcarbonitrile (Aldrich), 2-Picoline N-oxide (Aldrich) and silver hexafluoro antimonate (Aldrich) were used as received. Dichloromethane was distilled over CaH<sub>2</sub>. 2,2-Azobisisobutyronitrile (AIBN) was purified by re-crystallization from ethanol.

### Monomer Synthesis

Alkenoyl chloride (5ml) was added in one portion to a solution or suspension of the hydroxybiphenyl (5g) in aqueous potassium hydroxide (50ml, 50%) and dioxan (15 ml). The mixture was vigorously shaken and grew hot rapidly. After ten minutes of occasional shaking, a further portion (5 ml) of alkenoyl chloride was added. The mixture was then allowed to cool naturally, with occasional shaking, and poured into water (50 ml). The resulting precipitate was filtered off, washed with cold water until neutral to litmus, dried in vacuo and crystallized from ethanol: yield 60 %, phase transitions **K** (crystal) 103° C, **N** (Nematic) 129° C, **I** (Isotropic)<sup>11</sup>.

### Synthesis of Polytetrahydrofuran (PTHF) Macroinimers

Experiments were carried out in a nitrogen atmosphere. Freshly distilled THF was put into a Schlenk tube heated in vacuo with a heat gun and flushed with dry nitrogen after which stoichiometric amounts of methacryloyl chloride and AgSbF<sub>6</sub> stock solutions in THF were added to adjust the final concentration, respectively, under efficient stirring at 25° C. After a given time, an aliquot sample was removed for GPC characterization by syringe and poured into methanol. The remainder of the reaction mixture was terminated by the addition of a solution of 2-picoline N-oxide (10 mol equivalent of the initiator concentration) in CH<sub>2</sub>Cl<sub>2</sub>. The polymerization mixture was stirred for 30 minutes and after centrifugation, and the macroinimer was poured into methanol and cooled to -30° C. The precipitated polymer was filtered off and dried in vacuo.

## Graft Copolymerization of PTHF Macroinimer

LC monomer (1.2 mmol) was added to a solution of dimethylformamide (DMF) containing a given amount of the macroinimer and AIBN. The tube was degassed in vacuo and sealed under nitrogen. It was then placed into a thermostatically controlled bath at 65 °C. After a given time, the polymerization mixture was poured into methanol and the precipitated polymer was filtered off and dried in vacuo.

## Synthesis of Side Chain Block Copolymers

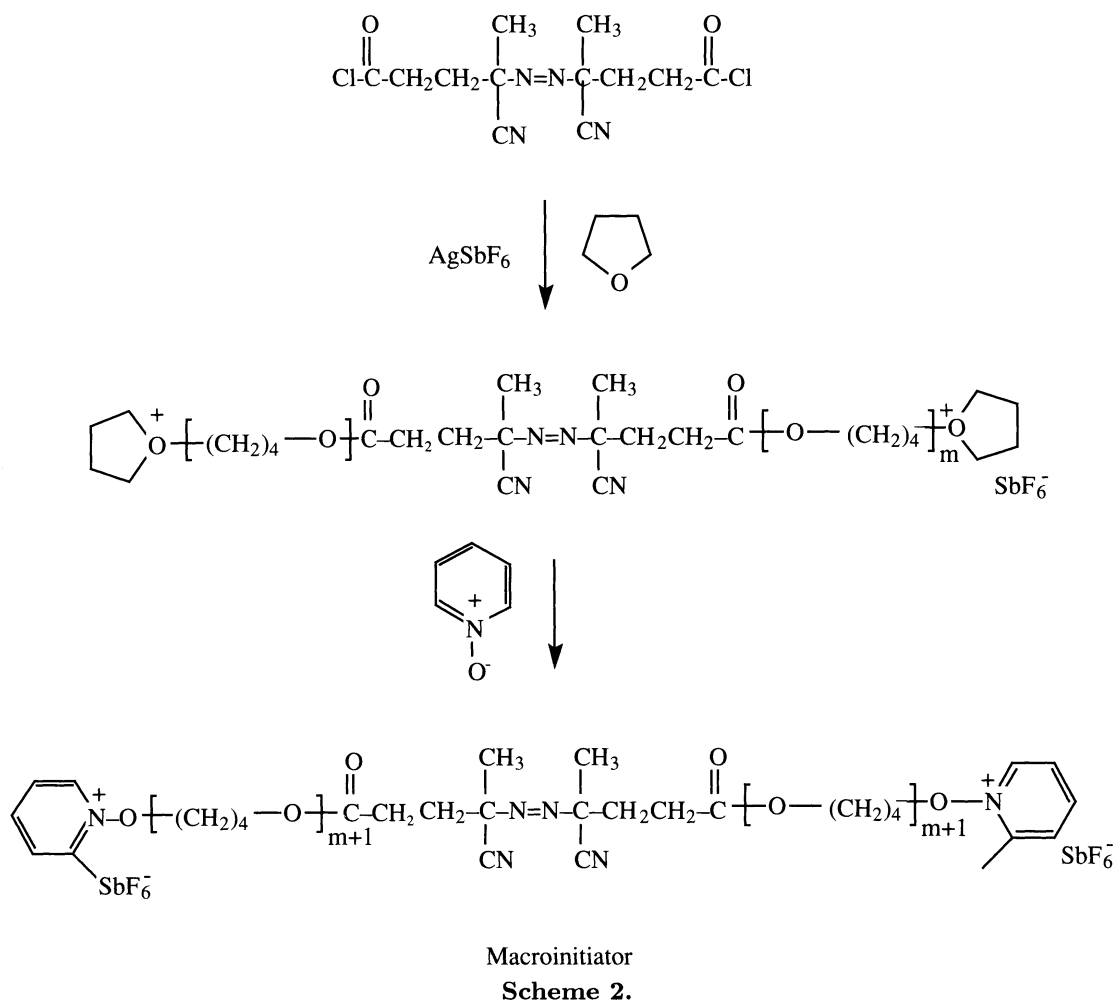
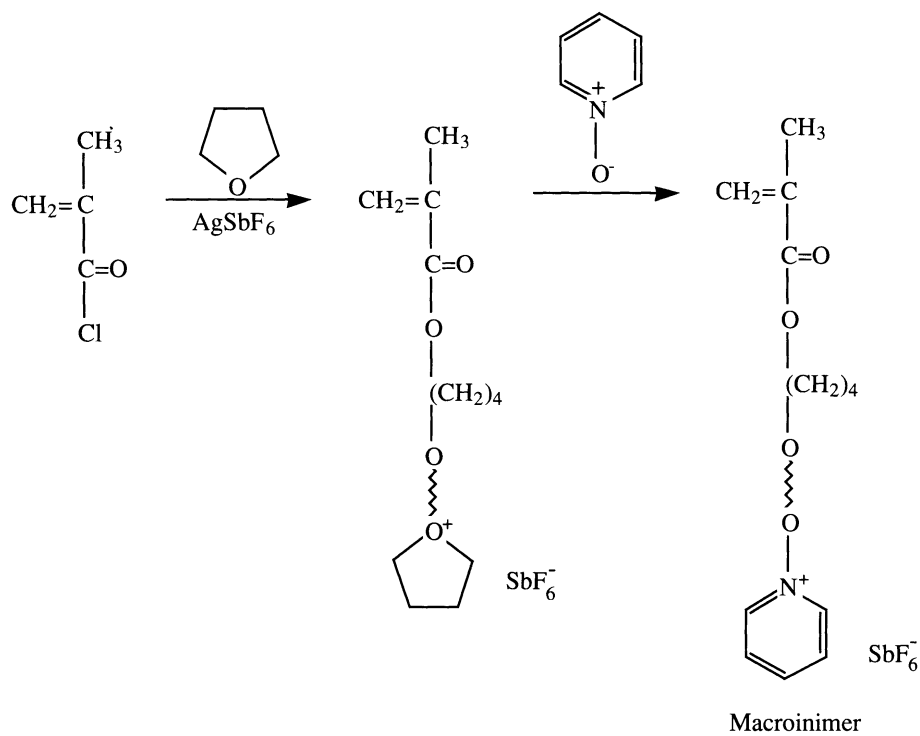
A given amount of the polymer (MI-C) was dissolved in DMF. The solution was put into a Pyrex tube and MMA and anthracene were added. The tube was degassed and sealed under nitrogen prior to irradiation at 350 nm in a Rayonet reactor. After a given time, the resulting polymer was poured into methanol. The precipitated polymer was filtered off and dried in vacuo.

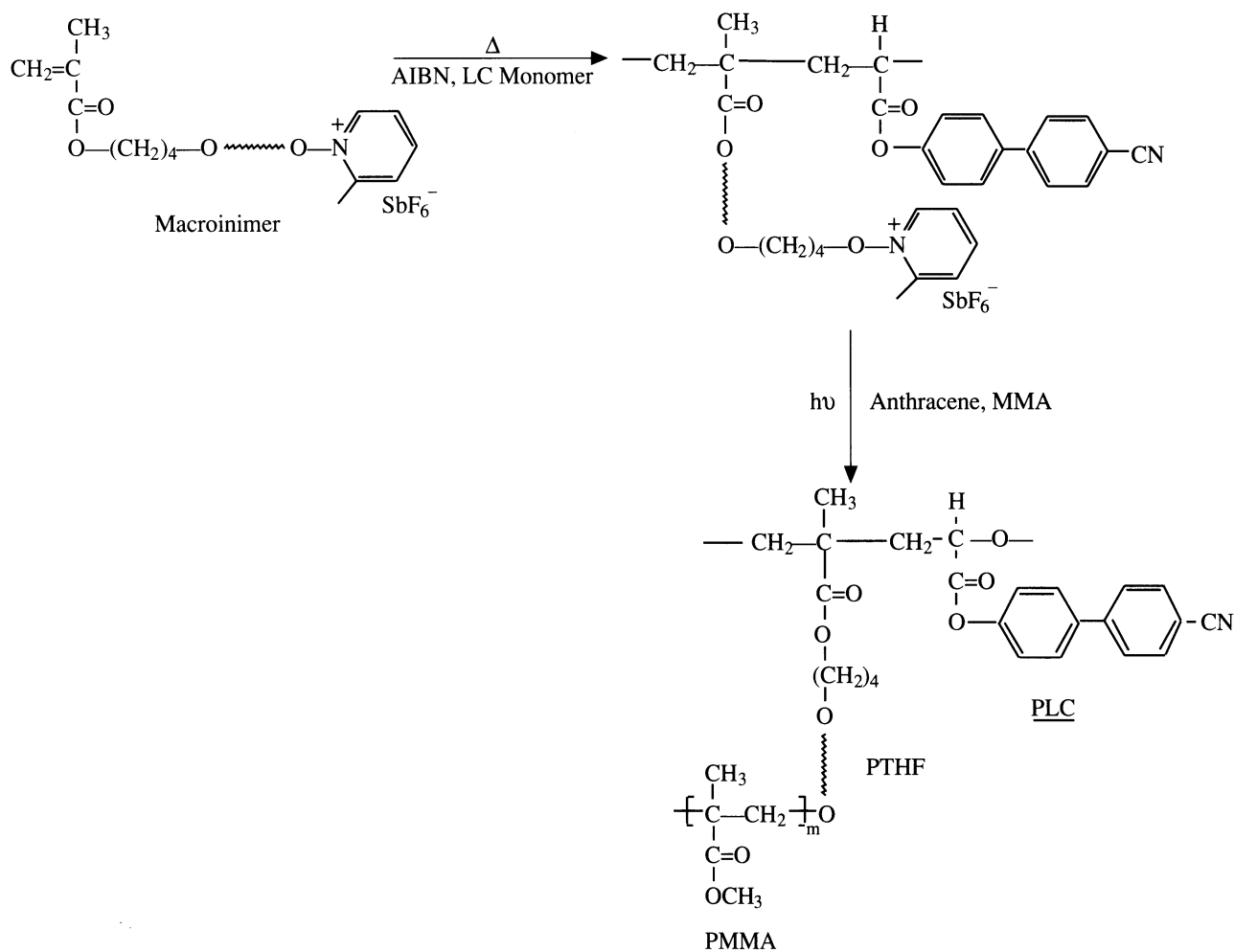
## Synthesis of PTHF Macroinitiator

Freshly distilled THF (15 ml) was put into a schlenk tube heated in vacuo with a heat gun and flushed with dry nitrogen, after which stoichiometric amounts of 4-4' azobis (4-cyanopentanoyl chloride) (ACPC) and AgSBF<sub>6</sub> were added under efficient stirring at room temperature respectively. After a given time, an aliquot sample was removed for g.p.c. characterization by syringe and poured into water. The remainder of the reaction mixture was terminated by the addition of a solution of 2-picoline N-oxide (2 mole equivalent of the initiator concentration) in CH<sub>2</sub>Cl<sub>2</sub>. After stirring for 30 minutes and centrifugation, the macroinitiator was poured into water. The precipitated polymer was filtered off and dried in vacuo.

## Block Copolymerization PTHF Macroinitiator

LC monomer was added to a solution of DMF containing a given amount of the macroinitiator. The tube was degassed in vacuo and sealed under nitrogen. It was then placed into a thermostatically controlled bath at 70 °C. After a given time, the termination reactions under closely controlled conditions. In this study, we employed oxo-carbenium salt as an initiator for the THF polymerization to obtain well-defined PTHF macroinimer and macroinitiator. N-Alkoxypridinium ion-terminated PTHF's were obtained by quenching the living ends of the polymers with 2-picolin N-oxide (Scheme 1). Experimental conditions and the molecular weights of the macroinitiator and macroinimers are shown in Table 1 and 4, respectively. The free radical polymerization of LC monomer with macroinimer and macroinitiator yielded graft copolymer MI-C (Table 5) and PLC-*b*-PTHF copolymers MA-B1, MA-B2 (Table 2), respectively. As seen in Table 2, the molecular weight of the resulting polymer and the conversion of LC monomer increased with the increase of the mole ratio of LC monomer to PTHF macroinitiator. The resulting graft copolymer and block copolymer with a photoactive group were then used in indirect photochemical polymerization of MMA in the presence of anthracene as a photosensitizer yielded side chain block copolymer MI-B and multi-block copolymer MA-MB, by the reactions depicted in Schems 3 and 4, respectively.




**Scheme 3.**
**Table 1.** Preparation<sup>a</sup> of Photoactive Polytetrahydrofuran Macroinitiator

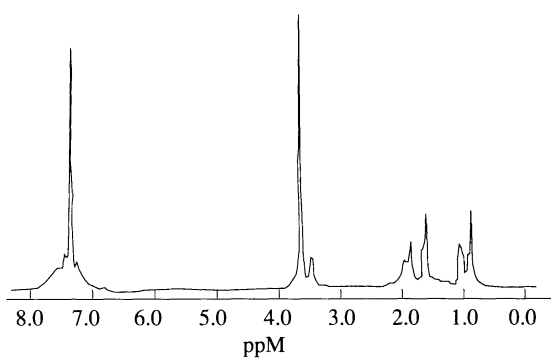
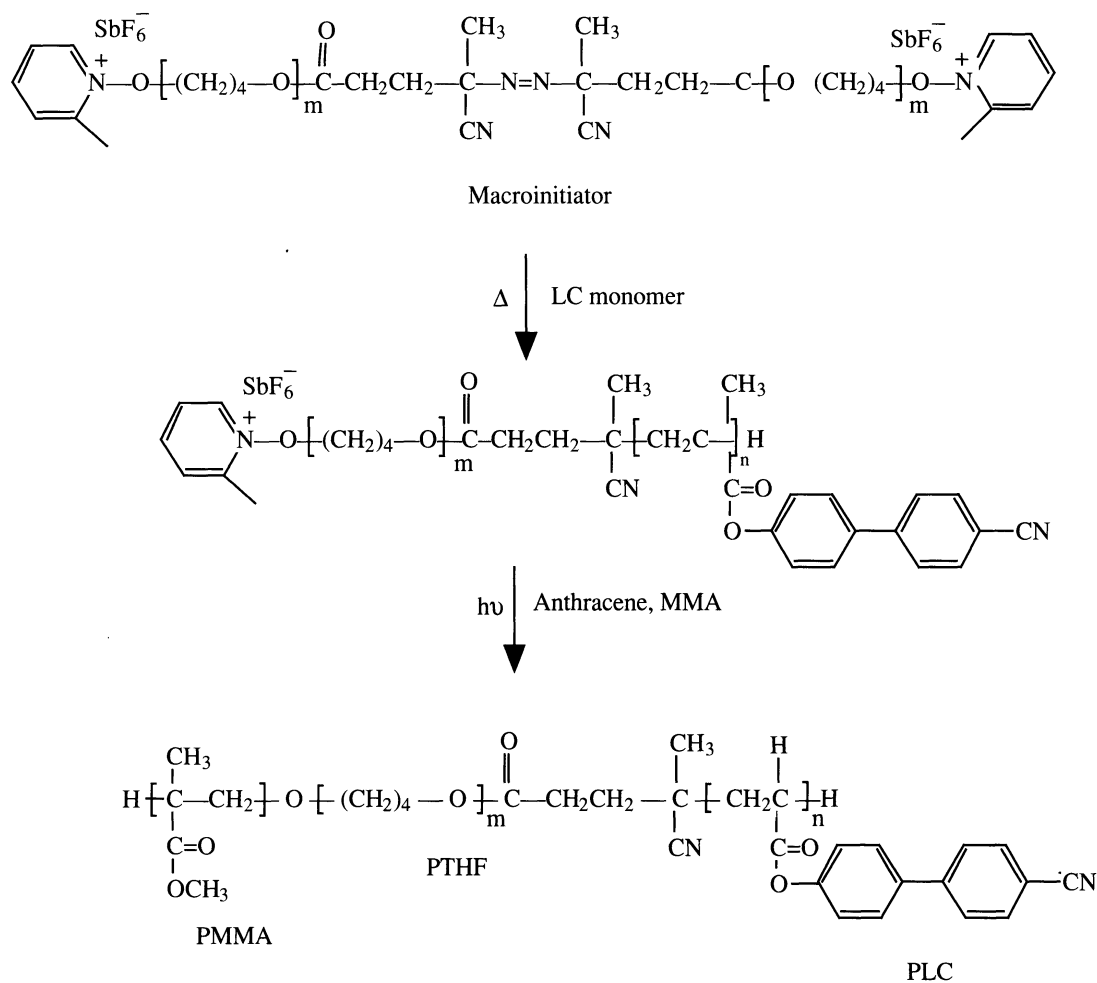
Code	N-Oxide (mol.l <sup>-1</sup> )	Time (min)	Conversion (%)	M <sub>n</sub> <sup>b</sup>	M <sub>w</sub> /M <sub>n</sub>
MA	2-Picoline (0.068)	3	27.5	27200	1.65

<sup>a</sup> Polymerization Conditions; [ACPC]=0.043 mol. l<sup>-1</sup>,

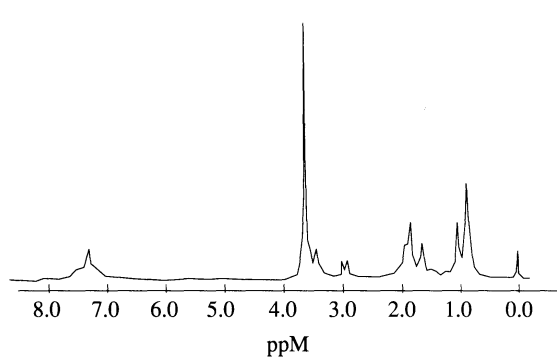
[AgSbF<sub>6</sub>]=0.08 mol.l<sup>-1</sup>, Temp.= 25°C.

<sup>b</sup> Determined by GPC based on PS standards

Side chain block and multiblock copolymers in which the mesogenic moiety was a 4-4'-cyano-biphenyl group were synthesized and characterized by <sup>1</sup>H-NMR spectra of the graft and block copolymers (Figure 1, 2) displayed signals at 7.2 ppm (C<sub>6</sub>H<sub>5</sub>), 3,6 ppm (-OCH<sub>3</sub>) and 3.2 ppm (-OCH<sub>2</sub>). The <sup>1</sup>H-NMR spectrum of the side chain block copolymer (Figure 1) shows large signals of PLC inits. These signals were insignificant in the case of the multi-block copolymer (Figure 2). although the mode of radical generation is the same in both cases, homopolymer formation in graft copolymerization may be due to the selectivity of propagating radicals towards monomers. Notably, only one kind of monomer in polymerization mixture was poured into methanol. The precipitated polymer was filtered off and dried in vacuo.



**Figure 1.**  $^1\text{H-NMR}$  spectrum of side chain block copolymer (MI-B)



**Figure 2.**  $^1\text{H-NMR}$  spectrum of multi-block copolymer (MA-MB)

## Synthesis of Multiblock Copolymers

A given amount of the block copolymer was dissolved in DMF. The solution was put into a Pyrex tube and MMA and anthracene were added. The tube was degassed and sealed under nitrogen prior to irradiation at 350 nm in a Rayonet reactor. After a given time, the resulting polymer was poured into methanol. The

precipitated polymer was filtered off and dried in vacuo.

**Table 2.** Results of Copolymerization<sup>a</sup> of Polytetrahydrofuran Macroinitiator with Liquid Crystalline Monomer

Code	PTHF macro-initiator (gr.l <sup>-1</sup> )	[LC]/[PTHF] (mol/mol)	Conversion (%)	M <sub>n</sub> <sup>b</sup>	M <sub>w</sub> /M <sub>n</sub>	Phase Transitions (°C)
MA-B1	28.57	180	58	9100	1.7	T <sub>m</sub> 30 S 265 I
MA-B2	20	440	90	11200	1.9	T <sub>m</sub> 30 S 270 I

<sup>a</sup>Conditions; Solvent=DMF, Time=2 days, Temp.=70°C.

<sup>b</sup>Determined by GPC based on PS standards.

T<sub>m</sub> = Melting temperature

## Analysis of Polymers

<sup>1</sup>H-NMR spectra were taken on a Bruker 200 instrument with solvent CDCl<sub>3</sub> and tetramethylsilane as the internal standard. GPC analyses were performed with a set-up consisting of a Waters pump (model 600E) and a Hewlett Packard column (Mixed-C PL gel 5μ). THF was used as the eluent at a flow rate of 1 ml. min<sup>-1</sup> and detection was achieved with a Waters differential refractometer (model 410). The thermal properties of the polymers were studied by DSC measurements (Perkin Elmer DSC 6 Model at a scanning rate of 5°C min<sup>-1</sup>) and hot-stage polarized light microscopy (Reichert Polyvar microscope equipped with programmable Mettler FP52 heating stage at a scanning rate of 10 K. min<sup>-1</sup>).

**Table 3.** Preparation<sup>a</sup> of multiblock Copolymers

Code	Prepolymer (gr.l <sup>-1</sup> )	Monomer (mol.l <sup>-1</sup> )	Conversion (%)	M <sub>n</sub> <sup>b</sup>	M <sub>w</sub> /M <sub>n</sub>	Phase Transitions (°C)
MA-MB	MA-B2 (66)	MMA (3.2)	22	16500	3.0	T <sub>m</sub> 30 T <sub>g</sub> 105 S 276 I

<sup>a</sup>Polymerization Conditions: Anthracene=5.10<sup>-3</sup> mol.l<sup>-1</sup>, Solvent=DMF, γ=350 nm, Time = 4h.

<sup>b</sup>Determined by GPC based on PS standards.

S: Smectic

I: Isotropic

**Table 4.** Preparation<sup>a</sup> of Polytetrahydrofuran Macroinimers

Code	2-Picoline N-Oxide (mol.l <sup>-1</sup> )	Time (min)	Conversion (%)	M <sub>n</sub> <sup>b</sup>	M <sub>w</sub> /M <sub>n</sub>
MI1	0.1	2	0.8	8600	1.07
MI2	0.1	5	1.3	12700	1.3

<sup>a</sup>Conditions; [THF]=12.3 mol.l<sup>-1</sup>; [MAC]=10<sup>-2</sup> mol.l<sup>-1</sup>, [AgSbF<sub>6</sub>]=10<sup>-2</sup> mol.l<sup>-1</sup> Temp= 25°C.

<sup>b</sup>Determined by GPC based on PS standards.

**Table 5.** Results of Copolymerization<sup>a</sup> of Polytetrahydrofuran Macroinimers Liquid crystalline Monomer

Code	PTHFmacroinimer (gr.l <sup>-1</sup> )	[LC]/[PTHF] (mol/mol)	Conversion (%)	M <sub>n</sub> <sup>b</sup>	M <sub>w</sub> /M <sub>n</sub>	Phase Transitions (°C)
MI-C	MI1 (20)	167	85	15900	2.4	T <sub>m</sub> 28 S 270 I

<sup>a</sup>Conditions; [AIBN]=5.10<sup>-3</sup> mol.l<sup>-1</sup>; Solvent=DMF, Time = 24 h, Temp = 65 °C.

<sup>b</sup>Determined by GPC based on PS standards.

## Results and Discussion

It is well known that<sup>12</sup> the initiation of THF polymerization by oxo-carbenium salts is quantitative and rapid and proceeds by an addition mechanism. Moreover, the polymerization is considered to be living, since it proceeds without chain transfer and is involved in block copolymerization, whereas two structurally different monomers, namely macroinimer and LC monomer, are involved in the first step of the latter case. Homopolymer of LC monomer formed this way could not be removed by extraction in a solvent because of the similar solubility properties of homopolymer and block copolymer. A clear proof of the block copolymer formation was obtained by GPC with dual detection by refractive index and ultraviolet recordings. The wavelength of 360nm, at which polytetrahydrofuran is transparent, was used for the ultraviolet detector. The GPC traces of sample MA-B2 obtained using both detectors are reported in Figure 3 as a typical example. They are practically superposable in terms of shape and peak position, thus indicating the formation of a block copolymer. Chromatograms recorded with macroinitiator, block copolymer and multi-block copolymer are also shown in Figure 4. The figure has three peaks, one at high elution volume pertaining to prepolymer and the other two at low elution volume pertaining to block copolymer and multi-block copolymer, respectively. The thermal behaviour of the polymers was investigated by hot-stage polarized microscopy and DSC measurement.

**Table 6.** Results of Block Copolymerization by Using Copolymers Derived From Macroinimer (MI-C)

Code	Prepolymer (gr.l <sup>-1</sup> )	Monomer (mol.l <sup>-1</sup> )	Conversion (%)	M <sub>n</sub> <sup>b</sup>	M <sub>w</sub> /M <sub>n</sub>	Phase Transitions (°C)
MI-B	MI-C (66)	MMA (3.1)	10.5	17600	3.1	T <sub>m</sub> 28 T <sub>g</sub> 106 S 270 I

<sup>a</sup>Conditions; Anthracene= 5.10<sup>-3</sup> mol.l<sup>-1</sup>; Solvent=DMF, λ = 350 nm  
Time = 4h,

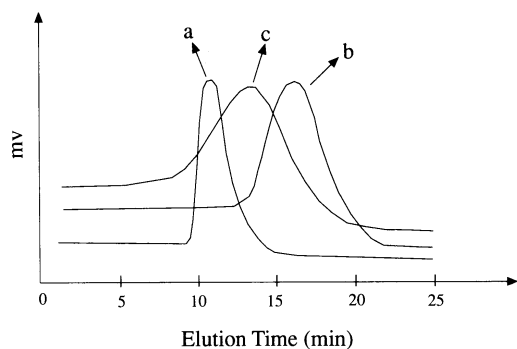
<sup>b</sup>Determined by GPC based on PS standards.

T<sub>m</sub>=Melting temperature

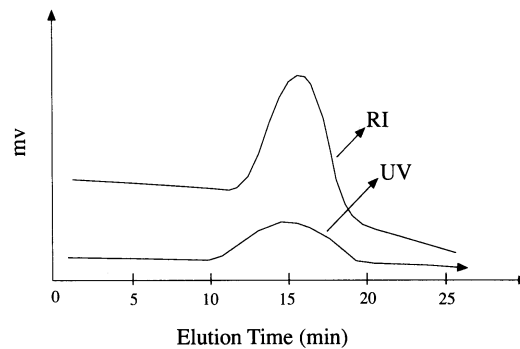
S: Smectic, I: Isotropic

The glass transition temperature of PTHF could not be detected. However, the melting transition of the PTHF segment gave an endothermic peak between 28-30 °C. The glass transition of the PMMA segment was observed at temperature between 105 and 110 °C by DSC experiments.





**Figure 3.** GPC traces of MA (a), MA-B2 (b), MA-MB (c)



**Figure 4.** Gel permeation chromatogram of MA-B2 detected by refractive index and ultraviolet recordings

The increase in the mesomorphic phase transition temperatures can be explained by the influence of the molecular weight of copolymers<sup>13</sup>. When the phase transition parameters of block copolymers are compared with those of the relevant homopolymers, it appears that the smectic-isotropic phase transition temperatures of the side chain and multiblock in both copolymers are quite different from their corresponding homopolymers. Most polymers with the same mesogen exhibit mesomorphic properties regardless of the nature of the backbone. X-Ray diffraction studies of these polymers suggests that the polymer backbones lie in essentially parallel planes within perpendicular smectic-like layers of the directly attached and rigid anisotropic side chain substituents<sup>14</sup>.

## Conclusion

LC copolymers consisting of different non-LC and LC blocks can be prepared by sequential cationic and free radical polymerizations. With this polymerization system, side chain and multi-block liquid crystalline copolymers containing the anisotropic properties of liquid crystal with polymeric properties were investigated. They are essentially microphase-separated systems which form a smectic mesophase different from the corresponding LC homopolymers. We are extending this procedure to the preparation of side chain block copolymers having flexible spacers in which we anticipate finding more profound effects of the multiple blocks on each other.

## Acknowledgement

We thank the *ITU Araştırma fonu* for financial support. A graduate fellowship from *TÜBİTAK (BDP program)* for Y. Hepuzer is gratefully acknowledged.

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