Synthesis of Liquid Crystalline–Amorphous Block Copolymers by the Combination of Atom Transfer and Promoted Cationic Polymerization

S. Demirhan, İ. E. Serhatli, A. Önen

Department of Chemistry, Istanbul Technical University, Maslak, Istanbul 34469, Turkey

ABSTRACT: Block copolymers of liquid crystalline 6-(4-cyanobiphenyl-4′-oxy) hexyl acrylate (LC6) and cyclohexene oxide (CHO) were obtained by the combination of atom transfer radical polymerization (ATRP) and promoted cationic polymerization (PCP). In the first part, a bifunctional initiator containing benzoin and halide groups in the same structure was used as an initiator in ATRP of LC6, in diphenyl ether in conjunction with CuBr/$N,N,N′,N″,N″$-pentamethyldiethylenetriamine as a catalyst. The obtained photoactive liquid crystalline polymers poly[6-(4-cyanobiphenyl-4′-oxy)hexyl acrylate] (PLC6), were used to induce polymerization of CHO through formation of electron donor polymeric radicals upon photolysis and subsequent oxidation to corresponding carbocations in the presence of onium salt. The spectral, thermal and optical measurements confirmed a full combination of ATRP and PCP, which resulted in the formation of AB-type block copolymers. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 568–575, 2007

Key words: atom transfer radical polymerization; cationic polymerization; block copolymers; liquid crystalline polymers; amorphous

INTRODUCTION

Block copolymers are useful in many applications where a number of different polymers are connected together to yield a material with hybrid properties. The desire to control polymer properties through the synthesis of block copolymers and complex macromolecular architectures is a continuing theme through polymer chemistry.[1–3] Block copolymers exhibit wide range of morphologies including lamellar, hexagonal-packed, cylindrical, and body centered cubic micellar structures, depending on the relative volume fractions of the blocks.[4,5] This clear picture of the morphology as a function of composition has primarily emerged from the investigation of diblock copolymers. The block copolymers with well defined structures such as architecture, composition, end group functionality, molecular weight and molecular weight distribution are very important. Several synthetic approaches have been developed successfully for the preparation of block copolymers, including sequential monomer addition, coupling reaction of ''living'' polymer chains and transformation mechanism in which terminally functional polymers were synthesized by one mechanism and subsequently employed to initiate the polymerization of a second monomer, by a different mechanism.[6] Recently ATRP has been applied to the synthesis of well defined macromolecular architectures such as block copolymers, graft copolymers, comb polymers, star polymers, hyperbranched polymers, and dendritic polymers.[7–10]

In spite of extensive studies on ATRP-living/controlled radical polymerization for the different monomers, its application to the synthesis of special polymers, such as liquid crystalline (LC) polymers, has been very rare. Gomes, Laus, and others reported liquid crystalline and amorphous block copolymers by living/controlled radical polymerization.[11–17]

The syntheses of block copolymers containing amorphous and LC segments are also popular and can originate a vast number of possible combinations of properties and structures.[18–26] The molecular design and synthesis of LC polymers, especially LC block copolymers, toward well defined polymer nano-architectures have gained considerable attention. Block copolymers with both LC properties and phase separation properties offer unique opportunities to manipulate LC order in nanometer scales.[27–29]
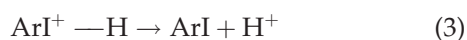
Since it was discovered by Dupont, photoinitiated polymerization has become an important industrial process.[30] The main positive attributes of photochemical processes are that they offer a rapid conversion of formulated reactive liquids to solids by radical or cationic means. Photoinitiated cationic polymerization has also gained a technological interest because of its range of application in coatings,
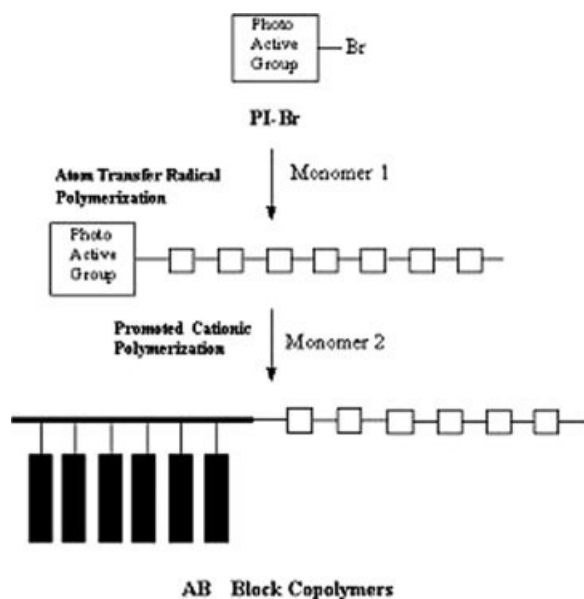
Scheme 1 Synthesis of AB type liquid crystalline-amorphous block copolymers via ATRP and PCP.

adhesives, inks, and resists.[31,32] Photoinitiated cationic polymerization is based on the photogeneration of acids and reactive cations. Onium salts and iron arene complexes are widely used as powerful photoinitiators for cationic polymerization.[33–36]

$$Ar_2I^+ \xrightarrow{h\upsilon} ArI^{+\bullet} + Ar^\bullet \quad (1)$$

$$ArI^{+\bullet} + R-H \rightarrow ArI^+ - H + R^\bullet \quad (2)$$

$$ArI^+ —H \rightarrow ArI + H^+ \quad (3)$$

To further improve the performance of these photoinitiators, the spectral response of onium salts can be extended to 300–400 nm region by using free radical sources, photosensitizers and charge transfer complexes.[37–40] Certain onium salts such as diphenyl iodonium and alkoxy pyridinium salts may be used to oxidize photochemically generated electron donating free radicals according to the reaction (4), thus generating reactive cations.[41,42]

$$—\overset{|}{\underset{|}{C}}^\bullet \;+\; On^+ \longrightarrow —\overset{|}{\underset{|}{C}}^+ \;+\; On^\bullet \quad (4)$$
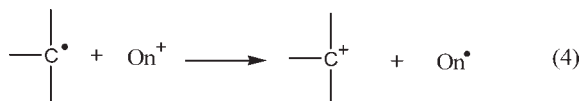
This method, so called free radical promoted cationic polymerization, has been employed for the synthesis of copolymers previously.[38,42]

Synthesis of polymers containing photo reactive groups in the main or at the side chains were also reported and find applications in various fields of UV curing as precursors for the synthesis of block and graft copolymers.[43–47] We have also synthesized functional LC polymers having photoactive benzoin groups at the chain end and utilize them as an initiator in the second stage to initiate free radical polymerization of a selected monomer to obtain block copolymers that combine the properties of different polymeric structures, into one macromolecular chain.[48]

This article describes the synthesis of AB type liquid crystalline-amorphous block copolymers via ATRP and PCP methods (Scheme 1).

EXPERIMENTAL

Materials

The LC monomer 6-(4-cyanobiphenyl-4′-oxy)-hexyl acrylate (LC6) was prepared according to the literature.[49] α-Methylol benzoin methyl ether (MBME) was prepared according to the modification method of Ahn et al.[50] Cyclohexene oxide (CHO) (Aldrich, Germany) and solvents were purified by conventional drying and distillation procedures. Other chemicals, diphenyl ether (Aldrich), Copper (I) Bromide (Aldrich), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) (Acros, Belgium), were used without further purification.

Synthesis of 2-methoxy-3-oxo-2,3-diphenylpropyl 2-bromopropanoate (PI-Br)

Under nitrogen 1.66 mL (15.68 mmol) 2-bromopropionyl bromide was added dropwise to a stirring mixture of 1.6 g (6.25 mmol) MBME and 2.19 mL (15.68 mmol) triethylamine in 150 mL of CHCl₃ in an ice bath for 30 min. After complete addition of the acid bromide, the reaction was stirred at room temperature for 3 h. The reaction mixture was washed with water (3 × 150 mL) and then dried over MgSO₄. After filtration and evaporation of
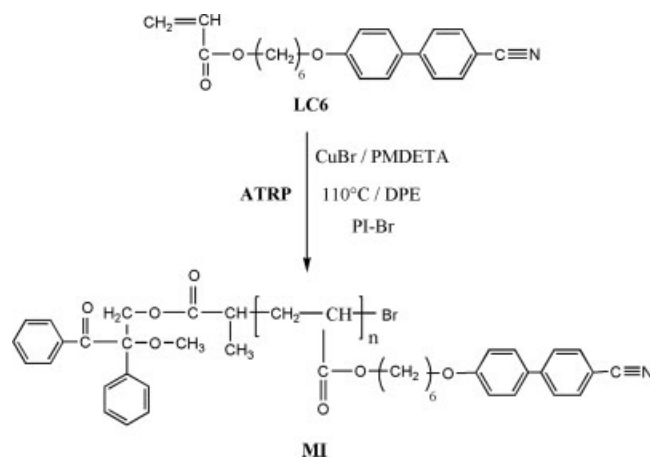
Scheme 2 Synthesis of photoactive liquid crystalline polymers via ATRP.

TABLE I
ATRP[a] of LC6 with PI-Br

Photoactive polymer	$[M]_o \times 10^4$ (mol L^{-1})	$[PIBr] \times 10^3$ (mol L^{-1})	Time (day)	$[I]_o/[CuBr]_o/$ $[PMDETA]_o/[M]_o$	Conv. (%)	M_n (GPC)[b]	$M_{n(theo)}$[c]	M_w/M_n
MI-1	3.6	4.7	6	1/1/1/75	30	5100	9300	1.51
MI-2	7.6	3.8	8	1/1/1/200	25	10400	13,500	1.40
MI-3	7.6	3.8	10	1/1/1/200	66	11300	20,559	1.31

[a] Temperature: 115°C, solvent: diphenylether.
[b] Determined from GPC, based on PSt standards.
[c] Calculated by $[M]_o/[I]_o \times$ conversion $\times MW_{monomer}$.

CHCl$_3$ a greasy yellowish product was obtained.[48] It was dried under vacuum and recrystallized from ethanol.

m.p.: 84–87°C, Yield: 47%. UV: λ_{max} = 338 nm, ε_{338nm} = 224 L mol^{-1} cm^{-1}.

^{1}H-NMR (CDCl$_3$), δ (ppm): 1.5–1.7 (d, 3H, —CH$_3$), 3.3–3.4 (s, 3H, —OCH$_3$), 4.2–4.3 [q, 1H, —CH(Br)], 4,7–4,8 (d, 1H, —CH$_2$), 5.0–5.1 (d, 1H, —CH$_2$), 7.2–7.5 (m, 8H, aromatic protons), 7.9–8.0 (d, 2H, aromatic protons). Elem. Anal. (391 g mol^{-1}) Calcl.: C, 58.31%; H, 4.85%. Found: C, 58.20%; H, 4.72%.

General procedure for ATRP of LC6

To a Schlenk tube equipped with magnetic stirrer, a vacuum and dry nitrogen were applied thrice, and then certain amounts of LC6, a solvent, a ligand (PMDETA), CuBr and PI-Br were added in that order under nitrogen. The reaction solution was bubbled by nitrogen for the removal of dissolved gases, and then the tube was immersed in an oil bath and held by a thermostat at 115°C with rigorous stirring. The polymerization was performed for a determined time and terminated by cooling to room temperature. The reaction mixture was dis-

solved in a large amount of THF. The THF solution was passed through a short alumina column for the removal of copper complex and then concentrated by evaporation. The polymer was precipitated into excess methanol and filtered. The polymer (MI) was dried under vacuum. The conversion was determined gravimetrically.

General procedure for promoted cationic polymerization of CHO

Appropriate solutions of obtained prepolymers (MI) and monomer (CHO) containing onium salt, namely diphenyliodonium hexafluorophosphate (Ph$_2$I$^+$), were placed in pyrex tubes. The mixtures were degassed with nitrogen in the usual manner prior to irradiation with a merry go round type photoreactor equipped with 16 Philips 8W/06 lamps emitting light nominally at 350 nm at 25°C. At the end of a
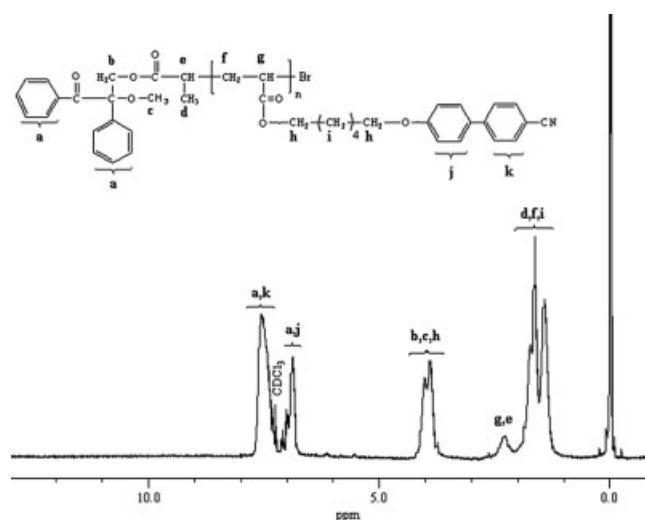

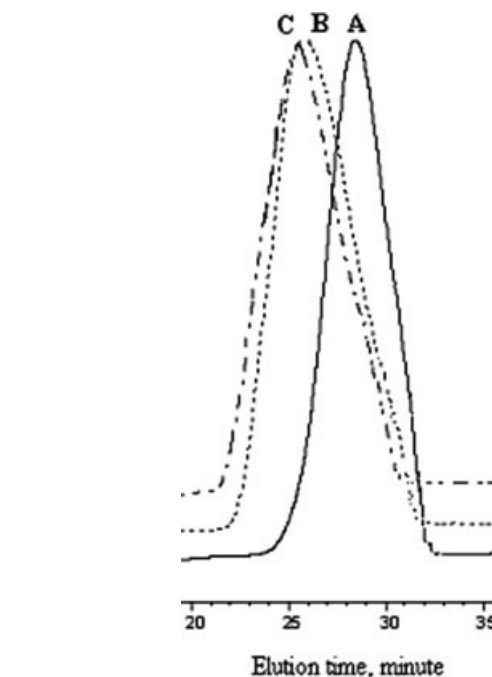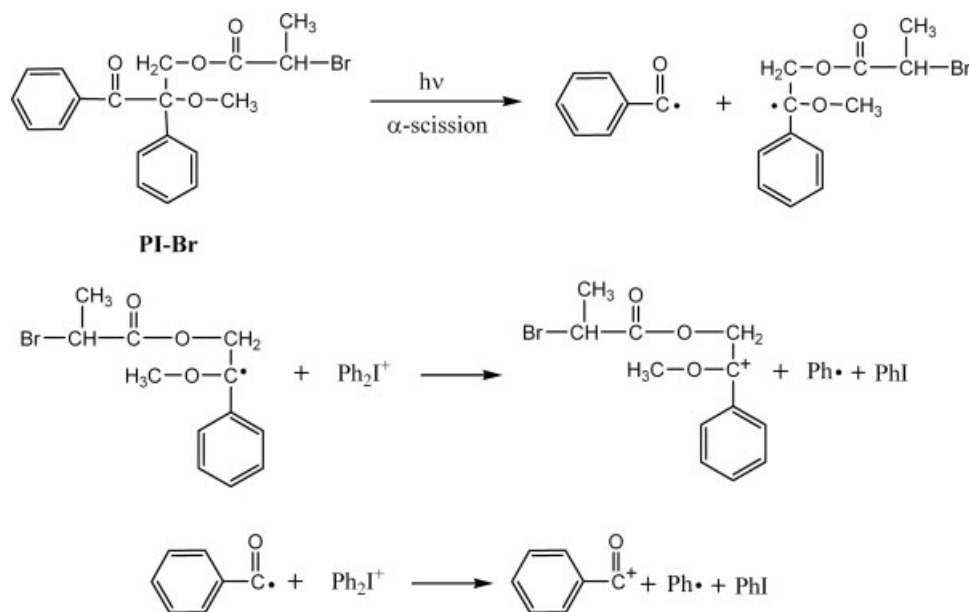**Figure 1**   ^{1}H-NMR spectrum of MI-1 in CDCl$_3$.

Figure 2   GPC chromatograms of MI-1 (A), MI-2 (B), MI-3 (C).

Scheme 3 Photochemical decomposition of PI-Br in the presence of Ph_2I^+.

given reaction time polymers were obtained from the reaction mixture by precipitation into methanol, filtered and dried *in vacuo*. The mixture of block copolymer and homopoly(CHO) (h-PCHO) was separated by successive extraction in boiling *n*-hexane which is selective solvent for homopoly(CHO).[38]

Analysis and characterization

FTIR was measured using Perkin–Elmer (USA) Spectrum One FTIR spectrometer, equipped with ATR sampling accessory. ^{1}H-NMR analysis were recorded on a Bruker (USA) 250 MHz Spectrometer with $CDCl_3$ as a solvent and tetramethylsilane as the internal standard. Gel permeation chromatography (GPC) analyses were carried out with a set up consisting of the Agilent (USA) pump and refractive-index detector (Model 1100) and four Waters (USA) Styragel columns (HR 5E, HR 4E, HR 3, and HR2). THF was used as the eluent at a flow rate of 0.3 mL min^{-1} at 30°C. The molecular weights of the

polymers were calculated with the aid of polystyrene standards. The thermal properties of the block copolymers were measured by differential scanning calorimetry (TA DSC Q10, USA) in a flowing nitrogen atmosphere from the room temperature to 300°C at scanning rate of 10°C min^{-1}. Leitz Laborlux (USA) 12 POL S type polarize optical microscope (POM) equipped with hotstage Mettler Toledo (USA) FP82 HT was used for optical examinations.

RESULTS AND DISCUSSION

In this study AB type amorphous, liquid crystalline block copolymers were synthesized via a two step procedure involving ATRP and promoted cationic polymerization (PCP). For this purpose a bifunctional initiator with benzoin and halide groups in the same structure (PI-Br) was synthesized and employed at the first stage to obtain photoactive liquid crystalline prepolymers. In the second stage these polymers were used as a free radical source for the PCP of CHO.

TABLE II
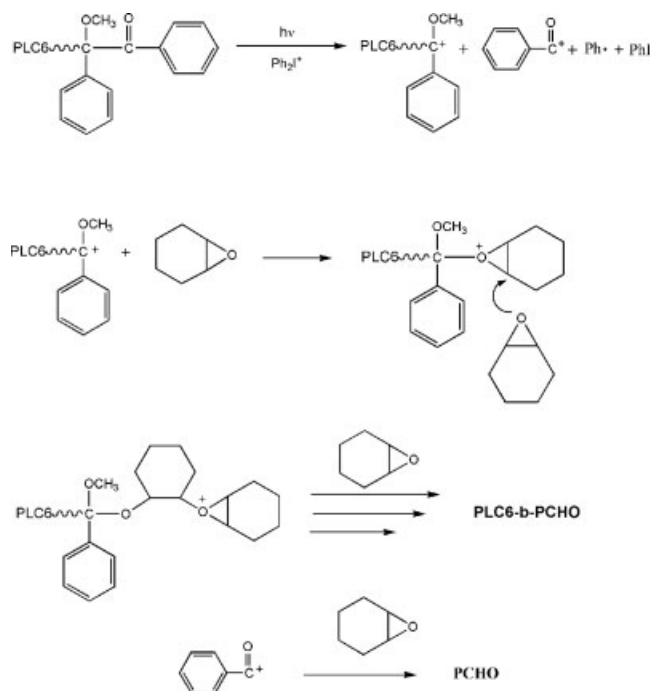**Promoted Cationic Polymerization^a of CHO Using Low Molar Mass Photoactivators in CH_2Cl_2**

Run	Photoactivator	Onium salt	Conv. (%)	M_n^b	M_w/M_n
1	MBME	EMP$^+$	44.54	2226	2.0
2	PI-Br	EMP$^+$	31.80	1875	1.8
3	PI-Br	Ph$_2$I$^+$	38.50	8500	1.9

^{a} $\lambda > 350$ nm; [photoactivator] = 5×10^{-3} mol L^{-1}; [onium salt] = 5×10^{-3} mol L^{-1}; [M] = 5.9 mol L^{-1}; time = 40 min.
^{b} Determined from GPC, based on PSt standards.
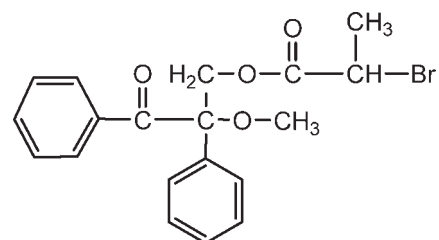
PI-Br

Scheme 4 PCP of CHO using photoactive PLC6.

Preparation of photoactive liquid crystalline polymers by using ATRP mechanism

In the first stage PI-Br was used in the ATRP of 6-(4-cyanobiphenyl-4′-oxy) hexyl acrylate (LC6) at 115°C using CuBr complexed by PMDETA as the catalyst to obtain photoactive liquid crystalline polymers having benzoin methyl ether (BME) groups at one chain end and bromine at the other chain end (Scheme 2).

Typical results concerning the polymerization of LC6 in the presence of PI-Br are presented in Table I. In the case of MI-1 30% conversion with M_n = 5100 and M_w/M_n = 1.51 was obtained for the reaction time of 6 days. When the reaction time was increased M_n values for the resulting polymers (MI-2 and MI-3) increased with a decrease in M_w/M_n values as indicated at Table I. This behavior proves that

the effective initiation of ATRP of LC6 took place. The theoretical molecular weights were higher than GPC values. This could be explained by the differences between polystyrene standards and poly LC segment.

^{1}H-NMR spectra of polymers prove the expected structure of liquid crystalline homopolymers with BME terminal groups at the chain end. The spectrum displays signals at 1.2–2.1 ppm —CH—CH$_2$ and —(CH$_2$)$_4$, 3.6–4.0 ppm —OCH$_2$, 6.2–7.5 ppm C$_6$H$_5$ and 7.0–8.0 ppm aromatic protons of the benzoin methyl ether groups, as illustrated in Figure 1. Figure 2 shows GPC chromatograms of liquid crystalline prepolymers.

Preparation of block copolymers by combination of ATRP and PCP

Poly(LC6)-b-poly(CHO) copolymers with different compositions were synthesized via PCP of CHO by utilizing photoactive liquid crystalline prepolymers.

As stated in the introduction, onium salts can be used to oxidize photochemically generated electron donating radicals producing reactive cations (reaction 4). For comparision with other benzoin type low molar mass photoinitiators, PI-Br was used in the PCP of CHO in conjunction with the onium salts (Scheme 3).

As can be seen from Table II, PI-Br was employed efficiently in promoted cationic polymerization of CHO. At the irradiation wavelength (λ = 350 nm) most of the emitted light is absorbed by benzoin chromophores (ε_{350nm} = 225 L mol^{-1} cm^{-1}) as the spectral sensitivity of iodonium salt is relatively poor in this region.

As stated previously our main interest is to synthesize block copolymers of LC6 and CHO by utilizing photoactive liquid crystalline polymers. UV irradiation of the photoactive LC prepolymers caused α-scission and yielded benzoyl and polymer bound alkoxybenzyl radicals. If the photopolymerization is

TABLE III
Promoted Cationic Polymerization[a] of CHO Using Photoactive PLC6

Product code[b]	[MI] (g L^{-1})	Conv. %	Composition of reaction mixture[c]		Composition[d] and molecular weight[e] of block copolymers			
			PCHO %	PLC6-b-CHO %	PCHO %	PLC6 %	M_n	M_w/M_n
CP1	40 (MI-1)	13	54	46	80	20	25,000	1.7
CP2	40 (MI-3)	14	47	53	87	13	41,000	2.0
CP3	100 (MI-3)	26	45	55	70	30	39,500	2.0

[a] λ > 350 nm; [Ph$_2$I$^+$] = 5 × 10^{-3} mol L^{-1}; time = 3 h.
[b] Represents extracted block copolymer.
[c] Calculated after exctraction with n-hexane.
[d] Calculated from ^{1}H NMR spectrum for extracted block copolymers.
[e] Determined from GPC, based on PSt standards for extracted block copolymers.

TABLE IV
Promoted Cationic Polymerization[a] of CHO Using Photoactive PLC6

Product code[b]	Time (h)	Conv. (%)	Composition of reaction mixture[c]		Composition[d] and molecular weight[e] of block copolymers			
			PCHO (%)	PLC6-b-CHO (%)	PCHO (%)	PLC6 (%)	M_n	M_w/M_n
CP4	1	10	33	67	91	9	25100	1.8
CP5	2	12	35	65	89	11	34600	1.9
CP6	3	14	45	55	70	30	39800	2.0
CP7	4	21	67	53	60	40	44200	2.1

[a] $\lambda > 350$ nm; $[Ph_2I^+] = 5 \times 10^{-3}$ mol L^{-1}; [MI-3] = 100 g L^{-1}.
[b] Represents extracted block copolymer
[c] Calculated after extraction with n-hexane.
[d] Calculated from ^{1}H NMR spectrum for extracted block copolymers.
[e] Determined from GPC, based on PSt standards.

carried out in the presence of CHO and Ph_2I^+, these radicals are oxidized to corresponding carbo-cations and initiate the polymerization of CHO. The efficiency of these processes depends on the redox potential of the system.

In our case, it would appear necessary for the polymer bound cation to initiate polymerization for successful block copolymerization but h-PCHO was also obtained due to the oxidation of benzoyl radicals to corresponding carbocations by Ph_2I^+ which has relatively high reduction potential (-0.2 V).[51] (Scheme 4).

Typical results concerning block copolymerization are presented in Tables III and IV. As can be seen

from Table III both the molecular weight and the concentration of the photoactive PLC6 (MI) affect the conversion, block yield, and composition of the block copolymer. When the concentration of the photoactive polymer was increased from 40 to 100 g L^{-1}, PLC6 segment increased significantly in the block copolymer structure. Table IV shows that conversion of CHO and LC6 ratio in the macromolecular chain increases with the increasing time. Homopoly(CHO) was removed from the reaction mixture by extraction with n-hexane, a selective solvent for PCHO.[38] Figure 3 shows the GPC chromatograms of representative photoactive liquid crystalline polymer and extracted block copolymer. The new peak at a higher molecular weight was ascribed to the block copolymer. The block copolymer structure was also characterized by means of IR and NMR spectral measurements.

The ^{1}H-NMR spectrum of the representative block copolymer, poly(LC6)-b- poly(CHO), is given in Figure 4. The composition of the copolymers was estimated from ^{1}H-NMR data with the ratio of the peak intensities at 3.8 ppm for ($-OCH_2$) protons of

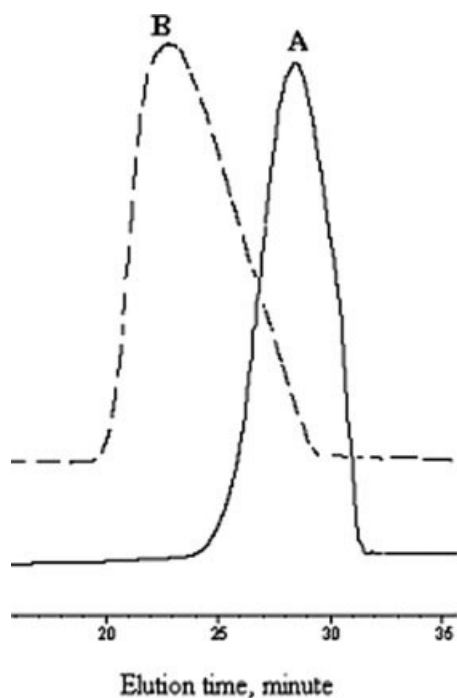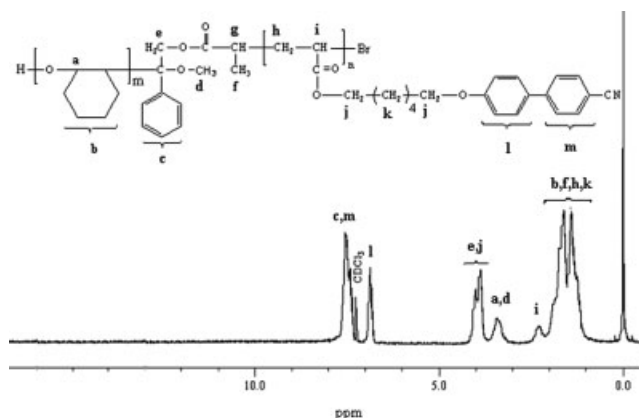**Figure 3** GPC chromatograms of MI-1 (A) and CP1 (B).

Figure 4 ^{1}H-NMR spectrum of poly(LC6)-b-poly(CHO) after extraction with n-hexane in CDCl$_3$.

TABLE V
Thermal and Liquid Crystalline Properties[a] of Related Polymers

Sample	$T_g{}^{b}$ (°C)	$T_g{}^{c}$ (°C)	T_{N-I} (°C)
h-PCHO	–	65–67	–
MI-1	45	–	116
MI-3	46	–	122
CP1	45	62	nd[d]
CP6	45	62	122
CP7	46	64	124

[a] Detected by DSC (5°C min^{-1}), second heating.
[b] Referred to PLC6 segment of polymer.
[c] Referred to PCHO segment of polymer.[52]
[d] Not detected; detected only by POM.

PLC6 and 3.4 ppm for (OCH) protons of PCHO. The IR spectra of the purified block copolymer also show the characteristic ether bond of the PCHO segment at 1090 cm^{-1} in addition to the usual PLC bands.

The thermal behavior of the block copolymers and prepolymers was studied by DSC (Table V). Homopolymers MI-1, MI-3 (Fig. 5) show one liquid crystalline mesophase. The glass transition temperatures of poly(LC6) segments of block copolymers (CP1, CP6, CP7) were detected at about 45–46°C, for the PCHO segments in all block copolymers the glass transition temperatures were obtained in a range between 62°C and 64°C depending on the degree of polymerization of PCHO (Fig. 6).[52] For the CP1 block copolymer nematic-isotropic transition temperatures were only observed by POM measurements. The phase transitions occur in the expected temperature ranges. Because of several polarizing microscopy experiments, it can be clearly stated that transitions from liquid crystalline to the isotropic phase could be detected.

In conclusion, block copolymerization via ATRP and PCP routes provides a versatile two-step method applicable to vinyl and nucleophilic monomers. It is obvious that this method can be applied
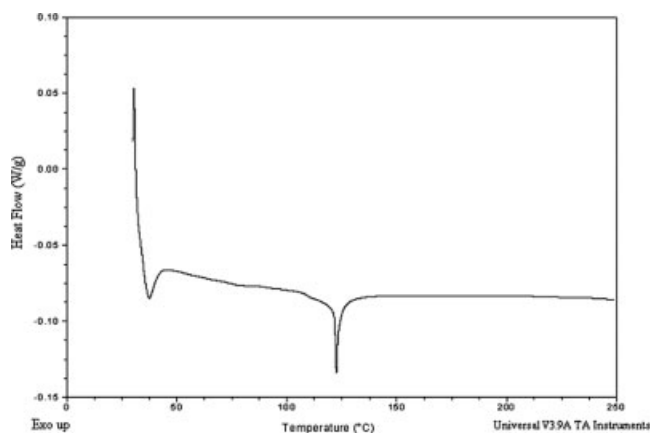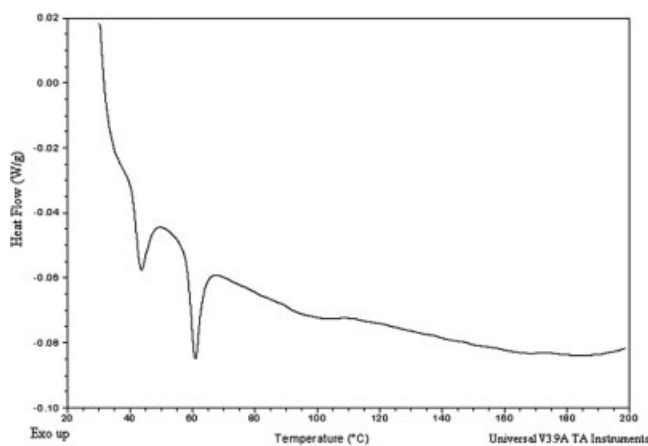

Figure 6 DSC curve of CP6.

to the synthesis of liquid crystalline-amorphous block copolymers.

References

1. Huang, C. F.; Kuo, S. W.; Chen, C. F. C. J Polym Res 2005, 12, 449.
2. Frechet, J. M. J. Science 1994, 263, 1710.
3. Webster, O. W. Science 1994, 251, 887.
4. Thomas, E. L.; Anderson, D. M.; Henkee, C. S.; Hoffman, D. Nature 1998, 334, 598.
5. Bates, F. S. Science 1991, 251, 898.
6. Allen, G.; Bevirington, J. C. Reactions in Comprehensive Polymer Science, Vol. 6; Pergamon: Oxford, 1998; Chapter 10.
7. Matyjaszewski, K.; Xia, J. Chem Rev 2001, 101, 2921.
8. Kamigaito, M.; Ando, T.; Sawamato, M. ChemRev 2001, 101, 3689.
9. Paik, H. J.; Teodorescu, M.; Xia, J.; Matyjaszewski, K. Macromolecules 1999, 32, 7023.
10. Çakir, T.; Serhatli, İ. E.; Önen, A. J Appl Polym Sci 2006, 99, 1993.
11. Barbosa, C. A.; Coelho, M. R. G.; Gomes, A. S.; Macromol Symp 2001, 168, 91.
12. Bignozzi, M. C.; Ober, C. K.; Laus, M.; Macromol Rapid Commun 1999, 20, 622.
13. He, X. H.; Zhang, H. L.; Wang, X. Y. Polym J 2002, 34, 523.
14. He, X. H.; Zhang, H. L.; Wang, X. Y. Polym Bull 2002, 48, 337.
15. Yian, Y.; Watanabe, K.; Kong, X.; Abe, J.; Iyoda, T. Macromolecules 2002, 35, 3739.
16. He, X.; Zhang, H.; Yan, D.; Wang, X. J Polym Sci Part A: Polym Chem 2003, 41, 2854.
17. He, X.; Yan, D. Macromol Rapid Commun 2004, 24, 949.
18. Galli, G.; Chiellini, E. In Structure and Transport Properties in Organized Polymeric Materials; Chiellini, E., Giordano, M., Leporini, D., Eds.; World Scientific: Singapore, 1997; p 35.
19. Adams, J.; Gronski, W. Makromol Chem Rapid Commun 1989, 10, 553.
20. Säenger, J.; Gronski, W. Macromol Chem Phys 1998, 199, 555.
21. Fischer, H.; Poser, S. Acta Polym 1996, 47, 413.
22. Adams, J.; Säenger, J.; Tefehne, C.; Gronski, W. Macromol Rapid Commun 1994, 15, 879.
23. Fischer, H.; Poser, S.; Arnold, M. Liq Cryst 1995, 18, 503.
24. Chien, J. T.; Thomas, E. L.; Ober, C. K.; Hwang, S. S. Macromolecules 1995, 28, 1688.

Figure 5 DSC curve of MI-3.

25. Serhatli, I. E.; Hepuzer, Y.; Yagci, Y.; Chiellini, E.; Rosati, A.; Galli, G. In Tailored Polymers and Applications; Yagci, Y., Mishra, M. K., Nuyken, O., Ito, K., Wnek, G., Eds.; VSP BV: Utrecht, 2000; pp 175–196.

26. Tian, Y.; Kong, X.; Nagase, Y.; Iyoda, T. J Polym Sci Part A: Polym Chem 2003, 41, 2197.

27. Chen, J. T.; Thomas, E. L.; Ober, J. K.; Mao, G. Science 1996, 273, 343.

28. Yamada, M.; Itoh, T.; Nakagawa, R.; Hiroa, A.; Nakahama, S.; Watanabe, J. Macromolecules 1999, 32, 282.

29. Mao, G. P.; Wang, J. G.; Ober, C. K. Chem Mater 1998, 10, 1538.

30. Plambeck, L. F. US Patent 2,760,863 (1956).

31. Belfield, K. D.; Crivello, J. V. Photoinitiated Polymerization; Oxford University Press: New York, 2003. ACS Symposium Series 847.

32. Neckers, D. C.; Jager, W. Chemistry and Technology of UV&EB Formulation for Coatings, Vol. VII; Inks&Paints, SITA Technology: London, 1998.

33. Crivello, J. V. Lam, J. H. W. J Polym Sci Polym Chem Ed 1980, 18, 2677.

34. Crivello, J. V.; Lam, J. H. W. J Polym Sci Polym Chem Ed 1980, 18, 2967.

35. Crivello, J. V. J Polym Sci Polym Chem Ed 1999, 87, 4241.

36. Meier, K.; Zweifel, H. J J Radiat Curing 1986, 13, 26.

37. Ledwith, A. Polymer 1978, 19, 1217.

38. Yagci, Y.; Onen, A.; Schnabel, W. Macromolecules 1991, 24, 4620.

39. Hua, Y.; Crivello, J. C. Polym Preprints 2001, 42, 781.

40. Yagci, Y.; Lukac, I.; Schnabel, W. Polymer 1993, 34, 1130.

41. Yagci, Y.; Schnabel, W.; Makromol Chem Makromol Symp 1992, 60, 133.

42. Galli, G.; Chiellini, E.; Yagci, Y.; Serhatli, E. I. Macromol Symp 1996, 107, 85.

43. Sato, T.; Maeda, R.; Seno, M.; Hirano, T. Eur Polym J 2002, 38, 1491.

44. Corrales, T.; Catalina, F.; Peinado, C.; Allen, N. S. J Photochem Photobiol A Chem 2003, 159, 103.

45. Ajayaghosh, A. Polymer 1995, 36, 2049.

46. Jiang, X.; Xu, H.; Yin, J. Polymer 2005, 46, 11079.

47. Yagci, Y.; Onen, A. J. Macromol Sci Chem A 1991, 28, 129.

48. Kacar, T.; Serhatli, I. E.; Onen, A. J Polym Sci Part A: Polym Chem 2003, 41, 1892.

49. Bamford, C. H.; Jenkins, A. D.; Wayne, R. P. Trans Faraday Soc 1960, 56, 932.

50. Ahn, K. D.; Ihn, K. J.; Kwon, I. C. J Macromol Sci Chem 1986, 23, 359.

51. Crivello, C. V.; Dietliker, K. Photoinitiators for Free Radical, Cationic and Anionic Photopolymerization, 2nd ed.; SITA Technology: London, 1998; Vol. III, p 400.

52. Thiam, M.; Spassky, N. Macromol Chem Phys 1999, 200, 2107.