Polymer Bulletin 48, 337-344 (2002)

Polymer Bulletin

Synthesis of side group liquid crystal-coil triblock copolymers with cyanobiphenyl moieties and PEG as coil segments by atom-transfer radical polymerization and their thermotropic phase behavior

Xiaohua He (✉) , Hailiang Zhang, Xiayu Wang (✉)

Department of Polymer Science and Engineering
College of Chemistry, Xiangtan University, Xiangtan 411105, People's Republic of China
Email: hxhcncn@yahoo.com, Tel.: +86-732-8293264, Fax: +86-732-8293264

Received: 12 March 2002/Revised version: 25 April 2002/ Accepted: 30 April 2002

Summary

A series of side group liquid crystal-coil(SGLC-coil) triblock copolymers with narrow polydispersity was synthesized by atom transfer radical polymerization (ATRP), which was designed to have LC conformation of poly(11-(4′-cyanophenyl-4″-phenoxy)undecyl methacrylate) and coil-conformation of polyethylene glycol (PEG) (Mn=6000) segment. The SGLC block was prepared with a rang of molecular weights from 3.5×10^3 to 1.4×10^4. The macro-initiator PEG6000-Br was synthesized with PEG and 2-Bromo-2-methylpropionyl bromide by reaction of acid bromide. Their characterization was investigated using proton nuclear magnetic resonance (^{1}H NMR), Fourier Transform Infrared (FT-IR) spectra, gel permeation chromatograph (GPC), differential scanning calorimetry (DSC) and polarized optical microscope (POM). All the block polymers exhibited a smectic A mesophase. The phase transition temperatures of the smectic to isotropic (T_S-T_I) phase increased and the crystallizability of PEG depressed with increasing of the molecular weight of the LC block.

Introduction

Block copolymers are unique class of materials. Block copolymers can be regarded as composite materials with domain sizes on sub-micrometer scales and offer an opportunity to engineer new, tailored materials using self-organizing liquid crystal components. In recent years, block copolymers containing liquid crystal (LC) segment have been extensively studied. By definition, LC block copolymers on LC segment and may have structures including rod-coil [1-5], side group LC-coil [6-10] and other block combinations [11]. Some research groups have reported the synthesis and characterization of side group LC-coil block copolymers. They have synthesized block copolymers by anionic [7] and cationic [8], and ring-opening metathesis [9] living polymerization, and they reported that these block copolymers displayed liquid crystalline behavior similar to homopolymers and formed a microphase separate structure. Besides living polymerization methods, polymer-analogous reaction [10] have also been employed, where one block carries functional groups to attach a reactive mesogen. This method is easier than direct living polymerization but the conversion may be not perfect.

It has been reported that side chain liquid crystal polymers with cyanobiphenyl moieties were synthesized by atom transfer radical polymerization (ATRP) [12]. Kasko and coworkers [12a] first successfully synthesized 3-arm star side chain liquid crystal polymers by ATRP. Chang and coworkers [12b] synthesized comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s by ATRP. In this paper, we synthesized the side group LC-coil block copolymer by ATRP, which has the cyanobiphenyl group as the mesogenic moiety and the poly ethylene glycol (PEG) as the coil segment. The cyanobiphenyl is a typical mesogen, and low molecular weight LC compounds containing the cyano groups are often used for display devices. PEG possesses many excellent properties, such as hydrophilic, nonionic crystalline, and which can complex monovalent metallic cations to produce new conductive materials [13]. The triblock copolymers were designated here “Block-60-m” (m=10—40; the theoretical degree of polymerization of triblock copolymers). The structure and thermotropic phase behavior of the triblock copolymers have been characterized. The morphologies and other aspects of these copolymers will be studied in the near future.

Experimental

Materials

4-(Dimethylamino)-pyridine (DMAP)(Acros,99%), CuBr (Adrich, 99.999%), 1,6-Dibromohexane (Acros,98%), 2.2′-dipyridine(dipy)(Acros,99%), 2-Bromo-2-methylpropionyl bromide(Acros,98%), Methacryloyl chloride (Aldrich, 96%), 11-bromo-1-undecane (Aldrich, 98%), 4′-hydroxy-4-biphenylcarbonitrile (Aldrich, 97%) were used without further purification. Chlorobenzene (C_6H_6Cl)(Acros, 99%) was purified by washing with concentrated sulfuric acid to remove residual thiophenes, followed by washing twice with water, once with 5% sodium carbonate solution, and again with water before being dried with anhydrous calcium chloride and distilled. Triethylamine(TEA) (Shanghai Chemical Reagents Co., A.R.grade) was refluxed with KOH and distilled. Methylene dichloride (CH_2Cl_2)(Shanghai Chemical Reagents Co., A.R.grade) was shaken with portions of concentrated sulfuric acid until the acid layer remained colorless, then washed with water, aqueous 5% Na_2HCO_3 and with water again, and finally distilled from CaH_2. Tetrahydrofuran (THF) (Shanghai Chemical Reagents Co., A.R.grade) was dried by distillation from CaH_2 under N_2. Polyethylene glycol (PEG) (Mn=6000) was purchased from Adrich. All other reagents were used as received.

Synthesis of Monomer

The monomer was prepared according to the similar method described by Kasko and Pugh [12a]:

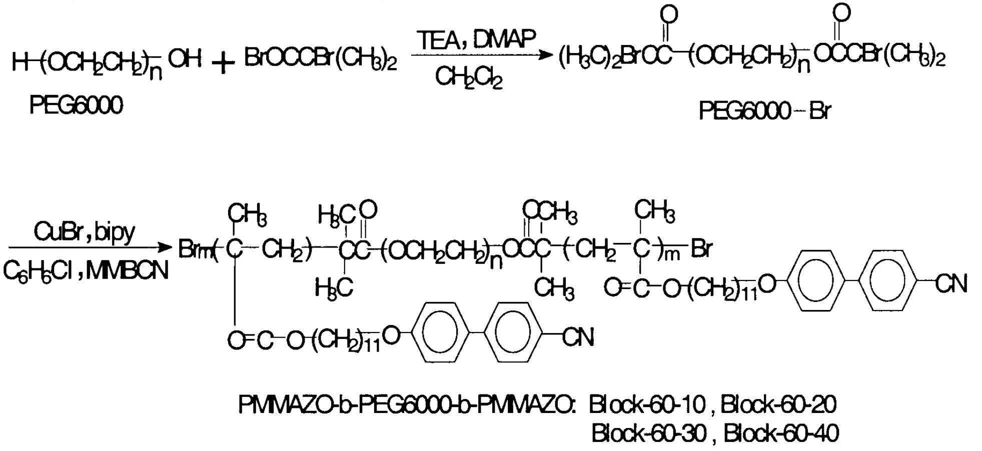
11-(4′-Cyanophenyl-4″-phenoxyl) undecanol was prepared in 86% yield. ^1H NMR: δ1.31(m, $(CH_2)_6$), 1.50(m, $CH_2CH_2CH_2OAr$), 1.59(m, CH_2CH_2OH), 1.81(m,CH_2CH_2OAr), 3.64(t,CH_2OH), 4.00(t,OCH_2), 7.00(d, 2 aromatic H ortho to OCH_2), 7.52(d, 2 aromatic H meta to OCH_2), 7.66(m, 4 aromatic H ortho and meta to

CN).

11-[(4′-Cyanophenyl-4″-phenoxyl) undecyl] Methacrylate(MMBCN) was prepared in 60% yield. ^{1}H NMR: δ1.31(m, $(CH_2)_7$), 1.68(m, $CH_2CH_2CH_2OAr$), 1.67(m, CH_2CH_2OAr), 1.81(m, $CH_2CH_2O_2C$), 1.95(s, CH_3), 4.00(t,CH_2OAr), 4.15(t, CH_2O_2C), 5.54(dd,1 olefinic H trans to CO_2), 6.10(dd, 1 olefinic gem to CO_2), 7.01(d, 2 aromatic H ortho to OCH_2), 7.52(d, 2 aromatic H meta to OCH_2), 7.68(m, 4 aromatic H ortho and meta to CN).

Preparation of PEG6000-Br macro-initiators

The synthesis of triblock copolymers was shown in Scheme 1.



Scheme 1

The macro-initiator was prepared according to the similar method described by Jankova and coworkers [14]: a certain amount of DMPA (0.92g, 7.5mmol) in 10mL of dry methylene chloride was mixed with TEA (0.7mL, 5mmol). The solution was transferred into a 250mL three-neck round-bottom flask equipped with condenser, dropping funnel, gas inlet/outlet, and a magnetic stirrer. After cooling to 0°C , 2-Bromo-2-methylpropionyl bromide (2.88g, 12.5mmol) in 10mL CH_2Cl_2 was added. PEG6000 (15.0g, 2.5mmol) in dry CH_2Cl_2 was added dropwise to the formed yellow dispersion in one hour under nitrogen, then the temperature was allowed to rise to room temperature. The reaction was continued under stirring for 24hrs. The solution was removed in rotary evaporator. The crude PEG6000-Br macro-initiator was dissolved in 50mL benzene, filtered and precipitated in cold ethyl ether. The crude PEG6000-Br macro-initiator was recrystallized in absolute ethanol two times and dried in vacuum.

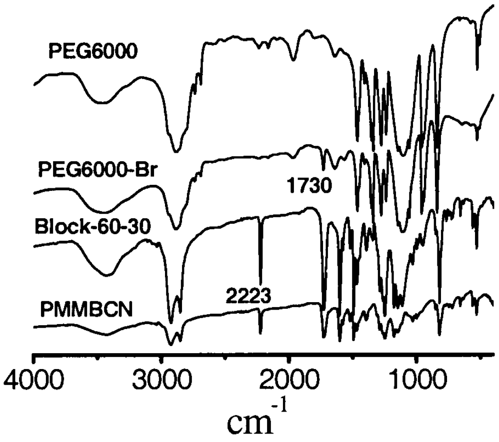
Synthesis of PMMBCN-b- PEG-b-PMMBCN

PMMBCN-b-PEG-b-PMMBCN triblock copolymers were synthesized by solution polymerization in chlorobenzene. Thus, in a typical solution polymerization, a polymerization tube was charged with PEG6000-Br macro-initiator (0.030g 0.005mmol), MMBCN (0.443g 0.10 mmol), CuBr (1.430mg 0.01 mmol), bipy (4.686 mg 0.03 mmol) and chlorobenzene (4.500g), and then after degassing with three freeze-thaw cycles, the tube was sealed off under vacuum. The reaction was carried out at 75°C for 10h, and was then cooled to room temperature. The sample was further diluted with tetrahydrofuran (THF), removed copper salts through a plugged column of neutral aluminum oxide and precipitated in a large volume of cold methanol. The sample purified by reprecipitating three times from THF to methanol and dried in a vacuum oven overnight at room temperature. The conversion of polymerization was determined gravimetrically.

Chartaterization.

Molecular weights M_n and polydispersity M_w/M_n were measured on a gel permeation chromatograph (Waters 150C) equipped with three Waters Styragel columns (10^3, 10^4 and 10^5 Å) using THF as an eluent at 35°C. The column system was calibrated by a set of mono-dispersed standard polystyrenes. ^1H NMR spectra were obtained on a 300 Varian NMR instrument using $CDCl_3$ as solvent, tetramethyl silane as the internal standard. Thermograms were obtained using a Perkin-Elmer DSC-7 instrument. Pure indium was used as a reference material to calibrate both the temperature scale and the melting enthalpy before the sample was tested. Samples with a typical mass of 5.0±0.1mg were encapsulated in sealed aluminum pans and were heated at 10°C /min heating rate from -20°C to 160°C under nitrogen for the first scan, immediately cooled at 10°C /min cooling rate to –20°C and then heated at 10 °C /min heating rate from –20°C to 160°C for the second scan. Polarized optical microscope (POM) observation was performed on a Leica DMLP microscope with a Leitz 350 hot stage. Fourier Transform Infrared (FT-IR) spectra were recorded on a Perkin-Elemer Spectrum one spectrometer.

Figure 1. FT-IR spectra of PEG6000 and Triblock polymers



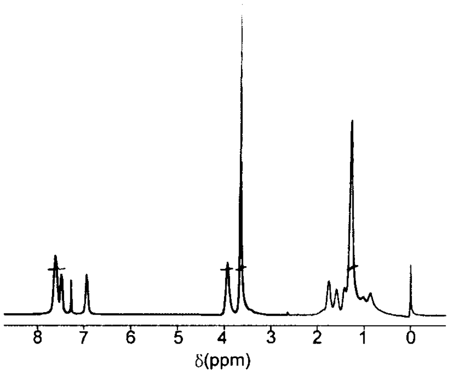


Figure 2. ^{1}H NMR spectrum

Results and Discussion

Preparation of macro-initiator PEG6000-Br and triblock copolymers

The PEG6000-Br macro-initiator was synthesized by reacting PEG with acid bromide (Scheme 1) and carried out at 0°C in the presence of TEA and DMPA. Figure 1 shows the FT-IR spectrum of the macro-initiator and part of triblock copolymers. The characteristic absorb peak of ester group at 1730cm^{-1} is observed on the FT-IR spectra for the PEG6000-Br macro-initiator because of the esterification.

The substitution of the hydroxyl groups was proved by ^{1}H NMR spectroscopy. A new signal appears at 1.91ppm on the ^{1}H NMR spectrum is observed for the PEG6000-Br macro-initiators after the esterification.

Table 1. Characterization data of Polymers

Polymer	Yield (%)	Mn ($\times 10^{-3}$)	M_W/Mn	DP[a]
PEG6000	--	12.9	1.02	--
PEG6000-Br	--	13.2	1.02	--
Block-60-10	65	37.3	1.13	10
Block-60-20	60	38.6	1.14	20
Block-60-30	63	41.1	1.15	30
Block-60-40	59	43.0	1.14	40
PMMBCN[b]	--	65.3	1.34	--

a: the theory degree of polymerization. b: synthesized by free polymerization

In order to make the hydroxyl groups be completely substituted, the ratio of the additional amount of 2-Bromo-2-methylpropionyl-bromide to that of PEG6000 was 2.5 times. By GPC analysis, it was found that synthesis of the PEG6000-Br macro-initiator involved no molecular weight reduction since narrow symmetrical signals were observed at essentially the same position as the starting PEG. The data are given in Table 1. The telechelic PEG6000-Br macro-initiator was used to initiate monomer MMBCN in the Chlorobenzene solution for formation of Block-60-n by ATRP. Figure 2 depicts the ^{1}H NMR spectrum of Block-60-30. A characteristic resonance originating from phenyl moieties at both 7.6, 7.5 and 6.9ppm can be observed from Figure 2. The characteristic absorb peak of phenyl group at 1602cm^{-1} and cyano group at 2223cm^{-1} in block copolymers can be also found (Fig. 1). Figure 3 shows the GPC traces of series of block copolymers. GPC analysis of the purified samples showed no signal of residual. PEG6000-Br macro-initiator and monomer MMBCN in the elution traces.The triblock copolymers possessed a symmetrical unimodal peak. The polydispersity of triblock copolymers was around 1.14(Tab. 1). The triblock polymers of narrow polydispersity were successfully synthesized by ATRP.

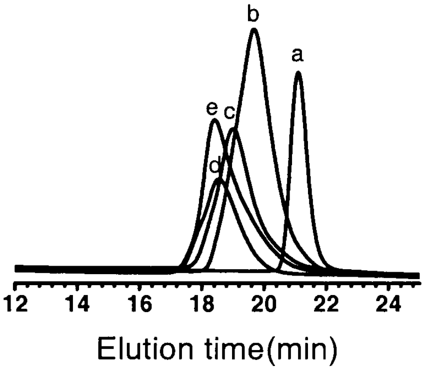


Figure 3. GPC traces: a. PEG6000, b. Block-60-10, c. Block-60-20 , d. Block-60-30, e. Block-60-40.

Thermotropic Phase Behavior

The phase behaviors of triblock copolymers were characterized by differential scanning calorimetry (DSC), thermal polarized microscopy (POM). The phase transition temperatures and the corresponding enthalpy changes of all samples obtained from the second heating and the first cooling scans are summarized in Table 2. Figure 4 presents the DSC second heating and first cooling traces of triblock copolymers. Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s is a thermotropic liquid crystalline polymer [12a], which can exhibit a smectic A (S_A) phase. The S_A focal conic fan texture can be observed. PMMBCN is also a S_A liquid crystalline polymer[15], which a focal conic fan texture can be seen from isotropic to liquid crystalline state. As can be observed from Figure 4, the triblock copolymers exhibit a crystalline phase and a smectic phase on the second heating. By combination of POM, the smectic phase is S_A. From the data of Table 2, it can be found that the transition temperatures of the S_A phase to the isotropic (T_S-T_I) change from 110.3°C to 117.5°C with increasing molecular weight of PMMBCN block. That is to say, the phase transition temperatures of T_S-T_I are affected by the molecular weight of PMMBCN block, which improve with increasing molecular weight of PMMBCN block. It may be possible that the increase degree of polymerization of PMMBCN is beneficial to stabilizing the liquid crystal phase. The result was established in side chain liquid crystal

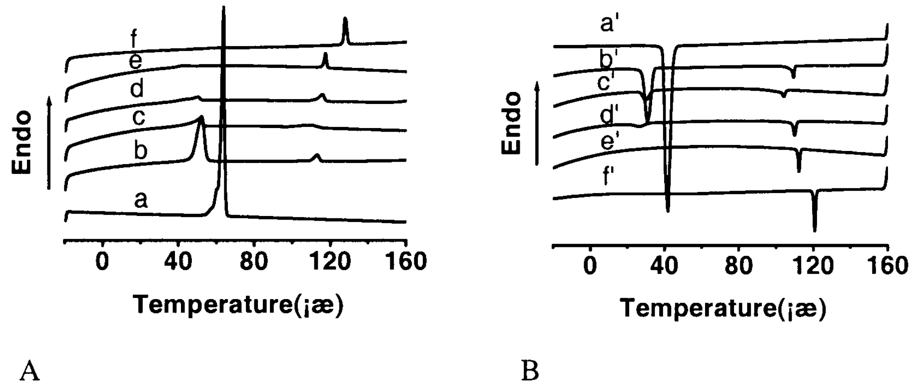


Figure 4. Second heating(**A**)and first cooling(**B**) DSC spectra of triblock copolymers: a, a'PEG6000; b, b' Block-60-10; c, c'. Block-60-20; d, d'Block-60-30; e, e'Block-60-40; f, f'PMMBCN

homopolymer [6a, 16]. On the other hand, the crystalline phase transition temperatures decrease from 63.2°C to 41.9°C , the corresponding enthylpy changes decrease from 174.7J/g to 2.0J/g for triblock copolymers with increasing molecular weight of PMMBCN block on second heating. It may be possible that increasing chain length of PMMBCN block inhibits the activity of the chain of PEG block

Table 2. Thermal transitions data of Polymers

Polymer	Phase transitions(°C) and corresponding enthalpy changes(J/g)^a	
	Second heating	first cooling
PEG6000	K 63.2(174.7) I	I 42.0(-168.5) K
Block-60-10	K 51.8(45.5) S_A 113.0(4.12) I	I 109.4(-4.2) S_A 30.9(-42.3) K
Block-60-20	K 51.0(10.0) S_A 110.3(5.4) I	I 104.2(-3.6) S_A 29.8(-7.6) K
Block-60-30	K 49.8(8.5) S_A 115.6(6.3) I	I 110.1(-6.0) S_A 26.6(-5.0) K
Block-60-40	K 41.9(2.0) S_A 117.5(5.4) I	I 113.4(-6.7) S_A 24.1(-4.7) K
PMMBCN	S_A 127.5(11.2) I	I 121.0(-10.8) S_A

a: S_A=smectic phase, K=crystalline phase, I=isotropic

and the crystallizability of block copolymers becomes poor. Polarized optical microscopic observations of all samples are consistent with the results of DSC. Transition from an isotropic liquid can be seen by the rapid formation of a focal conic fan texture with indicating a S_A phase.

Conclusion

A series of novel side group liquid crystal-coil (SGLC-coil) triblock copolymers with narrow molecular weight distributions was synthesized successfully by ATRP. Their characterization was investigated using gel permeation chromatograph (GPC), proton nuclear magnetic resonance (^{1}H NMR), Fourier transform infrared (FT-IR) spectra, differential scanning calorimetry (DSC) and polarized optical microscope (POM). It was observed that all the block polymers showed the S_A phase. The phase transition temperatures of T_S-T_I improved and the crystallizability of PEG of block copolymers became poor with increasing of the molecular weight of the LC block.

Acknowledgements. The Doctor Foundation of Xiangtan University (No: 00X2X003) was gratefully *acknowledged.*

Reference

1. Stupp SI, LeBonheur V, Walker K, Li LS, Huggins KE, Keser M, Amstutz A (1997) Science 276: 384
2. (a) Lee M, Cho BK, Zin WC (1996) Chem Commun 1787-1788 (b) Lee M, Cho BK, Kim H, Yoon JY, Zin WC (1998) J Am Chem Soc 120:9168-9179 (c) Lee M, Lee DW, Cho BK, Yoon JY, Zin WC (1998) J Am Chem Soc 120:13258-13259 (d) Lee M, Oh NK (1996) J Mater Chem 6(7):1079-1086
3. (a) Radzilowski LH, Stupp SI (1994) Macromolecules 27:7749-7753 (b) Radzilowski LH, Carragher BO, Stupp SI (1997) Macromolecules 30:2110-2119
4. Chen JT, Thomas EL, Ober CK, Hwang SS (1995) Macromolecules 28:1688-1697
5. Wan XH, Tu YF, Zhang D, Zhou QF (2000) Polym Int 49(3): 243-247
6. (a) Yamada M, Iguch T, Hirao A, Nakahama S, Watanabe J (1995) Macromolecules 28:50-58 (b) Yamada M, Itoh T, Nakagawa R, Hirao A, Nakahama SI, Watanable JI (1999) Macromolecules 32:282-289 (c) Yamada M, Iguchi T, Hirao A, Nakahama SI, Watanable JI (1998) Polym J 30(1):23-30
7. Percec V, Lee M (1992) Pure Appl Chem A29(9):723-740
8. Komiya Z, Schrock RR (1993) Macromolecules 26:1387-1392
9. (a) Mao GP, Wang JG, Clingman SR, Ober CK, Chen JT, Thomas EL (1997) Macromolecules 30:2556-2567 (b) Zaschke B, Frank W, Fisher H, Schmutzler K, Arnold M (1991) Polym Bull 27:1-8 (c) Fischer H, Poser S, Arnold M (1995) Macromolecules 28:6957-6962 (d) Fischer H, Poser S, Arnold M, Frank W (1994) Macromolecules 27:7133-7138 (e) Sänger J, Gronski W (1998) Macromol Chem Phys 199:555-561
10. (a) Moment A, Miranda R, Hanmond PT (1998) Macromol Rapid Commum 19(11):573-579 (b) Zheng WY, Hammond PT (1996) Macromol Rapid Commun 17:813-824
11. Wang JG, Mao GP, Ober CK, Kramer EJ (1997) Macromolecules 30:1906-1914

    (a) Kasko AM, Heintz AM, Pugh C (1998) Macromolecules 31:256-271 (b) Chang C, Pugh C (2001) Macromolecules 34:2027-2039
12. Kodera Y, Matsusthima A, Hiroto M, Nishimura H, Ishii A, Ueno T, Inada Y (1998) Prog Polym Sci 23:1233-1271
13. Jankobva K, Chen X, Kops J, Batsberg W (1998) Macromolecules 31:538-541
14. Craig AA, Imrie CT (1995) Macromolecules 28:3617-3624
15. Sagane T, Lenz RW (1989) Polymer 3 0:2269-2278