

Synthesis and Nanostructures of Amphiphilic Liquid Crystalline Block Copolymers with Azobenzene Moieties

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ABSTRACT: A series of novel amphiphilic liquid crystalline diblock copolymers consisting of poly(ethylene oxide) as hydrophilic segment (PEO) and poly(methacrylate) containing azobenzene moiety as hydrophobic liquid crystalline segments (AZO) were synthesized by the atom transfer radical polymerization (ATRP). The block copolymers were prepared with a range of number-averaged molecular weights from 12400 to 54200 with narrow polydispersities (ca. 1.14). Thermal investigation showed that the block copolymers exhibit smectic A (S_A), smectic C (S_C) and undefined smectic X (S_X) phases. Morphologies of the thin films of the block copolymers were investigated by transmission electron microscopy (TEM). Microphase separation, i.e., a PEO cylinder array with 20nm of periodicity in the AZO matrix, was observed. Smectic phase of the AZO domain may support the regular nanostructures.

Keyword: Amphiphilic block copolymer, Microphase separation, Atom transfer radical polymerization, Liquid crystalline, Cylinder array nanostructures.

Introduction

Block copolymers are self-assembled into periodic nanostructures such as lamellar, cylindrical, and spherical morphologies. The size and the shape of the microphase-separated domains can be controlled by molecular weight and composition of the block copolymer with a narrow polydispersity, which has drawn scientific and technological interests.^{1,2} Especially, of quite interest is to regard the individual micarodomains of the nanostructures based on the microphase separation as a specific reaction field or space.

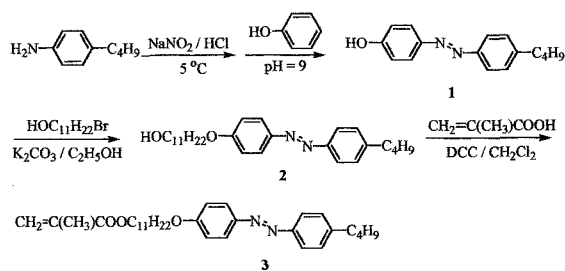
If any functional moieties are assembled into the block copolymers, the functionality might act as a probe to elucidate correlation of the restricted space of nanostructures and the functional properties, compared with the case of the uniform bulk materials. To further understand the nanostructure-functionality correlation in the functional block copolymers, we designed a series of multifunctional block copolymers consisting of poly(ethylene oxide) (PEO) with $M_n = 2000$ as the hydrophilic block, and poly(methacrylate) bearing photoisomerizable azobenzene mesogen (AZO) as hydrophobic block.³ Here, we adopted atom transfer radical polymerization (ATRP) method to design a series of block copolymers and observed nanostructures by TEM.

One of the most versatile controlled living radical polymerization method developed so far is the Cu-

catalyzed ATRP. The advantages of ATRP method are (1) easy preparative procedures, and (2) wide applicability of monomers with most of functional groups, leading to the promising polymer architectures polydispersity.^{4,5,6} In this paper, we report the synthesis of a series of amphiphilic liquid crystalline block copolymers by using ATRP method and the formation of periodic nanostructures based on microphase separation.

Experimental Section

Characterization. ¹H NMR spectra were measured by using a JEOL 270 instrument spectrometer operating at 270 MHz with TMS internal standard as a reference for chemical shifts. Molecular weights of polymers were determined by using a JASCO 860 gel permeation chromatography (Japan Spectroscopic Co., Ltd.) equipped with UV and RI detectors in reference of a series of standard polystyrenes with THF as eluent. Thermal behaviors were analyzed by using an SII Extra 6000 DSC system (Seiko Instruments Inc.) at a scanning rate of $\pm 10^\circ\text{C}/\text{min}$. Transmission electron microscopy (TEM, JEOL 1200 EXII) were carried out at an acceleration voltage of 200kV. TEM samples for the observation of nanostructures of the block copolymers were prepared by (1) spreading a 2 wt.% toluene solution onto a copper TEM grid, (2) annealing the film at 105°C for 24h, and (3) exposing to RuO₄ vapor at room temperature for 3 min so as to



Scheme 1

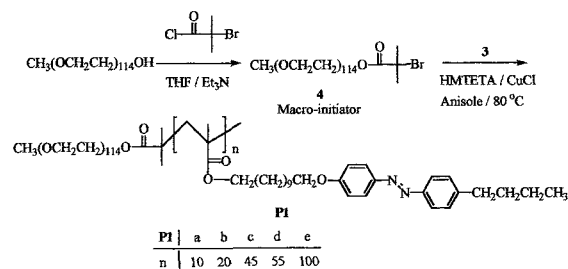
selectively stain the PEO block.

Materials. 2-Bromo-2-methylpropionyl chloride, 11-bromo-1-undecanol, 4-butylaniline, methacrylic acid, and dicyclohexylcarbodiimide (DCC), commercially available from Kanto Chem. Co. (Japan), were used without further purification. Poly(ethylene glycol) monomethyl ether with number-averaged molecular weight of about 5000 (Aldrich) was dried by azeotropic distillation with toluene. Anisole as the solvent for solution polymerization was purified by distillations from sodium with benzophenone. The ligand, 1,1,4,7,10,10-hexamethyldiethylenetriamine (HMTETA, Aldrich) was used as received without further purification. Catalyst Cu(I)Cl (Kanto Chem. Co., Japan) was washed successively with acetic acid and ether, then dried, and stored under nitrogen.

Preparation of Azobenzene Monomer. The synthesis of the monomer 11-[4-(4-butylphenylazo)phenoxy]-undecyl methacrylate **3** is indicated in Scheme 1 according to the conventional synthetic procedure.⁵

Preparation of PEO Macroinitiators of 4. The synthesis of the macroinitiator is shown in Scheme 2.

A solution of 5 g (1.0 mmol) of 2-bromo-2-methylpropionyl chloride in 30 ml of dry CH_2Cl_2 was added to a mixture of 830 μl (6.0 mmol) of triethylamine and 620 μl (5.0 mmol) of PEO monomethyl ether with an M_n of 5000 in 120 ml CH_2Cl_2 at room temperature, and then mixture was stirred for 18 h. After the mixture was filtered, washed 1M HCl aq, 0.5M NaHCO_3 aq. and braine. After dried by MgSO_4 the product was precipitated into ether. The solvent was stored, in a refrigerator to recrystallize the product. Yield; 1.4g (26%).



Scheme 2

$^1\text{H NMR}$ (CDCl_3), δ (ppm): 4.33 (dd, 2H, $-\text{OCH}_2\text{COO}-$), 3.73 (m, 158H, $-\text{CH}_2-$), 3.38 (s, 3H, $-\text{OCH}_3$), 1.94 (s, 6H, $((\text{CH}_3)_2\text{CBrCOO}-)$). The number averaged molecular weight M_n (GPC) determined by GPC with polystyrene standard and the polydispersity (M_w/M_n) are 8300 and 1.02, respectively. The number averaged molecular weight M_n (NMR) determined by $^1\text{H NMR}$ is 4700.

Preparation of Block Copolymers. The following is the typical preparative procedure of the amphiphilic block copolymers **PI d**. A 12mg (0.12 mmol) of Cu(I)Cl , 100mg (0.02 mmol) of **4**, and 492mg (1.00 mg) of the monomer **1** were mixed in a 10 ml ampule bottle, degassed, and filled with nitrogen. A 33 μl (28mg, 0.12 mmol) of HMTETA in 5 ml of anisole was added through a syringe. The mixture was degassed three times using the freeze-pump-thaw procedure and sealed under vacuum. After 30 min stirring at room temperature, the ampule was placed in the preheated 80°C oil bath for 24h. A solution was taken for $^1\text{H NMR}$ measurement. Conversion was 89%.³ The solution was passed through a neutral Al_2O_3 column with THF as eluent to remove the catalyst. The yellow filtrate was concentrated under reduced pressure and reprecipitated into acidic methanol and into hot ethanol. The yellow polymer was collected by filtration and dried under vacuum. Yield: 560mg (94%). M_n (GPC) = 28500, $M_w/M_n = 1.14$. ($^1\text{H NMR}$ (CDCl_3), δ (ppm): 7.84(d, 2H, $-\text{N}=\text{N}-\text{Ph}$), 7.74(d, 2H, $-\text{O}-\text{Ph}-\text{N}=\text{N}-$), 7.22(d, 2H, $-\text{N}-\text{Ph}-\text{C}-$), 6.89(d, 2H, $-\text{O}-\text{Ph}-\text{N}-$), 3.94(m, 4H, $-\text{COOCH}_2-$, $-\text{CH}_2-\text{O}-\text{Ph}$), 3.65(m, 8.2H, $-\text{OCH}_2\text{CH}_2-$), 2.65(t, 2H, $-\text{Ph}-\text{CH}_2-$.)

Table 1 Experimental Conditions^a and Molecular Weight Data of PEO-AZO synthesized by the ATRP Method

Sample	$[\text{M}]_0/[\text{I}]_0$ ^{b)}	Time ^{c)}	Conv. ^{d)} (%)	$DP(\text{AZO})$ ^{e)}	$M_n(\text{GPC})$ ^{f)}	$M_n(\text{calc.})$ ^{g)}	$M_n(\text{NMR})$ ^{h)}	M_w/M_n ⁱ⁾	LC content (wt%)	yield (%)
P1a	10	24	98	10	15000	9900	12400	1.09	59	63
P1b	20	24	96	20	17500	14400	14400	1.09	65	23
P1c	50	8	70	45	26500	22200	28000	1.14	82	53
P1d	50	24	89	55	28500	27100	31500	1.14	84	94
P1e	200	24	50	100	28000	38700	54200	1.11	90	42

a) [Initiator 4]: [HMTETA]:[Cu(I)Cl] = 1:2:2. Polymerization temperature is 80°C . b) Feed molar ratio of the monomer $[\text{M}]_0$ to initiator $[\text{I}]_0$. c) Polymerization time in hours. d) Conversion determined by $^1\text{H-NMR}$. e) Molecular weight of AZO block determined by $^1\text{H-NMR}$. f) Number average molecular weight, $M_n(\text{GPC})$ determined by GPC. g) $M_n(\text{calc.})$ desired from $M_n(\text{calc.}) = 4700 + [\text{M}]_0/[\text{I}]_0 \times \text{conv.} \times 492$. The figures of 4700 and 492 are the molecular weights of the initiator and the monomer respectively. h) $M_n(\text{NMR})$ determined by $^1\text{H-NMR}$ according to $4700 + 40 \times (I_{3.9}/I_{3.7}) \times 492$. i) Polydispersity determined by GPC.

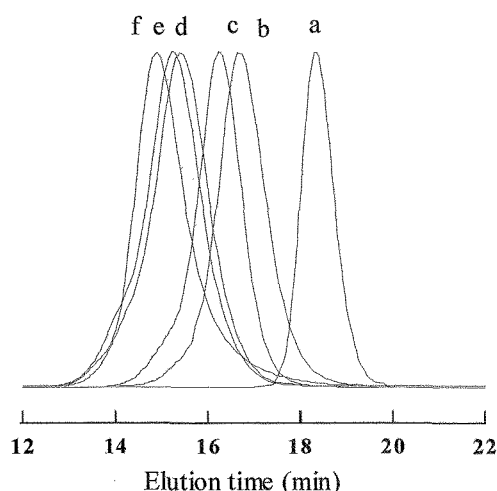


Figure 1 GPC traces of PEO-AZO block copolymers: (a) polyethylene oxide macroinitiator, (M_n (GPC) = 5000, M_w/M_n = 1.04), (b) **P1a**, (M_n (GPC) = 15000, M_w/M_n = 1.09), (c) **P1b**, (M_n (GPC) = 17500, M_w/M_n = 1.09), (d) **P1c**, (M_n (GPC) = 26500, M_w/M_n = 1.14) and (e) **P1d**, (M_n (GPC) = 28500, M_w/M_n = 1.14) (f) **P1e**, (M_n (GPC) = 28000, M_w/M_n = 1.11)

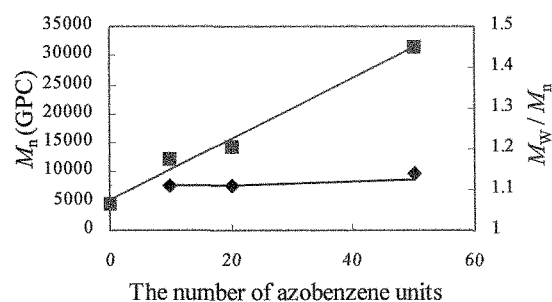


Figure 2 The dependence of molecular weight (M_n (GPC), ■) and polydispersity (M_w/M_n , ◆) on the number of AZO repeated units in block copolymers.

Results and Discussion

Synthesis by ATRP method. By ATRP method,⁵ a series of amphiphilic liquid crystalline block copolymers **P1a-P1e** were synthesized by using **4** as the macroinitiator ($M_n \approx 5000$) and Cu(1)Cl-HMTETA complex as the catalyst. Polymerization conditions and results are shown in Table 1. The feed monomer concentration ($[M]_0$) was kept 0.2M, and the monomer/initiator molar ratio, $[M]_0/[I]_0$, was systematically varied from 10 for **P1a** to 200 for **P1e**, to control their molecular weights. M_n (GPC) and polydispersity were determined by GPC with polystyrene standards. Conversion and M_n (NMR) were calculated by ¹H NMR.³ Figure 1 shows the GPC profiles of five block copolymers as a function of monomer/initiator molar ratio. The unimodal and narrow GPC curves corresponding to the block copolymers **P1a-P1e** shifted to high molecular weights with the increase of monomer molar ratio. Figure 2 gives the dependence of molecular weight and polydispersity on the number of the methacrylate units bearing azobenzene mesogen (AZO). The block

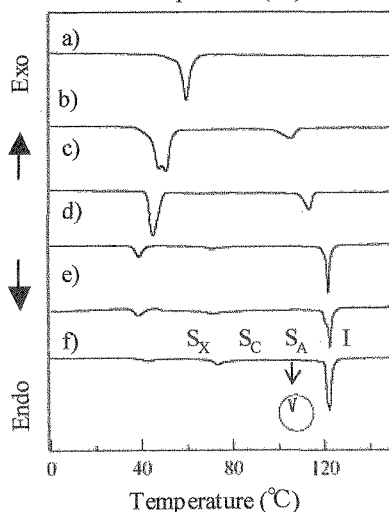
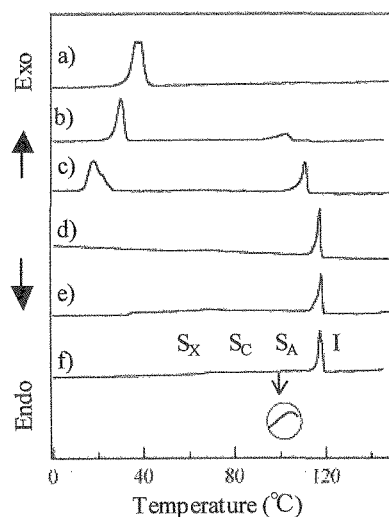
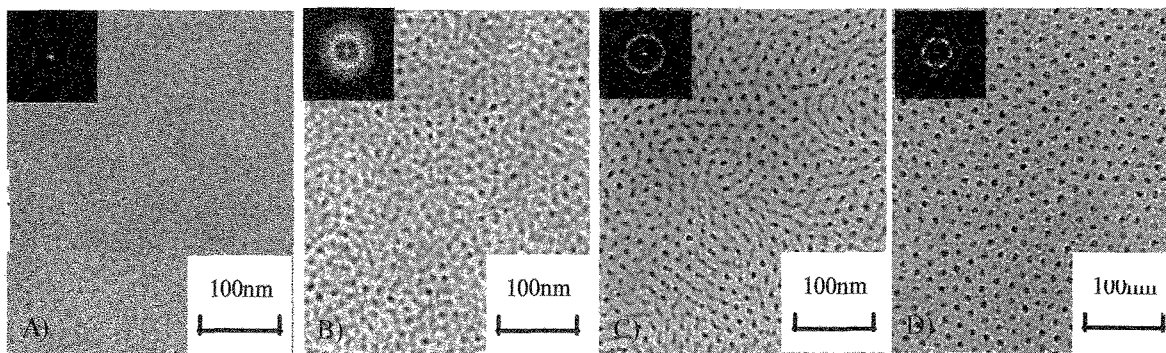


Figure 3 DSC thermograms of the first cooling (top) and the second heating (bottom) processes of (a) macroinitiator, diblock copolymers (b) **P1a**, (c) **P1b**, (d) **P1c**, (e) **P1d**, and (f) **P1e** on the second heating rate is 10°C/min.

Figure 4 TEM micrographs of block copolymer

copolymers exhibit narrow polydispersities in the range from 1.09 to 1.14, indicating controlled polymerization. The conversion in the primary stage increased linearly as a function of time. The M_n value increased monotonously, keeping a narrow polydispersity. These observations allow us to conclude the controlled living polymerization.

Thermal Properties. The block copolymers exhibit three kinds of smectic phases, i.e., smectic A (S_A), smectic C (S_C), and smectic X (S_X) phase between three transitions at 70°C for S_X-S_C , 100°C for S_C-S_A , and 120°C for S_A-I , which could be consistently determined by polarized optical micrograph (POM), differential scanning calorimetry (DSC), and X-ray diffraction. Figure 3 shows the second heating and first cooling DSC curves of the block copolymers **P1a-P1e**. The DSC curves were similar to series of PEO ($M_n \approx 2000$) block copolymers and homopolymers. In the case of **P1c**, on heating, two well-defined endothermic transitions at 73°C and 122°C, and



PEO114AZO45 annealed at different temperatures for 24h : A) r.t., B) 60°C, C) 80°C, and D) 105°C. The dark parts stained with RuO_4 are the PEO microdomains.

very small transition around 101°C were observed, respectively, which are reproducible on cooling. The transition temperatures of the smectic phase in **P1a-P1e** become higher with the increasing LC fraction. This tendency was observed in several kinds of LC-coil block copolymers^{7,8}, which was explained by the disordering of the LC structures in the vicinity of the microphase interface. On the other hand, the endothermic transition at 40°C of **P1c** was observed as a supercooling effect. This transition should be the melting point of the PEO block, which becomes lower with the increasing LC fraction.

TEM Observation of Nanostructures. The formation of periodic nanostructures based on microphase separation could be well imaged by TEM observation of the thin films. Figure 4 shows the TEM images of **P1c** thin films on carbon-deposited copper grids, which were annealed at different temperatures at r.t., 60°C, 80°C, and 105°C. The dark parts in the TEM image are PEO microdomains which were selectively stained by RuO_4 vapor. The PEO microdomains looked to be arranged as hexagonally packed cylinder array and/or spheres with a diameter about 7nm, which are dispersed into LC matrix **P1c**. As the increase of the annealing temperatures, the nanostructures observed in TEM images become more regular and clear. This observation may be interpreted by significance of high fluidity of the polymer around the isotropic temperature.

Conclusions

We have synthesized a new series of amphiphilic LC diblock copolymers with narrow polydispersities in the range of 1.08-1.14 by using ATRP method. Thermal investigation shows that the polymers exhibit S_A , S_C and S_X phases. For the block copolymers, cylinder and/or spherical morphologies of PEO block dispersed into LC block were clearly observed after annealing at 105°C for 24h. The size of nanostructures was 20nm and the PEO block diameter was 7nm. The microphase separations were more clear and orderly with the increase of annealing temperatures, i.e., the increase of fluidity.

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(Received December 21, 2002; Accepted April 28, 2003)