

Syntheses and Nanostructure of Amphiphilic Liquid Crystalline Block Copolymers with Various Mesogene Units

Sadayuki Asaoka,[†] Takayuki Uekusa,[†] Takeshi Yamada,[‡] Hirohisa Yoshida,[‡]
and Tomokazu Iyoda^{†*}

[†]CREST-JST, Chemical Resources Laboratory, Tokyo Institute of Technology

[‡]Department of Applied Chemistry, Graduate School of Engineering, Metropolitan University of Tokyo
4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
Tel: +81-45-924-5246, E-mail: iyoda@res.titech.ac.jp

Abstract: A series of novel amphiphilic liquid crystalline diblock copolymers consisting of poly(ethylene oxide) as hydrophilic segment and poly(methacrylate) tethered by tail-less azobenzene and stilbene as hydrophobic liquid crystalline segments were synthesized by the atom transfer radical polymerization. Thermal analysis together with temperature dependent polarized optical microscope observation of liquid crystalline phase implies that these copolymers exhibit in smectic liquid crystalline phase. Hexagonally packed cylindrical nanostructure was revealed by SAXS measurement for the copolymer bearing stilbene as mesogene.

Keyword: Amphiphilic diblock copolymer, Microphase separation, Atom transfer radical polymerization, Cylindrical nanostructure, Azobenzene mesogene, Stilbene mesogene

Introduction

Block copolymers are well known to give the highly-ordered nanostructures due to microphase separation. Fine control of the character and sequence of each block allows us to fabricate a wide variety of nanostructures such as lamellar, cylindrical, spherical, as well as more complicated cubic gyroid morphologies.¹

The controlled living radical polymerization enables us to obtain the block copolymer with narrow poly dispersities by easy preparative procedure, and can be applied to various kinds of olefinic monomers such as stylenes, acrylates and methacrylates.² We have already reported a series of amphiphilic diblock copolymers, consisting of poly(ethylene oxide) (PEO) as a hydrophilic segment and poly(methacrylate) tethered by liquid crystalline azobenzene unit as hydrophobic one, prepared by the atom transfer radical polymerization (ATRP).³

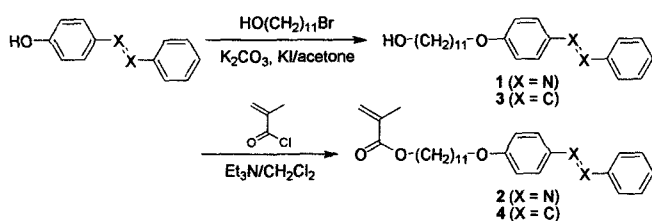
The wide angle X-ray diffraction (WAXD) together with the thermal analysis revealed that the liquid crystalline phases of these copolymers were assigned as the smectic (Sm) ones, of which tilt angles were varied through the phase transition from SmA at higher to SmC at lower temperature. The transmission electron microscopy (TEM) observations of morphologies in the thin solid films revealed highly ordered and hexagonally aligned cylindrical structures

due to the microphase separation, which were also supported by the small angle X-ray scattering (SAXS) of the annealed copolymer pellets. The smectic phase of liquid crystalline segments may reinforce the formation of such extremely ordered cylinder allays.

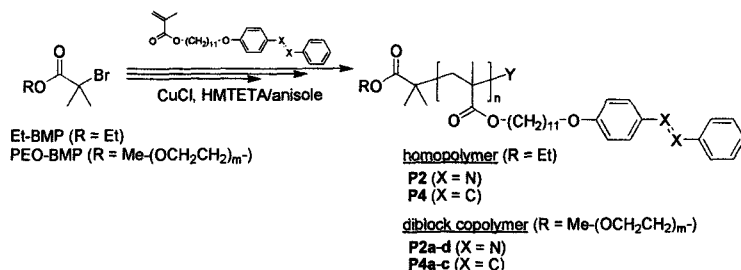
The liquid crystalline nature should play one of the most important roles to control the dimensions as well as the orderness of phase segregated nanostructures. Here a series of novel amphiphilic diblock copolymers were designed by tuning molecular interaction in liquid crystalline segments with different mesogene moieties. Since the liquid crystalline moieties have different hydrophobic properties and aggregation nature, each copolymer is supposed to afford various nanostructures. We wish to report the syntheses of novel amphiphilic block copolymers consist of alkyl tail (butyl group)-less azobenzene (**P2a-d**) and stilbene (**P4a-c**) for the studies on the effect of the molecular structure of liquid crystalline mesogenes, which varies the crystallinity, liquid crystalline phase and other thermal properties of the copolymer, to the nanostructures in the solid films.

Experimental Section

General. ¹H NMR spectra were measured by using a JEOL EX270 spectrometer. Molecular weights of polymers were determined by a gel permeation chromatography eluted by THF on KF803 and KF804



Scheme 1 Syntheses of liquid crystalline monomers.



Scheme 2 Syntheses of liquid crystalline homo- and amphiphilic diblock copolymers by ATRP.

column (Shodex) according to polystyrene standards using a JASCO liquid chromatography system equipped with 870-UV and RI-2031 Plus detectors. Thermal analyses were conducted on an SII Extra 6000 DSC system (Seiko Instruments Inc.) at a scanning rate of ± 10 °C/min. The temperature dependent polarized optical microscopic (POM) observation was conducted by using an Olympus BX51/BX52 microscope fitted with a Mettler Toledo FP900 thermo control system. Temperature dependent WAXD was measured with a Mac Science M21X-SRA using CuK α source, and SAXS measurements were carried out at the beam line 10C, Photon Factory, High Energy Accelerator Research Organization (Tsukuba, Japan) by using an one-dimensional position sensitive proportional counter (Rigaku) as detector.

Materials. Acetone and dichloromethane was fractionally distilled from potassium carbonate and calcium hydride, respectively. The other commercially available chemicals were used without further purification.

The ATRP macroinitiator α -methoxy-poly(ethylene oxide) ω -(2-bromo-2-methylpropionate) (PEO-BMP) was synthesized by esterification of poly(ethylene oxide) monomethyl ether ($M_n = 5000$, Aldrich) with 2-bromo-2-methylpropionyl bromide (TCI) according to same procedure as reported previously.³

The liquid crystalline monomers were prepared via the synthetic route as shown in Scheme 1 according to the following procedures;

11-[4-(phenylazo)phenoxy]undecan-1-ol (1). A mixture of potassium carbonate (10.5 g), potassium iodide (450 mg) and 4-(phenylazo)phenol (TCI, 10 g) in acetone (80 mL) was heated at reflux temperature for 30 minutes.

11-Bromo-1-undecanol (Wako, 15.4 g) was added to the suspension and then continued to heat at reflux temperature for 11 hours. After removal of solvent under reduced pressure, residual solid was washed with water, and then recrystallized from ethanol to afford yellow flakes (15.8 g, 85% yield). ¹H NMR (CDCl₃) δ 1.31-1.84 (m, 18H), 3.64 (t, $J = 6.6$ Hz, 2H), 4.04 (t, $J = 6.5$ Hz, 2H), 7.00 (d, $J = 8.9$ Hz, 2H), 7.40-7.50 (m, 3H), 7.86-7.93 (m, 4H); Anal. Calcd for C₂₃H₃₂N₂O₂: C, 74.96; H, 8.75; N, 7.60. Found: C, 75.18; H, 8.50; N, 7.62.

11-[4-(phenylazo)phenoxy]undecyl methacrylate (2). To dichloromethane (50 mL) solution of 1 (5 g) and triethylamine (2.1 g), dichloromethane (30 mL) solution of methacryloyl chloride (2.5 g) was added dropwise at 0 °C, and the reaction mixture was subjected to stir at room temperature for 12 hours. The solvent was once removed under reduced pressure, and then the residue was dissolved in chloroform and washed with 1N HCl, 5% NaHCO₃aq and brine. The solution was dried over MgSO₄ and evaporated to afford crude yellow solid, which was then subject to recrystallization in ethanol to give yellow powder (4.5 g, 76% yield). ¹H NMR (CDCl₃) δ 1.31-1.88 (m, 18H), 1.94 (s, 3H), 4.04 (t, $J = 6.6$ Hz, 2H), 4.14 (t, $J = 6.8$ Hz, 2H), 5.54 (s, 1H), 6.09 (s, 1H), 7.00 (d, $J = 9.2$ Hz, 2H), 7.40-7.53 (m, 3H), 7.85-7.95 (m, 4H); Anal. Calcd for C₂₇H₃₆N₂O₃: C, 74.28; H, 8.31; N, 6.42. Found: C, 74.08; H, 8.17; N, 6.43.

11-(4-styrylphenoxy)undecan-1-ol (3). Compound 3 was prepared from 4-hydroxystilbene (Across, 5.4 g) according to same procedure as 1. Colorless flakes (9.4 g, 94% yield) ¹H NMR (CDCl₃) δ 1.21-1.84 (m, 18H), 3.64 (t, $J = 6.5$ Hz, 2H), 3.97 (t, $J = 6.5$ Hz, 2H), 6.88 (d, $J = 8.6$ Hz, 2H), 7.01 (d, $J = 12.4$ Hz, 2H), 7.21 (d, $J = 7.3$ Hz, 1H), 7.34 (t, $J = 7.3$ Hz, 2H), 7.42-7.45 (m, 4H); Anal. Calcd for C₂₅H₃₄O₂: C, 81.92; H, 9.35. Found: C, 81.74; H, 9.55.

11-(4-styrylphenoxy)undecyl methacrylate (4). Compound 4 was prepared from 3 (9 g) according to same procedure as 2. Colorless powder (6.7 g, 62% yield) ¹H NMR (CDCl₃) δ 1.23-1.74 (m, 18H), 1.87 (s, 3H), 3.90 (t, $J = 6.5$ Hz, 2H), 4.06 (t, $J = 6.5$ Hz, 2H), 5.47 (s, 1H), 6.02 (s, 1H), 6.81 (d, $J = 8.9$ Hz, 2H), 7.01 (d, $J = 12.4$ Hz, 2H), 7.21 (d, $J = 7.3$ Hz, 1H), 6.94 (d, $J = 12.4$ Hz, 2H), 7.14 (d, $J = 7.3$ Hz, 1H), 7.27 (t, $J = 7.3$ Hz, 2H), 7.35-7.42 (m, 4H); Anal. Calcd for C₂₉H₃₈O₃: C, 80.14; H, 8.81. Found: C, 79.92; H, 8.93.

Table 1 Polymerization conditions^a and properties of homo- and diblock polymers synthesized via ATRP.

sample	[M] ₀ /[I] ₀ ^b	time ^c (h)	conv. ^d (%)	M _n		DP ^e	M _w /M _n ^f	LC content ^g (%)
				GPC ^e	NMR ^f			
P2	50	24	81	8300	ND	20 ^h	1.10	100
P2a	100	2	23	16600	20800	36	1.13	75
P2b	100	4	46	15900	24600	45	1.14	80
P2c	100	6	65	23100	35000	69	1.12	86
P2d	100	12	81	24100	42500	86	1.16	88
P4	50	15	77	10800	ND	35 ^h	1.19	100
P4a	100	6	49	15300	18500	31	1.13	73
P4b	100	12	55	21000	25500	47	1.27	80
P4c	100	15	77	25300	32500	63	1.20	85

^a[Initiator]/[HMTETA]/[CuCl] = 1:10:10, polymerized at 80 °C. ^bFed molar ratio of monomer [M]₀ and initiator [I]₀. ^cPolymerization time. ^dConversions determined by ¹H NMR. ^eNumber averaged molecular weight determined by GPC analysis based on polystyrene standards. ^fDetermined by ¹H NMR. ^gPolymerization degree calculated from M_n(NMR), unless noted otherwise. ^hCalculated based on M_n(GPC). ⁱPolydispersity determined by GPC. ^jLC weight fractions determined by DPs.

Polymerization. Block copolymers were prepared by ATRP (Scheme 2) according to a typical procedure for P4b as follows; copper(I) chloride (9.9 mg), macroinitiator PEO-BMP (55 mg) and monomer 4 (430 mg) were settled in a 10 mL tube and dissolved in anisole (10 mL). Anisole (5 mL) solution of 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Aldrich, 27μL) was added, and then the reaction mixture was degassed through 4 cycles of freeze-pump-thaw and sealed under vacuum. After 30 minutes' stirring at room temperature, the sealed tube was heated at 80 °C for 12 hours. The reaction mixture was passed through an activated neutral alumina (Merck) column using THF as eluent. The eluted solution was concentrated under reduced pressure, and reprecipitated in methanol. The precipitate was washed thoroughly with hot ethanol until residual monomer was completely removed, to afford colorless polymer powder.

Homopolymers were prepared according to the same procedure by using ethyl 2-bromo-2-methylpropionate as an initiator.

Results and Discussions

Preparation of Polymers via ATRP. A series of homopolymers P2, P4 and diblock copolymers P2a-d, P4a-c were synthesized by ATRP method with

unimodal and narrow poly dispersities, as summarized in Table 1. While the concentrations of monomer and initiator were fixed, the M_ns of polymers were controlled by specified reaction time. The fact that stilbene-tethered polymers (P4, P4b,c) gave relatively larger M_w/M_n values than the corresponding azobenzene polymers (P2, P2b,c) was attributable to the low solubility of stilbene-based polymer to anisole in higher M_n region.

Thermal Properties. As reported previously,³ diblock copolymer tethered by 4-(4-*n*-butylphenylazo)phenoxy mesogenes P5 showed two kinds of smectic phase with

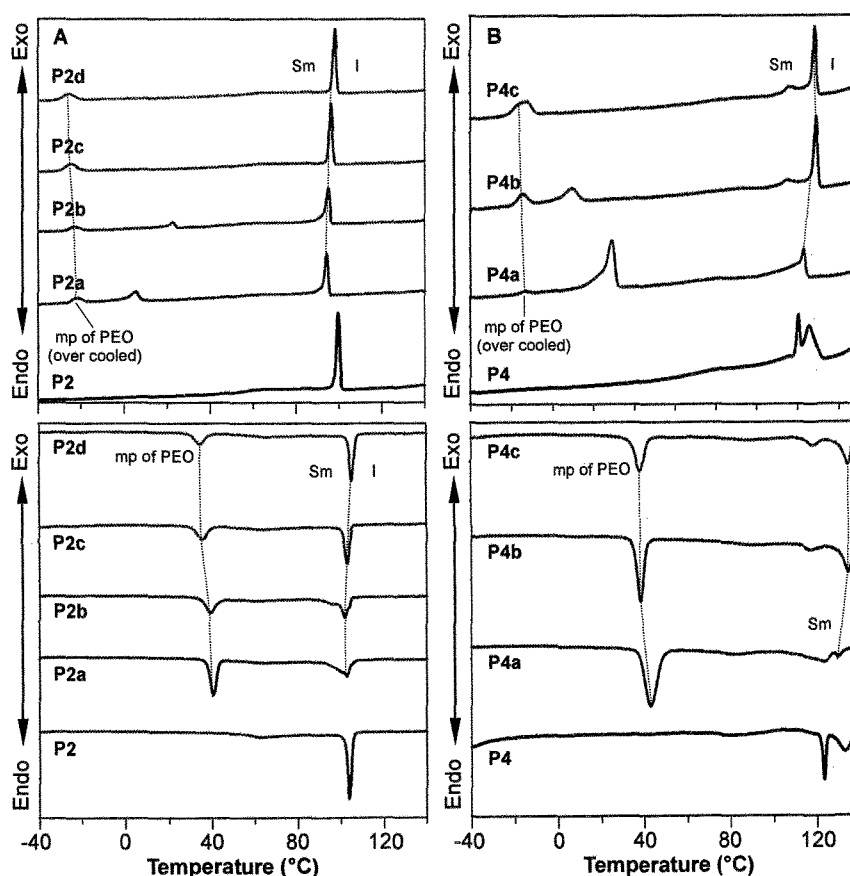


Figure 1 DSC curves of the homopolymers P2, P4 and diblock copolymers P2a-d, P4a-c on first cooling (upper traces) and second heating (lower traces) at a rate of ± 10 °C.

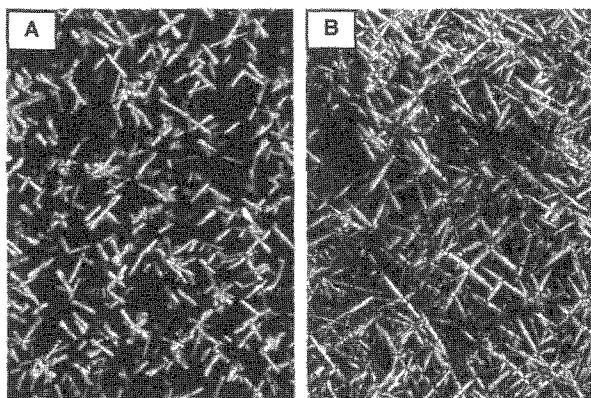
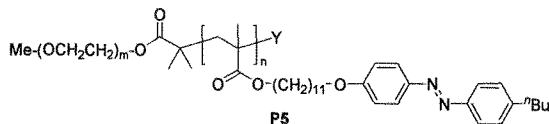


Figure 2 Typical polarized optical micrographs of (A) **P2b** and (B) **P4b** at 100 and 131 °C, respectively.



different tilt angles of the mesogene, i.e. SmA and SmC phases with their transitions SmX-SmC at 70 °C, SmC-SmA at 100 °C and SmA-I at 120 °C. The DSC curves of the homopolymers and diblock copolymers on the first cooling and second heating processes were shown in Figure 1. Azobenzene attached homopolymer **P2** and copolymer **P2a-d** had an isotropic transition temperature around 105 °C, which is lower than that of **P5** having *n*-butyl tail groups. Although a typical texture for Sm phases were observed by POM (Figure 2A for **P2b** at 100 °C), no obvious diffraction peaks on WAXD were obtained for them. The tail groups introduced in the mesogenes should therefore be indispensable to form well aligned smectic layer structure. Stilbene tethered polymers **P4** and **P4a-c** gave a set of transitions around 120 °C. Since the typical textures for Sm phases were obtained between them (Figure 2B for **P4b** at 131 °C), they are attributable to Sm-I transitions. A strong diffraction emerged at $2\theta \sim 20^\circ$ on WAXD by lowering temperature, which may indicate the enhancement of crystallinity in the liquid crystalline domain.

The isotropic transition temperatures for diblock copolymers **P2a-d** and **P4a-c** became higher with increasing the liquid crystalline segments. This tendency should be attributable to the disordering at the interface of microphase separation, as reported for LC-coil block copolymers. The transition at ca. 40 °C should be assigned as the melting point of PEO domain, which was lowered with increasing liquid crystalline fraction.

Analyses of Nanostructures. A periodic cylindrical nanostructure has been observed for **P5** in the wide range of polymerization degree of PEO and liquid crystalline segments, which was well imaged by using transmission electron microscopy (TEM). The periodicity and highly

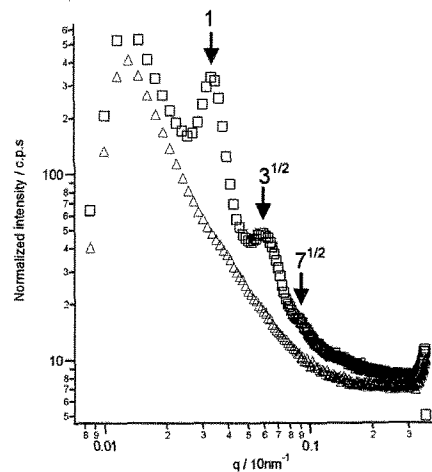


Figure 3 Static SAXS profile of **P4b** at 17 °C after annealing (squares) and at 157 °C (triangles).

ordered alignment of the cylindrical structure have also been detected by SAXS as a result of intense and clear diffraction peaks observed. In order to analyze the nanostructure of diblock copolymers **P2b** and **P4b**, SAXS measurements were conducted. While no obvious diffractions were observed for **P2b**, stilbene tethered copolymer **P4b** gave a set of diffractions after annealing, as shown in Figure 3. This diffraction pattern indicates hexagonally aligned cylindrical structure with the distance between each cylinders of 19.9 nm, which is comparable to that in **P5** with 45 azobenzene units of 19.7 nm.

Conclusions

A series of amphiphilic liquid crystalline diblock copolymers possessing tail-less azobenzene and stilbene units as mesogenes were synthesized with unimodal and narrow polydispersities in the range of 1.12-1.16 for **P2a-d** and 1.13-1.27 for **P4a-c** via ATRP. Thermal analysis implied that all the polymers may exhibit smectic phase, but the liquid crystalline phase was emerged in restricted temperature region due to the crystallization nature. The hexagonally packed cylindrical nanostructure was indicated by SAXS measurement for the copolymer having stilbene as mesogene, which dimensions was consistent with that of **P5**. Unfortunately, ordered nanostructures for **P4b** have not imaged by TEM yet, and further investigation is now underway.

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