

## 2D Nanophase Separation in Monolayers of Triblock Copolymer Having Azobenzene Moiety

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Nanophase (microphase) separation of block copolymer is attracting great attention in application for nanotechnologies. We synthesized three novel azobenzene-containing ABA-type triblock copolymers from poly(ethylene glycol) and azobenzene methacrylate via the atom transfer radical polymerization method. Monolayer behavior on water was investigated by surface pressure vs area isotherms and UV-Vis absorption spectrum measurements. Atomic force microscopy revealed that the monolayers transferred onto a mica substrate represented clear nanophase separation structures. UV-Vis absorption spectra measurements showed that the photoisomerization behavior in the nanostructures were quite different from that observed for an Az homopolymer without phase separation.

Key words: ABA triblock copolymer, azobenzene, nanophase separation structure, atom transfer radical polymerization, LB film, atomic force microscopy

### 1. INTRODUCTION

Nanometer scale surface patterns based on self-assembly have been considered as new material to replace high resolution lithographic technologies using X-ray or electron beam and interference lithography. In particular, nanophase separation structures of block copolymers have been recognized as an important target in this region.<sup>1-4</sup> For the construction of 2D polymer system, the Langmuir-Blodgett (LB) technique is a powerful tool.<sup>5</sup> Langmuir monolayer on water can provide characteristic nanostructures. Addition of light responsive function to the monolayer is expected to contribute a great deal in creation of new functional materials.

Our previous work showed photoinduced area changes of monolayers consisting of a poly(vinyl alcohol) having azobenzene (Az) unit in side chain on water.<sup>6</sup> The trans to cis photoisomerization of Az by UV irradiation gives rise to an expansion of the monolayer film at low pressures. On visible light irradiation, the reverse process takes place, and alternate irradiation result in the expansion and contraction with high reproducibility. Moreover, the transferred monolayer on a mica surface also exhibited large photoinduced morphological changes in humidified atmosphere as proved by atomic force microscopy (AFM).<sup>7</sup> The hydration on surface plays important role in the film motility on the mica surface. Introduction of photoresponsive actions in blockcopolymer monolayer is expected to provide new perspectives in nano-patterning. We expect that new photoresponsive nanomaterials may be created when the morphologies of 2D nanostructures formed by the monolayers of block copolymers can be altered by light.

In this paper, we report the synthesis and features of LB monolayers of novel ABA-type triblock copolymers where A and B correspond to Az containing polymethacrylate and poly(ethylene oxide) (PEO),

respectively. They were synthesized by atom transfer radical polymerization (ATRP) method<sup>8</sup> according to similar procedures reported by Tien et al.<sup>9</sup> The spreading behavior of the polymer on water was evaluated by the surface pressure vs area ( $\pi$ -A) isotherms. Monolayers on water were transferred onto a solid substrate, and morphologies of these films were observed by AFM. Furthermore, UV-visible spectroscopic measurements were conducted to confirm the photoisomerization behavior on a solid substrate.

### 2. EXPERIMENTAL

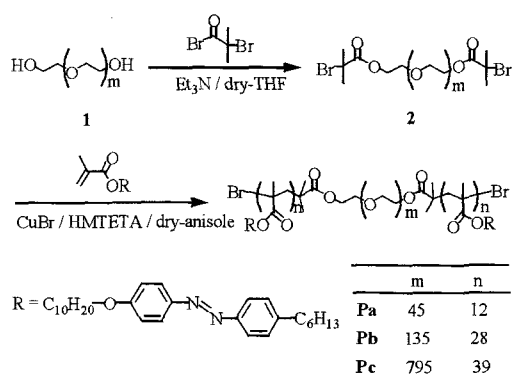
#### 2.1 Materials

Poly(ethylene oxide) with number-average weight of ca. 2000 (Kanto Chem. Co., Japan), 6000 (Kanto Chem. Co., Japan) and 10000 (Aldrich) were dried by azeotropic distillation with toluene. 2-Bromo-2-methylpropionyl bromide (Kanto Chem. Co., Japan) was used without further purification. Anisole as solvent for ATRP method was dehydrated by distillation from sodium with benzophenone. 1,1,4,7,10,10-hexamethyltrithylenetetraamine as ligand (HMTETA, Aldrich) was employed without further purification. Catalyst CuBr (Kanto Chem. Co., Japan) was washed with acetic acid containing HCl and ether.

#### 2.2 Preparation of PEO Macroinitiator of 2b

A solution of 200  $\mu$ l (1.20 mmol) of 2-bromo-2-methylpropionyl bromide was added to a mixture of 1 g (0.16 mmol) of PEO ( $M_n = 6000$ ) and 200  $\mu$ l (1.40 mmol) triethylamine in 30 ml of dry THF at room temperature, and then mixture was stirred for overnight. After the mixture was filtered, half of solvent was evaporated. The PEO macroinitiator was reprecipitated into cold ether. After dissolution in methanol, reprecipitation into cold ether was carried out. White solid was obtained. Yield: 750 mg (75 %). <sup>1</sup>H-NMR ( $CDCl_3$ ),  $\delta$  (ppm): 3.64 (m, 545H,  $-OCH_2CH_2-$ ), 1.94 (s, 12h,  $(CH_3)_2CBrCO-$ ).

#### 2.3 Typical Synthetic Procedure of Triblock Copolymer



Scheme 1

**(Pb)**

A portion 9 mg (0.09 mmol) of CuBr, 30 mg (5  $\mu$ mol) of **2b**, and 260 mg (0.01 mmol) of Az monomer were inserted in a 10 ml ampule tube, degassed, and filled with  $N_2$  gas. A 15  $\mu$ l (0.05 mmol) of HMTETA in 6 ml of anisole was added through a syringe. The mixture was degassed by freeze-pump-thaw procedure and sealed under vacuum. After 30 min stirring at room temperature, the ampule was placed in 70 °C oil bath for 48 h. The solution was passed through neutral alumina short column with chloroform to remove Cu catalyst. Solvent was concentrated under reduced pressure and added to hexane to remove Az monomer. Yellow solid was dissolved in chloroform, and was reprecipitated into methanol. The yellow polymer was collected by centrifugation and dried under vacuum. The conversion of polymerization was 69 % as estimated from  $^1H$ -NMR spectrum. Yield: 120 mg (43 %).  $M_n$  (GPC) = 32200,  $M_w/M_n$  = 1.13,  $M_n$  ( $^1H$ -NMR) = 35700.  $^1H$ -NMR ( $CDCl_3$ ),  $\delta$  (ppm): 7.83 (d,  $J$  = 8.9 Hz, 2H, Ph-H) 7.75 (d,  $J$  = 8.4 Hz, 2H, Ph-H), 7.23 (d,  $J$  = 8.5 Hz, 2H, Ph-H), 6.90 (d,  $J$  = 8.7 Hz, 2H, Ph-H), 3.92 (m, 4H,  $-COOCH_2-$ ,  $-CH_2-O-Ph$ ), 3.64 (m, 9.6H,  $-OCH_2CH_2-$ ), 2.61 (bt,  $J$  = 7.5 Hz, 2H,  $-CH_2-Ph$ ), 1.27-1.73 (bm, 24H,  $-CH_2-$ ), 0.86 (bt,  $J$  = 7.1 Hz, 3H,  $-CH_3$ ).

**Pa** and **Pc** were synthesized in same manners as described above.

## 2.4 Characterization

$^1H$ -NMR spectra were recorded on a JEOL 270GXS instrument spectrometer operating at 270 MHz with tetramethylsilane as the internal standard. Molecular weight and polydispersity of polymers were measured by gel permeation chromatography (GP) using a liquid chromatograph (Shodex UV-41) with a appropriate column (Shodex KF-803L and Shodex KF-805L) on tetrahydrofuran as eluent, which was calibrated with standard polystyrene.

The spreading behavior of the triblock copolymers were

evaluated on pure water (Milli-Q grade,  $18M\Omega\text{ cm}^{-1}$ ) using a Lauda FW-1 film balance at 20°C. The temperature of water subphase was controlled by water circulation using a Yamato-KOMATSU CTE-22W. UV-Vis absorption spectra on water were measured with an Ohtsuka Electronics MCPD-2000. AFM observations were carried out on a SPA400/SPI3800N system (Seiko Instruments) in the noncontact mode. The monolayers for AFM studies were transferred onto a fresh cleaved mica substrate by the conventional dipping method. UV-Vis absorption spectra on quartz substrate were measured on a JASCO MAC-1 spectrophotometer. Samples were prepared in the same way as those used for AFM measurements.

## 3. RESULTS AND DISCUSSION

## 3.1 Synthesis of triblock copolymers

Results of the polymerization are shown in Table 1. The polymerization should proceed equally from both end terminals of the PEO macroinitiator, polymerization degree (n) estimated by  $^1H$ -NMR and GPC shown here are the half of the total increment of molecular weight. The polymers exhibited narrow polydispersities in the range from 1.11 to 1.13 as determined by GPC. Thus, novel triblock copolymers were successfully synthesized by the controlled radical polymerization.

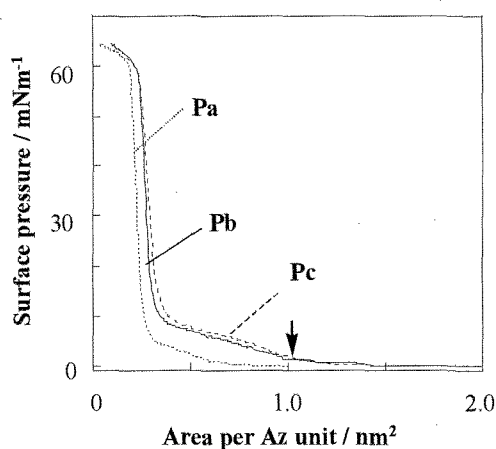
## 3.2 Surface Pressure-Area Isotherms

Figure 1 indicates the surface pressure vs area ( $\pi$ -A) isotherms of triblock copolymers spread from a chloroform solution onto the water surface at 20°C. The features of the curves can be basically regarded as a superposition of those for Az homopolymer and PEO, indicating that this ABA block copolymers are spread as "pure" 2D monolayers on water without 3D coil formation. This is reasonably understood from the fact that both blocks possess polar groups in the chain. Lift off areas per Az unit of **Pa-Pc** were 0.8, 1.4, and 1.5  $\text{nm}^2$ , respectively. Limiting areas per Az unit of **Pa-Pc** were 0.27, 0.31, and 0.32  $\text{nm}^2$ , respectively. **Pb** and **Pc** gave similar isotherms. However,  $\pi$ -A curve for **Pa** showed different characters. The origin of such behavior was suggested by UV-Vis absorption spectra of monolayer around the limiting area ( $10\text{ mN m}^{-1}$ ) on water (Figure 2). This fact indicates the formation of stronger H-type aggregates in the **Pa** monolayer than that in **Pb** monolayer. Absorption maximum ( $\lambda_{\text{max}}$ ) observed for **Pa** was positioned at 318 nm, which was blue shifted to more extent than that for **Pb** (324 nm). In addition, absorbance ratios of  $A_{\text{short}}/A_{\text{long}}$ , where  $A_{\text{short}}$  and  $A_{\text{long}}$   $\pi$ - $\pi^*$  correspond to absorbance of bands for

Table 1 ABA triblock copolymers synthesized by ATRP method

Polymer	$M_n$ (PEO) <sup>a)</sup>	m <sup>b)</sup>	n ( $^1H$ -NMR) <sup>c)</sup>	n (GPC) <sup>d)</sup>	$M_w/M_n$ <sup>e)</sup>	Conv. (%) <sup>f)</sup>	Yield (%)
<b>Pa</b>	2000	45	12	18	1.11	65	28
<b>Pb</b>	6000	135	28	26	1.13	69	43
<b>Pc</b>	10000	227	39	18	1.13	82	55

a) Number average molecular weight of starting material, PEO. b) Unit number of PEO. c) Polymerization degree of Az monomer estimated by  $^1H$ -NMR. d) Polymerization degree of Az monomer determined by GPC. e) Polydispersity determined by GPC. f) Conversion estimated by  $^1H$ -NMR.

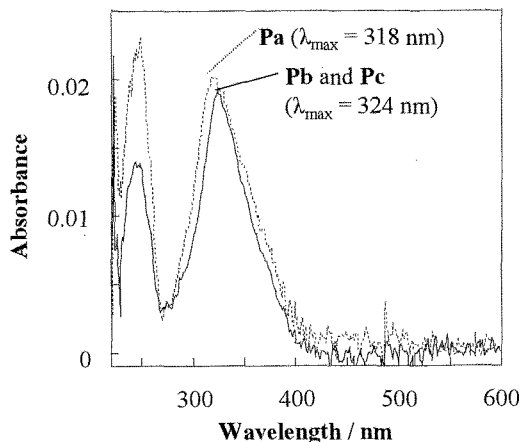


**Figure 1.** Surface pressure vs area ( $\pi$ -A) isotherms of triblock copolymers. **Pa-Pc** are represented by dot line, solid, and dashed lines, respectively.

phenyl ring (246 nm) and long axis transition of Az, respectively, varied; 1.12 for **Pa** and 0.73 for **Pb**. The absorbance ratio can be a measure of Az orientation. The Az in the **Pa** monolayer is oriented in a more perpendicular manner than that in the **Pb** monolayer. Thus, the block length of PEO modifies the aggregation and orientational state of Az in the monolayer.

### 3.3 Morphology Observations by AFM.

The monolayer was transferred onto a freshly cleaved mica surface by vertical dipping method at  $1 \text{ mNm}^{-1}$ . Topographical AFM images obtained for three polymers are shown in Figure 3. All images show the nano-phase separation structure of two block components. The height difference of the two phase were ca. 2 nm in all cases. The morphology of **Pa** was characterized by shapes of stone pavement. **Pb** and **Pc** gave mixture of dot and stripe shapes. To confirm the constituents of



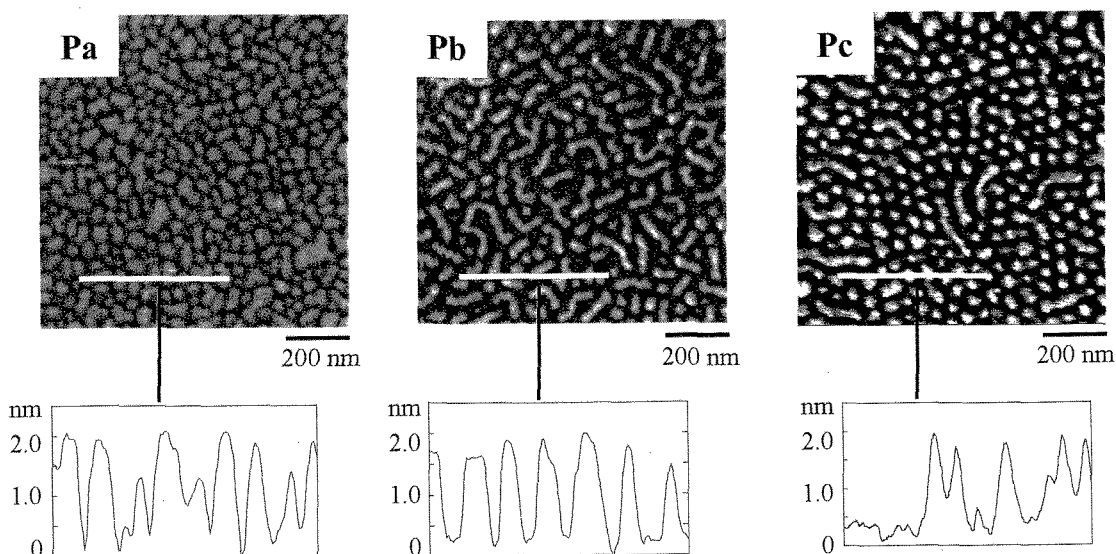
**Figure 2.** UV-visible absorption spectra of monolayers around the limiting area on water. **Pa** and **Pb** are represented by dot and solid lines, respectively.

each phase, a PEO homopolymer ( $M_n = 6000$ ) was added in the solution and spread onto water. Addition of PEO brought about an expansion of lower areas in the AFM image, indicating that the Az and PEO blocks occupy the area of higher and lower phases, respectively.

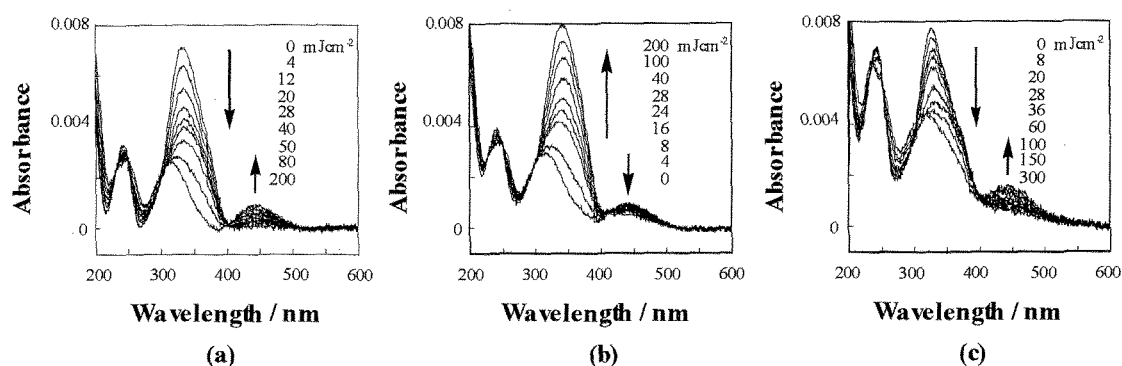
### 3.4 UV-Visible Absorption Spectra on Quartz Substrate.

Absorption spectral changes on illumination were observed for the monolayer of **Pb**. For comparison, a monolayer sample of Az homopolymer ( $M_n = 29000$ ,  $M_w/M_n = 1.6$ ) was also investigated. Figure 4 shows UV-Vis absorption spectrum of the polymers deposited on both side of quartz plate. The films were first irradiated with 365 nm light and successively with 436 nm light. For these measurements, monolayers were transferred at  $1 \text{ mNm}^{-1}$ .

The  $\lambda_{\text{max}}$  of the Az  $\pi$ - $\pi^*$  band of **Pb** monolayer



**Figure 3.** Topographical AFM images of monolayer films of triblock copolymers deposited on mica substrate at  $1 \text{ mNm}^{-1}$ . The AFM images are  $1 \mu\text{m}^2$  scans.



**Figure 4** UV-Vis absorption spectrum changes on quartz of monolayer of **Pb** and homopolymer. (a) illumination with UV light to **Pb** (trans-to-cis). (b) illumination with Visible light to **Pb** (cis-to-trans). (c) illumination with UV light to homopolymer (trans-to-cis).

was 334 nm (a). UV-irradiation readily induced the trans-to-cis photoisomerization. Light dose required to reach the photostationary state was 200 mJ cm<sup>-2</sup> and the conversion to cis form reached to ca. 90 %, which are comparable to that in solution. Also the spectral shape of the monolayer in the trans form characterized by  $A_{\text{short}}/A_{\text{long}}$  ratio was similar to that in solution. The spectrum was almost reverted on irradiation with visible light. Interestingly,  $\lambda_{\text{max}}$  showed further bathochromic shift to 344 nm. Thus, the environment of Az unit in the nanophase separated state is solution like in term of random orientation and high molecular motions allowed.

The spectral features and photoisomerization behavior of the Az homopolymer were obviously different from those of **Pb**. The  $\lambda_{\text{max}}$  showed a hypsochromic shift to 326 nm, indicating the feature of H-aggregation. The  $A_{\text{short}}/A_{\text{long}}$  ratio implies that the trans-Az was in more perpendicular orientation. Furthermore, the conversion to cis isomer reached only to a level of ca. 50 %. In the above manners, formation of nanostructures in the monolayer significantly alter the environment of Az in which the photoisomerization readily undergoes nearly as in solution. In the monolayer of the homopolymer, the promotion of aggregation and normal orientation of the Az side chains should be the consequence of cooperative packing behavior that requires large area sizes. For the block copolymers, on the other hand, the sizes of microphase separation domains at several ten nanometer levels seem too small for evolution of such cooperative nature. The same tendency is already reported for the bulk system.<sup>9</sup>

#### 4. CONCLUSIONS

We synthesized novel ABA triblock copolymers containing azobenzene with narrow polydispersity in the range of 1.11-1.13 by ATRP method.  $\pi$ -A isotherms were confirmed the formation of 2D monolayer on water without 3D coils. Nanophase separation structures of monolayer on mica substrate were observed by AFM images. In such phase separated state, the

environment of Az resembled that in solution. Efficient photoisomerization is anticipated to bring about a large structural alternation of nanostructures in the monolayer state. Work in this regard is now in progress.

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