Polystyrene-polysiloxane Diblock Copolymer having Liquid Crystalline Side Chains

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The polystyrene-*b*-poly(vinyl methylsiloxane) (PS-*b*-PVMS) main chain was synthesized via the anionic polymerization of styrene and cyclotrisiloxane monomer consecutively. The catalytic hydrosilylation of vinyl groups with the hydrosiloxane tethered by liquid crystalline stilbene mesogen unit afforded a diblock copolymer PS-*b*-PMS(Stb) with the narrow polydispersity ($M_N = 52100$, $M_W/M_N = 1.25$). This diblock copolymer exhibited liquid crystalline phase, and gave a lamellae-like nanostructure in the thin film thermally annealed at higher temperature than the isotropic-to-LC transition point.

Key words: polysiloxane, microphase segregated nanostructure, liquid crystalline polymer

1. INTRODUCTION

To create well-defined nanopatterns over large areas, a variety of patterning technologies including top-down and bottom-up methods have been developed. Fabrication of well-defined nanostructures for nanopatterning using the phase segregated nanostructure of block copolymers (BCPs) have been intensively studied because of the tunable dimensions and chemical properties with a flexible, simple, and low-cost process. Since the durability of polysiloxane upon reactive ion etching is considerably higher than conventional organic polymer such as polystyrene (PS), the diblock copolymer having a polysiloxane segment like PS-*b*-PDMS[1, 2] have been investigated for the purpose of application to the etching masks. Hayakawa et al. have reported that the block copolymers composed of polymethacrylate with polyoligomeric

silsesquioxane (POSS) in the side chain affords highly ordered lamellae and/or cylindrical nanostructure in the thin film,[3] which can be used as the BCP mask to fabricate the line and/or dot patterns on the substrate.

We have already reported the amphiphilic diblock copolymer having liquid crystalline side chains, which gave normally oriented cylindrical phase segregated nanostructure along with the direction of mesogen arrangement in the thin film.[4, 5] The side-chain LC block copolymers composed of a polysiloxane segment have also been synthesized to improve the regularity of the phase segregated nanostructures.[6-9] We wish to report here about the synthesis and nanostructure of polystyrene-polysiloxane diblock copolymer having liquid crystalline side chains with stilbene mesogens, which can be photo-crosslinked upon UV-light irradiation to fix the nanostructure (PS-*b*-PMS(Stb)).

Scheme 1 Synthesis of polystyrene-polysiloxane diblock copolymer having LC side chains.

2. EXPERIMENTAL SECTION

2.1 General

^1H NMR spectra were obtained on AV-300 spectrometers in chloroform- d . Molecular weights of polymers were determined by gel permeation chromatography (GPC) eluted by THF on a LF-804 column (Shodex) in reference of a series of standard polystyrene using a JASCO liquid chromatography system composed of a PU-980 HPLC pump and an 860-CO column oven (operated at 40 °C) equipped with an ERMA ERC-8710 UV and a Shodex RI-101 RI detector. Thermal analyses were conducted under N_2 flow on an SII DSC-6200 DSC system (Seiko Instruments Inc.) at a scanning rate of 5 °C/min. Temperature-dependent polarized optical microscopic (POM) observation was conducted under Ar flow by using an Olympus BX53 microscope fitted with a Imoto Machinery Co., Ltd. thermo-control system. Small-angle X-ray scattering (SAXS) measurements were carried out at the beamline 10 C in Photon Factory, High Energy Accelerator Research Organization (Tsukuba, Japan), by using a one-dimensional position-sensitive proportional counter (Rigaku) as a detector. Transmission electron microscope (TEM) images were obtained by using a Hitachi H-7100 electron microscope at an acceleration voltage of 100 kV. The samples for observation were prepared subject to the following procedure. The spin-coated films from the 2 wt % toluene solutions of the block copolymers on the fresh surface of mica substrates were annealed above the isotropic transition temperature under vacuum without any precise control of the heating and cooling rate. The obtained thin films were easily peeled from the substrates by soaked in water, and then transferred onto copper grids.

2.2 Materials

After treated with 2% sodium hydroxide aqueous solution, styrene was freshly distilled under reduced pressure once from calcium hydride and then from isopropylmagnesium chloride just prior to use. 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane purchased from Shinetsu was vacuum distilled from the calcium hydride. THF used for the anion polymerization was freshly distilled once from sodium containing benzophenone, and then from butyllithium just prior to use. *N*-methylpyrrolidone was distilled under reduced pressure from the calcium hydride. Toluene was distilled from melting sodium containing benzophenone. All other chemicals were used as purchased without further purification.

(*E*)-4-(4-Butylstyryl)phenol (1). The NMP (50 mL) solution of 4-vinylphenylacetate (12.7 g, 78.3 mmol), 1-bromo-4-butylbenzene (11.5 g, 54.0 mmol), $\text{Me}_2\text{N}(\text{CH}_2)_3\text{CO}_2\text{H}\cdot\text{HCl}$ (10.2 mg, 60.8 μmol), palladium acetate (15.4 mg, 68.6 μmol) and potassium carbonate (28.2 g, 204 mmol) was stirred at 130°C for 24 h under nitrogen atmosphere. The mixture was diluted CH_2Cl_2 , and washed with water, 1N HCl and brine. The organic layer dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified on the silica gel column chromatography by using hexane-ethyl acetate (5:1) as eluent, followed by recrystallization in methanol, to give colorless needles (8.1 g, 59%). ^1H NMR (CDCl_3) δ 7.40 (d, $J = 8.4$ Hz, 4H), 7.16 (d, $J = 8.1$ Hz, 2H), 6.97 (d, $J = 7.0$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 2H), 4.84 (s, 1H), 2.61 (t, $J = 7.7$ Hz, 2H), 1.63 (t, $J = 7.5$ Hz, 2H), 1.36 (q, $J = 7.5$ Hz, 2H), 0.93 (t, $J = 7.3$ Hz, 3H).

Figure 1 Synthesis of LC polystyrene-polysiloxane diblock copolymer by the combination of anionic polymerization and catalytic hydrosilylation. (a) ^1H NMR spectra of LC mesogen unit, back bone and diblock copolymer. (b) GPC profiles of the diblock copolymers, PS-b-PVMS (broken) and PS-b-PVMS(Stb) (full line).

(E)-1-(Allyloxy)-4-(4-butylstyryl)benzene (2). A mixture of **1** (9.0 g, 36 mmol), potassium hydroxide (4.2 g, 75 mmol), potassium Iodide (46 mg, 280 μ mol), allylbromide (9.5 g, 78 mmol), ethanol (300 mL) and water (15 mL) was stirred at 60 °C for 4 h under nitrogen atmosphere. After removal of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 and washed with water and brine. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was recrystallized in ethanol, to give colorless powder (9.3 g, 89 %). ^1H NMR (CDCl_3) δ 7.42 (t, J = 8.8 Hz, 4H), 7.16 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 6.9 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.06 (m, 1H), 5.42 (d, J = 17.3 Hz, 1H), 5.30 (d, J = 10.5 Hz, 1H), 4.56 (d, J = 5.3 Hz, 2H), 2.61 (t, J = 7.7 Hz, 2H), 1.60 (t, J = 7.7 Hz, 2H), 1.36 (q, J = 7.5 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H).

(E)-1-(3-(4-(4-Butylstyryl)phenoxy)propyl)-1,1,3,3-tetramethyldisiloxane (3). To the toluene (40 mL) solution of 1,1,3,3-tetramethyldisiloxane (40 mL, 227 mmol), the mixture of **2** (6.5 g, 22 mmol) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene (2.2%, 0.6 mL, 35 μ mol) in toluene (160 mL) was added dropwise and heated at 60 °C for 20 h under nitrogen atmosphere. After removal of the solvent under reduced pressure, the residue was purified on the silica gel column chromatography by using hexane-chloroform (1:1) as eluent, to yield colorless powder (7.7 g, 81%). ^1H NMR (CDCl_3) δ 7.41 (t, J = 8.1 Hz, 4H), 7.16 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 4.70 (m, 1H), 3.94 (t, J = 6.9 Hz, 2H), 2.61 (t, J = 7.3 Hz, 2H), 1.83 (m, 2H), 1.61 (t, J = 7.7 Hz, 2H), 1.37 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H), 0.67 (m, 2H), 0.18 (d, J = 2.7 Hz, 6H), 0.12 (s, 6H).

Polystyrene-*b*-poly(vinylmethylsiloxane) (PS-*b*-PVMS). To the mixture of *sec*-butyllithium hexane solution (1.02 M, 150 μ L, 153 μ mol) and anhydrous THF (3 mL), styrene (1 mL, 8.7 mmol) was added at -40 °C under nitrogen atmosphere, to change the color of reaction mixture from pale yellow to bright orange. After stirring for 10 min, the anhydrous THF (4 mL) solution of 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane (1.5 mL, 5.6 mmol) was added to the reaction mixture. After stirring for 16.5 h, trimethylchlorosilane (50 μ L, 390 μ mol) was added to terminate polymerization, followed by additional stirring for 2.5 h to ensure the complete termination. After removal of the solvent under reduced pressure, the residue was purified by reprecipitation in methanol,

to afford colorless powder (1.4 g). M_N = 36100, M_W/M_N = 1.21. ^1H NMR (CDCl_3) δ 7.05 (m, 3xH), 6.58 (m, 2xH), 6.78-5.75 (m, 3yH), 1.86-1.42 (m, 3xH), 0.14 (s, 3yH).

Polystyrene-*b*-poly(methylsiloxane) tethered by LC side chains (PS-*b*-PMS(Stb)). To the mixture of PS-*b*-PVMS (100 mg) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene (2.2%, 20 μ L, 1.2 μ mol) and toluene (0.5 mL), the toluene (0.5 mL) solution of **3** (210 mg) was added dropwise at 60 °C and heated for 4 days under nitrogen atmosphere. After the platinum catalyst was removed through the silica gel short column chromatography by using chloroform as eluent, the crude product was then purified by reprecipitation in methanol and sequential Soxhlet extraction with hexane, to give colorless powder (70 mg). M_N = 52100, M_W/M_N = 1.25. ^1H NMR (CDCl_3) δ 7.34 (br, 4zH), 7.09-6.58 (br, (5x + 4z)H), 5.95-5.76 (m, 3yH), 3.84 (s, 2zH), 2.56 (s, 2zH), 2.17-1.06 (m, (3x + 6z)H), 0.93-0.88 (m, 3zH), 0.59 (br, 2zH), 0.45 (s, 2zH), 0.07-0.04 (t, (3y + 6z)H).

3. RESULTS AND DISCUSSION

3.1 Synthesis of LC diblock copolymer

The main chain block copolymer PS-*b*-PVMS was synthesized via anionic polymerization of styrene followed by 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane. A small aliquot of the reaction mixture was taken to confirm the consumption of styrene monomer before adding the cyclosiloxane monomer, and then precipitated in methanol. Using this sample, the molecular weight and distribution of PS segment was determined as M_N = 32000 and M_W/M_N = 1.28 based on molecular standard samples of PS (Aldrich), respectively. The degree of polymerization (x) was determined as 308 from the M_N value.

The LC side chains were introduced via catalytic hydrosilylation of vinyl groups in the PVMS segment with the hydrodisiloxane units **3**. As shown in Figure 1b, the GPC profile for the product was shifted higher molecular weight region than that of PS-*b*-PVMS. On the ^1H NMR spectrum of the product shown in Figure 1a, while the peaks at 5.95-5.76 ppm assigned as vinyl protons in the PVMS segment (H_i) almost disappeared, a new peak assignable to protons (H_j) on the carbon connecting with the disiloxane group in the side chain, suggesting the side chains were almost quantitatively introduced at vinyl groups in the PVMS segment. The numbers of repeated units for vinylmethylsiloxane units (y) and LC-tethered methylsiloxane units (z)

Figure 2 DSC curves (a) of PS-*b*-PVMS (gray) and LC block copolymer PS-*b*-PMS(Stb) (black line) together with POM images (b) of LC block copolymer at 80 (left), 101 (center) and 130 °C (right).

Figure 3 SAXS profile (a) of **PS-*b*-PMS(Stb)**, and calculated molecular structure (b) of a LC side chain optimized by MM2 force field method.

were calculated to be 8 and 80 from the peak area ratio of H_i and H_j to H_b , respectively.

3.2 Thermal properties of LC diblock copolymer

The thermal properties of diblock copolymers were investigated by using differential scanning calorimetry (DSC). On the DSC curves shown in Figure 2a, while two second-order transitions at -23 and 82 °C assigned as glass transition of PVMS and PS segment, respectively, were observed for **PS-*b*-PVMS**, two large first-order transition peaks were observed at 90 and 115 °C for the LC diblock copolymer. A small glass transition of polymethylsiloxane back bone was also observed for the diblock copolymer at lower temperature than that of PVMS segment in **PS-*b*-PVMS** by 8 °C. On the temperature-dependent POM observation, once the LC diblock copolymer was heated to 130 °C, just black-out views with no texture were observed at the cross Nicole optical setting, suggesting an isotropic phase. A texture shown as the insets of Figure 2 appeared in the temperature range of 125 – 85 °C on cooling, exhibiting some LC phase. On further cooling below 85 °C, the texture slightly became obscure (Figure 2b).

As shown in Figure 3, a set of diffraction peaks at q of 2.10 and 4.08 nm^{-1} was exhibited in the wide angle region on SAXS profile, which can be assigned as $[001]$ and $[002]$ diffractions derived from the layer structure with the periodicity of 2.99 nm. The fully extended side chain length of 2.73 nm calculated by MM2 force field method, which was comparable to the calculated layer distance. The liquid crystalline phases of **PS-*b*-PMS(Stb)** could be therefore assigned as smectic phase.

3.3 Nanostructure in thin film

No peaks were observed for the bulk pellet of **PS-*b*-PMS(Stb)** in the small angle region on SAXS profile, suggesting the lack of periodicity in the phase segregated nanostructure. In order to investigate the nanostructure in the thin film of **PS-*b*-PMS(Stb)**, a spin-coat film from toluene solution was fabricated on mica substrate. The thin film was thermally annealed under vacuum for 3 h at 140 °C higher than the isotropic phase transition temperature. As shown in Figure 4, nanofibrils were observed in the thin film, where the side-chain LC polymethylsiloxane domain

Figure 4 TEM images of **PS-*b*-PMS(Stb)** spin-coat films, unstained (a) and stained (b) by RuO_4 . The scale bars are of 500 nm.

should be observed as dark region because of the relative high electron density of Si. The contrast between PS and LC polymethylsiloxane domains in the TEM image were emphasized by staining using RuO_4 . Although the possibility of cylindrical assemblies cannot be excluded, the weight fraction of polysiloxane segment including the LC side chain was calculated to be 55% , which might be reasonable value for exhibiting lamellae structure from the Flory-Huggins theory.

4. CONCLUSION

The LC diblock copolymer **PS-*b*-PMS(Stb)** composed of a polystyrene and a polymethylsiloxane segment tethered by stilbene LC mesogens as the side chains was synthesized by the combination of anionic polymerization and catalytic hydrosilylation with keeping narrow polydispersity. The LC diblock copolymer exhibited smectic LC phase, and gave a lamellae-like nanostructure in the thin films. Although the LC side chains were introduced in aiming to improve the regularity of the phase segregated nanostructure, the bulk sample of the block copolymer showed no periodicity on the SAXS profile.

5. REFERENCES

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