

Photoinduced 3D Ordering and Patterning of Microphase Separated Nanostructure in Polystyrene-Based Block Copolymer

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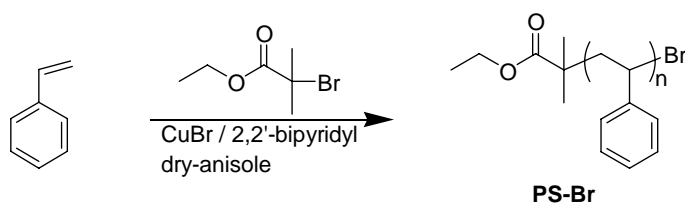
Supporting information

1. Synthesis of diblock copolymer

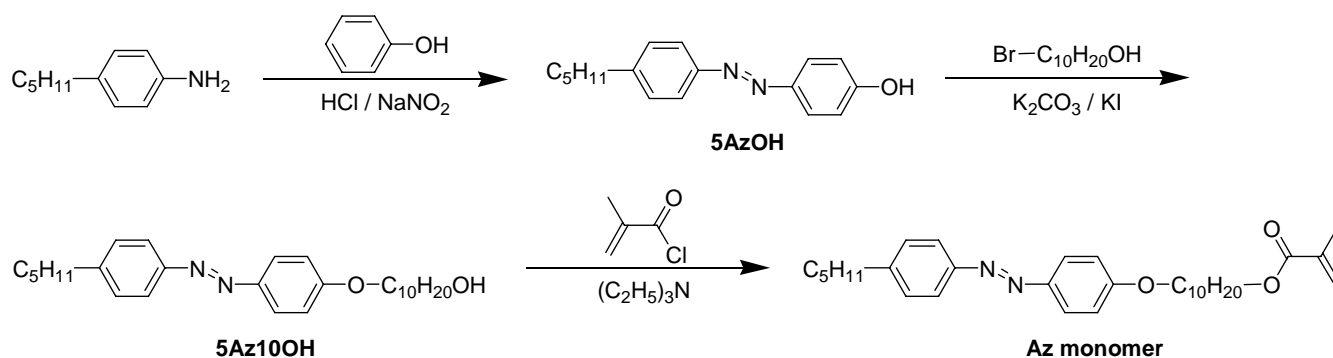
1.1 Materials

N,N'-Dimethyl formamide (DMF) as solvent was dehydrated by distillation from calcium hydride. Anisole and tetrahydrofuran (THF) as solvents was distilled from sodium with benzophenone. Styrene was purified by distillation to remove inhibitor before use. Catalyst CuBr (Kanto Chem. Co., Japan) was washed with acetic acid containing a drop of HCl solution and diethyl ether for several times, and dried in vacuum. Other compounds were used without further purification.

1.2 Preparation of Macroinitiator Polystyrene-Br (PS-Br)



A flask was charged with 7.17 mg of CuBr, degassed and filled with N₂ gas. 3.12 g of styrene, 9.75 mg of 2-bromoisobutyric acid and 78.1 mg of 2,2'-bipyridyl in 1 ml of anisole were degassed, filled with N₂ gas and added through a syringe. The mixture was degassed by freeze-pump-thaw procedure and sealed under vacuum. The flask was placed in oil bath at 110 °C for 11 h. The reaction mixture was dissolved in THF and passed through alumina column to remove Cu catalyst. After being concentrated, The THF solution was poured to methanol to remove styrene monomer. The final product was dried under vacuum. Yield: 350 mg (11.2 %). $M_n = 8000$ and $M_w/M_n = 1.05$ (evaluated by Gel Permeation Chromatography).



1.3.1 Preparation of 4-[(4'-Pentylphenyl) azo] phenol (5AzOH)

solution was stirred for 2 h at 5 °C and 3 h at room temperature. After this solution was neutralized with a diluted hydrochloric acid aqueous solution, the precipitate was filtered off and dissolved in ethyl acetate. The solution was washed with water, sodium bicarbonate aqueous solution and water and NaCl aqueous solution, and then, dried over anhydrous magnesium sulfate. The precipitate was recrystallized from hexane twice to give yellow platelet crystals.

Yield: 24.9 g (60.6 %)

1.3.2 4-(10-Hydroxydecyloxy)-4'-pentylazobenzene (5Az10OH)

Potassium carbonate (25.7 g, 186 mmol) and catalytic amount of potassium iodide were added to 5AzOH (10.0 g, 37.3 mmol) in dry DMF (90ml), and then mixture was stirred for 1 h at 60 °C. 10-Bromodecanol (15.9 g, 67.1 mmol) in dry DMF (10ml) was added dropwise to the solution. The solution was stirred for 4h at 60 °C. The reaction mixture was washed with water, sodium bicarbonate aqueous solution and NaCl aqueous solution, and then, dried over anhydrous magnesium sulfate. The solution was evaporated and separated out a solid. This product was recrystallized from methanol to give yellow solid.

Yield: 15.4 g (81.1 %).

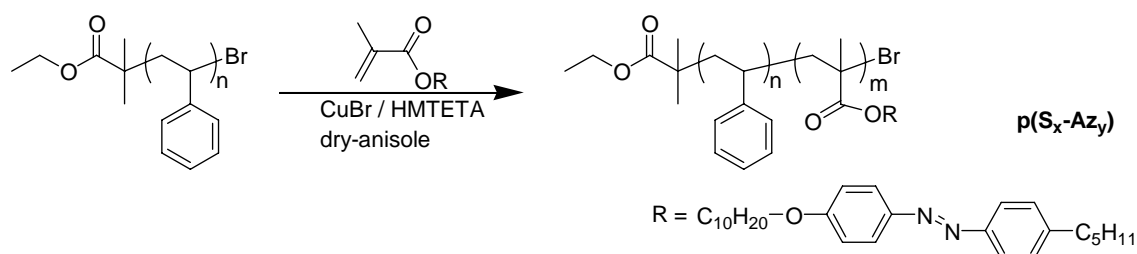
1.3.3 4-(10-Methacroydecyloxy)-4'-pentylazobenzene (Az monomer)

Triethylamine (7.16 g, 70.8 mmol) was added to 5Az10OH (15.0 g, 35.4 mmol) in dry THF solution. A dry THF solution of methacryloyl chloride (7.36 g, 70.8 mmol) was added dropwise to the solution at 0 °C. The mixture was stirred for 30 min at 0 °C and 12 h at room temperature. The

reaction mixture was evaporated, and chloroform was added. The solution was washed with water, sodium bicarbonate aqueous solution and NaCl aqueous solution, and then, dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was recrystallized from methanol. Yellow solid was obtained.

Yield: 10.4 g (60.0 %).

1.4 Preparation of Az-containing diblock copolymer (p(S_x-Az_y))



A 10 ml ampule tube was charged with 37.6 mg of PS-Br, 399 mg of Az monomer, 8.99 mg of HMTETA and 1 ml of THF. After several freeze-pump-thaw cycles, 5.59 mg of CuBr was immediately inserted in the ampule tube. The mixture was degassed by freeze-pump-thaw procedure and sealed under vacuum. The flask was placed in 70 °C oil bath for 17 h. The solution was passed through alumina column with chloroform. The solution was concentrated and precipitated in hexane, methanol and finally in hot hexane (60 °C). The precipitation process in each solvent was repeated twice, respectively. The final product was dried under vacuum. Yield: 70 mg (16.0 %). $M_n = 77000$ and $M_w/M_n = 1.21$ (GPC, **Figure S1**). The ^1NMR chart is shown in **Figure S2**. Thermal phase properties for Az polymer block: $\text{Sm}_X\text{-}90^\circ\text{C-Sm}_A\text{-}118^\circ\text{C-I}$, T_g of polystyrene = 102 °C (DSC chart is indicated in **Figure S3**).

2. Characterizations

Molecular weight and polydispersity were measured by gel permeation chromatography (GPC) using a liquid chromatograph (Shodex UV-41) with an appropriate combination of columns (Shodex KF-803L and Shodex KF-805L). THF was used as eluent, and polystyrene standards were used for calibration. ^1H -NMR spectrum was recorded on a JEOL 270GXS instrument spectrometer (270 MHz). Phase transition temperatures were measured with Seiko Instrument DSC6200/EXSTAR6000 (heating and cooling rates: 10 °C/min).

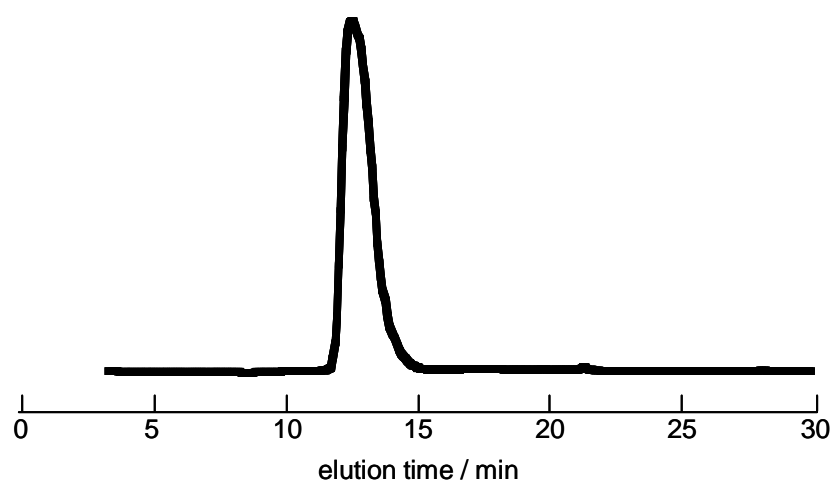


Figure S1. GPC chart of p(S₇₆-Az₁₄₀).

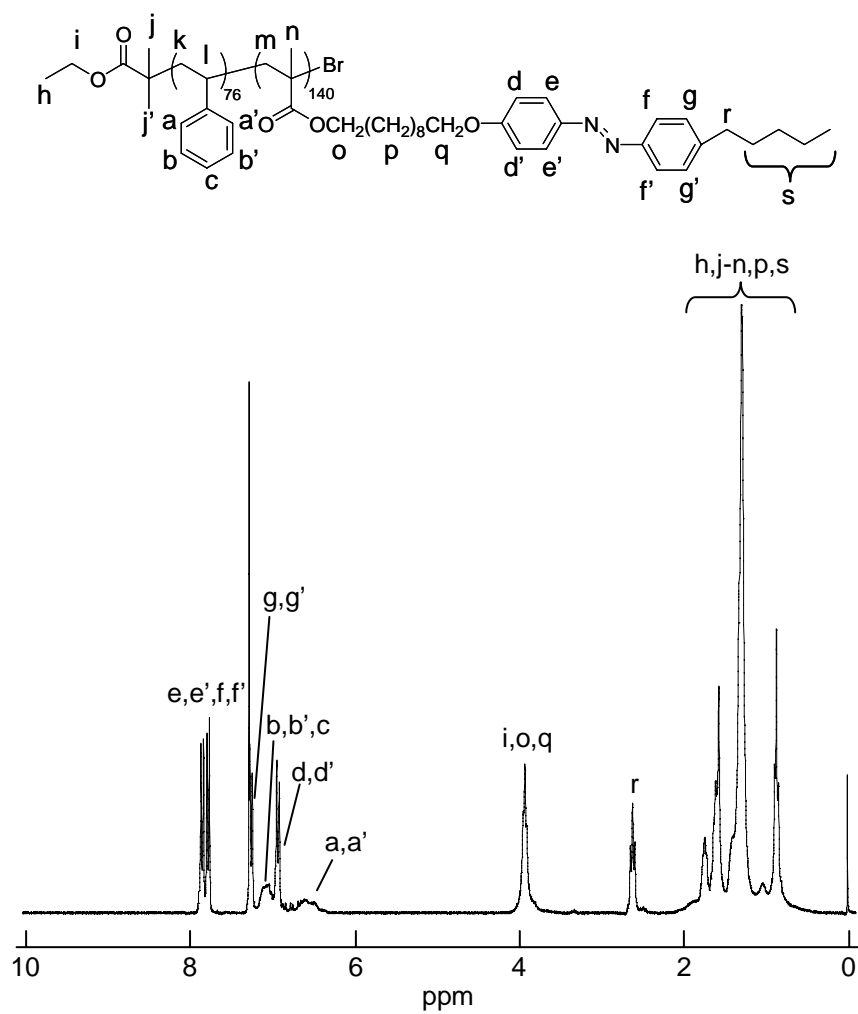


Figure S2. $^1\text{H-NMR}$ spectrum of $p(S_{76}\text{-Az}_{140})$.

Az polymer : glass-43 °C-SmX-90 Sm_X-90 °C-Sm_A-118 °C-Iso
 T_g of PS : 102 °C

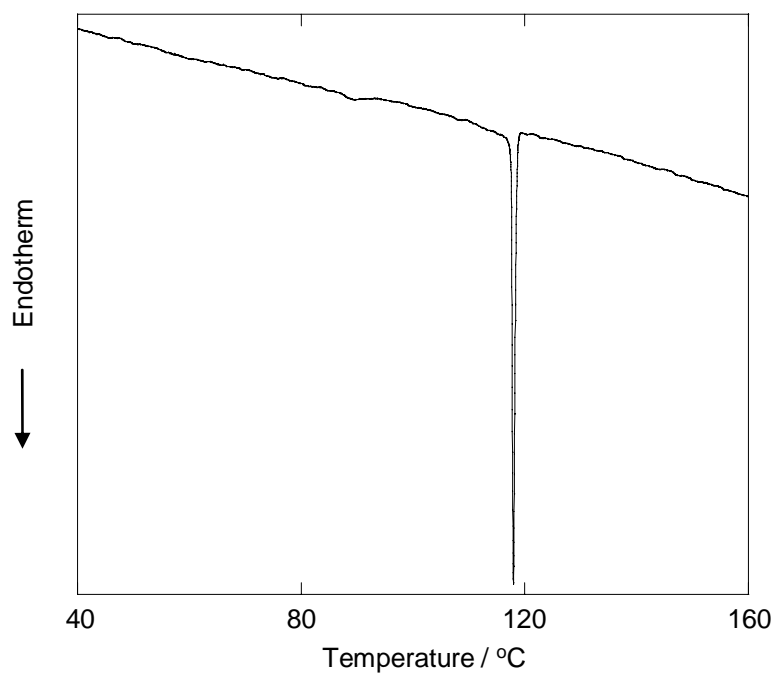


Figure S3. DSC chart of the p(S₇₆-Az₁₄₀) in a heating process.