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Photoinduced Nanoscale Cooperative Motion in a Novel Well-Defined Triblock Copolymer **

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1. Materials and characterization

1.1 Reagent

To get rid of the stabilizer (hydroquinone, 0.005%) in commercially available methyl methacrylate (MMA, 98%), MMA was washed twice with an aqueous solution of sodium hydroxide (5%) and twice with distilled water, then stirred over CaH_2 overnight and distilled under vacuum prior to polymerization. Ethyl 2-bromoisobutyrate (EBriB), triethylamine, methacryloxy chloride, triethylamine, 4-cyano-4'-hydroxybiphenyl, 6-chloro-1-hexanol, N,N-dimethylformamide (DMF), 4-ethoxyaniline and hydroquinone were commercially available (Kanto Chem. Co.) and used without further purification. Anisole and tetrahydrofuran (THF) were purified by distillation from sodium with benzophenone. The ligand, 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Aldrich) was used as received without further purification. The catalyst $\text{Cu}(\text{I})\text{Cl}$ was washed successively with acetic acid and ether, then dried.

1.2 Characterization

¹H NMR spectra were measured using a Lambda-300 spectrometer operating at 300 MHz with tetramethylsilane as an internal reference for chemical shifts. Molecular weights of the polymers were determined by gel permeation chromatography (GPC, JASCO) and referenced against standard polystyrenes with chloroform as eluent. The thermodynamic properties of the monomers and the polymers were analyzed by a differential scanning calorimeter (DSC, Seiko) at a heating and cooling rate of 10 °C/min. At least three scans were performed to check the reproducibility. The LC phases were evaluated with a polarizing optical microscope (POM, Olympus BH-2). The UV-Vis spectra were measured in a chloroform solution using a JASCO V-550 spectrophotometer. Atomic force microscopy (AFM) images of surface modulation in tapping mode were detected with a scanning probe microscope (Veeco Instruments Inc., Nanoscope IV) at room temperature.

2. Synthesis of monomers and block copolymers

2.1 Synthesis of monomers

6-(4-(4-Ethoxyphenylazo)phenoxy)hexyl methacrylate (M6AB2)

As shown in Scheme S1, the monomer M6AB2 was prepared by a diazo-coupling reaction between 4-ethoxyaniline and phenol in the presence of sodium nitrite and hydrochloric acid, followed by a reaction with 6-chloro-1-hexanol and methacryloyl chloride. ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): **d** = 1.17 (t, 3H), 1.36-1.42 (m, 4H), 1.64 (t, 2H), 1.74 (t, 2H), 1.88 (s, 3H), 3.97 (q, 2H), 4.03-4.12 (m, 4H), 5.48 (d, 1H), 6.04 (d, 1H), 6.92 (m, 4H), 7.78 (m, 4H). DSC: m.p. 106 °C. UV-Vis (chloroform): λ_{max} = 360 nm.

6-(4-Cyano-4'-biphenoxy) hexyl methacrylate (M6CB)

M6CB was prepared by a Schotten-Baumann reaction between methacryloyl chloride and (4-cyano-4'-biphenyloxy) hexyl-1-ol. (300 MHz, CDCl₃, 25°C, TMS): **d** =

1.45-1.55 (m, 4H), 1.71 (t, 2H), 1.82 (t, 2H), 1.92 (s, 3H), 3.98 (q, 2H), 4.15 (q, 2H), 5.53 (d, 1H), 6.08 (d, 1H), 6.95 (d, 2H), 7.52 (m, 2H), 7.60-7.68 (m, 4H). DSC: m.p. 74 °C. UV-Vis (chloroform): $\lambda_{\text{max}} = 298 \text{ nm}$.

2.2 Synthesis of block copolymers

The macroinitiator PMMA-Br

Polymerization of macroinitiator PMMA-Br was carried out in a Pyrex tube ampoule. After the monomer (MMA, 15.0 g, 150 mmol), catalyst (Cu(I)Cl (0.099 g, 1.0 mmol), ligand (HMTETA, 0.23 g, 1.0 mmol) and initiator (EBrIB, 0.195 g, 1.0 mmol) were added under the protection of argon, the mixture was degassed by three freeze-pump-thaw cycles and sealed under vacuum, then stirred for 30 min at room temperature. The reaction was carried out in a preheated oil bath at 100 °C. After 20 min, the reaction mixture was cooled in cold water because of a large amount of heat released in the bulk polymerization. Then the solid product was dissolved in THF and passed through a silica gel column to remove the catalyst, and the solvent was removed. The PMMA-Br was precipitated by pouring the concentrated solution into a large excess of methanol. Finally, the product was dried under vacuum until reaching constant weight. Polymer yield (7.2 g, 47%) was determined by gravimetry. The number-average molecular weight, M_n (GPC), and the polydispersity index (M_w/M_n) were 16,000 and 1.17, respectively. The glass-transition temperature (T_g , DSC) of 120 °C was obtained.

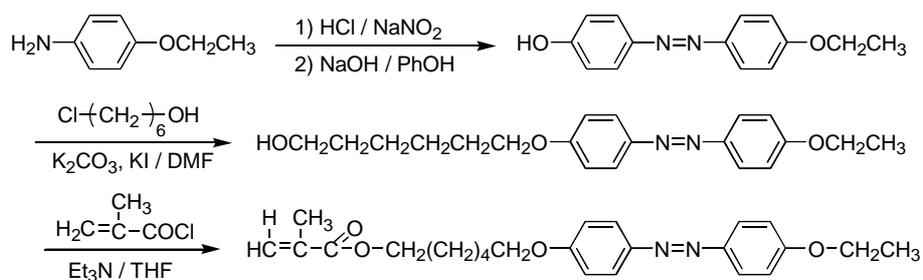
The diblock copolymer PMMA-*b*-PM6CB

PMMA-Br (1.6 g, 0.1 mmol), Cu(I)Cl (9.9 mg, 0.1 mmol), and M6CB (2.46 g, 7.0 mmol) were mixed in a 50 mL ampule, degassed and filled with argon. HMTETA (23.0 mg, 0.1 mmol) in anisole (30.0 mL) was added. The mixture was degassed by three freeze-pump-thaw cycles and sealed under vacuum, placed in an oil bath preheated at 80 °C for 24 h. Then the solution was passed through a column (silica gel)

with THF as eluent and the filtrate was precipitated into hot methanol (60 °C). The copolymer was collected and dried. Yield: 1.9 g (52%). Mn (GPC) = 28,200, Mw/Mn = 1.15. Tg = 122 °C. No liquid-crystalline (LC) phase transition peak was obtained and no LC texture was observed under POM (20-200 °C).

The triblock copolymer PMMA-*b*-PM6CB-*b*-PM6AB2

The triblock copolymer was prepared using the obtained diblock copolymer and M6AB2 as a macroinitiator and a monomer, respectively, by the procedure similar to that describe above for the preparation of diblock copolymer. Yield: 0.6 g (73%). Mn (GPC) = 30,400, Mw/Mn = 1.11. Tg = 118 °C. No liquid-crystalline (LC) phase transition peak was obtained and no LC texture was observed under POM (20-200 °C).



Scheme S1. Synthetic route of the monomer M6AB2.

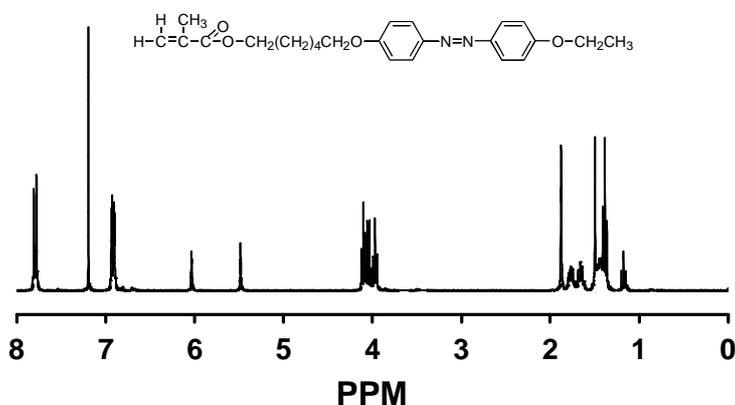


Figure S1. ^1H NMR of monomer M6AB2.

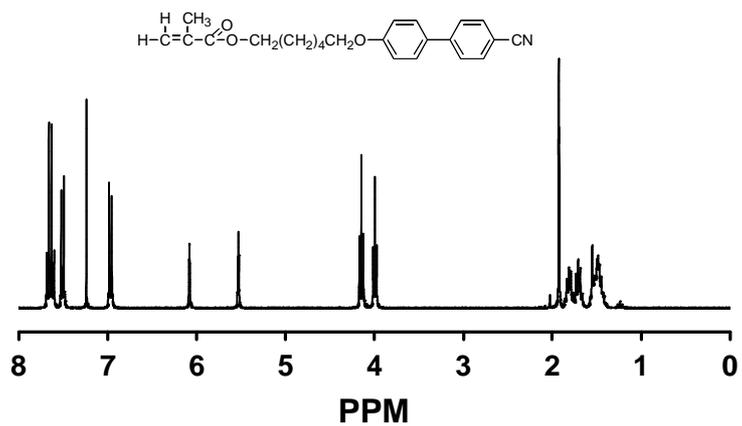


Figure S2. ^1H NMR of monomer M6CB.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

1 cm

Figure S3. Photograph of a triblock copolymer film with 200- μm thickness.