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Synthesis of Well-defined Mechanochromic Polymers Based on a Radical-Type Mechanochromophore by RAFT Polymerization:Living Radical Polymerization from a Polymerization Inhibitor

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Experimental Section

Materials. All solvents and reagents were purchased from Sigma-Aldrich, FUJIFILM Wako Pure Chemical Corporation, Tokyo Chemical Industry, and Kanto Chemical, and used as received unless otherwise noted. DABBF-diol was synthesized according to the previous report.¹ Methyl acrylate (MA), Methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), hexyl methacrylate (HMA), styrene (St), di(ethylene glycol) methacrylate (DEGMA), and 2-hydroxyethyl methacrylate (HEMA) were passed through basic alumina column (Merck KGaA) to remove inhibitors prior to use. *N*-isopropylacrylamide (NIPAM) was recrystallized in hexane prior to use.

Instruments and Measurements. ¹H NMR spectroscopic measurements were carried out at 25 °C using Bruker AVANCE III HD500 spectrometer (500MHz) in chloroform-*d* (CDCl₃) with tetramethylsilane (TMS) as internal standard and DMSO*d*₆. The LED method for DOSY measurement was used. Pulse program: ledbpgp2s, diffusion time: 40 ms, diffusion gradient length: 2000 us, maximum gradient strength: 51 g/cm.² Gel permeation chromatography (GPC) measurements in tetrahydrofuran (THF) were carried out at 40 °C on TOSOH HLC-8320 GPC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), a differential refractive index detector, and a UV-vis detector. THF was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene (PS) standards were used to calibrate the GPC system. GPC measurements in dimethylformamide were carried out at 30 °C on JASCO HSS-1500 system equipped with a two columns (TOSO TSK gel G2000HXL and GMHXL), a differential refractive index detector, and a UV-vis detector. DMF containing 0.01 M LiBr was used as the eluent at a flow rate of 0.85 mL/min. PS standards were used to calibrate the GPC system. FT-IR spectroscopic measurement was recorded on a JASCO FT/IR-4100 with a KBr or NaCl plate. UV-Vis absorption measurement was recorded on a JASCO V-650 with CHCl₃ or solid state.

Grinding tests. Grinding tests were performed on a Retsch Mixer Mill MM 400. The applied force was controlled by vibrational frequency and grinding time. A powdered sample (50 mg) was placed in the grinding jar and ground for 10 min at 30 Hz.

Electron paramagnetic resonance (EPR) spectroscopy. EPR measurements were carried out on a JEOL JES-X₃20 Xband ESR spectrometer equipped with a JEOL DVT temperature controller. The powder sample was transferred into an EPR glass capillary, weighed, and the capillary was sealed after being degassed. The spectra of ground samples were measured using a microwave power of 0.05 or 0.1 mW and a field modulation of 0.2 mT with a time constant of 0.03 s and a sweep rate of 0.125 mT/s at 25 °C. The concentration of the radicals formed from the cleavage of **DABBF-based polymers** was determined by comparing the area of the observed integral spectrum with a 0.01 mM solution of 4-hydroxy-2,2,6,6tetramethylpiperidin-1-oxyl (TEMPOL) in benzene under the same experimental conditions. The *g* value was calculated according to the following equation: $g = hv/\beta$ H where *h* is the Planck constant, *v* is the microwave frequency, β is the Bohr magneton and H is the magnetic field.

Synthetic Procedure

Synthesis of PMMA by free radical polymerization. MMA ($_{314}$ mg, $_{3.14}$ mmol) and $_{2,2}$ '-azobis(isobutyronitrile) (AIBN) (1.03 mg, 6.27 µmol) were added to a test tube. Then, freeze-pump-thaw was carried out three times and the test tube was filled with nitrogen, after that the solution was heated at 70 °C. After 2.5 h, the reaction was stopped by cooling. To dilute the solution, chloroform was added to the test tube and the reaction mixture was precipitated in ice-cold methanol. The resulting white solid was filtered, dried under vacuum. M_n and PDI values were determined by analytical GPC with polystyrene standards in THF. $M_n = 64$ 000, PDI = 2.53.

Synthesis of PMMA by free radical polymerization in the presence of DABBF-diol. MMA ($_{314}$ mg, $_{3.14}$ mmol), AIBN ($_{1.03}$ mg, $_{6.27}$ µmol), and DABBF-diol ($_{50.6}$ mg, $_{6.39}$ µmol) were added to a test tube. Then, freeze-pump-thaw was carried out three times and the test tube was filled with nitrogen, after that the solution was heated at 70 °C. After 8 h, the reaction was stopped by cooling. To dilute the solution, chloroform was added to the test tube and the reaction mixture was precipitated in ice-cold methanol. The resulting white solid was filtered, dried under vacuum. M_n and PDI values were determined by analytical GPC with polystyrene standards in THF. $M_n = 177$ 000, PDI = 2.31.

Synthesis of PMMA by RAFT Polymerization in the presence of DABBF-diol. MMA (1.24 g, 12.4 mmol), AIBN (1.58 mg, 9.62 µmol), 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid (10.0 mg, 24.8 µmol), and DABBF-diol (9.81 mg, 12.4 µmol) were added to a test tube. Then, freeze-pump-thaw was carried out three times and the test tube was filled with nitrogen, after that the solution was heated at 70 °C. After 6.5 h, the reaction was stopped by cooling. To dilute the solution, chloroform was added to the test tube and the reaction mixture was precipitated in ice-cold methanol. The resulting white solid was filtered, dried under vacuum. M_n and PDI values were determined by analytical GPC with polystyrene standards in THF. $M_n = 19$ 000, PDI = 1.12.

Synthesis of DABBF-based CTA. 4-Cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid (3.49 g, 8.65 mmol), *N*,*N*'-diisopropylcarbodiimide (DIC) (1.09 g, 8,64 mmol), **DABBF-diol** (2.30 g, 2.91 mmol), 4-dimethylaminopyridine (70.1 mg, 0.574 mmol), and chloroform (70.0 mL) were added to a 100 mL round-bottomed flask. The reaction mixture was stirred at room temperature for 24 h. After concentrating the reaction solution, hexane was added, and the by-product derived from the precipitated DIC was removed by filtration. After concentrating the crude product was purified twice by column chromatography on silica gel using hexane/ethyl acetate (4/1 and 3/1), and dried in vacuo to give 1.54 g **DABBF-based CTA** (0.99 mmol, 34%) as yellow amorphous solid. 'H NMR (500 MHz, CDCl₃): δ / ppm 0.88 (t, *J* = 6.94, 6H, CH₃), 1.17–1.40 (m, 52H, CH₂/CH₃), 1.87 (d, *J* = 4.58, 6H, CH₃), 2.34–2.54 (m, 4H, CH₂) 2.64 (m, 4H, CH₂) 3.32 (t, *J* = 6.67, 4H, CH₂), 4.06 (m, 4H, CH₂), 4.31 (t, *J* = 6.29, 4H, CH₂), 7.29 (brs, 12H, aromatic proton) ;¹³C NMR (125 MHz, CDCl₃) : δ / ppm 216.91, 171.47, 158.75, 149.11, 133.50, 132.38, 132.30, 132.15, 118.99, 113.12, 64.14, 61.98, 61.91, 50.90, 46.30, 37.04, 34.69, 34.35, 33.81, 31.90, 31.54, 29.73, 29.62, 29.54, 29.42, 29.34, 29.07, 28.92, 28.45, 27.65, 24.88, 22.69, 14.28, 14.22, 14.20, 14.15 ; FT-IR (NaCl, cm⁻¹) : 3583, 2925, 1796, 1739, 1510, 1255, 1185, 1088, 800, 714, 430; FAB-MS (m/z): calcd for C₈₈H₁₂₄N₂O₁₀S₆Na, 1583.7478; found, 1583.7443.

General procedure of RAFT polymerization using DABBF-based CTA. Synthesis of PMMA-CTA (PMMA5-CTA): MMA (3.40 g, 34.0 mmol), AIBN (3.41 mg, 20.8 µmol), and DABBF-based CTA (105 mg, 67.2 µmol) were added to a test tube. Then, freeze-pump-thaw was carried out three times and the test tube was filled with nitrogen, after that the solution was heated at 70 °C. After 13 h, the reaction was stopped by cooling. To dilute the solution, chloroform was added to the test tube and the reaction mixture was precipitated in ice-cold methanol. The resulting yellow solid was filtered, dried under vacuum. M_n and PDI values were determined by analytical GPC with polystyrene standards in THF. $M_n = 30$ 600, PDI = 1.19. ¹H NMR (500 MHz, CDCl₃): δ / ppm 0.84–1.25 (m, 3H, CH₃), 1.81–1.95 (m, 2H, CH₂), 3.60 (br, 3H, CH₃). In a similar manner, PMMA-CTA with different molecular weight were synthesized.

PEMA-CTA, **PBMA-CTA**, and **PHMA-CTA** were synthesized in the similar manners as PMMA-CTA. **PEMA-CTA**; [EMA] : [AIBN] : [**DABBF-based CTA**] = 499 : 0.332 : 1 [mol], 70 °C, 20 h, M_n = 47 800, PDI = 1.14. **PBMA-CTA**; [BMA] : [AIBN] : [**DABBF-based CTA**] = 501 : 0.328 : 1 [mol], 70 °C, 27 h, M_n = 27 700, PDI = 1.14. **PHMA-CTA**; [HMA] : [AIBN] : [**DABBF-based CTA**] = 499 : 0.328 : 1 [mol], 70 °C, 27 h, M_n = 19 600, PDI = 1.23.

PEMA-CTA; ¹H NMR (500 MHz, CDCl₃): δ / ppm 0.89-1.04 (m, 3H, CH₃), 1.25-1.27 (m, 3H, CH₃), 1.82-2.05 (m, 2H, CH₂), 4.04 (m, 2H, CH₂). **PBMA-CTA**; ¹H NMR (500 MHz, CDCl₃): δ / ppm 0.87-1.03 (m, 6H, CH₃), 1.40 (br, 2H, CH₂), 1.61 (m, 2H, CH₂), 1.81-2.01 (m, 2H, CH₂), 4.04 (m, 2H, CH₂). **PHMA-CTA**; ¹H NMR (500 MHz, CDCl₃): δ / ppm 0.81-1.03 (m, 6H, CH₃), 1.25-1.61 (m, 8H, CH₂), 1.80-1.95 (m, 2H, CH₂), 3.92 (br, 2H, CH₂).

Synthesis of PS-CTA by RAFT Polymerization. Styrene (0.958 g, 9.20 mmol), AIBN (0.755 mg, 4.60 µmol), and DABBFbased CTA (17.8 mg, 11.4 µmol) were added to a test tube. Then, freeze-pump-thaw was carried out three times and the test tube was filled with nitrogen, after that the solution was heated at 70 °C. After 20 h, the reaction was stopped by cooling. To dilute the solution, methanol was added to the test tube and the reaction mixture was precipitated in ice-cold hexane. The resulting yellow solid was filtered, dried under vacuum. M_n and PDI values were determined by analytical GPC with polystyrene standards in THF. $M_n = 6$ 000, PDI = 1.17. ¹H NMR (500 MHz, DMSO- d_6): δ / ppm 1.06–1.80 (m, 2H, CH₂), 1.87– 2.10 (m, H, CH), 6.58 (m, 2H, CH₂), 7.05–7.12 (m, 2H, CH₂).

Synthesis of PDEGMA-CTA by RAFT Polymerization. DEGMA (1.10 g, 5.84 mmol), AIBN (0.420 mg, 2.56 µmol), and **DABBF-based CTA** (18.1 mg, 11.7 µmol) were added to a test tube. Then, freeze-pump-thaw was carried out three times and the test tube was filled with nitrogen, after that the solution was heated at 60 °C. After 20 h, the reaction was stopped by cooling. To dilute the solution, methanol was added to the test tube and the reaction mixture was precipitated in ice-cold hexane. The resulting yellow solid was filtered, dried under vacuum. M_n and PDI values were determined by analytical GPC with polystyrene standards in THF. M_n = 10 700, PDI = 1.47. ¹H NMR (500 MHz, DMSO- d_6): δ / ppm 0.78–0.95 (m, 3H, CH₃), 1.24-1.87 (m, 2H, CH₂), 3.27 (br, 3H, CH₃), 3.46 (br, 2H, CH₂), 3.54 (br, 2H, CH₂), 3.60 (br, 2H, CH₂), 4.01 (br, 2H, CH₂).

Synthesis of PHEMA-CTA by RAFT Polymerization. HEMA (803 mg, 6.17 mmol), AIBN (0.410 mg, 2.50 µmol), DABBFbased CTA (9.50 mg, 6.08 µmol), and THF (250 µL) were added to a test tube. Then, freeze-pump-thaw was carried out three times and the test tube was filled with nitrogen, after that the solution was heated at 70 °C. After 20 h, the reaction was stopped by cooling. To dilute the solution, methanol was added to the test tube and the reaction mixture was precipitated in ice-cold hexane. The resulting yellow solid was filtered, dried under vacuum. M_n and PDI values were determined by analytical GPC with polystyrene standards in DMF. $M_n = 99$ 000, PDI = 1.24. 'H NMR (500 MHz, DMSO- d_6): δ / ppm 0.77-0.94 (m, 3H, CH₃), 1.78-1.98 (m, 2H, CH₂), 3.57 (br, 2H, CH₂), 3.89 (br, 2H, CH₂), 4.83 (s, 1H, OH).

RAFT Polymerization of MA. (Entry 13) MA (1.34 g, 15.6 mmol), AIBN (0.870 mg, 5.30 µmol), and **DABBF-based CTA** (30.2 mg, 19.5 µmol) were added to a test tube. Then, freeze-pump-thaw was carried out three times and the test tube was filled with nitrogen, after that the solution was heated at 70 °C. After 13 h, the reaction was stopped by cooling. To dilute the solution, chloroform was added to the test tube and the reaction mixture was precipitated in ice-cold methanol. The resulting yellow solid was filtered, dried under vacuum.

RAFT Polymerization of NIPAM. NIPAM (2.90 g, 25.6 mmol), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (0.800 mg, 2.59 µmol), **DABBF-based CTA** (39.8 mg, 25.5 µmol), and DMF (5 mL) were added to a test tube. Then, freeze-pump-thaw was carried out three times and the test tube was filled with nitrogen, after that the solution was heated at room temperature. After 24 h, the reaction was stopped by cooling.

Evaluation of living properties of polymerization. A stock solution of MMA (2.21 g, 22.1 mmol), AIBN (2.08 mg, 12.7 μ mol), and **DABBF-based CTA** (68.2 mg, 43.7 μ mol) were prepared. Aliquots (0.5 mL) were transferred to four test tubes. Then, freeze-pump-thaw was carried out three times and the test tubes were filled with nitrogen, after that the solution was heated at 70 °C for 8 h, 10 h, 12 h, and 18 h. The reaction was stopped by cooling. The conversion were determined by 'H NMR spectra of a portion of the polymerization mixture in CDCl₃. M_n and PDI were determined by GPC profiles.

Transformation of PMMA-CTA to PMMA-SH. PMMA5-CTA (1.10 g, 35.9 mmol, M_n = 30 600, PDI = 1.19), propylamine (112 mg, 1.89 mmol), tributylphosphine (76.7 mg, 0.379 mmol), and degassed THF (5 mL) were add to a Schlenk flask. The reaction mixture was stirred at room temperature for 5 h under nitrogen. After concentrating the solution was precipitated in ice-cold methanol. The resulting white solid was filtered, dried under vacuum to get 0.97 g polymer. ¹H NMR (500 MHz, CDCl₃): δ / ppm 0.85–1.22 (m, 3H, CH₃), 1.81–1.95 (m, 2H, CH₂), 3.60 (br, 3H, CH₃).

Transformation of PMMA-SH to PMMA-T. PMMA5-SH (300 mg, 9.80 µmol, M_n = 30 600, PDI = 1.19), phenyl isocyanate (22.6 µL, 0.207 mmol), triethylamine (57.7 µL, 0.414 mmol), and degassed THF (3 mL) were add to schlenk flask. The reaction mixture was stirred at room temperature for 22 h under nitrogen. After concentrating the solution was precipitated in icecold methanol. The resulting white solid was filtered, dried under vacuum to get 227 mg polymer. ¹H NMR (500 MHz, CDCl₃): δ / ppm 0.83–1.22 (m, 3H, CH₃), 1.81–1.95 (m, 2H, CH₂), 3.60 (br, 3H, CH₃).

Synthesis of PMMA-b-PHMA-b-PMMA-CTA. MMA (3.40 g, 34.0 mmol), AIBN (3.41 mg, 20.8 µmol), and **PHMA1-CTA** (105 mg, 23.9 µmol) were added to a test tube. Then, freeze-pump-thaw was carried out three times and the test tube was filled with nitrogen, after that the solution was heated at 70 °C. After 7 h, the reaction was stopped by cooling. To dilute the solution, chloroform was added to the test tube and the reaction mixture was precipitated in ice-cold methanol. The resulting yellow solid was filtered, dried under vacuum. M_n and PDI values were determined by analytical GPC with polystyrene standards in THF. M_n = 38 000, PDI = 1.21. ¹H NMR (500 MHz, CDCl₃): δ / ppm 0.85–1.25 (m, 3H, CH₃), 1.81–1.99 (m, 2H, CH₂), 3.60 (br, 3H, CH₃).



Figure S1. 'H NMR spectrum of DABBF-based CTA (500 MHz, CDCl₃, 298 k).



Figure S2. ¹³C NMR spectrum of DABBF-based CTA (125 MHz, CDCl₃, 298 k).



Figure S3. GPC profiles of obtained polymers in Table 1 (eluent, THF or DMF for PHEMA-CTA).



Figure S4. GPC profile of PMA-CTA in Table 1 (eluent, THF).



Figure S5. DOSY spectrum of PMMA1-CTA ($M_n = 10500$), (500 MHz, CDCl₃, 298 k).



Figure S6. (a) MALDI-TOF MS spectrum of PMMA1-CTA (M_n = 3 400) and (b) the extended figure in the chemical shift range from 1550 to 2150 m/z. Since the polymer containing the DABBF moiety is detected in the state where the central C-C bond cleaves and that sodium is added in the MALDI-TOF mass spectroscopy, the theoretical m/z was calculated based on this cleaved structure.



Figure S₇. 'H NMR spectra of the polymerization of MMA in the presence of DABBF-based CTA.

(500 MHz, CDCl₃, 298 k)



Figure S8. GPC profiles of the polymerization of MMA in the presence of DABBF-based CTA (eluent, THF).



Figure S9. (a) GPC profiles of PHMA1-CTA (red) and PMMA-*b*-PHMA-*b*-PMMA-CTA (blue) (eluent, THF) and (b) 'H NMR spectrum of PMMA-*b*-PHMA-*b*-PMMA-CTA (500 MHz, CDCl₃, 298 k).



Figure S10. DOSY spectrum of PMMA-*b*-PHMA-*b*-PMMA-CTA. (500 MHz, CDCl₃, 298 k)



Figure S1. (a) ¹H NMR spectra of PMMA3-SH ($M_n = 14300$) (black) and PMMA3-CTA ($M_n = 14300$) (blue) in the chemical shift range from 2.7 to 3.7 ppm (500 MHz, CDCl₃, 298 k) and (b) UV-vis spectra recorded between 250 and 400 nm for PMMA5-CTA ($M_n = 30600$) (blue) and PMMA5-SH ($M_n = 30600$) (black) (1 mg·mL⁻¹, in CHCl₃).



Figure S12. ¹H NMR spectra of PMMA3-SH (M_n = 14 300) (blue) and PMMA3-T (M_n = 14 300) (black) in the chemical shift range from 7.1 to 7.9 ppm (500 MHz, CDCl₃, 298 k).



Figure S13. GPC profiles of PMMA-CTA, PMMA-SH, and PMMA-T (eluent, THF).



Figure S14. Photographs of PMMA5-T (M_n = 30 600) after a grinding test and solvent addition (THF).



Figure S15. EPR spectra of PMMA4-T and PMMA4-SH ($M_n = 22 000$) before and after grinding.



Figure S16. EPR spectra of DABBF-diol before and after grinding.¹



Figure S17. DSC profile of PMMA₄-T.



Figure S18. EPR spectra of PMMA-b-PHMA-b-PMMA-T before and after grinding.

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