Supporting Information

Bottlebrush Polymer-Reinforced Transparent Multiphase Plastics

Yoshihiro Yamauchi*, Sadaki Samitsu, Kenta Goto, Masayuki Takeuchi

*To whom correspondence should be addressed. E-mail: YAMAUCHI.Yoshihiro@nims.go.jp

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Materials and Methods

1. Materials

Unless otherwise noted, chemicals were used as received from Sigma-Aldrich [2bromoisobutyryl bromide (98%), 3-bromopyridine (99%), Grubbs catalyst (second generation), and anisole (99.7%)], Tokyo Chemical Industry [ethyl vinyl ether (98%) and N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA; 99%)], and Wako Pure Chemical Industries [CuCl₂ (95%), deoxidized dichloromethane (99%), ethanol (99.5%), and methanol (99.8%)]. Diethyl ether and tetrahydrofuran (THF) were purchased from Wako Pure Chemical Industries and dried by passing through an activated alumina column (Innovative Technology, Inc., PureSolv). CDCl₃ (99.8%) was purchased from Cambridge Isotope Laboratories. The third-generation Grubbs catalyst was prepared from the second-generation Grubbs catalyst as previously described.^[S1] CuCl (Wako Pure Chemical Industries) was sequentially washed with glacial acetic acid, ethanol, and diethyl ether, filtered, and dried under vacuum before use. n-Butyl acrylate and t-butyl methacrylate were purchased from Tokyo Chemical Industry and passed through a basic alumina column before use. 2-endo,3-endo-Bis(2-bromoisobutyryloxymethyl)-5norbornene was synthesized as previously reported by one of us.^[S2] The epoxy resin used to embed plastic samples was purchased from Struers (SpeciFix-40). Polishing suspensions (microcrystalline diamond suspensions MetaDi 9 µm and MetaDi 3 µm; colloidal silica suspension MasterMet), water-resistant abrasive paper (CarbiMet 320), and polishing buffs (TriDent, VerduTex, and MasterTex) were purchased from Buehler.

2. General remarks

¹H NMR spectra were recorded on a JEOL JNM-ECS400 spectrometer. Chemical shifts are given in ppm downfield from the signal of the internal standard, tetramethylsilane. Analytical SEC was performed at 40 °C on a TOSOH HLC-8320GPC system equipped with a refractive index detector and two linearly connected polystyrene gel columns (TSKgel SuperMultiporeHZ-M, TOSOH) using THF as the eluent at a flow rate of 0.35 mL min⁻¹. Polystyrene standards (SM-105, Shodex) were used for calibration. Photoinduced radical polymerization was conducted using a xenon short-arc lamp (500 W, OPM2-502H, USHIO).

3. Synthesis of the polymers

Poly[2-endo,3-endo-bis(2-bromoisobutyryloxymethyl)-5-norbornene] (NB): P1, P2, and **P3** were synthesized by ring-opening metathesis polymerization of **NB** at 25 °C in a vacuum-type glovebox (MDB-1KP-LRMH2, MIWA) filled with nitrogen as reported previously by one of us.^[S2] The conversion was calculated based on the consumption of **NB**, which was monitored by ¹H NMR spectroscopy.

P1: A stirred CH_2Cl_2 solution (1.0 mL) of the third-generation Grubbs catalyst (10.0 mg, 11.3 µmol) was treated with a CH_2Cl_2 solution (0.60 mL) of **NB** (256 mg, 566 µmol), stirred for 15 min, treated with ethyl vinyl ether (0.20 mL, 2.1 mmol), and stirred for 30 min. The resulting mixture was diluted with CH_2Cl_2 and added to methanol. The formed precipitate was collected by centrifugation and dried under reduced pressure to furnish **P1** as a white solid (230 mg). Conversion exceeded 99%.

SEC (THF, 40 °C): $M_n = 1.4 \times 10^4$, $M_w = 1.5 \times 10^4$, $M_w/M_n = 1.07$.

P2: A stirred CH_2Cl_2 solution (1.6 mL) of the third-generation Grubbs catalyst (4.0 mg, 4.5 µmol) was treated with a CH_2Cl_2 solution (0.80 mL) of **NB** (409 mg, 905 µmol), stirred for 15 min, treated with ethyl vinyl ether (0.20 mL, 2.1 mmol), and stirred for 30 min. The resulting mixture was diluted with CH_2Cl_2 and added to methanol. The formed precipitate was collected by centrifugation and dried under reduced pressure to yield **P2** as a white solid (352 mg). Conversion exceeded 99%.

SEC (THF, 40 °C): $M_n = 4.7 \times 10^4$, $M_w = 4.9 \times 10^4$, $M_w/M_n = 1.04$.

P3: A stirred CH_2Cl_2 solution (0.2 mL) of the third-generation Grubbs catalyst (0.50 mg, 0.56 µmol) was treated with a CH_2Cl_2 solution (0.30 mL) of **NB** (153.2 mg, 338.8 µmol), stirred for 15 min, treated with ethyl vinyl ether (0.20 mL, 2.1 mmol), and stirred for 30 min. The resulting mixture was diluted with CH_2Cl_2 and added to methanol. The formed precipitate was collected by centrifugation and dried under reduced pressure to furnish **P3** as a white solid (139 mg). Conversion exceeded 99%.

SEC (THF, 40 °C): $M_n = 1.7 \times 10^5$, $M_w = 1.8 \times 10^4$, $M_w/M_n = 1.05$.

BP1: An anisole solution (12 mL) of **P1** (92 mg) and *n*-butyl acrylate (42 mL, 36 mmol) was degassed by bubbling with argon for 30 min. The mixture was treated with CuBr₂ (4.4 mg, 20 μ mol) and CuBr (57.4 mg, 400 μ mol), stirred for 10 min, treated with PMDETA (92 μ L, 440 μ mol), and stirred at 70 °C for 18 h. The resulting mixture was exposed to air and added to methanol (500 mL). The obtained precipitate was purified by dissolution in chloroform and precipitation from methanol (5 cycles). The purified residue was dried under reduced pressure to yield **BP1** as a wax (2.62 g).

SEC (THF, 40 °C): $M_n = 3.2 \times 10^5$, $M_w = 3.8 \times 10^4$, $M_w/M_n = 1.20$.

BP2: An anisole solution (12 mL) of **P2** (92 mg) and *n*-butyl acrylate (42 mL, 36 mmol) was degassed by bubbling with argon for 30 min. The mixture was treated with CuBr₂ (4.4 mg, 20 µmol) and CuBr (57.4 mg, 400 µmol), stirred for 10 min, treated with PMDETA (92 µL, 440 µmol), and stirred at 70 °C for 15 h. The resulting mixture was exposed to air and added to methanol (500 mL). The formed precipitate was purified by dissolution in chloroform and precipitation from methanol (5 cycles). The purified residue was dried under reduced pressure to yield **BP2** as a wax (2.11 g). SEC (THF, 40 °C): $M_n = 5.9 \times 10^5$, $M_w = 7.5 \times 10^4$, $M_w/M_n = 1.27$.

BP3: An anisole solution (12 mL) of **P3** (92 mg) and *n*-butyl acrylate (42 mL, 36 mmol) was degassed by bubbling with argon for 30 min. The mixture was treated with CuBr₂ (4.4 mg, 20 µmol) and CuBr (57.4 mg, 400 µmol), stirred for 10 min, treated with PMDETA (92 µL, 440 µmol), and stirred at 70 °C for 18 h. The resulting mixture was exposed to air and added to methanol (500 mL). The formed precipitate was purified by dissolution in chloroform and precipitation from methanol (5 cycles). The purified residue was concentrated to dryness under reduced pressure to yield **BP3** as a wax (2.39 g). SEC (THF, 40 °C): $M_n = 1.1 \times 10^6$, $M_w = 1.3 \times 10^4$, $M_w/M_n = 1.21$.

Cleavage of the BP1 side chains: A solution of BP1 (28 mg) in 1,4-dioxane (3.0 mL) and *n*-BuOH (3.0 mL) was treated with aqueous HCl (12 M, 20 μ L) and stirred at reflux for 384 h. The resulting mixture was cooled to room temperature and concentrated to dryness under reduced pressure. The residue, containing poly(*n*-butyl acrylate) derived from the side chains of BP1, was dissolved in THF (5.0 mL) and subjected to analytical SEC.

SEC (THF, 40 °C): $M_n = 1.2 \times 10^4$, $M_n/M_w = 1.09$.

Cleavage of the BP2 side chains: The side chains of BP2 were cleaved in a similar manner as BP1.

SEC (THF, 40 °C): $M_{\rm n} = 1.3 \times 10^4$, $M_{\rm n}/M_{\rm w} = 1.10$.

Cleavage of the BP3 side chains: The side chains of BP3 were cleaved in a similar manner as BP1.

SEC (THF, 40 °C): $M_{\rm n} = 1.1 \times 10^4$, $M_{\rm n}/M_{\rm w} = 1.08$.

4. Preparation of the plastics

Preparation of plastic without filler: 2-Hydroxy-2-methylpropiophenone (20 μ L, 113 μ mol) was mixed with *t*-butyl methacrylate (2.3 mL, 14.0 mmol) at 25 °C. The solution was irradiated with a xenon arc lamp, whereupon radical polymerization proceeded nearly quantitatively within 1 h to afford the filler-free plastic.

Preparation of plastic filled with 4 wt% BP1: **BP1** (90 mg) was dispersed in *t*-butyl methacrylate (2.3 mL, 14.0 mmol) at room temperature, and the solution was treated with 2-hydroxy-2-methylpropiophenone (20 μ L, 113 μ mol). The reaction mixture was stirred at room temperature for 24 h and irradiated with a xenon arc lamp, whereupon radical polymerization proceeded nearly quantitatively within 1 h to afford the desired plastic.

Preparation of plastic filled with 10 wt% BP1: **BP1** (226 mg) was dispersed in *t*-butyl methacrylate (2.3 mL, 14.0 mmol) at room temperature, and the solution was treated with 2-hydroxy-2-methylpropiophenone (20 μ L, 113 μ mol). The plastic was prepared in a similar manner as the plastic filled with 4 wt% **BP1**.

Preparation of plastic filled with 4 wt% BP2: The plastic was prepared in a similar manner as the plastic filled with 4 wt% **BP1**.

Preparation of plastic filled with 10 wt% BP2: The plastic was prepared in a similar manner as the plastic filled with 10 wt% **BP1**.

Preparation of plastic filled with 4 wt% BP3: The plastic was prepared in a similar manner as the plastic filled with 4 wt% **BP1**.

Preparation of plastic filled with 10 wt% BP3: The plastic was prepared in a similar manner as the plastic filled with 10 wt% **BP1**.

Preparation of plastic filled with 4 wt% LP: The plastic was prepared in a similar manner as the plastic filled with 4 wt% **BP1**.

Preparation of plastic filled with 10 wt% LP: The plastic was prepared in a similar manner as the plastic filled with 10 wt% **BP1**.

5. Experimental characterization procedures

5.1. Dynamic light scattering (DLS) measurements

DLS measurements were performed on a Zetasizer Nano ZSP instrument (Malvern Panalytical) at 25 °C using a solvent-resistant microcuvette (ZEN0040) for *t*-butyl methacrylate with 0.1, 1, 2, 4, 6, 8, and 10 wt% **BP**. First, the 10 wt% **BP** solutions were prepared by stirring the **BP**s and *t*-butyl methacrylate at 25 °C and 1000 rpm for 24 h in the dark. Subsequently, this solution was diluted with *t*-butyl methacrylate and stirred for 12 h to furnish the 0.1, 1, 2, 4, 6, and 8 wt% **BP** solutions.

5.2. Refractive index (n_D) measurements

Refractive index measurements of LP and BPs were performed on a RA-620 refractometer (Kyoto Electronics Manufacturing Co. LTD.) at 20 °C using a Na-D line (589.3 nm) LED as the light source.

5.3. Differential scanning calorimetry (DSC) measurements

DSC measurements were performed on a Q2000 instrument (TA Instruments) in the range of -80 °C to 150 °C at a constant heating rate of 10 °C min⁻¹. Each sample (LP (13.4 mg), **BP1** (8.8 mg), **BP2** (11.0 mg), **BP3** (9.9 mg), the matrix polymer [poly(*t*-butyl methacrylate)] without filler (9.4 mg), the plastic containing 10 wt% LP (7.3 mg), the plastic containing 10 wt% **BP1**(13.1 mg), the plastic containing 10 wt% **BP2** (10.6 mg), and the plastic containing 10 wt% **BP3** (7.0 mg)) was encapsulated in an aluminum pan with lids (Tzero Pan and Tzero Lid for waxes or Tzero Hermetic Lid for solids, TA Instruments), and measured using the vacant pans with the lids as the references.

5.4. Visible spectrum transmittance measurements

Visible spectrum transmittance measurements were performed on a V-630 spectrophotometer (Jasco) in the range of 380–800 nm using a glass cuvette of 1 mm thickness for the samples, according to the preparation of plastics (section 4).

5.5. AFM measurements

5.5.1. Single molecular observation of the bottlebrush polymers (BP1–BP3)

AFM images were recorded on a MultiMode 8 instrument using a NCHV-A silicon probe (Bruker, resonance frequency = 320 kHz, spring constant = 42 N m⁻¹) in tapping mode. Samples were prepared by spin-coating of freshly cleaved mica surfaces with chloroform solutions of **BP1**, **BP2**, and **BP3** for 60 s at 2000 rpm.

5.5.2. Observation of the plastics surfaces

Plastic surfaces were mechanically polished in four steps. First, a sample embedded in

epoxy resin was roughly polished by a water-resistant abrasive paper in water. Further polishing was achieved using an appropriate combination of polishing suspension and buff: MetaDi 9 μ m, TriDent; MetaDi 3 μ m, VerduTex; MasterMet, MasterTex. The surface texture of the polished specimens was imaged using a reflective optical microscope. AFM images were collected on an MFP-3D Infinity instrument using an AC240TS-R3 silicon probe (Asylum Research, resonance frequency = 70 kHz, spring constant = 2 N m⁻¹) in tapping mode for height profiles or in contact mode for elastic and adhesive mapping.

5.6. Vickers Hardness Tests

The Vickers indentation fracture toughness was measured using a Vickers hardness tester (Akashi AVK-A). A 1-kgf load was applied to a flat sample surface by a pyramidal diamond indenter for 15 s. In addition to the indent diagonal used in the conventional Vickers hardness test, the operation produced thin cracks growing from each indent diagonal when the applied load was sufficiently large to fracture a brittle plastic. The fracture toughness (K_{IC}) was determined as:

$$K_{\rm IC} = 0.018 \left(\frac{E}{H}\right)^{0.5} \frac{P}{c^{3/2}}$$

where *E* is the Young's modulus, *H* is the Vickers hardness, *P* is the applied load, and *c* is half of the total crack length. The reported K_{IC} is the average of 3–5 tests. The Young's modulus was measured using a microindenter (DUH-211, Shimadzu).

5.7. Dynamic mechanical analysis (DMA) measurements

Temperature-sweep viscoelasticity was measured using a dynamic mechanical analyzer (RSA III, TA Instruments) with a compressive mode. Temperature-sweep measurements of the storage (*E'*) and loss (*E''*) moduli were performed from 0 °C to 130 °C at a constant heating rate of 2.5 °C min⁻¹, frequency of 1 Hz, and 0.1% strain. The sample dimensions were ϕ 4.67 mm × 8.06 mm (plastic without filler), ϕ 4.64 mm × 8.34 mm (plastic containing 10 wt% **LP**), ϕ 4.34 mm × 11.93 mm (plastic containing 10 wt% **BP1**), ϕ 4.63 mm × 9.21 mm (plastic containing 10 wt% **BP2**), and ϕ 4.65 mm × 7.04 mm (plastic containing 10 wt% **BP3**).

6. Supporting Figures (Figs. S1–S11)



Fig. S1 ¹H NMR spectra (400 MHz, CDCl₃, 300 K) of (a) **P1**, (b) **P2**, (c) **P3**, (d) **BP1**, (e) **BP2**, and (f) **BP3**.



Fig. S2 Height images of the bottlebrush polymers (a) BP1, (b) BP2, and (c) BP3.



Fig. S3 SEC analysis of the side chains cleaved from the bottlebrush polymers: (a) reaction scheme and (b) SEC profiles of (i) **BP1**, (ii) **BP2**, and (iii) **BP3**.



Fig. S4 Aggregation behavior of the bottlebrush polymers in *t*-butyl methacrylate determined by DLS measurements. Correlation coefficients of (a) **BP1**, (b) **BP2**, and (c) **BP3** at various concentrations.



Fig. S5 AFM surface analyses of the matrix containing (a) 4 wt% and (b) 10 wt% **BP3**: (i) height, (ii) elasticity, and (iii) adhesion.



Fig. S6 AFM surface analyses of the matrix containing (a) 4 wt% and (b) 10 wt% **BP1**: (i) height, (ii) elasticity, and (iii) adhesion.



Fig. S7 AFM surface analyses of the matrix containing (a) 4 wt% and (b) 10 wt% **BP2**: (i) height and (ii) elasticity.



Fig. S8 AFM surface analyses of the matrix (a) containing 4 wt% **LP** and (b) without filler: (i) height and (ii) elasticity.



Fig. S9 Physical properties of the matrix containing the fillers (a) LP, (b) BP1, (c) BP2, and (d) BP3: (i) Vickers hardness and (ii) fracture toughness values.



Fig. S10 Average molecular weights of the matrix polymers constituting plastics filled with BPs at loadings of (a) 0 wt%, (b) 2 wt%, (c) 4 wt%, and (d) 10 wt%.



Fig. S11 Dynamic mechanical analysis profiles of (a) the matrix, (b) the matrix containing 10 wt% LP, (c) the matrix containing 10 wt% BP1, (d) the matrix containing 10 wt% BP2, and (e) the matrix containing 10 wt% BP3. The measurements were conducted with a compressive mode. The increased E' or distorted plots observed around the softening temperature of the samples probably indicate that the sample softening occurred faster than the dynamic control time-scale.

References

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- S2. Y. Yamauchi, K. Yamada, N. N. Horimoto, Y. Ishida, Polymer 2017, 120, 68.