<Supporting Information>

Synthesis, Isolation via Self-Assembly, and Single-Molecule Observation of a [60]Fullerene-End-Capped Isotactic Poly(methyl methacrylate)

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Experimental Section

Measurements. NMR spectra were recorded on a Varian Unity Inova 500 spectrometer (500 MHz for ¹H and 125 MHz for ¹³C) in chloroform-d or 1,2-dichlorobenzene- d_4 using tetramethylsilane (TMS) as the internal standard. Fast atom bombardment (FAB) mass spectra were obtained using a JEOL JMS-HX110A mass spectrometer (Tokyo, Japan). Size exclusion chromatography (SEC) measurements were performed with a Jasco PU-2080 liquid chromatograph (Hachioji, Japan) equipped with a refractive index (Jasco, RI-2031) and a UV-visible (330 nm; Jasco UV-2070) detector. A Tosoh (Tokyo, Japan) TSKgel α-M [30 cm for CH₃OH/THF (3/7, v/v)] or two Tosoh TSKgel Multipore H_{XI}-M (30 cm for toluene) SEC columns were connected in series at a flow rate of 1.0 mL/min. The molecular weight calibration curves were obtained with poly(methyl methacrylate) (PMMA) standards (Shodex, Tokyo, Japan). Preparative SEC purifications were carried out with a JAI LC-928 chromatograph (Japan Analytical Industry (JAI), Tokyo, Japan) equipped with two JAIGEL-1H columns (60 cm) using chloroform as the eluent at a flow rate of 3.8 mL/min. Absorption spectra were measured in a 2- or 10-mm quartz cell using a Jasco V-570 spectrophotometer. Dynamic light scattering (DLS) measurements were performed on a Photal DLS-7070YN spectrometer (Otsuka Electronics, Osaka, Japan) equipped with a 10mW

He-Ne laser (632.8 nm). Atomic force microscopy (AFM) observations were done using a Nanoscope IV (Veeco Instruments, Santa Barbara, USA) in the tapping mode in air. A silicon cantilever (resonance frequency; ca. 300 kHz, length; 125 µm) was used.

Materials. *n*-Butyllithium (*n*-BuLi, 1.6 M solution in pentane) and *sec*-butyllithium (*s*-BuLi, 1.4 M solution in cyclohexane) were obtained from Aldrich. Anhydrous toluene (water content < 0.005%) obtained from Wako (Osaka, Japan) was mixed with a small amount of *n*-BuLi and distilled under high vacuum just before use. Tetrahydrofuran (THF) was refluxed and distilled over CaH₂ and finally distilled under reduced nitrogen pressure over lithium aluminum hydride just before use. *tert*-Butyl methacrylate (*t*-BuMA) obtained from Tokyo Kasei (TCI, Tokyo, Japan) was repeatedly washed with aqueous NaOH, then purified by fractional distillation under reduced nitrogen pressure, dried over CaH₂, and vacuum-distilled just prior to polymerization. 1,1-Diphenylethylene (DPE, Aldrich), diisopropylamine (Wako), and methyl isobutyrate (Wako) were purified by distillation over CaH₂. [60]Fullerene (C₆₀) was obtained from TCI and used as a toluene solution. CH₃OH, dimethyl sulfoxide (DMSO), CH₃I, and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) were purchased from Wako and used without further purification.

Preparation of PMMA-C₆₀. (1,1-Diphenyl-3-methylpentyl)lithium (*s*-BuDPE-Li) used as an initiator was the reaction products of *s*-BuLi (2.97 mL, 3 mmol) with DPE (0.53 mL, 3mmol) in THF (3mL) at room temperature. Anionic polymerization of *t*-BuMA was carried out in a dry glass ampule under a dry nitrogen atmosphere. The initiator solution (12.5 µmol in 20 mL toluene) was prepared in the ampule, and the polymerization reaction was initiated by adding the monomer (1.64 mL, 10 mmol) to the initiator solution at -78 °C. After completion of the polymerization, 80 µmol of C₆₀ in a toluene (20 mL) and THF (2 mL) mixture was slowly added to the mixture at -78 °C. After 3h at -78 °C, the polymerizaztion was quenched with CH₃OH containing a small amount of aqueous 14 N HCl. The mixture was then poured into a large amount of CH₃OH, and the precipitate was collected by filtration, washed with CH₃OH, and then dried under vacuum to give the C₆₀-end-capped poly(*t*-BuMA) (poly(*t*-BuMA)-C₆₀) together with unreacted C₆₀.

The poly(*t*-BuMA)- C_{60} was hydrolyzed by refluxing in CH₃OH/THF (1/1, v/v) containing a small amount of aqueous 14 N HCl. After 12 h, the reaction mixture was poured into a large amount of acetone to precipitate the polymeric product, which was then collected by filtration, washed with acetone, and then dried under vacuum, yielding the C_{60} -end-capped poly(methacrylic acid) (PMAA- C_{60}).

To a solution of PMAA-C₆₀ (400 mg, 4.6 unit mmol) in DMSO (30 mL) were added CH₃I (0.74 mL, 12 mmol) and DBU (0.90 mL, 6 mmol), and the mixture was stirred at room temperature for 90 min. The resulting C₆₀-end-capped poly(methyl methacrylate) (PMMA-C₆₀) was precipitated into a large amount of CH₃OH, collected by filtration, washed with CH₃OH, and then dried under vacuum. The precipitate contained unreacted C₆₀, which could be removed by preparative SEC using chloroform as the eluent. The PMMA-C₆₀ was finally obtained from a benzene solution by freeze-drying. The conversion was determined to be 100% based on its ¹H NMR spectrum (Figure S-1 in Supporting Information).

PMMA prepolymer was prepared in the same way by quenching the living poly(t-BuMA) with CH₃OH containing a small amount of aqueous 14 N HCl, followed by hydrolysis of the pendant esters and methyl esterification with CH₃I in the presence of DBU. The characteristics of the PMMA-C₆₀ and the PMMA prepolymer are summarized in Table S-1.

Table S-	• 1. Poly	merization of	<i>t-</i> BuMA with	s-BuDPE-Li in	Toluene at -	-78 °C for 90 min ^a
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C ₆₀ in feed			tacticity (%) ^c				_	
run	(µmol)	\overline{M} n ^b	$\overline{M}w/\overline{M}n^{\mathrm{b}}$	mm	mr	rr	$f_{\rm C60}(\%)^{\rm d}$	
1	_	118,000	1.14	97.7	1.9	0.4	_	PMMA
2	80	115,000	1.14	97.5	1.9	0.6	40	PMMA-C ₆₀

^a *t*-BuMA, 10 mmol; *s*-BuDPE-Li, 12.5 μ mol; toluene, 20 mL; yield, 100 %. ^b Determined by SEC as its methyl ester. PMMA standards were used for the calibration. ^c Determined from ¹H NMR signals due to the α -methyl protons for PMMA derived from poly(*t*-BuMA) (See Figure S-1 in Supporting Information). ^d Functionality of C₆₀ estimated on the basis of the absorbance at 330 nm in its UV–vis spectrum (See Figure S-2 in Supporting Information).

Preparation of MIB-C₆₀. A model compound of PMMA-C₆₀ was prepared according to Scheme S-1.

Scheme S-1. Preparation of MIB-C₆₀



Lithium diisopropylamide (LDA) was prepared from *n*-BuLi and diisopropylamine under a dry nitrogen atmosphere in THF at -78 °C for 2 h. Methyl α -lithioisobutyrate (0.67 M in THF, 0.4 mL, 0.27 mmol) generated from the reaction of methyl isobutyrate with the LDA was allowed to react with C₆₀ (109 mg, 0.15 mmol) in toluene (50 mL) at -78 °C. After 30 min, the reaction was quenched with CH₃OH containing a small amount of aqueous 14 N HCl. After the solvent was evaporated under reduced pressure, the crude product was purified by preparative SEC to give 18 mg of the model compound (MIB-C₆₀) as a dark brown powder in 20% yield. ¹H NMR (1,2-dichlorobenzene-*d*₄, 60 °C, TMS) δ 6.61 (s, -C₆₀-H, 1H), 3.98 (s, -OCH₃, 3H), 2.22 (s, -CH₃, 6H). ¹³C NMR (1,2-dichlorobenzene-*d*₄, 60 °C, TMS) δ 175.78 (C=O), 154.21, 152.95, 147.49, 147.28, 147.18, 146.96, 146.37, 146.34, 146.16, 146.09,

145.81, 145.44, 145.32, 145.24, 144.76, 144.43, 143.18, 142.93, 142.59, 142.57, 142.23, 142.13, 142.08, 141.58, 141.48, 141.43, 140.25, 139.00, 137.20, 136.54 (sp²-carbons of C₆₀), 71.17 (isobutyrate-bound carbon of C₆₀), 58.32 (H-bound carbon of C₆₀), 53.25 (quaternary carbon of isobutyrate), 52.37 (-OCH₃), 24.04 (-CH₃). FAB-MS: m/e 823 (M+H)⁺.



Figure S-1. ¹H NMR spectrum of PMMA-C₆₀ before isolation by SEC in chloroform-*d* at 55 °C.



Figure S-2. UV–vis spectra of C_{60} (a), MIB- C_{60} (b), PMMA- C_{60} before isolation by SEC (c, d). The spectra were measured in toluene (a–c) and CH₃OH/THF (3/7, v/v) (d).



Figure S-3. Time-dependent SEC changes of PMMA-C₆₀ (f_{C60} = 40%, concentration = 2 mg/mL) in CH₃OH/THF (3/7, v/v) (a–d) and H₂O/THF (1/9, v/v) (e–h) at room temperature. The SEC was measured using CH₃OH/THF (3/7, v/v) (a–d) or H₂O/THF (1/9, v/v) (e–h) as the eluent after the samples had been allowed to stand for an appropriate time in the solvent mixtures.



Figure S-4. Histogram analysis of DLS measurement of PMMA-C₆₀ (Mn = 115,000, $f_{C60} = 40\%$, concentration = 2 mg/mL) in CH₃OH/THF (3/7, v/v) after storing the sample at room temperature for 96 h.



Figure S-5. RI (solid line) and UV (330 nm, dotted line) detected SEC curves of PMMA-C₆₀ before ($f_{C60} = 40\%$) (a, c) and after ($f_{C60} \sim 100\%$) (b) purification by SEC fractionation using toluene (a, b) and H₂O/THF (1/9, v/v) (c) as the eluent. The SEC curve (c) was obtained after the sample had been allowed to stand at room temperature for 24 h. The fraction marked by brackets in (c) was collected, and then injected into the SEC system (b).



Figure S-6. SEC curves and ¹³C NMR spectra of low MW PMMA (a) and low MW PMMA-C₆₀ (b). The low MW PMMA was prepared by the polymerization of *t*-BuMA (3 mmol) with *s*-BuDPE-Li (0.2 mmol) in toluene (6 mL) at -78 °C, followed by hydrolysis and methylation with CH₃I in the presence of DBU. The low MW PMMA-C₆₀ was prepared by end-capping the poly(*t*-BuMA) anion with C₆₀ (0.3 mmol), followed by hydrolysis and methylation with CH₃I in the presence of DBU. The fractions marked by brackets in SECs were collected, and then subjected to the ¹³C NMR measurements.