Synthesis and Characterization of C_{60}-Anchored Multiarmed Polymers with Well-Defined Structures

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ABSTRACT: A multistep procedure for preparing novel C_{60}-anchored multiarmed polymers with well-defined structures was developed. First, di-, tetra- and octabromo-functionalized molecules with a malonate ester core were synthesized and used as functional initiators for growing two-, four-, and eight-armed poly(*tert*-butyl acrylate) (PtBA) with well-controlled molecular weight, by atom transfer radical polymerization. Then, C_{60}-anchored polymers were synthesized by the effective Bingel reaction between C_{60} and the malonate ester core of the multiarmed polymers. The NMR analyses of the products demonstrated that C_{60} had been covalently bonded to the polymers and UV−vis studies of these polymers revealed strong characteristics of "closed" 6−6-ring-bridged methanofullerene derivatives. As indicated by GPC chromatograms, the molecular weights of the polymers were comparable before and after they are attached to C_{60} molecules, suggesting that these polymers were monosubstituted C_{60} derivatives. Furthermore, the C_{60} contents in these polymers were determined from their light absorbance at 326 nm based on Beer's law and were found to be very close to the theoretical value based on the assumption that C_{60}-derived polymer was a monoadduct. Additionally, highly water-soluble C_{60}-anchored multiarmed poly(acrylic acid) were obtained in quantitative yield by the hydrolysis of the C_{60}-anchored multiarmed PtBA in the presence of trifluoroacetic acid at room temperature.

Introduction

Fullerene has attracted considerable interest because of its unique chemical and physical properties during recent decades.[1] However, the poor solubility and processability of the C_{60} molecule have limited its range of applications in material science. Incorporation of the C_{60} molecule into the main chain of organic polymers or as a pendant group into the side chain of a polymer, yielding polymeric derivatives of C_{60}, improved the solubility and processability of C_{60}.[2] However, many synthetic procedures commonly led to uncontrolled multiarmed or highly cross-linked intractable solids of fullerene-derived polymers because of the multifunctionality and the activity of C_{60} in chemical reactions. Some methods have been presented for preparing soluble polymeric C_{60} derivatives with well-defined structures. Hawker[3] reported a simple method to prepare polystyrene-C_{60} derivatives by reacting azide end group functionalized polymers with C_{60}. Mathis et al.[4] synthesized star-shaped C_{60}-bonded polystyrene and polyisoprene by adding "living" anionic polymers onto a C_{60} core. Moreover, Fukuda et al.[5] described the preparation of C_{60}-bound polystyrene with a narrow molecular distribution by the reaction of C_{60} with TEMPO-end-capped polystyrene. Our group[6] also prepared starburst C_{60}-linked polyurethanes with six well-defined polymeric arms via the condensation between polyhydroxylated C_{60} and isocyanate-terminated polyether prepolymers. Recently, Li et al.[7] and Wang et al.[8] separately prepared functional polystyrene and poly(*tert*-butyl acrylate) with well-defined molecular weights via atom transfer radical polymerization (ATRP), and then introduced C_{60} to these polymers to generate C_{60}-end-bonded polymers. The former was prepared by the radical addition of bromo-terminated polystyrene on a C_{60} molecule, while the latter was prepared by the cycloaddition reaction of azide end-group-functionalized poly(*tert*-butyl acrylate) with C_{60} molecules. However, successful procedures for preparing well-defined multiarmed C_{60}-containing polymers remain rare and challenging.

With this concern, this work demonstrates the multistep synthesis of C_{60}-anchored multiarmed polymers with well-defined numbers of arms and chain lengths. First, a series of malonate ester-bearing polybromo-functionalized molecules was synthesized and adopted as initiators for synthesizing multiarmed poly(*tert*-butyl acrylate) via the ATRP of *tert*-butyl acrylate in the presence of CuBr/*N*,*N*′,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA). Herein, the ATRP technique developed by Matyjaszewski is established to be an effective and attractive method for "living"/controlled radical polymerization.[9] The dynamic equilibrium of the transfer of halogen atoms between dormant polymer chains and ligands is such that the polymerization can be effectively controlled to produce polymers with predictable molecular weights and low polydispersity. Moreover, this method also makes accessible various polymer architectures and composites, such as block copolymers, graft copolymers and hyperbranched polymers.[10] Then, C_{60} was functionalized with multiarmed polymers by Bingel cyclopropanation[11] between the fullerene cage and the malonate ester, to afford the C_{60}-containing starburst polymers with well-defined polymer arms. Additionally, water-soluble C_{60}-anchored multiarmed poly(acrylic acid) was obtained by the acidic hydrolysis of the hydrophobic C_{60}-anchored polymers.

Experimental Section

Materials and Instruments. Pure C_{60} (>99%) was purchased from BuckyUSA and used as received. 2-Bromoisobutyryl bromide, *p*-xylylene glycol, 3,4-dihydro-2H-pyran, DOWEX resin 50W×8, malonic acid, 1-hydroxybenzotriazole (HOBT), *N*,*N*′-dicyclohexylcarbodiimide (DCC), *p*-toluenesulfonic acid monohydrate (TsOH),

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Meldrum's acid, 4-(dimethylamino)pyridine (DMAP), *tert*-butyl acrylate (tBA), *N*,*N*′,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), copper(I) bromide, iodine, and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) were all obtained as high-purity reagent-grade chemicals (>99%) from Acros and used without further purification. Acetonide-2,2-bis(methoxy)propionic anhydride was prepared according to the literature.[12] All organic solvents were AR grade and purchased either from TEDIA or Mallinckrodt. Dichloromethane (CH_2Cl_2), triethylamine (Et_3N), toluene, pyridine, and *n*-hexane were dried over calcium hydride (CaH_2) under N_2 before use. Tetrahydrofuran (THF) and ether were distilled over sodium under N_2 in the presence of benzophenone as the indicator prior to use. The monomer (tBA) was extracted three times with 5% aqueous NaOH and then washed with distilled water. After the monomer was dried over $CaCl_2$ and the drying agent filtered off, the monomer was distilled in a vacuum, stored in a Schlenk flask and degassed over three freeze−pump−thaw cycles; N_2 backfilling then ensured that the polymerization reaction proceeded in an inert atmosphere.

Gel permeation chromatography (GPC) was conducted at 40 °C using two Jordi DVB mixed-bed columns (250 × 10 mm; suitable for separating polymers with molecular weights ranging from 1×10^2 to 1×10^7 g mol^{-1}) for the organic phase, and at 35 °C using two Shodex 803 HQ columns (300 × 8 mm; suitable for separating polymers with molecular weights ranging from 1×10^2 to 1×10^6 g mol^{-1}) for the water phase, on a JASCO instrument equipped with UV−vis and refractive index (RI) detectors connected in series. THF and 20% acetonitrile in water with 0.05 M sodium nitrate were used as the eluent at flow rates of 1.0 mL/min and 0.5 mL/min in these two systems. Thirteen linear polystyrene samples (Aldrich) with molecular weights ranging from 7×10^2 to 2×10^6 g mol^{-1} and six linear poly(styrenesulfonate) (Polymer standards service) samples with molecular weights ranging from 1×10^3 to 4×10^5 g mol^{-1} were used as standards for establishing the calibration curves for organic and water phase systems, respectively. Moreover, matrix-assisted laser desorption ionization/time-of-flight (MALDI−TOF) mass spectrometry was preformed on a Bruker AutoFlex MALDI−TOF system in positive ion mode using α-cyano-4-hydroxycinnamic acid (CHCA) as the desorption matrix. The sample solution was prepared by mixing 1.0 μL of the analyte solution (1.0×10^{-3} M in THF), 1.0 μL of NaTFA solution (0.1 M in THF) and 10 μL of the matrix solution (0.1 M in THF). Then 0.5 μL of the mixed solution was then transferred onto a direct sample probe and dried under reduced pressure. The dried samples were then irradiated with a pulse nitrogen laser (337 nm) in the ion source of a linear time-of-flight mass spectrometry. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER SPECTROSPIN-400 MHz spectrometer at room temperature using $CDCl_3$ or DMSO-d_6 as the solvent, and the solvent signal was adopted as an internal standard. Ultraviolet−visible absorption (UV−vis) spectra and Fourier transform infrared absorption (FT-IR) spectra were recorded on a Hitachi U-3410 spectrometer and on a JASCO FT/TR 480 spectrometer, respectively.

Monoesterification of Symmetrical Diol (1). A round-bottomed flask charged with *p*-xylylene glycol (4.30 g, 31.1 mmol), THF (100 mL), and Et_3N (3.40 mL, 24.2 mmol) was cooled to 0 °C using an ice/water bath. Then, a solution of 2-bromoisobutyryl bromide (3.53 g, 15.4 mmol) in 25 mL of THF was added dropwise. The reaction mixture was stirred overnight and warmed to room temperature. After the solvent was removed by rotary evaporation, the mixture was transferred to a separation funnel with 150 mL of diethyl ether and extracted with 2 × 50 mL of $NaHCO_3$ and 2 × 50 mL of brine, consecutively. The organic phase was dried over $MgSO_4$ and filtered; the solvent was evaporated. The obtained crude product was purified by flash column chromatography on SiO_2, and eluted with diethyl ether/hexane (70:30) to yield **1** as a pale yellow oil (5.87 g, 66%). ^{1}H NMR ($CDCl_3$): δ = 7.36 (s, 4H, Ar**H**), 5.18 (s, 2H, −ArC**H**$_2$OCO), 4.69 (s, 2H, −C**H**$_2$OH), 1.93 (s, 6H, −C(C**H**$_3$)). ^{13}C NMR ($CDCl_3$): δ = 171.40 (−CH_2O***C***O), 140.86 (Ar ***C***), 134.43 (Ar ***C***), 127.91 (Ar ***C***), 127.02 (Ar ***C***), 67.23 (−***C***H$_2$OCO), 64.56 (−***C***H$_2$OH), 55.59 (−***C***(CH$_3$)), 30.57 (−C(***C***H$_3$)).

Monotetrahydropyranylation of Symmetrical Diol (2). A solution of *p*-xylylene glycol (5.53 g, 40.1 mmol), 3,4-dihydro-2H-pyran (6.0 mL, 2.5% v/v) and DOWEX resin 50W×8 (4.00 g) in 240 mL of toluene was stirred at 30 °C for 3.5 h. After the resin was filtered off, the solvent was removed by rotary evaporation. The obtained crude product was purified by flash column chromatography on SiO_2, and eluted with diethyl ether/hexane (70:30) to yield **2** as a colorless oil (7.40 g, 83%). ^{1}H NMR ($CDCl_3$): δ = 7.33 (d, 2H, Ar**H**), 7.32 (d, 2H, Ar**H**), 4.76 (d, 1H, −OC**H**$_2$Ar), 4.68 (t, 1H, −OC**H**O), 4.66 (s, 2H, −C**H**$_2$OH), 4.48 (d, 1H, −OC**H**$_2$Ar), 3.93−3.87 (m, 1H, −C**H**$_2$O), 3.55−3.50 (m, 1H −C**H**$_2$O), 1.88−1.51 (m, 6H, −C**H**$_2$C**H**$_2$). ^{13}C NMR ($CDCl_3$): δ = 140.26 (Ar ***C***), 137.27 (Ar ***C***), 127.87 (Ar ***C***), 126.85 (Ar ***C***), 97.51 (−O***C***HO), 68.43 (−Ar***C***H$_2$O), 64.61 (−***C***H$_2$OH), 61.98 (−***C***H$_2$O), 30.37 (−CH_2CH_2***C***H_2CHO_2), 25.28 (−***C***$H_2CH_2CH_2$-CHO_2), 19.14 (−CH_2***C***$H_2CH_2CHO_2$).

Synthesis of Ditetrahydropyran-Capped Malonate Ester (3). Compound **2** (7.35 g, 33.1 mmol), malonic acid (1.64 g, 15.7 mmol) and HOBT (710 mg, 5.26 mmol, 9.93% w/w) were mixed in 40 mL of dry CH_2Cl_2 and 10 mL of dry THF in a round-bottom flask. After the reaction flask had been flushed with N_2, a solution of DCC (7.15 g, 34.6 mmol) in 10 mL of dry CH_2Cl_2 was added. After being stirred for 1 h, the reaction mixture was heated to 40 °C for 24 h. Following the reaction, the *N*,*N*′-dicyclohexylurea (DCU) was filtered off in a glass filter and the solvent was evaporated. The obtained crude product was purified by flash column chromatography on SiO_2, and eluted with diethyl ether/hexane (70:30) to yield **3** as a colorless oil (7.46 g, 93%). ^{1}H NMR ($CDCl_3$): δ = 7.34 (d, 4H, Ar**H**), 7.29 (d, 4H, Ar**H**), 5.14 (s, 4H, −ArC**H**$_2$OCO), 4.77 (d, 2H, −OC**H**$_2$Ar), 4.68 (t, 2H, −OC**H**O), 4.48 (d, 2H, −OC**H**$_2$Ar), 3.92−3.87 (m, 2H, −C**H**$_2$O), 3.56−3.51 (m, 2H, −C**H**$_2$O), 3.44 (s, 2H, −(OOC)$_2$C**H**$_2$), 1.87−1.51 (m, 12H, −C**H**$_2$C**H**$_2$). ^{13}C NMR ($CDCl_3$): δ = 166.16 (−O***C***OCH$_2$), 138.63 (Ar ***C***), 134.33 (Ar ***C***), 128.35 (Ar ***C***), 127.88 (Ar ***C***), 97.67 (−O***C***HO), 68.30 (−Ar***C***H$_2$O), 67.00 (−***C***H$_2$OCO), 62.03 (−***C***H$_2$O), 41.47 (−OCO***C***H$_2$), 30.46 (−CH_2CH_2***C***H_2CHO_2), 25.37 (−***C***H_2-$CH_2CH_2CHO_2$), 19.24 (−CH_2***C***$H_2CH_2CHO_2$).

Synthesis of Malonate Ester-Based Diol ([G#0]-(OH)$_2$). A solution of compound **3** (7.50 g, 14.6 mmol) and TsOH (570 mg, 3.00 mmol) in 125 mL of methanol was stirred at room temperature for 4 h. The solvent was removed by rotary evaporation and then the mixture was transferred to a separation funnel with 100 mL of ethyl acetate (EA) and extracted with 2 × 50 mL of 1 M HCl, and 2 × 50 mL of brine, consecutively. The organic phase was dried over $MgSO_4$ and filtered and the solvent was evaporated. Crystallization of the residue from EA/hexane afforded **[G#0]-(OH)$_2$** as a white solid (2.22 g, 45%). ^{1}H NMR ($CDCl_3$): δ = 7.27 (s, 8H, Ar**H**), 5.14 (s, 4H, −ArC**H**$_2$OCO), 4.66 (s, 4H, −C**H**$_2$OH), 3.45 (s, 2H, −(OOC)$_2$C**H**$_2$). ^{13}C NMR ($CDCl_3$): δ = 166.19 (−O***C***OCH$_2$), 141.07 (Ar ***C***), 134.23 (Ar ***C***), 128.26 (Ar ***C***), 126.94 (Ar ***C***), 66.92 (−***C***H$_2$OCO), 64.49 (−***C***H$_2$OH), 41.55 (−OCO***C***H$_2$).

Synthesis of Dibromo-Functionalized Initiator ([G#0]-Br$_2$). Method A. A mixture of **1** (1.00 g, 3.50 mmol) and Meldrum's acid (531 mg, 3.68 mmol) was heated at 110−120 °C for 3 h. The obtained mixture was vacuum-dried at room temperature to give **1′** as a pale-yellow oil, which was used without further purification. The dibromo-functionalized initiator was then prepared by reacting the solution of **1** (952 mg, 3.31 mmol), **1′** (1.28 g, 3.43 mmol) and DMAP (81.0 mg, 0.663 mmol) in CH_2Cl_2 (10 mL) with the DCC (787 mg, 3.81 mmol) solution in CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature under N_2 for 24 h. Following the reaction, the resulting mixture was filtered through a glass filter to remove DCU and the solvent was evaporated. The crude product was then purified by flash column chromatography on SiO_2, and eluted with diethyl ether/hexane (70:30) to give **[G#0]-Br$_2$** as a colorless oil (1.86 g, 88%).

Method B. A round-bottomed flask charged with **[G#0]-(OH)$_2$** (172 mg, 500 μmol), THF (20 mL) and pyridine (200 μL, 2.45 mmol) was cooled to 0 °C using an ice/water bath. Then, a solution of 2-bromoisobutyryl bromide (280 mg, 1.22 mmol) in 5 mL of THF was added dropwise. The reaction mixture was stirred for 6 h

and allowed to warm to room temperature. After the solvent was removed by rotary evaporation, the mixture was transferred to a separation funnel with 50 mL of CH_2Cl_2 and extracted with 2 × 50 mL of 1 M HCl and 2 × 50 mL of brine, consecutively. The organic phase was dried over $MgSO_4$ and filtered; the solvent was evaporated. The obtained crude product was purified by flash column chromatography on SiO_2, and eluted with diethyl ether/hexane (70:30) to yield **[G#0]-Br$_2$** as a colorless oil (309 mg, 96%). ^{1}H NMR ($CDCl_3$): δ = 7.34 (d, 4H, Ar**H**), 7.33 (d, 4H, Ar**H**), 5.18 (s, 4H, −ArC**H**$_2$OCO), 5.15 (s, 4H, −ArC**H**$_2$OCO), 3.46 (s, 2H, −(OOC)$_2$C**H**$_2$), 1.93 (s, 12H, −C(C**H**$_3$)). ^{13}C NMR ($CDCl_3$): δ = 171.19 (−ArCH$_2$O***C***O), 165.98 (−O***C***OCH$_2$), 135.53 (Ar ***C***), 135.18 (Ar ***C***), 128.32 (Ar ***C***), 127.91 (Ar ***C***), 66.92 (−Ar***C***H$_2$-OCO), 66.66 (−Ar***C***H$_2$OCO), 55.49 (−***C***(CH$_3$)), 41.31 (−OCO***C***H$_2$), 30.57 (−C(***C***H$_3$)). MALDI−TOF. Calcd: $[M]^+$ m/z = 642.3. Found: $[M + Na]^+$ = 665.1.

Synthesis of Malonate Ester-Based Tetraol ([G#1]-(OH)$_4$). A solution of **[G#0]-(OH)$_2$** (693 mg, 2.01 mmol), DMAP (81.2 mg, 0.665 mmol), and acetonide-2,2-bis(methoxy)propionic anhydride (1.73 g, 5.23 mmol) in 21 mL of dry CH_2Cl_2 and 7 mL of dry pyridine was stirred overnight at room temperature. After completion, the excess anhydride was quenched by stirring the reaction mixture with 2 mL of 1:1 pyridine/water solution. The organic phase was diluted by adding 100 mL of CH_2Cl_2 and extracted with 3 × 50 mL of $NaHSO_4$ (1 M), 3 × 50 mL of Na_2CO_3 (10%) and 3 × 50 mL of brine. The organic phase was dried over $MgSO_4$ and filtered; the solvent was evaporated. A solution of the precursor (1.20 g, 1.80 mmol) and TsOH (70.0 mg, 0.368 mmol) in 50 mL of methanol was stirred at room temperature for 4 h. The solvent was removed by rotary evaporation and then the mixture was transferred to a separation funnel with 100 mL of EA and extracted with 2 × 50 mL of 1 M HCl and 2 × 50 mL of brine, consecutively. The organic phase was dried over $MgSO_4$ and filtered; the solvent was evaporated to give **[G#1]-(OH)$_4$** as a colorless oil (1.04 g, 93%). ^{1}H NMR ($CDCl_3$): δ = 7.30 (s, 8H, Ar**H**), 5.18 (s, 4H, −ArC**H**$_2$OCO), 5.14 (s, 4H, −ArC**H**$_2$OCO), 3.91 (d, 4H, −C**H**$_2$-OH), 3.71 (d, 4H, −C**H**$_2$OH), 3.46 (s, 2H, −(OOC)$_2$C**H**$_2$), 1.06 (s, 6H, −CC**H**$_3$). ^{13}C NMR ($CDCl_3$): δ = 173.95 (−ArCH$_2$O***C***O), 166.10 (−O***C***OCH$_2$), 136.27 (Ar ***C***), 135.06 (Ar ***C***), 128.42 (Ar ***C***), 127.89 (Ar ***C***), 68.17 (−***C***H$_2$OCO), 66.82 (−***C***H$_2$OCO), 65.96 (−***C***H$_2$OH), 41.88 (−***C***CH$_3$), 41.40 (−OCO***C***H$_2$), 18.49 (−C***C***H$_3$).

Synthesis of Malonate Ester-Based Octaol ([G#2]-(OH)$_8$). A solution of [G#1]-(OH)$_4$ (925 mg, 1.60 mmol), DMAP (129 mg, 1.06 mmol), and acetonide-2,2-bis(methoxy)propionic anhydride (2.76 g, 8.36 mmol) in 27 mL of dry CH_2Cl_2 and 9 mL of dry pyridine was stirred overnight at room temperature. After completion, the excess anhydride was quenched by stirring the reaction mixture with 2 mL of 1:1 pyridine/water solution. The organic phase was diluted with 100 mL of CH_2Cl_2 and extracted with 3 × 50 mL of $NaHSO_4$ (1 M), 3 × 50 mL of Na_2CO_3 (10.0%) and 3 × 50 mL of brine. The organic phase was dried over $MgSO_4$ and filtered; the solvent was evaporated. The obtained crude product was purified by flash column chromatography on SiO_2, and eluted with diethyl ether to yield Acetonide-protected precursor as a colorless oil. A solution of the precursor (841 mg, 700 μmol) and TsOH (35.0 mg, 0.184 mmol) in 50 mL of methanol was stirred at room temperature for 4 h. The solvent was removed by rotary evaporation and then the mixture was transferred to a separation funnel with 100 mL of EA and extracted with 2 × 50 mL of 1 M HCl and 2 × 50 mL of brine, consecutively. The organic phase was dried over $MgSO_4$ and filtered; the solvent was evaporated. Crystallization of the residue from hexane afforded **[G#2]-(OH)$_8$** as a white solid (667 mg, 40%). ^{1}H NMR (DMSO-d_6): δ = 7.24 (s, 8H, Ar**H**), 5.06 (s, 8H, −ArC**H**$_2$OCO), 4.22 (d, 4H, −C**H**$_2$OCO), 4.13 (d, 4H, −C**H**$_2$OCO), 3.54−3.46 (m, 16H, −C**H**$_2$OH), 3.41 (s, 2H, −(OOC)$_2$C**H**$_2$), 1.19 (s, 6H, −CC**H**$_3$), 0.95 (s, 12H, −CC**H**$_3$). ^{13}C NMR (DMSO-d_6): δ = 173.84 (−CH$_2$O***C***O), 171.88 (−ArCH$_2$O***C***O), 165.33 (−O***C***OCH$_2$), 134.92 (Ar ***C***), 134.56 (Ar ***C***), 127.56 (Ar ***C***), 127.47 (Ar ***C***), 65.82 (−***C***H$_2$OCO), 65.50 (−***C***H$_2$OCO), 64.15 (−***C***H$_2$OCO), 63.92 (−***C***H$_2$OH), 49.37 (−***C***CH$_3$), 45.52 (−***C***CH$_3$), 40.53 (−OCO***C***H$_2$), 17.10 (−C***C***H$_3$), 16.19 (−C***C***H$_3$).

Synthesis of Tetrabromo-Functionalized Initiator ([G#1]-Br$_4$). A round-bottomed flask charged with **[G#1]-(OH)$_4$** (1.00 g, 1.73 mmol), THF (40 mL), and pyridine (1.00 mL, 12.3 mmol) was cooled to 0 °C using an ice/water bath. Then, a solution of 2-bromoisobutyryl bromide (1.94 g, 8.47 mmol) in 20 mL of THF was added dropwise. The reaction mixture was stirred for 6 h and allowed to warm to room temperature. After the solvent was removed by rotary evaporation, the mixture was transferred to a separation funnel with 50 mL of EA and extracted with 2 × 50 mL of 1 M HCl and 2 × 50 mL of brine, consecutively. The organic phase was dried over $MgSO_4$ and filtered; the solvent was evaporated. The obtained crude product was purified by flash column chromatography on SiO_2 and eluted with diethyl ether/hexane (90:10) to yield **[G#1]-Br$_4$** as a colorless oil (1.41 g, 70%). ^{1}H NMR ($CDCl_3$): δ = 7.32 (s, 8H, Ar**H**), 5.15 (s, 8H, −ArC**H**$_2$-OCO), 4.38 (d, 4H, −C**H**$_2$OCO), 4.32 (d, 4H, −C**H**$_2$OCO), 3.46 (s, 2H, −(OOC)$_2$C**H**$_2$), 1.84 (s, 24H, −C(C**H**$_3$)), 1.33 (s, 6H, −CC**H**$_3$). ^{13}C NMR ($CDCl_3$): δ = 172.14 (−CH$_2$O***C***O), 170.93 (−CH$_2$O***C***O), 166.12 (−O***C***OCH$_2$), 135.63 (Ar ***C***), 135.49 (Ar ***C***), 128.55 (Ar ***C***), 128.53 (Ar ***C***), 66.82 (−***C***H$_2$OCO), 66.68 (−***C***H$_2$-OCO), 66.26 (−***C***H$_2$OCO), 55.28 (−***C***(CH$_3$)), 46.74 (−***C***CH$_3$), 41.41 (−OCO***C***H$_2$), 30.57 (−C(***C***H$_3$)), 17.86 (−C***C***H$_3$). MALDI−TOF. Calcd: $[M]^+$ m/z = 1172.5. Found: $[M + Na]^+$ = 1195.8.

Synthesis of Octabromo-Functionalized Initiator ([G#2]-Br$_8$). A round-bottomed flask charged with [G#2]-(OH)$_8$ (631 mg, 0.606 mmol), THF (40 mL), and pyridine (1.00 mL, 12.3 mmol) was cooled to 0 °C using an ice/water bath. Then, a solution of 2-bromoisobutyryl bromide (1.70 g, 7.39 mmol) in 20 mL of THF was added dropwise. The reaction mixture was stirred for 6 h and allowed to warm to room temperature. After the solvent was removed by rotary evaporation, the mixture was transferred to a separation funnel with 50 mL of EA and extracted with 2 × 50 mL of 1 M HCl and 2 × 50 mL of brine, consecutively. The organic phase was dried over $MgSO_4$ and filtered; the solvent was evaporated. The obtained crude product was first purified by flash column chromatography on SiO_2, and eluted with diethyl ether/hexane (90:10). Then crystallization of the residue from methanol afforded **[G#2]-Br$_8$** as a white solid (867 mg, 64%). ^{1}H NMR ($CDCl_3$): δ = 7.33 (s, 8H, Ar**H**), 5.16 (s, 4H, −ArC**H**$_2$OCO), 5,-14 (s, 4H, −ArC**H**$_2$OCO), 4.34−4.22 (m, 24H, −C**H**$_2$OCO), 3.47 (s, 2H, −(OOC)$_2$C**H**$_2$), 1.88 (s, 48H, −C(C**H**$_3$)), 1.27 (s, 6H, −CC**H**$_3$), 1.24 (s, 12H, −CC**H**$_3$). ^{13}C NMR ($CDCl_3$): δ = 171.84 (−CH$_2$O***C***O), 171.58 (−CH$_2$O***C***O), 170.85 (−CH$_2$O***C***O), 166.15 (−O***C***OCH$_2$), 135.61 (Ar ***C***), 135.50 (Ar ***C***), 128.64 (Ar ***C***), 128.51 (Ar ***C***), 66.77 (−***C***H$_2$OCO), 65.95 (−***C***H$_2$OCO), 65.89 (−***C***H$_2$-OCO), 55.32 (−***C***(CH$_3$)), 46.70 (−***C***CH$_3$), 46.65 (−***C***CH$_3$), 41.34 (−OCO***C***H$_2$), 30.57 (−C(***C***H$_3$)), 17.76 (−C***C***H$_3$), 17.68 (−C***C***H$_3$). MALDI−TOF. Calcd: $[M]^+$ m/z = 2232.9. Found: $[M + Na]^+$ = 2255.6.

Preparation of Two-Armed Polymers via ATRP Procedure. A round-bottomed flask was charged with **[G#0]-Br$_2$** (64.9 mg, 100 μmol), PMDETA (42.0 μL, 200 μmol), and CuBr (28.4 mg, 200 μmol), and purged with N_2. Deoxygenated acetone (1.50 mL) and tBA (6.00 mL, 41.3 mmol) were then added, after which the solution was placed in an oil bath whose temperature was thermostatically maintained at 70 °C and vigorously stirred. The polymerization was carried out for 4 h, 8 h and 12 h for preparing polymers **2**−**1**, **2**−**2**, and **2**−**3**, respectively. Following the reaction, the mixture was diluted with a small amount of CH_2Cl_2 and passed through a neutral alumina column for catalyst removal. The solution was then precipitated twice in a large excess of 30% H_2O/methanol with vigorous stirring. The precipitate was collected using a centrifuge and vacuum-dried to yield two-armed polymer as a white glassy solid. The monomer conversions for polymers **2**−**1**, **2**−**2**, and **2**−**3**, as determined by GPC, were 28%, 37%, and 55%, respectively, and their molecular weight characteristics are shown in Table 1.

Preparation of Four-Armed Polymers via ATRP Procedure. A round-bottomed flask was charged with **[G#1]-Br$_4$** (59.2 mg, 50.0 μmol), PMDETA (42.0 μL, 200 μmol), and CuBr (28.4 mg, 200 μmol), and purged with N_2. Deoxygenated acetone (1.50 mL)

Table 1. Molecular Weight Characteristics of Two-, Four-, and Eight-Armed Poly(*tert*-butyl acrylate) and Their C_{60} Adducts

		polymer			C_{60}-anchored polymer			
	run	$M_{n,GPC}$[a]	$M_{n,NMR}$[b]	M_w/M_n	$M_{n,GPC}$[a]	$M_{n,GPC}$[c]	M_w/M_n	C_{60} cont (%)[d]
2-armed	2−1	14 000	15 400	1.11	13 200	14 000	1.12	4.7 (4.5)
	2−2	18 300	20 200	1.12	17 100	17 200	1.14	3.9 (3.4)
	2−3	29 500	29 900	1.11	28 000	28 200	1.19	2.2 (2.3)
4-armed	4−1	19 100	21 400	1.17	20 800	19 900	1.14	3.7 (3.3)
	4−2	30 600	33 900	1.11	32 600	31 600	1.11	2.8 (2.1)
	4−3	38 900	44 100	1.13	41 900	40 500	1.13	1.6 (1.6)
8-armed	8−1	31 200	46 500	1.09	34 600	34 300	1.10	1.4 (1.5)
	8−2	42 800	65 000	1.09	48 100	48 300	1.10	1.0 (1.1)
	8−3	98 200	131 000	1.10	99 000	100 000	1.13	0.4 (0.5)

[a] Determined via gel permeation chromatography analysis with RI detector in THF; low-dispersed polystyrenes were used as calibration standards. [b] The number-average molecular weights were calculated from the number-average degree of polymerization (DP_n) of each arm; $M_{n,NMR} = (DP_{per\ arm} \times 128.17 \times n) + M_i$, where 128.17 and M_i stand for the molar mass of *tert*-butyl acrylate and initiator; n stands for the arm numbers. [c] Measured by GPC analysis with UV−vis detector at 350 nm. [d] Calculated based on the absorbance of C_{60}-anchored polymers at 326 nm according to Beer's law; the data in parentheses denote the theoretical values based on the C_{60}-monoadduct structure.

and tBA (6.00 mL, 41.3 mmol) were then added, after which the solution was placed in an oil bath whose temperature was thermostatically maintained at 70 °C and vigorously stirred. The polymerization was carried out for 3, 7, and 13 h for preparing polymers **4**−**1**, **4**−**2**, and **4**−**3**, respectively. Following the reaction, the mixture was diluted with a small amount of CH_2Cl_2 and passed through a neutral alumina column for catalyst removal. The solution was then precipitated twice in a large excess of 30% H_2O/methanol with vigorous stirring. The precipitate was collected using a centrifuge and vacuum-dried to yield two-armed polymer as a white glassy solid. The monomer conversions for polymers **4**−**1**, **4**−**2** and **4**−**3**, as determined by GPC, were 19%, 31% and 50%, respectively, and their molecular weight characteristics are shown in Table 1.

Preparation of Eight-Armed Polymers via ATRP Procedure. A round-bottomed flask was charged with **[G#2]-Br$_8$** (55.9 mg, 25.0 μmol), PMDETA (42.0 μL, 200 μmol), and CuBr (28.5 mg, 200 μmol), and purged with N_2. Deoxygenated acetone (1.50 mL) and tBA (6.00 mL, 41.3 mmol) were then added, after which the solution was placed in an oil bath whose temperature was thermostatically maintained at 70 °C and vigorously stirred. The polymerization was carried out for 2, 4, and 8 h for preparing polymers **8**−**1**, **8**−**2**, and **8**−**3**, respectively. Following the reaction, the mixture was diluted with a small amount of CH_2Cl_2 and passed through a neutral alumina column for catalyst removal. The solution was then precipitated twice in a large excess of 30% H_2O/methanol with vigorous stirring. The precipitate was collected using a centrifuge and vacuum-dried to yield two-armed polymer as a white glassy solid. The monomer conversions for polymers **8**−**1**, **8**−**2**, and **8**−**3**, as determined by GPC, were 21%, 30% and 60%, respectively, and their molecular weight characteristics are shown in Table 1.

Preparation of C_{60}-Anchored Two-Armed Polymers via Bingel Cyclopropanation. A round-bottom flask was charged with two-armed polymer **2**−**1** (0.16 g, 10 μmol), C_{60} (8.6 mg, 12 μmol), I_2 (5.1 mg, 20 μmol), and toluene (20 mL) under N_2. DBU (6.1 mg, 40 μmol) was then added to the solution at room temperature, and the mixture was stirred for 24 h. The solvent was evaporated and the crude filtrate was passed through a neutral silica gel column and eluted with $CHCl_3$ varied gradually to 30:70 THF/$CHCl_3$, to yield C_{60}-anchored polymer as a red-brown glassy solid (97 mg, 60%).

Preparation of C_{60}-Anchored Four-Armed Polymers via Bingel Cyclopropanation. A round-bottom flask was charged with four-armed polymer **4**−**2** (0.35 g, 10 μmol), C_{60} (8.6 mg, 12 μmol), I_2 (5.1 mg, 20 μmol), and toluene (20 mL) under N_2. DBU (6.1 mg, 40 μmol) was then added to the solution at room temperature, and the mixture was stirred for 24 h. The solvent was evaporated and the crude filtrate was passed through a neutral silica gel column and eluted with $CHCl_3$ varied gradually to 30:70 THF/$CHCl_3$, to yield C_{60}-anchored polymer as a red-brown glassy solid (0.19 g, 55%).

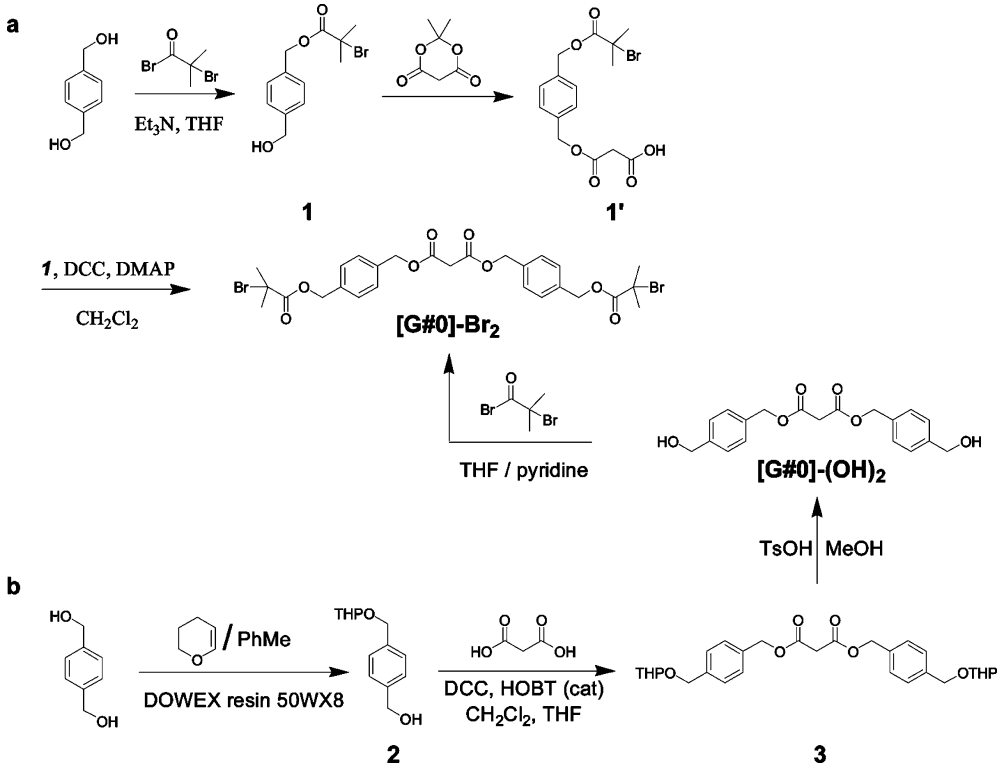
Preparation of C_{60}-Anchored Eight-Armed Polymers via Bingel Cyclopropanation. A round-bottom flask was charged with eight-armed polymer **8**−**2** (0.66 g, 10 μmol), C_{60} (8.6 mg, 12 μmol), I_2 (5.1 mg, 20 μmol), and toluene (20 mL) under N_2. DBU (6.1 mg, 40 μmol) was then added to the solution at room temperature, and the mixture was stirred for 24 h. The solvent was evaporated and the crude filtrate was passed through a neutral silica gel column and eluted with $CHCl_3$, to yield C_{60}-anchored polymer as a red-brown glassy solid (0.33 g, 50%).

Synthesis of Dibromo-Functionalized C_{60} Derivative as a Model Compound (4). A round-bottom flask was charged with **[G#0]-Br$_2$** (270 mg, 0.420 mmol), C_{60} (306 mg, 0.425 mmol), I_2 (161 mg, 0.634 mmol), and toluene (640 mL). The DBU (193 mg, 1.27 mmol) solution in toluene (5 mL) was added to the solution, and the mixture was stirred at room temperature for 6 h. Then, the reaction mixture was filtered through a short plug of a silica gel column using CH_2Cl_2 to remove unreacted C_{60}, and concentrated. The obtained crude product was purified by flash column chromatography on SiO_2, and eluted with CH_2Cl_2/hexane (70:30) to give **4** as a dark-red glassy product (262 mg, 46%). ^{1}H NMR ($CDCl_3$): δ = 7.43 (d, 4H, Ar**H**), 7.37 (d, 4H, Ar**H**), 5.45 (s, 4H, −ArC**H**$_2$-OCO), 5,20 (s, 4H, −ArC**H**$_2$OCO), 1.94 (s, 12H, −C(C**H**$_3$)). ^{13}C NMR ($CDCl_3$): δ = 171.36 (−CH_2O***C***O), 163.27 (−O***C***OCH_2), 145.20−138.99 (***C***$_{60}$), 136.16 (Ar ***C***), 134.60 (Ar ***C***), 129.10 (Ar ***C***), 128.04 (Ar ***C***), 71.27 (bridgehead ***C***), 68.49 (−***C***H$_2$OCO), 66.99 (−***C***H$_2$OCO), 55.56 (−***C***(CH$_3$)), 51.60 (−OCO***C***H$_2$), 30.73 (−C(***C***H$_3$)). MALDI−TOF. Calcd: $[M]^+$ m/z = 1360.3. Found: $[M + H]^+$ = 1361.5, $[M + Na]^+$ = 1383.5.

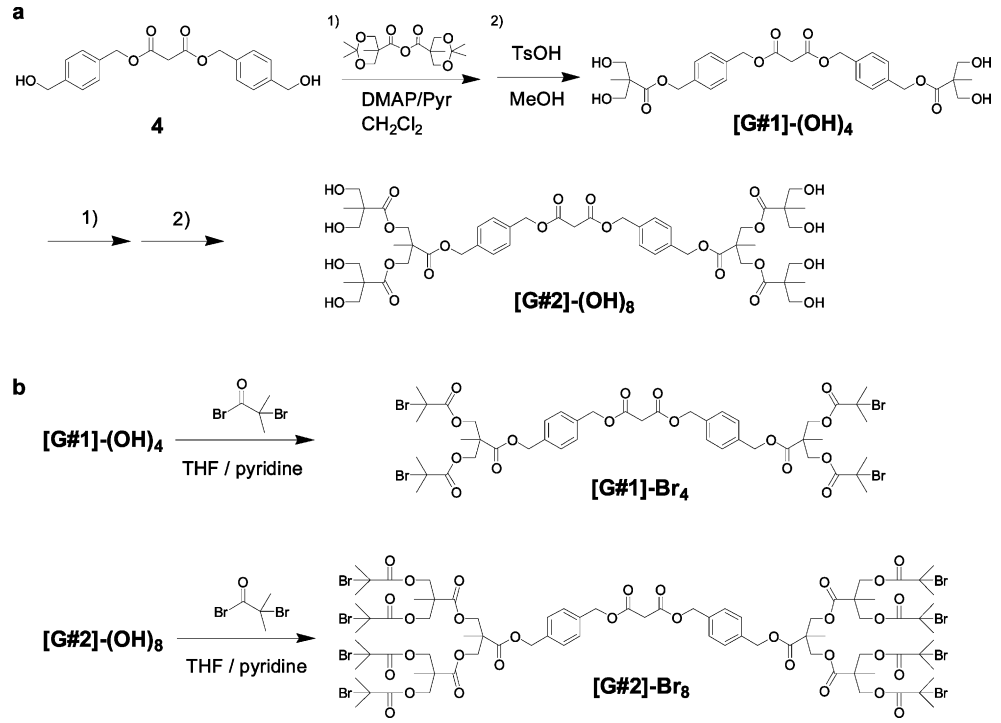
Results and Discussion

Synthesis and Characterization of Di-, Tetra-, and Octabromo-Functionalized Initiators. Scheme 1 illustrates two simply synthetic routes for preparing malonate ester-bearing dibromo-functionalized initiator, **[G#0]-Br$_2$**. One method[13] with an overall yield of 58% involved the monosubstitution of symmetrical diol with 2-bromoisobutyryl bromide in the presence of Et_3N, to yield α-bromo ester-derived alcohol **1**; the subsequent reaction of **1** with 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid) at 120 °C yielded the corresponding monoester **1′** of malonic acid, and DCC-promoted esterification of malonate monoester **1′** with alcohol **1** yielded the initiator. Another method with an overall yield of 33% involved the monotetrahydropyranylation of symmetrical diol, affording alcohol **2**;[14] the DCC-promoted esterification of alcohol **2** with malonic acid in the presence of HOBT yielded ditetrahydropyran-protected malonate ester **3**; the subsequent deprotection of **3** with a catalytic amount of *p*-toluenesulfonic acid (TsOH) yielded the functional diol with a malonate ester core, **[G#0]-(OH)$_2$**, and the acylation of the functional diol in the presence of 2-bromoisobutyryl bromide and pyridine yielded the initiator.

Scheme 1. Synthesis of Dibromo-Functionalized Initiator with a Malonate Ester Core, [G#0]-Br_2



Scheme 2. Synthesis of Tetra- and Octabromo-Functionalized Initiators with a Malonate Ester Core, [G#1]-Br_4 and [G#2]-Br_8



Additionally, as presented in Scheme 2, the malonate ester-containing tetraol, **[G#1]-(OH)**$_4$, was synthesized by treating **[G#0]-(OH)**$_2$ with acetonide-protected 2,2-bis(hydroxymethyl)-propionic anhydride, followed by the deprotection of hydroxyl groups with a catalytic quantity of TsOH.[15] Similarly, the octaol that contained eight primary hydroxyl end groups, **[G#2]-(OH)**$_8$, was prepared by repeating the synthetic procedure described above, using **[G#1]-(OH)**$_4$ as the starting material. Finally, the tetrabromo- and octabromo-functionalized initiators in 65% and 24% overall yield were prepared by the acylation of the functional tetraol and octaol with 2-bromoisobutyryl bromide and pyridine.

NMR and MALDI−TOF−MS methods were adopted to elucidate the chemical structures and molecular weights of these initiators. The ^{1}H NMR spectrum of **[G#0]-Br**$_2$ exhibited signals that corresponded to the peripheral methyl groups at 1.9 ppm, malonate protons at 3.4 ppm, two sets of benzylic protons at 5.1−5.2 ppm and aromatic rings at 7.3 ppm. All of this information verified the basic structure of the dibromo-functionalized molecule with a malonate ester core. The ^{1}H NMR spectra of

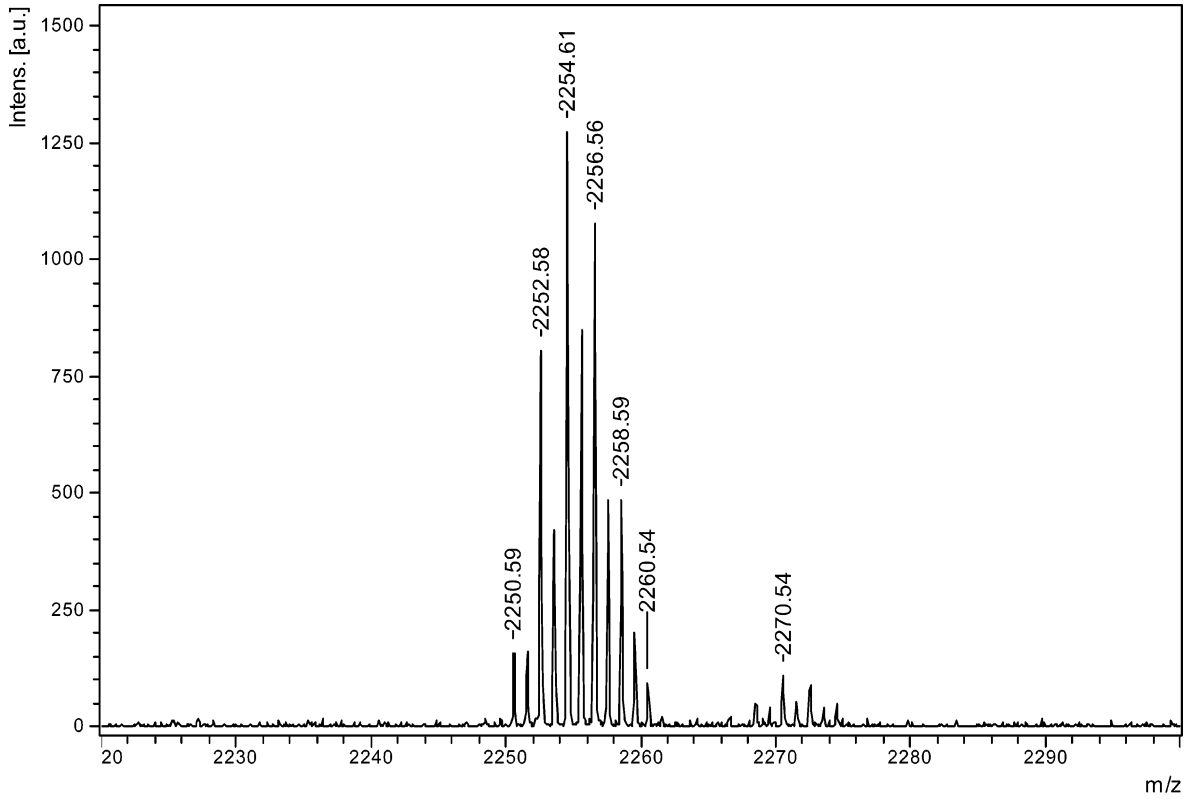
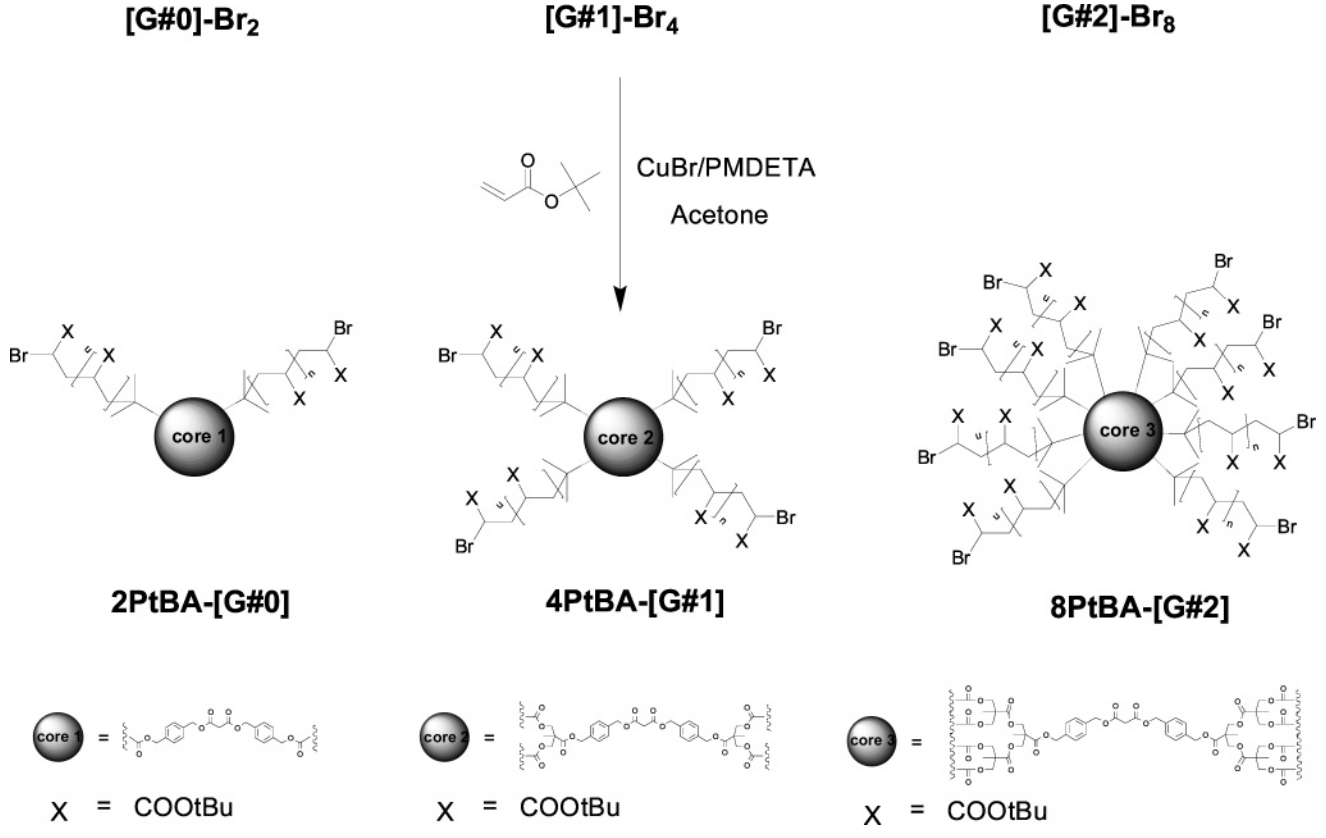


Figure 1. Matrix-assisted laser desorption ionization/time-of-flight (MALDI−TOF) spectrum of octabromo-fucntionalized initiator (**[G#2]-Br**$_8$) with calculated molecular weight of 2255.9 Da (sodium adduct).

[G#1]-Br$_4$ and **[G#2]-Br**$_8$ displayed not only the signals of the above protons at the same chemical shifts, but also the signals of the bis-MPA-based building blocks at 1.2−1.3 (methyl protons) and 4.2−4.4 (methylene protons) ppm, respectively. The integration ratios of each peak in the ^{1}H NMR spectra were consistent with the theoretical number of protons in these

Scheme 3. Synthesis of Two-, Four-, and Eight-Armed Poly(*tert*-butyl acrylate) via Atom Transfer Radical Polymerization Technique



initiators. Moreover, ^{13}C NMR analyses of these initiators confirmed the ^{1}H NMR results. MALDI−TOF−MS, a powerful tool for analyzing dendrimer, offered useful information regarding the purity and molecular weights of these initiators. The results of these analyses all agree with the calculated values. Figure 1 depicts the example of **[G#2]-Br$_8$**. The mass peaks with an isotopic distribution at an average *m*/*z* of 2256 and 2272 correspond to sodium and potassium adduct ions; the values exactly matched the theoretical calculations.

Synthesis and Characterization of Multiarmed Polymers and Their C_{60} Adducts. As shown in Scheme 3, the malonate ester-bridged two-, four-, and eight-armed poly(*tert*-butyl acrylate) (PtBA) were obtained by the ATRP of tBA monomer in the presence of CuBr/PMDETA complex, using **[G#0]-Br$_2$**, **[G#1]-Br$_4$**, and **[G#3]-Br$_8$** as initiators, respectively. Herein, ATRP, living/controlled radical polymerization, provided an efficient means of creating the polymers with a defined degree of polymerization (DP), through manipulating either the initial molar ratio of monomer to initiator or the conversion of the monomer, by altering the reaction time.[10] The monomer conversion was controlled not to exceed 60%, to prevent intermolecular coupling of a star-shaped polymer, which usually occurred while the polymer chains propagated at high conversion.[16] Table 1 summarizes the molecular weight characteristics of two-, four- and eight-armed PtBAs with various DPs. The resulting very narrow molecular-weight distributions (M_w/M_n) and single symmetric curves of all multiarmed star polymers synthesized herein eliminated the occurrence of star−star coupling and revealed well-controlled chain-growth during ATRP. Furthermore, the number-averaged molecular weights (M_n) of these star polymers were determined from both GPC chromatograms using linear polystyrene as standards and ^{1}H NMR spectra using the peak area ratio of α-protons on the PtBA backbone to the peripheral methyl protons on the core initiators. The discrepancy between the M_n values determined by the GPC and NMR increased with the number of arms, probably because the GPC method commonly underestimates the M_n values of branched polymers, such as dendrimers and star polymers, because of their conformation toward a more globular architecture, causing a smaller molecular size than random-coiled polystyrene standards. Similar results have also been reported for systems of eight-armed[16] and 12-armed[17] star-shaped PMMA. Thus, the

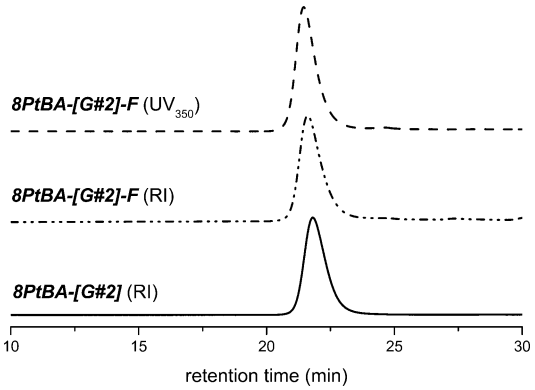
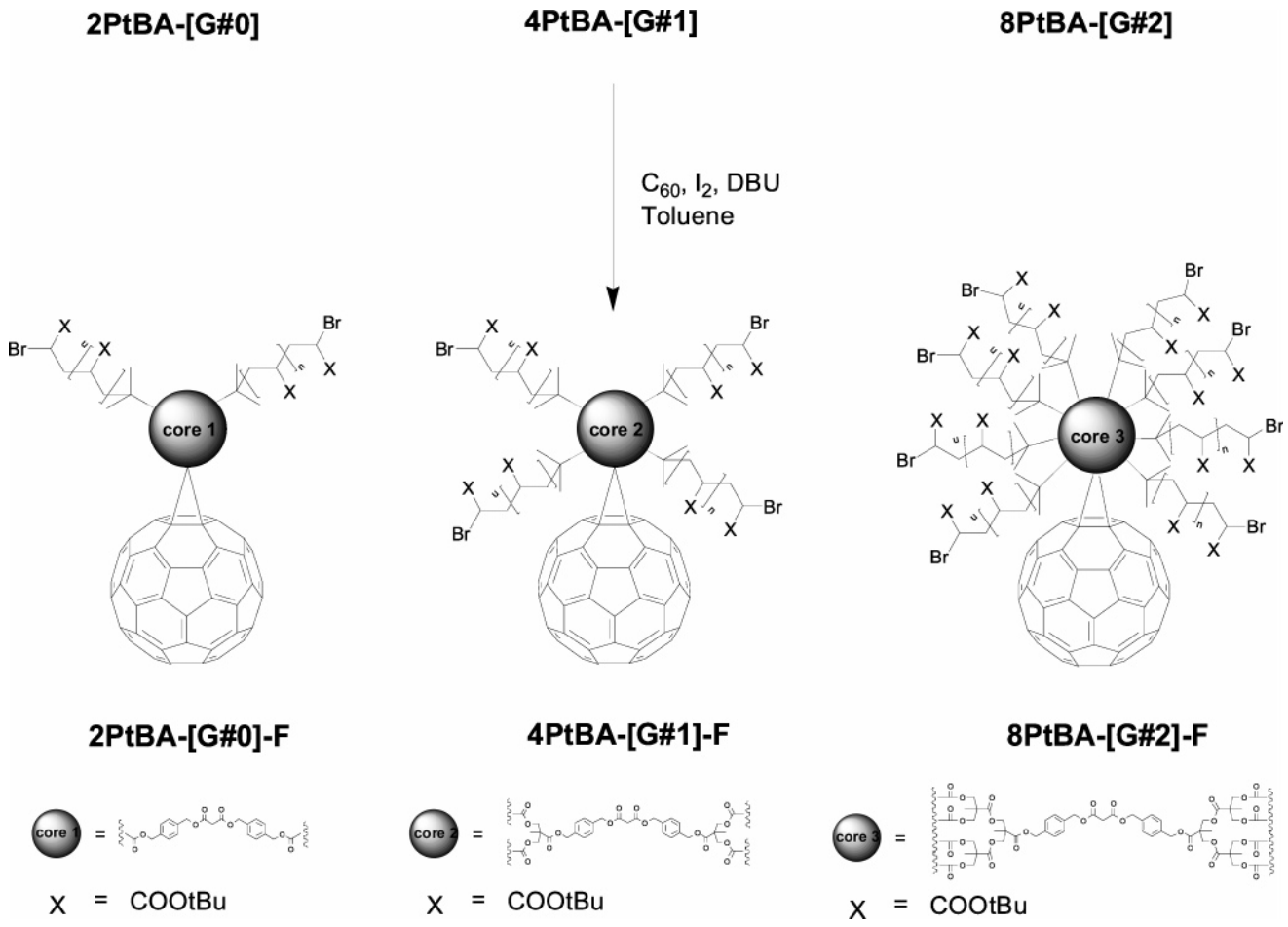


Figure 2. Gel permeation chromatograms (GPC) for C_{60}-anchored eight-armed poly(*tert*-butyl acrylate) (**8PtBA-[G#2]-F**) by refractive index (RI) and UV−vis dual detector and for eight-armed poly(*tert*-butyl acrylate) (**8PtBA-[G#2]**) by RI detector.

Scheme 4. Synthesis of C_{60}-Anchored Two-, Four-, and Eight-Armed Poly(*tert*-butyl acrylate) via Bingel Cyclopropanation



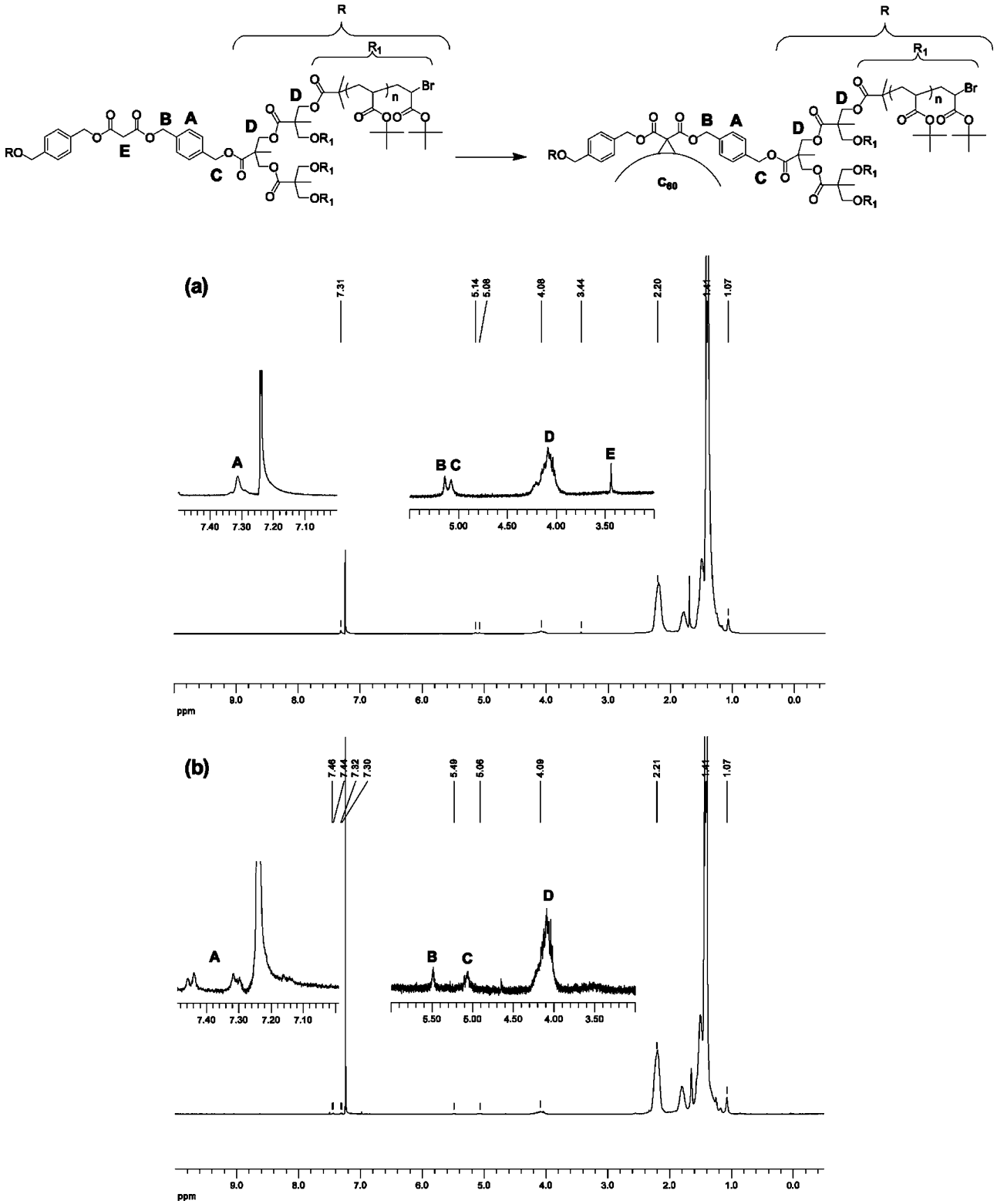


Figure 3. ^{1}H nuclear magnetic resonance spectra for (a) eight-armed poly(*tert*-butyl acrylate) (**8PtBA-[G#2]**) and (b) C_{60}-anchored eight-armed poly(*tert*-butyl acrylate) (**8PtBA-[G#2]-F**) in $CDCl_3$ at room temperature. The insets of parts a and b zoom in on the 3.0−6.0 ppm region.

M_n values determined by the NMR method for all samples prepared herein are more accurate, and they are very close to the target values calculated from the monomer-to-initiator molar ratio. This fact also indicates that the ATRP of tBA from these multifunctionalized initiators was a well-controlled process.

The grafting of C_{60} onto malonate ester-bridged star-shaped polymers is based on the Bingel reaction,[11] as shown in Scheme 4. It was conducted by treating C_{60} with corresponding multi-armed polymers, iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature to yield C_{60}-anchored two-, four-, and eight-armed PtBA. Figure 2 presents an example of GPC analyses, displaying traces of the eight-armed polymer, **8PtBA-[G#2]**, and its C_{60} adduct, **8PtBA-[G#2]-F**, obtained using UV and RI dual detectors. The tBA segments are only detectable by an RI detector but the C_{60} cage is detectable by both RI and UV detectors that are operated at 350 nm, and the

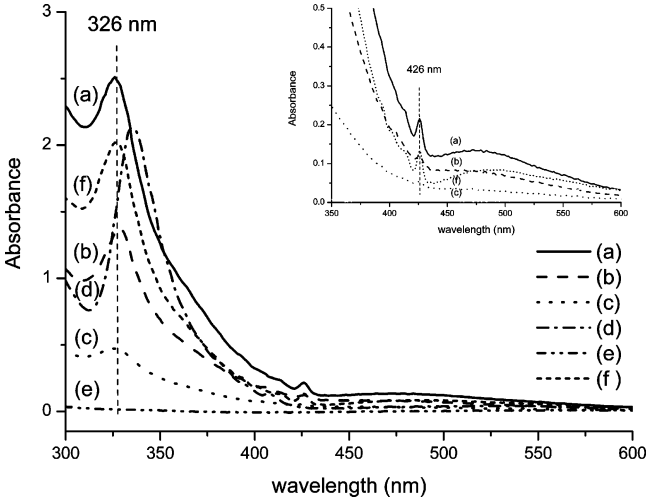


Figure 4. Ultraviolet-visible (UV−vis) absorption spectra of (a) C_{60}-anchored two-armed poly(*tert*-butyl acrylate) (**2PtBA-[G#0]-F**, M_n = 13 200 g mol^{-1}), (b) C_{60}-anchored four-armed poly(*tert*-butyl acrylate)-(**4PtBA-[G#1]-F**, M_n = 32 600 g mol^{-1}), (c) C_{60}-anchored eight-armed poly(*tert*-butyl acrylate) (**8PtBA-[G#2]-F,** M_n = 48 100 g mol^{-1}), (d) C_{60}, (e) two-armed poly(*tert*-butyl acrylate) (**2PtBA-[G#0]**), and (f) model compound **4** in CH_2Cl_2 at room temperature. The inset shows the 350−600 nm regions in detail and reveals a sharp band at 426 nm for both compound **4** and C_{60}-anchored polymers.

features of the GPC chromatograms of **8PtBA-[G#2]-F** obtained by RI and UV detectors are almost identical, revealing the presence C_{60} molecules in the structures of C_{60}-anchored polymers. Table 1 presents the molecular weight distributions of two-, four-, and eight-armed systems, and the similar M_n values of the polymers before and after they were attached to the C_{60} molecule establish that the monosubstituted C_{60} derivatives can be obtained by reacting 1 equiv of multiarmed polymers with 1 equiv of C_{60} molecules.

The chemical structures of multiarmed polymers and their C_{60} adducts were carefully analyzed by ^{1}H NMR. Figure 3 presents an example of **8PtBA-[G#2]** and **8PtBA-[G#2]-F**. The peaks from 1.4 to 2.2 ppm in Figure 3, parts a and b, are assigned to the protons on the PtBA backbone of the eight-armed polymer. Moreover, the signals from the initiator core can be visualized upon expanding the region related to that in the ^{1}H NMR spectrum of the octabromo-functionalized initiator, **[G#2]-Br**$_8$. In Figure 3a, the peak centered at 7.31 ppm (A) is attributed to the aromatic protons; the peaks centered at 5.14 (B) and 5.07 (C) ppm correspond to the two sets of benzylic protons; the peaks between 4.0 and 4.3 ppm (D) correspond to the bis-MPA building block, and the peak centered at 3.44 ppm (E) is attributed to the malonate protons. A comparison with the original peaks in the initiator spectrum demonstrates that these peaks in the polymer spectrum are broader and shifted slightly upfield. This result strongly suggests that the monomer of tBA was successfully polymerized from all initiating sites of the initiator to yield eight-armed PtBA.[17] The disappearance of peak E in Figure 3b after the polymer attached to the C_{60} molecule to yield the C_{60}-anchored polymer verifies the successful Bingel cyclopropanation between the malonate ester core of **8PtBA-[G#2]** and C_{60}. Additionally, since the C_{60} molecule has a strong electron-withdrawing capacity, peak B, assigned to the benzylic protons of the initiator core that neighbors the C_{60} moiety, was apparently shifted downfield from 5.14 to 5.49 ppm. Peak A, corresponding to the aromatic protons, also split from a singlet signal into two pairs of doublet signals, because the presence of C_{60} molecule changed the electron density. The NMR analyses of both the two and the four-armed systems exhibit are analogous to that of eight-armed system. These observations clearly reconfirmed that C_{60} was covalently bonded to the polymers.

Figure 4 displays the UV−vis absorption spectra of C_{60}-anchored multiarmed PtBA in CH_2Cl_2. All C_{60}-anchored PtBA including two-, four-, and eight-armed systems have an absorp-

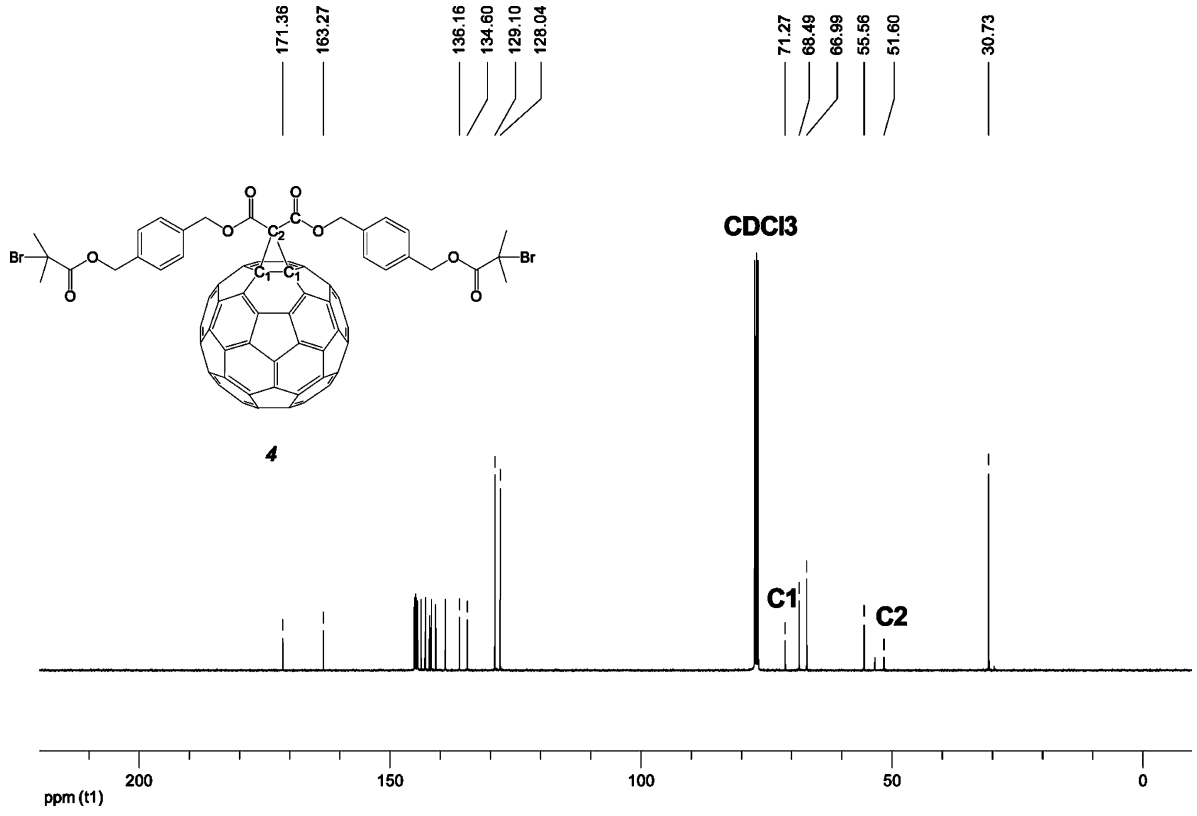


Figure 5. ^{13}C nuclear magnetic resonance spectrum for model compound **4** in $CDCl_3$ at room temperature.

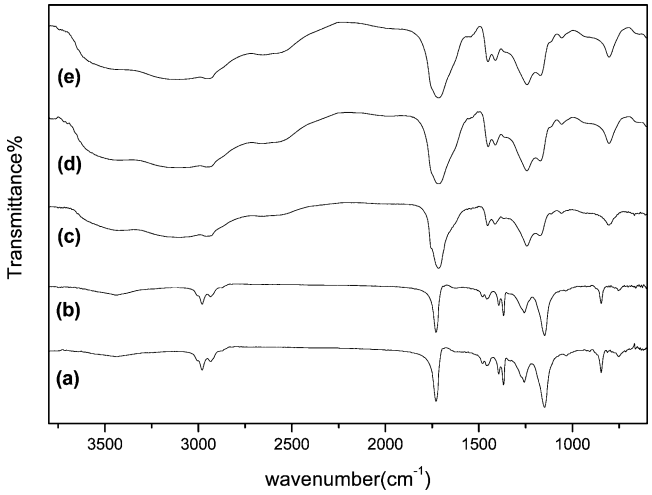


Figure 6. Fourier transform infrared absorption (FT-IR) spectra of (a) two-armed poly(*tert*-butyl acrylate) (**2PtBA-[G#0]**), (b) C_{60}-anchored two-armed poly(*tert*-butyl acrylate) (**2PtBA-[G#0]-F**), (c) C_{60}-anchored two-armed poly(acrylic acid) (**2PAA-[G#0]-F**), (d) C_{60}-anchored four-armed poly(acrylic acid) (**4PAA-[G#1]-F**), and (e) C_{60}-anchored eight-armed poly(acrylic acid) (**8PAA-[G#2]-F**) in KBr pellets.

tion band centered at 326 nm, with a tail that extends to around 600 nm. The PtBA backbone and initiator core cannot absorb incident light at these wavelengths, so the absorption profile for the polymers entirely corresponds to the C_{60} moiety. However, the absorption band of the C_{60}-anchored polymers is blue-shifted from the absorption maximum of pure C_{60} molecules (Figure 4d). Diederich et al. found that this blue-shift indicates that the C_{60}-anchored polymer is a "closed" 6−6-ring-bridged methanofullerene derivative.[18] ^{13}C NMR is a powerful tool for determining whether the bonding in the fullerene derivative is of the π-(6−5-ring-bridged) or σ-(6−6-ring-bridged) form. However, determining the type of bonding on a C_{60} cage in C_{60}-anchored PtBA is difficult because the signal from the PtBA backbone severely suppresses the signal from the two bridged carbons of C_{60} in ^{13}C NMR. The dibromo-functionalized C_{60} derivative **4** was prepared by directly treating the malonate ester derivative, **[G#0]-Br**$_2$, with C_{60} under the same preparation conditions as used to prepare the C_{60}-anchored polymers, providing a model compound for ^{13}C NMR analysis, whose UV−vis absorption profile could also be examined to determine the type of bonding between the malonate ester moiety of multiarmed polymers and the C_{60} molecule. Figure 5 presents the ^{13}C NMR spectrum of model compound **4**, and the clear appearance of the peak at 71.27 ppm is attributed to the sp^3 bridgehead carbon atom (C1) of the "close" transannular bond on the C_{60} cage. This finding is a clear evidence of the formation of 'closed' 6−6-ring-bridged methanofullerene derivatives in the DBU- and iodine-promoted Bingel reaction.[18] Moreover, the UV−vis absorption band of compound **4** (Figure 4f) is blue-shifted by 9 nm from the absorption maximum of the C_{60} molecule, which result is consistent with the observation of the 9 nm blue-shift of the absorption band of the C_{60}-anchored polymer. The presence of a sharp band centered at 426 nm for both compound **4** and the C_{60}-anchored polymers (inset in Figure 4) is also regarded as characteristic of a "closed" 6−6-ring-bridged methanofullerene derivative.[19] Consequently, these results confirmed that the bonding between the malonate ester moiety of multi-armed PtBA and C_{60} molecules is σ-homoaromatic, reinforcing the conclusion that the formation of covalent bonds between fullerene and polymer yield C_{60}-anchored multiarmed PtBA.

Figure 4 also demonstrates that the absorbance of light at 326 nm by the two-, four-, and eight-armed polymers with identical concentrations of 1 gL^{-1} in CH_2Cl_2 decreases as the number of polymer arm increases. This is because the increase in both the number of arms and the M_n values of the polymers results in the reduction of the weight percentage of C_{60} moiety in the sample, which is directly proportional to the light absorbance of the material, according to Beer's law. C_{60}-anchored polymers and model compound **4** are methanofullerene derivatives, so both compounds were assumed to share similar UV−vis absorp-

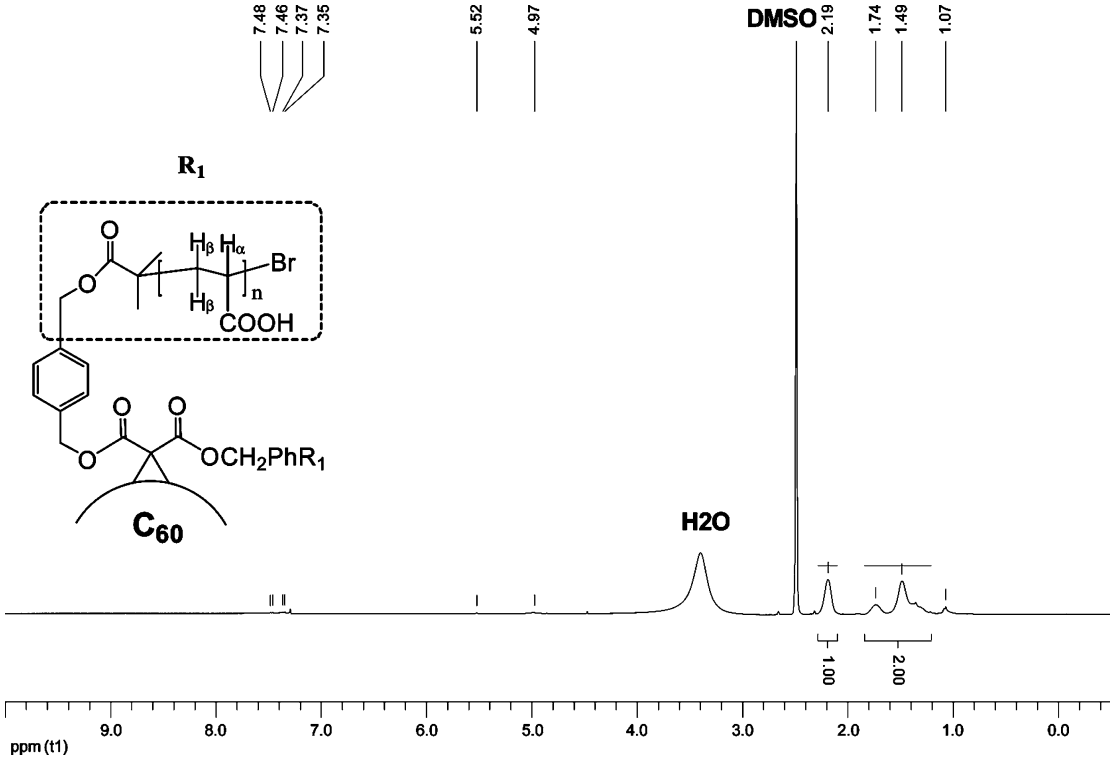


Figure 7. ^{1}H nuclear magnetic resonance spectrum for C_{60}-anchored two-armed poly(acrylic acid) (**2PAA-[G#0]-F**) in DMSO-d_6 at room temperature.

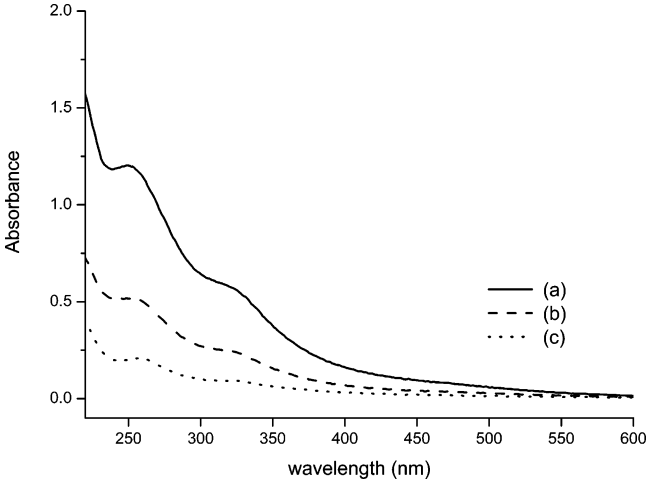


Figure 8. Ultraviolet-visible (UV−vis) absorption spectra of (a) C_{60}-anchored two-armed poly(acrylic acid) (**2PAA-[G#0]-F**), (b) C_{60}-anchored four-armed poly(acrylic acid) (**4PAA-[G#1]-F**), and (c) C_{60}-anchored eight-armed poly(acrylic acid) (**8PAA-[G#2]-F**) in H_2O at room temperature.

tion profiles and identical molar absorbtivities. Accordingly, the C_{60} contents of the polymers can be estimated from the UV−vis absorbance of the CH_2Cl_2 solution of polymers at 326 nm, according to Beer's law and the calibration curve established using a series of known concentrations of model compound **4** in CH_2Cl_2. The results in Table 1 show that the C_{60} contents in two-, four-, and eight-armed systems drop as the M_n values of the polymers increase, and they are close to the theoretical values based on the assumption that the C_{60}-derived polymer is a monoadduct.

Hydrolysis of C_{60}-Anchored Multiarmed PtBA. Subsequent hydrolysis of C_{60}-anchored multiarmed PtBA in the presence of trifluoroacetic acid (TFA) as an acidic promoter afforded C_{60}-anchored multiarmed poly(acrylic acid) (PAA) with excellent solubility in water. GPC analyses show that the resultant C_{60}-derived water-soluble polymers retained a very narrow molecular-weight distribution and the loss of *tert*-butyl groups on the PtBA backbone reasonably reduced the M_n values. These results indicate that TFA treatment did not alter the linkages between the C_{60}-derived core and polymer backbone. FT-IR analyses of a series of C_{60}-anchored polymers provided useful information for monitoring the reactions, especially the hydrolysis of *tert*-butyl groups. In the example of the two-armed system shown in Figure 6, the FT-IR spectra of the two-armed polymers after (Figure 6b) attachment to a C_{60} molecule did not differ from that before (Figure 6b), but the broad peak at 3000−3500 cm^{-1}, attributed to the absorption of carboxylic acid and the disappearance of the sharp peaks at 1393 and 1368 cm^{-1}, attributed to the absorption of the *tert*-butyl groups in Figure 6c−e, which correspond to two-, four-, and eight-armed C_{60}-anchored PAA respectively, clearly indicate the successful hydrolysis of the corresponding C_{60}-anchored multiarmed PtBA.[8,20] Figure 7 displays an example of ^1H NMR analysis of C_{60}-anchored two-armed PAA and shows that all of the *tert*-butyl groups were completely removed because the peak at 1.4 ppm disappeared and the integration ratio of the peak of the β-protons to the peak of the α-protons on the PAA backbone equals 2, perfectly matching the theoretical value. Figure 8 presents the UV−vis spectra of the C_{60}-anchored two-, four-, and eight-armed PAA solubilized in water, revealing that the characteristic peaks of the C_{60} moiety at 250 and 320 nm become broader with nonpronounced maxima than the absorption spectra of their parent C_{60}-anchored PtBA. According to the earlier studies, this behavior is caused by the amphiphilic character of C_{60}-anchored PAA, which may be responsible for micellar aggregation in water.[8,20,21] The hydrophobic cores, C_{60} molecules and aliphatic ester dendrons, form an actual cluster with the hydrophilic carboxyl groups that protrude into water as surrounding shells.

Conclusion

Novel di-, tetra-, and octabromo-fuctionalized molecules with a malonate ester core weresynthesized and adopted as effective initiators in preparing well-controlled multiarmed polymers using the ATRP method. The Bingel cyclopropanation between C_{60} molecule and the malonate ester-bearing poly(*tert*-butyl acrylate) was demonstrated to be an efficient route for synthesizing multiarmed C_{60}-anchored poly(*tert*-butyl acrylate) with well-defined and well-controlled structure and molecular weight. Both GPC and ^1H NMR studies of the C_{60}-anchored polymers verified that C_{60} had been covalently bonded to the polymer to yield monosubstituted C_{60} derivatives. The UV−vis analyses of the C_{60}-anchored polymers not only reconfirmed this successful reaction but also revealed that the bonding was σ-homoaromatic between the polymer and C_{60}. Additionally, the water-soluble C_{60}-anchored multiarmed poly(acrylic acid) was obtained by simple acidic treatment of the hydrophobic C_{60}-anchored multiarmed poly(*tert*-butyl acrylate). Further investigations of these hydrophilic C_{60}-anchored polymers are being conducted to elucidate their micellar behavior and optoelectronic properties.

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Supporting Information Available: Figures showing ^1H NMR spectra of multiarmed poly(*tert*-butyl acrylate)s, C_{60}-anchored poly(*tert*-butyl acrylate)s, and C_{60}-anchored poly(acrylic acid)s. This material is available free of charge via the Internet at http://pubs.acs.org.

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