Supplementary Information

A Novel [60]Fullerene-Appended Initiator for Living Cationic Polymerization and its Application to the Synthesis of [60]Fullerene-End-Capped Poly(vinyl ether)s

Jin Motoyanagi, Ryo Miyabara, Masashi Suzuki, Sadao Miki and Masahiko Minoda*

Department of Chemistry and Materials Technology, Graduate School of Science and Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan.
E-mail: minoda@kit.ac.jp

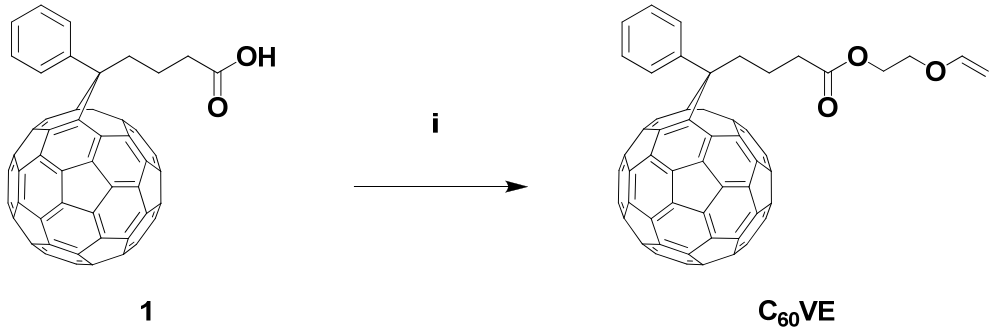
Measurements.

^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker model AC-500 spectrometer, operating at 500 and 125 MHz, respectively, where chemical shifts (δ in ppm) were determined with respect to non-deuterated solvent residues as internal standards. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI–TOF–MS) was performed on an Applied Biosystems BioSpectrometry Workstation™ model Voyager–DE™ STR spectrometer using 9-nitroanthracene as a matrix. Preparative gel permeation chromatography (SEC) was performed at 25 °C by using 21.5 mm x 300 mm polystyrene gel columns (TOSOH TSKgel G2000H, G2500H and G3000H) on a TOSOH model CCPE equipped with RI-8022 RI detector. Analytical GPC was performed at 40 °C, using 8.0 mm x 300 mm polystyrene gel columns (Shodex KF-804 x 2) on a TOSOH model DP-8020 equipped with a UV-8000 variable-wavelength UV-vis detector and a RI-8022 RI detector. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) ratio were calculated from the chromatographs with respect to 15 polystyrene standards (Scientific Polymer Products, Inc.; M_n = 580-670000, M_w/M_n = 1.01-1.07). UV-vis spectra were recorded on a SHIMADZU Type UV-2550 spectrometer.

Materials.

Ethylene glycol mono vinyl ether (TCI, 95%), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (TCI, 98%), 4-dimethylaminopyridine (DMAP; TCI, 98%), TFA (Wako, 98%) and ethylaluminum dichloride ($EtAlCl_2$; Wako, 1.0 M in n-hexane) were used as received. Phenyl-C_{61} butyric acid was prepared according to a literature[1] with some modifications. Isobutyl vinyl ether (**IBVE**; Aldrich, 99%) was dried overnight over KOH pellets, and distilled twice over CaH_2. 2-Methoxyethyl vinyl ether (**MOVE**; Maruzen Petrochemical, 99.9%) was distilled twice over CaH_2 under reduced pressure. Anhydrous solvents for reactions were purchased from Kanto Chemicals.

Preparation of C_{60}VE.



Scheme 1 *Reagents and conditions*: (i) ethylene glycol mono vinyl ether, DMAP, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride,1,2-dichlorobenzene, 25 °C.

Compound C_{60}VE. To a 1,2-dichlorobenzene solution (45 mL) of a mixture of phenyl-C_{61} butyric acid (**1**; 450 mg, 0.50 mmol), ethylene glycol mono vinyl ether (0.92 mL, 100 mmol) and DMAP (60 mg, 0.50 mmol) was added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (190 mg, 1.0 mmol) and the mixture was stirred for 16 h at 25 °C under N_2. The reaction mixture was washed with water, dried over Na_2SO_4 and evaporated to dryness. The residue was chromatographed on SiO_2 with toluene as an eluent to allow isolation of **C_{60}VE** as purple solid (445 mg, 0.46 mmol) in 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (m, 2H), 7.55 (m, 2H), 7.43 (m, 1H), 6.46 (m, 2H), 4.28 (m, 2H), 4.19(m, 1H), 4.05 (m, 1H) 3.85 (m, 2H), 2.17 (t, J =7.5 Hz, 2H), 1.64 (m, 2H), 1.48 (m, 2H) ppm. ^{13}C NMR

[1] J. C. Hummelen, B. W. Knight, F. LePeq, F. Wudl, J. Yao and C. L. Wilkins, *J. Org. Chem.*, 1995, **60**, 532-538.

(125 MHz, $CDCl_3$): δ 172.94, 151.49, 147.47, 146.54, 145.31, 144.91, 144.62, 144.37, 144.09, 143.88, 143.78, 143.69, 143.27, 143.22, 143.18, 143.14, 142.86, 142.62, 142.36, 142.26, 142.05, 142.01, 141.44, 141.16, 140.60, 139.89, 139.83, 138.93, 138.46, 138.30, 138.17, 138.04, 136.82, 135.19, 130.89, 130.65, 128.80, 127.89, 127.82, 87.26, 79.99, 65.81, 62.73, 61.09, 35.40, 34.02, 19.92. MALDI–TOF–MS: Calcd. for $C_{75}H_{19}O_3$ $[M+H]^+$: m/z = 967.13; Found: 967.34.

Cationic polymerization of vinyl ether monomers with C_{60}VE-TFA.

The preparation of **C_{60}VE-TFA** and polymerization of vinyl ether monomers were carried out under a dry nitrogen atmosphere in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure is given below. To a toluene solution (3.8 mL) of **C_{60}VE** (39 mg, 40 μmol) was added 1 equivalent TFA (5.0 mM in toluene; 0.25 mL, 40 μmol) at 0 °C under N_2, and the mixture was stirred for 15 h at 0 °C under N_2. And then, to the reaction mixture were added of prechilled toluene (2.6 mL), **IBVE** (0.52 mL, 4.0 mmol), dioxane (0.80 mL, 9.4 mmol) and $EtAlCl_2$ (in hexane, 1.0 M; 0.10 mL, 0.10 mmol) at 0 °C under N_2. After stirring for 15 h, the polymerization was quenched with an excess of prechilled MeOH (1 mL) containing a small amount of NH_3 aq. The monomer conversion was determined by GC measurement. The quenched reaction mixture was poured into toluene and then washed with dil. HCl and water to remove the aluminum-containing residues, and evaporated to dryness under reduced pressure. The residue was subjected to preparative GPC, where the first band was collected and evaporated to dryness to give **C_{60}-PIBVE** as purple oil.

Characterization of C_{60}-PMOVE.

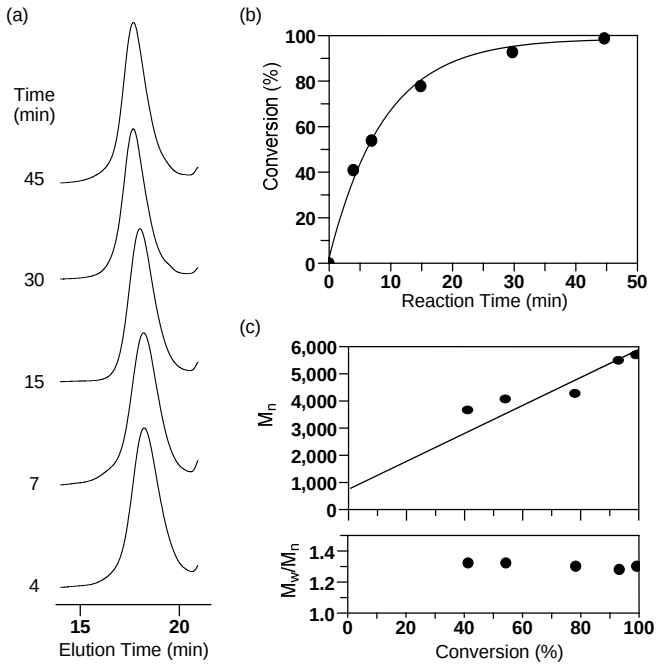


Fig. S1. (a) SEC curves of **C_{60}-PMOVE** using THF as the eluent, (b) time-conversion curve for the polymerization of **MOVE** and (c) M_n and M_w/M_n value of **C_{60}-PMOVE** plotted against monomer conversion. Polymerization was conducted with **C_{60}VE-TFA**/$EtAlCl_2$/dioxane in toluene at 0 °C ([**MOVE**]$_0$ = 500 mM, [$EtAlCl_2$]$_0$ = 12.5 mM, [dioxane]$_0$ = 1.2 M, [**C_{60}VE-TFA**]$_0$ = 5.0 mM).