

Electronic Supplementary Information (ESI)

Surface Segregation of a Branched Polymer with Hydrophilic Poly[2-(2-ethoxy)ethoxyethyl vinyl ether] Side-chains

S. Sugimoto,^a Y. Oda,^{*b} T. Hirata,^b R. Matsuyama,^b H. Matsuno^{b,c} and K. Tanaka^{*a,b,c}

^a Department of Automotive Science, Kyushu University, Fukuoka 819-0395, Japan

^b Department of Applied Chemistry, Kyushu University, Fukuoka 819-0395, Japan

^c International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka 819-0395, Japan

*To whom correspondence should be addressed

TEL: +81-92-802-2878, FAX: +81-92-802-2880

E-mail: k-tanaka@cstf.kyushu-u.ac.jp, y-oda@cstf.kyushu-u.ac.jp

Materials

2-(2-Ethoxy)ethoxyethyl acetate (EOEOEA) was prepared from 2-(2-ethoxy)ethoxyethyl vinyl ether [EOEOVE; (Maruzen Petrochemical, Co., Ltd.)] and acetic acid (Wako Pure Chemical Industries, Ltd.; > 99.7%). Obtained EOEOEA was distilled twice over calcium hydride before use. EOEOVE was washed with 10% aqueous sodium hydroxide and then with water, dried overnight over potassium hydroxide pellets, and distilled over calcium hydride and then metallic sodium. 1,4-Dioxane (Kanto Chemical Co., Inc.; > 99.7%) was distilled over calcium hydride and then lithium aluminum hydride. Toluene (Kanto Chemical Co., Inc.; > 99.7%) for living cationic polymerization was distilled over calcium hydride and then metallic sodium. 2-Hydroxyethyl methacrylate [HEMA; (Kanto Chemical Co., Inc.; > 95.0%)] was distilled with calcium hydride before use. Commercial $\text{Et}_{1.5}\text{AlCl}_{1.5}$ (Nippon Aluminum Alkyls, Co.; 1.0 M solution in toluene) was used without further purification. Methyl methacrylate [MMA; (Wako Pure Chemical Industries, Ltd.; > 98.0%)] was washed with 10% aqueous sodium hydroxide and then with water, dried overnight with MgSO_4 , and distilled twice with calcium hydride before use. Toluene for radical polymerization was distilled with calcium hydride before use. Ethyl 2-bromoisobutyrate [EtBr*i*Bu; (Tokyo Chemical Industry Co., Ltd.; > 98.0%)] and 4,4'-dinonyl-2,2'-bipyridyl [dNbp*y*; (Sigma-Aldrich Co. LLC.; > 97.0%)], CuBr (Sigma-Aldrich Co. LLC.; > 99.9%) were used without further purification.

Living Cationic Polymerization

Cationic polymerization of EOEOVE was carried out under dry nitrogen in a flask equipped with a three-way stopcock at 233 K. The reaction was initiated by the addition of the $\text{Et}_{1.5}\text{AlCl}_{1.5}$ toluene solution into the monomer solution under dry nitrogen and terminated by the addition of HEMA. The quenched reaction mixture was washed with water to remove the initiator residues, was evaporated to dryness under reduced pressure, and then vacuum-dried overnight. The obtained products, referred to PEOEOVE-MA macromonomers, were purified by dialysis against methanol for at least 3 days in a 1k MWCO dialysis tube.

Atom Transfer Radical Polymerization

Radical polymerization of PEOEOVE-MAs with MMA was carried out under dry nitrogen in a flask equipped with a three-way stopcock. The mixture of PEOEOVE-MA, MMA, CuBr, and dNbp*y* with the predetermined ratios was dried and degassed several times by freeze-pump-

thaw cycles in the flask. The total monomer concentration was kept constant at 50 wt%. After an addition of the EtBr*i*Bu toluene solution into the mixture, the reaction mixture was then heated in an oil bath at 363 K. After a prescribed time, the reaction mixture was cooled to room temperature. The obtained products were purified by passing through an activated aluminum column to remove the catalyst residues and dried under reduced pressure. The products were dissolved in tetrahydrofuran (THF), and then they were subjected to gel permeation chromatography (GPC) measurements using three polystyrene gel columns (TSKgel MultiporeH_{XL}-M, flow rate = 1.0 mL/min) for Fig. 1 or two columns (Shodex KF-804L, flow rate = 0.8 mL/min) for Fig. S1. The conversion of MMA and PEOEOVE-MAs were determined by gravimetry and ¹H-NMR analysis, respectively.

Atomic Force Microscopic (AFM) Observations

The cantilever tip used for the measurements was microfabricated from Si, and its spring constant and resonance frequency in air were 2.8 Nm⁻¹ and 75 kHz, respectively. The tip radius was ~ 5 nm. The drive frequency used in water was 30 kHz, which was on the lower frequency side of the resonance. To avoid possible deformations of the sample surface during the observation, the ratio of the set point to the free amplitude of the cantilever was maintained at ~ 0.9 (10% damping of the amplitude of oscillation).

Molecular Characteristics of PEOEOVE-MAs and PMMA-g-PEOEOVEs

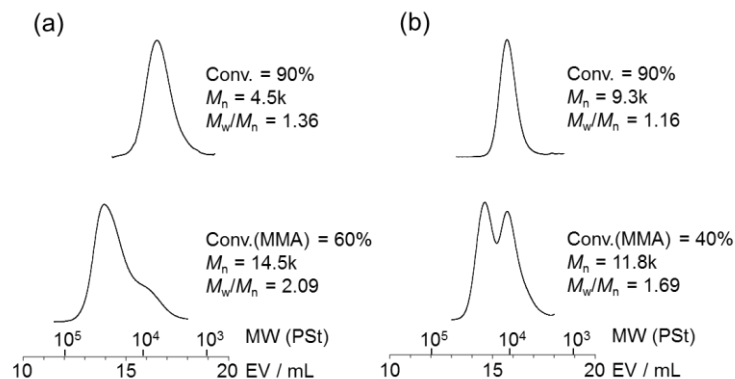


Fig. S1 MWD curves for (a) PEOEOVE-MA5k and (b) PEOEOVE-MA9k (upper) and for the obtained products by radical copolymerization of (a) PEOEOVE-MA5k or (b) PEOEOVE-MA9k with MMA (lower). Cationic polymerization conditions: $[EOEOVE]_0 = 0.57$ M, $[EOEOEA]_0 = 9.2$ mM (PEOEOVE-MA9k), 18.4 mM (PEOEOVE-MA5k), $[Et_{1.5}AlCl_{1.5}]_0 = 20$ mM, $[1,4\text{-dioxane}] = 1.2$ M, in toluene at 233 K for 2 h. Radical copolymerization conditions: $[PEOEOVE\text{-}MA5k]_0 = 400$ mM or $[PEOEOVE\text{-}MA9k]_0 = 193$ mM, $[MMA]_0 = 72$ M, $[EtBr_iBu]_0 = 150$ mM, $[CuBr] = 150$ mM, $[dNbpy] = 300$ mM, in toluene at 363 K for 6 h (PEOEOVE-MA9k) or for 12 h (PEOEOVE-MA5k).

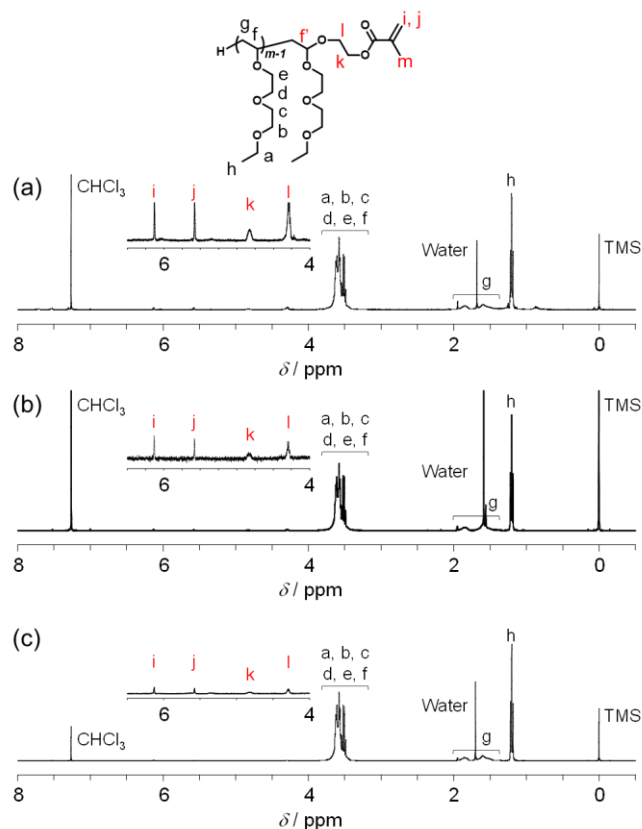


Fig. S2 1H -NMR spectra for (a) PEOEOVE-MA3k, (b) PEOEOVE-MA5k and (c) PEOEOVE-MA9k acquired in $CDCl_3$ with tetramethyl silane (TMS) as an internal standard.

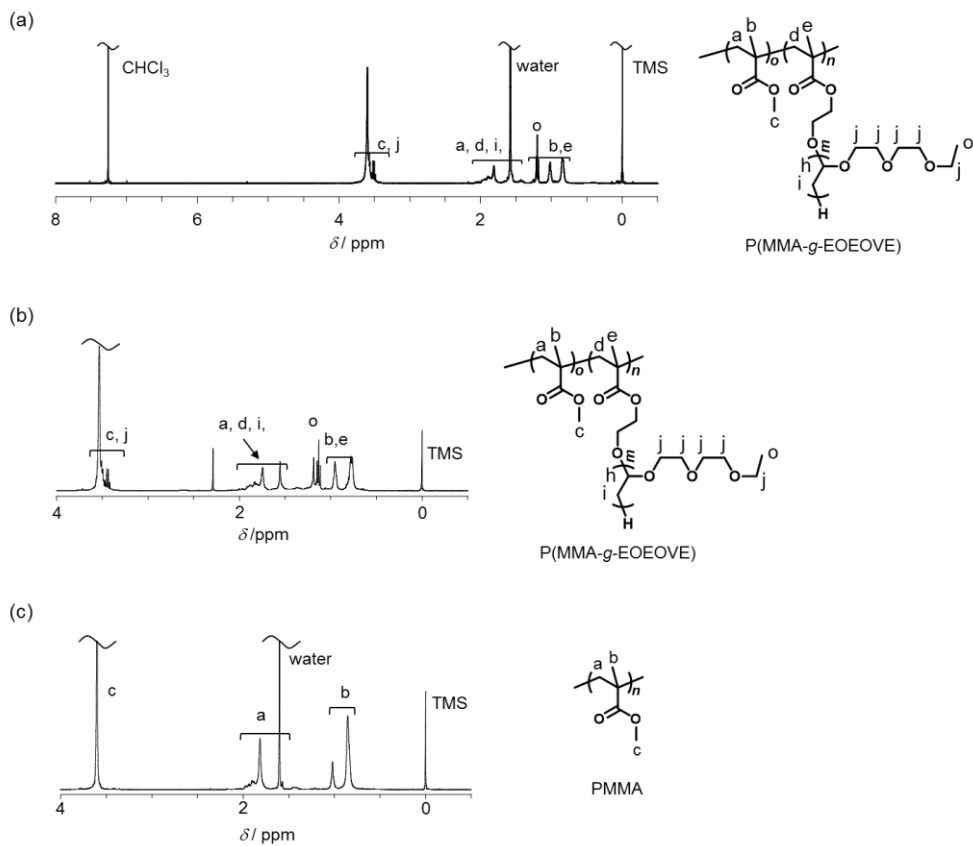


Fig. S3 ^1H NMR spectra for the products obtained by ATRP of MMA with (a) PEOEOVE-MA3k, (b) PEOEOVE-MA5k and (c) PEOEOVE-MA9k measured in CDCl_3 with TMS. It is noted that the spectra for (b) and (c) were acquired after removing of the remained PEOEOVE-MAs by preparative GPC.

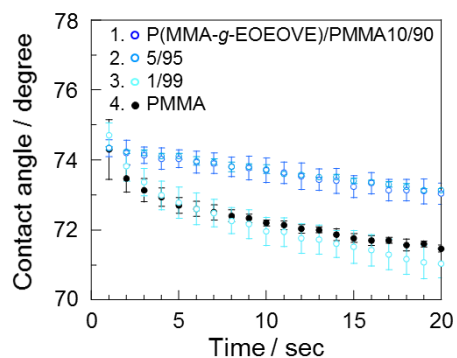


Fig. S4 (a) Time dependence of contact angles of a water droplet for the PMMA homogeneous film and P(MMA-g-EOEOVE)/PMMA blend films with the various blend ratios; (1/99), (5/95) and (10/90).