

Electronic Supplementary Information

Aqueous Emulsion Polymerizations of Methacrylates and Styrene via Reversible Complexation Mediated Polymerization (RCMP)

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1. Experimental section.

Materials. Methyl methacrylate (MMA) (>99.8%, Tokyo Chemical Industry (TCI), Japan), styrene (>99.0%, TCI), benzyl methacrylate (BzMA) (>98.0%, TCI), glycidyl methacrylate (GMA) (>95.0%, TCI), 2-hydroxyethyl methacrylate (HEMA) (>95.0%, TCI), sodium iodide (NaI) (>99.0%, Sigma-Aldrich, USA), potassium iodide (KI) (>99.5%, TCI), tetrabutylammonium iodide (BNI) (>98.0%, TCI), tributylmethylphosphonium iodide (BMPI) (>98.0%, TCI), Tween-80 (the ester group derived from oleic acid ($\geq 58.0\%$) and from primarily linoleic, palmitic, and stearic acids (balance), Sigma-Aldrich), FES-77 (33.0% of FES and 67.0% of water, BASF, Shanghai), and 2,2'-azobis(2-methylpropionamide) dihydrochloride (V50) (95%, Wako Pure Chemical, Japan) were used as received. 2-Hydroxyethyl 2-iodoisobutyrate (2-HEI) (>90.0%), 2-hydroxyethyl 2-iodo-2-phenylacetate (2-HEPhI) (>85.0%), and 2-iodophenylacetic acid (2-IPhA) (>94.0%) were provided through the courtesy of Godo Shigen Co., Ltd. (Japan) and used as received.

Measurement. The GPC analysis using THF as the eluent was performed on a Shimadzu LC-2030C Plus liquid chromatograph (Kyoto, Japan) equipped with both a Shodex KF-804L mixed gel column (300 × 8.0 mm; bead size = 7 μm; pore size = 1500 Å) and a Shodex LF-804 mixed gel column (300 × 8.0 mm; bead size = 6 μm; pore size = 3000 Å). The flow rate was 0.7 mL/min (40 °C). Sample detection and quantification were conducted using a Shimadzu differential refractometer RID-20A. The column system was calibrated with standard poly(methyl methacrylate)s (PMMA)s.

The GPC analysis using DMF as the eluent was performed on a Shimadzu (Kyoto, Japan) LC-2030C plus liquid chromatograph equipped with two Shodex LF-804 columns (300 × 8.0 mm; bead size = 6 μm; pore size = 3000 Å) and one KD-802 column (300 × 8.0 mm; bead size = 6 μm; pore size = 150 Å). The eluent (DMF) contained LiBr (10 mM). The flow rate was 0.34 mL/min (40 °C). The sample detection and quantification were conducted using a Shimadzu differential refractometer RID-20A. The column system was calibrated with standard poly(methyl methacrylate)s (PMMA)s or standard polystyrenes (PSts).

The ¹H NMR spectra were recorded on Bruker (Germany) AV500 spectrometer (500 MHz) or AV300 (300 MHz) at ambient temperature. CDCl₃ (for purified polymers), acetone-*d*₆ (for crude methacrylate polymers), and tetrahydrofuran-*d*₈ (for crude styrene polymers) (Cambridge Isotope Laboratories, USA) were used as the solvents for the NMR analysis, and the chemical shift was calibrated using residual undeuterated solvents or tetramethylsilane (TMS) as the internal standard. The monomer conversion was determined with ¹H NMR.

The polymer shown in Fig. 6 was purified with a preparative GPC (LC-9204, Japan Analytical Industry, Tokyo) equipped with JAIGEL 1H and 2H polystyrene gel columns (600×40 mm; bead size = 16 μm; pore size = 20-30 (1H) and 40-50 (2H) Å). Chloroform was used as the eluent at a flow rate of 14 mL/min (room temperature).

The DLS measurement was carried out on a Malvern Zetasizer Nano ZSP (Worcestershire, UK) at room temperature. The test angle for the DLS analysis was 173° (backscattering detection).

The UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 (Kyoto, Japan) at room temperature with a quartz cell with an optical path length of 1 cm.

General procedure for polymerization. In a typical run, a mixture of a monomer (25.0 g, 30.0-50.0 wt%), an alkyl iodide initiator, an azo initiator, catalysts, emulsifier (1.7-10.0 wt%), and deionized water (44.4-66.7 wt%) was heated in a reaction vessel at 60–80 °C under argon atmosphere with mechanical stirring (1000 rpm). The vessel was a 100 mL jacketed cylindrical reaction vessel (ChemGlass, USA) connected with an overhead mechanical stirrer (Heidolph, Germany) and immersed in a water bath (Lauda, Germany). After a prescribed time t , an aliquot (2 mL) of the solution was taken out by a syringe, cooled to room temperature, and analyzed with GPC (DMF as eluent) and ^1H NMR.

Synthesis of PMMA-I for chain-end fidelity analysis (Fig. 6). A mixture of MMA (25.0 g, 8 M, 30.0 wt%), 2-HEPhI (0.8 g, 80 mM), V50 (0.3 g, 40 mM), BNI (0.9 g, 80 mM), NaI (0.4 g, 80 mM), emulsifiers (Tween80/FES77 (3:1 (w/w))) (2.8 g, 3.3 wt%), and deionized water (54.9 g, 66.7 wt%) was heated in a reaction vessel at 60 °C for 1 h under argon atmosphere with mechanical stirring. At 1 h (monomer conversion = 43%), an aliquot (10 mL) of the mixture was taken out, cooled to room temperature, reprecipitated in methanol/water (2/1 (v/v)) (200 mL), and dried. The polymer was diluted with chloroform (10 mL) and subsequently purified with preparative GPC. The purified PMMA-I ($M_n = 3900$ and $D = 1.09$) was obtained as a yellow solid and subsequently analyzed with GPC (THF as eluent) and ^1H NMR.

Partitioning test of initiators using UV-Visible spectroscopy. A mixture of MMA (6.0 g, 100 equiv), alkyl iodide (1 equiv), and water (12.0 g) was stirred at 60 °C for 30 min under magnetic stirring. After 30 min, stirring was stopped, reaction mixture was settled down at 60 °C for 10 min to separate the organic (MMA) and aqueous phases. An aliquot (0.005 g) of each phase was separately taken out, diluted with 5 g methanol, and the absorption was measured with UV-Vis spectrophotometer (Fig. 4). The partitions of the initiator in the two phases were calculated from equations 1 and 2:

(Partition of initiator in MMA) = (absorbance of the initiator in organic (MMA) phase) / [(absorbance of initiator in organic phase) + 2 × (absorbance of initiator in aqueous phase)] (equation 1)

(Partition of initiator in water) = 1 – (partition of initiator in MMA) (equation 2)

Solid content test (Table 3 (entry 1)). An empty dry glass petri dish covered with aluminum foil was weighed (G1). An aliquot (1.5 g) of the MMA polymerization mixture (Table 3 (entry 1)) was put on the petri dish and weighed (G2). After that, the petri dish was dried in the oven at 90 °C for 1 day, subsequently desiccated for overnight, and reweighed (G3). The solid content is calculated from equation 3:

(Solid content) = (G3 – G1) / (G2 – G1) (equation 3)

Particle size analysis (Table 3 (entry 1)). Particle size was analyzed using DLS for the samples in Table 3 (entry 1). An aliquot (0.01 g) of the reaction mixture was diluted with water (25 times) and analyzed using DLS (Fig. S1).

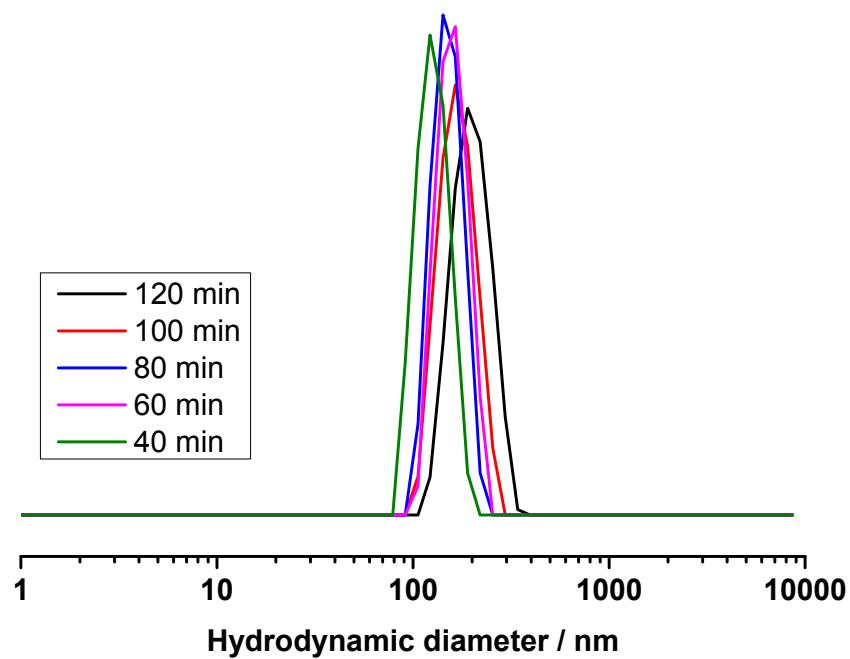


Fig. S1. DLS intensity-distribution curves for the MMA/2-HEPhI/NaI/BNI/V50 (8000/80/80/80/40 mM) system using a mixture of Tween80 and FES77 emulsifiers (3/1 (w/w)) (Table 3 (entry 1)). The polymerization times are indicated in the figure.

2. Combination of different catalysts.

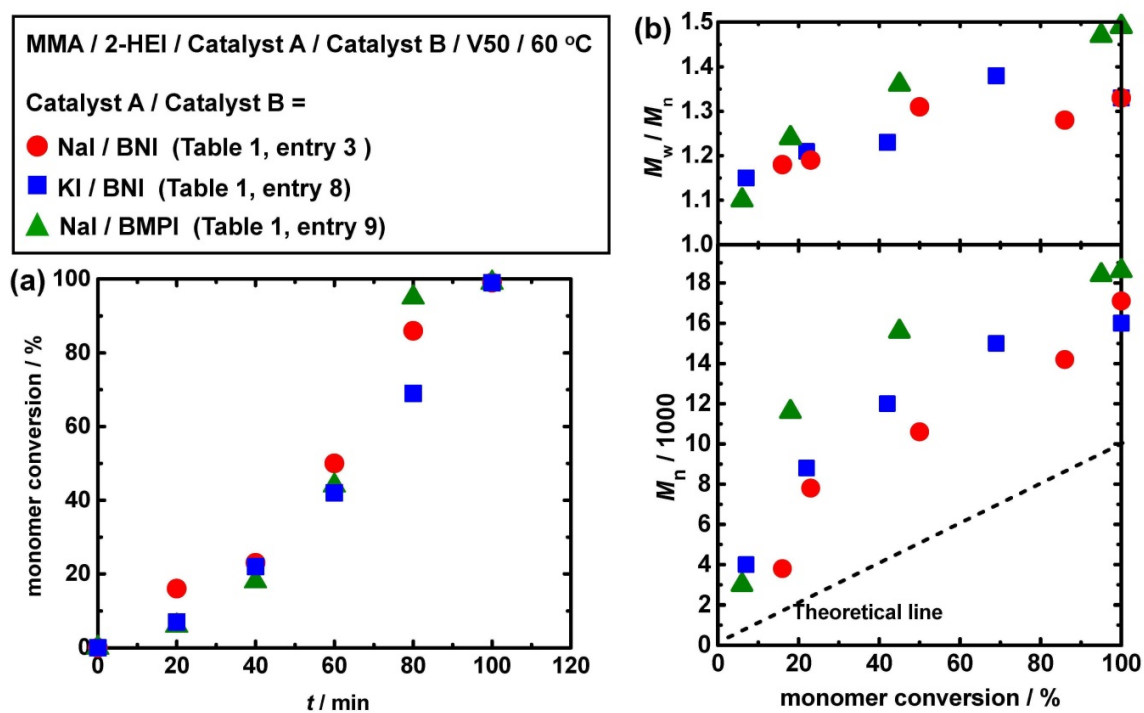


Fig. S2. Plots of (a) monomer conversion vs t and (b) M_n and M_w/M_n vs monomer conversion for the MMA/2-HEI/catalysts/V50 systems (60 °C) (Table 1, entries 3, 8, and 9). The symbols are indicated in the figure.

3. ^1H NMR analysis of PGMA.

Fig. S3 shows the ^1H NMR spectrum of the poly(glycidyl methacrylate) (PGMA) obtained in Table 4 (entry 2) and purified via reprecipitation in methanol (non-solvent) ($M_n = 16000$ and $D = 1.50$ after purification). The CH proton in the epoxide group (c) and the CH_3 protons in the polymer backbone (a) appeared at 3.24 and 0.84-1.35 ppm, respectively. According to the peak area for proton c and protons a in the ^1H NMR spectrum, the fraction of the retained epoxide functionality in the polymer chain was nearly 100% (98% as calculated).

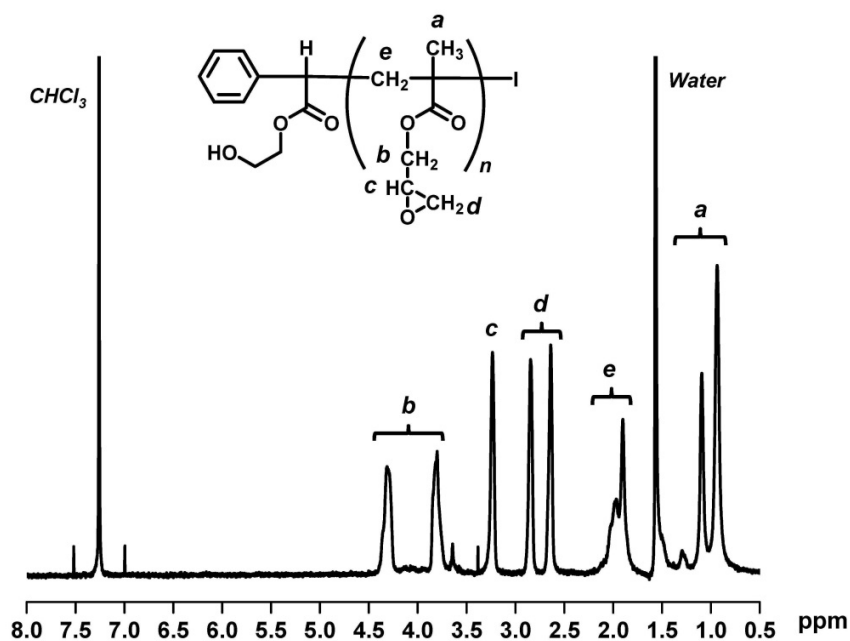


Fig. S3. ^1H NMR (CDCl_3) spectrum of PGMA obtained in Table 4 (entry 2) ($M_n = 16000$ and $D = 1.50$ after purification).