

Electronic Supplementary Information (ESI)

Use of Poly(methyl methacrylate) with Unsaturated Chain End as Macroinitiator Precursor in Organocatalyzed Living Radical Block Polymerization

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1. Experimental Section

Materials. Methyl methacrylate (MMA) (>99%, Mitsubishi Chemical Corporation (MCC), Japan), sodium 2-(methacryloyloxy)ethanesulfonate (>98%, MCC), 2,2'-azobis(2-methylpropionamide) dihydrochloride (V-50) (>98%, Wako Pure Chemical, Japan), 1,1,3,3-tetramethylbutylperoxy-2-ethylhexanoate (Perocta O) (>90%, NOF Corporation, Japan), cobalt (II) acetate tetrahydrate (>99%, Wako), diphenyl glyoxime (>98%, Tokyo Chemical Industry (TCI), Japan), boron trifluoride diethyl ether complex (>98%, TCI), potassium hydroxide (>85%, Wako), sodium sulfate (>99.5%, TCI), diethyl ether (>99.5%, TCI), butyl acrylate (BA) (>99%, TCI), tetrabutylammonium iodide (BNI)

(>98%, TCI), 2,2'-azobis(2-methylpropionitrile) (AIBN) (98%, Wako), iodine (I₂) (>98%, TCI), 2-iodo-2-methylpropionitrile (CP-I) (>95%, TCI), hexane (>99%, International Scientific Pte Ltd., Singapore), and tetrahydrofuran (THF) (>99.5%, Kanto Chemical, Japan) were used as received.

Synthesis of Dispersant for Dispersion Polymerization. 61.6 g of 17% aqueous potassium oxide solution, 19.1 g of MMA, and 19.3 g of deionized water were charged into a reaction vessel equipped with a stirrer, condenser tube, and thermometer. The mixture was stirred at room temperature. After the confirmation of an exothermic peak, the mixture was stirred for additional 4 h. Subsequently, the mixture was cooled to room temperature to obtain an aqueous potassium methacrylate solution.

900 g of deionized water, 60 g of sodium 2-(methacryloyloxy) ethanesulfonate, 10 g of the aforementioned aqueous potassium methacrylate solution, and 12 g of MMA were placed in a reaction vessel equipped with a stirrer, condenser tube and thermometer. The mixture was heated to 50 °C under a nitrogen atmosphere. 0.08 g of V-50 was added into the reaction vessel and the mixture was further heated at 60 °C. Subsequently, MMA was continuously added dropwise for 75 min at a rate of 0.24 g/min using a syringe pump. After holding the reaction mixture at 60 °C for 6 h, the mixture was cooled to room temperature to obtain a dispersant as a transparent aqueous solution with a solid content of approximately 10%.

Synthesis of Cobalt Complex for Dispersion Polymerization. 2.00 g (8.03 mmol) of cobalt (II) acetate tetrahydrate, 3.86 g (16.1 mmol) of diphenyl glyoxime, and 100 mL of diethyl ether deoxygenated by nitrogen bubbling were placed in a reaction vessel equipped with a stirrer. The mixture was kept stirring for 2 h at room temperature under a nitrogen atmosphere.

Next, 20 mL of boron trifluoride diethyl ether complex was added, and the mixture was kept stirring for additional 6 hours. The resulting mixture was filtered, and the solid was washed with diethyl ether and then vacuum-dried for 12 h at 20 °C to obtain 5.02 g (7.93 mmol, yield: 99%) of cobalt complex as a brown solid.

Dispersion Polymerization for Synthesis of PMMA-Y. 145 g of deionized water, 0.1 g of sodium sulfate, and 0.26 g of the dispersant synthesized above were placed in a reaction vessel equipped with a stirrer, condenser tube, and thermometer, and the mixture was stirred to obtain a homogeneous aqueous solution. To this solution, 100 g of MMA, 0.005 g of cobalt complex, and 0.1 g of Perocta O were added to obtain an aqueous dispersion, which was subsequently heated to 80 °C under a nitrogen atmosphere. The temperature was held at 80 °C for 4 h and then heated to 92 °C and was held for additional 2 h. The aqueous dispersion was cooled to 40 °C and filtered with a filter cloth. The filtrate was washed with deionized water and dried for 16 h at 40 °C to obtain PMMA-Y as white beads ($M_n = 3,900$).

Measurement. The GPC analysis was performed on a Shodex GPC-101 liquid chromatograph (Tokyo, Japan) equipped with two Shodex KF-804L mixed gel columns (300 × 8.0 mm; bead size = 7 μm; pore size = 20–200 Å). The eluent was tetrahydrofuran (THF) at a flow rate of 1.0 mL/min. Sample detection and quantification were conducted using a Shodex differential refractometer RI-101 calibrated with known concentrations of polymer in solvent. The monomer conversion was determined from the peak area. The column system was calibrated with standard polystyrenes and poly(methyl methacrylate)s (PMMA)s.

NMR. The NMR spectra were recorded on a Bruker (Germany) BBFO spectrometer (400 MHz) at ambient temperature. $CDCl_3$ (Cambridge Isotope Laboratories, USA) was used as a solvent, and the chemical shift was calibrated using the residual undeuterated solvent or tetramethylsilane (TMS) as the internal standard.

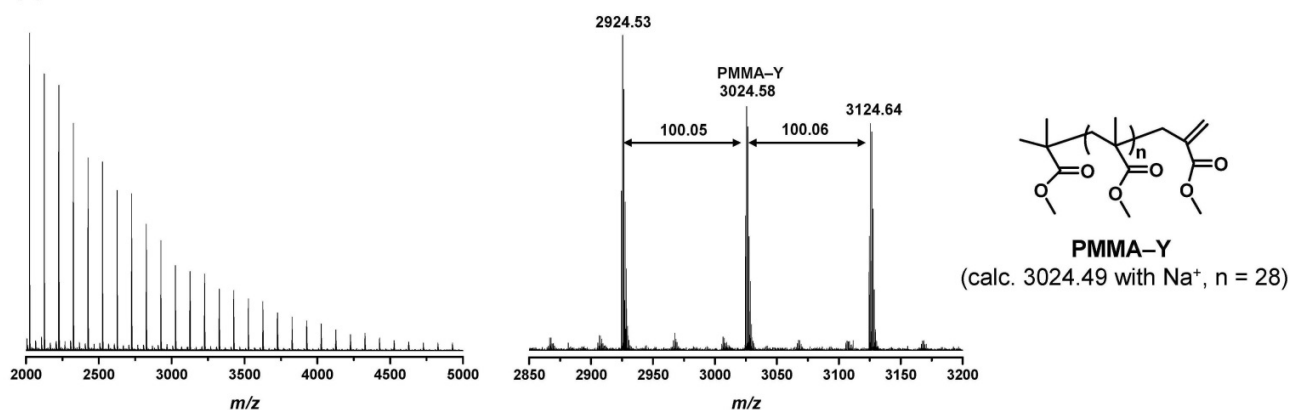
Gradient Polymer Elution Chromatography (GPEC). The GPEC analysis was performed at 40°C on a HPLC alliance e2695 liquid chromatograph (Waters, Milford, USA) equipped with a TSKgel ODS-100V column (TOSOH, Tokyo, Japan) (150 × 4.6 mm; bead size = 5 μm). The eluent was a gradient solvent of acetonitrile/THF from 100/0 to 0/100 in 10 min at a flow rate of 1 mL/min. Sample detection was conducted using a PDA 2998 detector (Waters).

MALDI-TOF-MS. The matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra were recorded on a JMS-S3000 SpiralTOF (JEOL, Japan) at an accelerating potential of 20 kV in the positive spiral mode. We prepared the polymer solutions (PMMA–Y: 10 g/L in THF and organocatalyzed LRP reaction mixture: 10 g/L in THF), matrix solution (DCTB: 60 g/L in THF), and cationization agent solution (NaTFA: 10 g/L in THF). The MALDI-TOF-MS samples were prepared by the dried droplet method.¹ The polymer solutions (in THF), NaTFA solution (in THF) and the DCTB solution (in THF) were mixed in a ratio of 1/1/2 (v/v/v). The mixed solution was deposited on the target plate spot and dried in the air at room temperature.

General Procedure for Polymerization. In a typical run (Table 1 (entry 1)), a mixture of BA (2.00 g), PMMA-Y (0.304 g), CP-I (0.0152 g), and BNI (0.231 g) was heated in a Schlenk flask at 110 °C under an argon atmosphere with magnetic stirring. After a prescribed time t , an aliquot (0.1 mL) of the solution was taken out by a syringe, quenched to room temperature, diluted by THF to a known concentration, and analyzed by GPC.

2. MALDI-TOF-MS Data

(a) PMMA-Y



(b) Organocatalyzed LRP (Table 1 (entry 1) at 8 h)

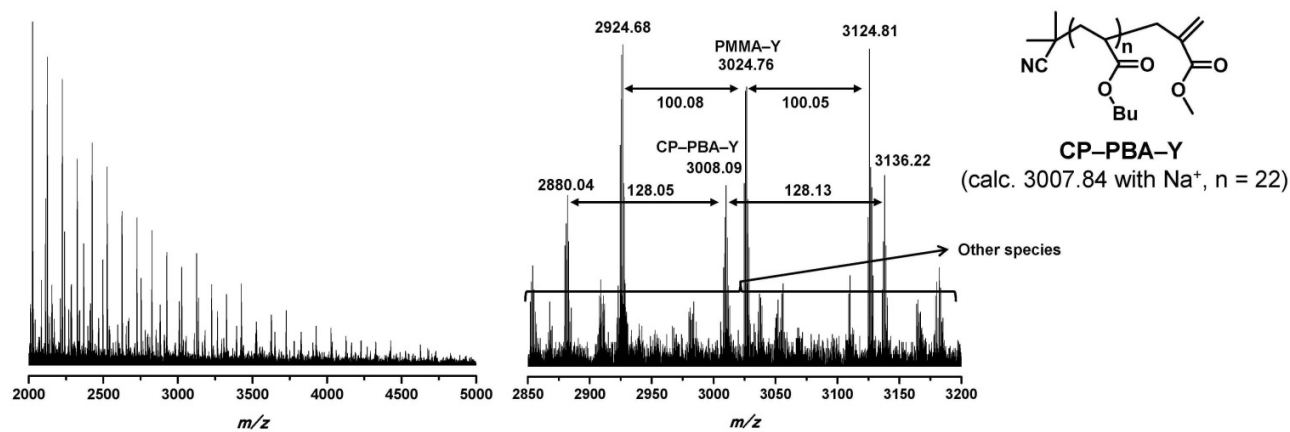


Fig. S1. MALDI-TOF-MS spectra of (a) PMMA-Y and (b) the polymer obtained in the organocatalyzed LRP (Table 1 (entry 1) at 8 h).

Reference

- (1) K. Kim, A. Hasneen, H. Paik and T. Chang, *Polymer*, 2013, **54**, 6133–6139.