Electronic Supplementary Information (ESI)

Synthesis of Block Copolymers Using Poly(methyl methacrylate) with Unsaturated Chain End through Kinetic Studies

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1. Experimental Section

Materials. Methyl methacrylate (MMA) (>99%, Mitsubishi Chemical Corporation (MCC), Japan), Methyl acrylate (MA) (>99%, MCC), sodium 2-(methacryloyloxy)ethanesulfonate (>98%, MCC), 2,2'-azobis(2-methylpropionamidine) 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 (Et_2O) (>99.5%, TCI), styrene (St) (>99%, TCI), acrylonitrile (AN) (>99%, Kanto Chemical, Japan), 2-methoxyethyl acrylate (MEA) (>98%, TCI), poly(ethylene glycol) methyl ether acrylate (PEGA) (98%, Sigma-Aldrich, US), butyl acrylate (BA) (>99%, TCI), *tert*-butyl peroxybenzoate (PBZ) (98%, NOF), 2,2'-azobis(2,4-dimethylvaleronitrile) (V65) (95%, Wako), 1,1'-

azobis(cyclohexane-1-carbonitrile) (V40) (98%, Wako), 2.2′-azobis(2-methylpropionitrile) (AIBN) (98%, Wako), tetrabutylammonium iodide (BNI) (>98%, TCI), iodine (I_2) (>98%, TCI), 2-iodo-2-methylpropionitrile (CP−I) (>95%, TCI), ethylene carbonate (>99%, TCI), diglyme (>99%, TCI), *N,N*-dimethylformamide (DMF) (>99.5%, Kanto), hexane (>99%, International Scientific Pte Ltd., Singapore), tetrahydrofuran (THF) (>99.5%, Kanto), silver trifluoroacetate (AgTFA) (>99.99%, Sigma-Aldrich), and *trans*-2-[3-(4-t-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (>99%, Sigma-Aldrich) 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 h. 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).

Dispersion Polymerization for Synthesis of PMMA-Y (higher molecular weight). 145 g of deionized water, 0.1 g of sodium sulfate, and 0.18 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, 95 g of MMA, 5 g of MA, 1.6 mg of cobalt complex, and 0.13 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 = 12,000).

Measurement. For Figures S3 and S4, 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 = 1500 Å). The eluent was dimethyl formamide (DMF) at a flow rate of 0.8

mL/min (40 °C). The DMF eluent included LiBr (10 mM). Sample detection and quantification were conducted using a Shodex differential refractometer RI-101 calibrated with known concentrations of polymer in solvent. The column system was calibrated with standard poly(methyl methacrylate)s (PMMAs).

For Figures 5, 11, and S8, the GPC analysis was performed on a Shimadzu LC-2030C Plus liquid chromatograph (Kyoto, Japan). The Shimadzu LC-2030C Plus GPC was 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 eluent was tetrahydrofuran (THF) at a flow rate of 0.7 mL/min. Sample detection and quantification were conducted using a Shimadzu differential refractometer RID-20A. The column system was calibrated with standard PMMAs.

Viscosity Analysis. The viscosity analysis (Figure 7) was performed on a Viscotek GPC-TDA 302 (Malvern Panalytical, Malvern, UK) equipped with a TSKgel guard column HXL-H (40 × 6.0 mm), two TSKgel GMHXL (300 × 7.8 mm; bead size = 9 μm) and a TSKgel G2500HXL (300 × 7.8 mm; bead size = 5 μm) (TOSOH, Tokyo, Japan). The eluent was THF at a flow rate of 1.0 mL/min (40 °C). Sample detection and quantification were conducted using triple detector (refractive index, differential pressure and 90 degree light scattering). The column system was calibrated with standard polystyrenes.

NMR. The NMR spectra were recorded on a Bruker (Germany) BBFO spectrometer (400 MHz) at ambient temperature. $CDCl_3$ (Cambridge Isotope Laboratories, USA) or DMSO–d_6 (Cambridge Isotope Laboratories) 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 1260 Infinity liquid chromatograph (Agilent, Santa Clara, USA) equipped with a TSKgel ODS-100V column (TOSOH) (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 Corona Veo RS detector (Thermo Fisher, Waltham, USA).

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, Tokyo, Japan) at an accelerating potential of 20 kV in the positive spiral mode. We prepared a polymer solution (PMMA–Y: 10 g/L in THF or polymerization mixture: 10 g/L in THF), a cationization agent solution (AgTFA: 10 g/L in THF), and a matrix solution (DCTB: 60 g/L in THF). The polymer solution, the AgTFA solution, and the DCTB solution were mixed in a ratio of 1/1/4 (v/v/v). The mixed solution was deposited on the target plate spot and dried in the air at room temperature.

General Procedure for Block Copolymerization of St. In a typical run, a mixture of St (0.833 g, 8.00 mmol), PMMA-Y (0.156 g, 0.04 mmol), CP-I (7.8 mg, 0.04 mmol), and PBZ (conventional radical initiator) (11.65 mg, 0.06 mmol) was added to a Schlenk flask and the mixture was bubbled with argon for 10 min. The Schlenk flask was then heated at 120°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, cooled to room temperature, diluted with THF to a known concentration, and analyzed by GPC.

Procedure for Block Copolymerization of AN. A mixture of AN (0.318 g, 6.00 mmol), PMMA-Y (0.117 g, 0.03 mmol), CP-I (5.85 mg, 0.03 mmol), AIBN (0.493 mg, 0.003 mmol), BNI (0.443 mg, 0.12 mmol), and ethylene carbonate (50wt%, 0.480 g) was added to a Schlenk flask and the mixture was bubbled with argon for 10 min. The Schlenk flask was then heated at 75°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, cooled to room temperature, diluted with DMF to a known concentration, and analyzed by GPC.

Procedure for Block Copolymerization of MEA. A mixture of MEA (1.04 g, 8.00 mmol), PMMA-Y (0.156 g, 0.04 mmol), CP-I (7.8 mg, 0.04 mmol), and BNI (118 mg, 0.32 mmol) was added to a Schlenk flask and the mixture was bubbled with argon for 10 min. The Schlenk flask was then heated 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, cooled to room temperature, diluted with THF to a known concentration, and analyzed by GPC.

Procedure for Block Copolymerization of PEGA. A mixture of PEGA (1.92 g, 4.00 mmol), PMMA-Y (0.156 g, 0.04 mmol), CP-I (7.8 mg, 0.04 mmol), and BNI (118 mg, 0.32 mmol) was added to a Schlenk flask and the mixture was bubbled with argon for 10 min. The Schlenk flask was then heated 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, cooled to room temperature, diluted with DMF to a known concentration, and analyzed by GPC.

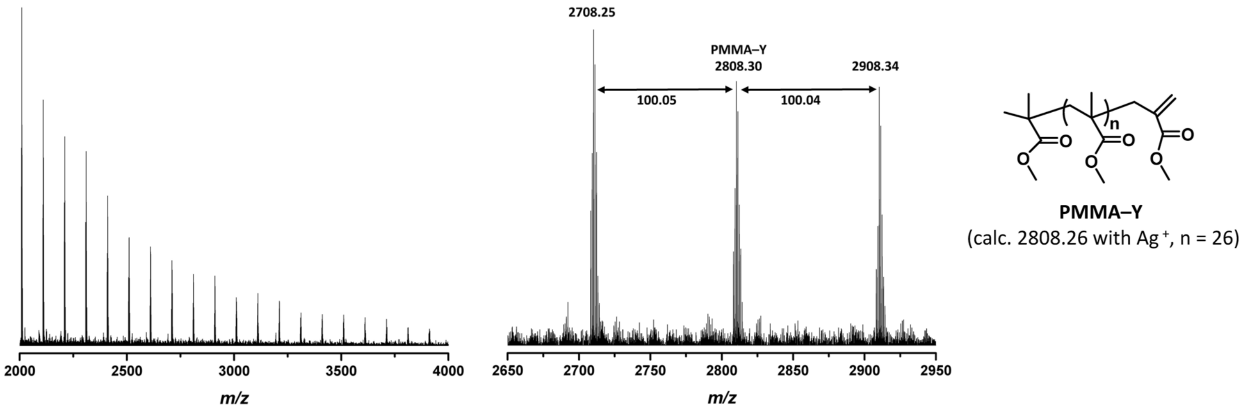
2. Reaction conditions, MALDI-TOF-MS spectra, data plots, GPC chromatograms, and ^{1}H NMR spectra.

Table S1. Reaction conditions for the polymerizations of St with PMMA–Y at different temperatures (Table 1 (entry 1) and Figs 2-4)).

Entry	T (°C)	In[a]	$[\mathrm{St}]_0/[\mathrm{PMMA{-}Y}]_0/[\mathrm{CP{-}I}]_0/[\mathrm{In^a}]_0$ (mM)
1	40	V65	8000/40/40/400
2	60	V65	8000/40/40/36
3	80	AIBN	8000/40/40/12
4	100	V40	8000/40/40/20
5	110	V40	8000/40/40/12
6	120	PBZ	8000/40/40/40

[a] Conventional radical initiator. V65 = 2,2'-azobis(2,4-dimethylvaleronitrile), AIBN = 2,2-azobis(2-methylpropionitrile) (AIBN), V40 = 1,1'-azobis(cyclohexanecarbonitrile), and PBZ = *tert*-butyl peroxybenzoate (PBZ).

(a) PMMA–Y



(b) Polymerization of styrene with PMMA–Y at 120 °C (Table 2 (entry 1) at 30 min)

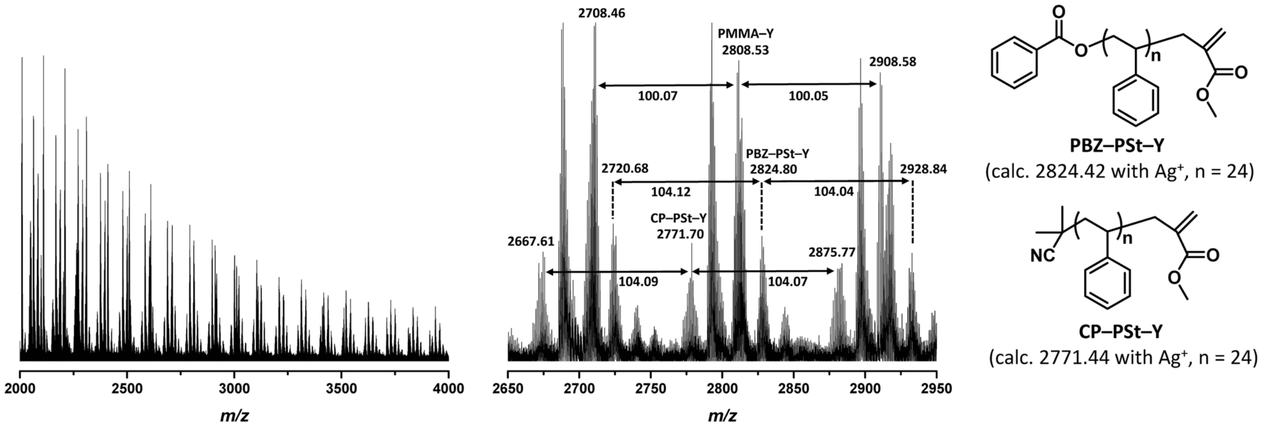


Fig. S1 MALDI-TOF-MS spectra of (a) PMMA–Y and (b) the polymer obtained in the styrene/PMMA–Y/CP–I/PBZ system at 120 °C (Table 2 (entry 1) at 30 min).

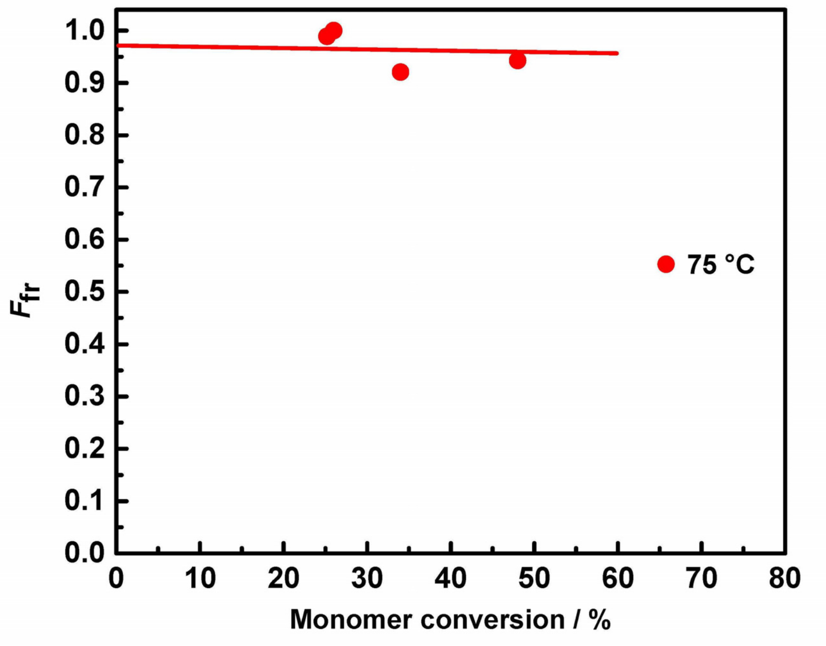


Fig. S2 Plot of F_{fr} vs monomer conversion for the AN/PMMA–Y/CP–I/AIBN/ BNI system at 75 $^{\mathrm{o}}$C (Table 1 (entry 2) and Table 2 (entry 3)).

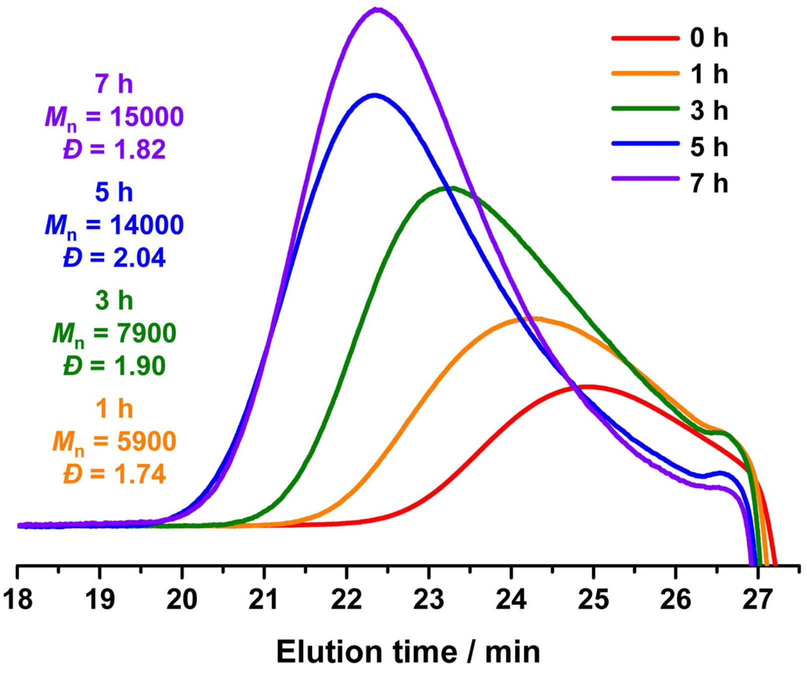


Fig. S3 GPC chromatograms (DMF-GPC) for the AN/PMMA–Y/CP–I/AIBN/EC/BNI system (75 ^{o}C). The reaction condition is given in Table 2 (entry 3).

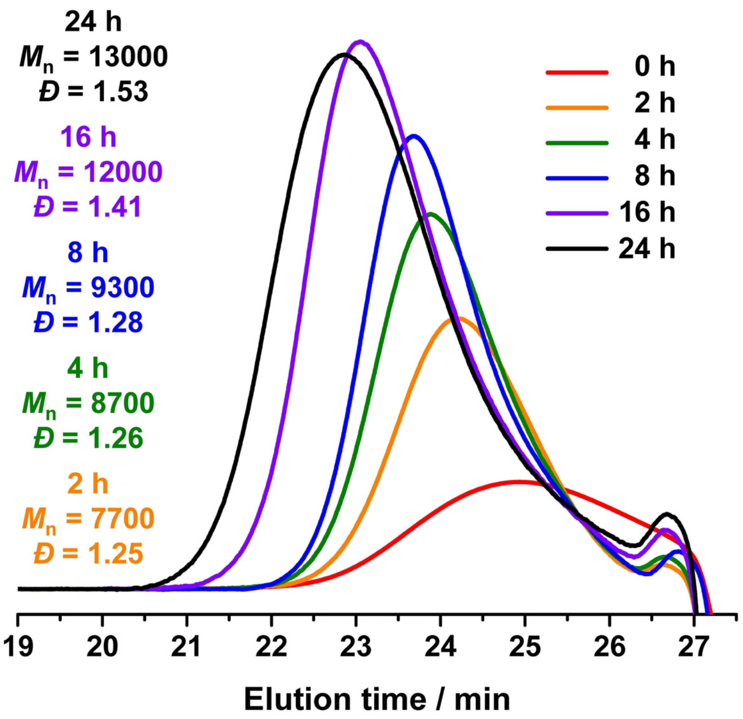


Fig. S4 GPC chromatograms (DMF-GPC) for the PEGA/PMMA–Y/CP–I/BNI system (110 ^{o}C) The reaction condition is given in Table 2 (entry 5).

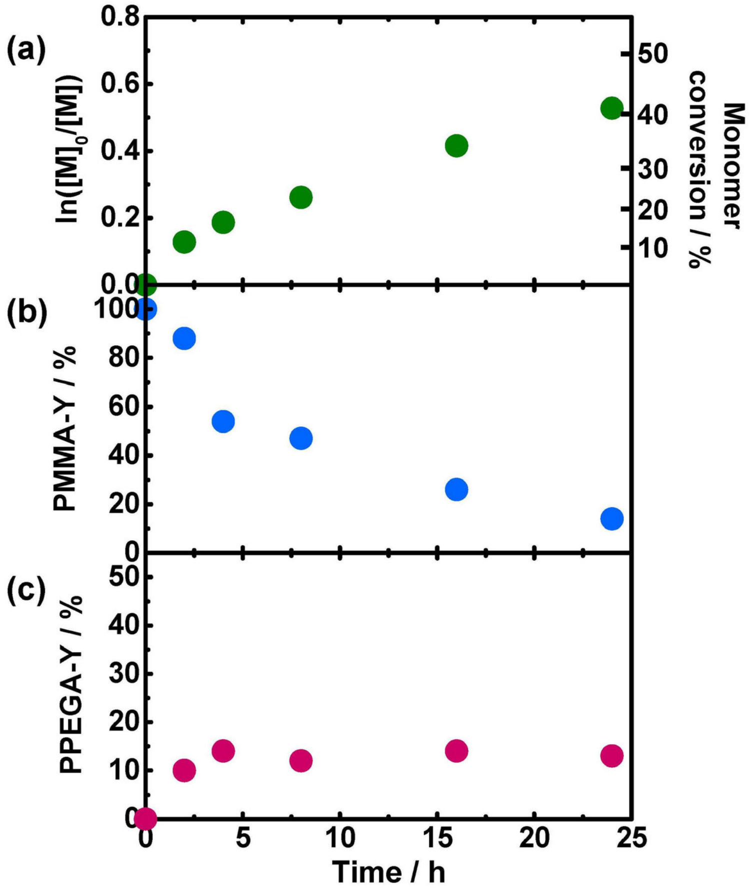


Fig. S5 Plots of (a) ln([M]$_0$/[M]), (b) fraction of PMMA–Y, and (c) fraction of PPEGA–Y vs time *t* for the PEGA/PMMA–Y/CP–I/BNI system (110 °C). The reaction condition is given in Table 2 (entry 5).

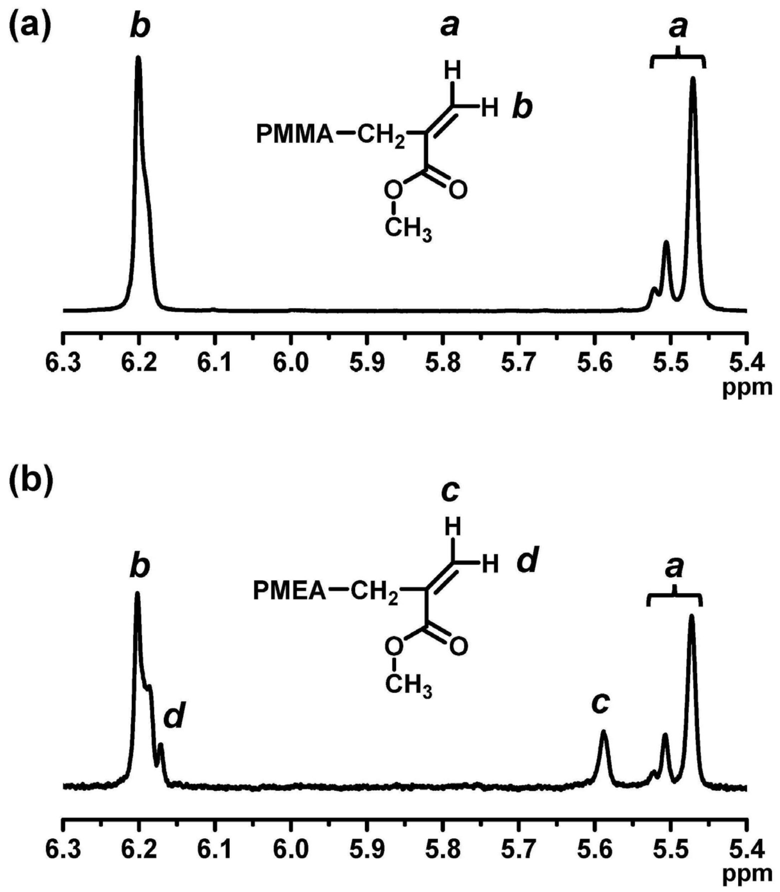


Fig. S6. ^{1}H NMR spectra ($CDCl_3$) in the range of 5.4–6.3 ppm at t = (a) 0 and (b) 4 h for the MEA/PMMA–Y/CP–I/BNI system (110 °C). The reaction condition is given in Table 2 (entry 4).

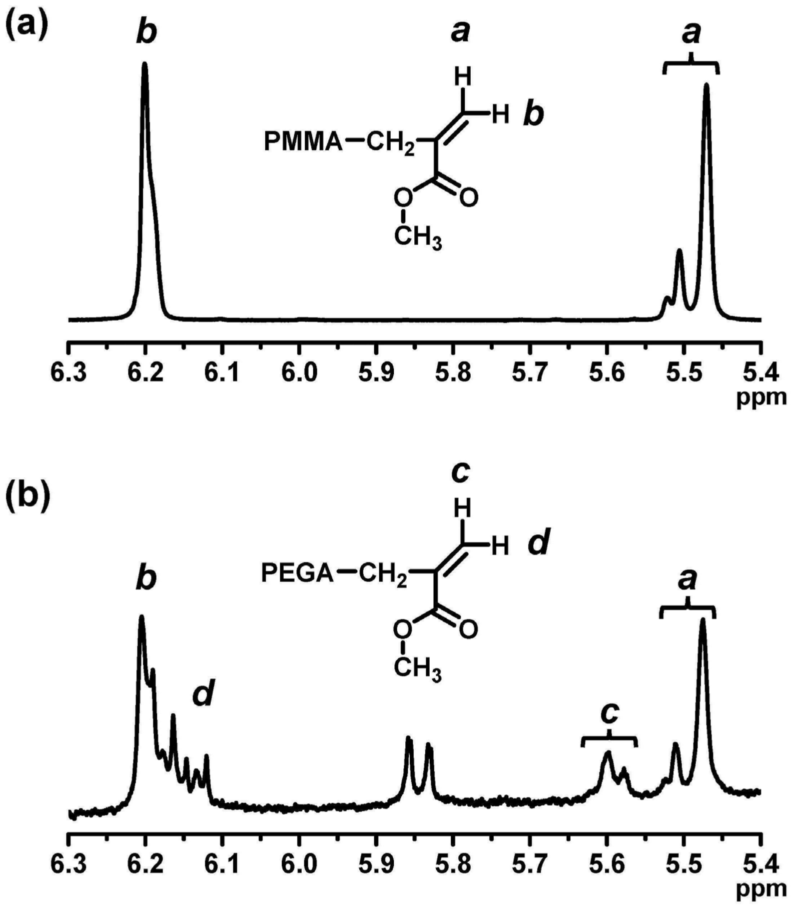


Fig. S7. ^{1}H NMR spectra ($CDCl_3$) in the range of 5.4–6.3 ppm at t = (a) 0 and (b) 4 h for the PEGA/PMMA–Y/CP–I/BNI system (110 °C). The reaction condition is given in Table 2 (entry 5).

We attempted to remove PEGA monomer from the block copolymer by reprecipitation into a Et_2O/hexane mixture. However, despite changing the ratio of Et_2O/hexane, we were not able to fully remove the monomer. In the NMR spectra, peak c from PEGA–Y is not overlapped with any peak of the PEGA monomer. Hence we can determine the concentration of PEGA–Y and the fragmentation from the peak ratio of c and a.

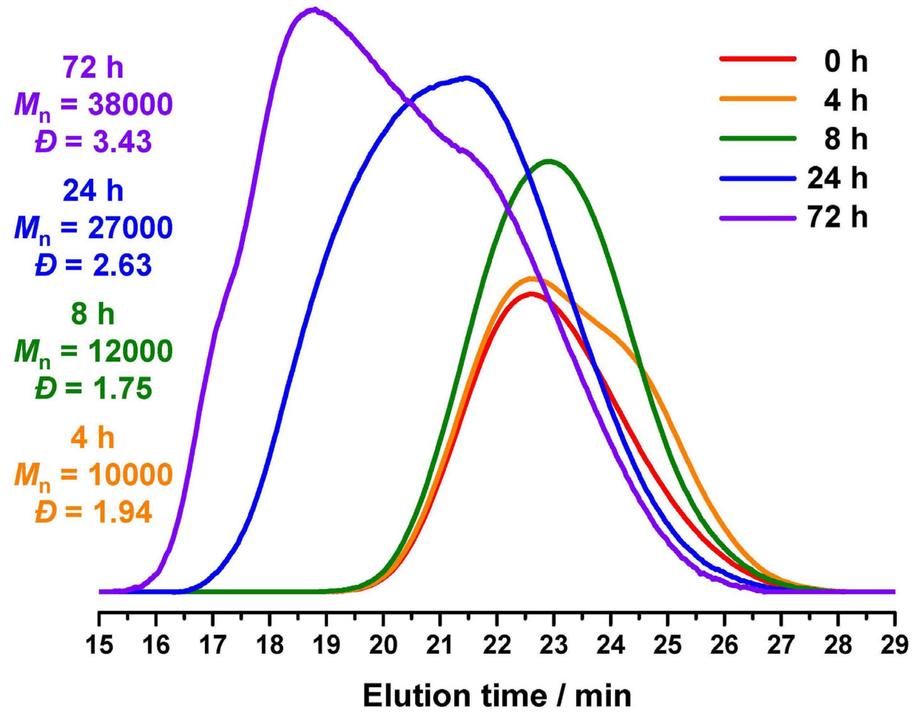


Fig. S8 GPC chromatograms (THF-GPC) for the BA/PMMA–Y/CP–I/BNI system (110 °C). The reaction condition is given in Table 4.