

Supporting Information

Comprehensive Study on Chain-End Transformation of Polymer-Iodides with Amines for Synthesizing Various Chain-End Functionalized Polymers

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1. Experimental Section

Materials. Methyl methacrylate (MMA) (>99.8%, Tokyo Chemical Industry (TCI), Japan), styrene (St) (>99%, TCI), butyl acrylate (BA) (>99%, TCI), 2-iodo-2-methylpropionitrile (2-cyano-2-propyl iodide (CP-I)) (>95%, TCI), tetrabutylammonium iodide (Bu₄NI) (>98%, TCI), 2,2'-azobis(2-methylpropionitrile) (AIBN) (98%, Wako Pure Chemical, Japan), 2-phenylethylamine (>98%, TCI), 1-aminopropan-2-amine (>98%, TCI), 3-aminopropyltriethoxysilane (>98%, TCI), 2-aminoethanethiol (>95%, TCI), 2-aminoethanol (>99%, TCI), 4-amino-1-butanol (>98%, TCI), ethylenediamine (>99%, Kanto Chemical, Japan), 1,4-diaminobutane (>98%, TCI), 1,6-diaminohexane (>99%, TCI), 2-phenylethanethiol (>97%, TCI), diethylene glycol dimethyl ether (diglyme) (>99%, TCI), 1-butanol (>99%, Kanto), *N,N*-dimethylformamide (DMF) (>99.5%, Kanto), hexane (>99%, International Scientific Pte Ltd., Singapore), methanol (>99%, International Scientific), tetrahydrofuran (THF) (>99.5%, Kanto), trans-2-[3-(4-*t*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (>99%, Fluka Chemicals Ltd., UK), dithranol (>98%, Fluka), NaI (>99.5%, Kanto), and sodium trifluoroacetate (NaTFA) (>98%, TCI) were used as received.

Analytical GPC. 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 = $7 \mu\text{m}$; pore size = $20\text{--}200 \text{ \AA}$). The eluent was THF at a flow rate of 1.0 mL/min (40°C). 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.

Preparative GPC. Polymers were 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 = $16 \mu\text{m}$; pore size = $20\text{--}30$ (1H) and $40\text{--}50$ (2H) \AA). Chloroform was used as eluent at a flow rate of 14 mL/min (room temperature).

NMR. The NMR spectra of the polystyrene (PSt) and poly(methyl methacrylate) (PMMA) in Figure 3 were recorded on an AV500 spectrometer (500 MHz) (Bruker, Germany) at ambient temperature; ^1H : spectral width 5000.00 Hz , acquisition time 6.554 sec , and pulse delay 1.000 sec . The NMR spectrum of poly(butyl acrylate) (PBA) in Figure 5 was recorded on a BBFO400 spectrometer (400 MHz) (Bruker) at ambient temperature; ^1H : spectral width 4000.00 Hz , acquisition time 8.192 sec , and pulse delay 1.000 sec .

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 Ltd., Japan) at an accelerating potential of 20 kV in the positive spiral mode. We prepared the polymer solution (PBA: 10 g/L , PSt: 15 g/L , or PMMA: 10 g/L , in THF in all cases), matrix solution (DCTB: 10 g/L , or dithranol: 60 g/L , in THF in both cases), and cationization agent solution (NaI: 10 g/L in methanol, or NaTFA: 10 g/L in THF). The MALDI-TOF-MS samples were prepared by the dried droplet method.¹ For the PBA samples, the PBA solution (in THF) and the DCTB solution (in THF) were mixed in a ratio of $1/4$ (v/v). First, $5 \mu\text{L}$ of the NaI solution (in methanol) was deposited on the target plate and dried in the air at room temperature. Second, $5 \mu\text{L}$ of the mixed PBA/DCTB solution (in THF) was deposited on the same

target plate spot and dried in the air at room temperature. The solutions were deposited in this two-step manner, because NaI is not soluble in THF. For the PSt and PMMA samples, NaTFA was used as a cationization agent which is soluble in THF. The polymer, matrix, and cationization agent solutions (all in THF) were mixed together in ratios of 1/5/1 (v/v/v) for PMMA/DCTB/NaTFA and 1/2/1 (v/v/v) for PSt/dithranol (or DCTB)/NaTFA. Then, 5 μ L of the mixed solution was deposited on the target plate and dried in the air at room temperature.

Preparation of PBA-I. A mixture of BA (20 g (8 M)), CP-I (80 mM), and Bu₄NI (320 mM) was heated in a 100 mL flask at 110 °C for 6 h under an argon atmosphere with magnetic stirring, yielding a PBA-I with $M_n = 5200$ and $M_w/M_n = 1.36$ (monomer conversion = 36.7%) (before purification). The reaction mixture was diluted with THF, and the polymer was reprecipitated in a water/methanol mixture (50/50 wt%). After further purification with preparative GPC, a PBA-I with $M_n = 5300$ and $M_w/M_n = 1.36$ was obtained (Table 1 (entry 1)).

Preparation of PSt-I. A mixture of St (10 g (8 M)), CP-I (160 mM), AIBN (60 mM), and Bu₄NI (40 mM) was heated in a 100 mL flask at 80 °C for 9 h under an argon atmosphere with magnetic stirring, yielding a PSt-I with $M_n = 4200$ and $M_w/M_n = 1.25$ (monomer conversion = 85.0%) (before purification). The reaction mixture was diluted with THF, and the polymer was reprecipitated in methanol. After further purification with preparative GPC, a PSt-I with $M_n = 4500$ and $M_w/M_n = 1.21$ was obtained (Table 1 (entry 2)).

Preparation of PMMA-I. A mixture of MMA (10 g (8 M)), CP-I (80 mM), and Bu₄NI (80 mM) was heated in a 100 mL flask at 70 °C for 35 min under an argon atmosphere with magnetic stirring, yielding a PMMA-I with $M_n = 3000$ and $M_w/M_n = 1.16$ (monomer conversion = 27.1%) (before purification). The reaction mixture was diluted with THF, and the polymer was reprecipitated in hexane. After purification with preparative GPC, a PMMA-I with $M_n = 3100$ and $M_w/M_n = 1.15$ was obtained (Table 1 (entry 3)).

Chain-End Functionalization. A mixture of a polymer-I (20 wt%), an amine (20 eq or 2 eq), and a solvent (80 wt%) in a reaction tube was capped with a stopcock in the atmospheric air, heated at a prescribed temperature in the dark for a prescribed time with magnetic stirring, and quenched to room temperature. The mixture was diluted by THF, and then the polymer was reprecipitated in a non-solvent (methanol/water (50/50 wt%) for PBA, methanol for PSt, and hexane for PMMA). The polymer was further purified with preparative GPC and dried overnight. The obtained polymer was subjected to MALDI-TOF-MS and ^1H NMR analyses.

2. MALDI-TOF-MS Spectra

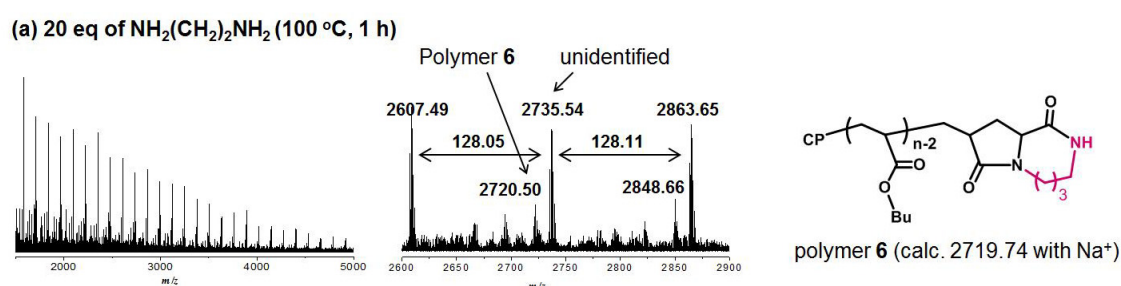
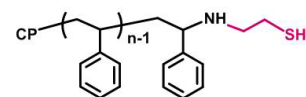
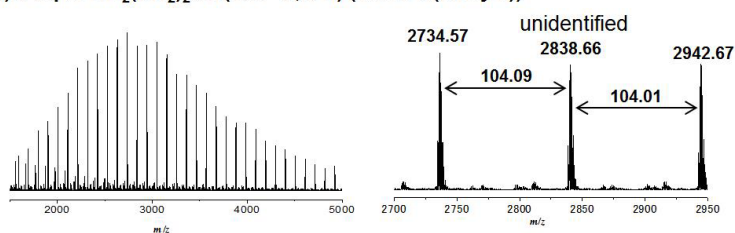


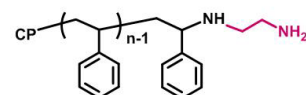
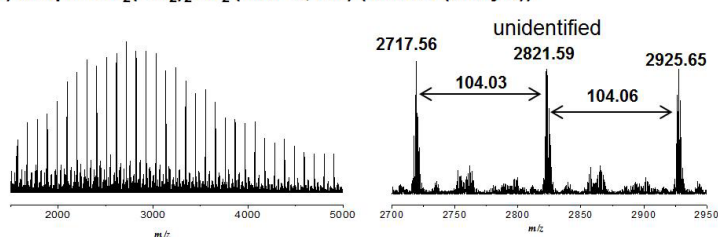
Figure S1. MALDI-TOF-MS spectrum of polymer obtained with a reaction of PBA-I (polymer 1) (1 eq, 20 wt%) with $\text{NH}_2(\text{CH}_2)_4\text{NH}_2$ (20 eq) in diglyme (40 wt%) and 1-butanol (40 wt%) at 100 °C for 1 h.

(a) 5 eq of $\text{NH}_2(\text{CH}_2)_2\text{SH}$ (100 °C, 8 h) (Table 3 (entry 6))

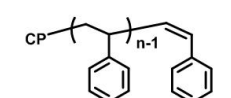


polymer **8** (calc. 2768.63 with Na^+)

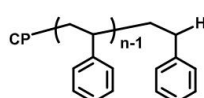
(b) 5 eq of $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$ (100 °C, 8 h) (Table 3 (entry 8))



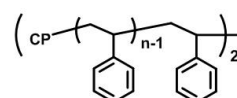
polymer **8** (calc. 2751.67 with Na^+)



PSt-macromonomer
(calc. 2795.66 with Na^+)



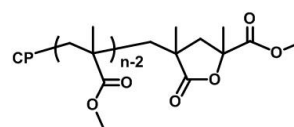
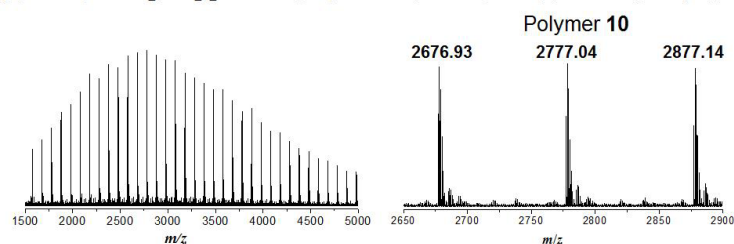
PSt-H
(calc. 2797.68 with Na^+)



CP-PSt-PSt-CP
(calc. 2864.72 with Na^+)

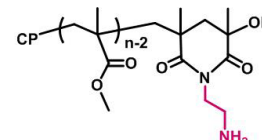
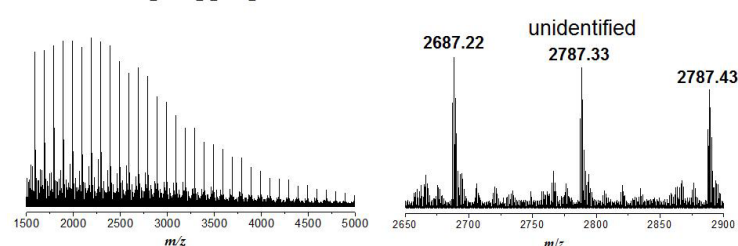
Figure S2. MALDI-TOF-MS spectra of polymers obtained with reactions of PSt-I (polymer **7**) with NH_2R in Table 3 (entries 6 and 8). The amines are given in the figure.

(a) 20 eq of $\text{NH}_2(\text{CH}_2)_2\text{SH}$ with polymer **10** (120 °C, 48 h) (Table 5 (entry 5))



polymer **10** (calc. 2677.38 with Na^+)

(b) 20 eq of $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$ with polymer **10** (120 °C, 48 h) (Table 5 (entry 7))



polymer **12** (calc. 2705.42 with Na^+)

Figure S3. MALDI-TOF-MS spectra of polymers obtained with reactions of polymer **10** with NH_2R in Table 5 (entries 5 and 7). The amines are given in the figure.

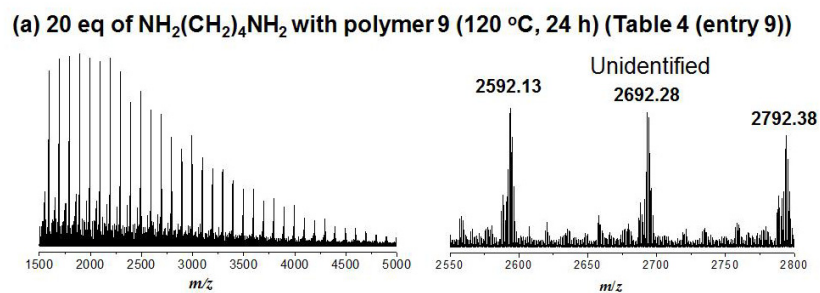


Figure S4. MALDI-TOF-MS spectrum of polymers obtained with a reaction of PMMA-I (polymer 9) with $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$ in Table 4 (entry 9).

Reference

- (1) Kim, K.; Hasneen, A.; Paik, H.; Chang, T. MALDI-TOF MS characterization of polystyrene synthesized by ATRP. *Polymer* **2013**, 54, 6133-6139.