

Supporting Information

One-pot synthesis of graft copolymer by combination of free radical polymerization and polyaddition

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Measurement conditions

^1H (400 MHz) Nuclear magnetic resonance (NMR) spectra were measured on a JEOL ECX-400 instrument using tetramethylsilane as an internal standard at ambient temperature (CDCl_3). The copolymer compositions and the M_{nNMR} values were calculated from integral ratios of the aromatic protons in the stem polymer and the $-\text{COOCH}_3$ protons in the graft chains. Size exclusion chromatography (SEC) measurements were performed on; using a Tosoh HPLC HLC-8220 system equipped with refractive index and ultraviolet detectors at a flow rate of 0.6 mL/min using *N,N*-dimethylformamide (DMF) containing 10 mM LiBr as an eluent at 40 °C, or a Viscotek TDA302 system equipped with a refractive index detector at a flow rate of 1.0 mL/min using chloroform as an eluent at 40 °C. The column set for HLC-8220 system was as follows: three consecutive hydrophilic vinyl polymer-based gel columns [TSK-GELs (bead size, exclusion limit): SuperAW5000 (7 μm , 4×10^6), SuperAW4000 (6 μm , 4×10^5), SuperAW3000 (4 μm , 6×10^4), 15 cm each] and a guard column [TSK-guard column Super AW-H, 3.5 cm]. Polystyrene standards were employed for calibration. The column set for Viscotek TDA302 system was as follows: four consecutive hydrophilic vinyl polymer-based gel columns [TSK-GELs (bead size, exclusion limit): GMH_{XL} (9 μm , 4×10^8), G4000H_{XL} (5 μm , 4×10^5), G3000H_{XL} (5 μm , 6×10^4), and G2500H_{XL} (5 μm , 2×10^4) 30 cm each] and a guard column [TSK-guard column H_{XL}-H, 4.0 cm]. Polystyrene standards were employed for calibration.

Materials

AIBN was recrystallized from methanol. 1,4-Dioxane was distilled over sodium under a nitrogen atmosphere. MMA was dried over CaH_2 and distilled under reduced pressure. Trimethylene dipiperidine was recrystallized from *n*-hexane. The bisphenol-A-type five-membered cyclic carbonate was prepared from bisphenol-A diglycidyl ether and CS_2 (ref 7 in the manuscript). Other reagents were used as received.

Typical polymerization procedure

A typical procedure for synthesis of polythiourethane-*g*-polyMMA follows. A dioxane (1.25 mL) solution of bisphenol-A type bifunctional cyclic dithiocarbonate (0.25 mmol), trimethylene dipiperidine (0.25 mmol), and AIBN (0.10 mmol) were stirred at room temperature under a nitrogen atmosphere for 18 h. Then, MMA (7.50 mmol) was added. The mixture was stirred at 60 °C for 24 h after the vessel was degassed and sealed. The polymer was isolated by precipitation with methanol or hexane from the THF solution.

Results of polymerization

Graft copolymerization of various feed ratios of MMA from *in situ* prepared poly(thiourethane) at 60°C. ^{a)}

Run	Feed ratio [MMA] / [SH]	Conv. of MMA [%] ^{b)}	yield [%] ^{d)}	copolymer composition [MMA / SH] ^{b)}	$M_n \times 10^{-4} (M_w / M_n)^c)$		
					RI	Viscosity	RALLS
1	15	>99	93.5 ^{d)}	14.7	1.92 (3.90)	2.64 (5.42)	13.4 (2.12)
2	30	>99	87.3 ^{d)}	28.9	3.51 (2.80)	4.87 (3.74)	12.0 (2.56)
3	40	>99	89.7 ^{e)}	41.2	3.95 (2.82)	5.23 (3.64)	12.6 (2.58)
4	60	>99	92.9 ^{e)}	70.9	4.39 (2.92)	4.82 (3.89)	21.2 (2.18)
5	80	>99	93.2 ^{e)}	81.6	7.43 (2.44)	10.0 (3.35)	28.4 (2.70)
6	120	>99	88.7 ^{e)}	136	8.95 (2.66)	10.9 (3.10)	35.3 (2.66)
7	200	99.4	84.5 ^{e)}	176	10.0 (3.34)	14.2 (2.47)	49.5 (5.95)
8	400	97.3	82.1 ^{e)}	415	12.3 (2.43)	34.6 (2.39)	87.0 (7.74)

^{a)} The stem polymer was prepared from BPA5DT and TMDP in 1,4-dioxane (1.25ml) at 60 °C for 18 h in degassed tube. Graft copolymerization with MMA was conducted in degassed sealed tubes at 60 °C for 24 h. ^{b)} Determined by ¹H-NMR spectroscopy. ^{c)} Estimated by SEC (polystyrene standard, THF). ^{d)} Isolated yield after precipitation with *n*-hexane. ^{e)} Isolated yield after precipitation with methanol.

Figure S1. ^1H NMR spectrum of the polymers.

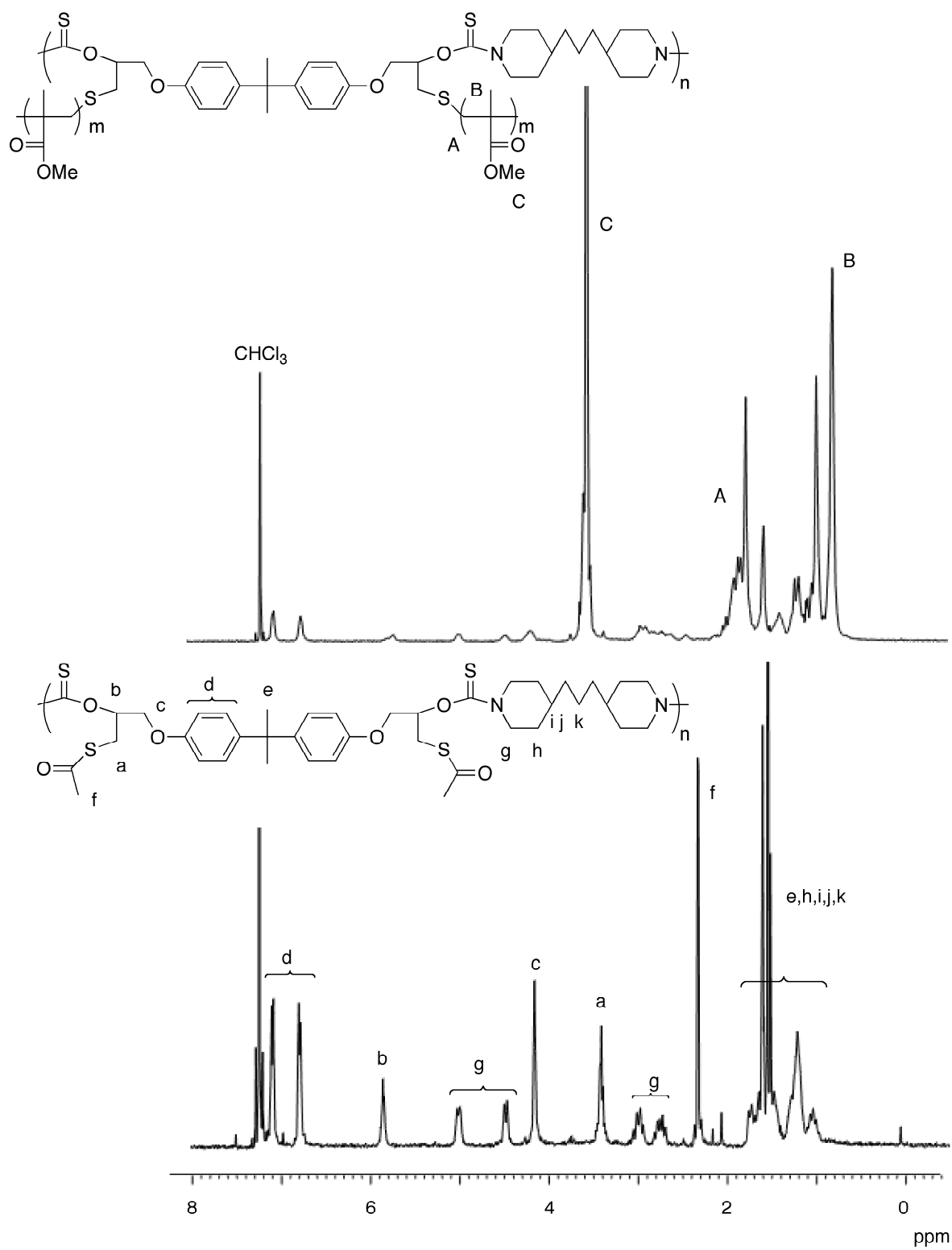


Figure S2. SEC profiles of the graft copolymers (RALLS).

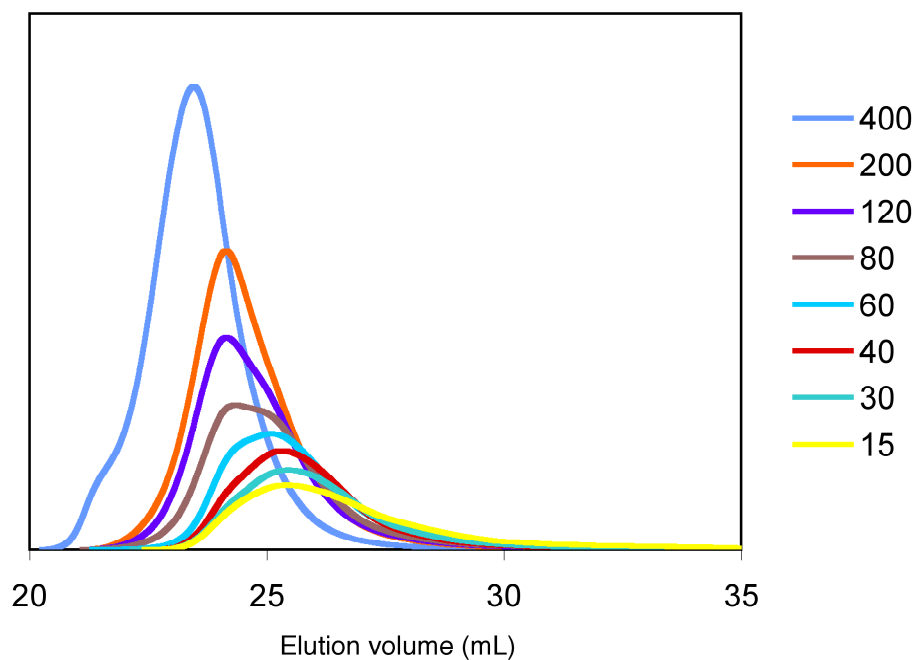


Figure S3. Conversion versus M_{nRALLS} relationship in radical polymerization of MMA in the presence of poly(mercapto-thiourethane) ($[MMA]/[SH] = 120$).

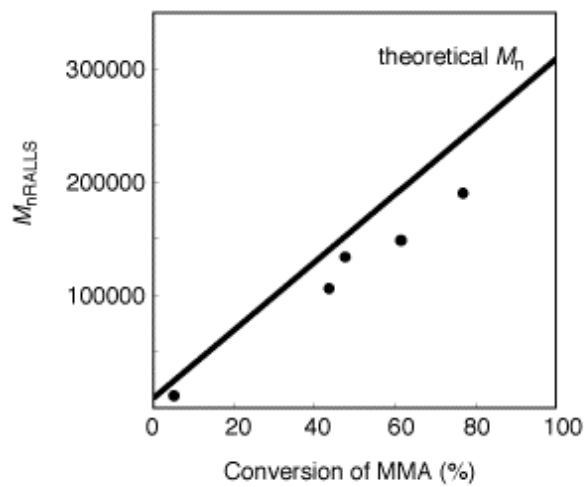


Figure S4. Time versus conversion and $\ln([MMA]_0/[MMA])$ relationships in radical polymerization of MMA in the presence of poly(mercapto-thiourethane) ($[MMA]/[SH] = 120$).

