

Supplementary Information

for

Anionic Polymerization of Acrylic Thioester by Using Organic Base

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Experimental

General

NMR spectra were recorded in CDCl₃ (ACROS ORGANICS, Chloroform-d for NMR, 0.03 v/v% TMS) with a Bruker AVANCE III 400 (400 MHz for ¹H) spectrometer. The chemical shift values in the ¹H and ¹³C NMR spectra are relative to TMS and CDCl₃, respectively, as an internal standard. The IR spectra were recorded on a FT/IR-460 Plus spectrometer. Electrospray ionization mass spectrometry (ESI-MS) was performed for samples dissolved into MeOH and THF with a Waters Synapt G2 HDMS tandem quadrupole orthogonal acceleration time-of-flight instrument. The eluent for GPC measurements was THF for tandem Shodex LF-404 columns. GPC was performed at 40°C, and UV (254 nm) and RI detectors were used. Polystyrene standards were used for GPC calibration. Gas chromatography was performed with a Shimadzu GC-21014 machine equipped with a Phenomenex Zebron ZB-5 capillary GC column (30m x 0.25 mm x 0.25 μm). A GC calibration was done by using toluene as an internal standard. Silica gel column chromatography was performed by using Kanto Chemical Silica Gel 60N (spherical, neutral). Acrylic acid (KANTO) and (4-*t*-butylphenyl)methanethiol (Sigma-Aldrich) were used as received. *S*-*n*-Dodecyl propanethioate was prepared from dodecane-1-thiol (KISHIDA, Japan) and propanoic acid (KANTO, Japan) with *N,N'*-dicyclohexylcarbodiimide (WAKO, Japan) by the same method as that used to prepare **1**. Dry THF and CH₂Cl₂ were purchased from KANTO CHEMICAL CO. DMF (KISHIDA) was dried over CaH₂ (NACALAI TESQUE, Japan) and distilled. DBU (WAKO or KANTO), MTBD (TCI, Japan), TBD (Sigma-Aldrich), DMAP (KISHIDA), DABCO (WAKO) were distilled or recrystallized before use. *t*-BuOK (TCI), LiBr (KISHIDA), LiI (KISHIDA), LiPF₆ (WAKO), LiNTf₂ (KANTO), CsI (WAKO), CsNTf₂ (TCI), and phenothiazine (KANTO) were used as received.

Isolation of side products **2** and **3**

According to the procedure mentioned for the polymerization of **1** (234 mg, 1 mmol), however, THF was employed as the solvent in place of DMF, and MTBD (5 mol% for **1**) was used as the base. The reaction mixture was subjected to silica-gel column chromatography (CH₂Cl₂/hexane = 1/1 v/v) to isolate **2** (*R*_f=0.45, 21 mg) and **3** (*R*_f=0.4, 38 mg). ¹H NMR spectra of **2** (CDCl₃, Fig. S9): δ 7.32 (m, 4H, aromatic), 7.20 (m, 4H, aromatic), 4.11 (s, 2H, (O=C)SCH₂), 3.69 (s, 2H, PhCH₂S), 2.76 (m, 4H, SC₂H₄(C=O)), 1.30 (s, 9H, C(CH₃)₃), 1.29 (s, 9H, C(CH₃)₃). ¹H NMR of **3** (CDCl₃, Fig. S10): δ 7.24 (m, 4H, aromatic), 7.15 (m, 4H, aromatic), 6.05 (s, 1H, CH=C), 5.54 (s, 1H, CH=C), 4.07 (s, 2H, benzyl), 4.02 (s, 2H, benzyl), 2.67 (m, 4H, C₂H₄(C=O)), 1.22 (m, 18H, C(CH₃)₃).

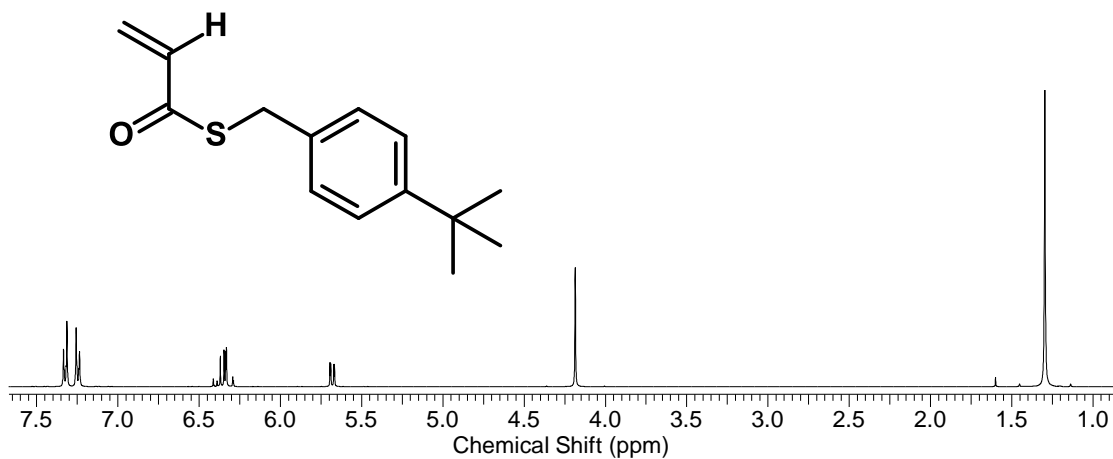


Fig. S1 ^1H NMR spectrum (CDCl_3) of *S*-(4-*t*-butylbenzyl) thioacrylate (**1**).

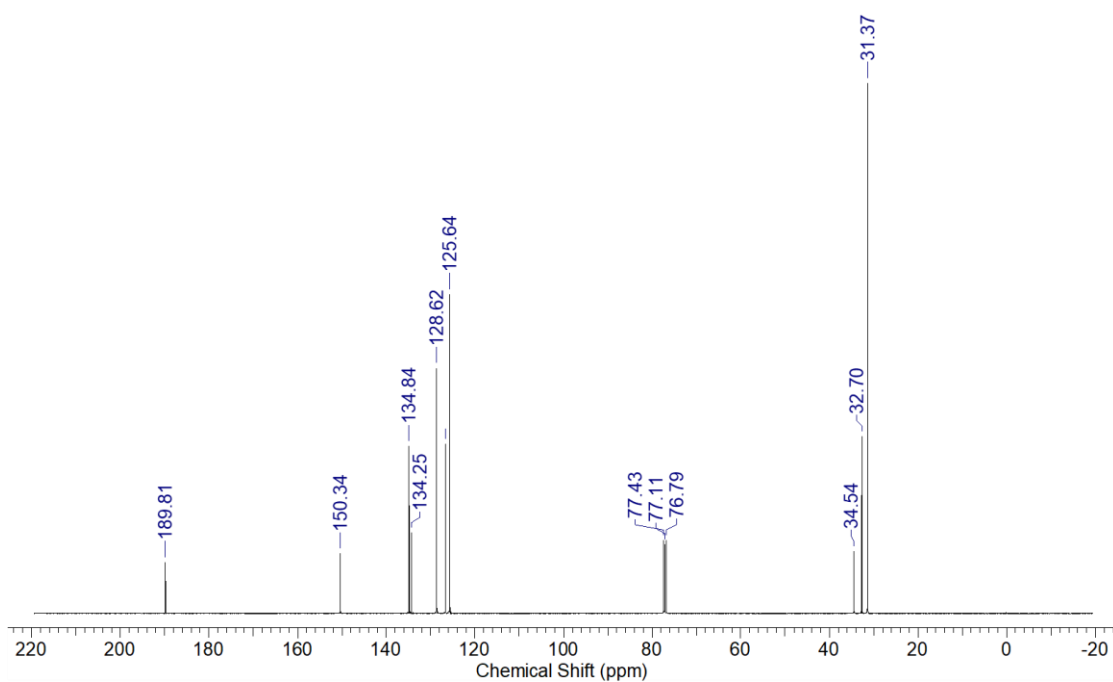


Fig. S2 ^{13}C NMR spectrum (CDCl_3) of *S*-(4-*t*-butylbenzyl) thioacrylate (**1**).

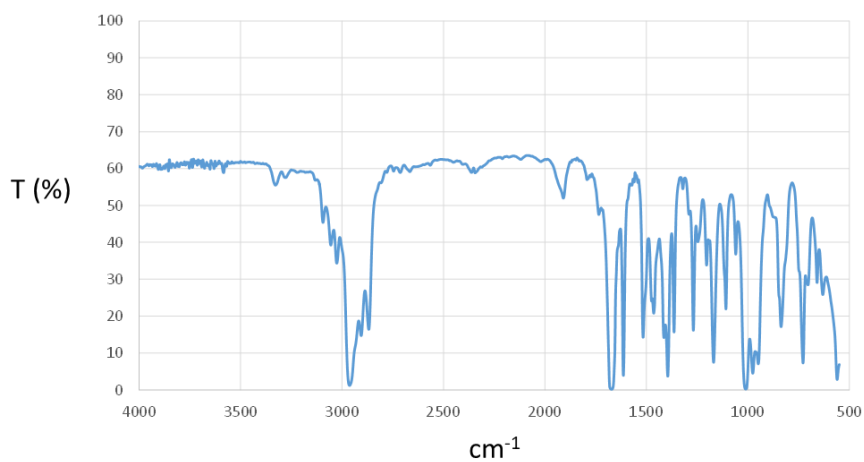


Fig. S3 IR spectrum of *S*-(4-*t*-butylbenzyl) thioacrylate (**1**). $\nu_{\text{C=O}}$: 1672 cm^{-1}

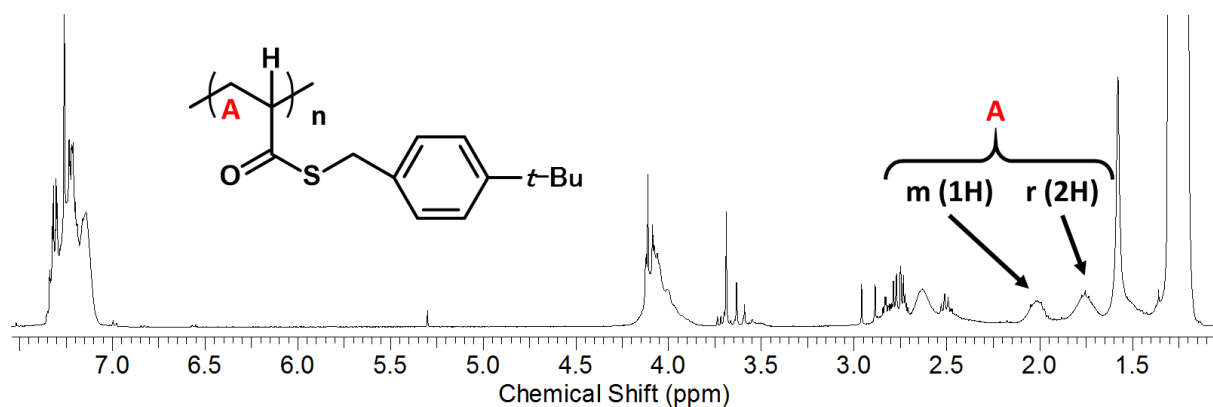


Fig. S4 ^1H NMR spectrum (CDCl_3) of the reaction mixture (run 1, Table 1). Another methylene proton of the meso isomer should be contained in the signal around 1.5 ppm.

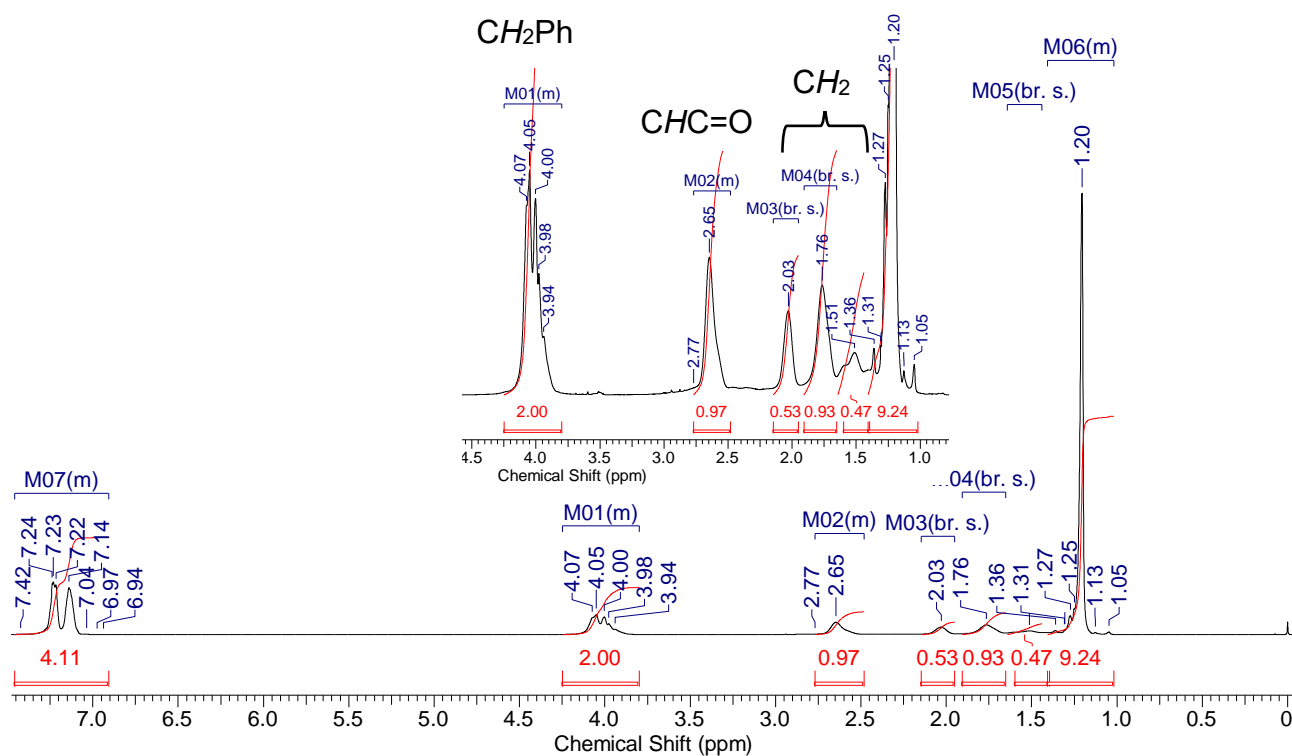


Fig. S5 ^1H NMR spectrum (CDCl_3) of the polymer (m:r=53:47, $M_n=24800$, $M_w=74200$) prepared under the condition of Run 17.

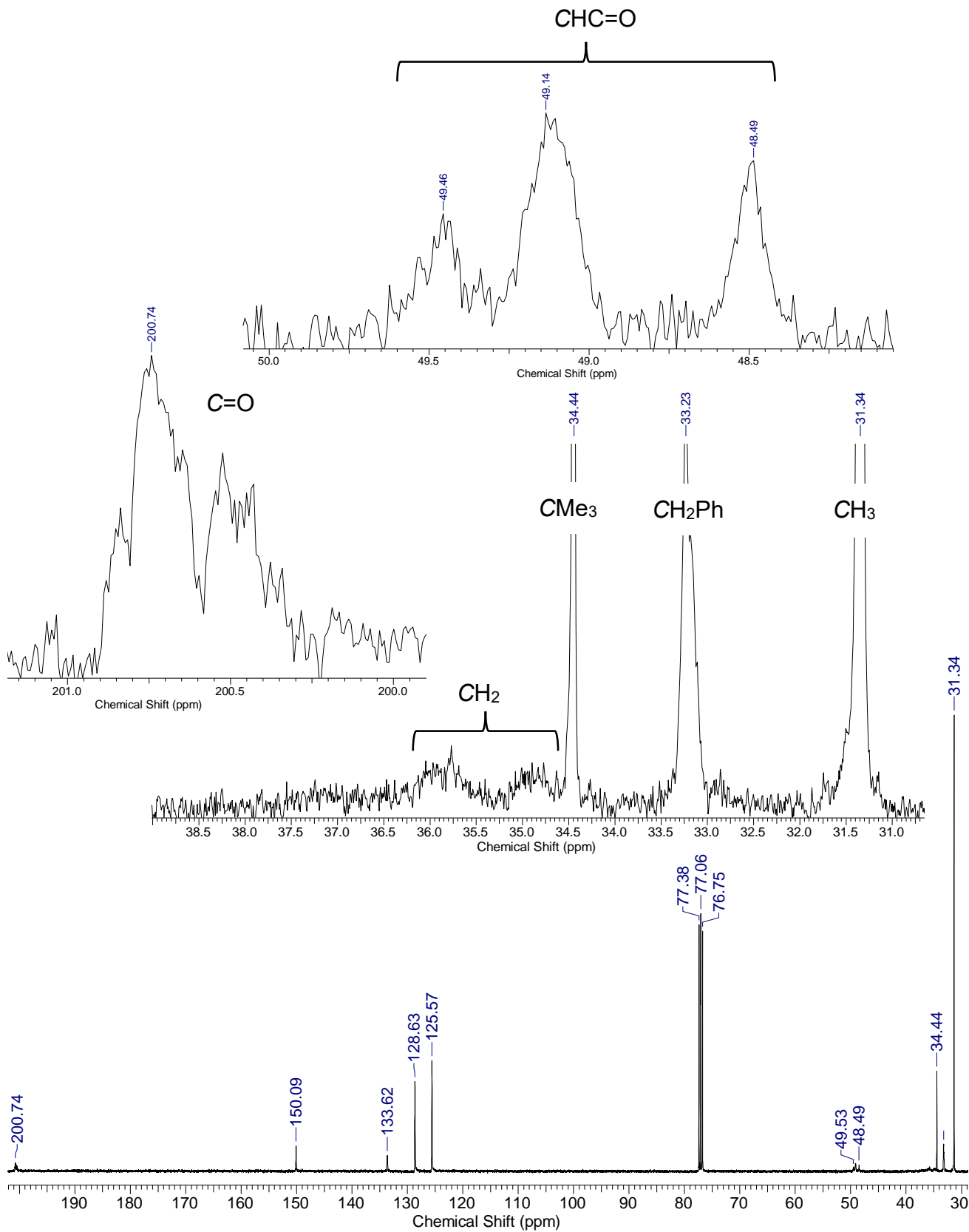


Fig. S6 ^{13}C NMR spectrum (CDCl_3) of the polymer ($m:r=53:47$, $M_n=24800$, $M_w=74200$) prepared under the condition of Run 17.

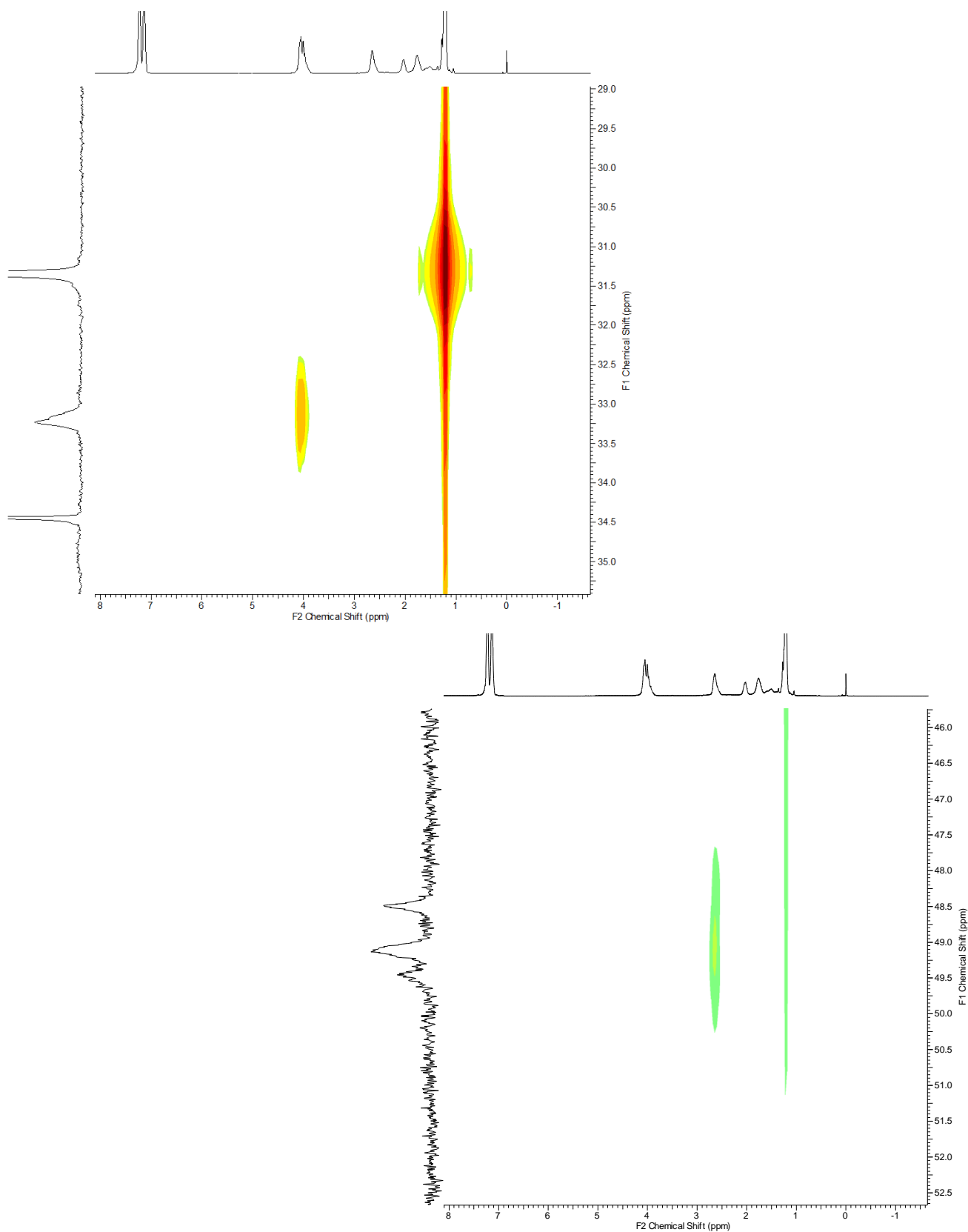


Fig. S7 HMQC NMR spectrum of the polymer ($m:r=53:47$, $M_n=24800$, $M_w=74200$) prepared under the condition of Run 17. The expanded areas are shown to assign the ^{13}C signals due to the benzylic (a) and methine (b) carbons, respectively.

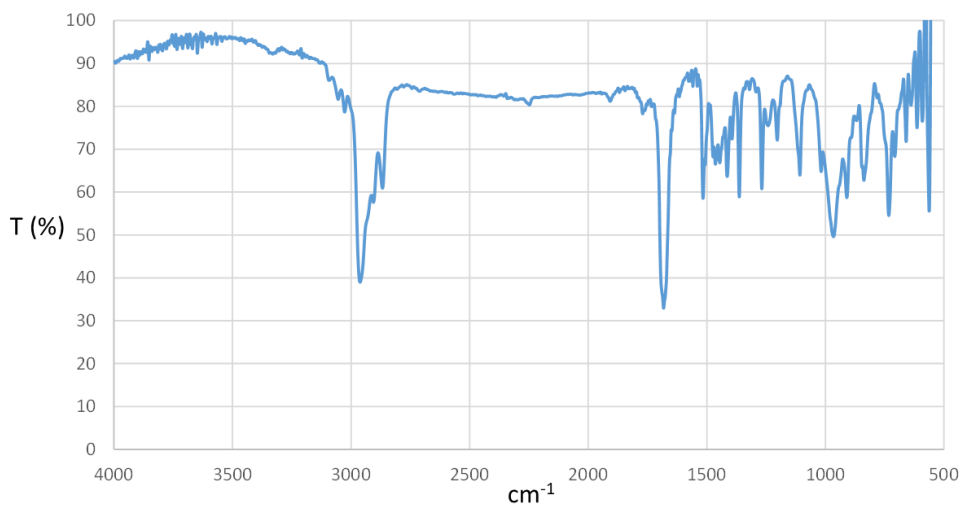


Fig. S8 IR spectrum of the polymer (m:r=53:47, $M_n=24800$, $M_w=74200$) prepared under the condition of Run 17. $\nu_{C=O}$: 1682 cm^{-1}

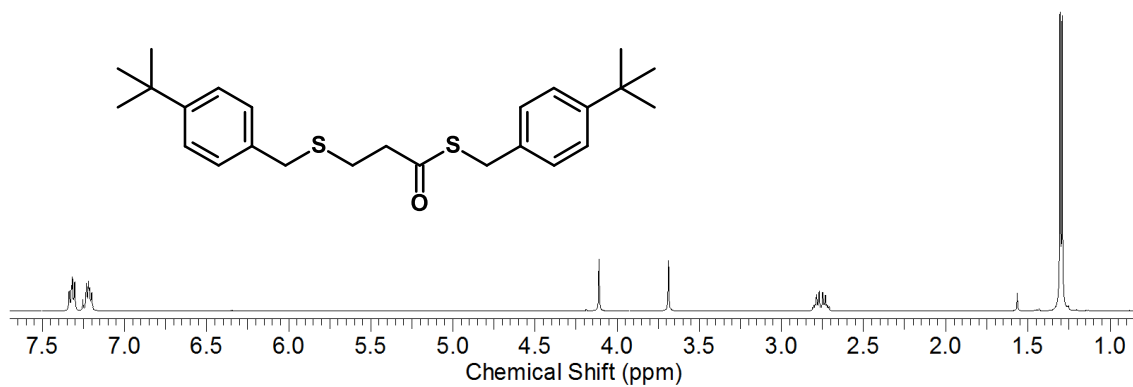


Fig. S9 ^1H NMR spectrum (CDCl_3) of **2**

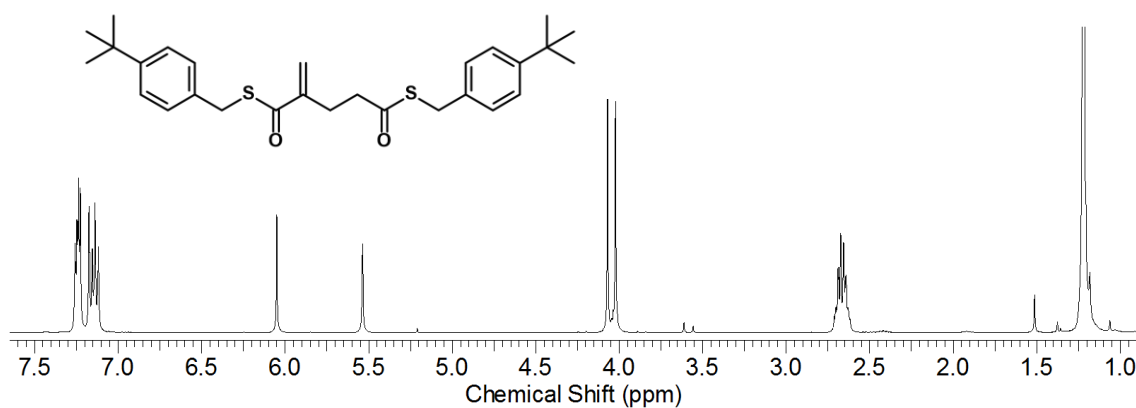


Fig. S10 ^1H NMR spectrum (CDCl_3) of **3**.

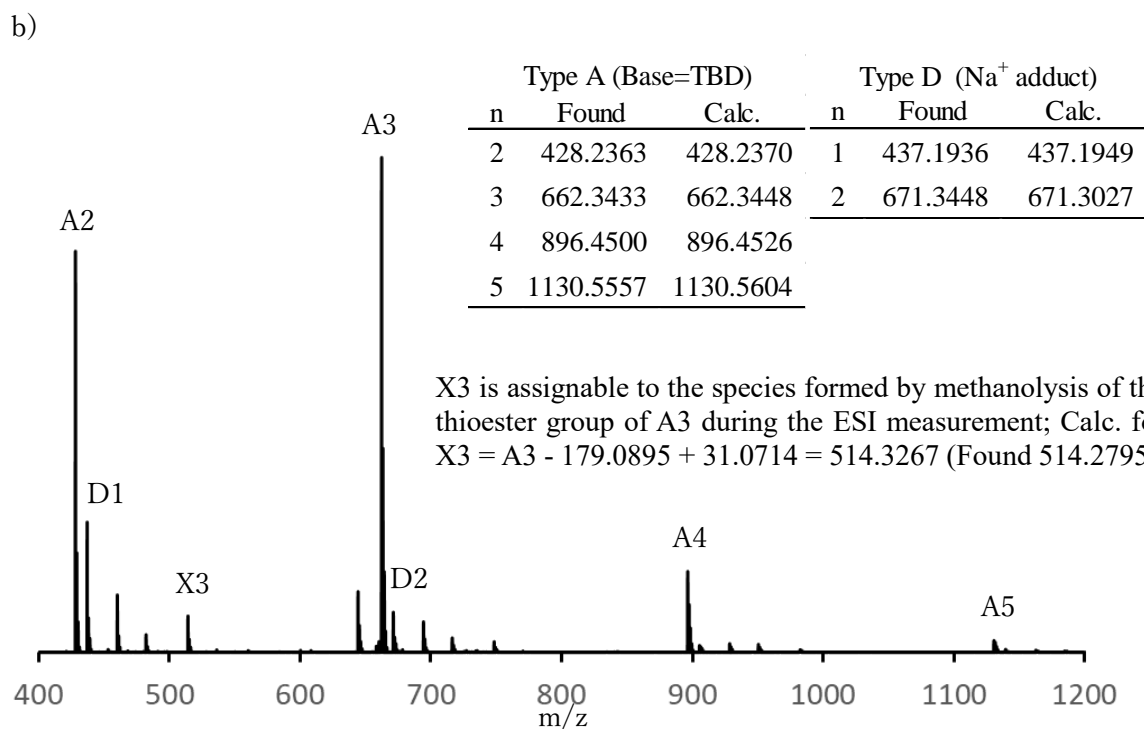
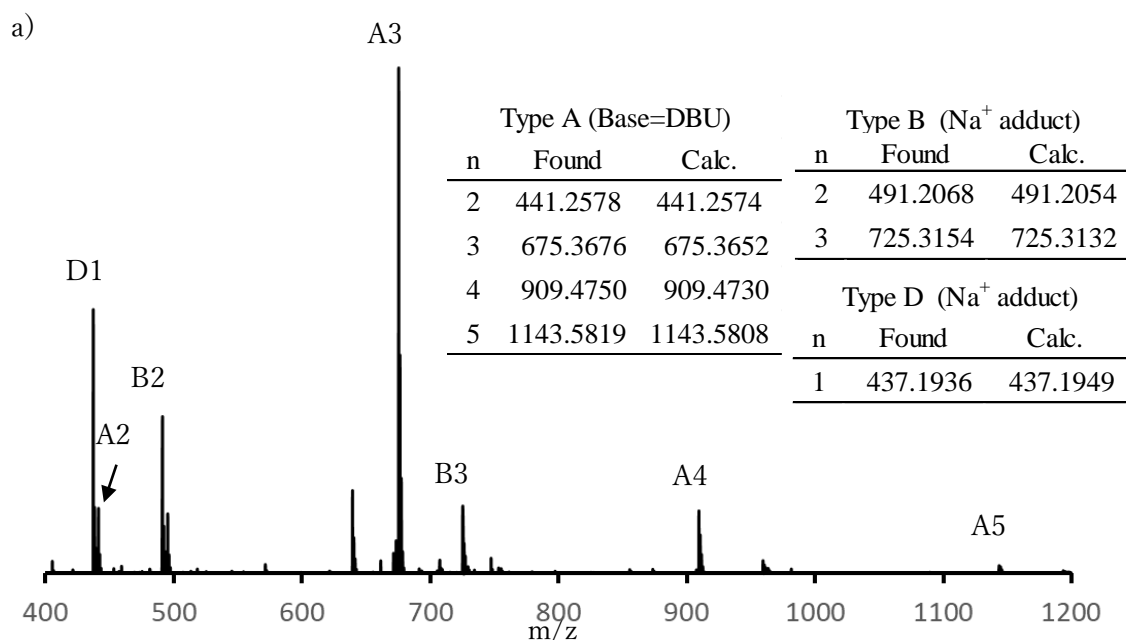


Fig. S11 ESI MS spectra of the reaction mixtures of Runs 23 (a) and 25 (b). The combination of alphabetical and numerical labels for the peak assignment shows the peak group structures (A-D) in Fig. 1 and the number of repeating units (n) of them, respectively.