Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Postpolymerization Modification of Sterically Demanding Poly(methacrylic acid) with Allen Sulfonamides

Hyun Gyu Shin,[a] *Tapas R. Pradhan,*[b] *Jin Kyoon Park*[*b] *and Jeung Gon Kim*[*a]

[a] Department of Chemistry and Research Institute of Physics and Chemistry, Jeonbuk National University, Jeonju, 54896, Republic of Korea

[b]Department of Chemistry and Institution for Functional Materials, Pusan National University, Busan, Republic of Korea 46241.

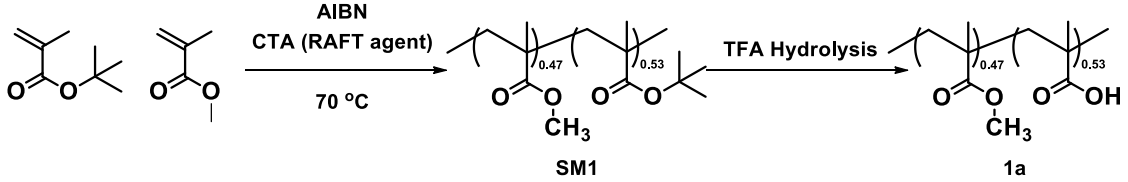
1. General Considerations

Unless noted otherwise, all reagents from commercial vendors (Aldrich, Alfa Aesar, TCI, or Acros) were used without further purification. All reactions were performed using flame-dried glassware and HPLC-grade solvent dried by 4Å molecular sieves. Thin layer chromatography (TLC) was conducted on silica gel 60 F254 plates and visualized by 254 nm UV light or $KMnO_4$ staining solution. Silica-gel (60 Å, 40-63 μm) used in flash chromatography was purchased from Zeochem.

2. Measurement

Gel permeation chromatography (GPC) analyses with refractive index (RI) detection were used to determine the number-average molecular weights (M_n) and polydispersity ($Đ$). Measurements were carried out using an instrument composed of a Waters 1515 isocratic pump, a 2414 differential refractive index detector, and a column-heating module with Shodex KF-G 4A guard column, HK-403, and HK404L columns in series. The columns were eluted with tetrahydrofuran (THF, HPLC grade, Daejung Chemical Company) at 40 °C at 0.5 mL min^{-1}. The calibration curve used 12 monodisperse poly(methyl methacrylate) standards (Agilent Technologies). ^1H NMR and ^{13}C NMR spectra were recorded by a 400 MHz Bruker Avance III HD Fourier transform NMR spectrometer at the Future Energy Convergence Core Center (FECC). Infrared spectra were measured by an ABB MB3000 FT-IR spectrometer equipped with an attenuated total reflectance module. The TGA thermogram recorded by Rigaku Thermo plus EVO2 was determined from 20 °C to 800 °C (10 °C min^{-1}) under N_2. High-resolution mass spectra (HR-MS) were obtained using JEOL JMS-700.

3. Synthesis of poly[(methyl methacrylate)-*co*-(methacrylic acid)]



Scheme S1. Synthesis of pre-polymer **1a**

3.1 Synthesis of poly[(methyl methacrylate)$_{0.47}$-*co*-(t-butyl methacrylate)$_{0.53}$] SM1

Methyl methacrylate (MMA) and *t*-butyl methacrylate (*t*-BMA) were filtered by a neutral alumina column to remove the inhibitor. The mixture of MMA (1 equiv., 2.9 mL, 27 mmol), *t*-BMA (1 equiv., 4.4 mL, 27 mmol,), AIBN (0.0012 equiv., 5.3 mg, 0.033 mmol), and CTA (4-Cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl]pentanoic acid)[1] (0.0060 equiv., 66 mg, 0.16 mmol) in 1,4-dioxane (1.5 mL) were degassed by

freeze-pump-thaw (3 cycles). The resulting mixture was heated at 70 °C for 20 h. The reaction was cooled to room temperature, and the cap was opened in the air for quenching. The solution was diluted with 15 mL dichloromethane (DCM) and precipitated in hexane several times. The product was dried under a vacuum oven at 70 °C to a yellow solid (4.2 g). The composition of copolymer **SM1** was calculated by ^{1}H NMR. M_n= 43.9 kg/mol; $Đ$ = 1.14; [PMMA]:[P*t*BMA] = 0.47:0.53.

3.2 Synthesis of poly[(methyl methacrylate)$_{0.47}$-*co*-(methacrylic acid)$_{0.53}$] 1a

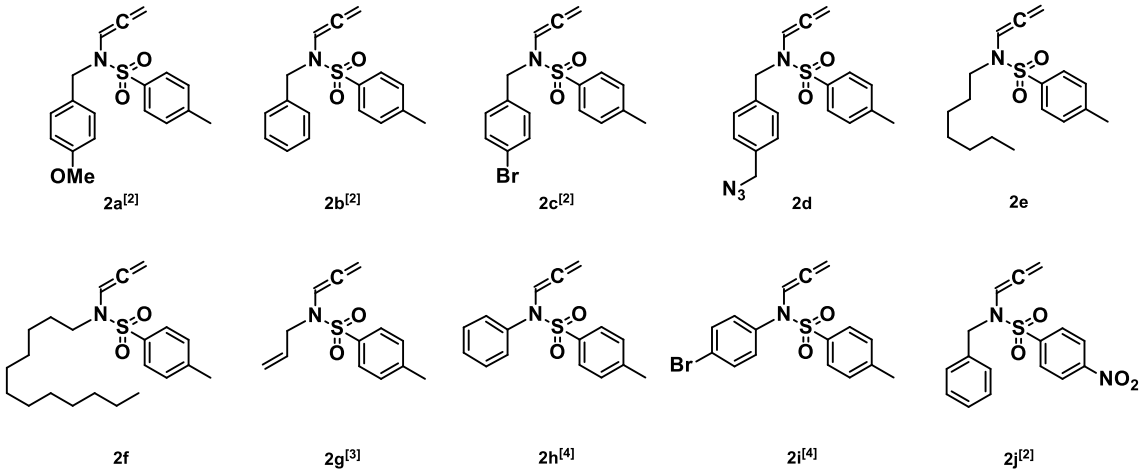
The **SM1** (4.2 g) was diluted with 15 mL $CHCl_3$. Trifluoracetic acid 25 mL (excess amount, around 10 equiv. to *t*-butyl ester functionality) was slowly added to the solution. After overnight stirring, 30 mL MeOH and excess water were added to precipitate the yellow product. The solid was dried under a vacuum oven at 70 °C to give the polymer **1a** (3.3 g).

3.3 Synthesis of poly [(methyl methacrylate)$_{0.18}$-*co*-(methacrylic acid)$_{0.82}$] 1b, and poly (methacrylic acid) 1c and poly [(methyl methacrylate)$_{0.51}$-*co*-(acrylic acid)$_{0.49}$] 1d

The copolymers **1b**, **1c, 1d** were synthesized using the same procedure in different monomer ratios. Monomer ratio for **SM2**, MMA (1.2 mL, 11 mmol) and *t*-BMA (7.1 mL, 44 mmol). M_n= 44.5 kg/mol; $Đ$ = 1.18; [PMMA]:[P*t*BMA] = 0.18:0.82. After TFA treatment, copolymer **1b** was gained as a yellow solid (1.6 g). Monomer for P*t*BMA, **SM3**, *t*-BMA (8.8 mL, 54 mmol). M_n= 35.1 kg/mol; $Đ$ = 1.23. After TFA treatment, copolymer **1c** was gained as a yellow solid by washing $CHCl_3$ (2.9 g). Monomer ratio for **SM4,** MMA (2.9 mL, 27 mmol) and *t*-butyl acrylate(*t*-BA) (4.0 mL, 27 mmol). M_n= 52.6 kg/mol; $Đ$ = 1.30; [PMMA]:[P*t*BA] = 0.51:0.49. TFA treatment produced copolymer **1d** as a yellow solid (3.2 g).

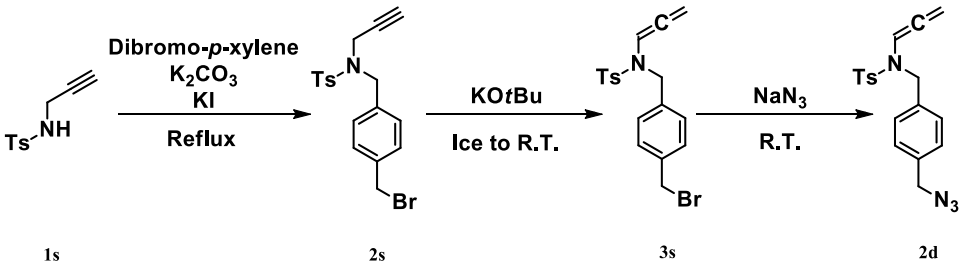
4. Synthesis of allene sulfonamide

The allene sulfonamides (**2a-2i**) were obtained according to the reported procedure, except for **2d**, **2e**, and **2f**.[2-5] (**Scheme S2**).



Scheme S2. Series of allene sulfonamides synthesized for postpolymerization modification.

4.1 Representative Procedure: Synthesis of 2d



Scheme S3. Synthetic route of **2d**

The precursor of allene sulfonamide **1s** was synthesized according to the literature procedure.[4] To the solution of propargyl sulfonamide **1s** (1 equiv., 4.2 g, 20 mmol) in acetone (0.3 M), K_2CO_3 (2 equiv., 5.5 g, 40 mmol) and KI (2 equiv., 6.6 g, 40 mmol) were added. The mixture was heated to reflux, and a 1.0 M solution of α,α′-dibromo-*p*-xylene (1 equiv., 5.3 g, 20 mmol) in acetone was slowly added for a half hour. After refluxing overnight, the mixture was poured into the pad of celite to remove salts. The resulting mixture was purified using column chromatography, hexanes:ethyl acetate = 9:1 (v/v). Product **2s** was obtained as a white solid (49%, 3.9 g).

The propargyl sulfonamide **2s** (0.88 g 2.2 mmol) was diluted in THF (0.5 M). After the flask was cooled to 0 ºC, potassium *tert*-butoxide (0.5 equiv. 0.13 g 1.1 mmol, 1 M in THF) was slowly added for 30 min with stirring under an inert condition. The mixture was stirred for 16 h at room temperature. Ethyl acetate

(10 mL) was added and washed with deionized water. The aqueous layer was extracted with ethyl acetate (20 mL) twice. The combined organic layer was dried over Na_2SO_4, and the mixture was purified by column chromatography, hexanes:ethyl acetate = 9:1 (v/v). The product **3s** was obtained as a white solid (57%, 0.50 g).

To the precursor **3s** (0.30 g, 0.77 mmol) in DMF (0.3 M) in a round bottom flask, NaN_3 (3 equiv., 0.15 g, 0.23 mmol) was added. The solution was stirred overnight at room temperature. DCM (5 mL) was added, and the mixture was washed with H_2O. The aqueous layer was extracted with DCM twice. The combined organic layer was dried over Na_2SO_4. The crude mixture was purified by column chromatography, hexanes:ethyl acetate = 9:1 (v/v). The compound **2d** was obtained as a white solid (84%, 0.23 g).

5. General procedure for postpolymerization modification (PPM)

Poly[(methyl methacrylate)-*co*-(methacrylic acid)] **1a** (10 mg, 0.057 mmol of carboxylic acid functionality) and *p*-methoxy benzyl allene sulfonamide **2a** (54 mg, 0.14 mmol, 2.5 equiv. to carboxylic acid) was added to 1 mL V-shaped vial. 1,4-Dioxane (0.19 mL, 0.3 M to carboxylic acid functionality) was added to the vial, and the mixture was placed in a pre-heated reaction block at 100 °C. After 20 h, the solution was diluted with 0.5 mL DCM and precipitated in MeOH twice. The combined precipitate was dried in a vacuum at room temperature to produce the final product. (conversion: 92%, M_n = 51.6 kg/mol, $Đ$ = 1.16).

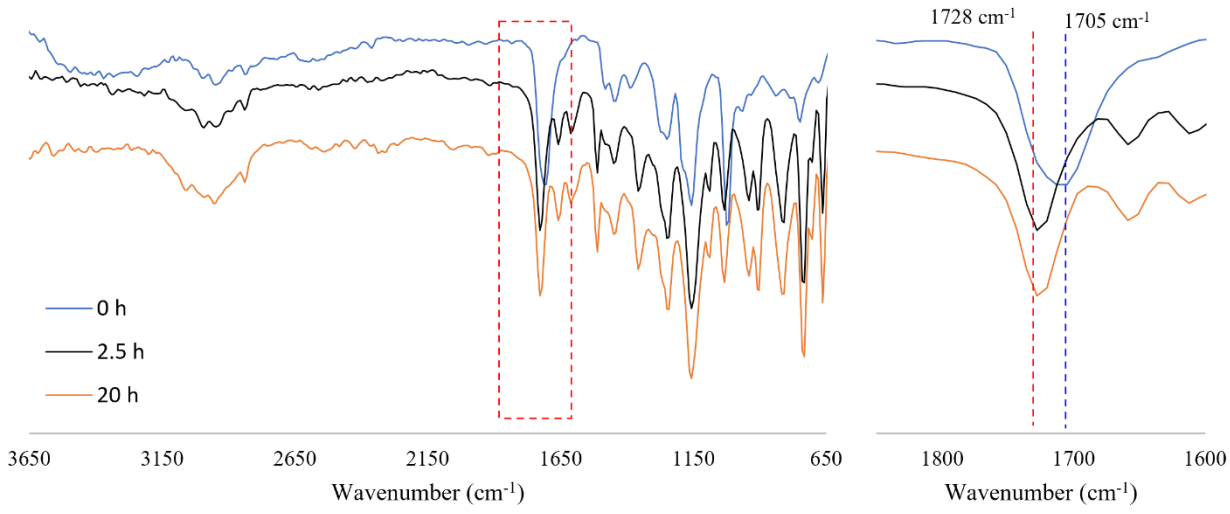


Figure S1. IR spectra of 0 h (**1a**), isolated polymer (after 2.5 h), and product **P1** (20 h)

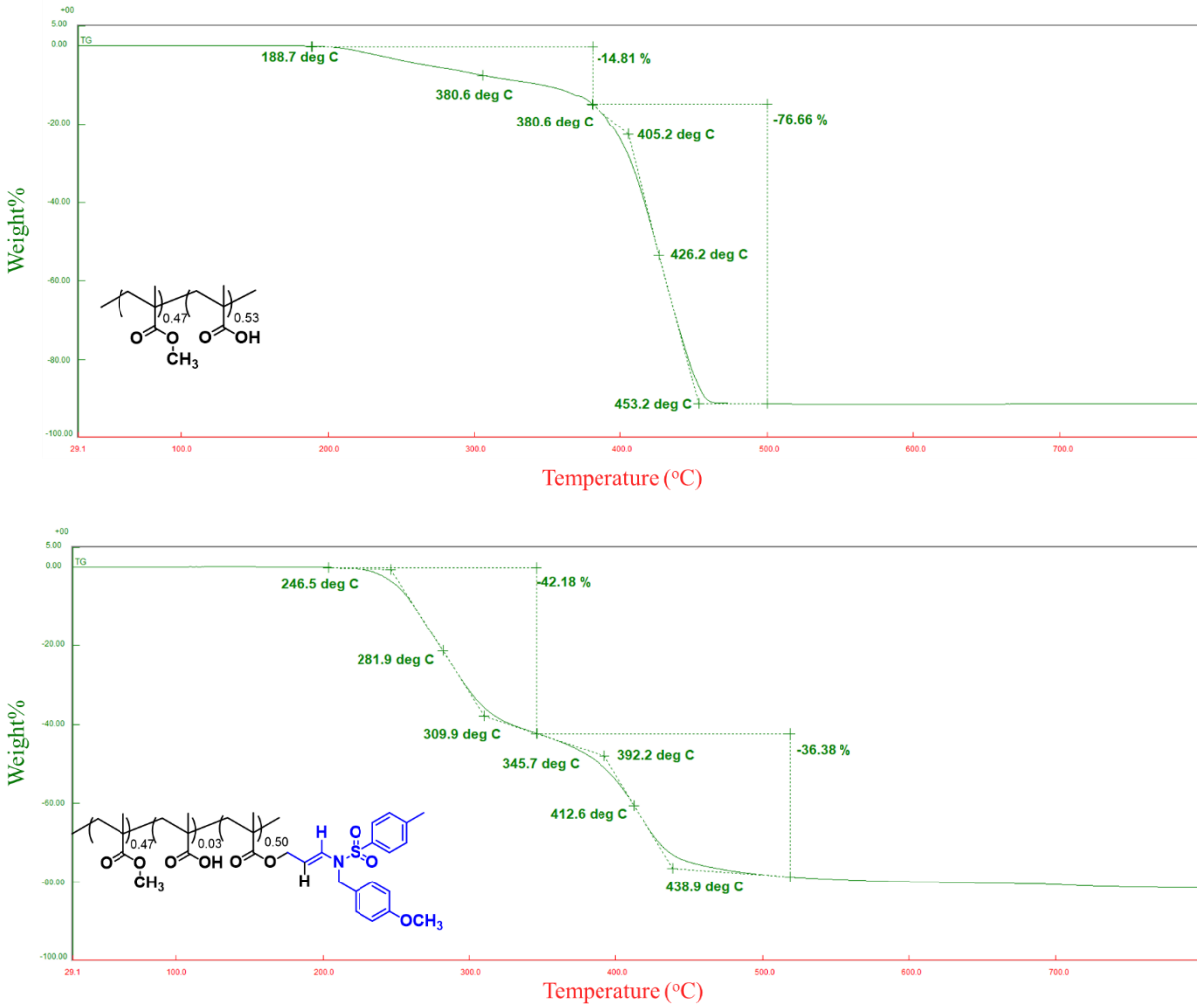


Figure S2. TGA curve of **1a** (top) and **P1** (bottom).

6. Reference

1. J. C. Foster, S. C. Radzinski, X. Zou, C. V. Finkielstein and J. B. Matson, *Mol. Pharmaceutics*, 2017, **14**, 1300–1306.

2. W.-F. Zheng, G.-J. Sun, L. Chen and Q. Kang, *Adv. Synth. Catal.,* 2018, **360**, 1790–1794.

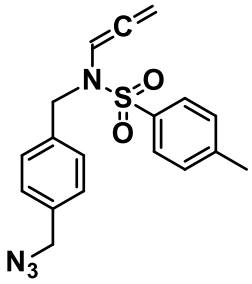
3. F. Yan, H. Liang, B. Ai, W. Liang, L. Jiao, S. Yao, P. Zhao, Q. Liu, Y. Dong and H. Liu, *Org. Biomol. Chem.*, 2019, **17**, 2651–2656.

4. S. Suárez-Pantiga, C. Hernández-Díaz, M. Piedrafita, E. Rubio and J. M. González, *Adv. Synth. Catal.*, 2012, **354**, 1651–1657.

5. T. R. Pradhan, H. E. Lee, G. A. Gonzalez-Montiel, P. H. Cheong and J. K. Park, *Chem. Eur. J.*, 2020, **26**, 13826–13831.

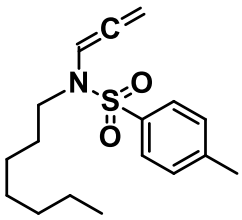
7. Characterization of New Compounds

***N*-(4-(azidomethyl)benzyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (2d)**



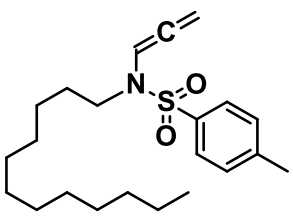
^{1}H NMR (400 MHz, acetone-d_6) δ 7.79 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 4.1 Hz, 4H), 6.85 (t, J = 6.3 Hz, 1H), 5.20 (d, J = 6.3 Hz, 2H), 4.43 (s, 2H), 4.37 (s, 2H), 2.46 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6) δ 202.94, 145.06, 137.81, 136.52, 135.95, 130.82, 129.29, 129.06, 128.16, 100.84, 88.49, 54.78, 50.48, 21.47 ppm; HRMS (EI^+) Calculated for $C_{18}H_{18}N_4O_2S[M]^+$: 354.1150, found: 354.1147; melting point : 56 °C; white solid.

***N*-Heptyl-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (2e)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 6.75 (t, J = 6.2 Hz, 1H), 5.20 (d, J = 6.3 Hz, 1H), 3.03 – 2.98 (m, 2H), 2.34 (s, 3H), 1.49 – 1.42 (m, 2H), 1.23 – 1.14 (m, 8H), 0.79 (t, J = 6.9 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.57, 143.64, 135.61, 129.75, 127.18, 100.20, 87.41, 46.69, 31.75, 28.92, 27.91, 26.51, 22.62, 21.58, 14.12 ppm; **HRMS** (FAB^+) Calculated for $C_{17}H_{26}NO_2S[MH]^+$: 308.1684, found: 308.1681; light yellow oil.

***N*-Dodecyl-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (2f)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.74 (t, J = 6.2 Hz, 1H), 5.20 (d, J = 6.3 Hz, 2H), 3.04 – 2.97 (m, 2H), 2.33 (s, 3H), 1.43 (dd, J = 14.1, 6.9 Hz, 2H), 1.47 – 1.40 (m, 2H), 1.23 – 1.13 (m, 18H), 0.79 (t, J = 6.9 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.56, 143.60, 135.62, 129.73, 127.16, 100.20, 87.37, 46.68, 31.97, 29.71, 29.68, 29.62, 29.55, 29.40, 29.26, 27.90, 26.55, 22.74, 21.55, 14.15 ppm; **HRMS** (FAB^+) Calculated for $C_{22}H_{36}NO_2S[MH]^+$: 378.2467, found: 378.2464; light yellow oil.

8. Spectral Data:

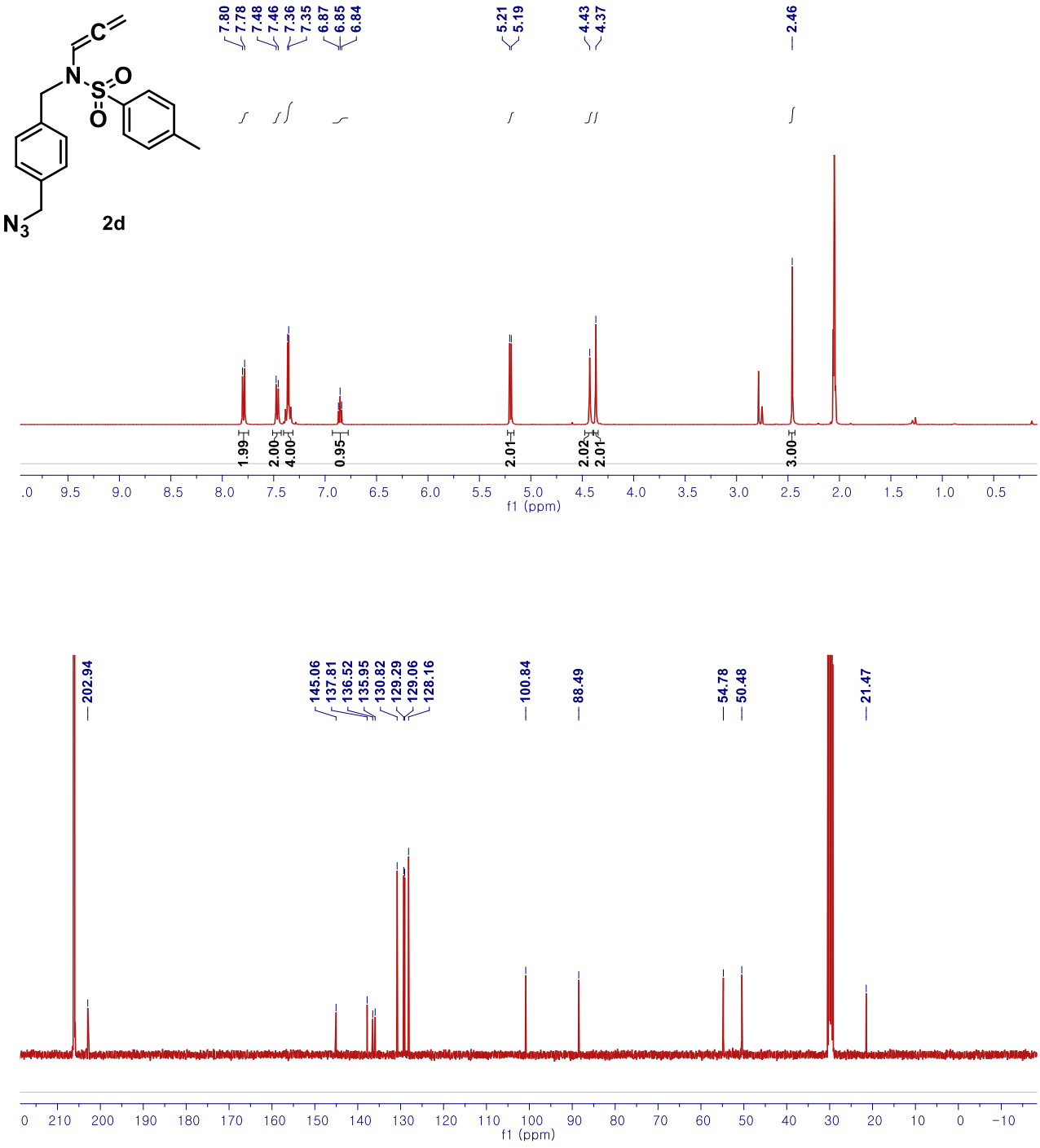


Figure S3. ^{1}H NMR and ^{13}C NMR spectra of **2d**.

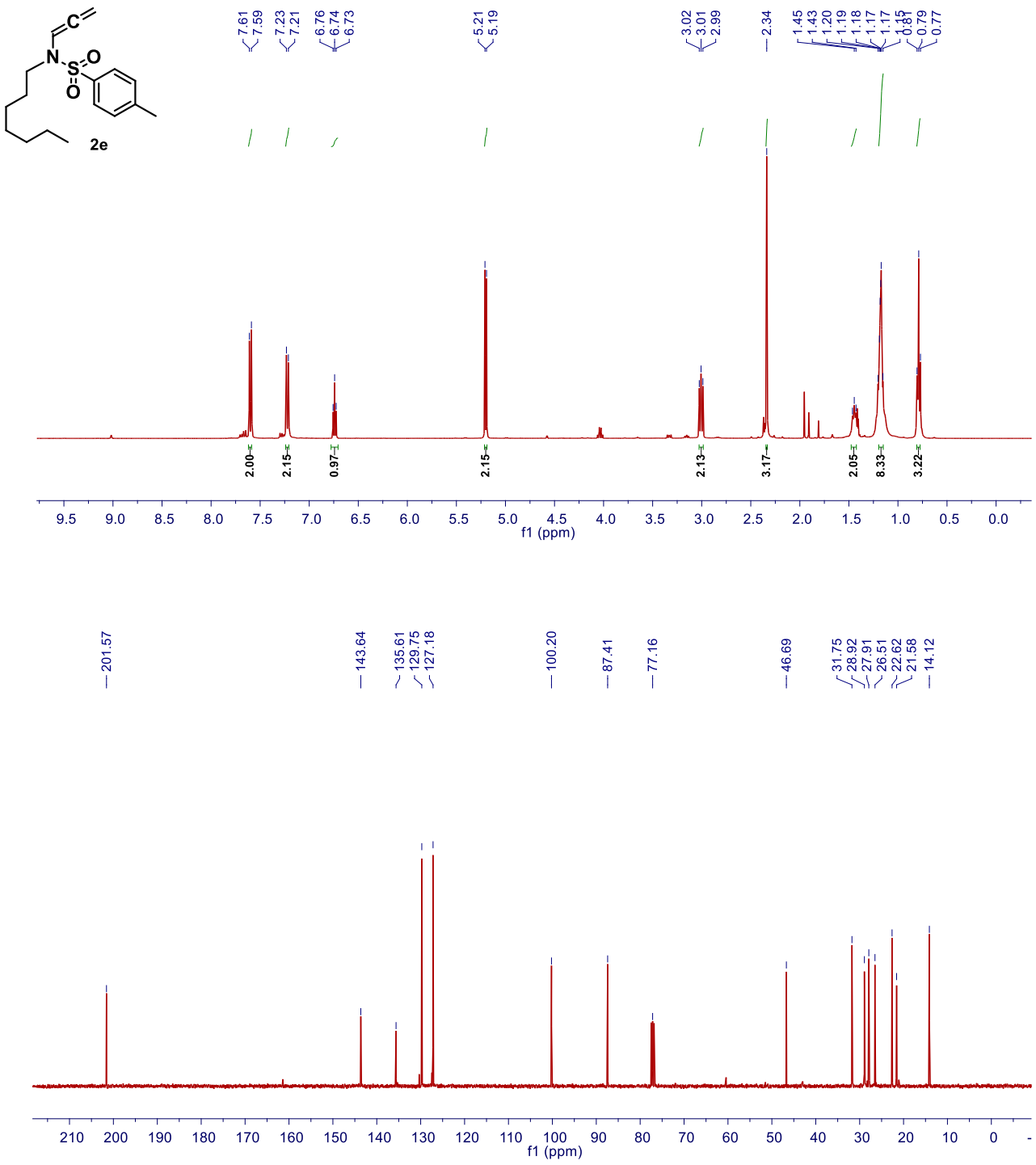


Figure S4. ^{1}H NMR and ^{13}C NMR spectra of **2e**.

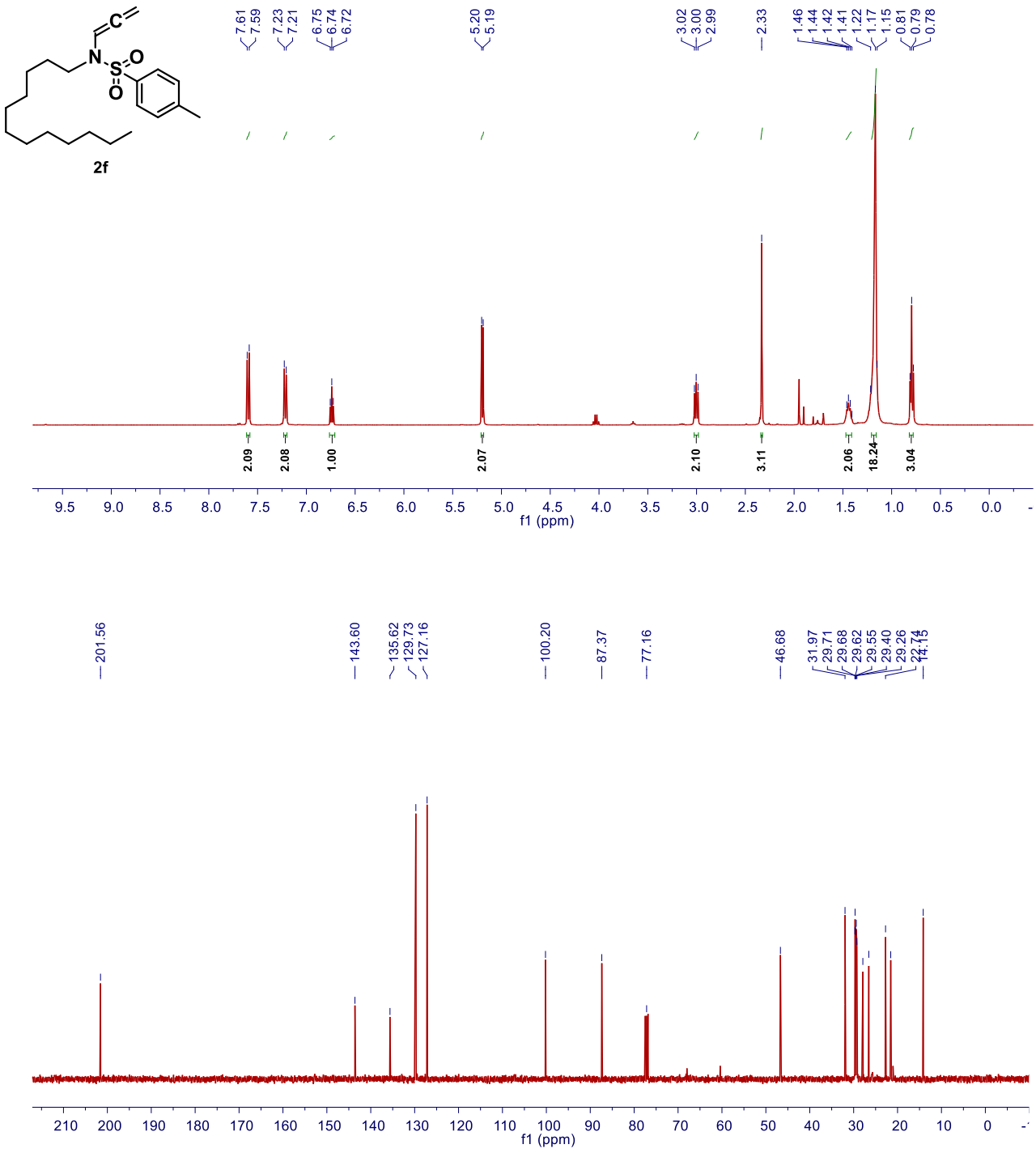


Figure S5. ^{1}H NMR and ^{13}C NMR spectra of **2f**.

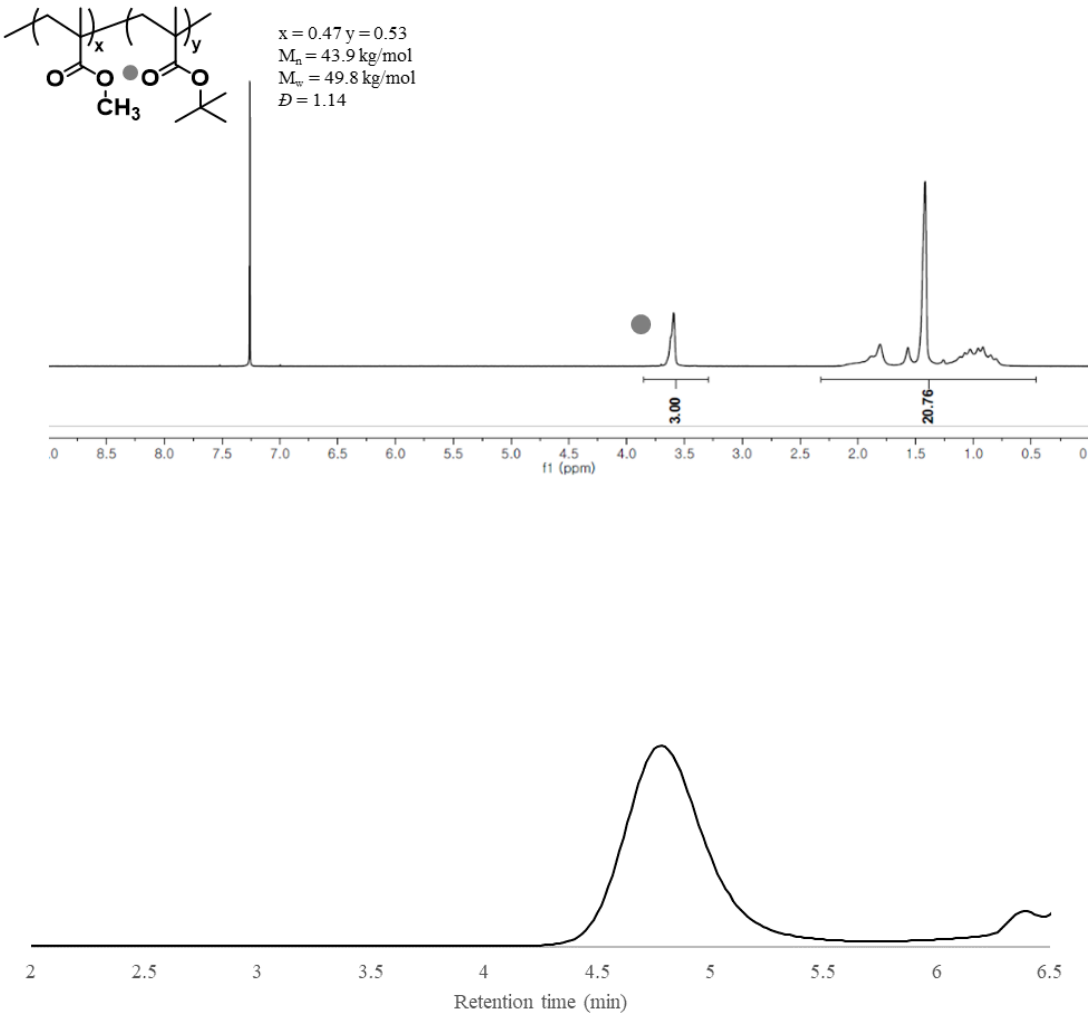


Figure S6. ^{1}H NMR (acetone-d_6) and GPC spectra of poly[(methyl methacrylate)$_{0.47}$-*co*-(*t*-butyl methacrylate)$_{0.53}$] (**SM1**)

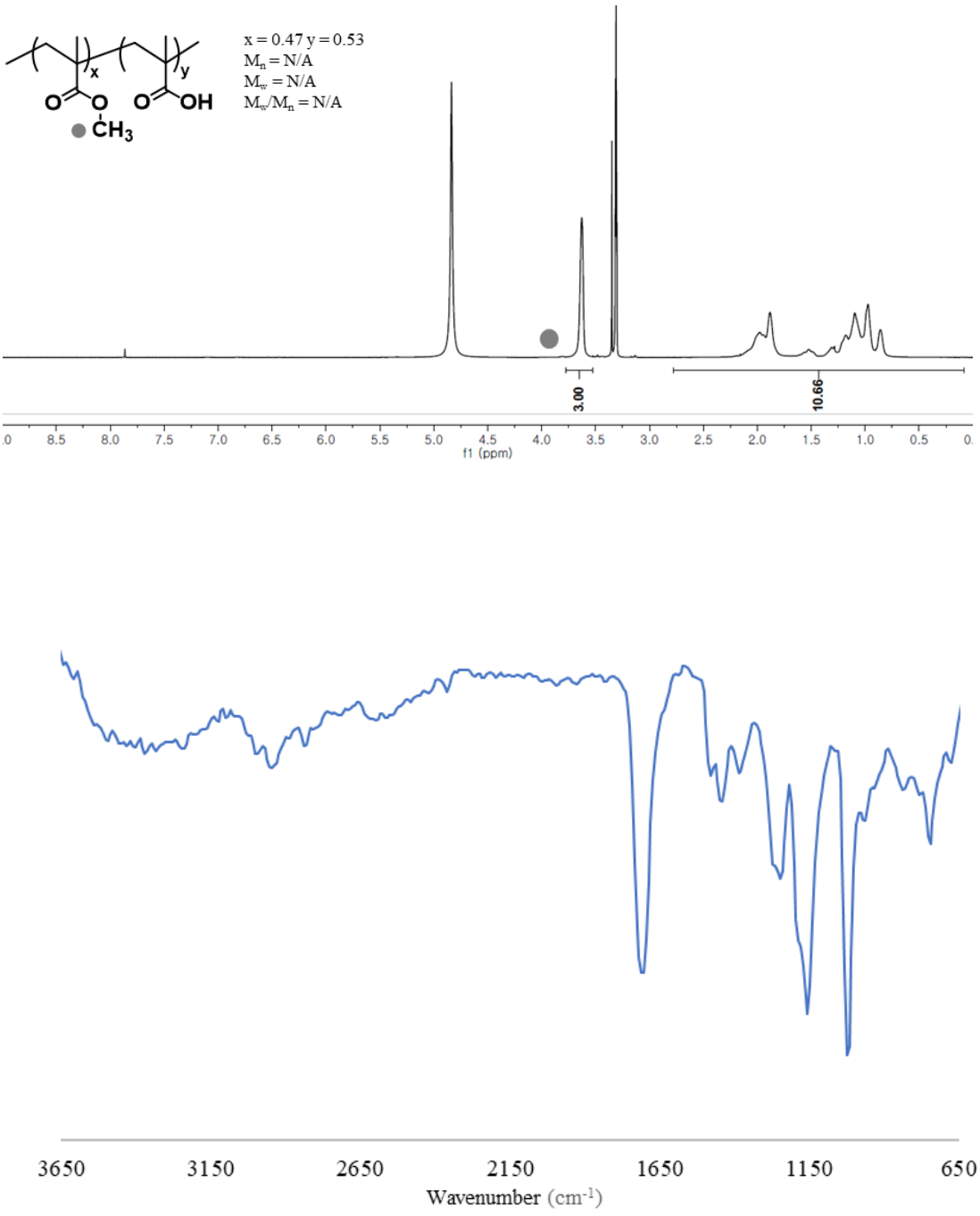


Figure S7. ^{1}H NMR and FT-IR spectra of **1a (**CD_3OD:$CDCl_3$ = 9:1 (v/v))

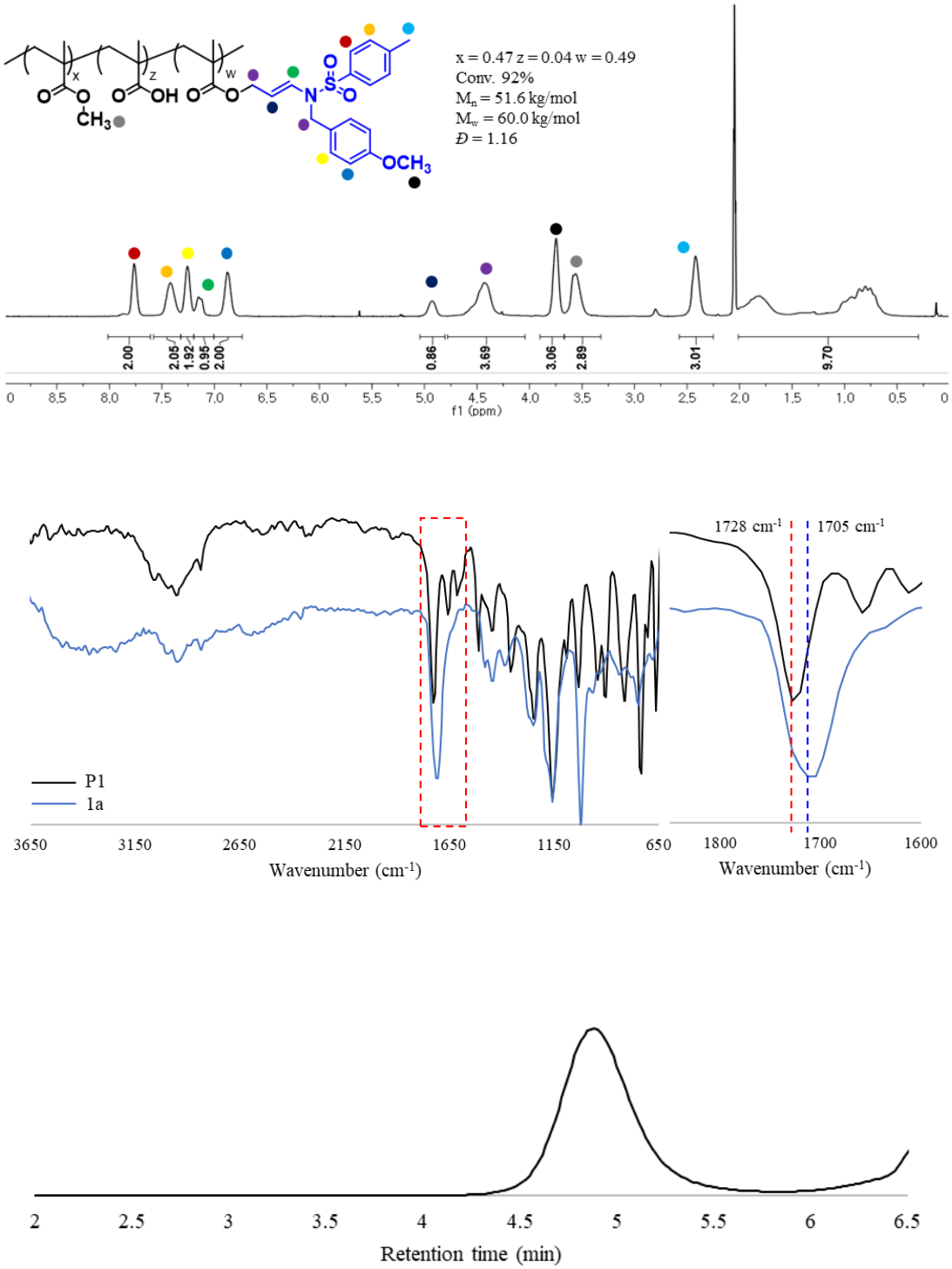


Figure S8. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P1**

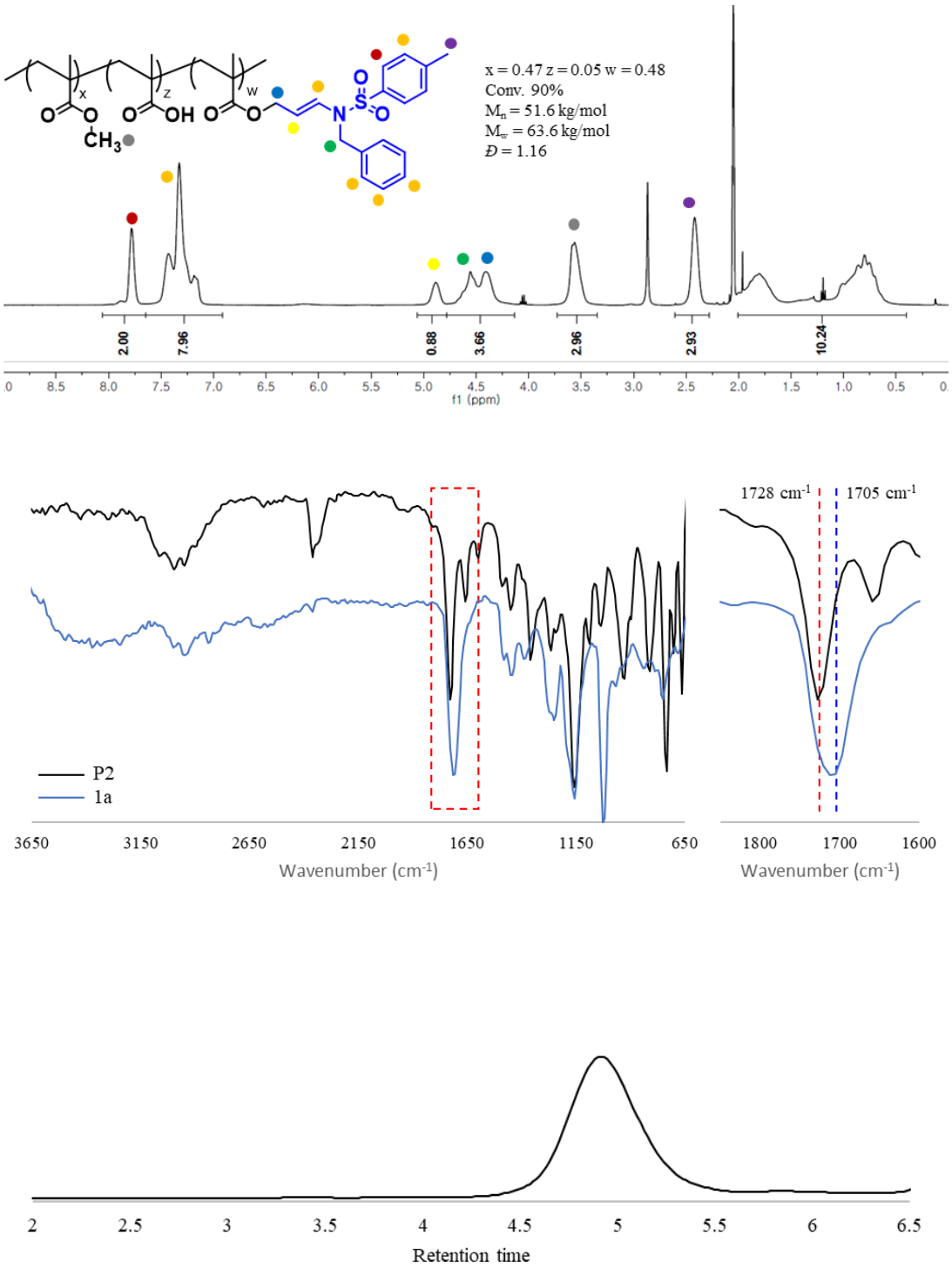


Figure S9. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P2**

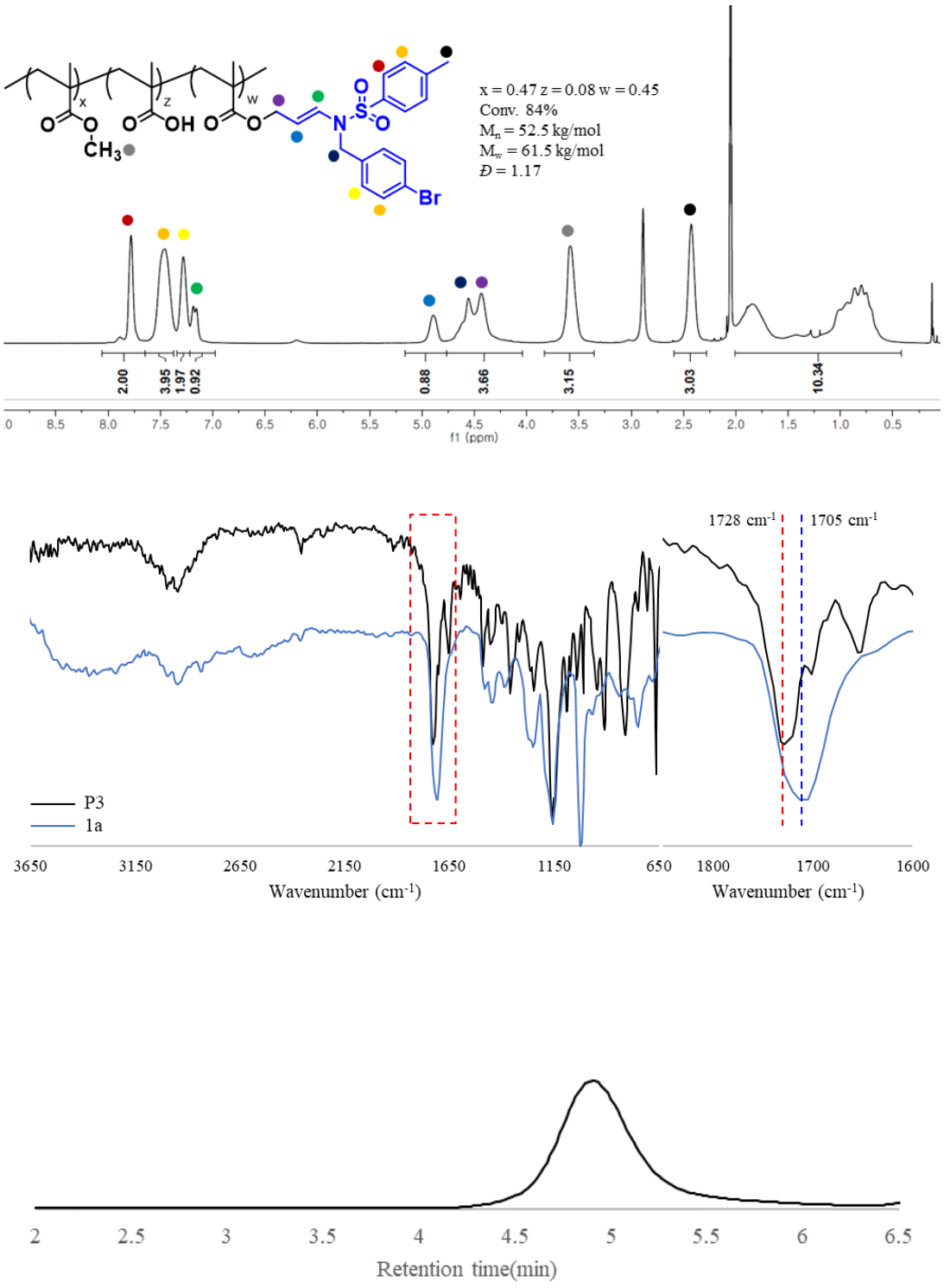


Figure S10. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P3**

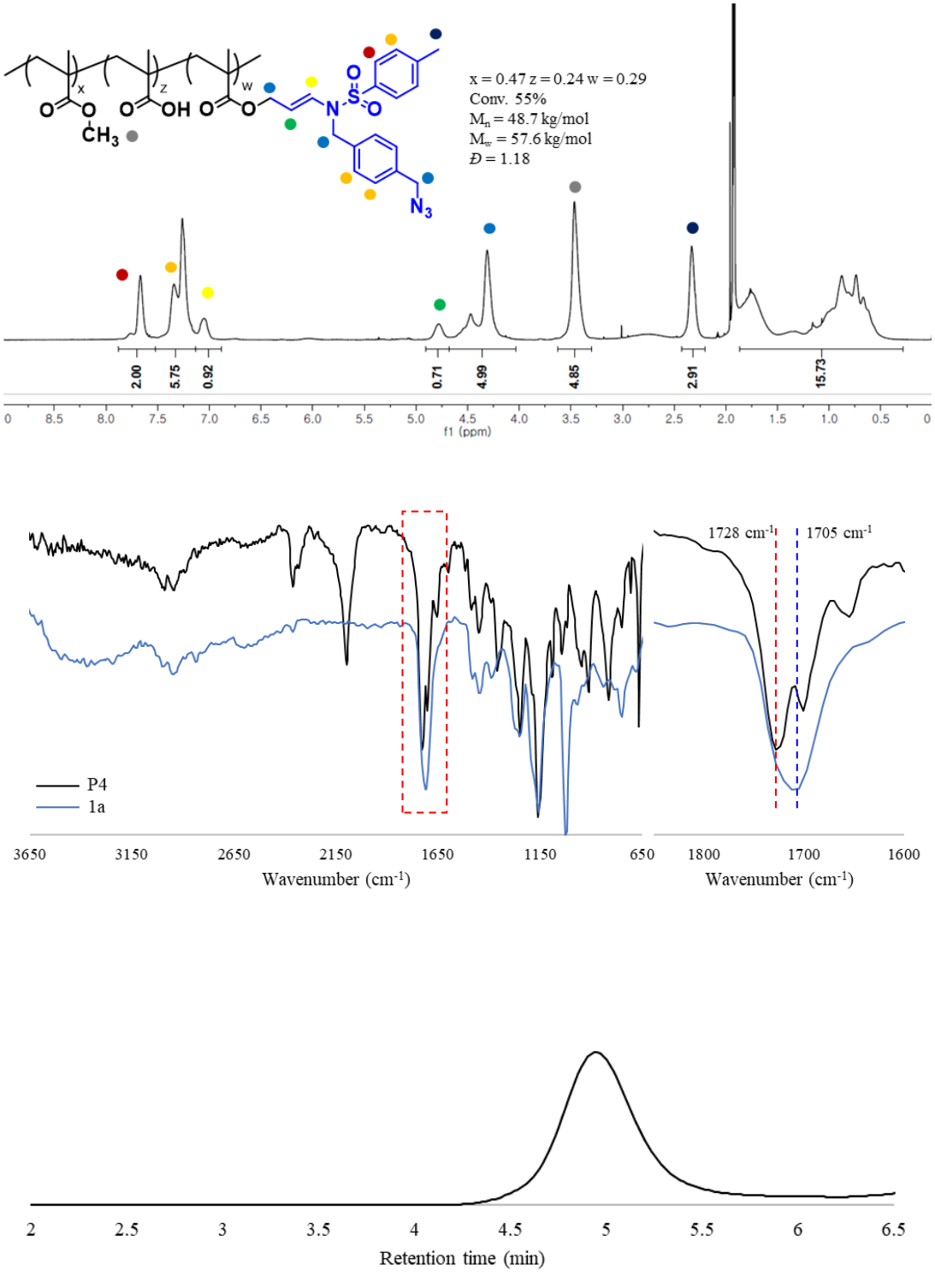


Figure S11. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P4**

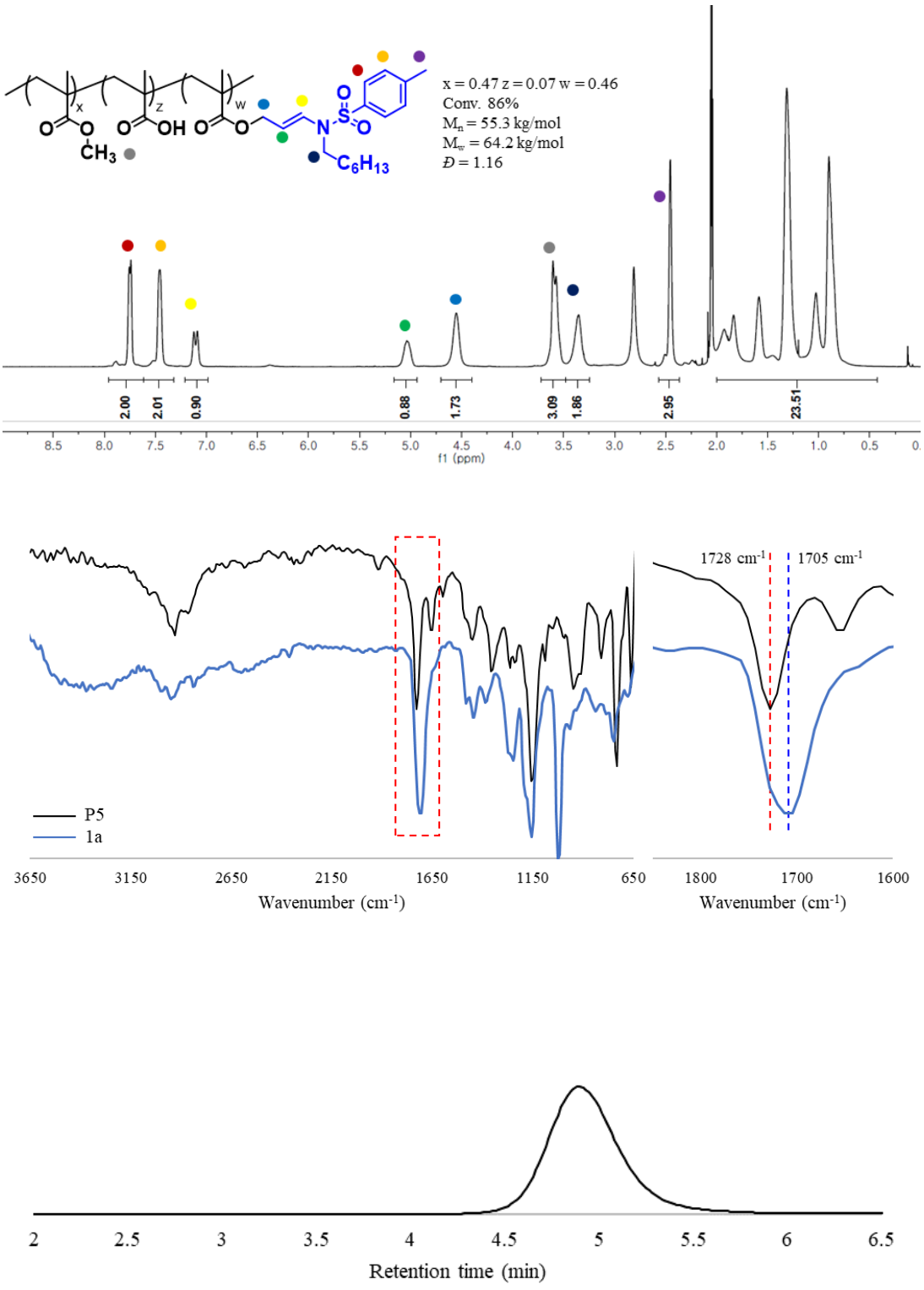


Figure S12. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P5**

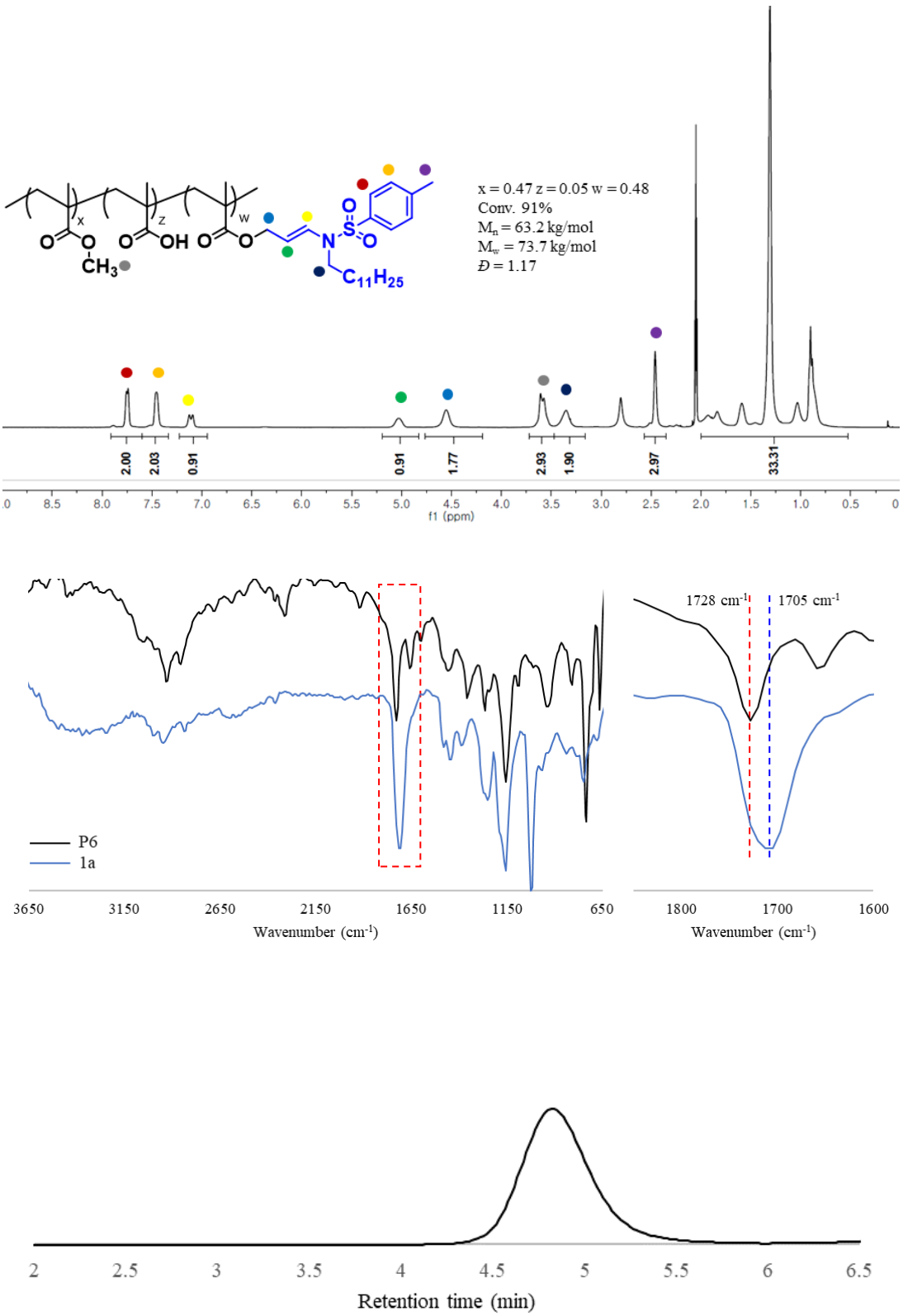


Figure S13. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P6**

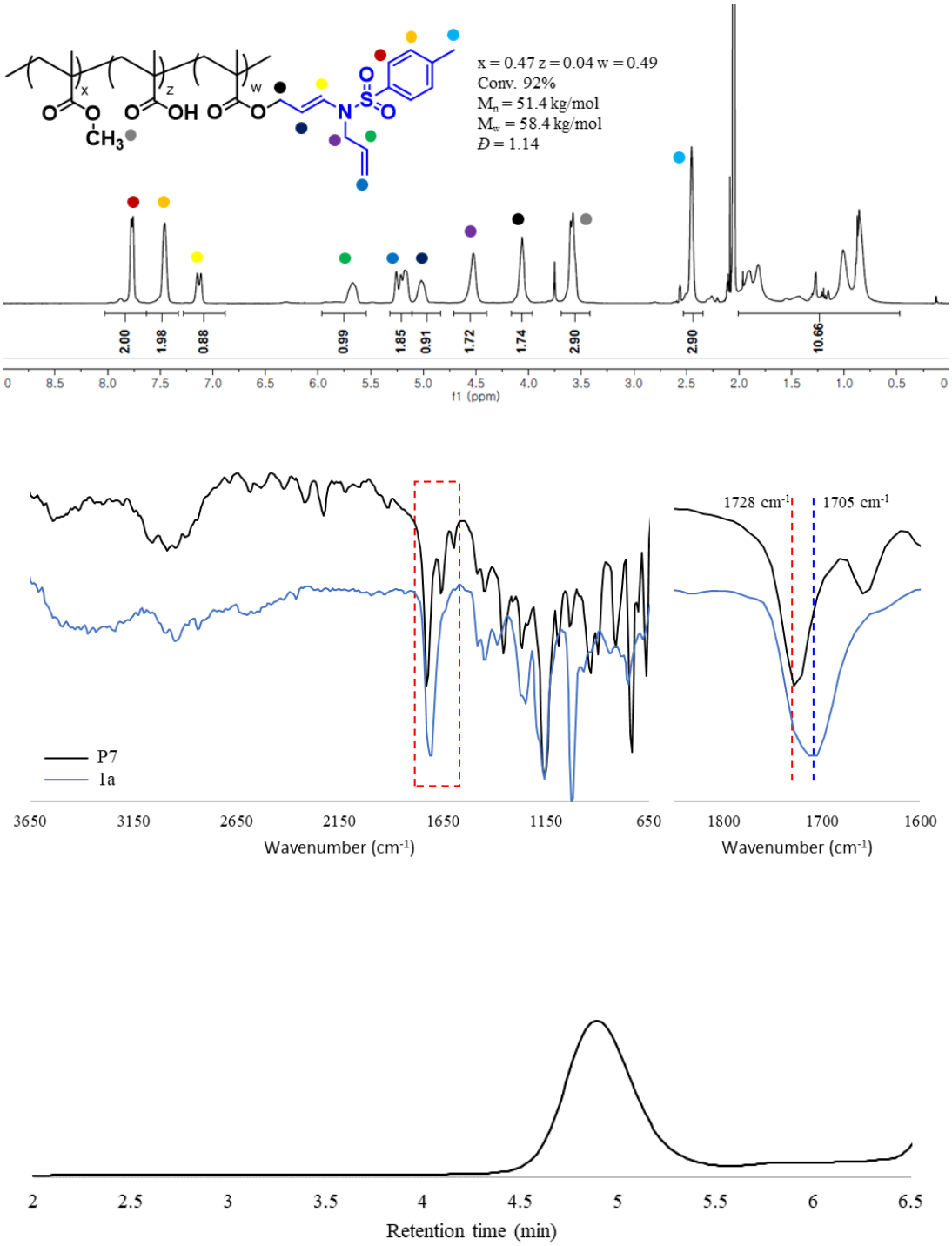


Figure S14. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P7**

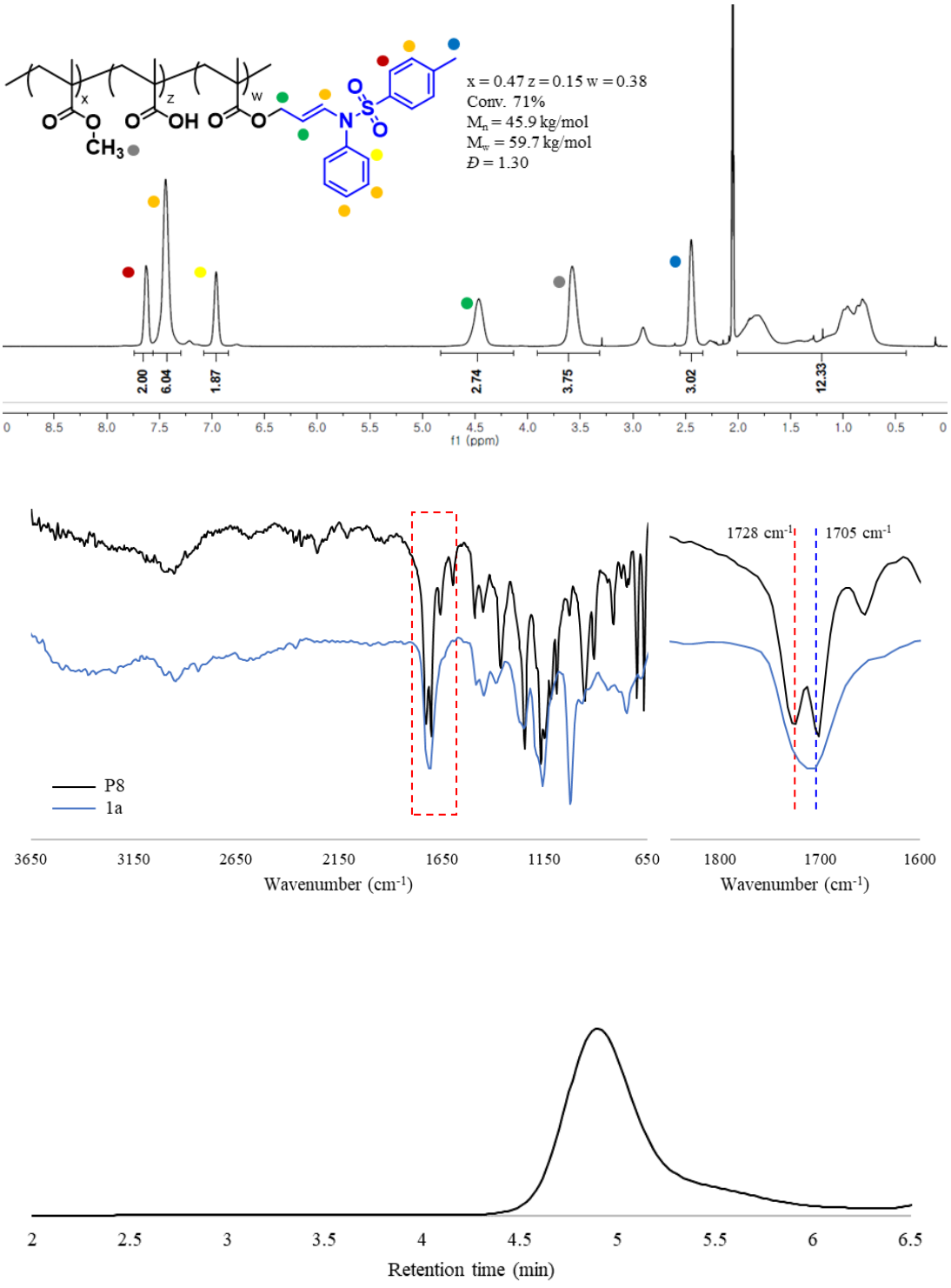


Figure S15. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P8**

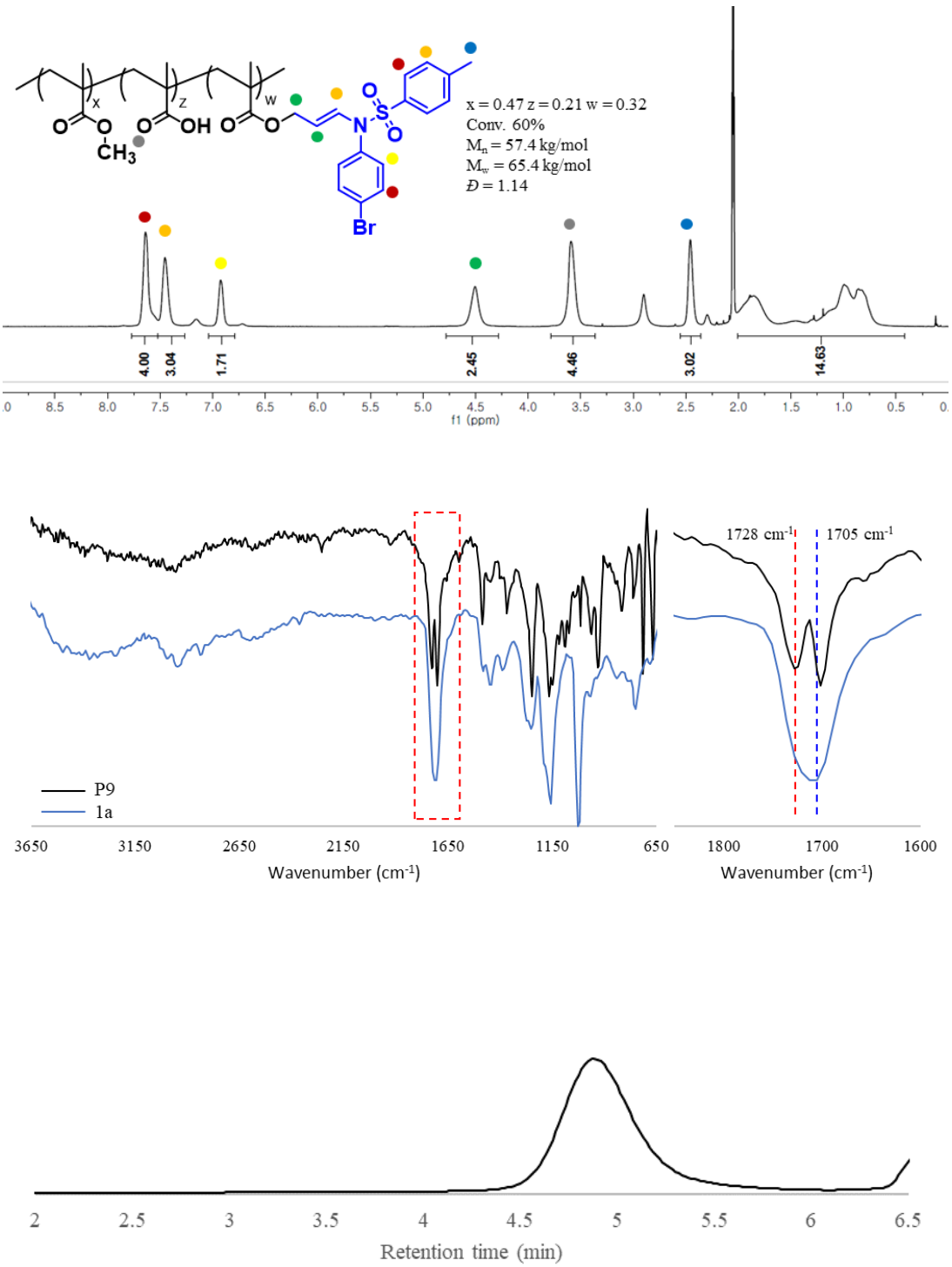


Figure S16. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P9**

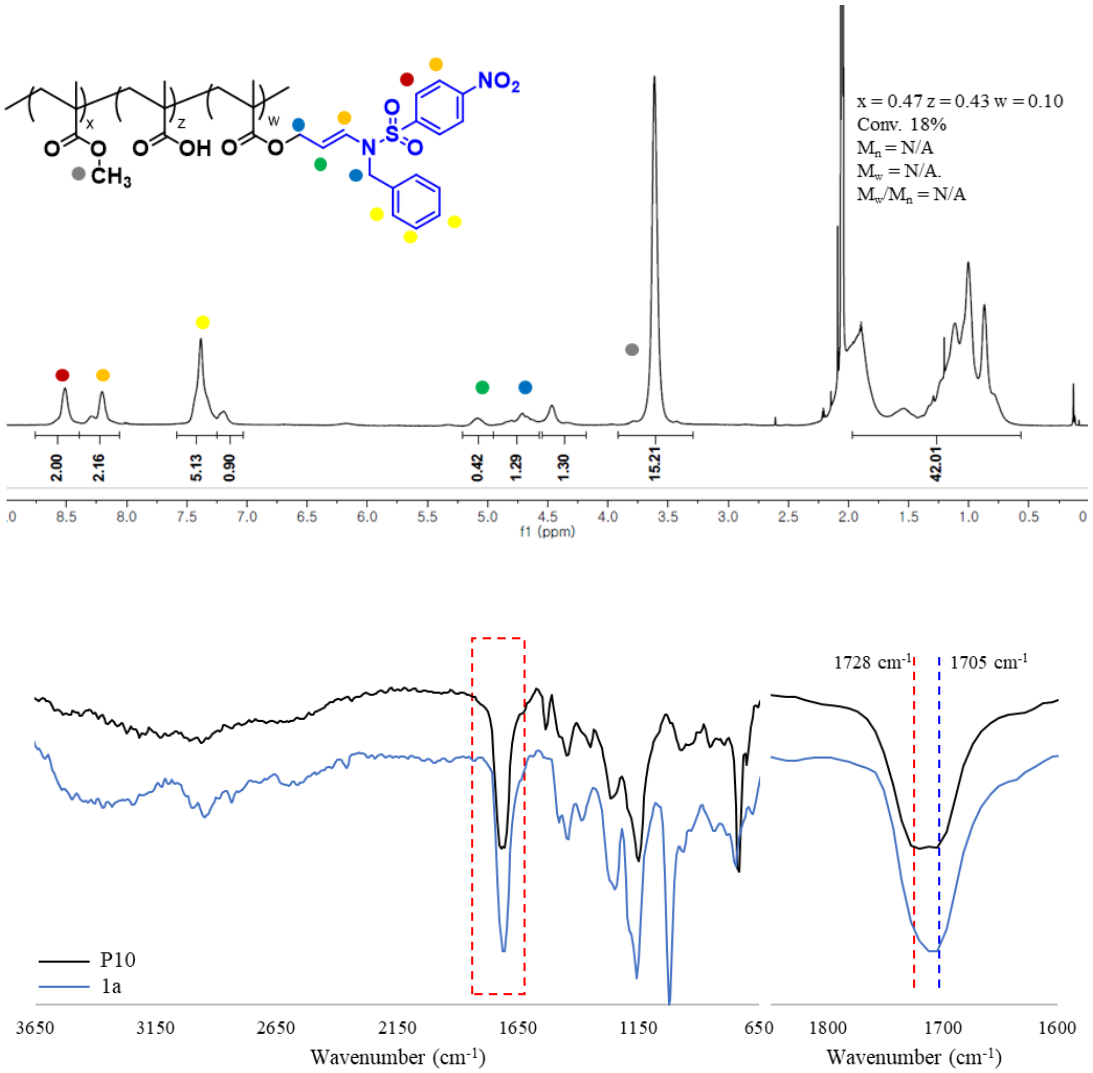


Figure S17. ^{1}H NMR (acetone-d_6) and FT-IR spectra of **P10**

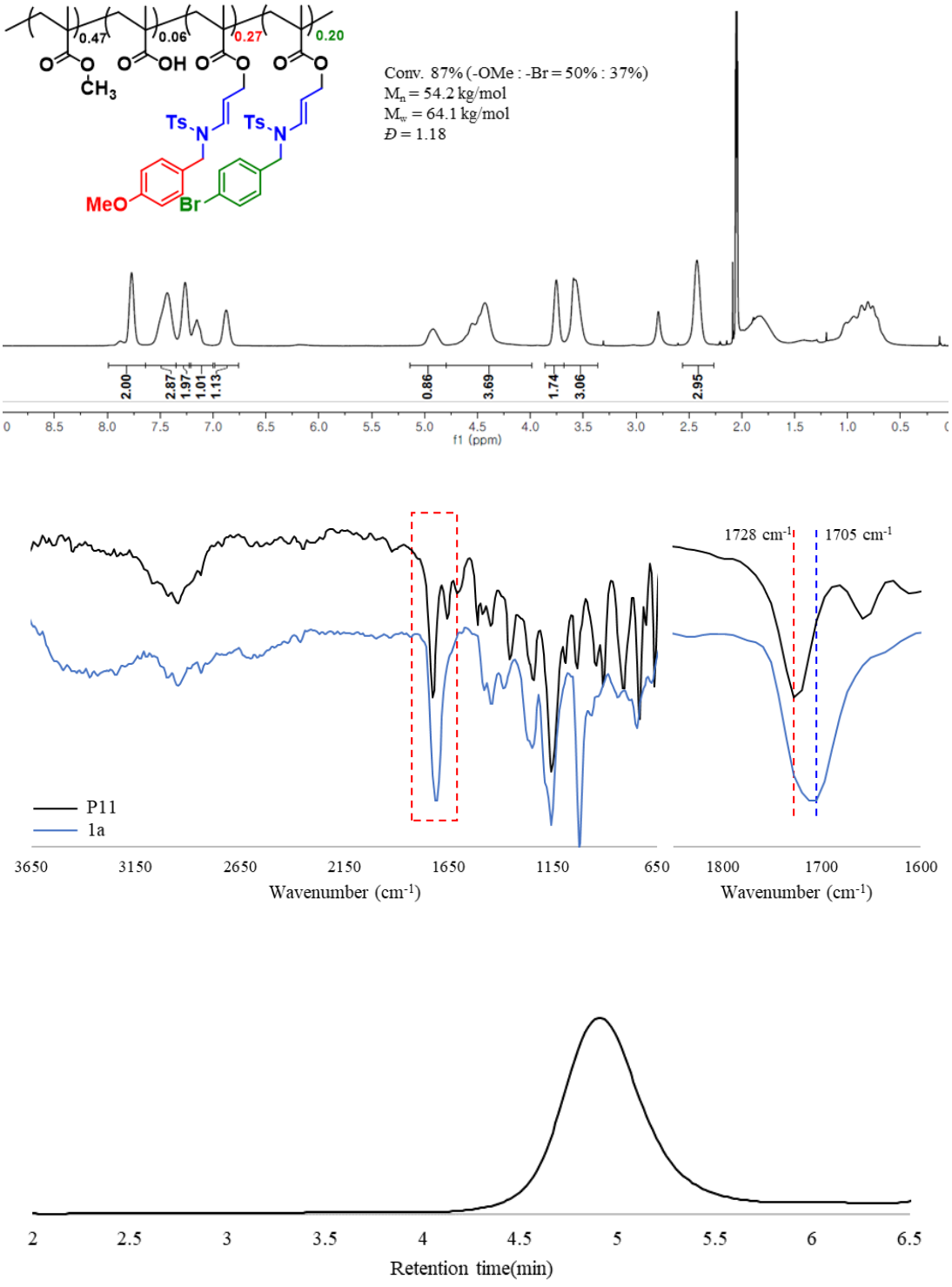


Figure S18. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P11**

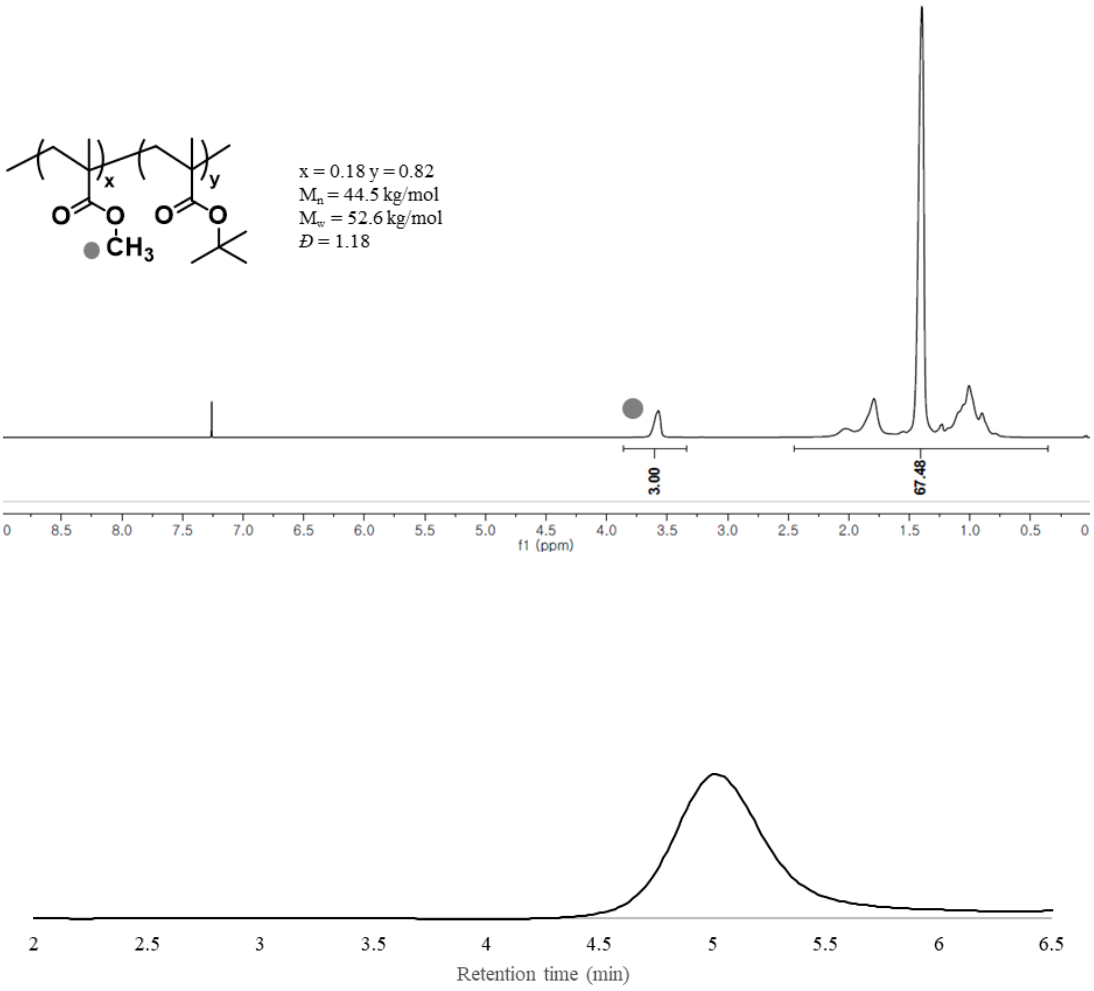


Figure S19. ^{1}H NMR ($CDCl_3$) and GPC spectra of poly[(methyl methacrylate)$_{0.18}$-*co*-(*t*-butyl methacrylate)$_{0.82}$] (**SM2**)

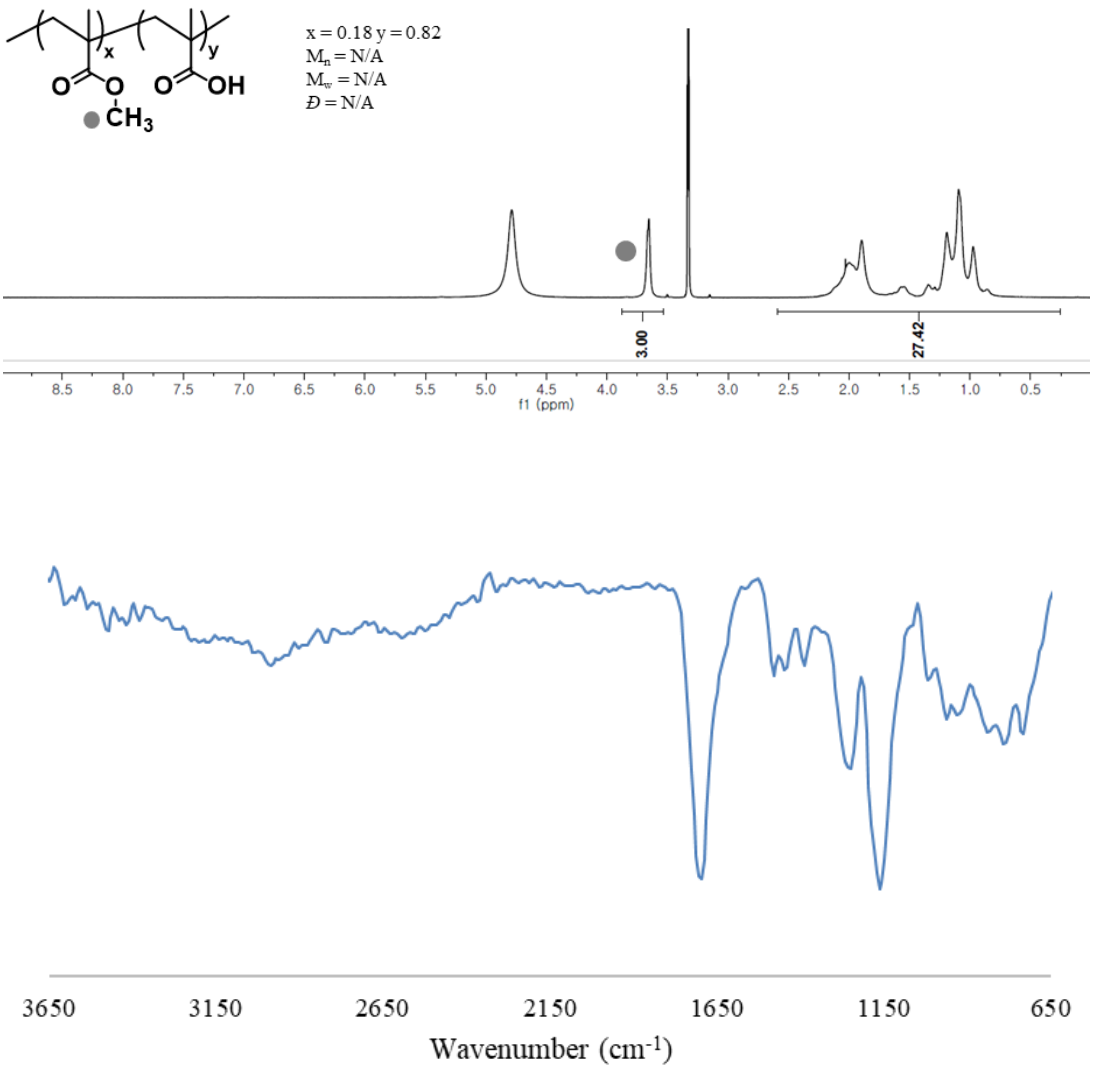


Figure S20. ^{1}H NMR and FT-IR spectra of **1b (**CD_3OD:$CDCl_3$ = 9:1 (v/v))

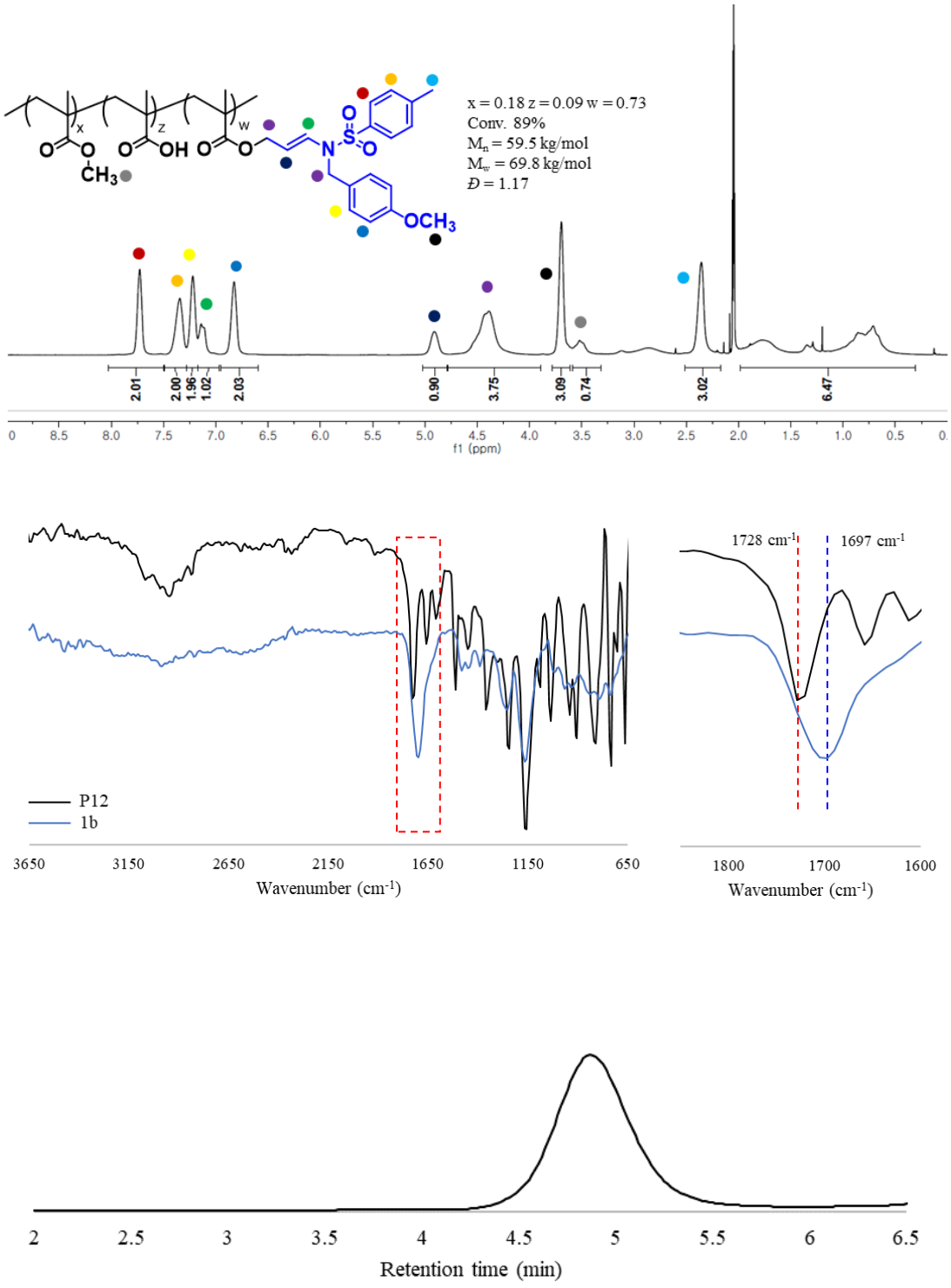


Figure S21. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P12**

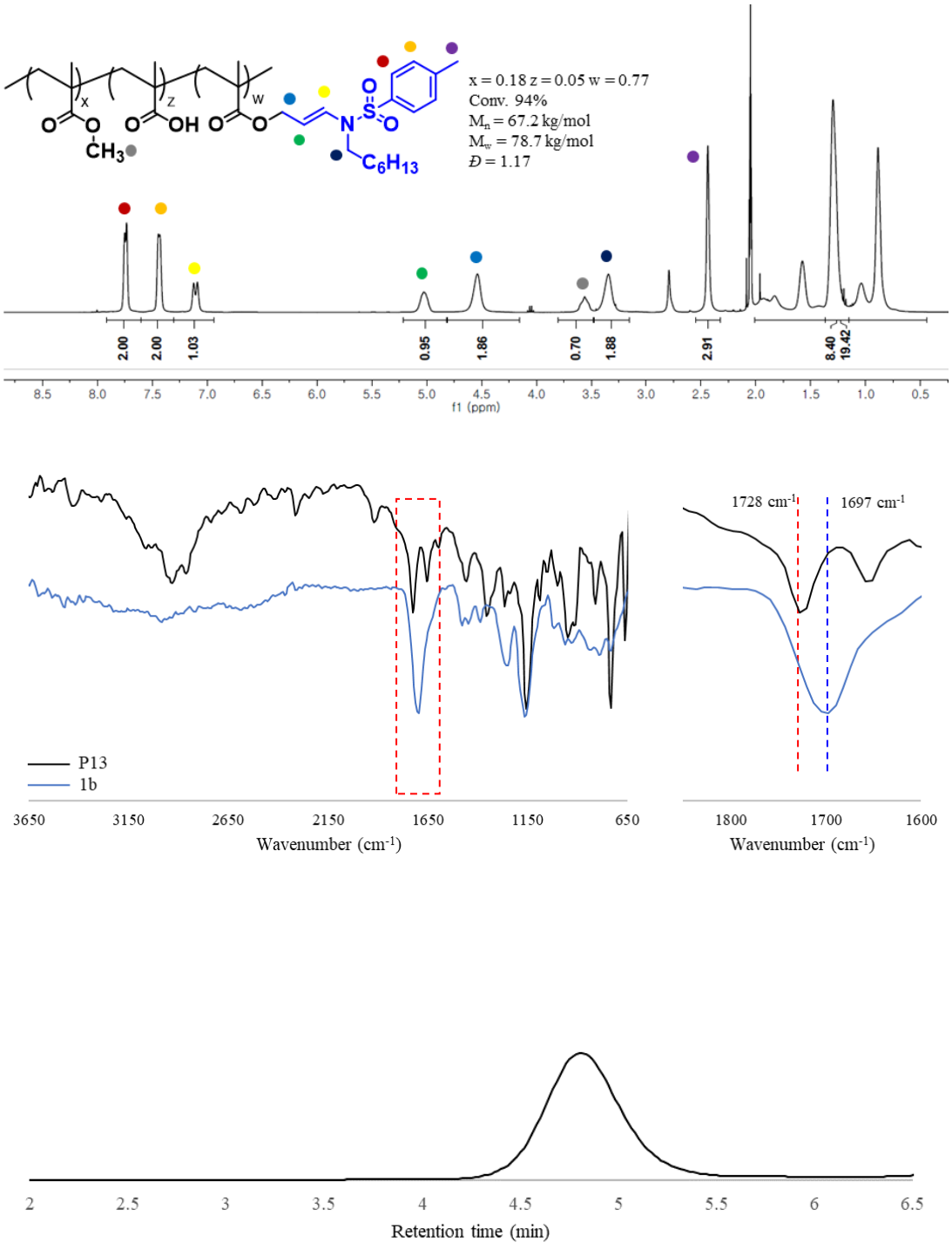


Figure S22. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P13**

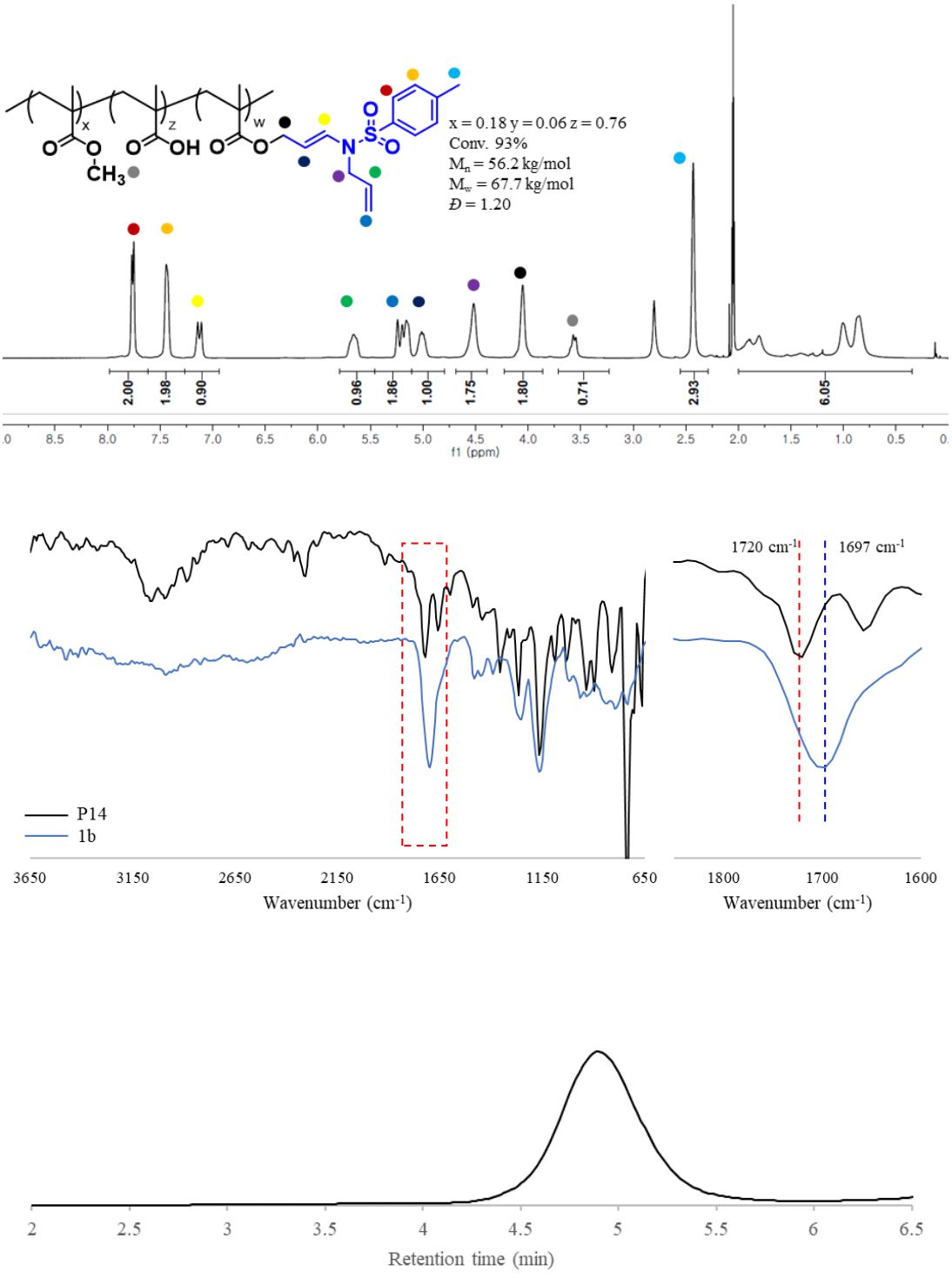


Figure S23. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P14**

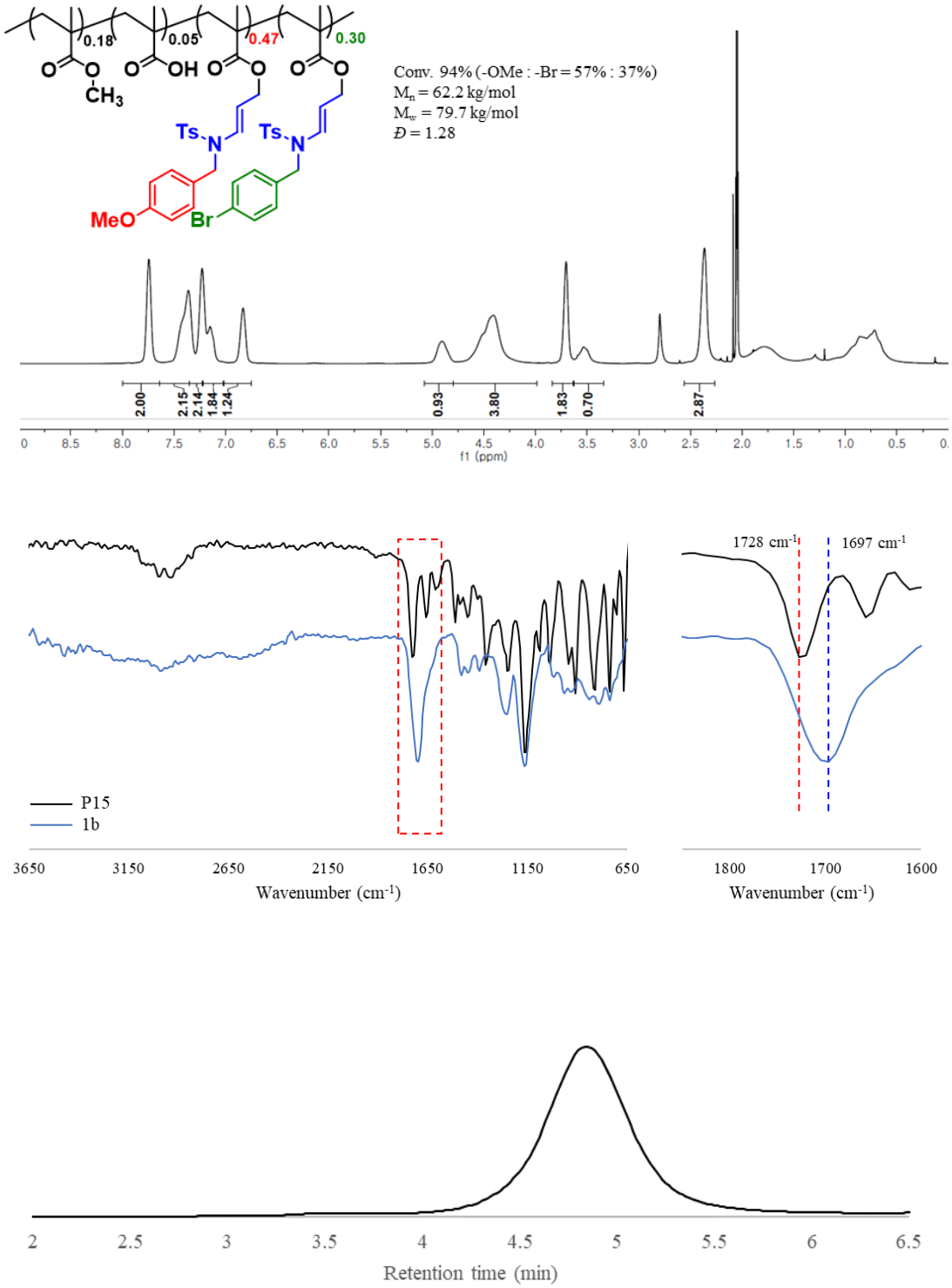


Figure S24. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P15**

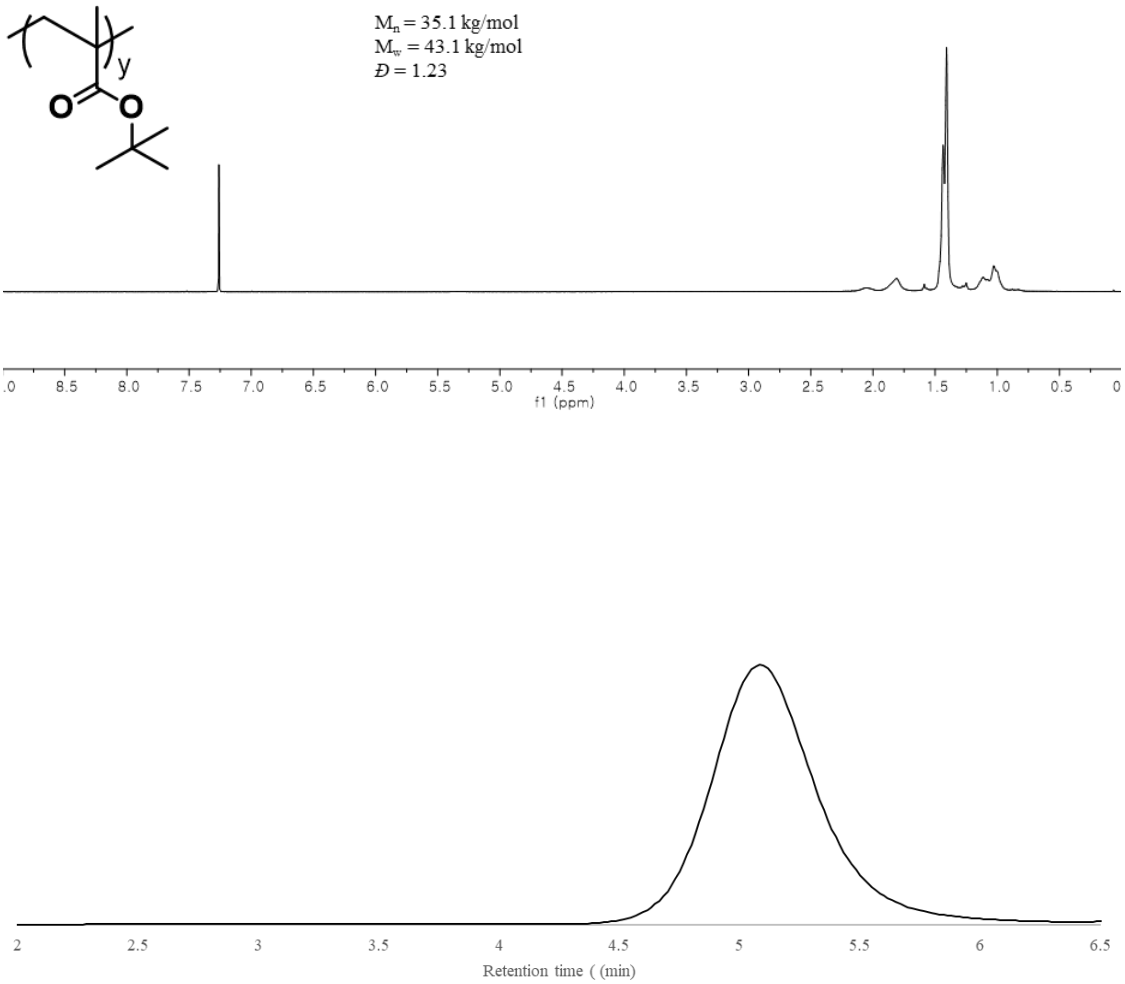


Figure S25. ^{1}H NMR ($CDCl_3$), and GPC spectra of **SM3**

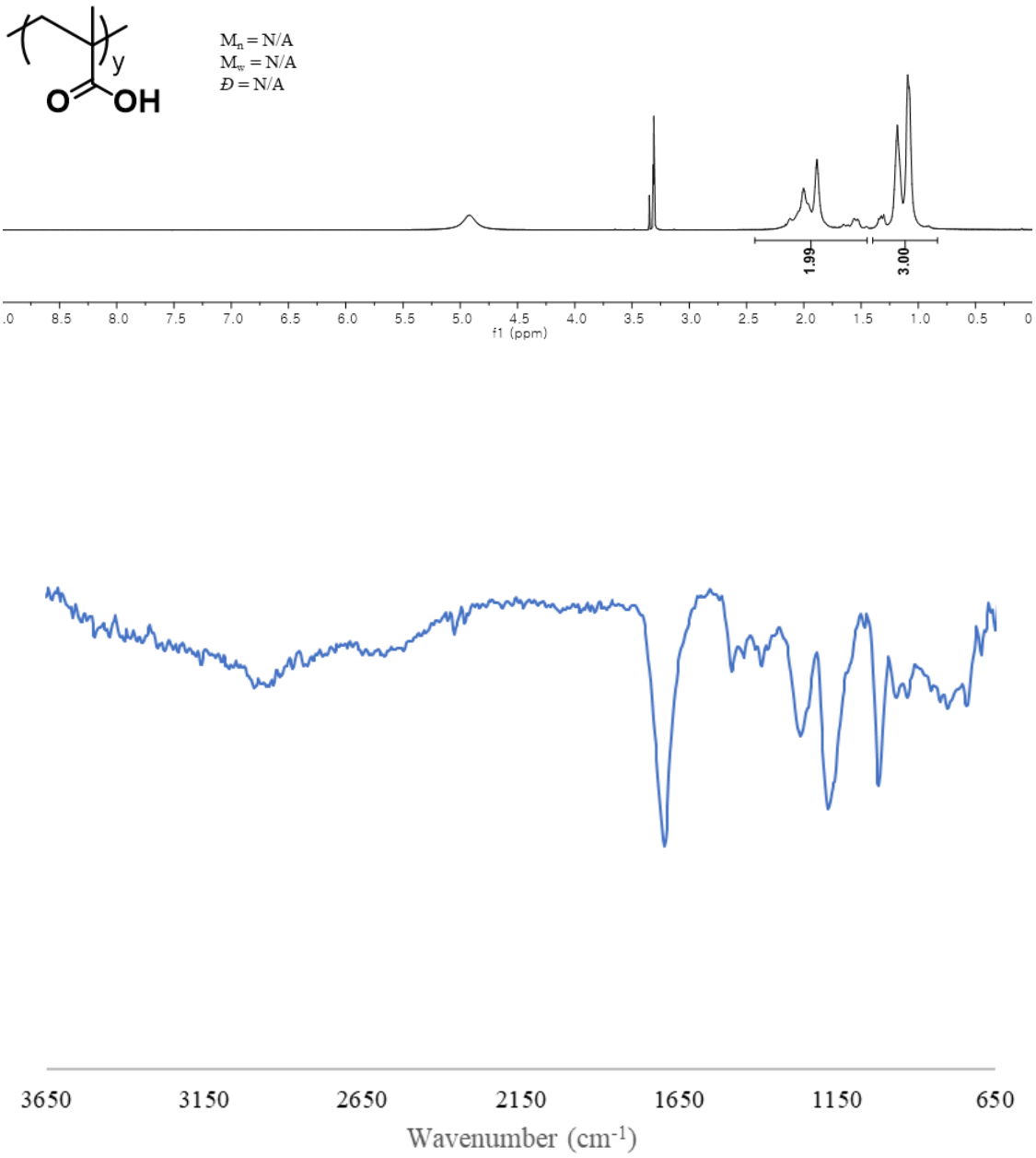


Figure S26. ^{1}H NMR (**(**CD_3OD:D_2O = 9:1 (v/v)) and FT-IR spectra of **1c**

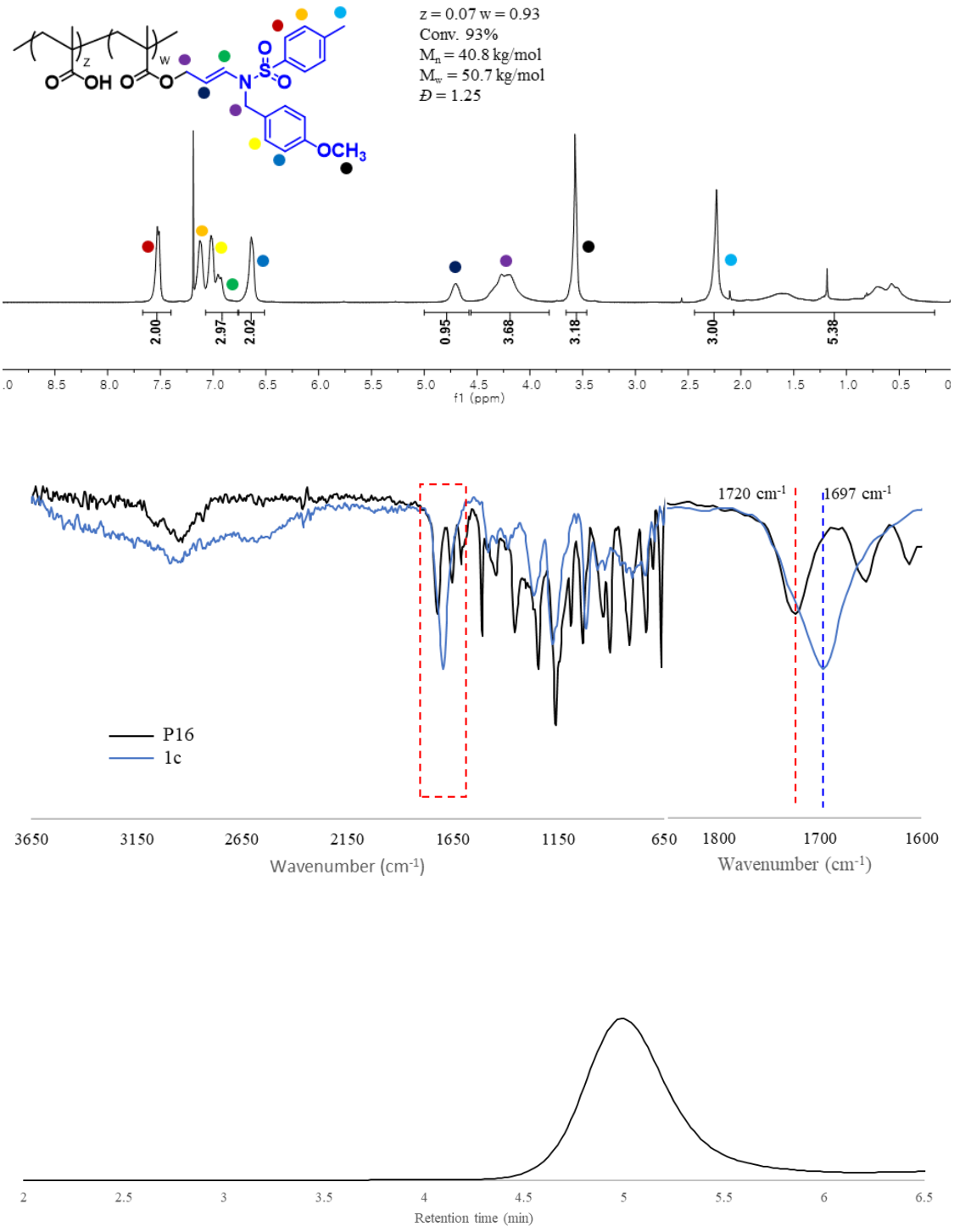


Figure S27. ^{1}H NMR ($CDCl_3$), FT-IR, and GPC spectra of **P16**

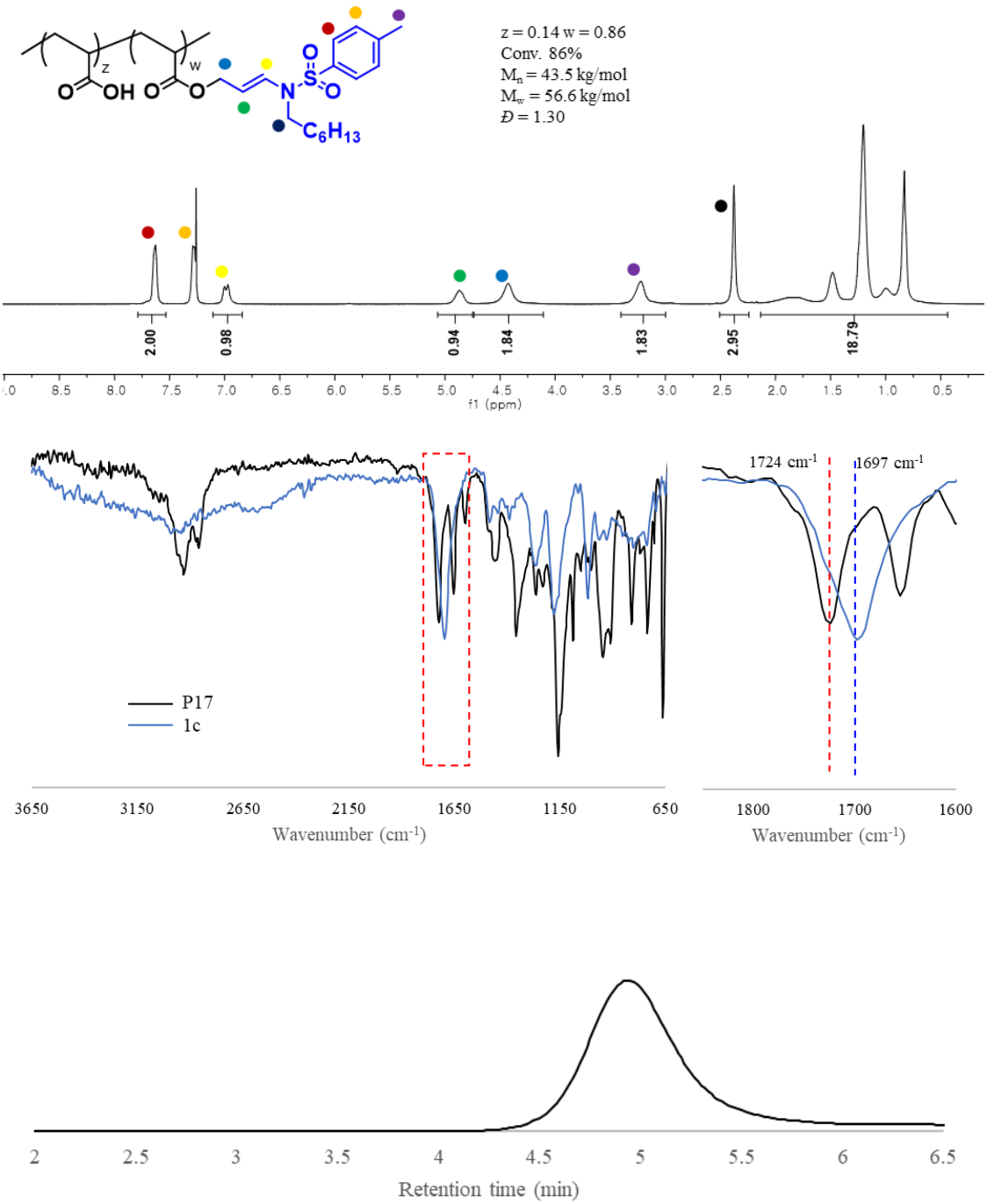


Figure S28. ^{1}H NMR ($CDCl_3$), FT-IR, and GPC spectra of **P17**

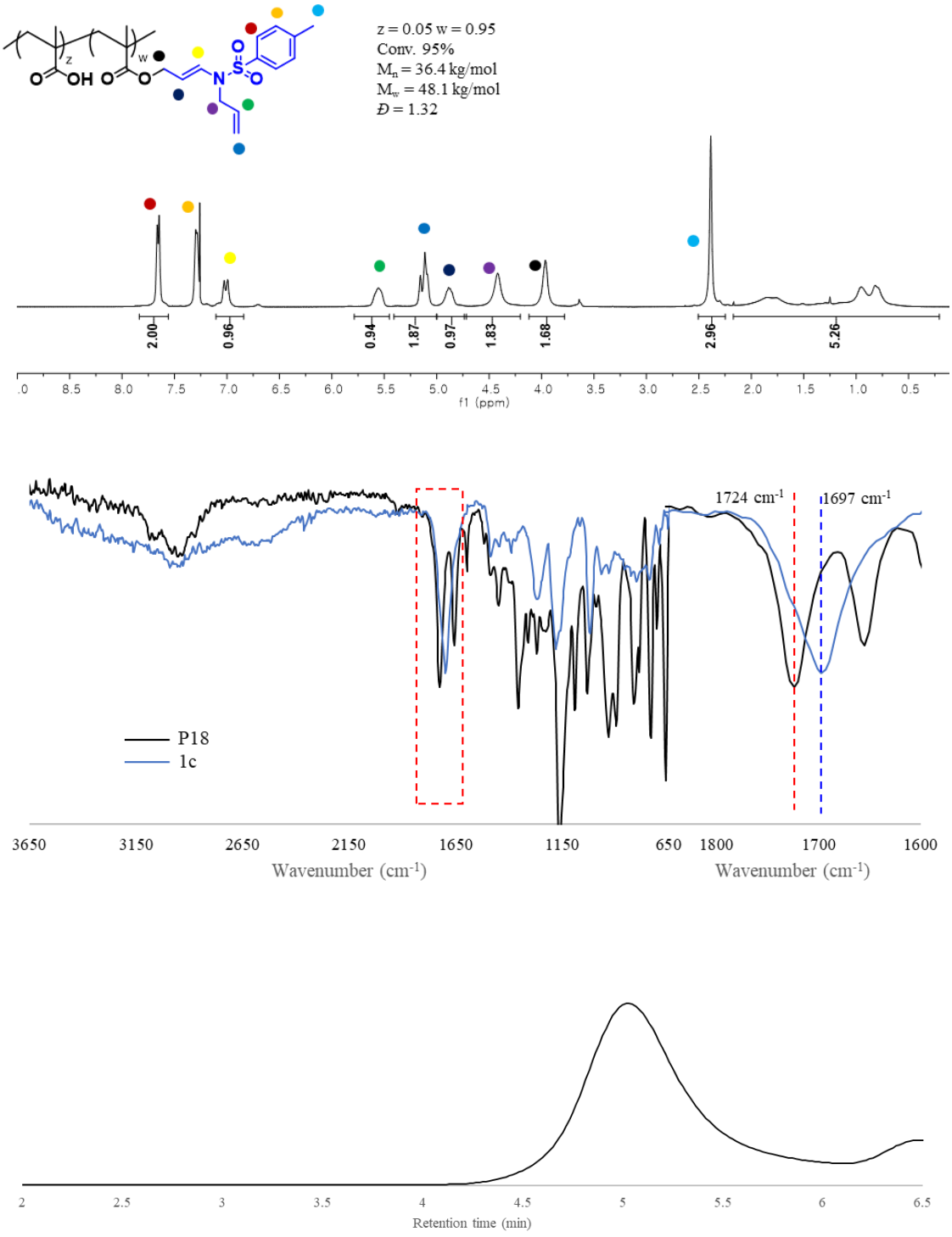


Figure S29. ^{1}H NMR ($CDCl_3$), FT-IR, and GPC spectra of **P18**

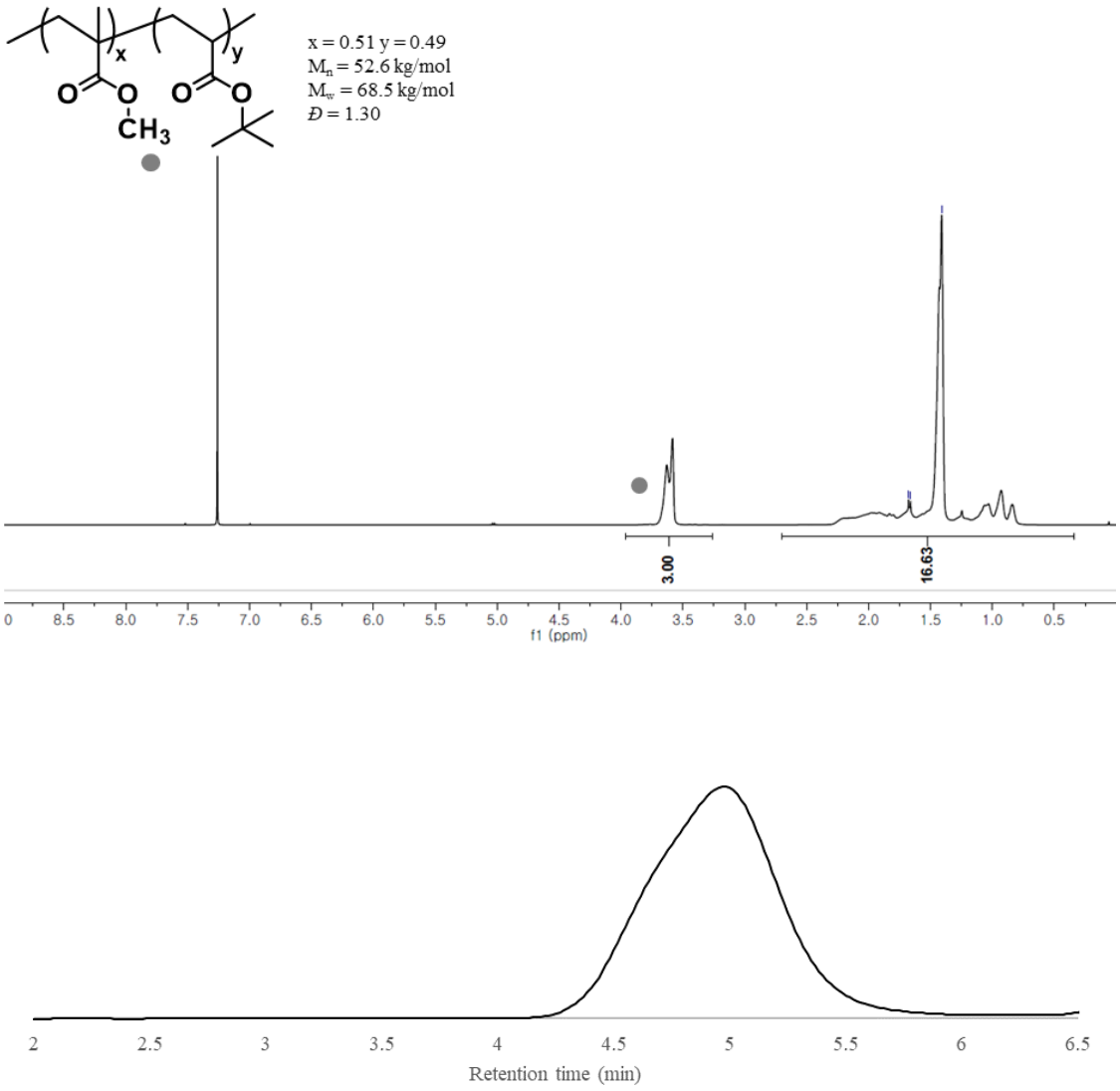


Figure S30. ^{1}H NMR ($CDCl_3$) and GPC spectra of poly[(methyl methacrylate)$_{0.51}$-*co*-(*t*-butyl acrylate)$_{0.49}$] (**SM4**)

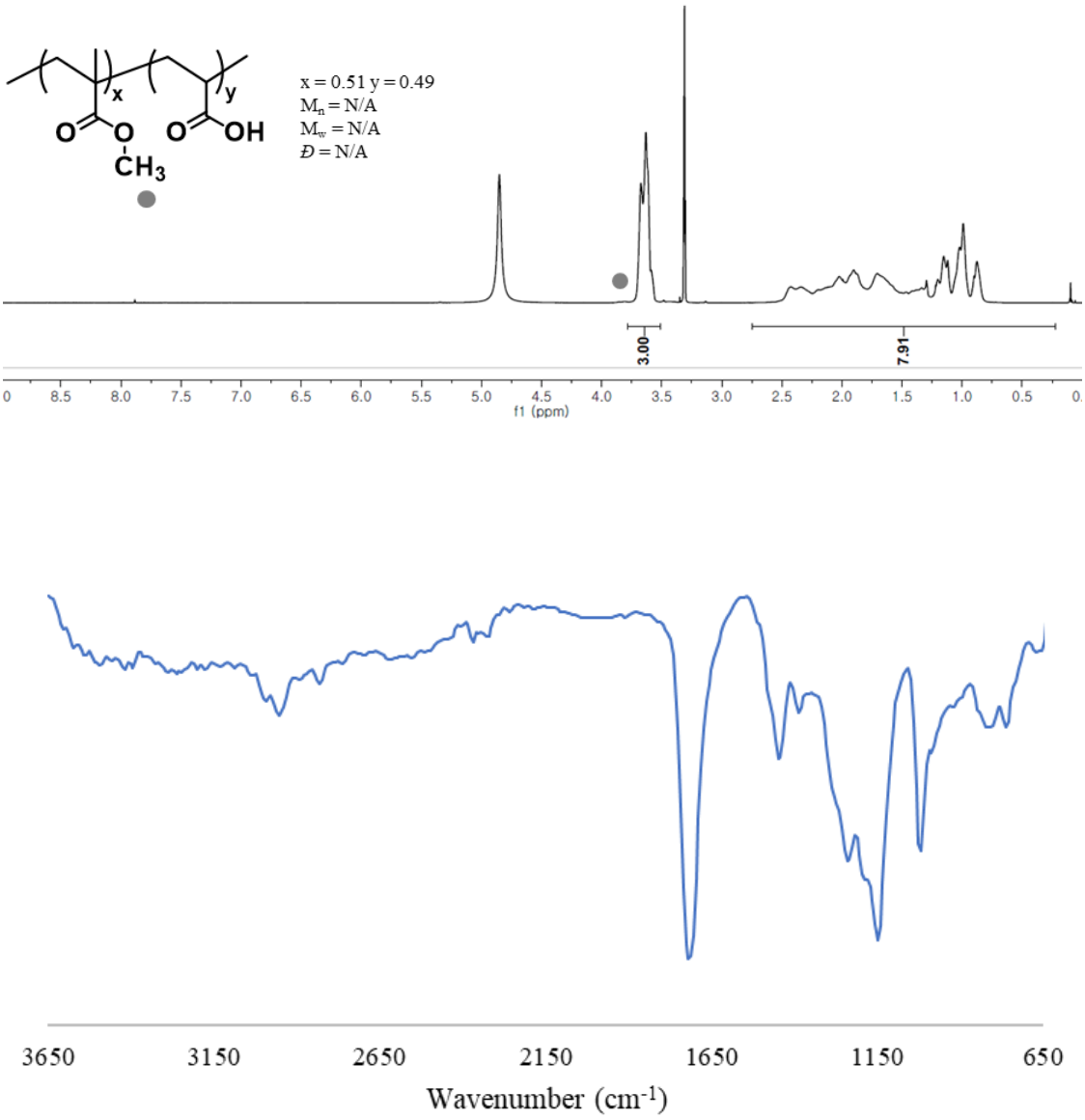


Figure S31. ^{1}H NMR and FT-IR spectra of **1d (**CD_3OD:$CDCl_3$ = 9:1 (v/v))

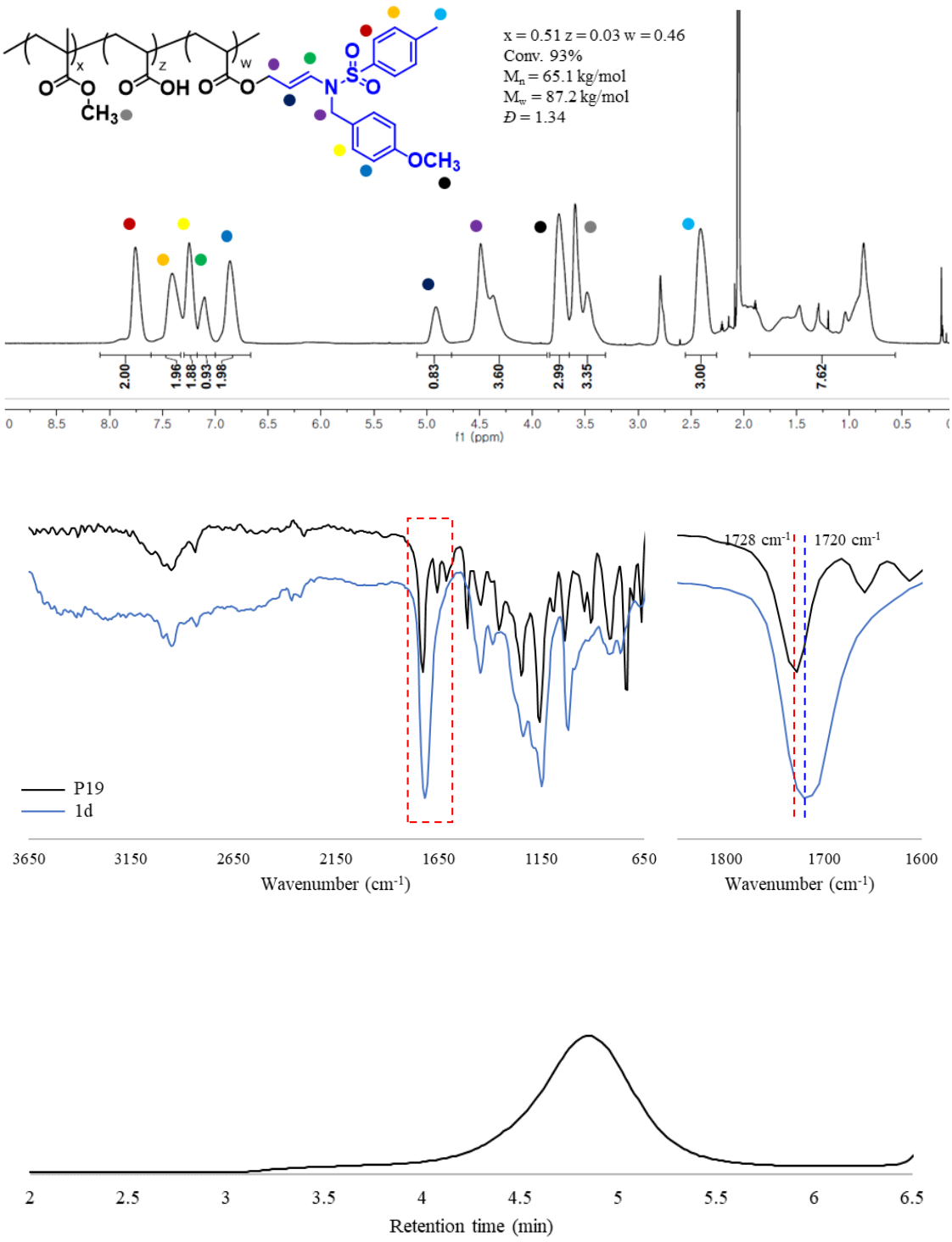


Figure S32. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P19**

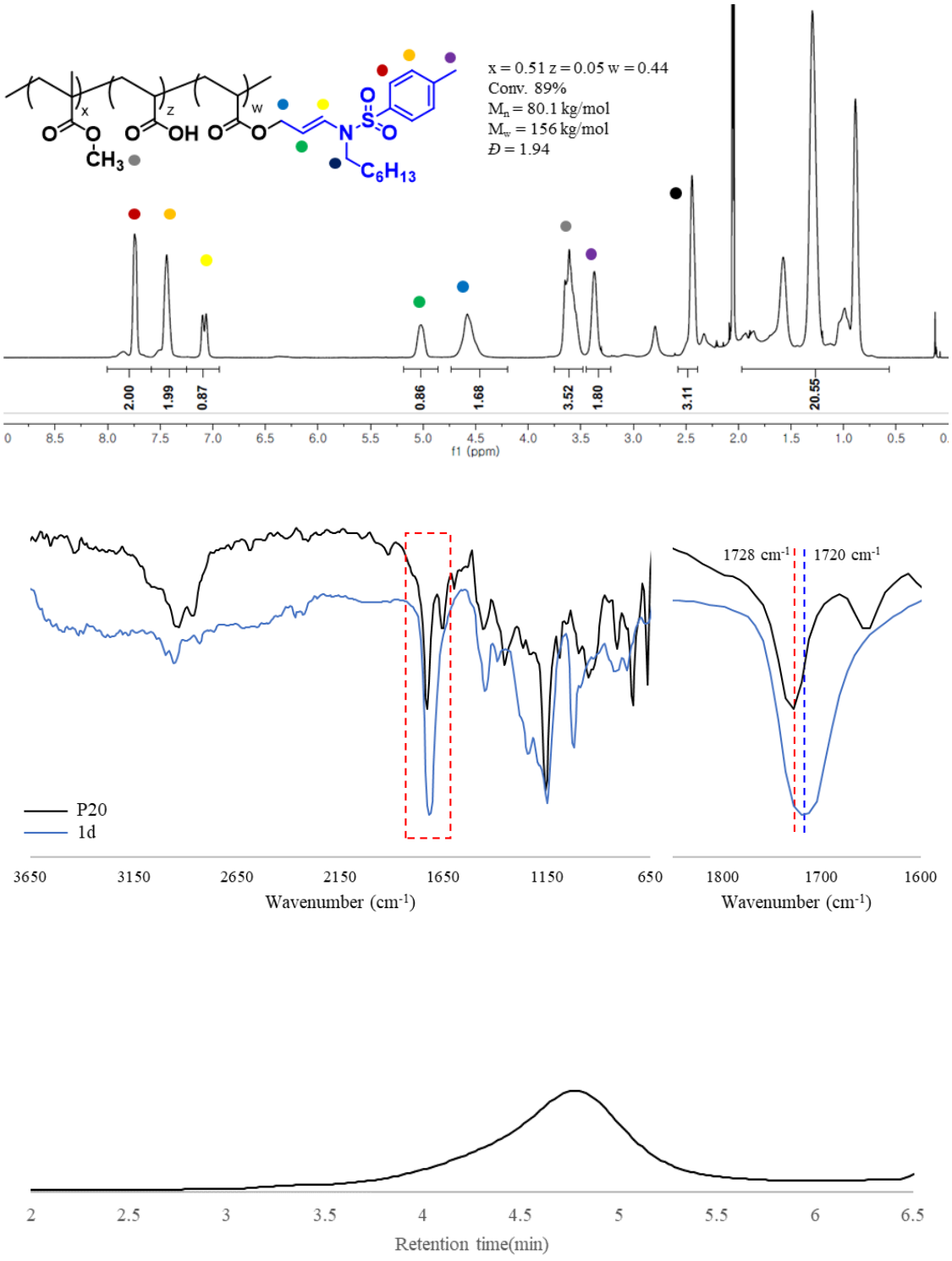


Figure S33. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P20**

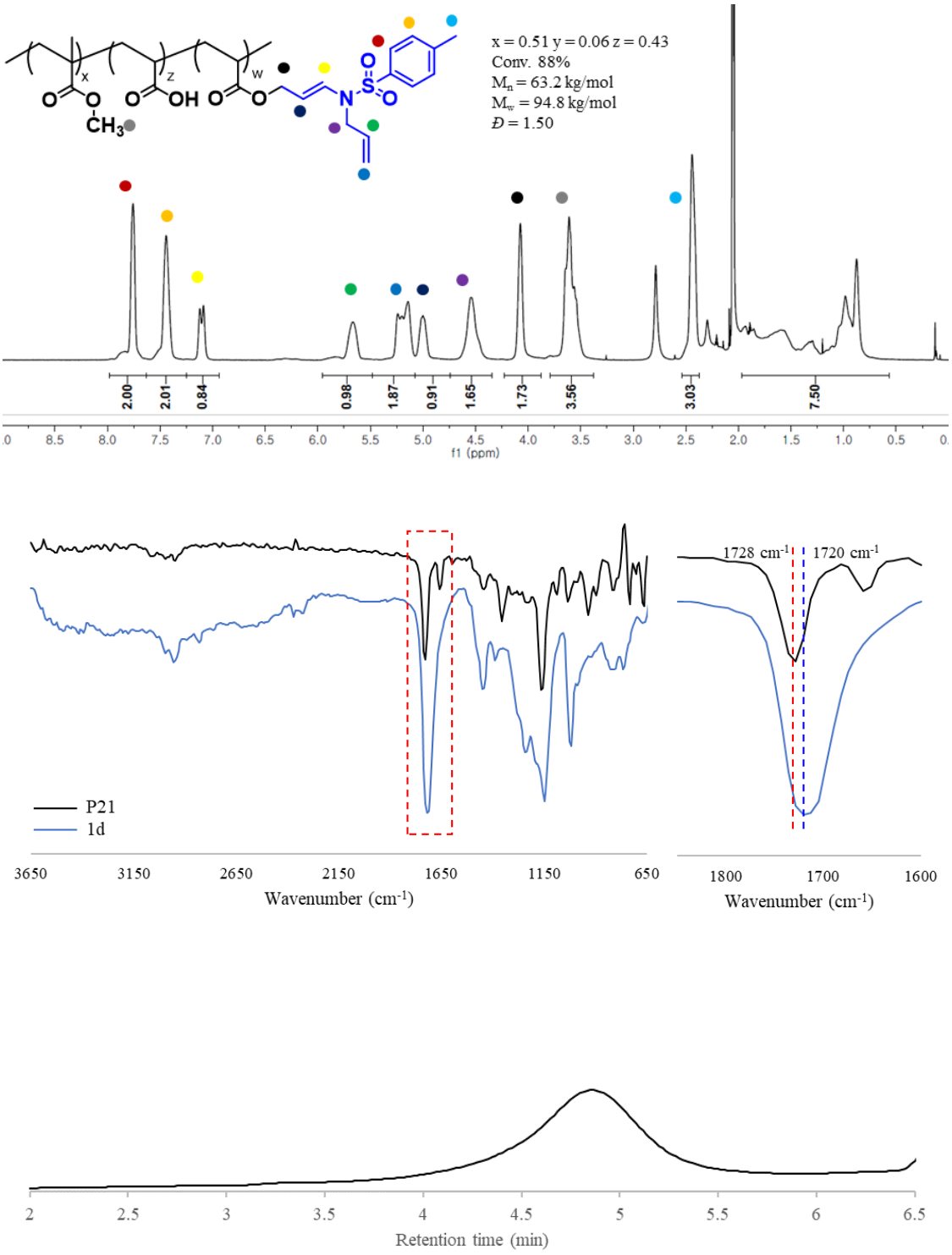


Figure S34. ^{1}H NMR (acetone-d_6), FT-IR, and GPC spectra of **P21**