

Supporting Information

Mechanochemical Post-Polymerization Modification: Solvent Free Solid-State Synthesis of Functional Polymers

Nuri Ohn and Jeung Gon Kim*

Department of Chemistry and Institute of Physical Science, Chonbuk National University,

567 Baekje-daero, deokjin-gu, Jeonju-si, Jeollabuk-do 54896 Republic of Korea

jeunggonkim@jbnu.ac.kr

1. General Considerations. Chemical reagents obtained from commercial sources (Aldrich, Alfa Aesar, TCI and Acros) were used without further purification. Retsch Mixer Mill MM 400 was used for the ball-milling experiments with a 10 mL stainless-steel vessel and 7 mm stainless-balls. A Teflon seal was placed between the vessel and the top closure.

2. Measurements. ^1H -NMR spectra were obtained on a 400 MHz Bruker Avance III HD Fourier transform NMR spectrometer and referenced to the residual protonated solvent. Gel permeation chromatography (GPC) analyses with refractive index (RI) detection were used to determine the number-average molecular weights (M_n), weight-average molecular weights (M_w), and polydispersities (M_w/M_n). The RI 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-804, KF-803, and KF-802.5 columns in series. The columns were eluted with tetrahydrofuran (preservative-free HPLC grade, Fisher or Daejung Chemical Company) at 40 °C and 1.0 mL/min and calibrated using 14 monodisperse polystyrene standards (purchased from Alfa Aesar). Infrared spectra were obtained on a Bruker Alpha Fourier transform IR spectrometer equipped with ATR module.

3. Synthesis. 4-Vinylbenzaldehyde was prepared according to Wooley's protocol¹ Solid ammonium carbamate salts were synthesized following Lee's procedure.²

Synthesis of Poly(styrene-*co*-4-vinylbenzaldehyde) (PS-*co*-P4VBA) (Table 1, SM). A solution of styrene (13 mL, 0.11 mmol), 4-vinylbenzaldehyde (5.0 g, 38 mmol), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (0.18 g, 0.49 mmol), and 2,2'-azobis(2-methylpropionitrile) (16 mg, 0.098 mmol) in 1,4-dioxane (20 mL) was placed in a 50-mL Schlenk flask. Three freeze-pump-thaw cycles were performed to remove residual gases. The flask was placed in a preheated oil bath at 70 °C. After 20 hours, the reaction was opened to air to quench the polymerization reaction. The solution was precipitated in hexanes to give a yellow powder. The polymer was reprecipitated in hexanes/dichloromethane. The resulting product was dried under vacuum at room temperature. GPC (THF, PS standard): M_n =6.80 kg/mol; M_w = 8.36 kg/mol; M_w/M_n = 1.23.

Synthesis of Poly(4-vinylbenzaldehyde) (Table 2, SM). A solution of 4-vinylbenzaldehyde (3.8 g, 28 mmol), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (34 mg, 0.095 mmol), and 2,2'-azobis(2-methylpropionitrile) (3.0 mg, 0.019 mmol) in 1,4-dioxane (3.8 mL) was placed in a 50-mL Schlenk flask. Three freeze-pump-thaw cycles were performed to remove residual gases. The flask was placed in a preheated oil bath at 70 °C. After 20 hours, the reaction was opened to air to quench the polymerization reaction. The solution was precipitated in methanol to give a yellow powder. The polymer was reprecipitated in methanol/dichloromethane. The resulting product was dried under vacuum at room temperature. GPC (THF, PS standard): M_n =19.1 kg/mol; M_w = 20.1 kg/mol; M_w/M_n = 1.05.

Synthesis of Polystyrene-*block*-poly(4-vinylbenzaldehyde) (Table 3, SM). A mixture of styrene (50 mL, 0.43 mol) and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid

¹ Sun, G.; Cheng, C.; Wooley, K. L. Reversible Addition Fragmentation Chain Transfer Polymerization of 4-Vinylbenzaldehyde. *Macromolecules* **2007**, *40*, 793–795.

² Kang, P.; Lee, K. M.; Lee, W. K.; Lee, K. H.; Lee, B.; Cho, J.; Hur, N. H. One-pot Solvent-free Reductive Amination with a Solid Ammonium Carbamate Salt from CO₂ and Amine. *RSC Adv.* **2014**, *4*, 46203–46207.

(0.16 g, 0.44 mmol) was placed in a 500-mL Schlenk flask. Three freeze-pump thaw cycles were performed to remove residual gases. The flask was placed in a preheated reaction block at 120 °C. After 2 hours, the reaction was opened to air to quench the polymerization reaction. The solution was precipitated in methanol to give a yellow powder. The polymer was reprecipitated in methanol/dichloromethane. The resulting product was dried under vacuum at 70 °C. A mixture of the resulting polystyrene ($M_n = 10.6$ kg, $M_w/M_n = 1.05$, 1.0 g), 4-vinylbenzaldehyde (1.8 g, 13 mmol), and 2,2'-azobis(2-methylpropionitrile) (2.0 mg, 0.012 mmol) in 1,4-dioxane (8 mL) was placed in a 50-mL Schlenk flask. Three freeze-pump-thaw cycles were performed to remove residual gases. The flask was placed in a preheated oil bath at 70 °C. After 20 hours, the reaction was opened to air to quench the polymerization reaction. The solution was precipitated in methanol to give a yellow powder. The polymer was reprecipitated in methanol/dichloromethane. The resulting product was dried under vacuum at room temperature. GPC (THF, PS standard): $M_n = 14.9$ kg/mol; $M_w = 17.4$ kg/mol; $M_w/M_n = 1.17$.

4. Representative procedure of the mechanochemical post-polymerization modifications (Table 1, entry 2). To a stainless-steel milling container (10 mL volume) were added poly(styrene-*co*-4-VBA) (0.10 g) and benzyl ammonium carbamate salt (90 mg) followed by three stainless-steel milling balls (7 mm in diameter). The tightly sealed vial was placed in a vibrational ball mill and subjected to milling for 30 min with a 30 Hz frequency. The resulting powder was precipitated in dichloromethane/hexanes. A powder was obtained after drying in vacuo (93 mg). A portion was subjected to ^1H -NMR spectroscopy and GPC measurements to determine the conversion and molecular weight. > 99% conversion; GPC data (THF, PS standard): $M_n = 8.00$ kg/mol, $M_w = 9.68$ kg/mol; $M_w/M_n = 1.21$.

5. Polymer stability test under a ball-milling condition

a) Aldehyde polymer test: Poly(styrene-*co*-4-VBA) (0.10 g, 42% aldehyde) was subjected to milling for an hour with a 30 Hz frequency in a stainless-steel container (10 mL) having three stainless-steel milling balls (7 mm in diameter). The molecular weight change was monitored by GPC and ^1H -NMR (Table S1 and figure S1).

b) Schiff base polymer test: Representative procedure (table 1, entry 2) was conducted except a reaction time. The ball-milling was continued to 2 hours to monitor structural alternations and degradations. At 1 and 2 hr, the vibration was interrupted to take a small portion of the solid reaction mixture for GPC and ^1H -NMR (Table S1 and figure S2).

Table S1. Polymer stability test.

	SM			1 hr			2 hr		
	M_n	M_w	D	M_n	M_w	D	M_n	M_w	D
	kg/mol								
Poly(styrene- <i>co</i> -4-VBA), 30 Hz Ball-Milling	6.97	8.35	1.20	6.80	9.50	1.40			
Poly(styrene- <i>co</i> -4-VBA) with benzyl ammonium carbamate, 30 Hz Ball-Milling	6.97	8.35	1.20	7.57	9.16	1.21	7.41	9.13	1.23

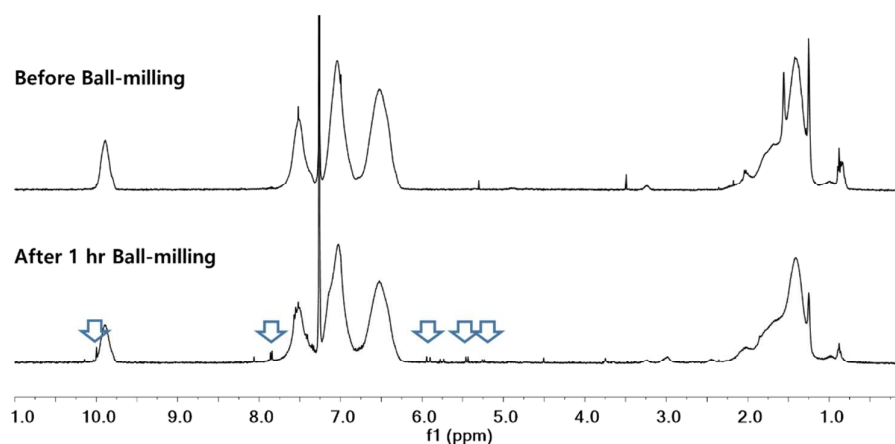


Figure S1. ^1H -NMR spectra of a ball-milling stability test of poly(styrene-*co*-4-VBA).

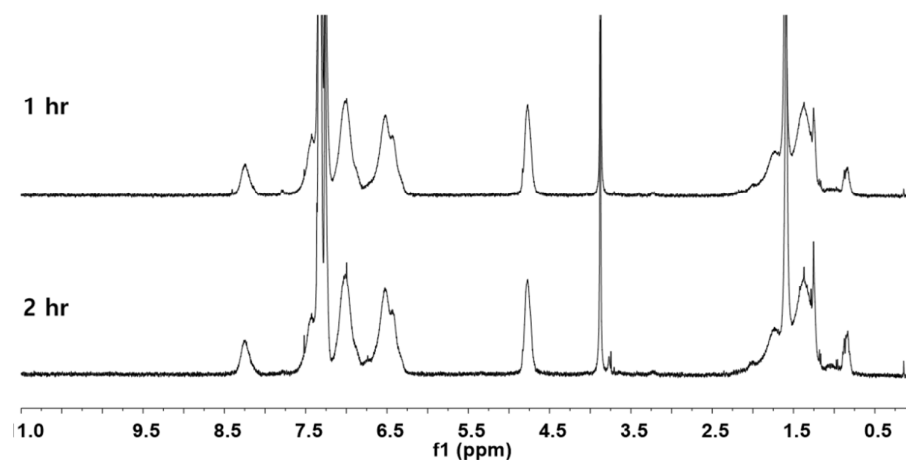


Figure S2. ^1H -NMR spectra of a ball-milling stability test of the imine polymer from

poly(styrene-*co*-4-VBA) with benzyl ammonium carbamate.

6. Ball-Milling vs. Solution vs. Solvent Free reaction comparison.

- a) Ball-milling reaction: Representative procedure was applied to the mixture of poly(4-VBA) (0.10 g, table 2, SM) and *p*-anisidine (0.19 g, 1.5 mmol). Separate reactions of 30 min and 60 min vibrations were conducted. Reaction rates were measured using ¹H-NMR.

Same procedure was conducted with poly (styrene-*co*-4-VBA) (0.10 g, table 1, SM) and *p*-anisidine (0.078 g).

- b) Solution reaction (RT): To a 5 mm NMR tube were added poly(4-VBA) (0.010 g, table 2, SM) and *p*-anisidine (0.019 g, 0.15 mmol) followed by CDCl₃ (0.8 mL). The reaction rate was measured by ¹H-NMR at 10, 20, 30, 40, 50, 60, 120, and 180 min.

- c) Solution reaction (50 °C): The same reaction set-up of RT experiment was conducted. The reaction rate was measure by ¹H-NMR at 10, 20, 30, 40, 50, 60, 120, and 180 min.

- d) Solvent free reaction (70 °C): The mixture of poly(4-VBA) (0.10 g, table 2, SM) and *p*-anisidine (0.19 g, 1.5 mmol) in a 4 mL vial equipped with an egg-shape stir-bar was placed on a preheated reaction block. At 10, 30, and 60 min, three samples from distinct positions were collected for ¹H-NMR measurement to obtain conversions.

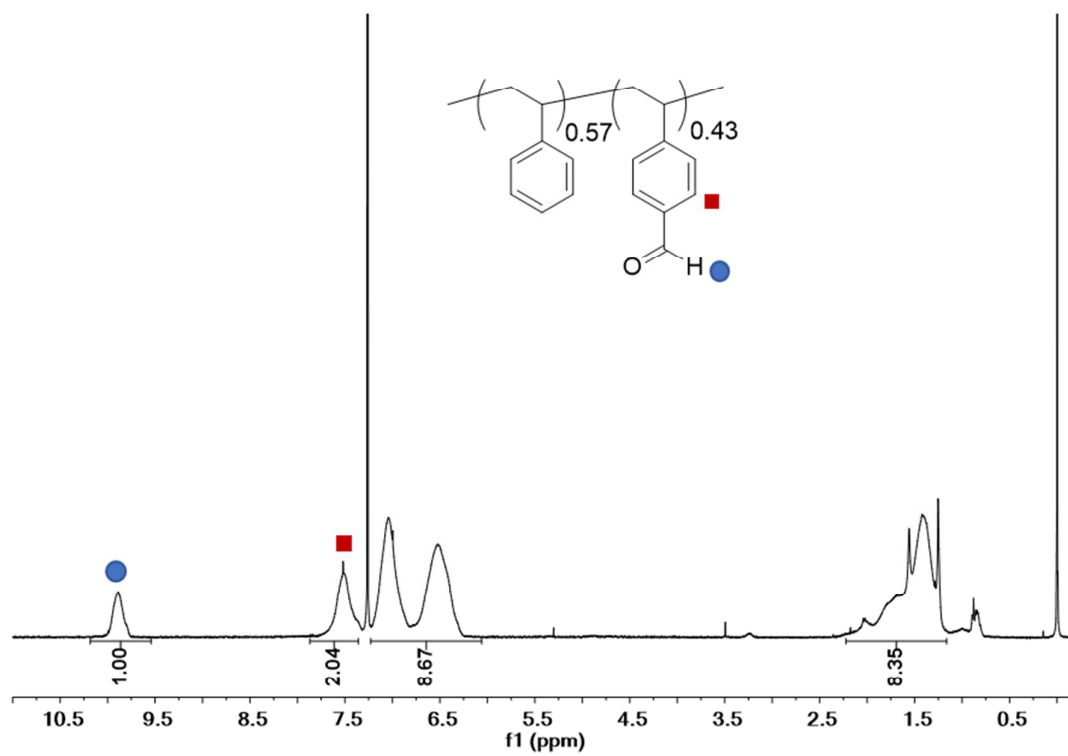
Same procedure was conducted with poly (styrene-*co*-4-VBA) (0.10 g, table 1, SM).

Table S2. Ball-mill vs. solution vs. solvent-free reaction comparison.

polymer	Conditions	Conversion (%)							
		10 min	20 min	30 min	40 min	50 min	60 min	120 min	180 min
1	Ball-mill			68			>99		
2	poly(4-VBA) (Table 2, SM)	1		2			3	11	12
3		6	9	12	14	15	17	27	34
4	Solvent-free			78/86/93			85/88/91		
5	poly(styrene- <i>co</i> - 4-VBA) (Table 1, SM)	98	>99	>99					
6		6/60/75	33/53/76	63/92/94					

Table 1, SM

^1H -NMR



FT-IR

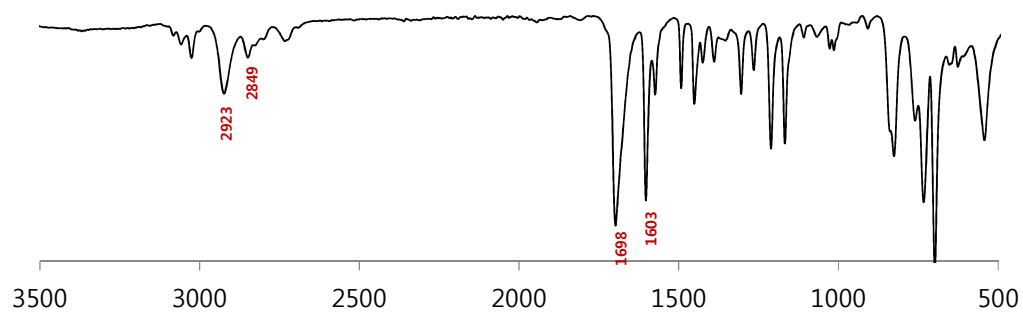
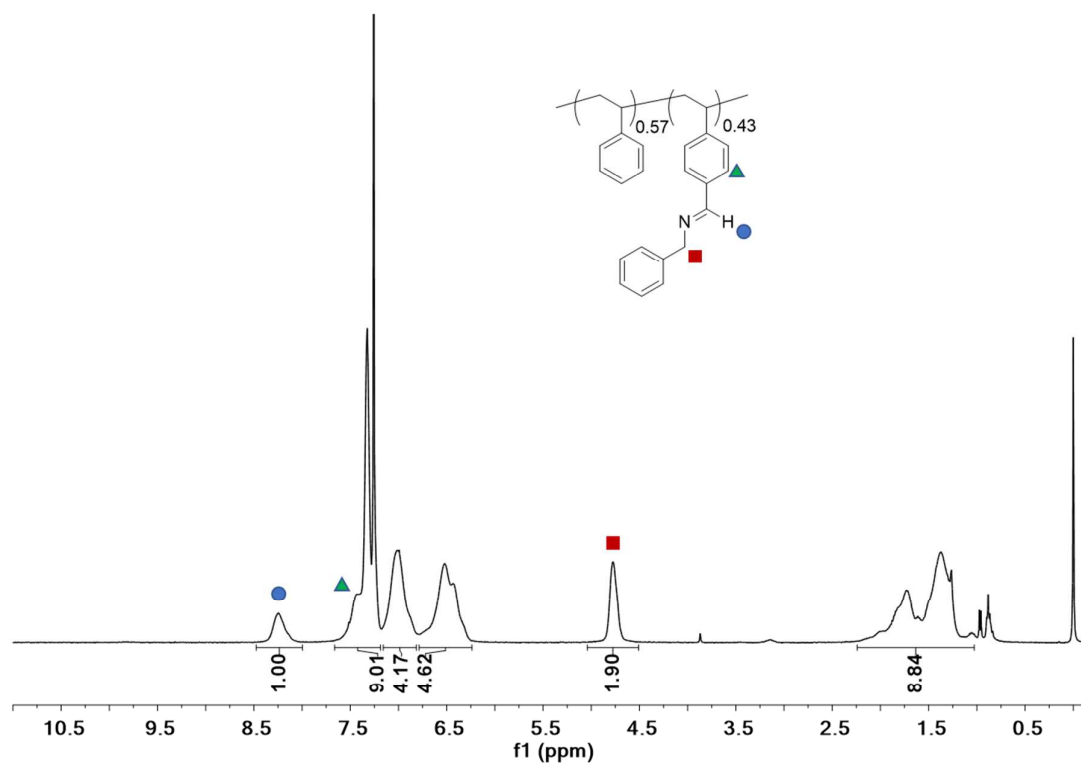


Table 1, Entry 1

The final product (114 mg) was obtained after two precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

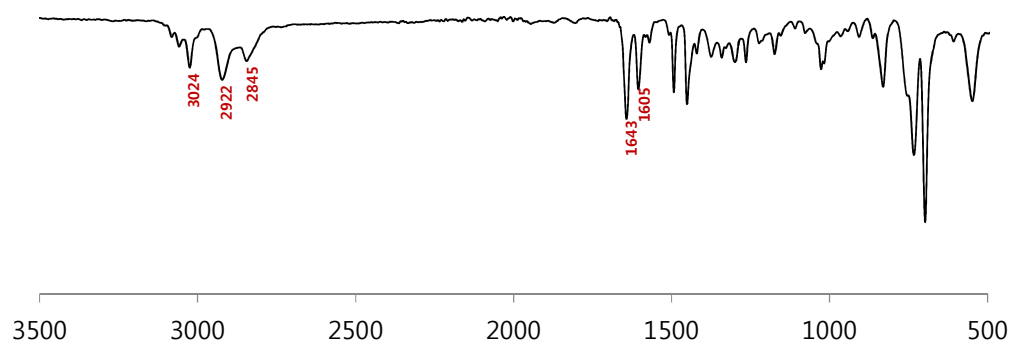
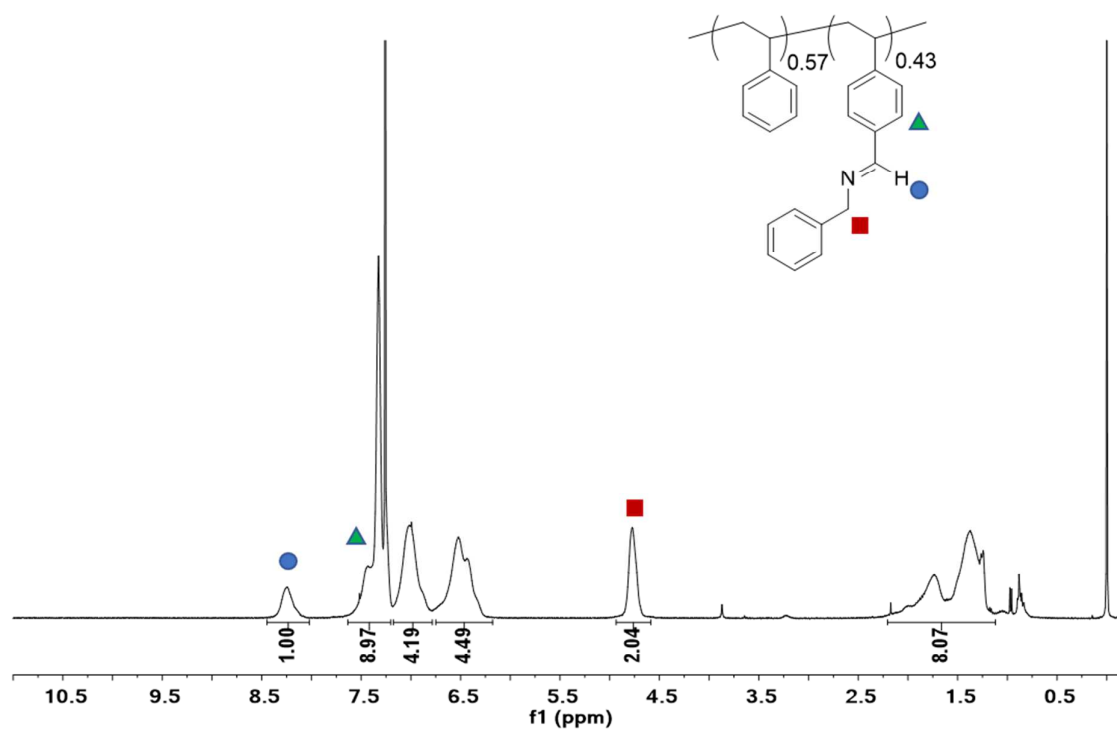


Table 1, Entry 2

The final product (93 mg) was obtained after a precipitation in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

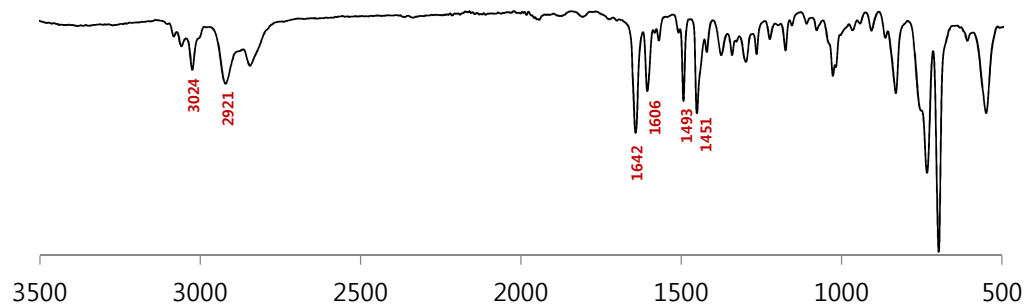
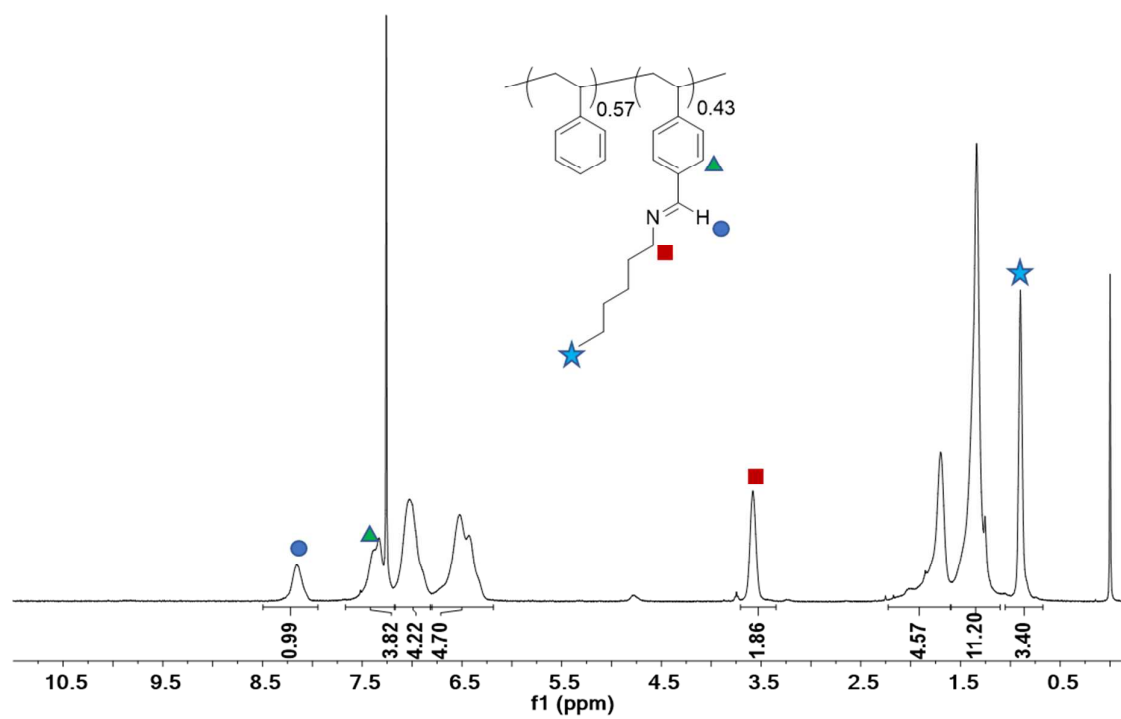


Table 1, Entry 3

The final product (47 mg) was obtained after two precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

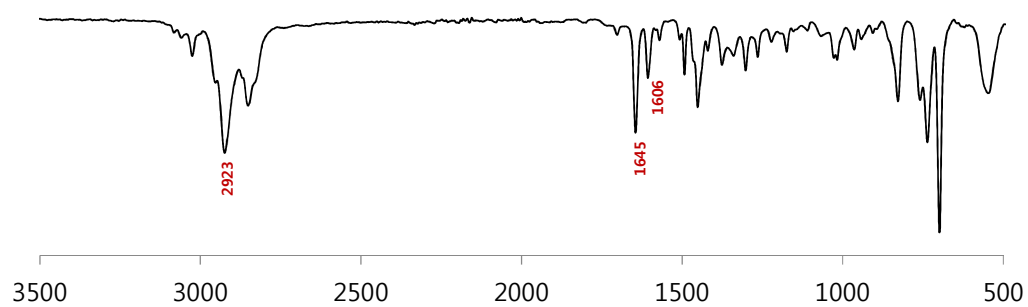
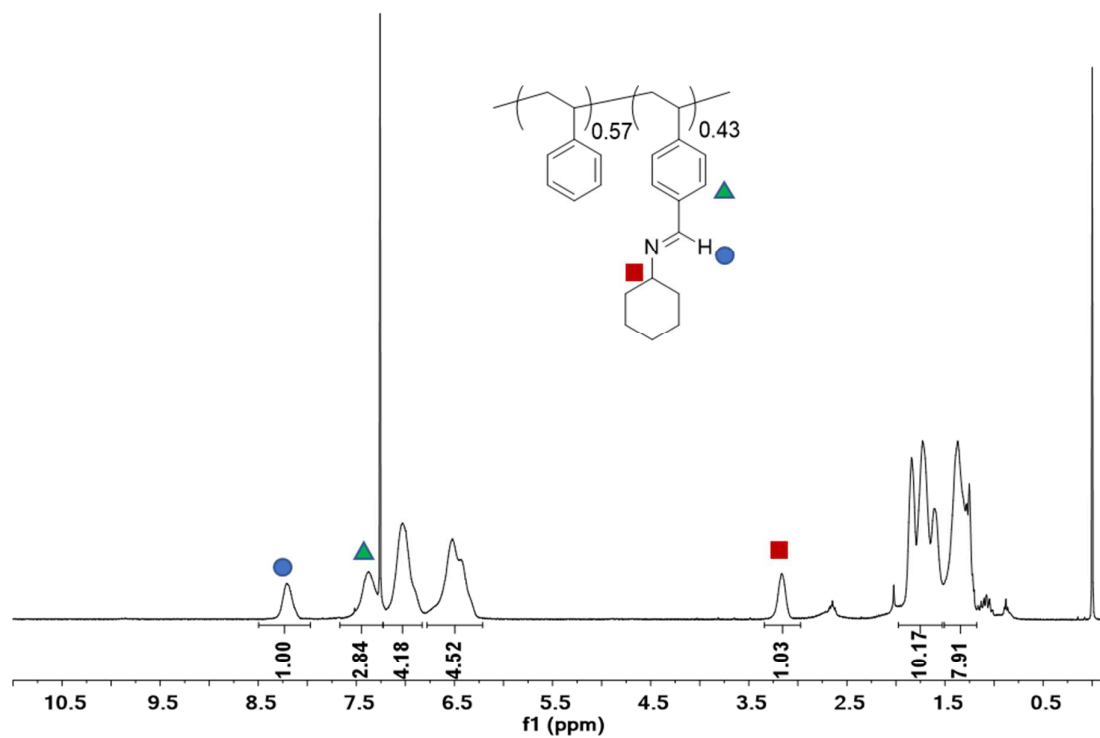


Table 1, Entry 4

The final product (53 mg) was obtained after four precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

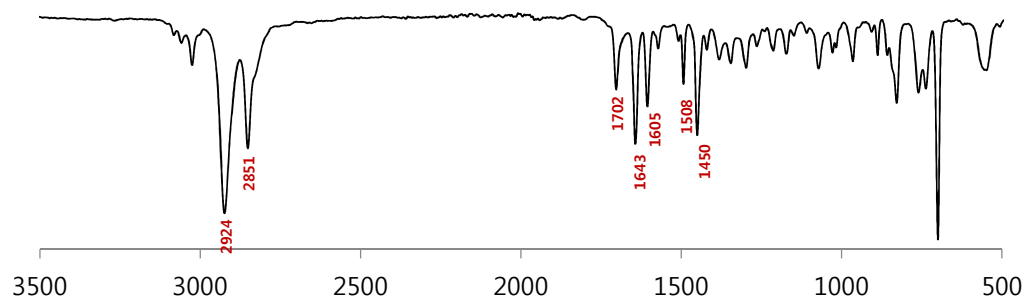
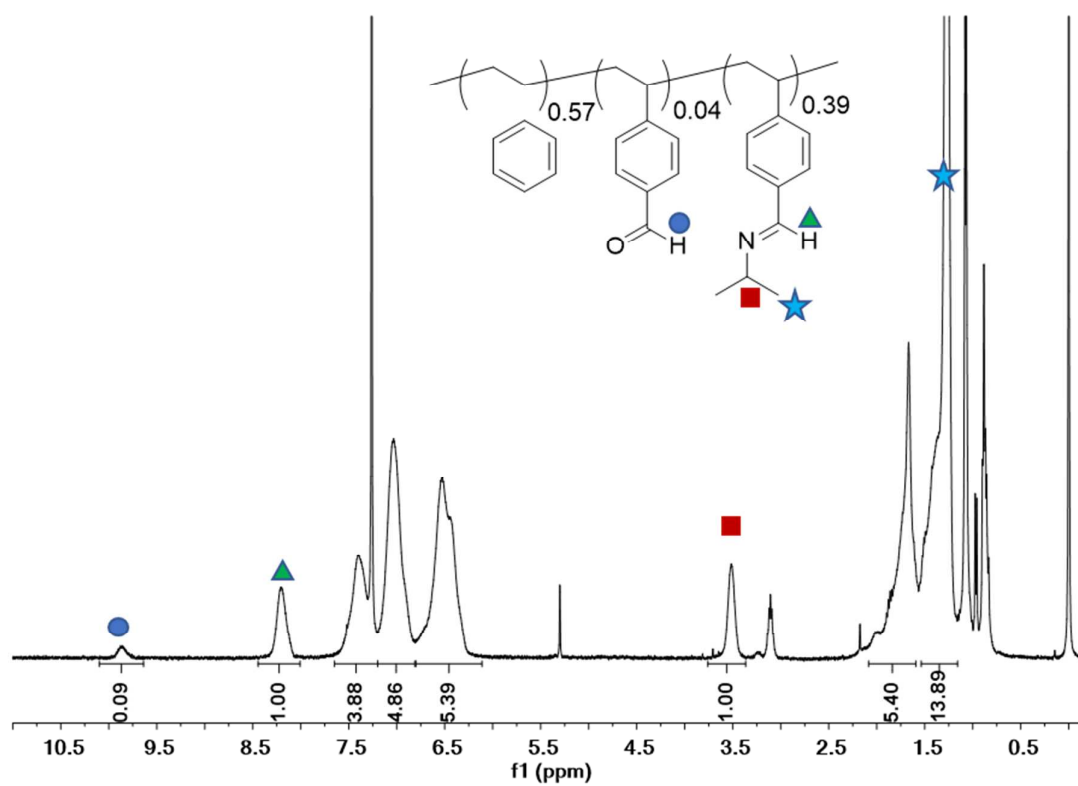


Table 1, Entry 5

The final product (9 mg) was obtained after five precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

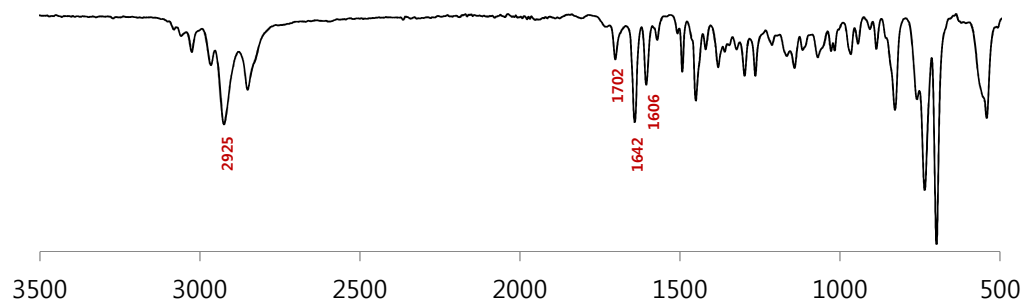
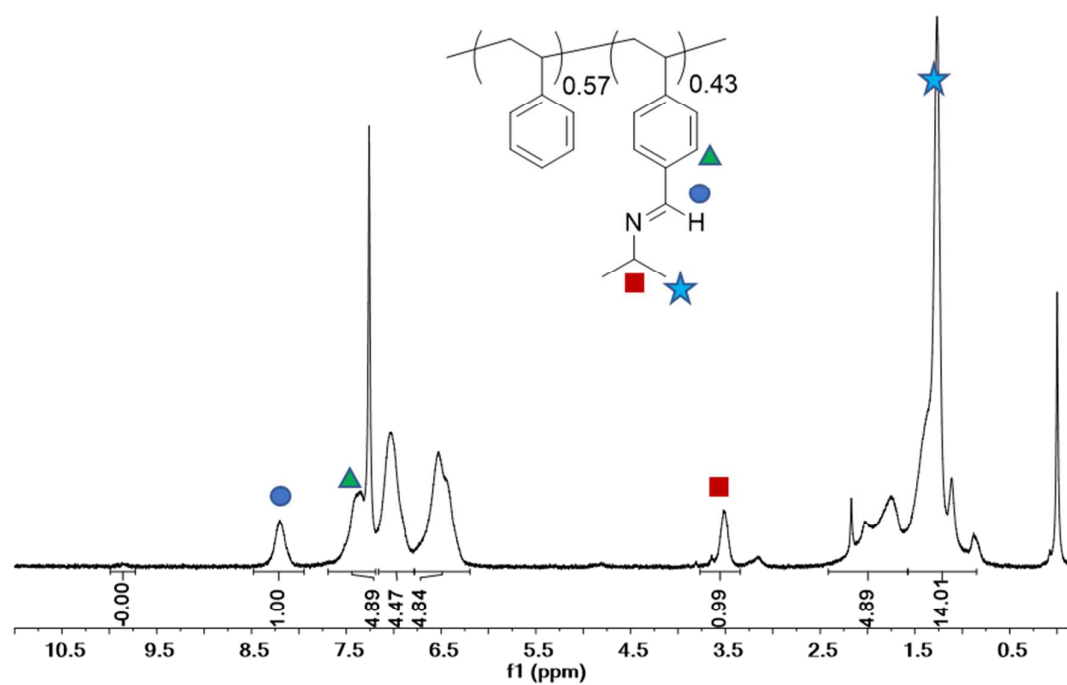


Table 1, Entry 6

The final product (6 mg) was obtained after four precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

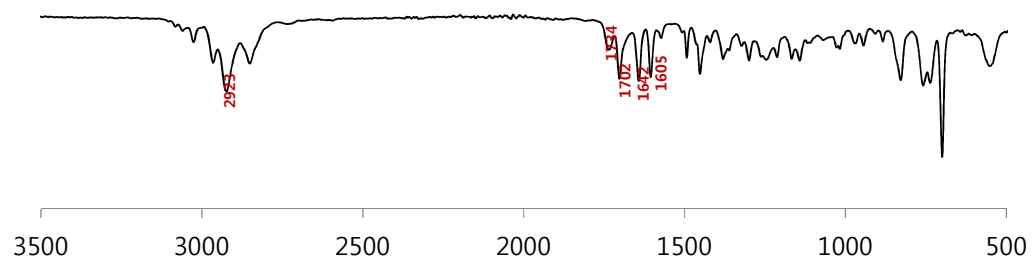
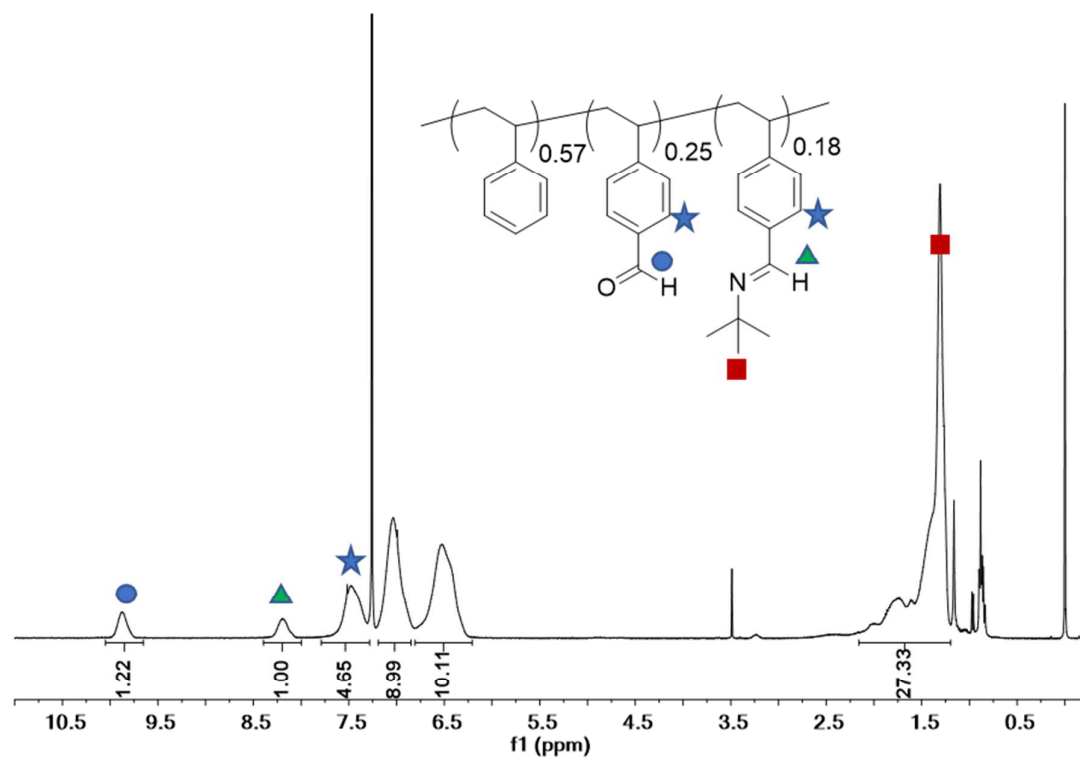


Table 1, Entry 7

The final product (89 mg) was obtained after two precipitations in CH₂Cl₂/Hexanes

¹H-NMR



FT-IR

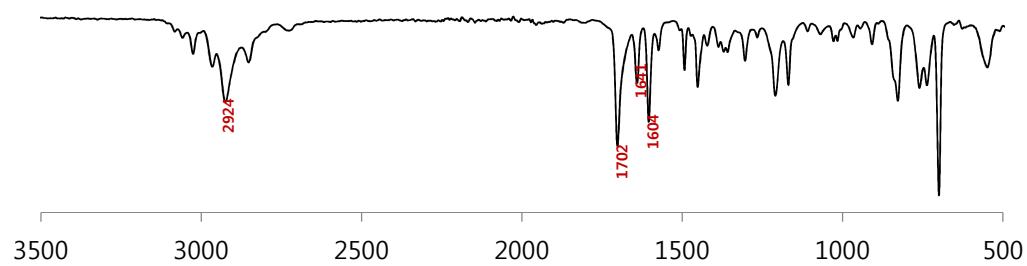
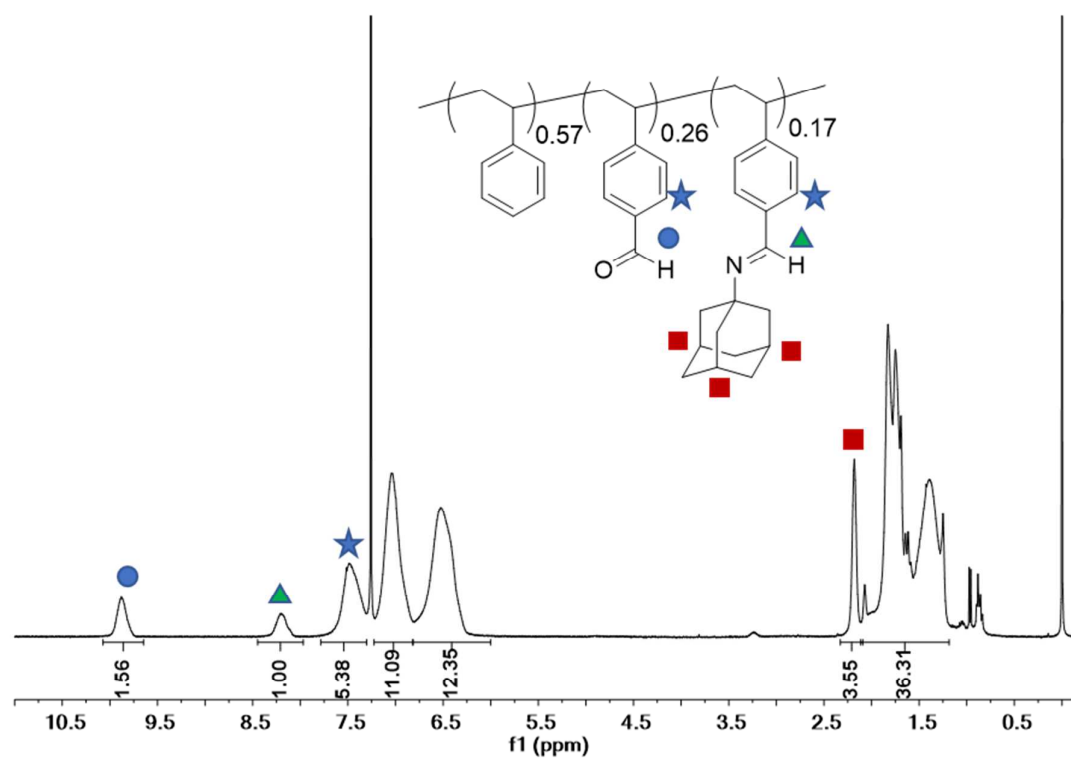


Table 1, Entry 8

The final product (112 mg) was obtained after two precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

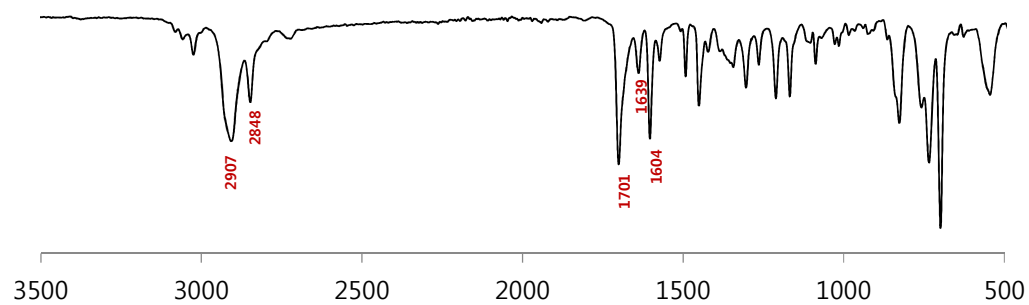
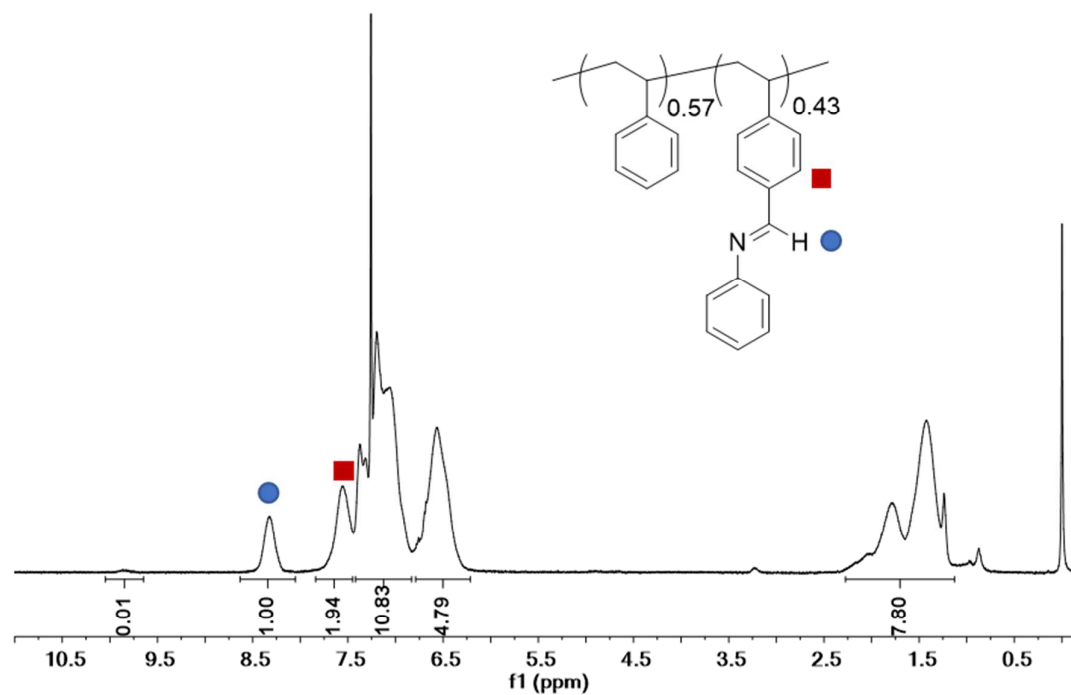


Table 1, Entry 9

The final product (100 mg) was obtained after a precipitation in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

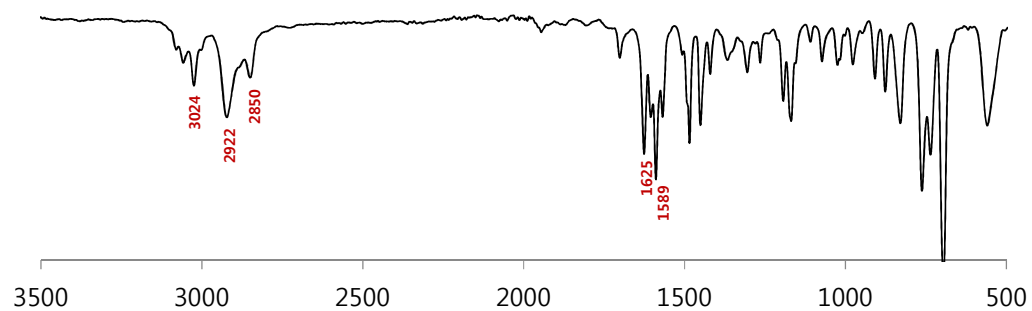
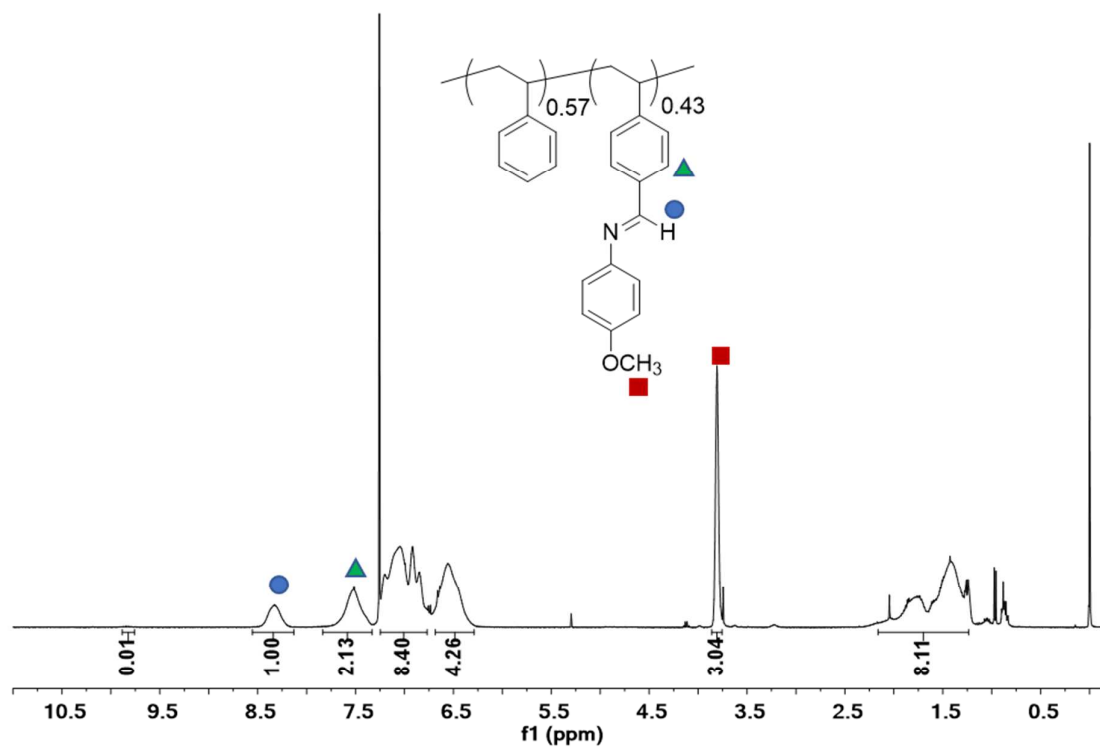


Table 1, Entry 10

The final product (117 mg) was obtained after three precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

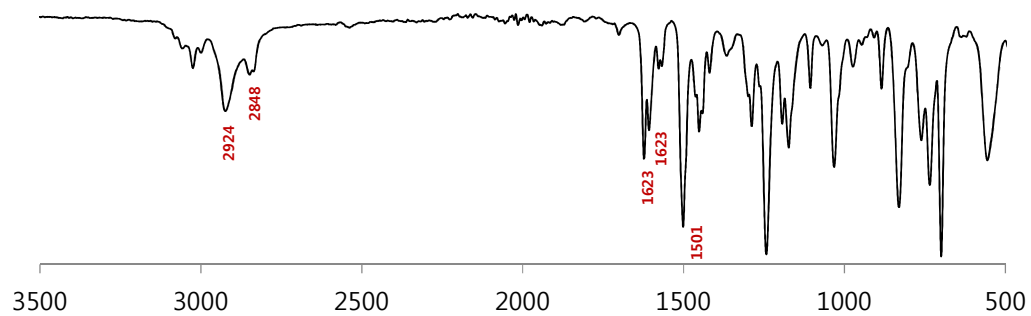
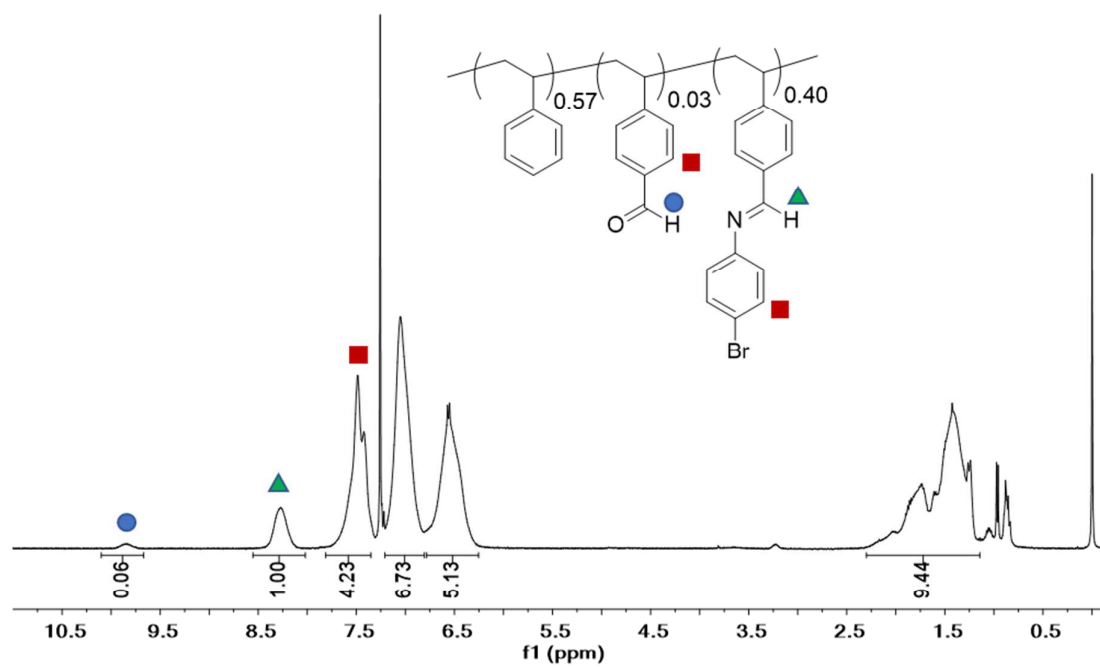


Table 1, Entry 11

The final product (120 mg) was obtained after two precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

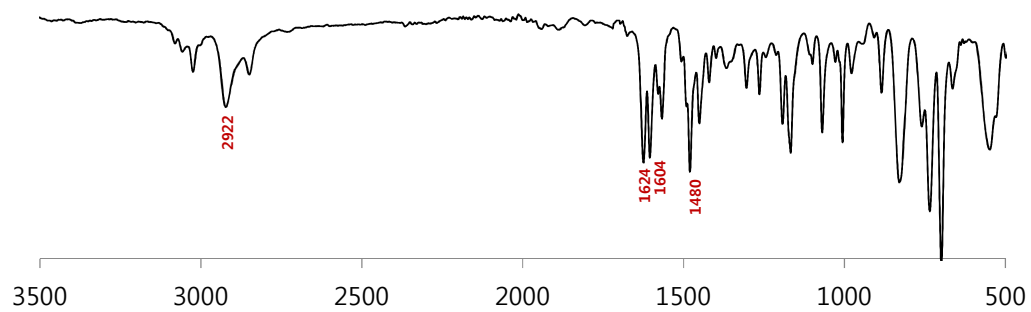
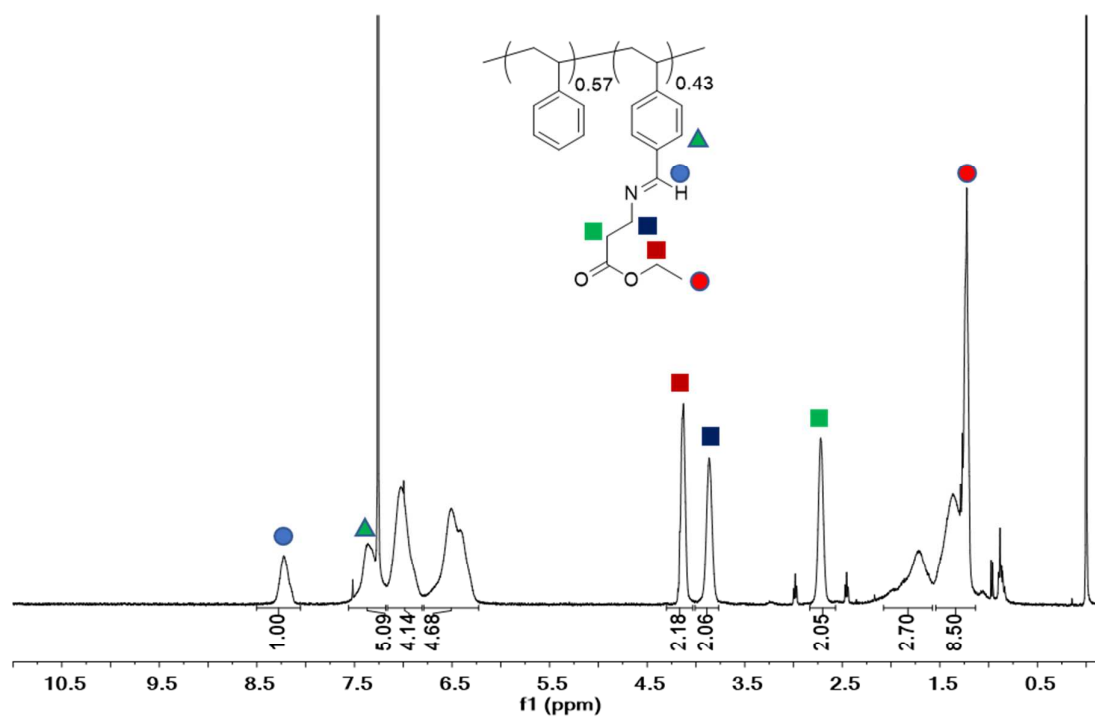


Table 1, Entry 13

The final product (165 mg) was obtained after two precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

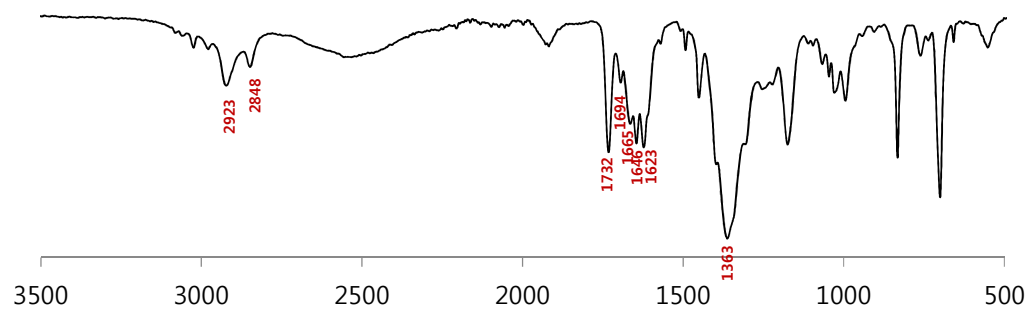
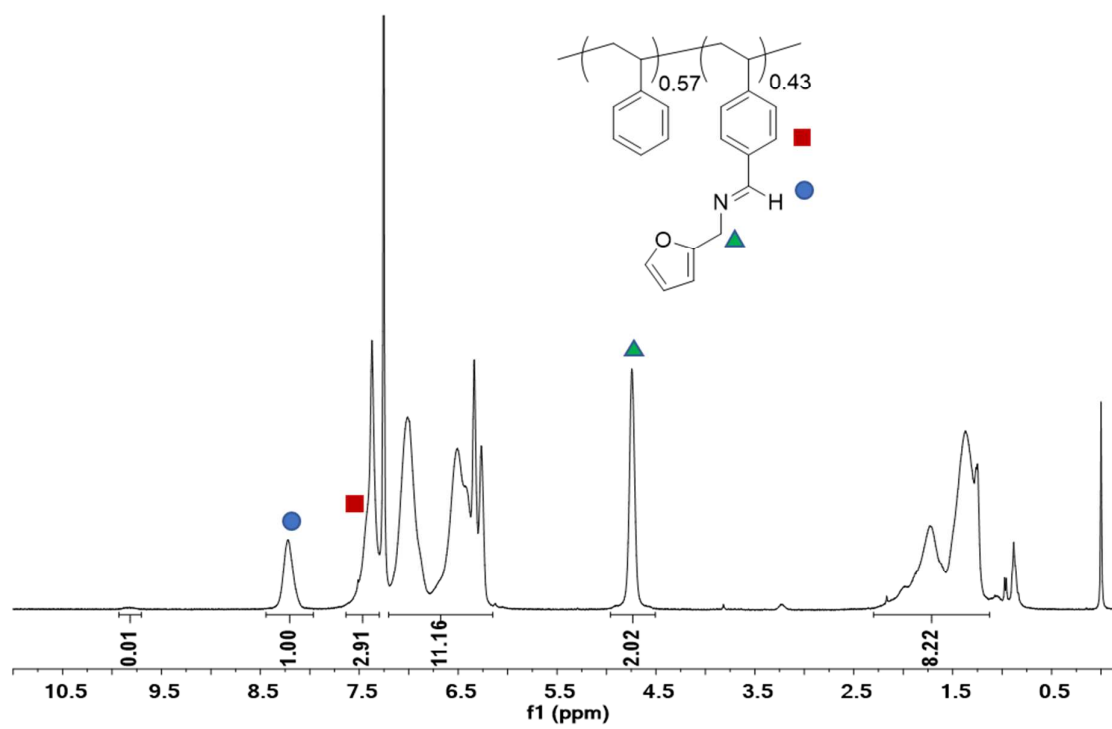


Table 1, Entry 14

The final product (84 mg) was obtained after a precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

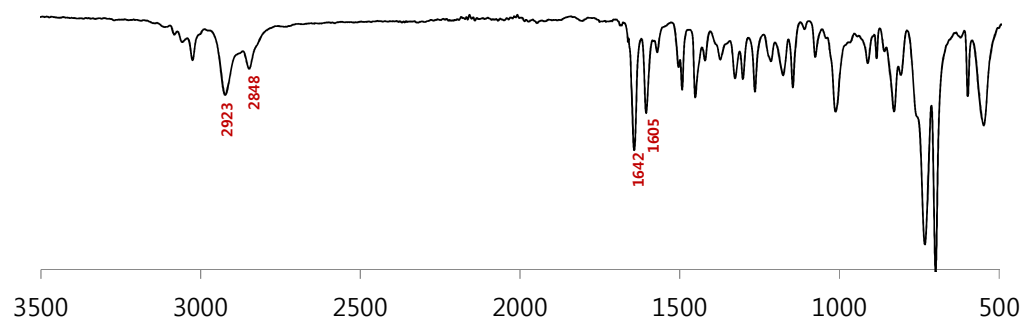
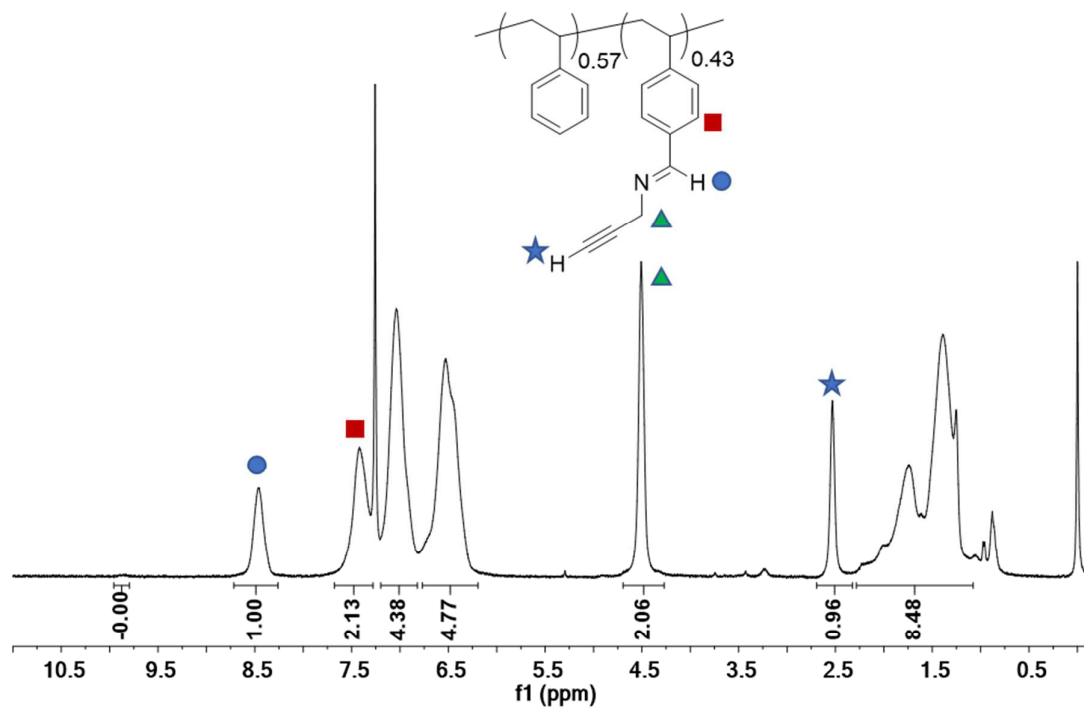


Table 1, Entry 15

The final product (87 mg) was obtained after a precipitations in CH_2Cl_2 /Hexanes.

^1H -NMR



FT-IR

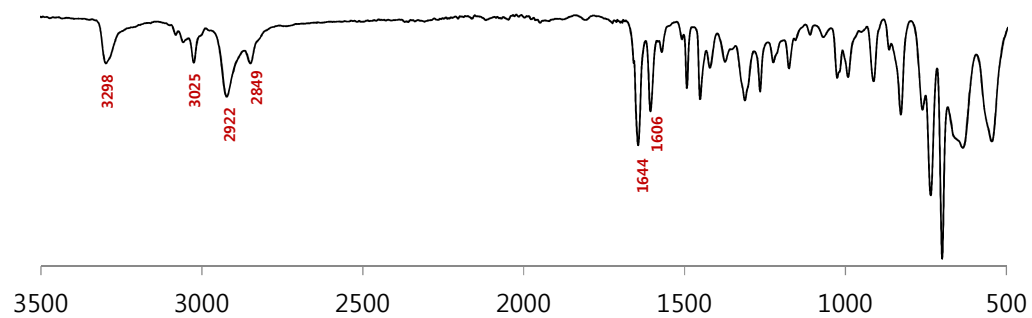
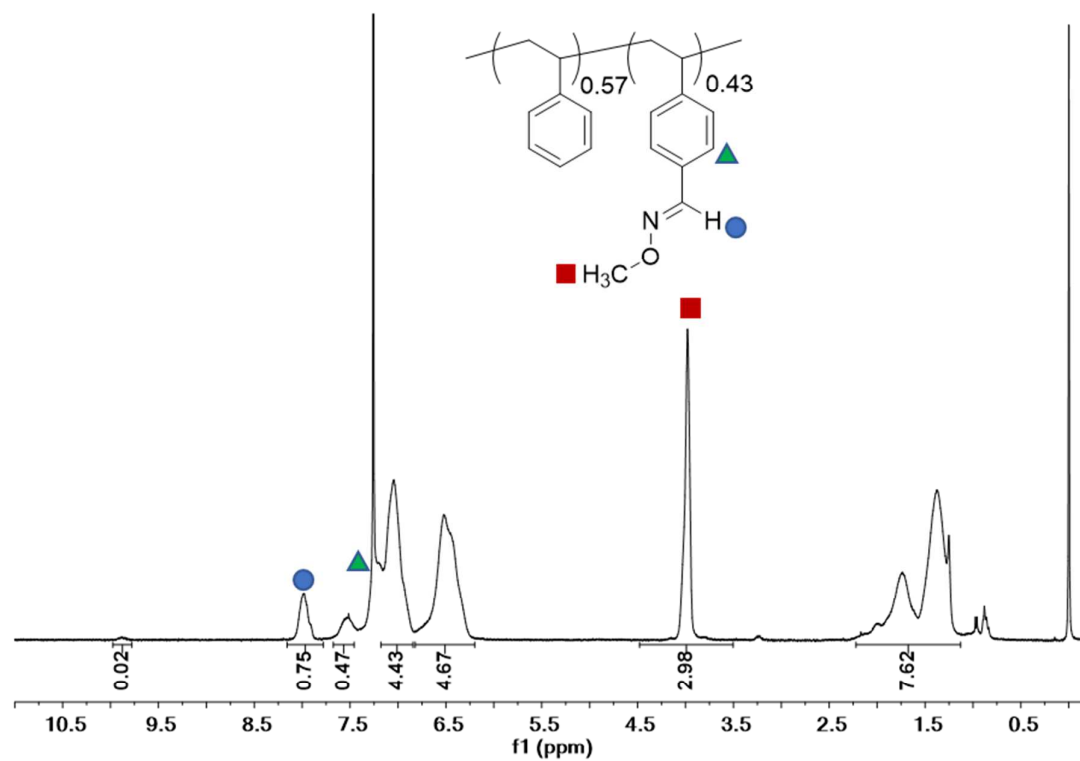


Table 1, Entry 16

The final product (78 mg) was obtained after a precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

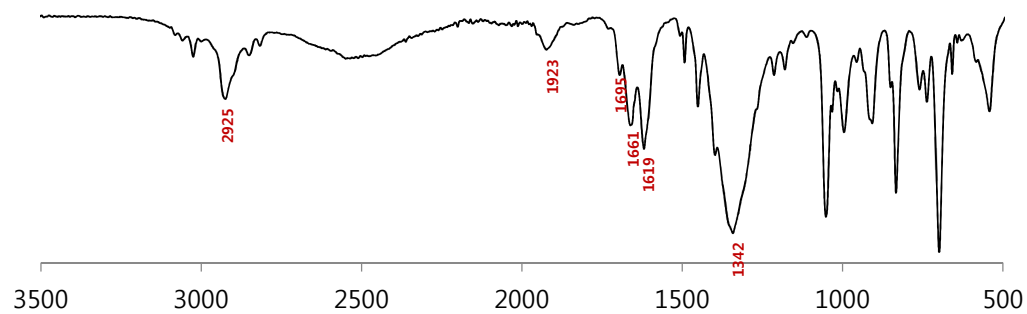
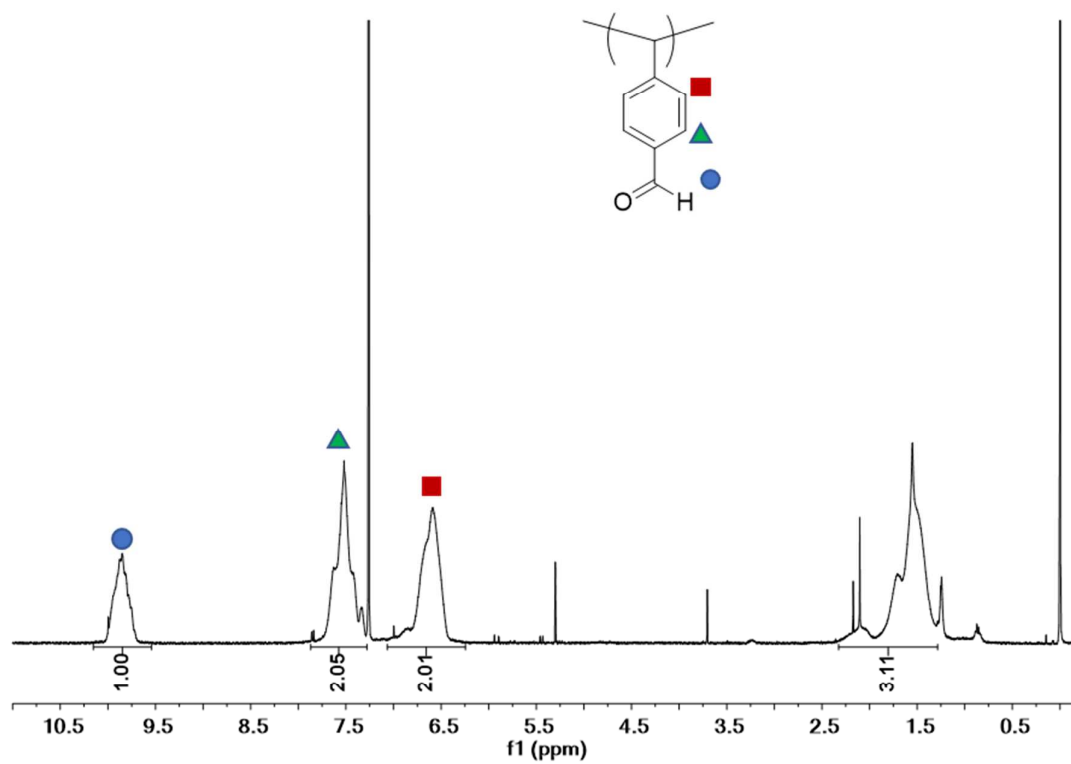


Table 2, SM

^1H -NMR



FT-IR

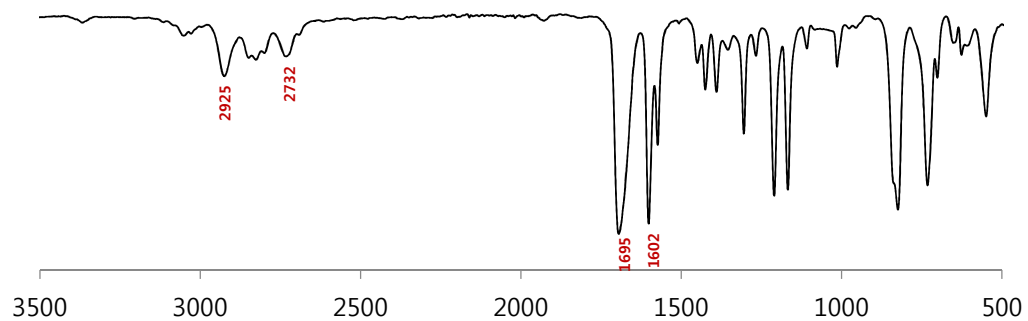
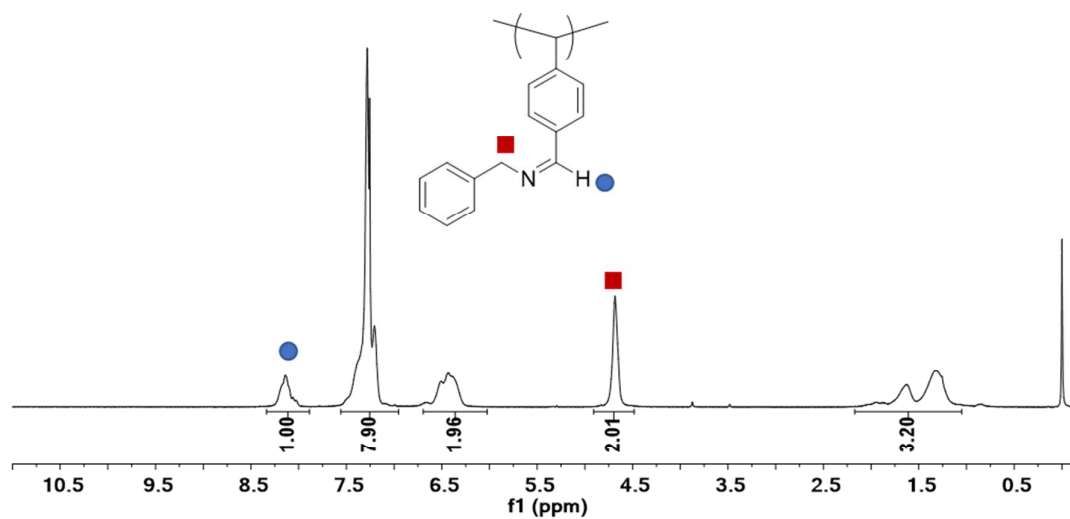


Table 2, Entry 1

The final product (82 mg) was obtained after three precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

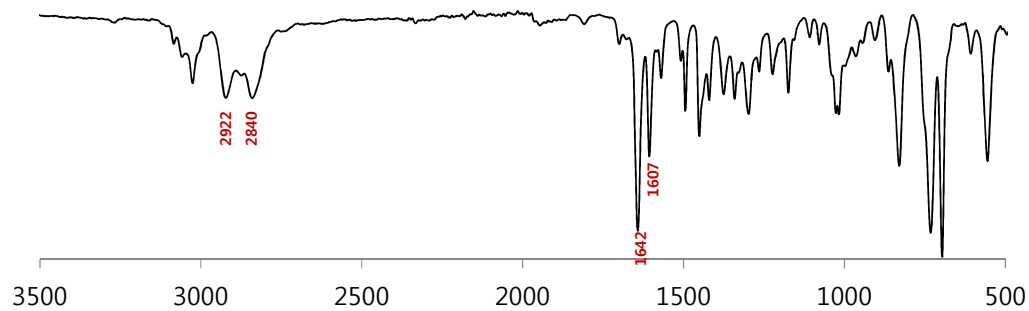
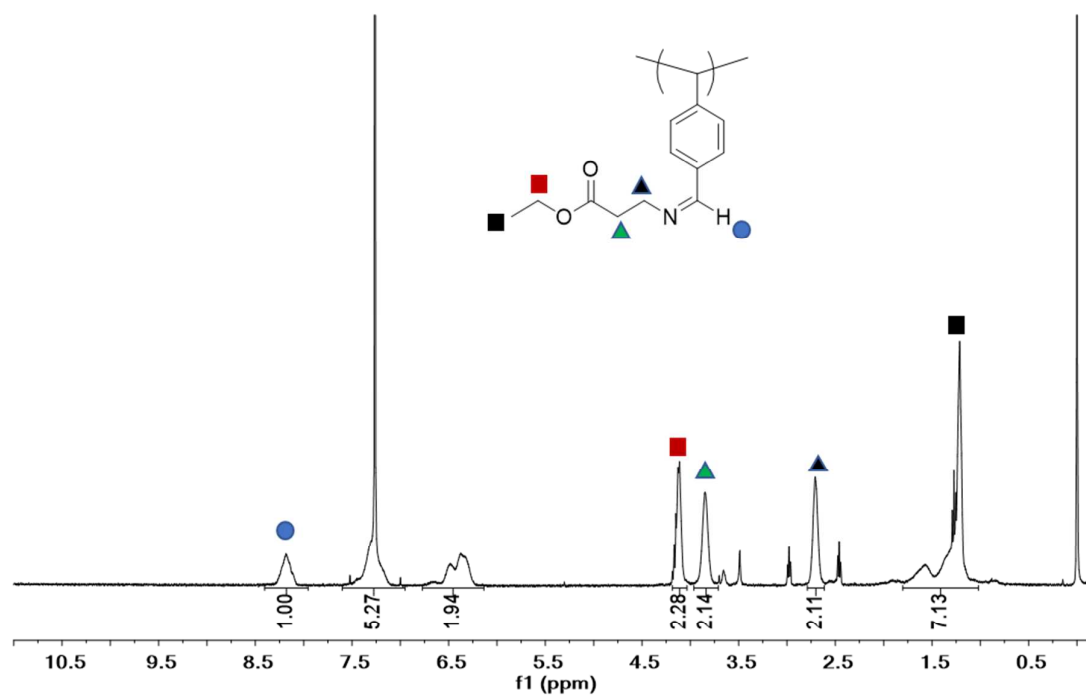


Table 2, Entry 2

The final product (48 mg) was obtained after three precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

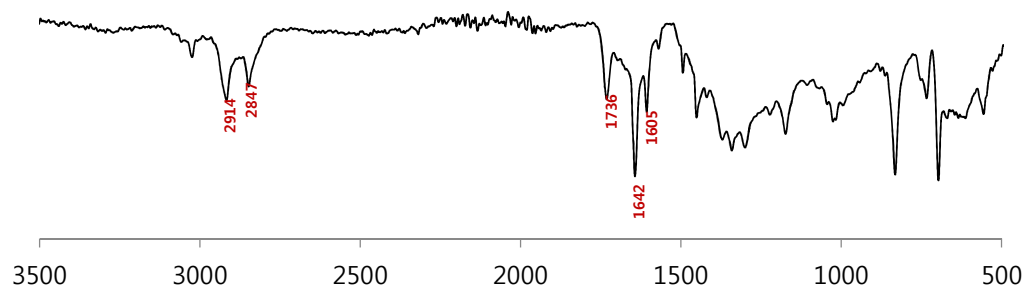
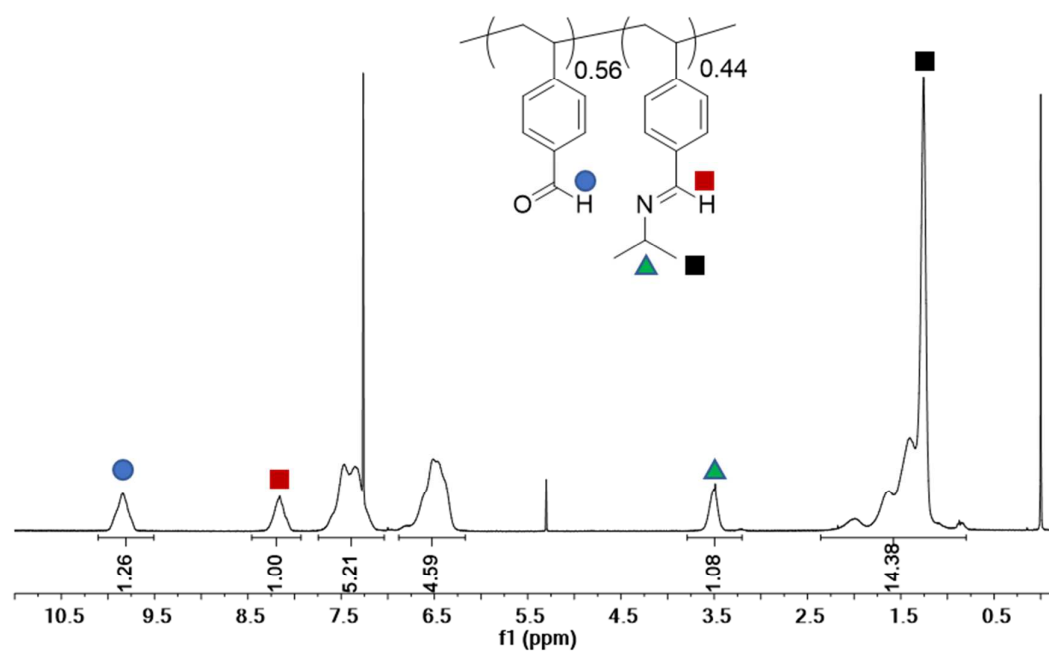


Table 2, Entry 3

The final product (45 mg) was obtained after four precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

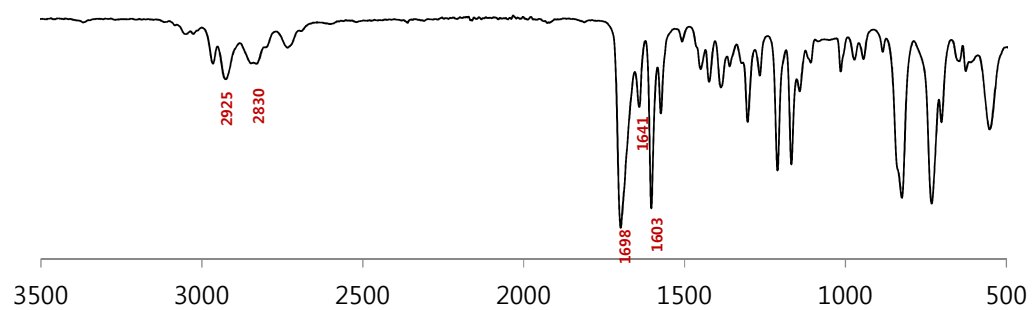
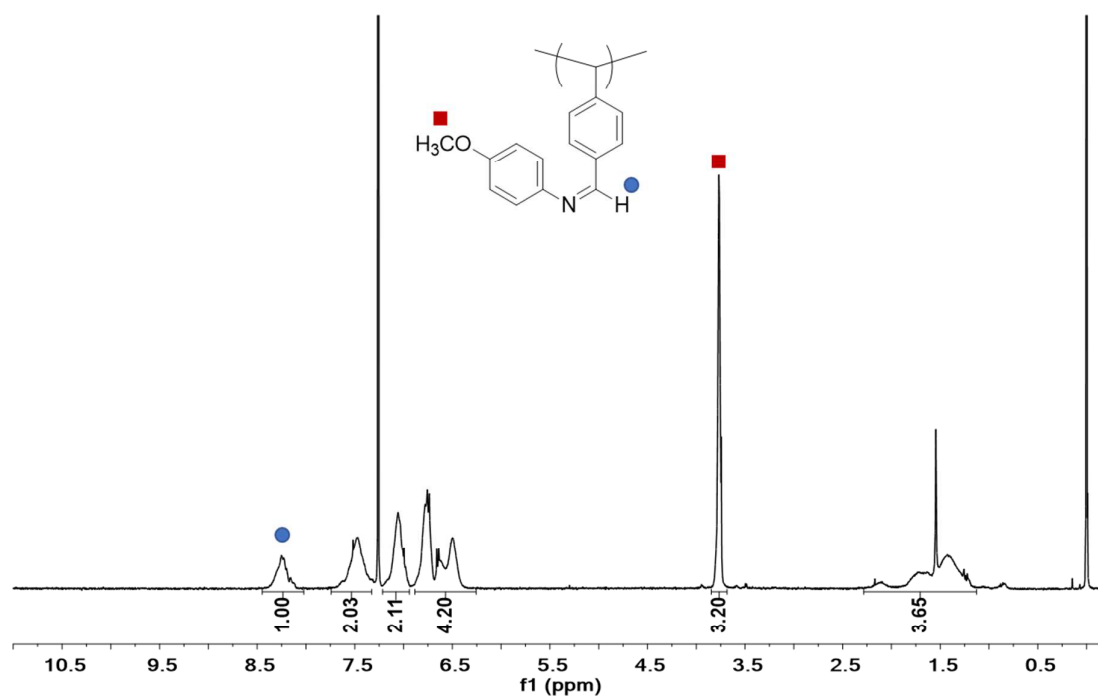


Table 2, Entry 4

The final product (152 mg) was obtained after four precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

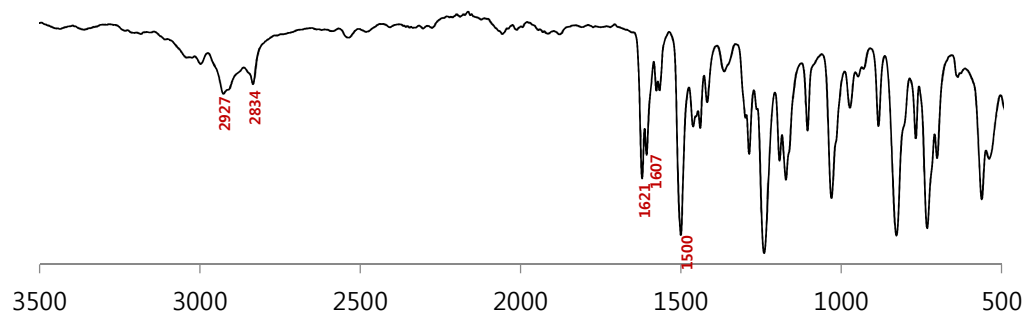
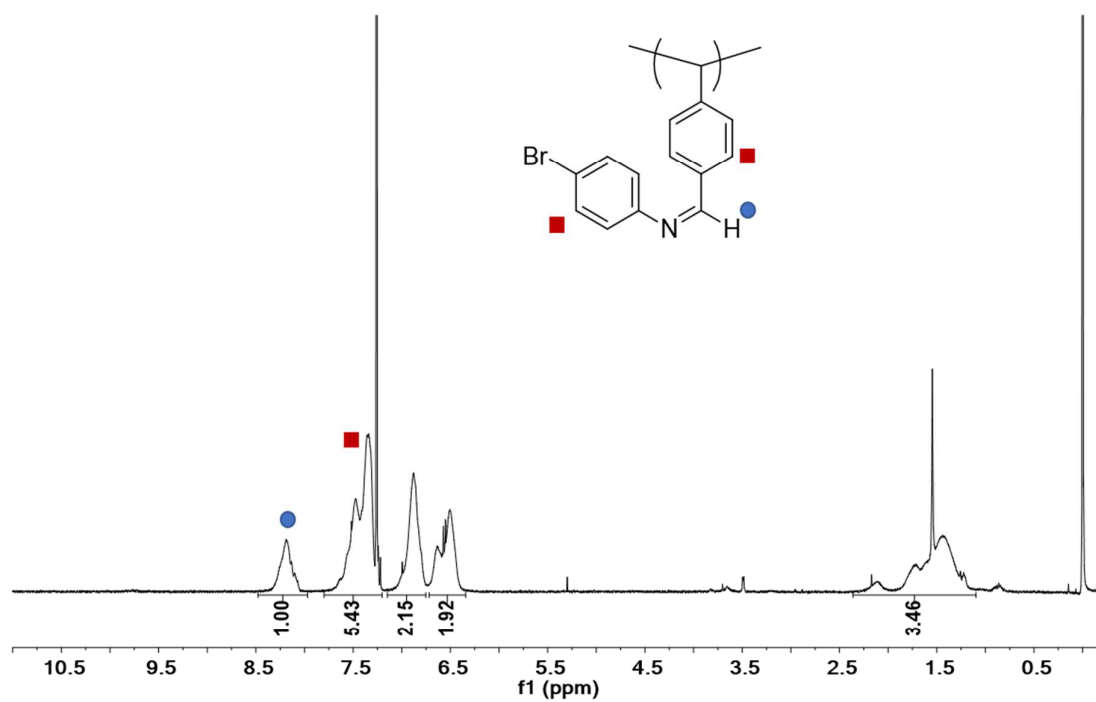


Table 2, Entry 5

The final product (179 mg) was obtained after four precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

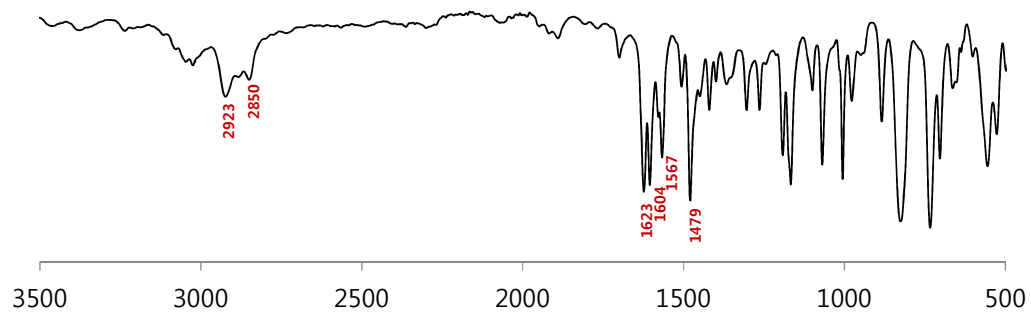
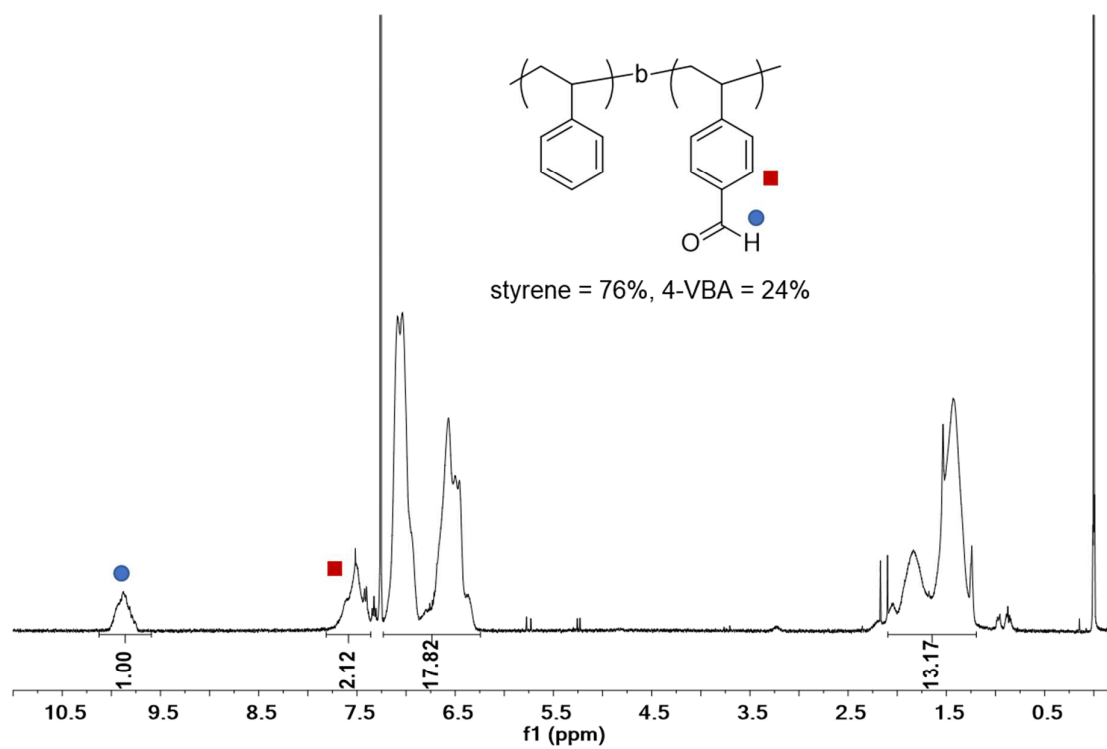


Table 3, SM

^1H -NMR



FT-IR

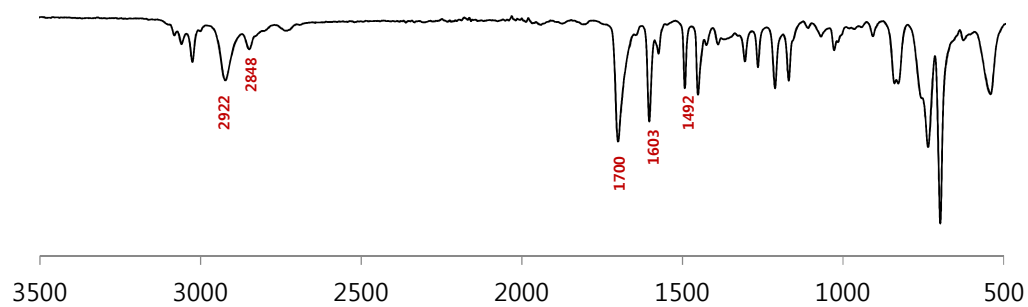
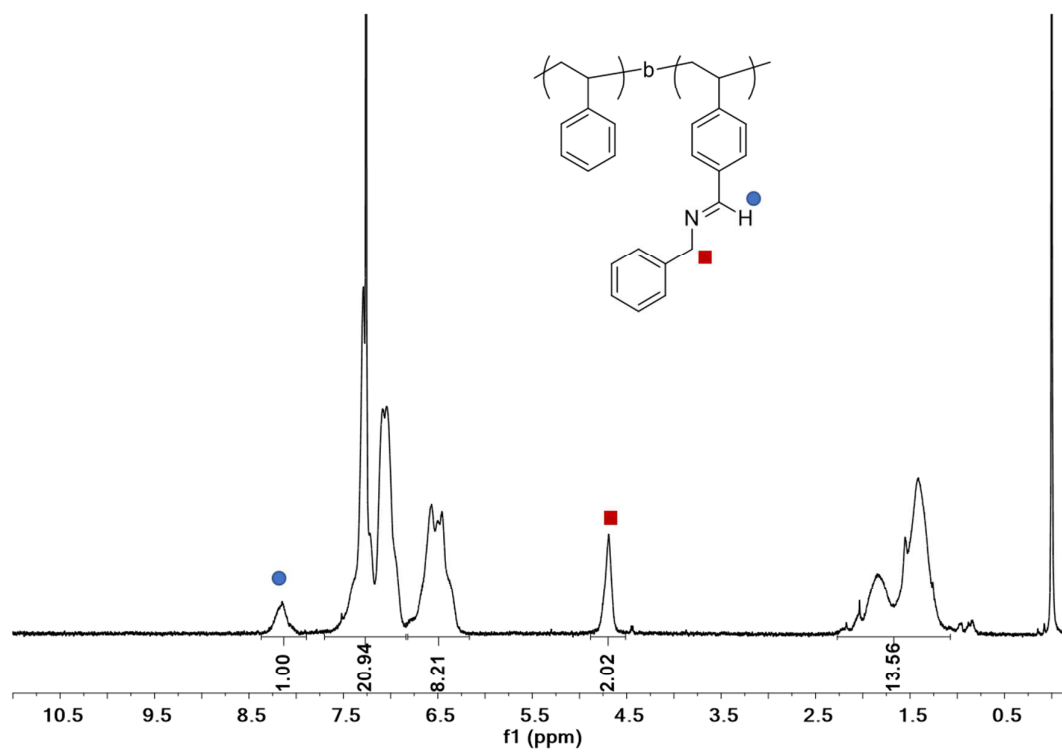


Table 3, Entry 1

The final product (114 mg) was obtained after two precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

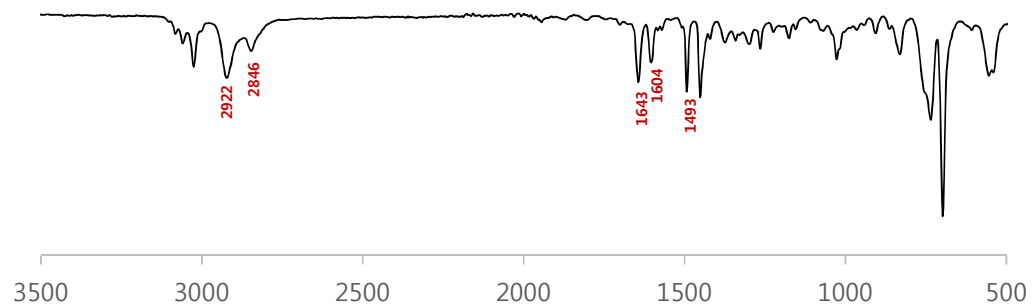
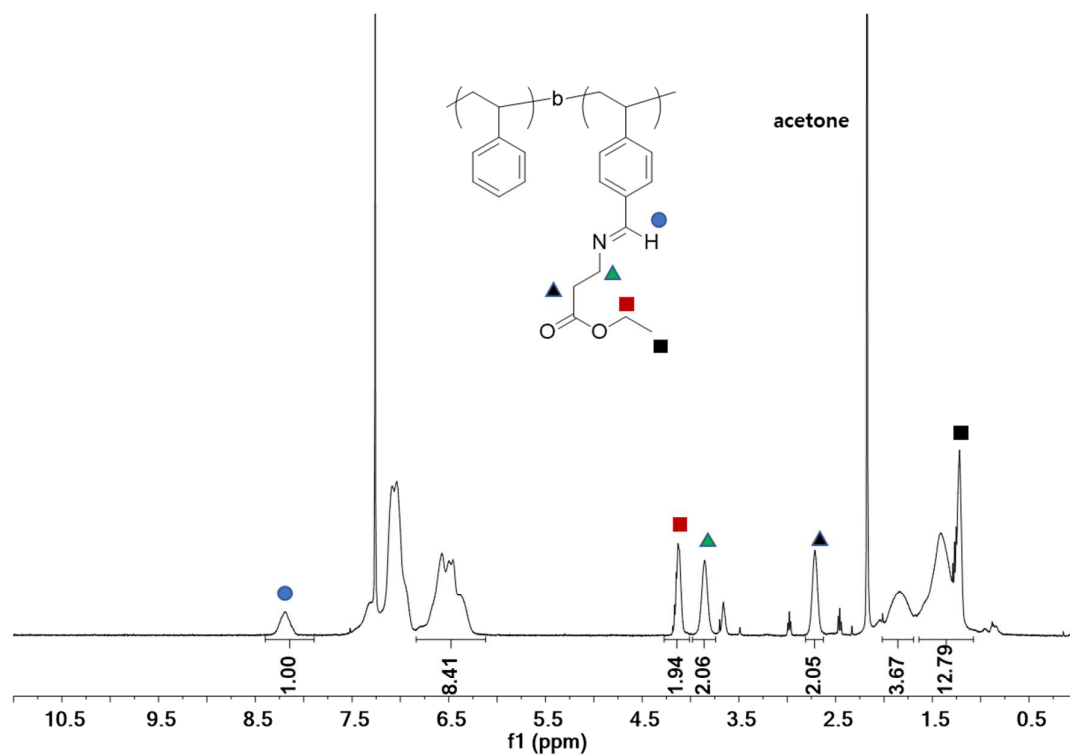


Table 3, Entry 2

The final product (20 mg) was obtained after two precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

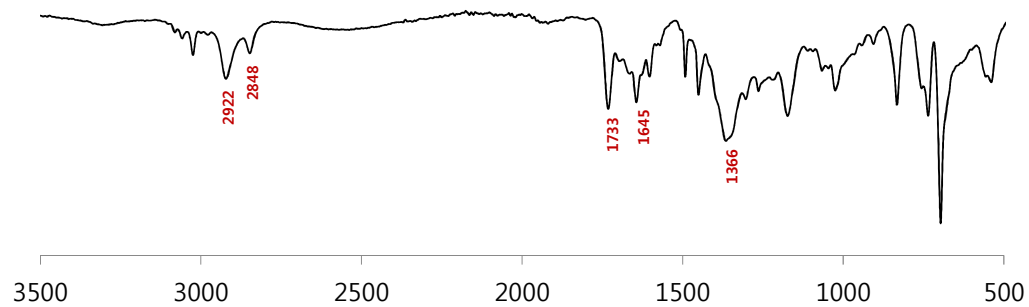
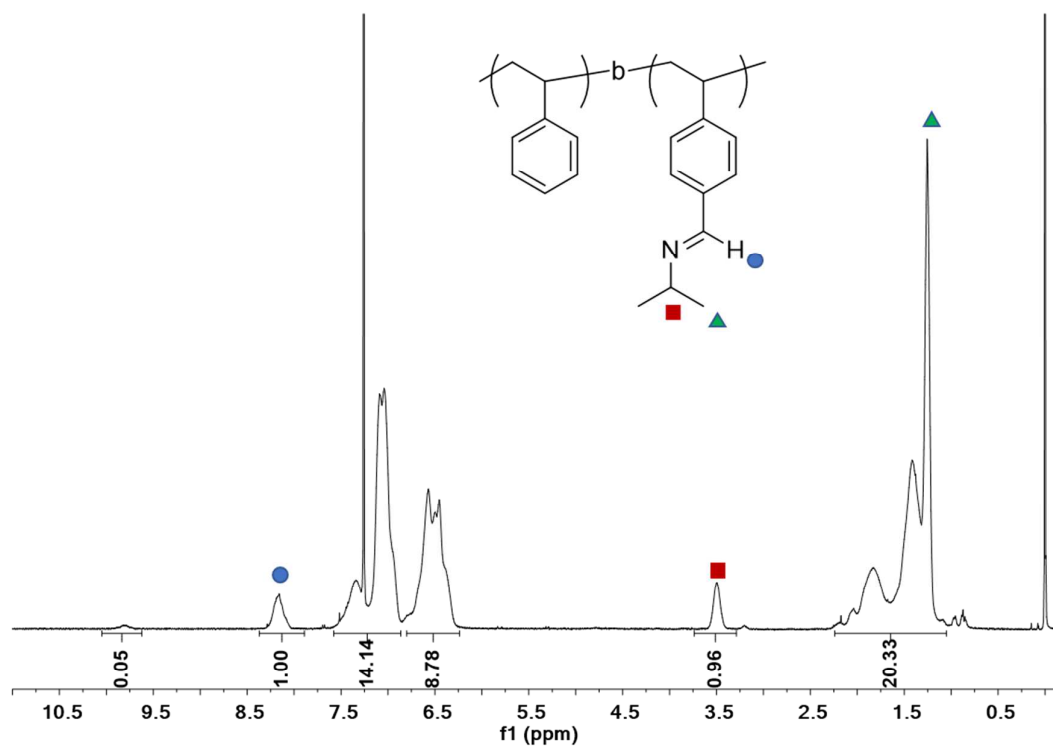


Table 3, Entry 3

The final product (91 mg) was obtained after two precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

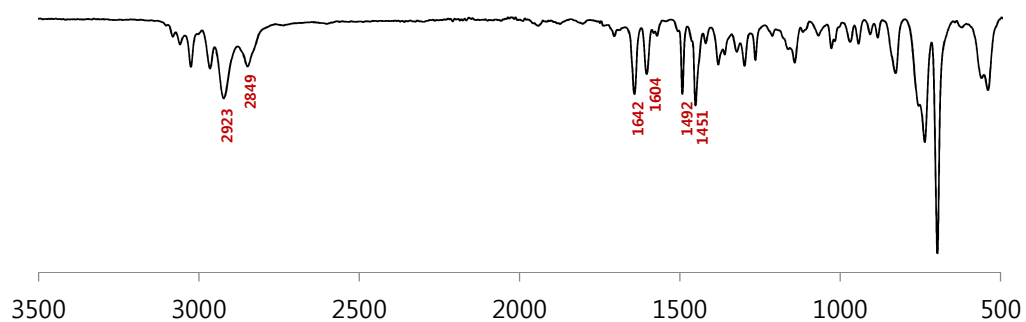
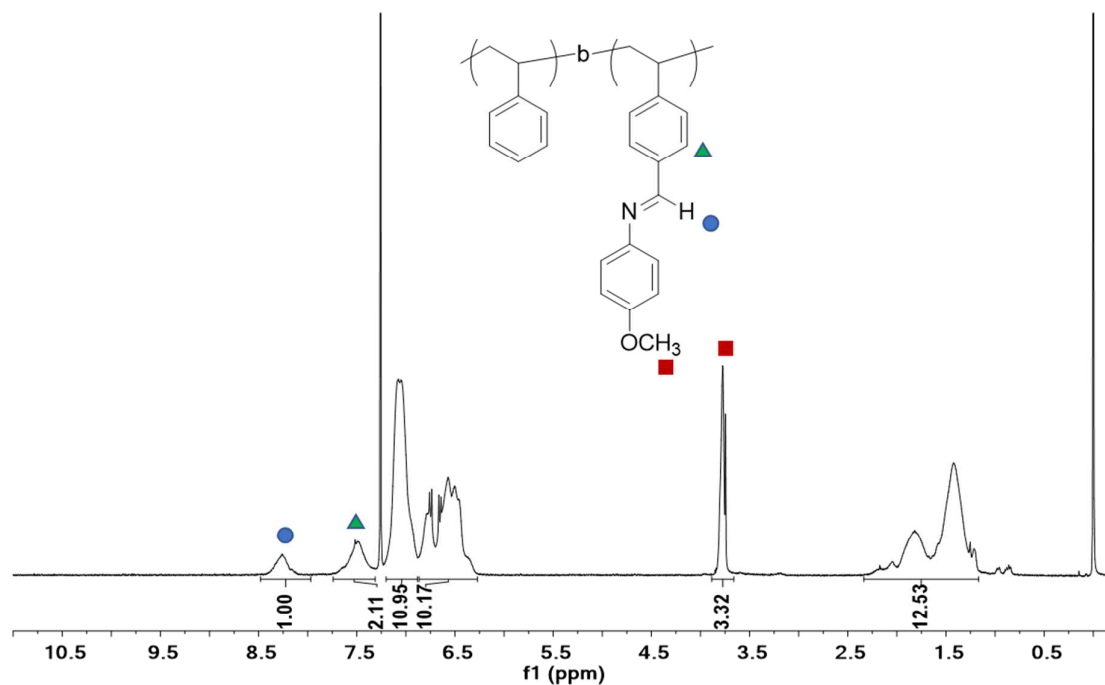


Table 3, Entry 4

The final product (99 mg) was obtained after two precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

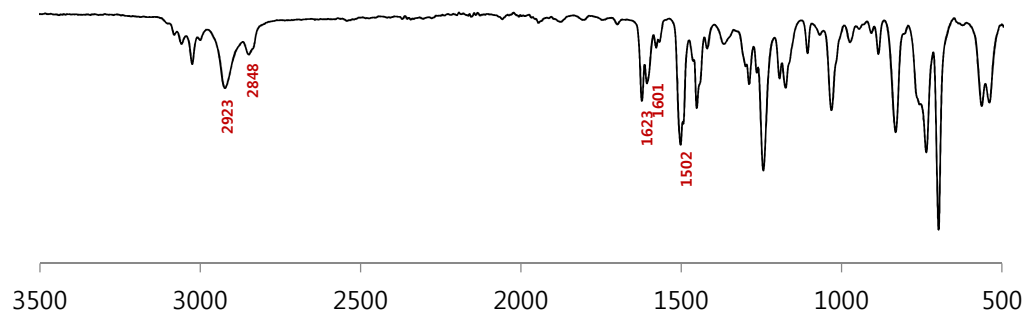
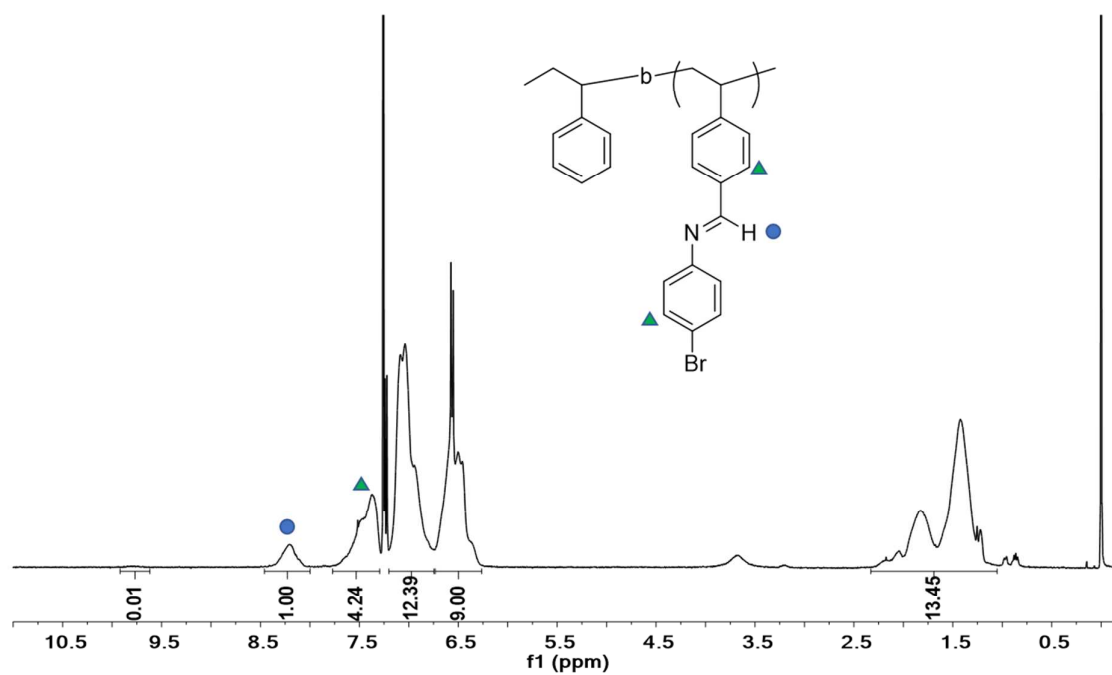


Table 3, Entry 5

The final product (23 mg) was obtained after two precipitations in CH₂Cl₂/Hexanes.

¹H-NMR



FT-IR

