Base catalyzed polymerization of safrole oxide (2)

Polymerization using TBAF

The conditions for polymerizations are described in Table S1. Safrole oxide **2** (178 mg, 1.00 mmol), Bu_4NF (0.1 mol), added as $Bu_4NF.3H_2O$ or as 1 M solution in THF, in toluene (2.0 mL) and the solvent along with moisture was evaporated using a gentle stream of N_2. The mixture was then heated under N_2 at 70 °C for 24 h. Thereafter, 4:1 (v/v) methanol/water (10 mL) was added to quench the polymerization, and polymer **5** was extracted with ether. The ether layer was dried (Na_2SO_4) and concentrated to obtain the polymer.

Polymerization using TBAH

As described in Table S1, safrole oxide **2** (237 mg, 1.33 mmol), TBAH 40% in water (28 mg, 0.0432 mmol) and toluene (5.0 mL) were mixed and the solvent along with the moisture was evaporated using a gentle stream of N_2. Heating at 70 °C for 15 h was followed by quenching with methanol/water and then polymer **5** was extracted with ether. The ether layer was dried (Na_2SO_4) and concentrated to obtain the polymer.

Attempted synthesis of diphenylsilyl protected 4-allylcatechol (11)[1]

Tris(pentafluorophenyl)borane (5.6 mg, 0.01 mmol) was added under N_2 at 25 ºC to a stirred solution of eugenol **10** (871 mg, 5.3 mmol) and diphenylsilane (1.11 g, 6.0 mmol, 1.1 equiv) in dichloromethane (5 mL) in a RB flask (50 mL) fitted with a condenser. The exothermic reaction was completed within minutes with the evolution of a gas. The reaction mixture upon silica gel chromatography using hexane/ether as eluant gave 4-allylcatechol **12** (77%): δ_H

($CDCl_3$): 3.27 (2H, d, *J* 6.7 Hz), 5.03 - 5.07 (2H, m), 5.88 – 5.96 (1H, m), 6.62 (1H, dd, *J* 2.2 Hz, *J* 7.9 Hz), 6.71 (1H, d, *J* 2.2 Hz), 6.79 (1H, d, *J* 7.9 Hz); δ_C ($CDCl_3$): 39.51, 115.37, 115.59, 115.72, 121.02, 133.25, 137.64, 141.70, 143.48 ($CDCl_3$ middle carbon: 77.04), $\nu_{max.}$ (KBr): 3422, 3078, 3005, 2978, 2904, 1697, 1639, 1605, 1520, 1444, 1413, 1356, 1281, 1192, 1147, 1112, 995, 964, 916, 814, and 789 cm^{-1}.

General Procedure for attempted block copolymerization

Block copolymerization of **2** and **7** was unsuccessful. After completion of polymerization of monomer **2**, the second monomer **7** was added. However, the sequence led to the formation of two homopolymers.

When 1 M $^{i}Bu_3Al$ solution in hexane was used for polymerization a two-phase system developed in which the homopolymer of **2** remained in the more viscous phase, while that of **7** remained in the less viscous layer. When $^{i}Bu_3Al$ solution (25% in toluene) was used for polymerization, the system remained in one phase. But after work up, the material separated into two phases with the upper phase having the homopolymer of allyl glycidyl ether **7**, while the lower phase contained the homopolymer of safrole oxide **2**.

Reference in Supporting Information.

1 J. Heo, T. Kang, S. G. Jang, D. S. Hwang, J. M. Spruell, K. L. Killops, J. H. Waite and C. J. Hawker, *J. Am. Chem. Soc.*, 2012, **134** (49), 20139–20145.

Table S1. Polymerization of safrole oxide **2**[a]

Entry	Solvent	Catalyst (mmol)	Temp (°C)	Time (h)	Yield (%)
1	Neat[b]	TBAF.3H_2O (0.06)	85	18	Trace
2	Neat[b]	TBAF.3H_2O (0.06)	90	18	Trace
3	Neat[b]	TBAH 40% H_2O (0.05)	85	18	≈100
4	Neat[c]	TBAH 40% H_2O (0.03)	50	24	45
5	Neat[c]	TBAH 40% H_2O (0.03)	50	66	55
6	THF[d]	TBAH 40% H_2O (0.03)	50	24	Trace
7	THF[d]	TBAH 40% H_2O(0.03)	50	66	Trace
8	Neat[b]	TBAH 40% H_2O (0.05)	70	18	78
9	Neat[b]	TBAH 40% H_2O (0.02)	90	2	≈100
10	Neat[b]	TBAH 40% H_2O(0.02)	100	18	≈100
11	Neat[b]	TBAH 40% H_2O (0.04)	100	2	77
12	Neat[b]	TBAH 40% H_2O (0.04)	100	4	86
13	Neat[b]	TBAH 40% H_2O (0.04)	100	24	94
14	Neat[b]	NaO^{t}Bu (0.05)	100	18	0

[a] 1.00 mmol; [b] Toluene was added and removed under N_2; [c] Toluene was added and removed under N_2 then dried under vacuum; [d] THF was added and removed under N_2. then dried under vacuum.

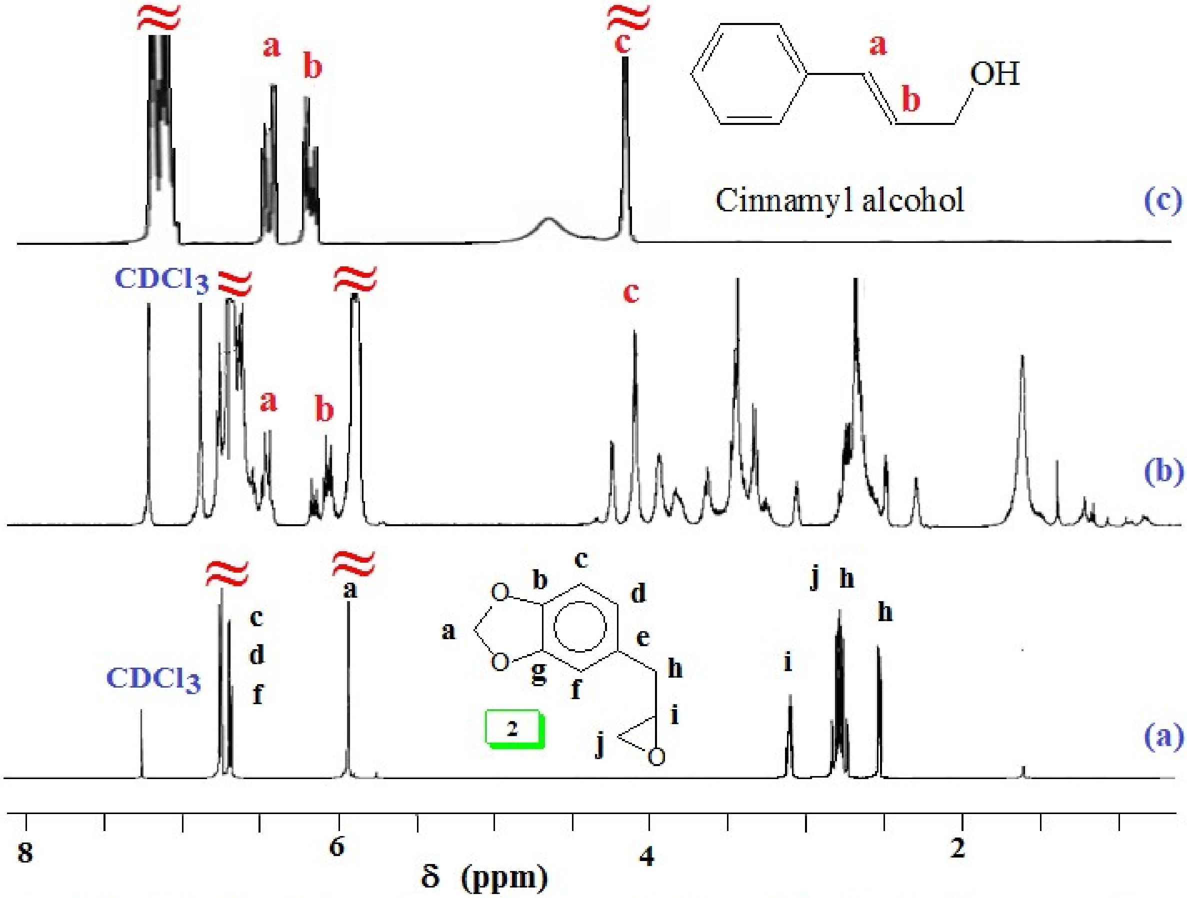

Fig. S1. ^{1}H NMR spectra of (**a**) safrole oxide **2,** (**b**) base catalyzed polymerized product from **2**, (**c**) cinnamyl alcohol in $CDCl_3$.

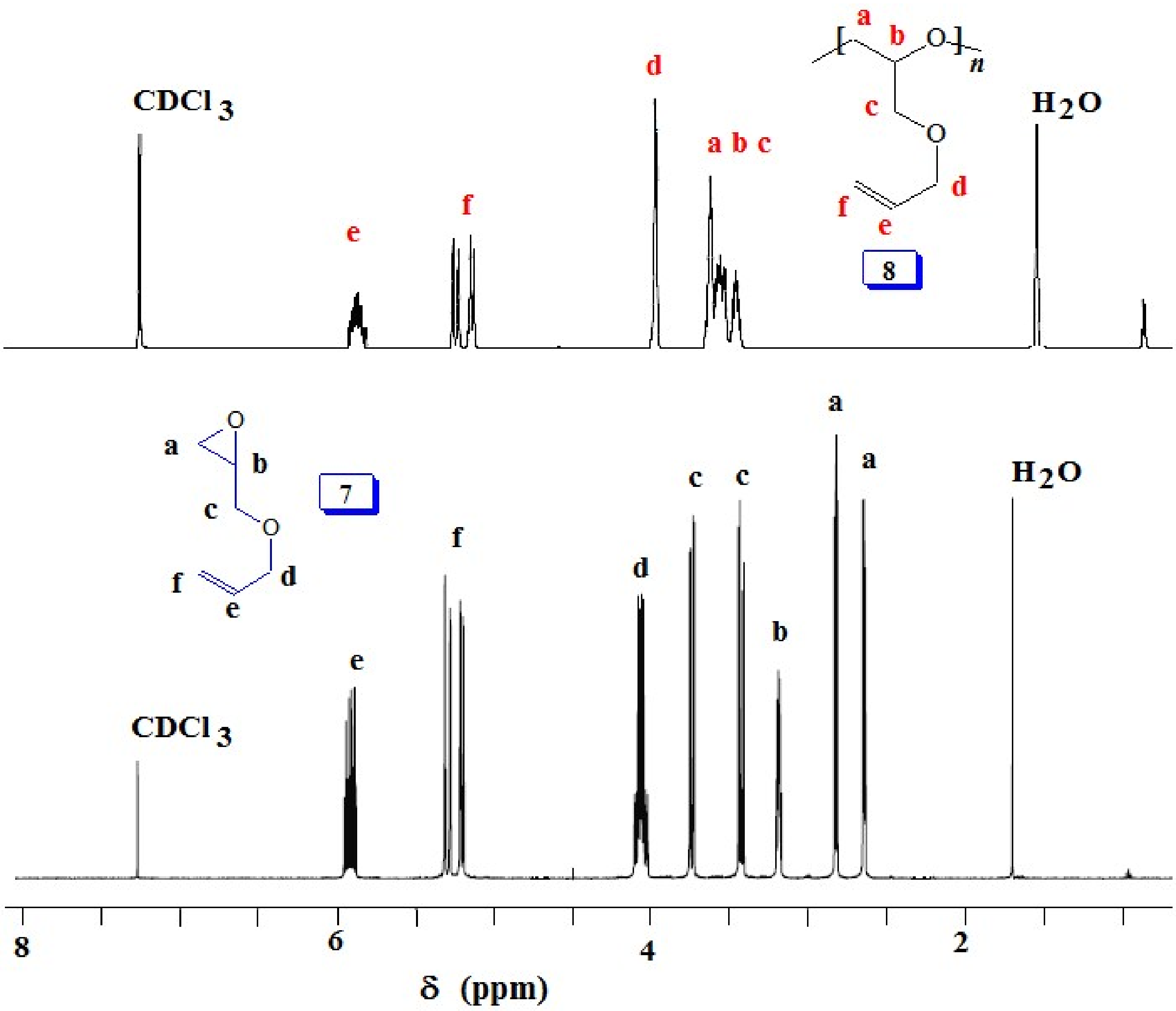

Fig. S2. ^{1}H NMR spectra of (**a**) AGE **7** and (**b**) polymer **8** in $CDCl_3$.

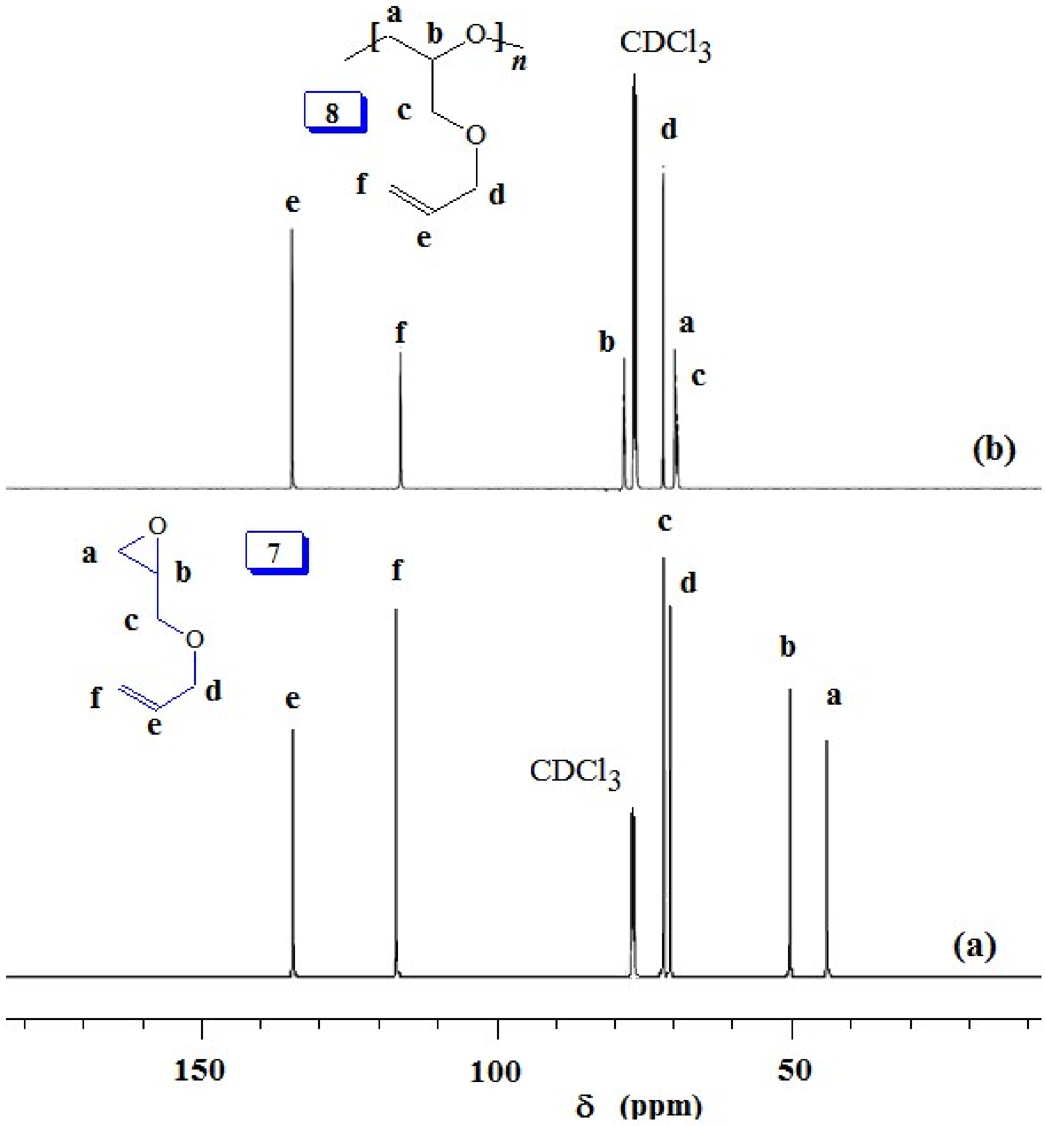

Fig. S3. ^{13}C NMR spectra of (**a**) AGE **7** and (**b**) polymer **8** in CDCl$_3$.

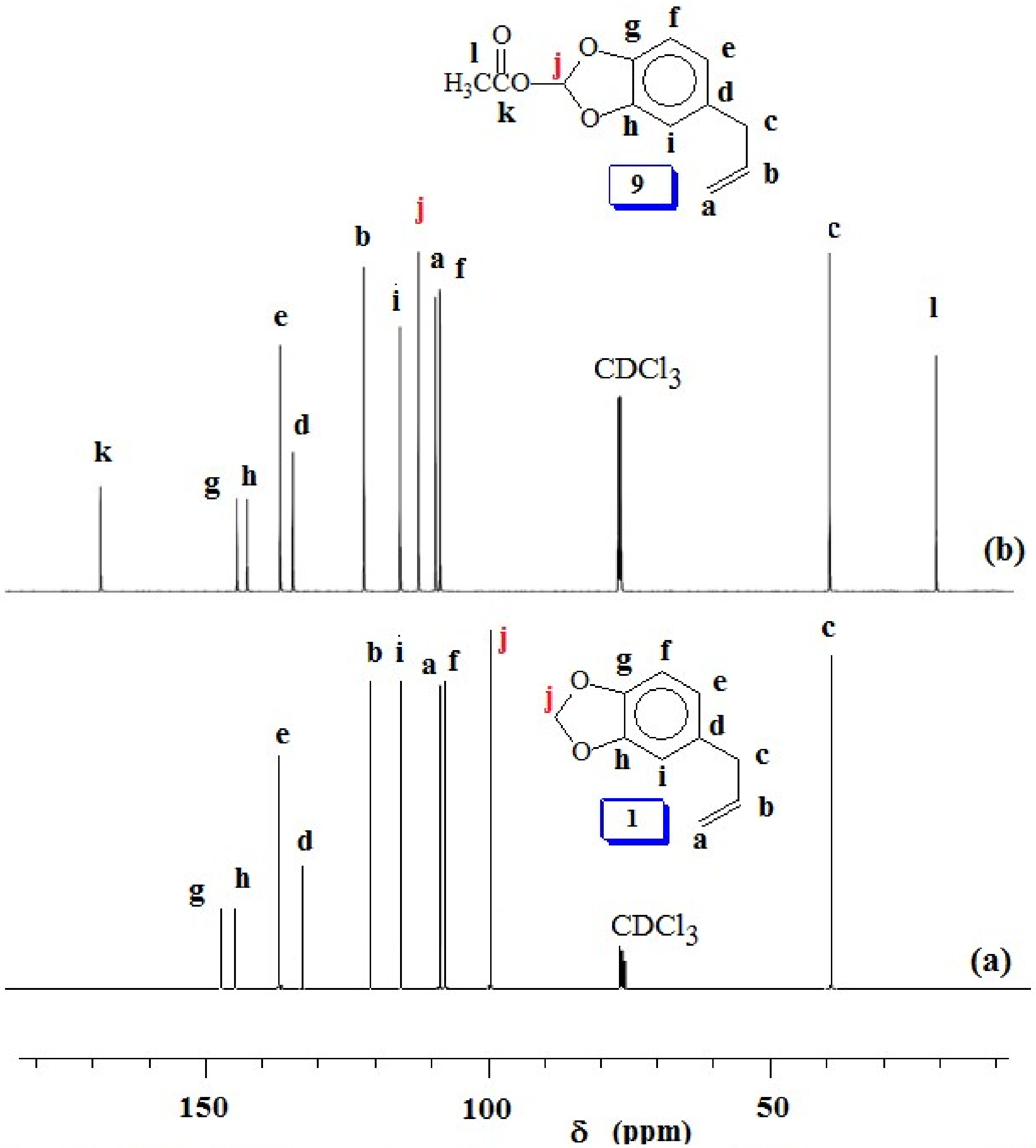

Fig. S4. ^{13}C NMR spectra of (**a**) safrole **1** and (**b**) acetoxysafrole **9** in $CDCl_3$.

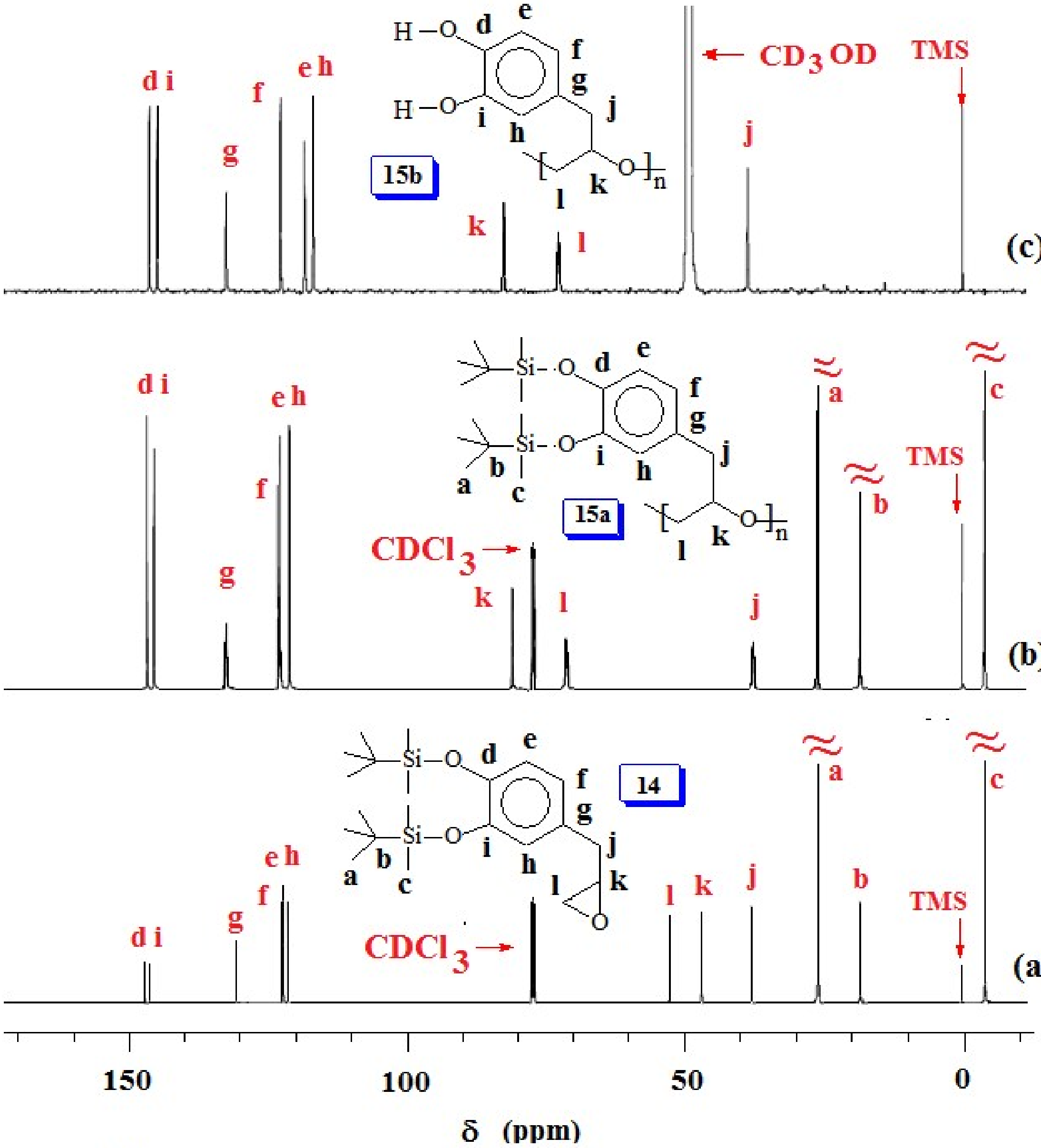

Fig. S5. ^{13}C NMR spectra of (**a**) **14** and (**b**) **15a** in $CDCl_3$; and (**c**) **15b** in CD_3OD.

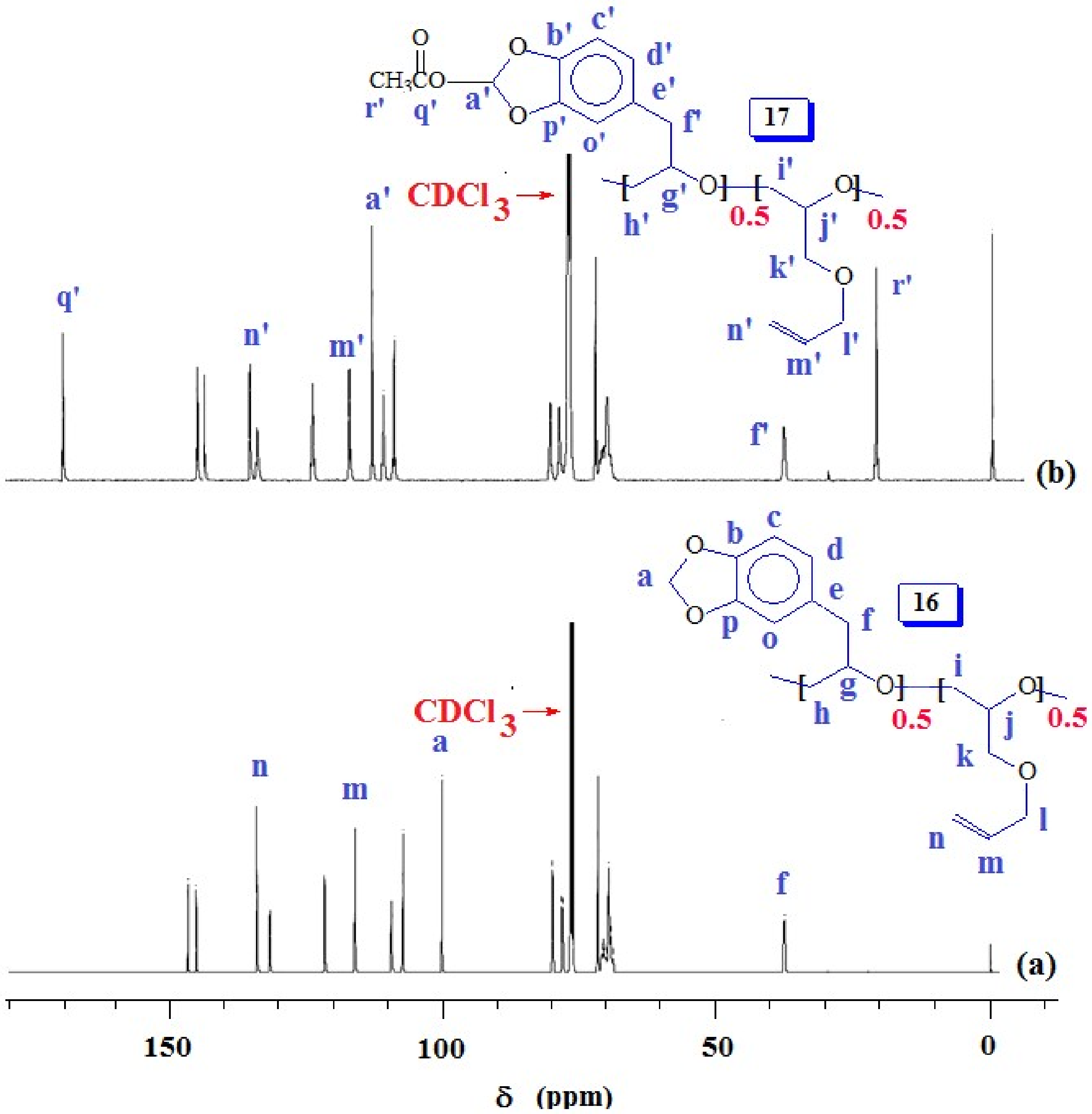

Fig. S6. ^{13}C NMR spectra of (**a**) 1:1 random copolymer **16** and (**b**)) 1:1 random copolymer **17** in CDCl$_3$.

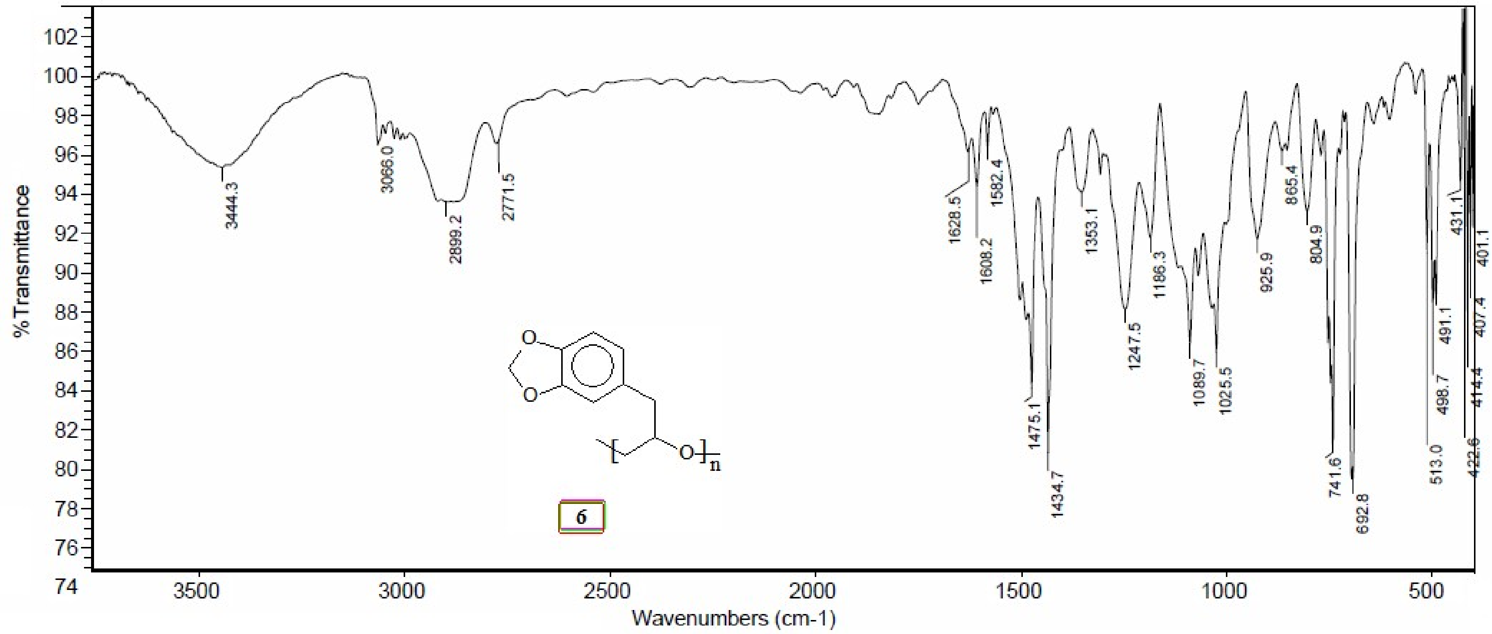

Fig. S7. IR spectrum of polymer **6**.

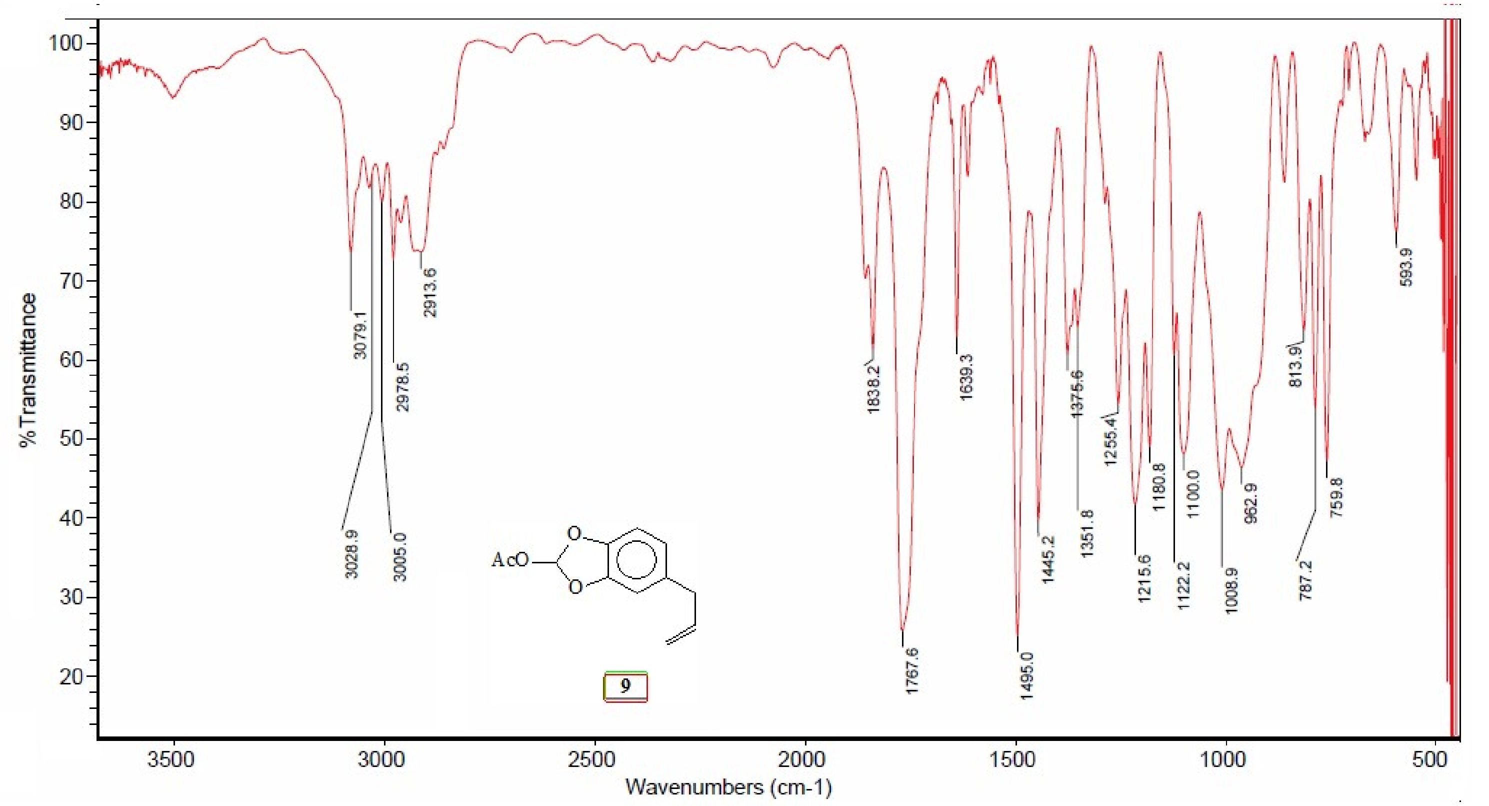

Fig. S8. IR spectrum of polymer **9**.

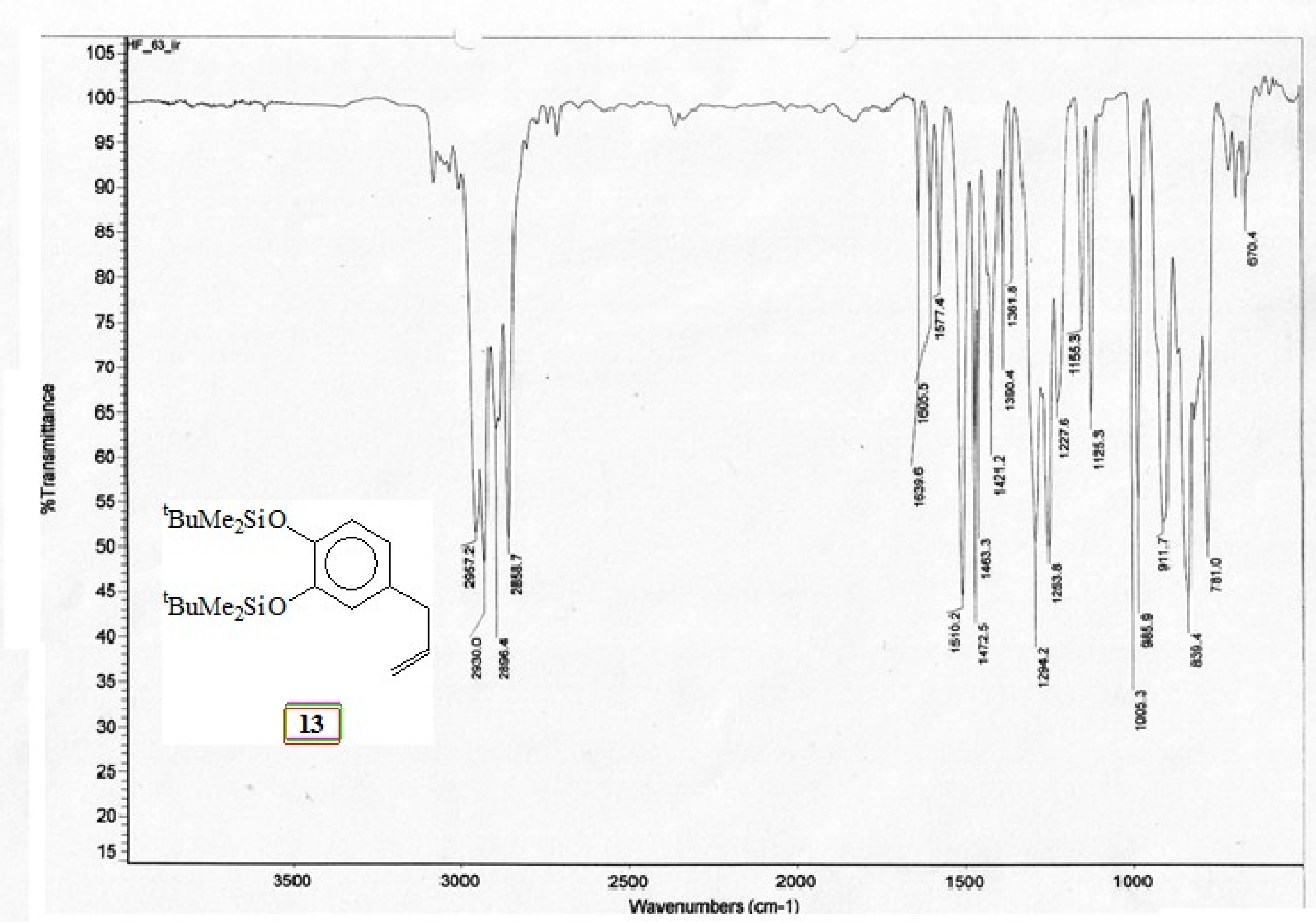

Fig. S9. IR spectrum of polymer **13**.

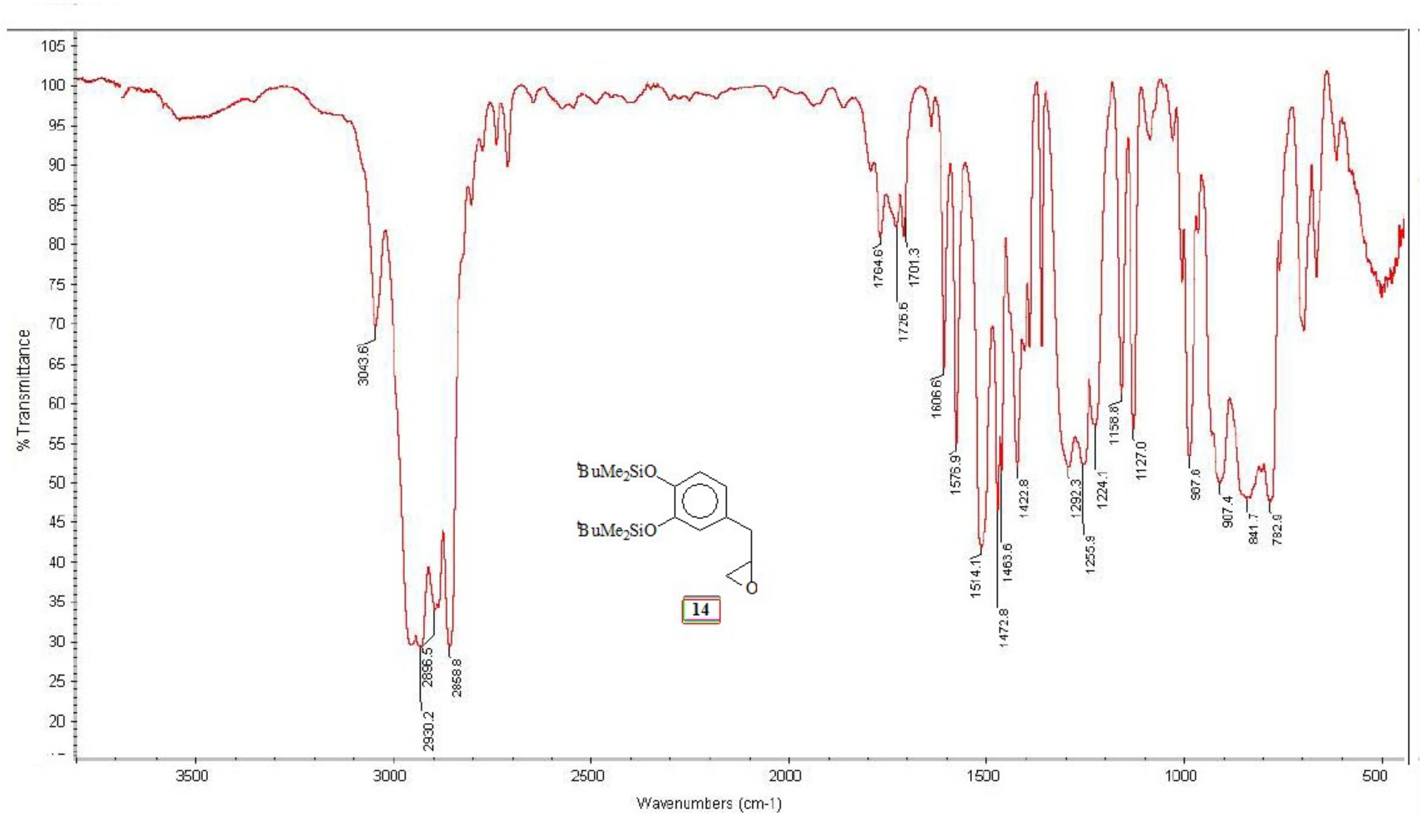

Fig. S10. IR spectrum of polymer **14**.

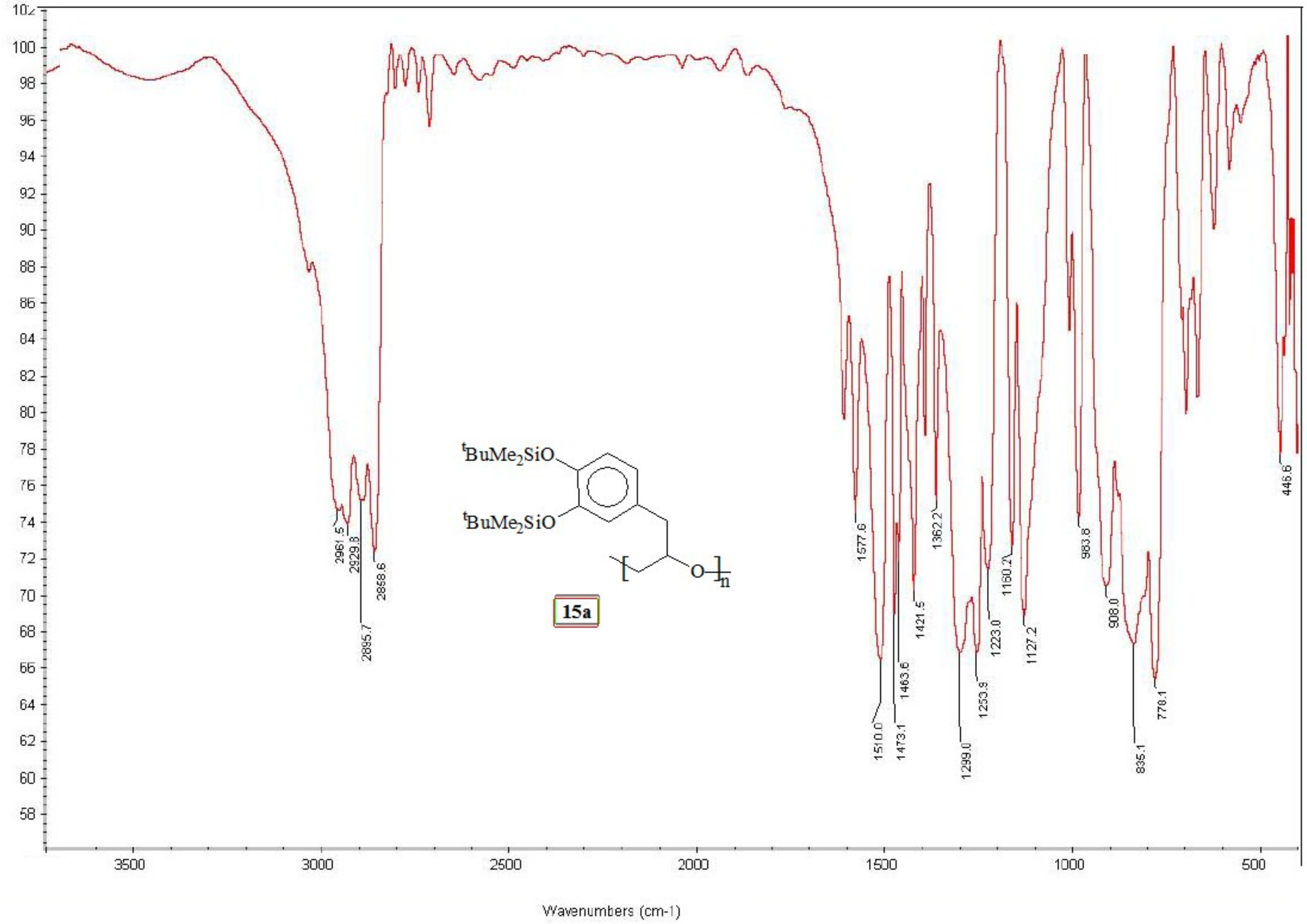

Fig. S11. IR spectrum of polymer **15a**.

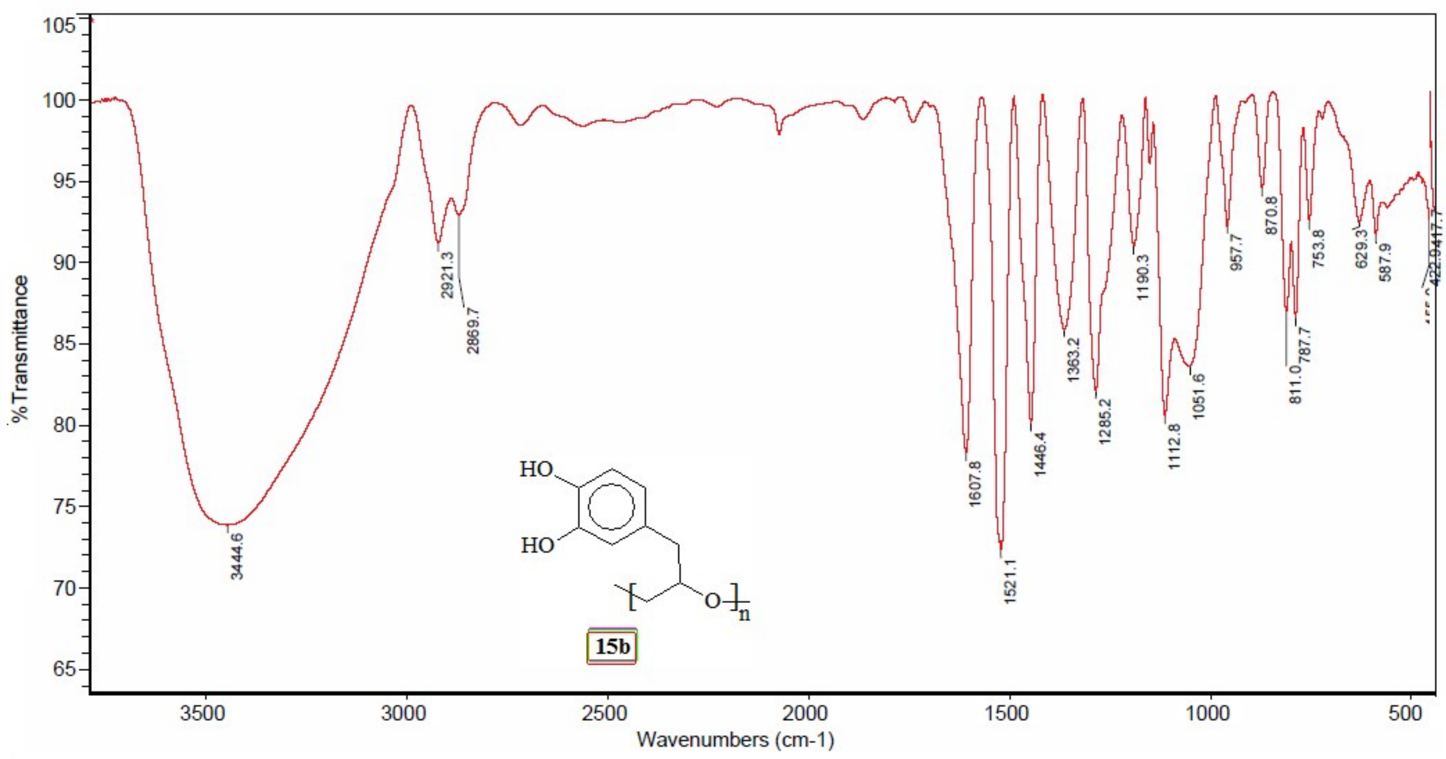

Fig. S12. IR spectrum of polymer **15b**.

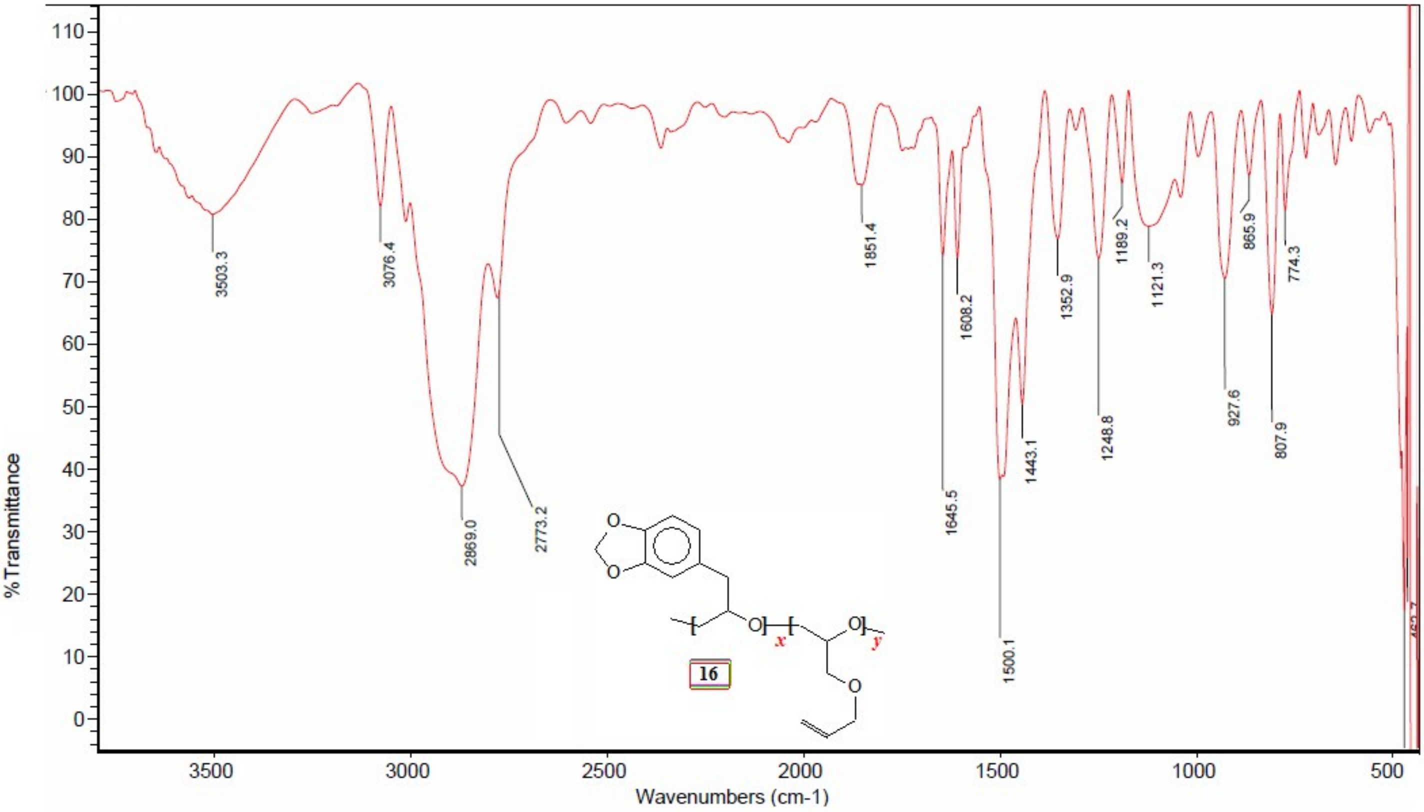

Fig. S13. IR spectrum of polymer **16**.

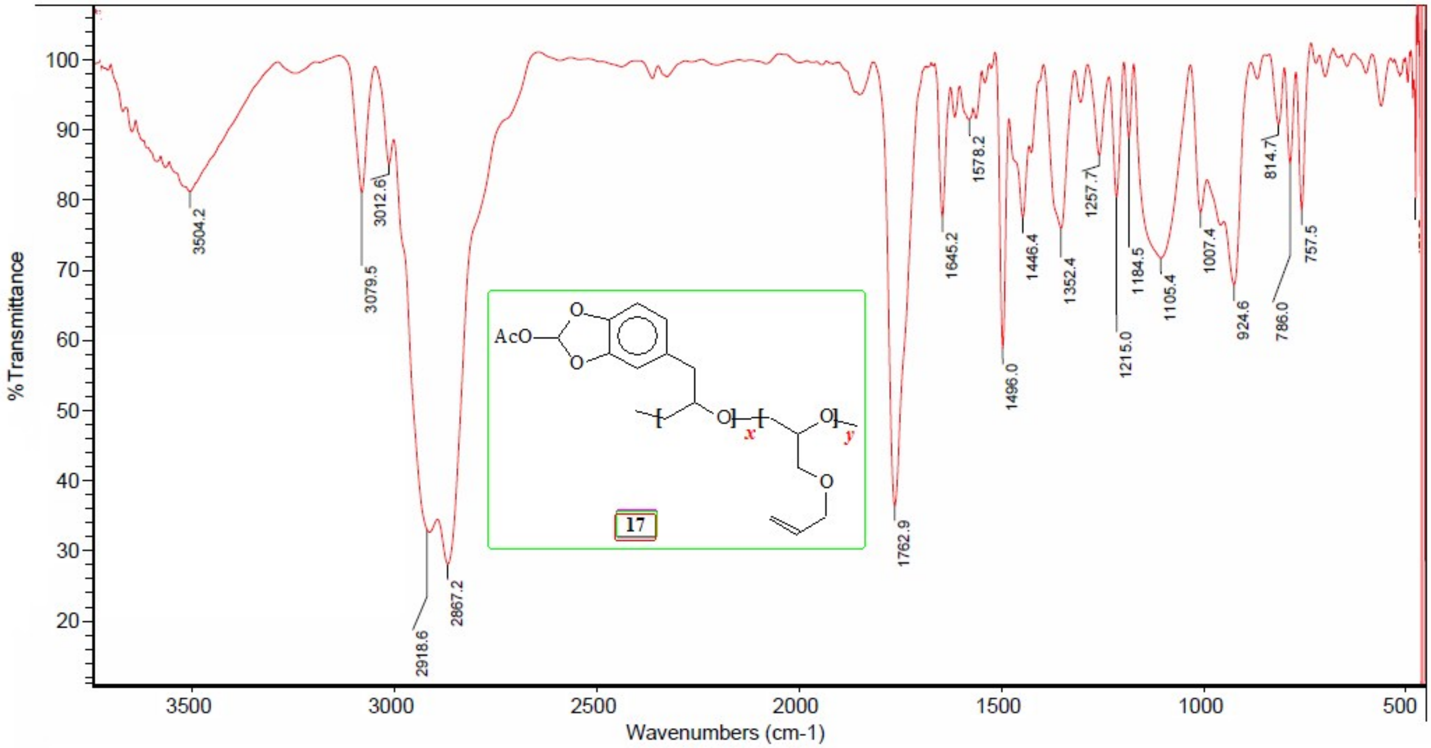

Fig. S14. IR spectrum of polymer **17**.

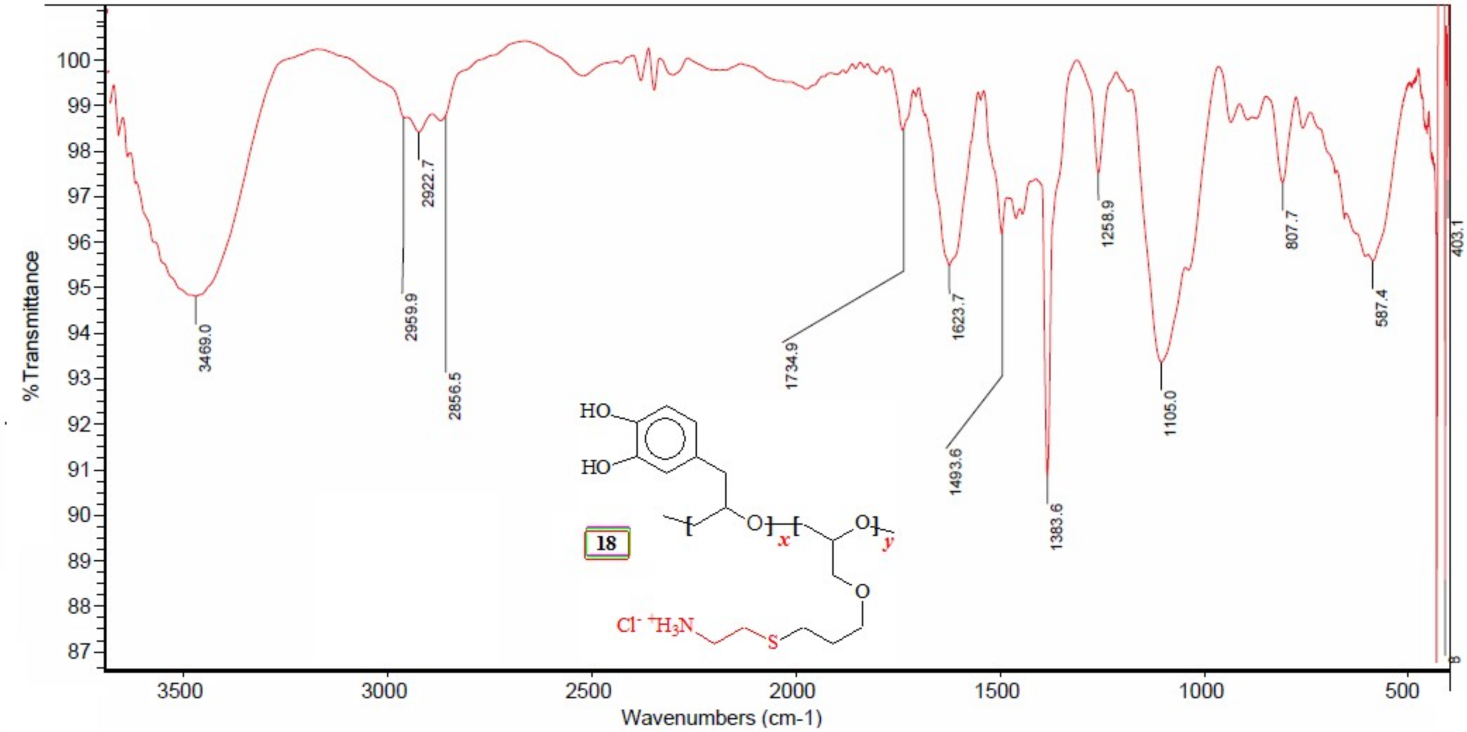

Fig. S15. IR spectrum of polymer **18**.

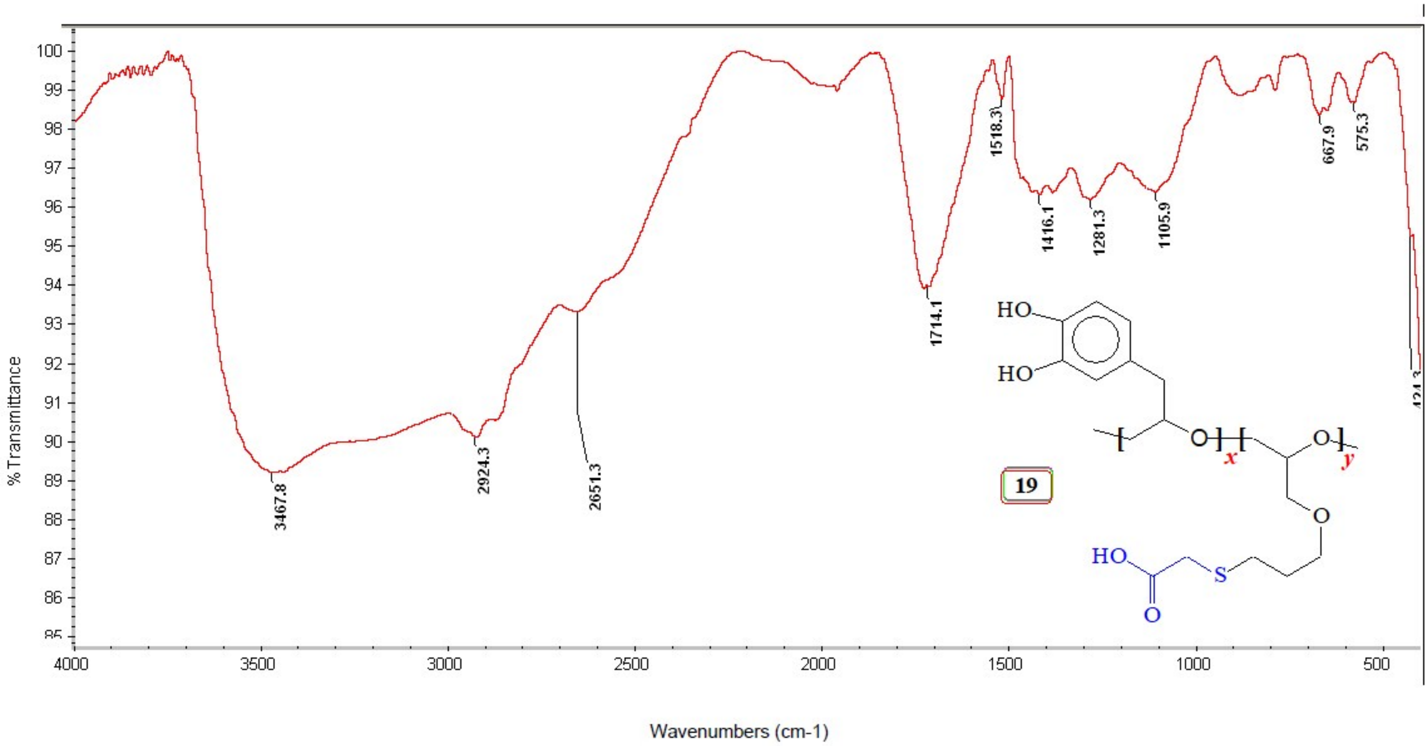

Fig. S16. IR spectrum of polymer **19**.

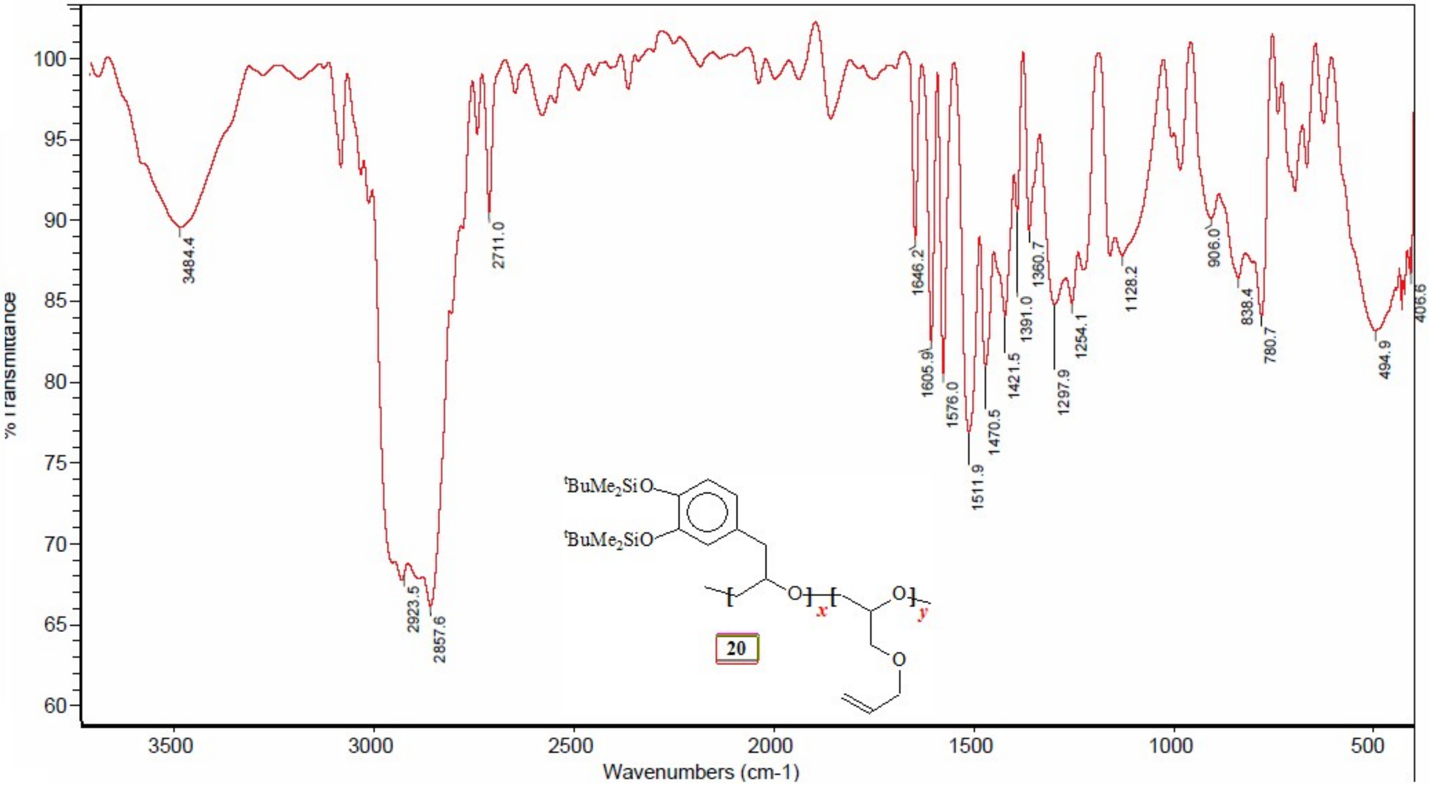

Fig. S17. IR spectrum of polymer **20**.

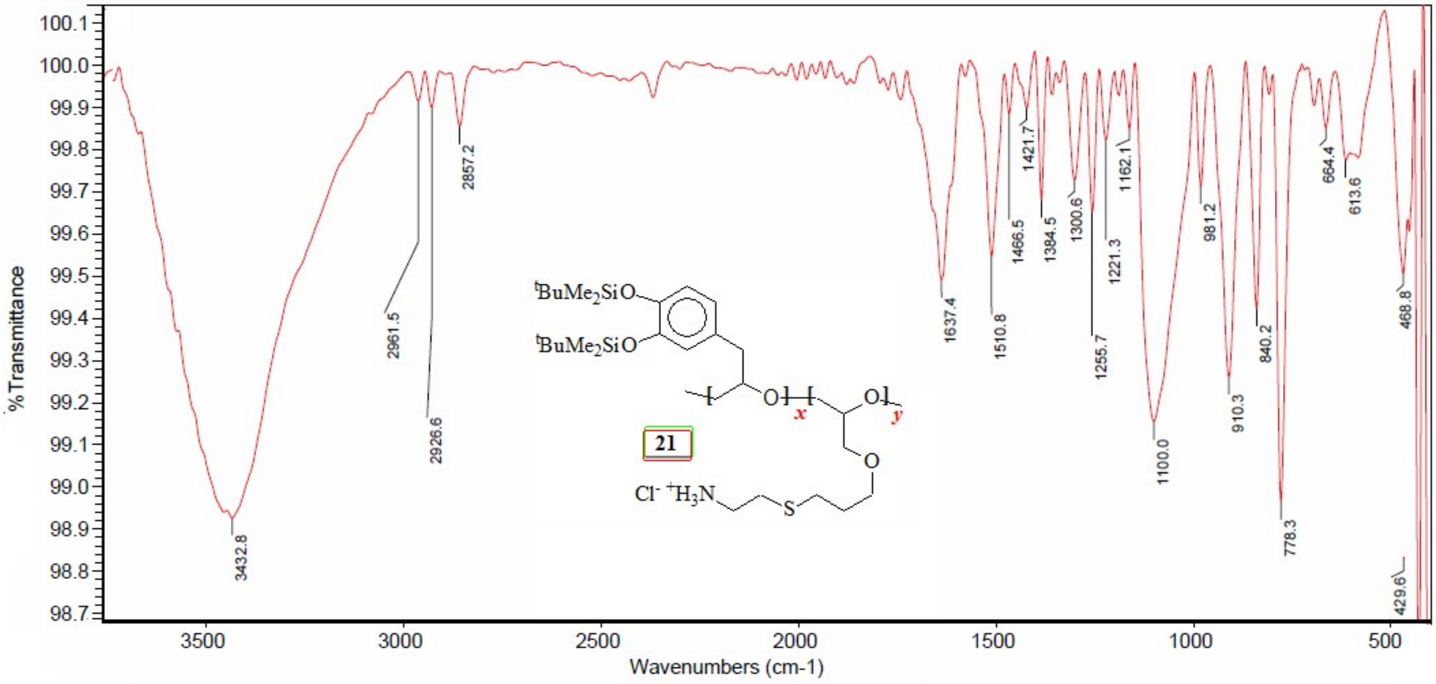

Fig. S18. IR spectrum of polymer **21**.

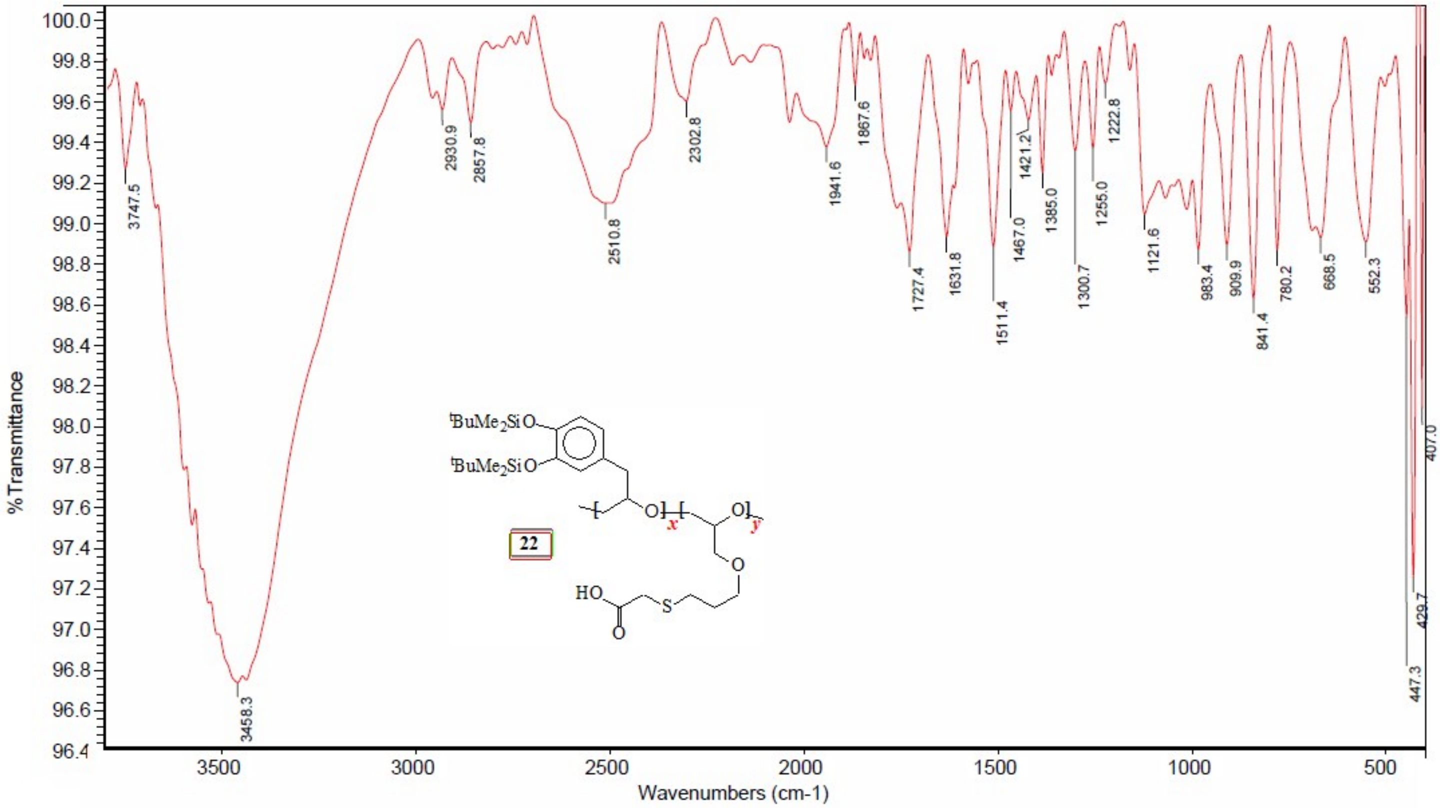

Fig. S19. IR spectrum of polymer **22**.

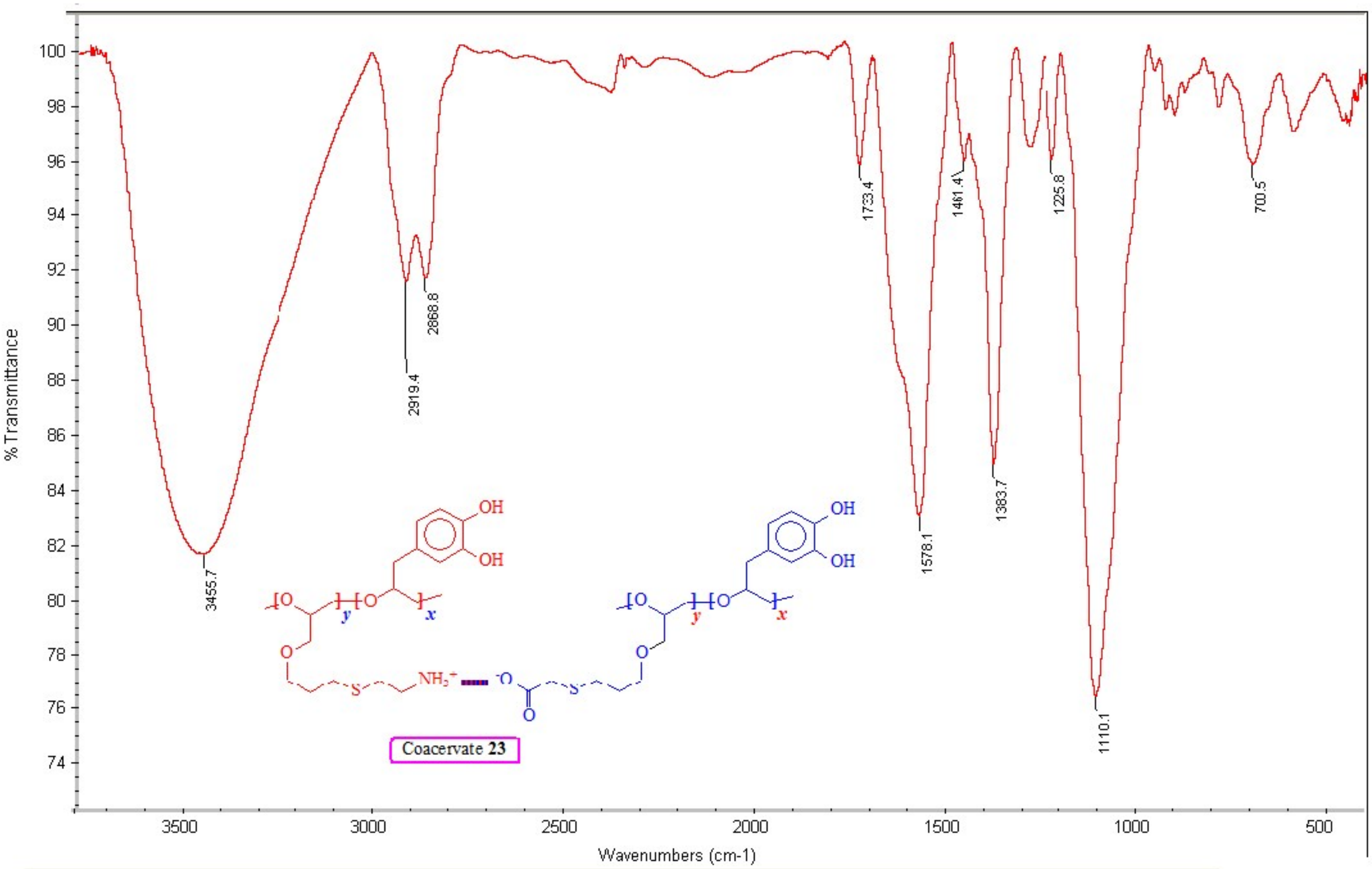

Fig. S20. IR spectrum of coacervate **23**.