Supporting Information

C−H Polyaddition of Dimethoxyarenes to Unconjugated Dienes by Rare Earth Catalysts

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Experimental Section

Experimental Section

General Procedure and Materials All manipulations of air and moisture-sensitive compounds were performed under a dry nitrogen atmosphere by use of standard Schlenk techniques or a nitrogen-filled Mbraun glovebox. Nitrogen was purified by being passed through a Dryclean column DC-A4 (4 Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. Norbornadiene and 1,9-decadiene were purchased from Kanto Chemical Co. Int and Tokyo Chemical Ind. Co. Ltd, dried over CaH_2, and vacuum-transferred prior to polymerization experiments. $[Ph_3C][B(C_6F_5)_4]$ was purchased from Strem Chemical Corporation and used without purification. Cp´Ln($CH_2C_6H_4NMe_2$-*o*)$_2$ (Cp´ = C_5Me_5, $C_5Me_4SiMe_3$; Ln = Sc, Y, Gd, Sm, Lu),[1-2] 1,4-divinylbenzene and 4,4′-divinylbiphenyl[3] were synthesized according to literatures. The deuterated solvents benzene-d_6 (99.6 atom % D), THF-d_8 (99.6 atom % D), $CDCl_3$ (99.8 atom % D), and 1,1,2,2-tetrachloroethane-d_2 (99.6 atom % D) were obtained from Kanto Chemical Co. Inc. and Cambridge Isotope. The NMR data of the polymers were obtained on a Bruker AVANCE III HD 500 NMR (FT, 500 MHz for ^{1}H; 125 MHz for ^{13}C) spectrometer at 120 °C or 26.8 °C with 1,1,2,2-$C_2D_2Cl_4$ as a solvent. The molecular weights and the molecular weight distributions of all the copolymers were determined at 145 °C by high temperature gel permeation chromatography (HT-GPC) on a HLC-8121GPC/HT apparatus (Tosoh Corporation). 1,2-Dichlorobenzene (DCB) was employed as an eluent at a flow rate of 1.0 mL/min. The molecular weights and the molecular weight distributions of copoly(1,4-dimethoxybenzene/1,9-decadiene) was determined at 40 °C by gel permeation chromatography (GPC) on a HLC-8320 GPC apparatus (Tosoh Corporation), THF was employed as an eluent at a flow rate of 0.35 mL/min. The calibration was made by use of polystyrene standard (Tosoh Corporation). The DSC measurements were performed on a DSC 6220 (S Ⅱ Corporation) at a rate of 10 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to 300 °C (or 250 °C), cooling at 10 °C/min to –10 °C (or –100 °C), and then recording the second DSC scan.

A Typical Procedure for the Polyaddition of dimethoxybenzene to norbornadiene (Table S1, Entry 1). In a glovebox, a toluene solution (1.0 mL) of $[Ph_3C][B(C_6F_5)_4]$ (23.1 mg, 0.025 mmol) was slowly added to a toluene solution (1.0 mL) of $C_5Me_5Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (11.2 mg, 0.025 mmol) under magnetic stirring in a 20 mL Schlenk tube. After the mixture was stirred for 5 min, dimethoxybenzene (138 mg, 1.0 mmol) and norbornadiene (92 mg, 1.0 mmol) were added. The Schlenk tube was sealed and taken out of the glovebox and then heated at 70 °C for 24 hours. The polymerization was quenched by addition of methanol (50 mL, containing 5% butylhydroxytoluene (BHT) as a stabilizing agent). Then the mixture was poured into methanol (200 mL) to precipitate the polymer product. The precipitated polymer was dried under vacuum at 60 °C to a constant weight (230 mg, 100% yield).

The experimental results of the copolymerization of 1,4-dimethoxybenzene with 2,5-norbornadiene by various rare earth catalysts are summarized in Table S1.

Table S1. Copolymerization of 1,4-dimethoxybenzene with 2,5-norbornadiene by various rare earth catalysts[a]

Entry	Ln[a]	Yield[b] (%)	2,5/2,6[c]	M_n ($\times 10^3$)[d]	M_w/M_n[d]	T_g[e] (°C)
1	**1-Sc**	100	1.21	9.80	2.00	199
2	**1-Y**	0	-	-	-	-
3	**1-Sm**	0	-	-	-	-
4	**1-Gd**	0	-	-	-	-
5	**1-Lu**	19	n.d.	0.62	1.79	n.d.
6	**2-Sc**	64	1.20	1.63	1.59	127
7	**2-Y**	0	-	-	-	-

[a]Reaction conditions: [M] (0.025 mmol), $[Ph_3C][B(C_6F_5)_4]$ (0.025 mmol), 1,4-dimethoxybenzene (1 mmol): norbornadiene (1 mmol), toluene (2 mL), 70 °C, 24 h; [b]Isolated yield; [c]Calculated from the ^{13}C NMR spectrum; [d]Determined by GPC against polystyrene standards at 145 °C in *o*-dichlorobenzene; [e]Measured by DSC.

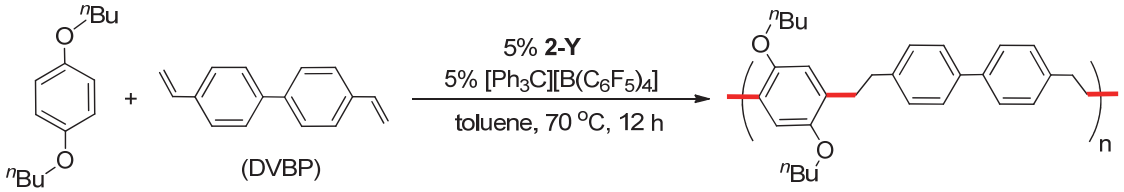
(1) Li, X.; Nishiura, M.; Mori, K.; Mashiko, T.; Hou, Z. *Chem. Commun.* **2007**, 4137.

(2) Nishiura, M.; Baldamus, J.; Shima, T.; Mori, K.; Hou, Z. *Chem. Eur. J.* **2011**, *17*, 5033.

(3) Ludwiczak, M.; Majchrzak, M.; Marciniec, B.; Kubicki, M. *J. Organomet. Chem.* **2011**, *696*, 1456.

The copolymerization of 1,4-dibutoxybenzene (DBB) with 4,4'-divinylbiphenyl (DVBP) (Scheme S1) and 1,4-dimethoxybenzene (DMB) with 1,9-decadiene (Scheme S2) were carried out in a similar fashion.

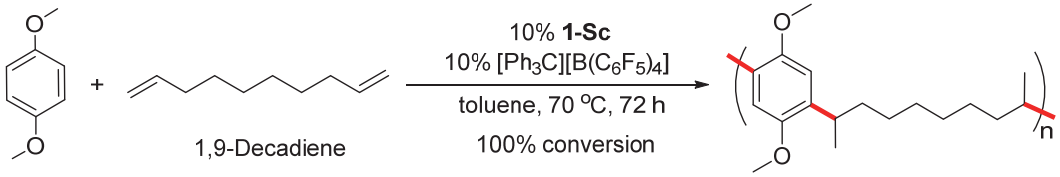
Scheme S1. C-H Polyaddition of 1,4-dibutoxybenzene to 4,4′-divinylbiphenyl



(DBB)

yield 67%, M_n = 2570, M_w/M_n = 2.61

Scheme S2. C-H Polyaddition of 1,4-dimethoxybenzene to 1,9-decadiene



DMB

26% (MeOH-insoluble), M_n = 2160, M_w/M_n = 1.23, T_g = -16 °C
74% (MeOH-soluble), M_n = 470, M_w/M_n = 2.27

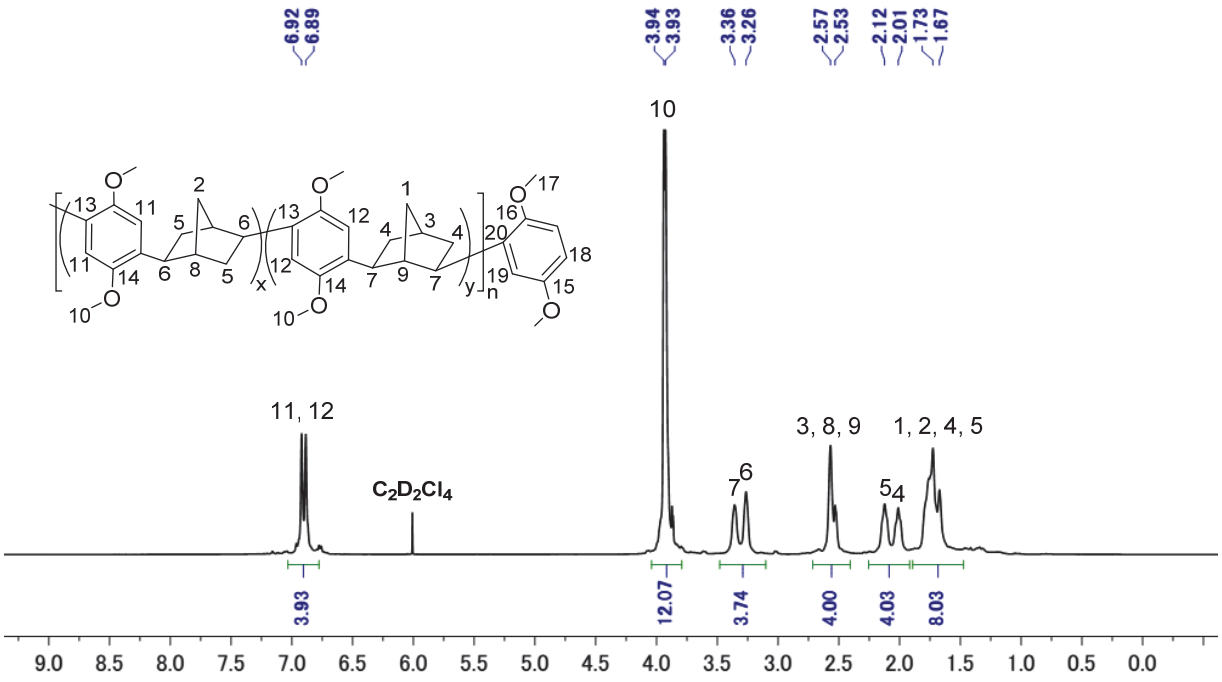


Figure S1. ^{1}H NMR spectrum (500 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/ norbornadiene) (Table 1, Entry 6)

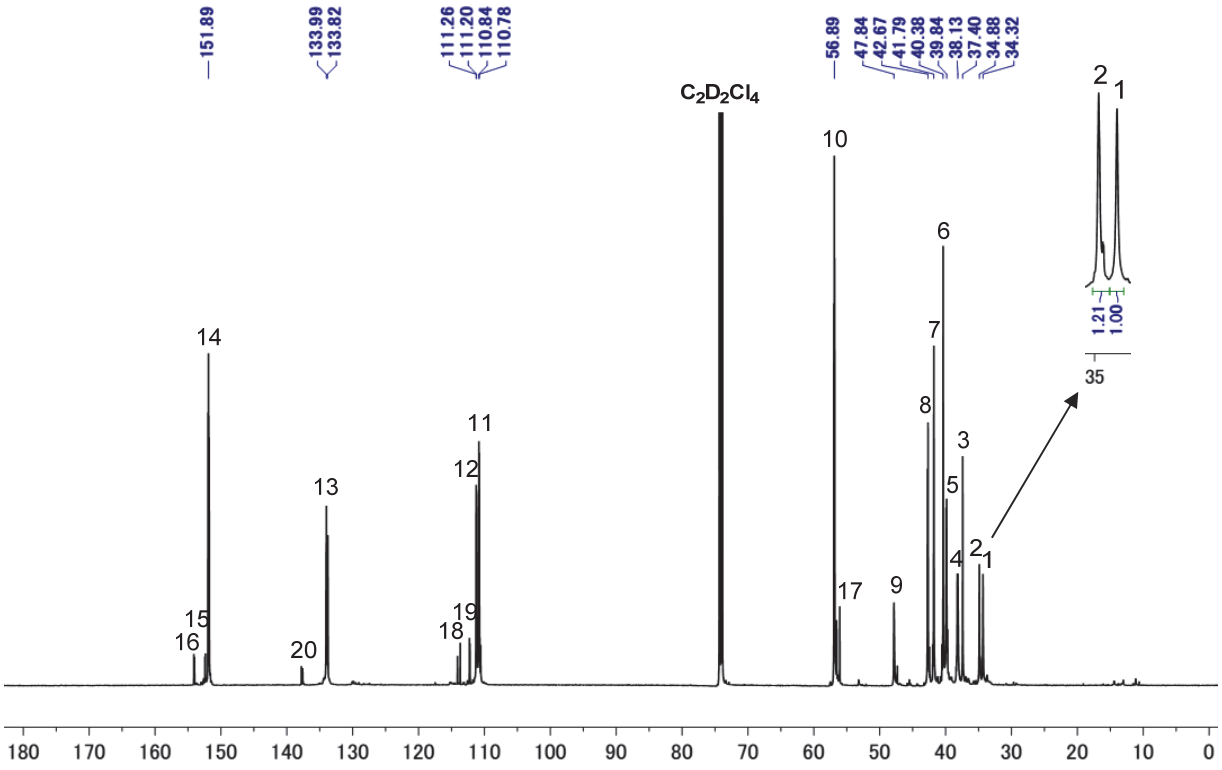


Figure S2. ^{13}C NMR spectrum (125 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/ norbornadiene) (Table 1, Entry 6)

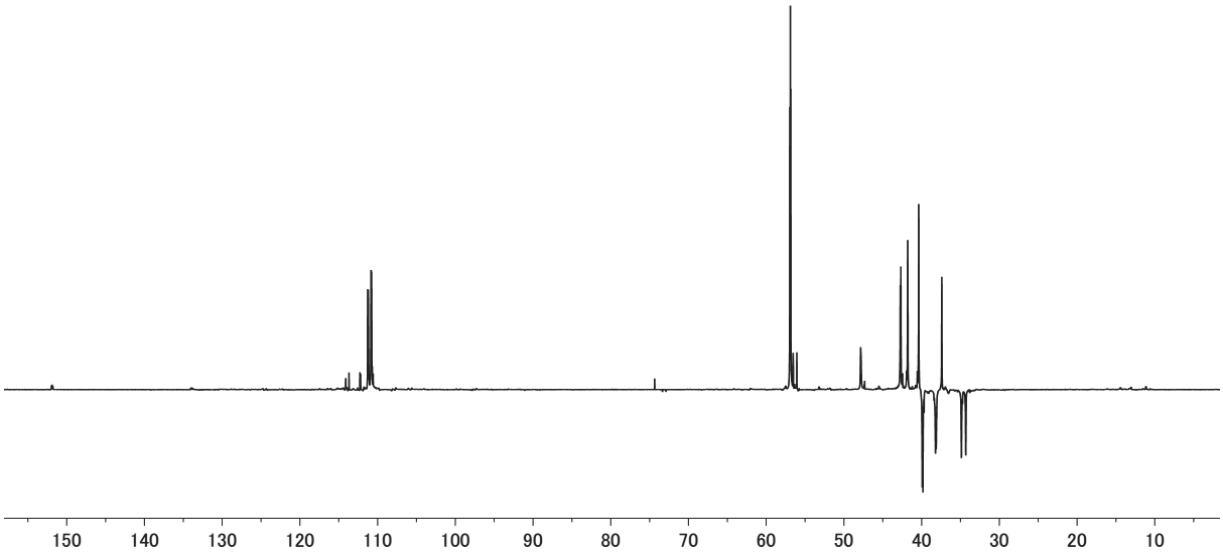


Figure S3. DEPT135-^{13}C spectrum (125 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/ norbornadiene) (Table 1, Entry 6)

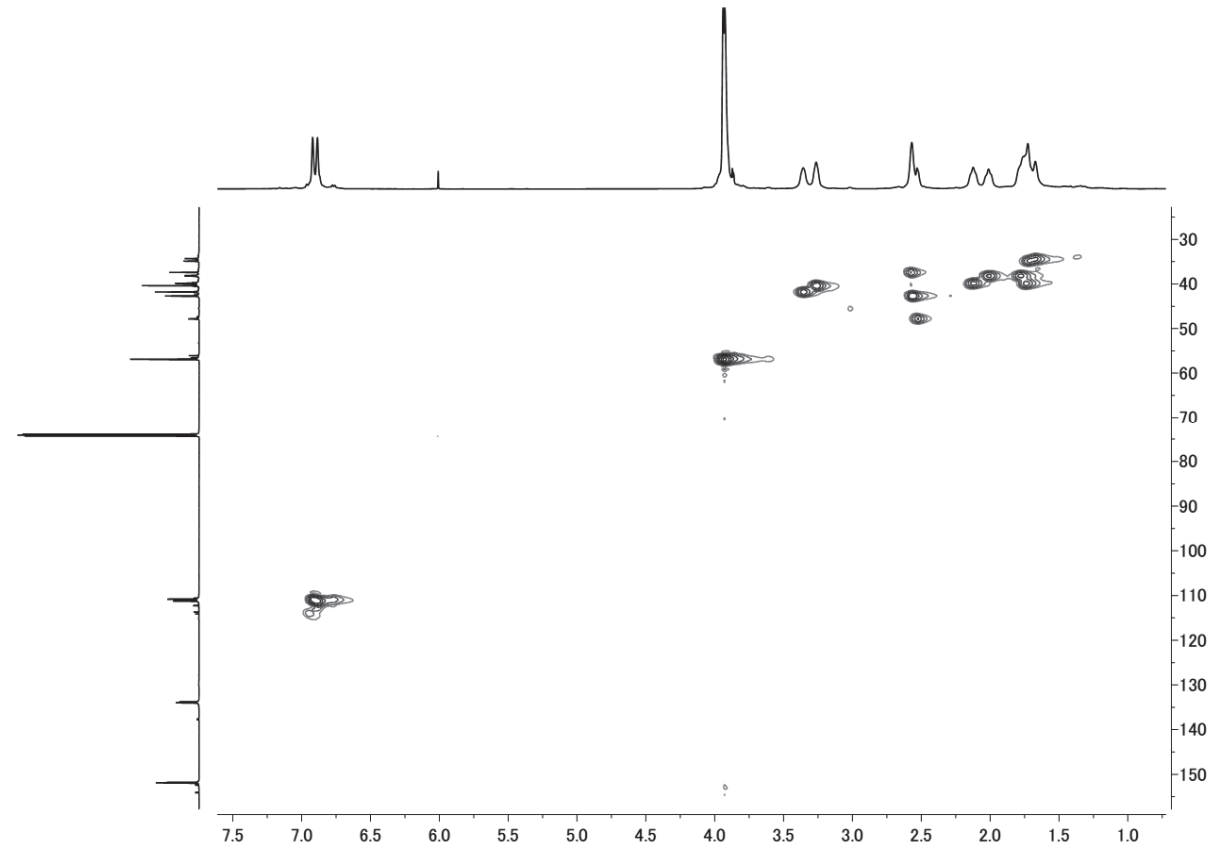


Figure S4. HSQC spectrum ($C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/norbornadiene) (Table 1, Entry 6)

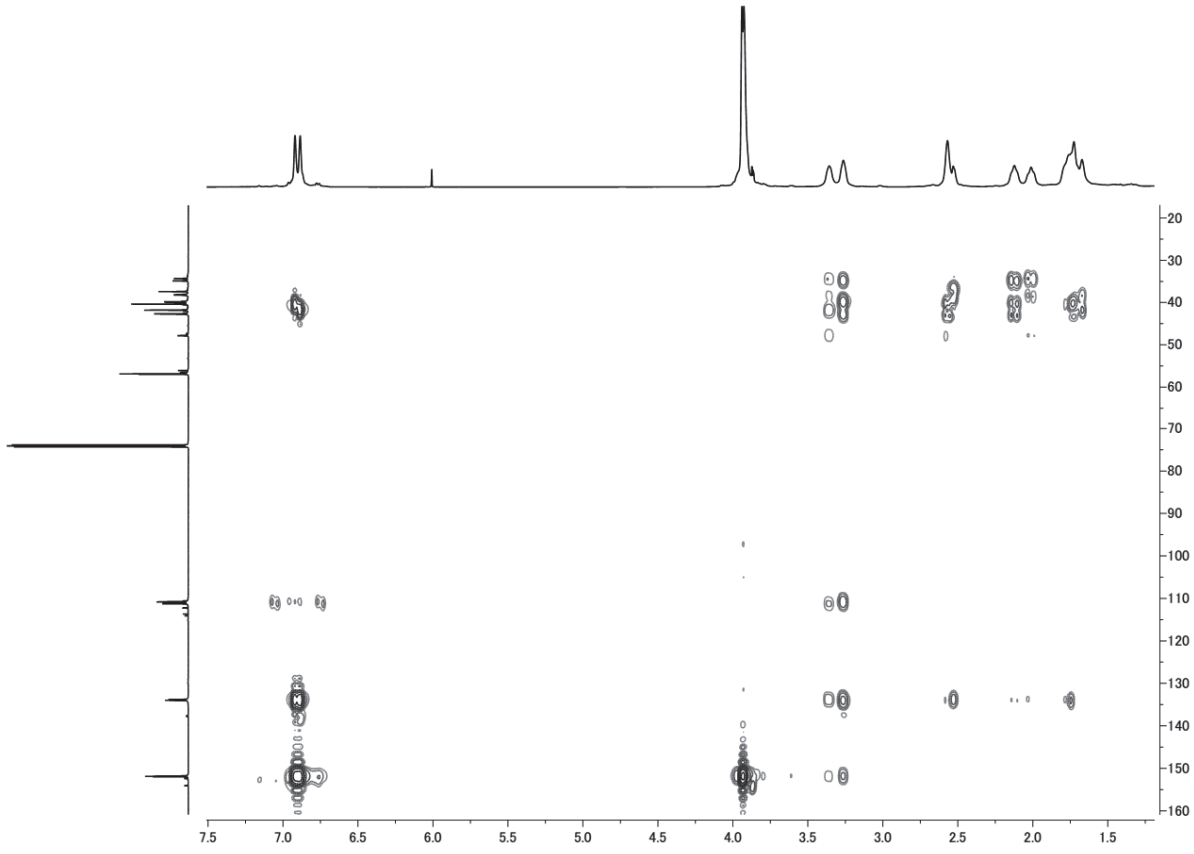


Figure S5. HMBC spectrum ($C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/norbornadiene) (Table 1, Entry 6)

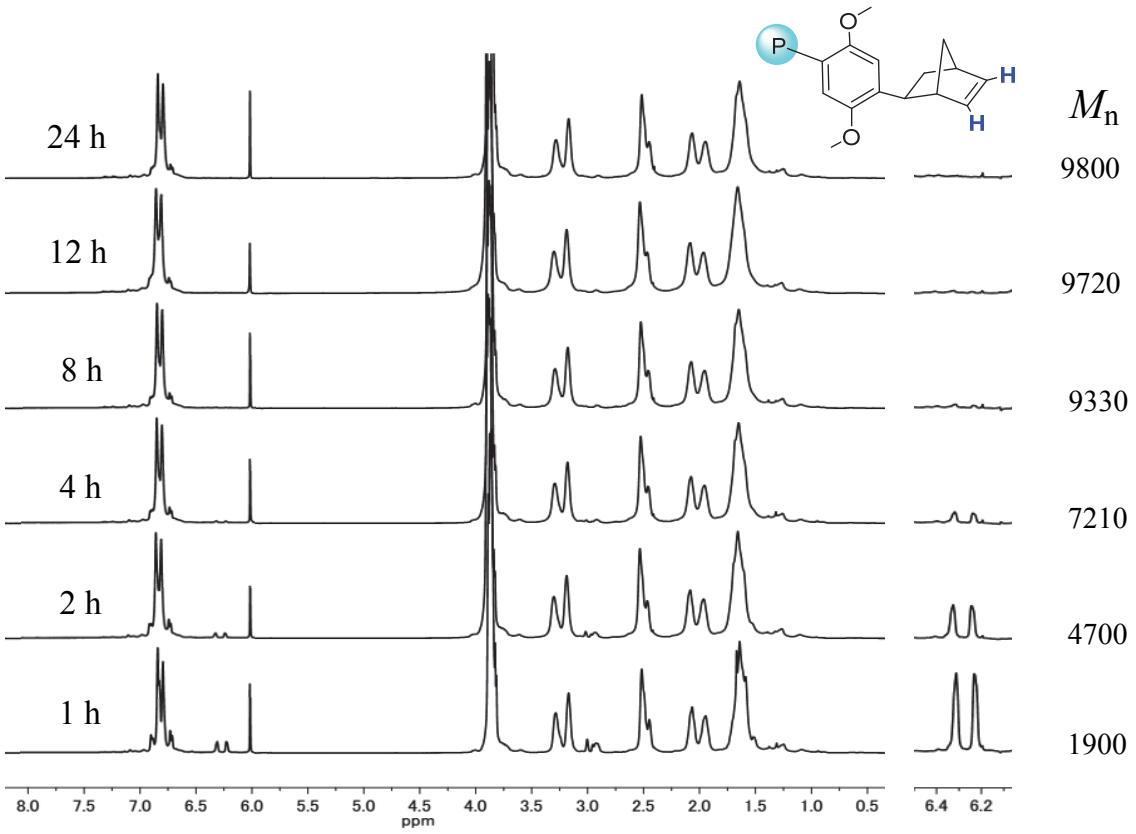


Figure S6. ^{1}H NMR spectrum of copoly(1,4-dimethoxybenzene/norbornadiene) in different polymerization time (Table 1, Entries 1-6)

The ^{1}H-NMR has shown the detailed information about the resultant polymers in various polymerization times when the monomer/catalyst ratio was 40. The peaks between 6.1-6.5 ppm which assigned to the double bond proton in the norbornadiene unit as the chain end group became weaker gradually along with the polymerization time and the increase of M_n.

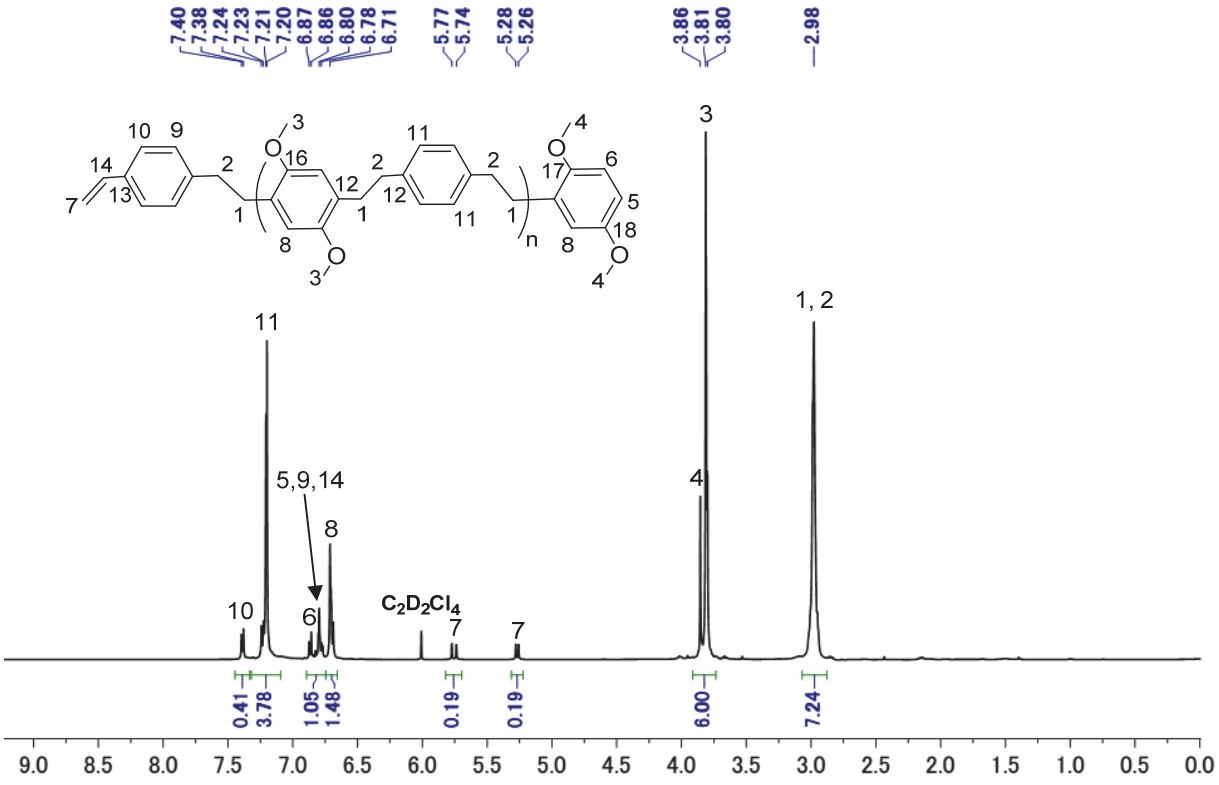


Figure S7. ^{1}H NMR spectrum (500 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/1,4-divinylbenzene) (Table 2, Entry 3)

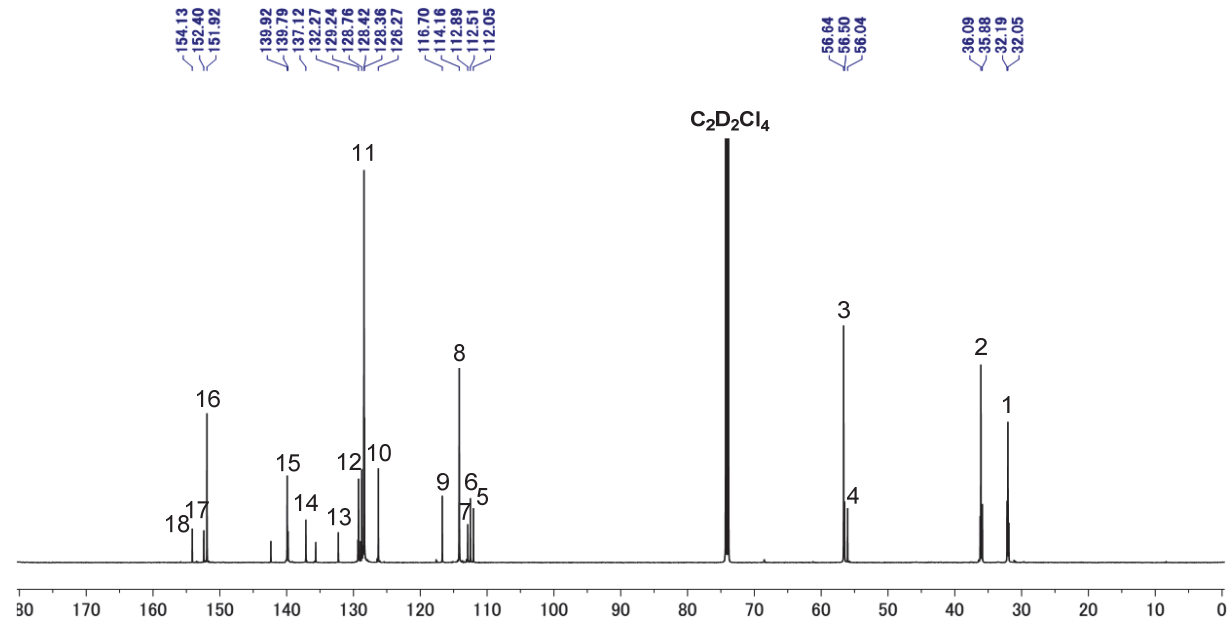


Figure S8. ^{13}C NMR spectrum (125 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/1,4-divinylbenzene) (Table 2, Entry 3)

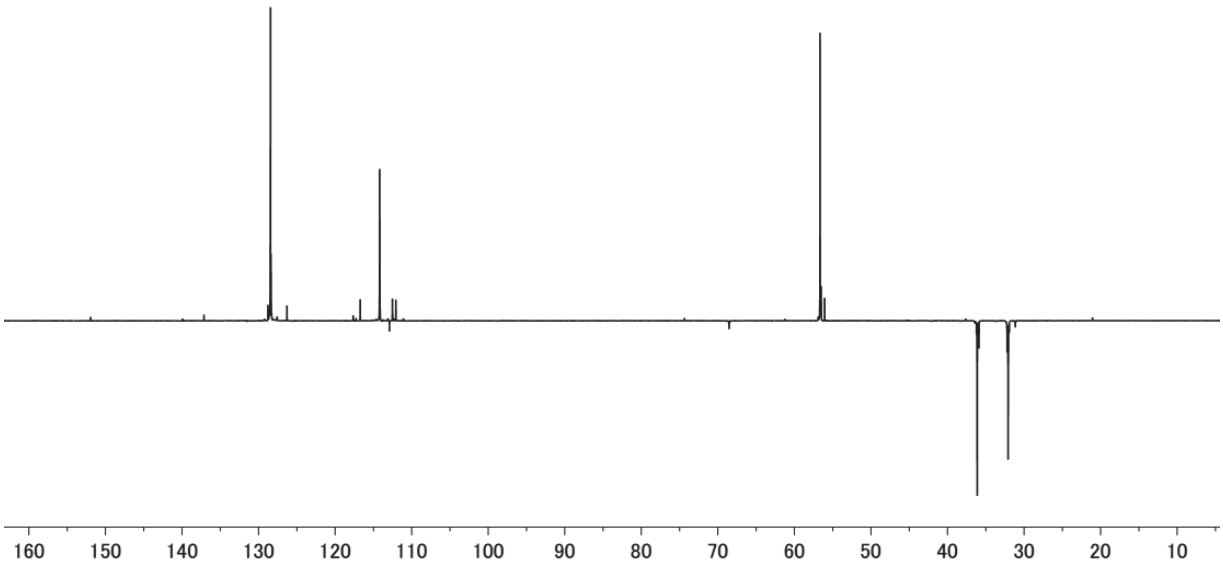


Figure S9. DEPT135-^{13}C spectrum (125 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/1,4-divinylbenzene) (Table 2, Entry 3)

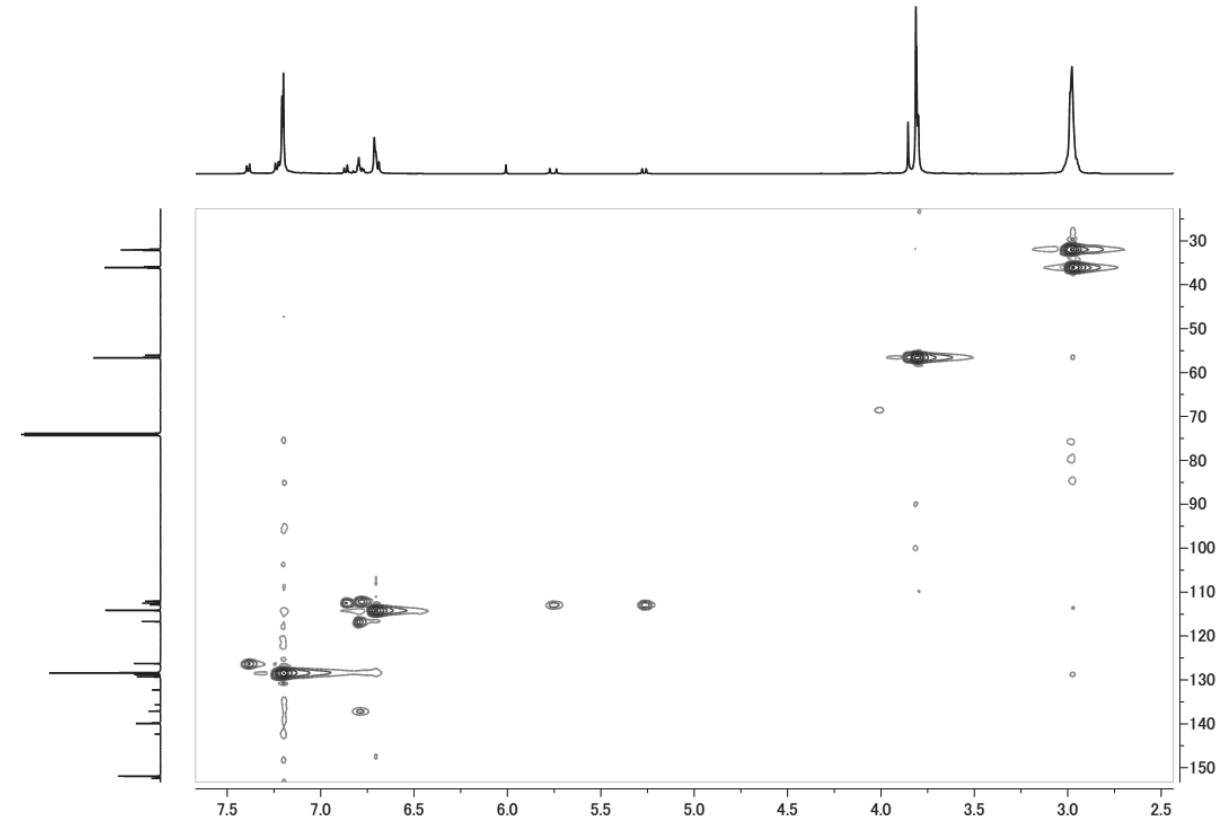


Figure 10. HSQC spectrum ($C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/1,4-divinylbenzene) (Table 2, Entry 3)

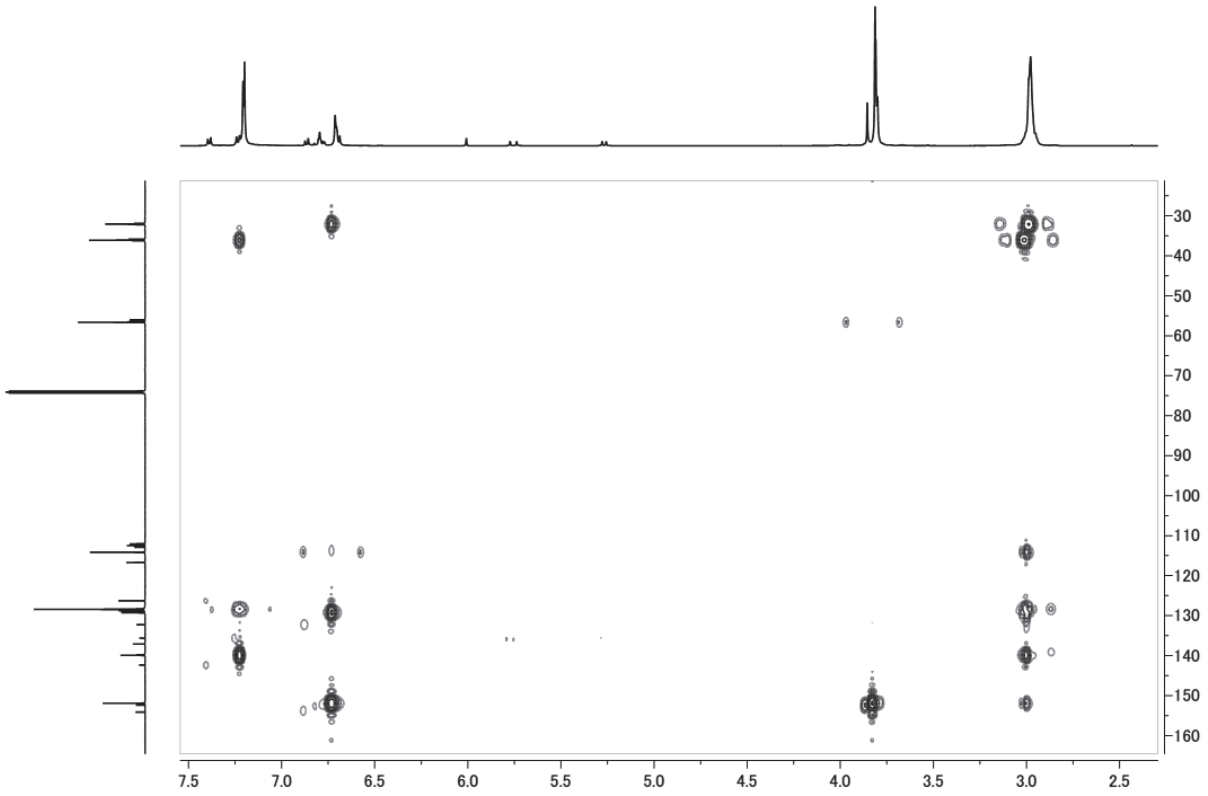


Figure S11. HMBC spectrum ($C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/1,4-divinylbenzene) (Table 2, Entry 3)

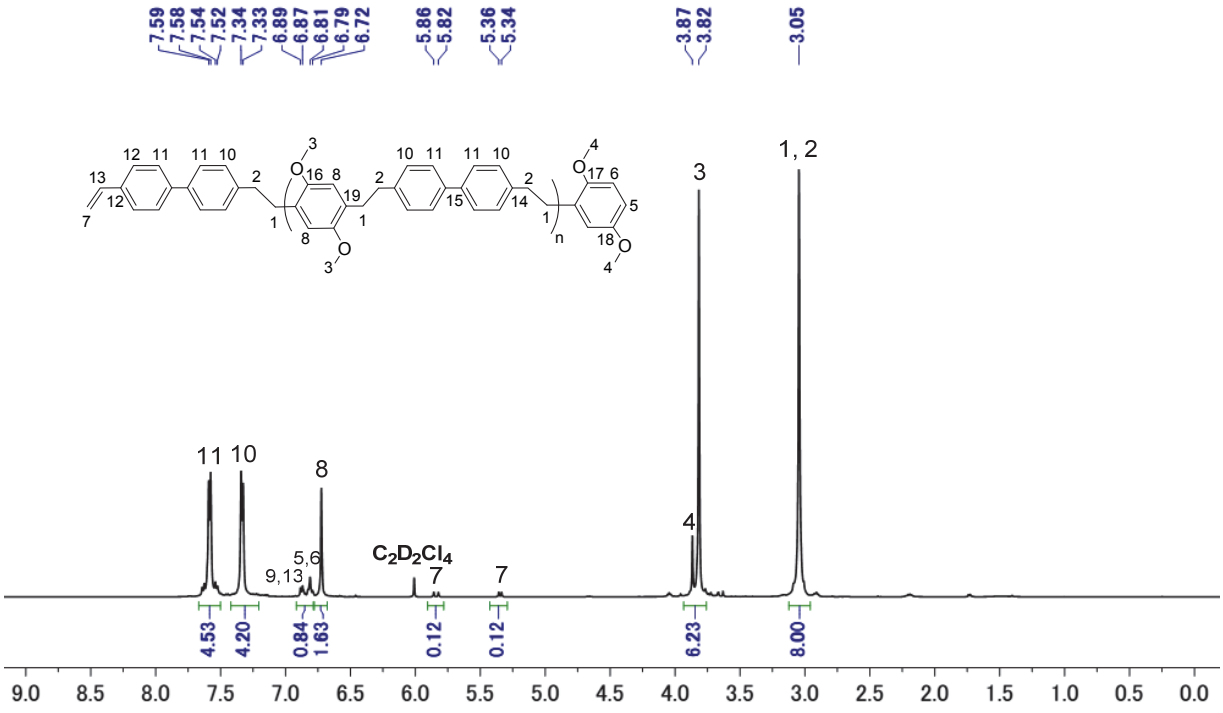


Figure S12. ^{1}H NMR spectrum (500 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/4,4′-divinylbiphenyl)

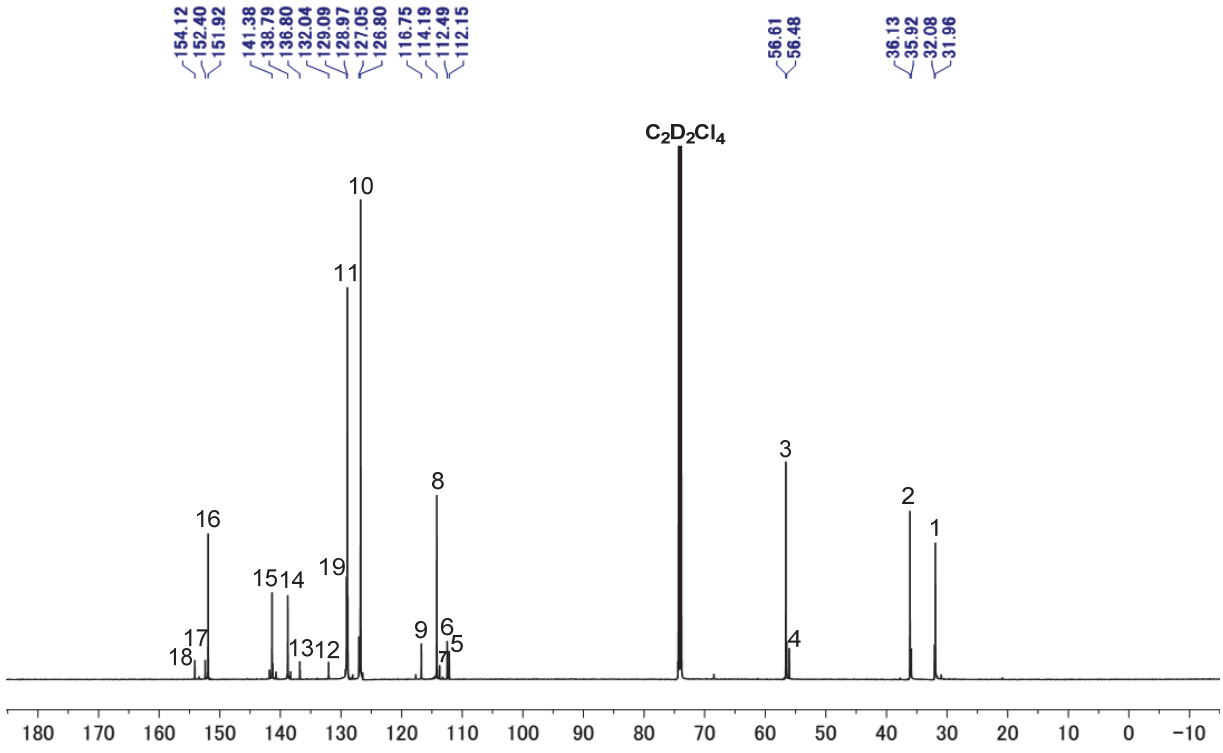


Figure S13. ^{13}C NMR spectrum (125 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/4,4′-divinylbiphenyl)

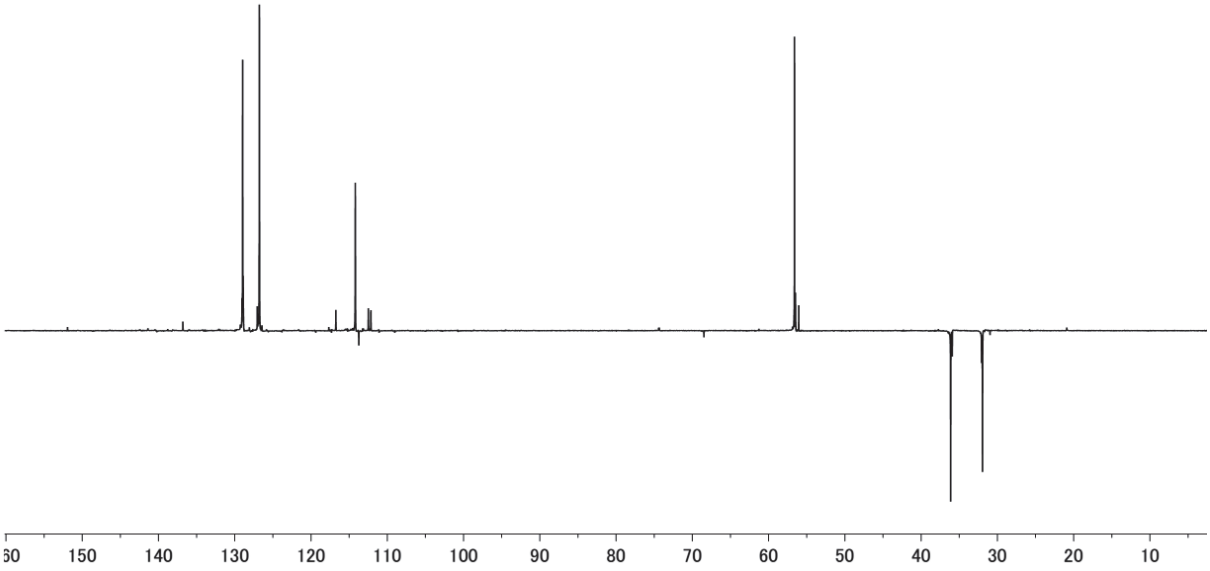


Figure S14. DEPT135-^{13}C spectrum (125 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/4,4′-divinylbiphenyl)

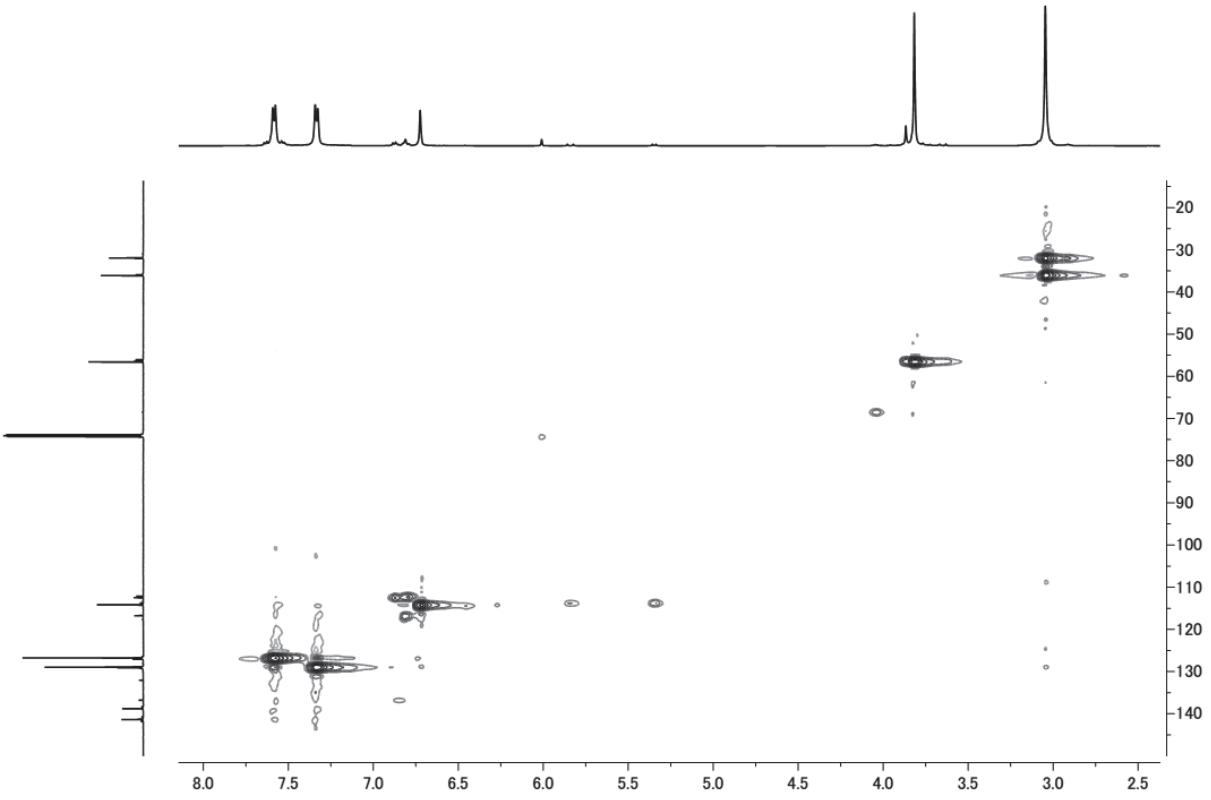


Figure S15. HSQC spectrum ($C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/4,4′-divinylbiphenyl)

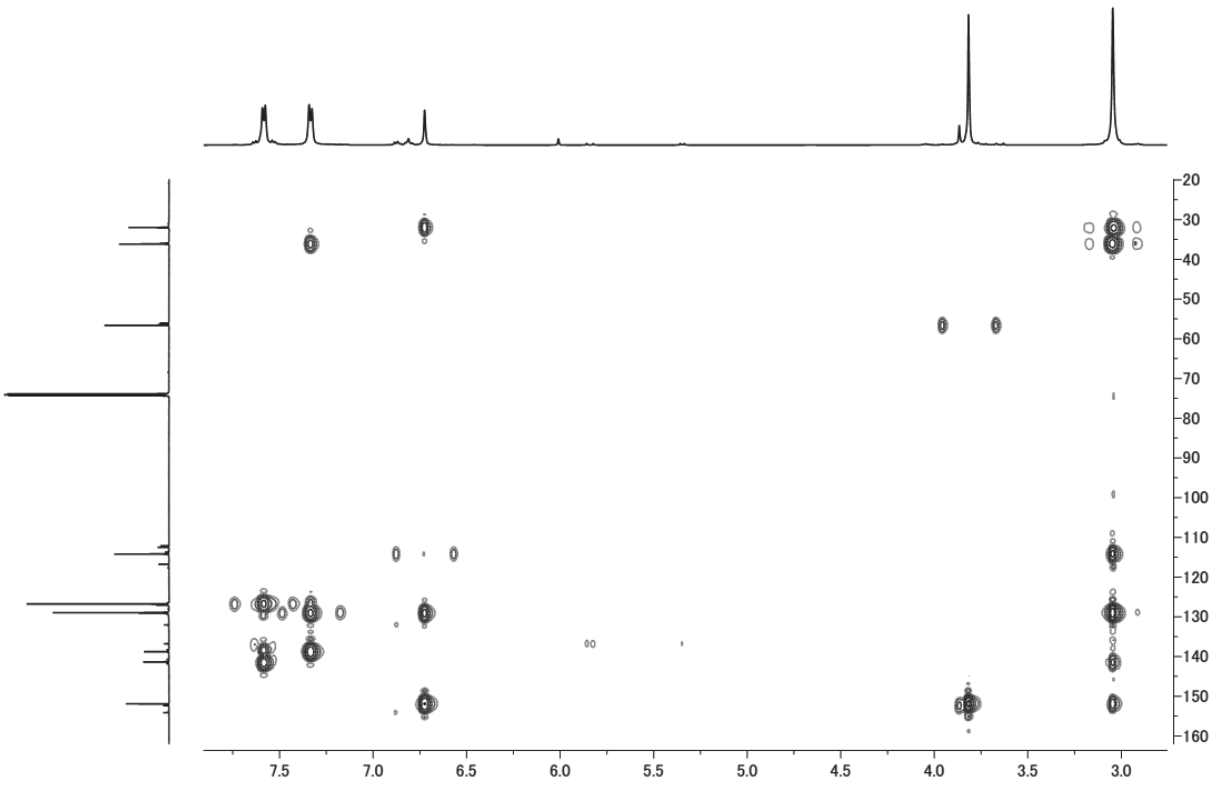


Figure S16. HMBC spectrum ($C_2D_2Cl_4$, 120 °C) of copoly(1,4-dimethoxybenzene/4,4′-divinylbiphenyl)

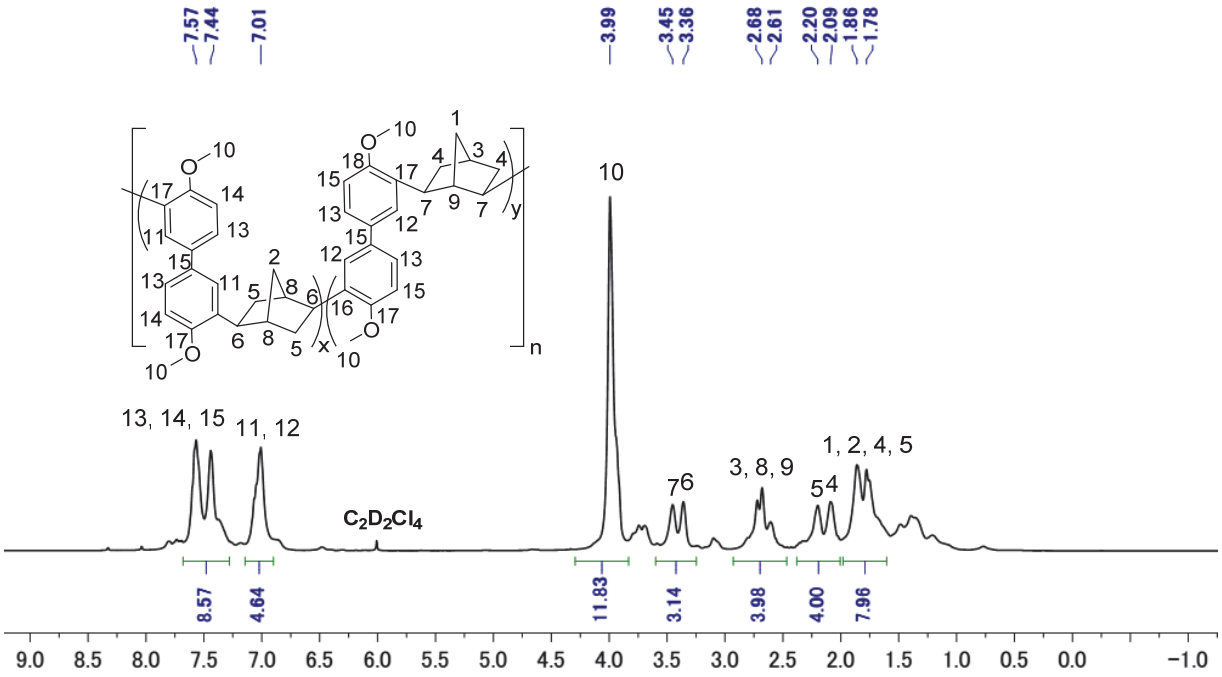


Figure S17. ^{1}H NMR spectrum (500 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(4,4′-dimethoxybiphenyl/ norbornadiene)

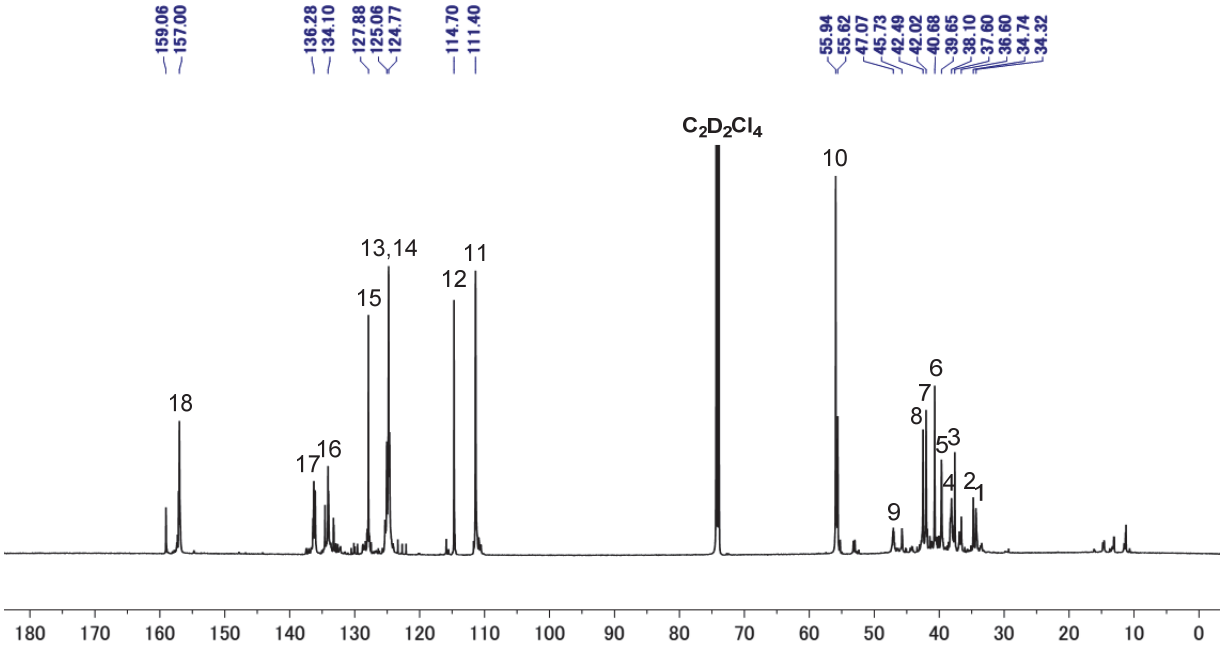


Figure S18. ^{13}C NMR spectrum (125 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(4,4′-dimethoxybiphenyl/ norbornadiene)

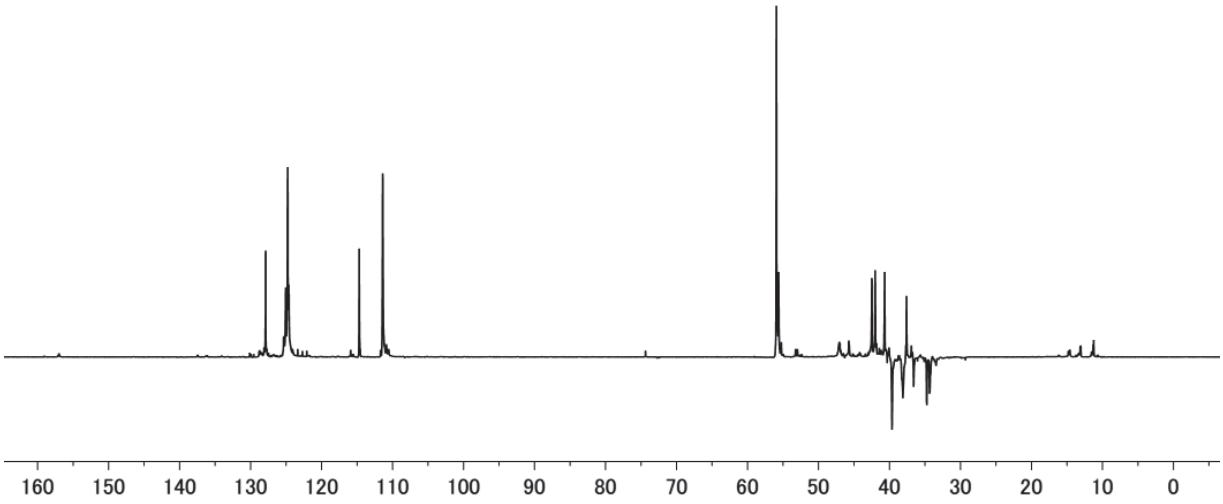


Figure S19. DEPT135-^{13}C spectrum (125 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(4,4′-dimethoxybiphenyl/ norbornadiene)

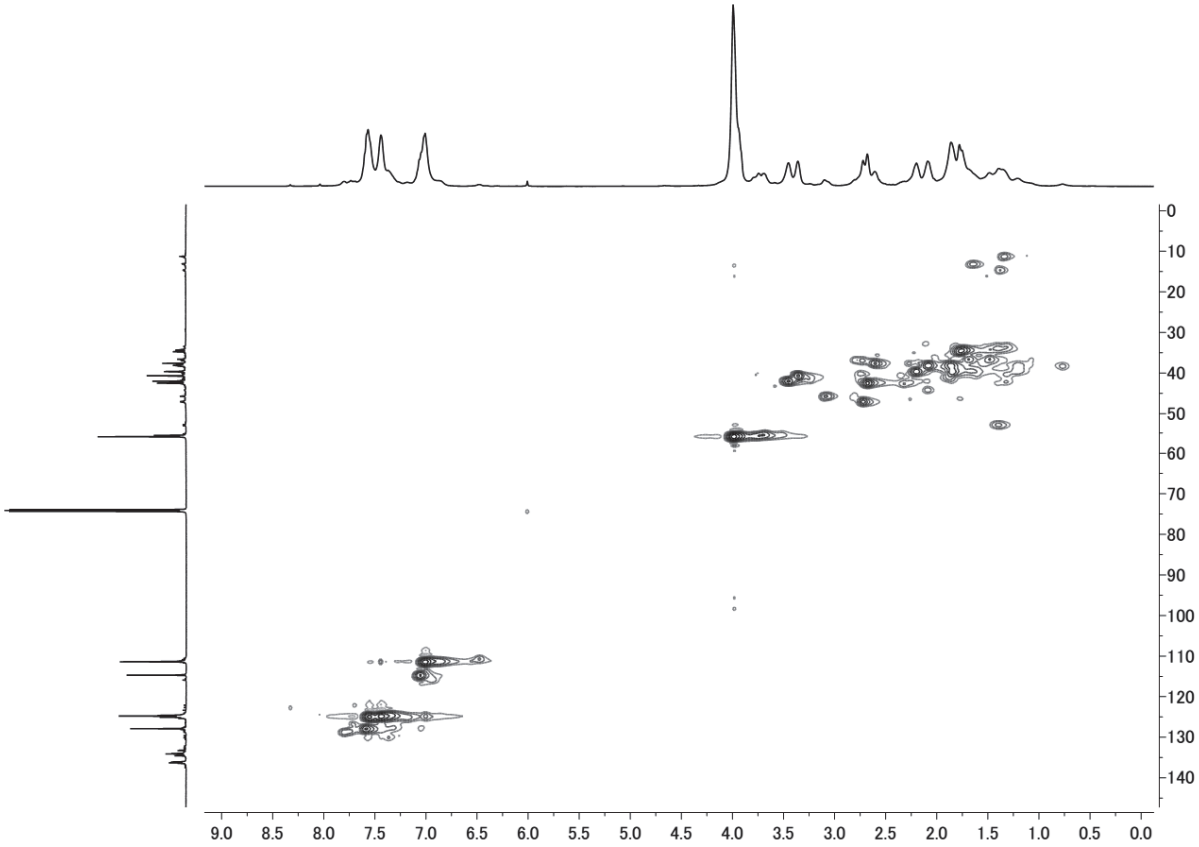


Figure S20. HSQC spectrum ($C_2D_2Cl_4$, 120 °C) of copoly(4,4′-dimethoxybiphenyl/norbornadiene)

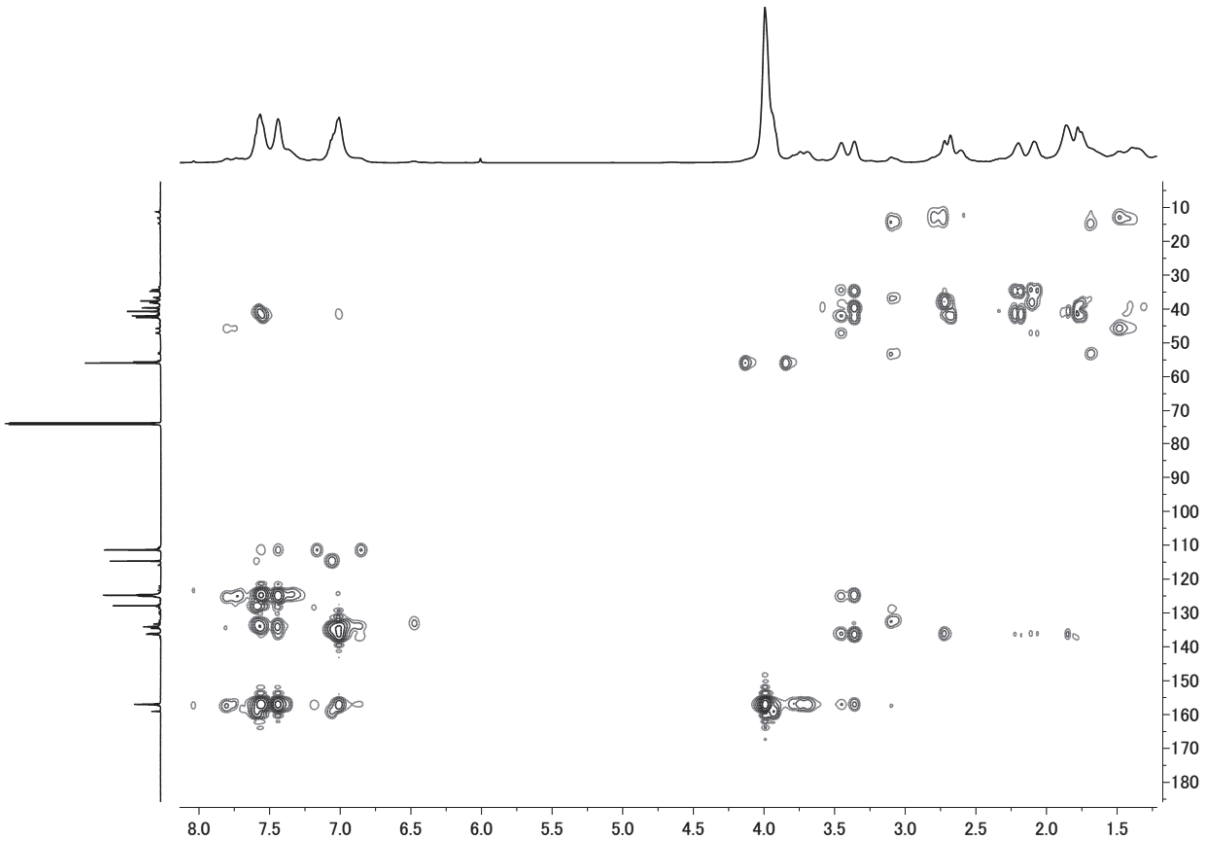


Figure S21. HMBC spectrum ($C_2D_2Cl_4$, 120 °C) of copoly(4,4′-dimethoxybiphenyl/norbornadiene)

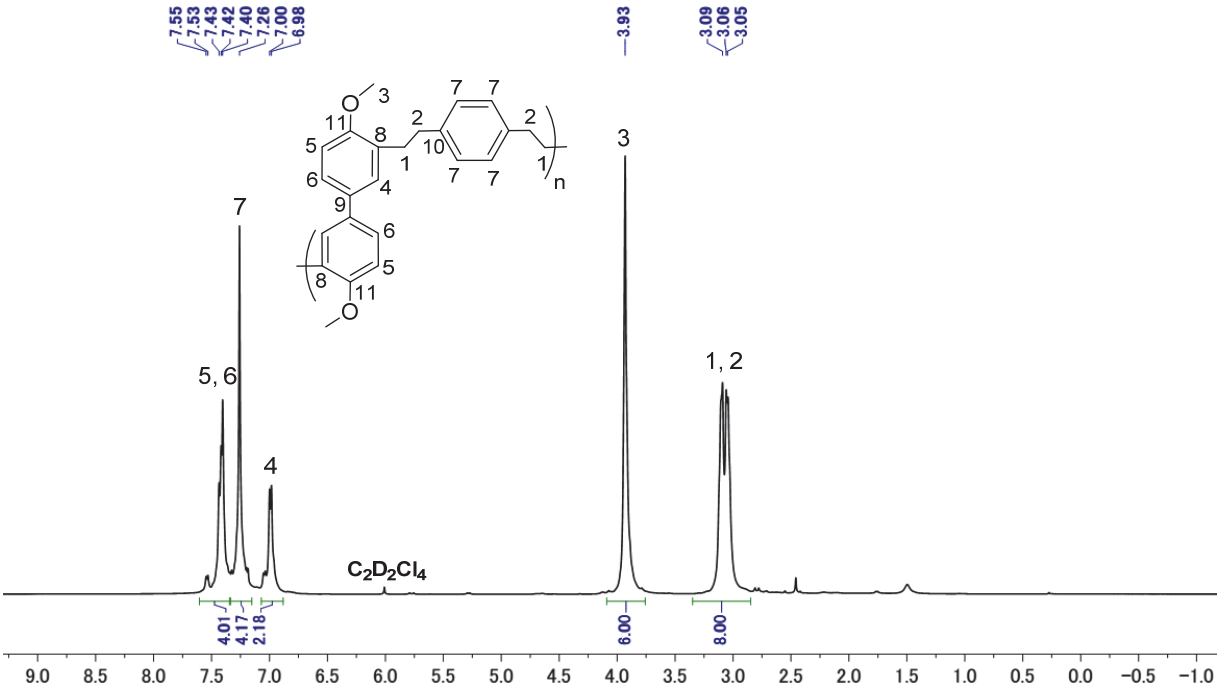


Figure S22. ^{1}H NMR spectrum (500 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(4,4′-dimethoxybiphenyl/1,4-divinylbenzene)

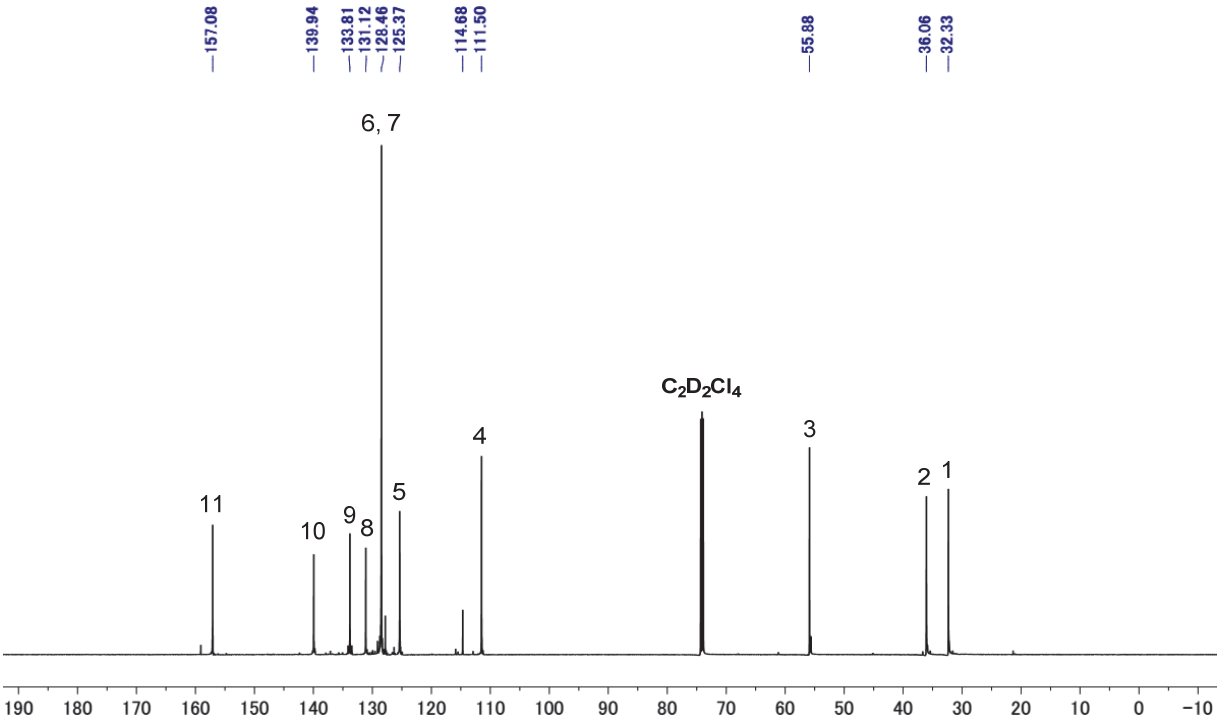


Figure S23. ^{13}C NMR spectrum (125 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(4,4′-dimethoxybiphenyl/1,4-divinylbenzene)

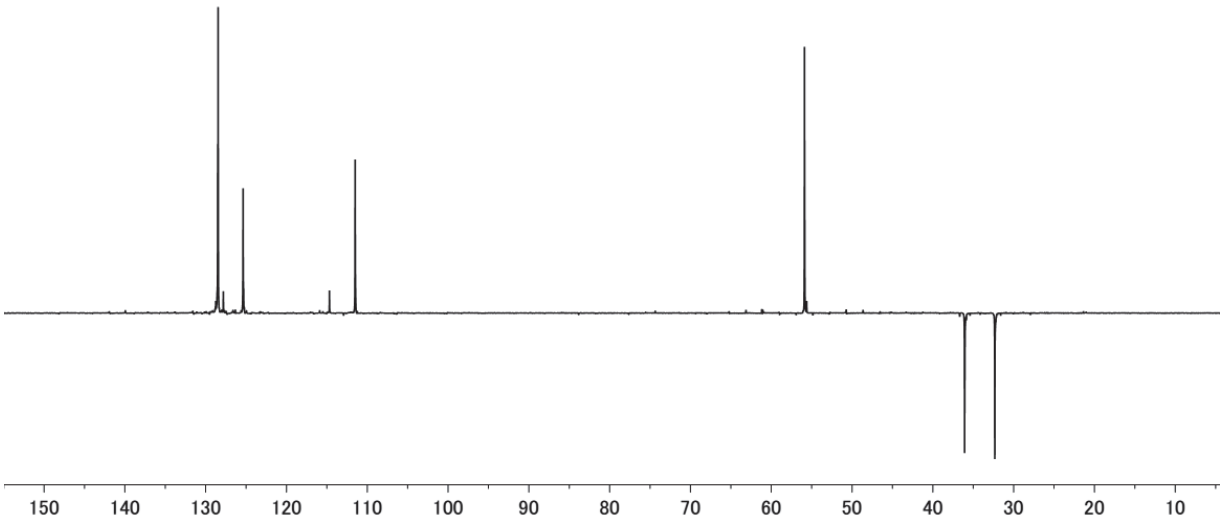


Figure S24. DEPT135-^{13}C spectrum (125 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(4,4′-dimethoxybiphenyl/1,4-divinylbenzene)

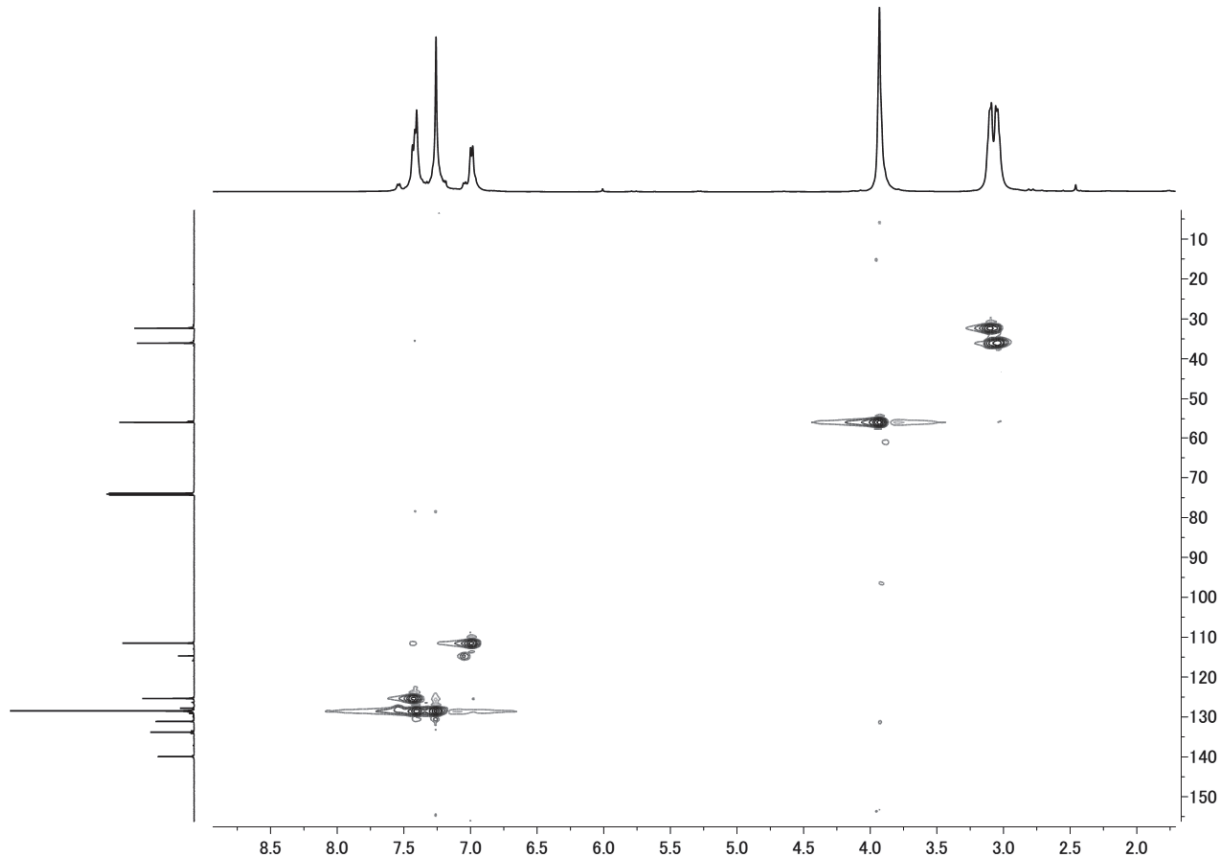


Figure S25. HSQC spectrum ($C_2D_2Cl_4$, 120 °C) of copoly(4,4′-dimethoxybiphenyl/1,4-divinylbenzene)

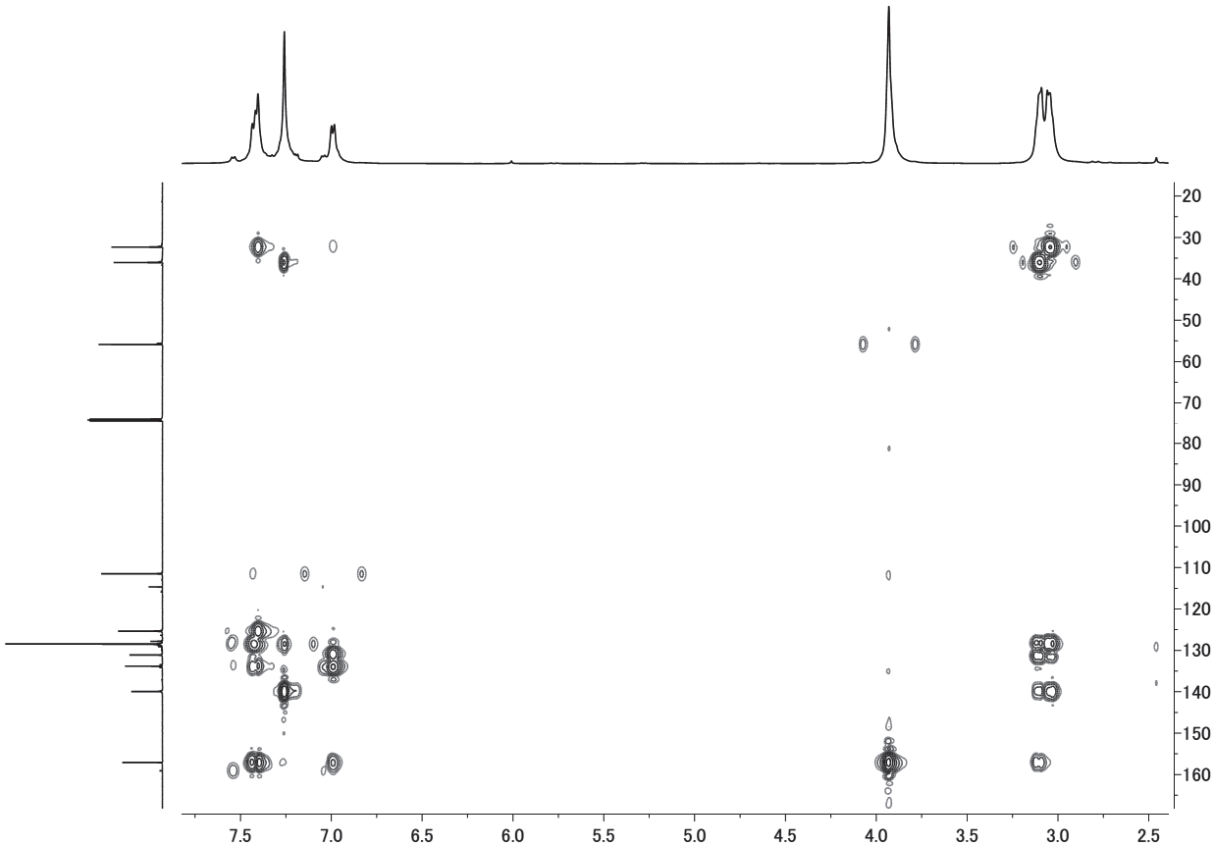


Figure S26. HMBC spectrum ($C_2D_2Cl_4$, 120 °C) of copoly(4,4′-dimethoxybiphenyl/1,4-divinylbenzene)

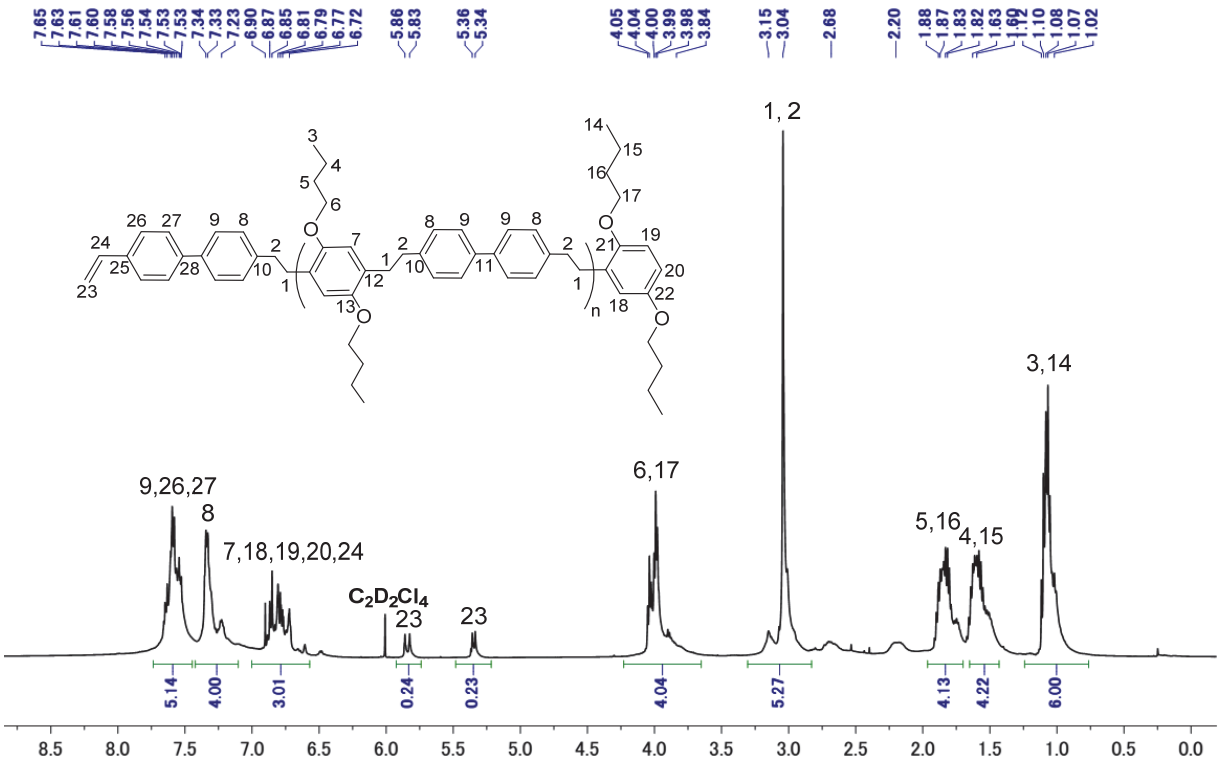


Figure S27. ^{1}H NMR spectrum (500 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(1,4-dibutoxybenzene/4,4′-divinylbiphenyl)

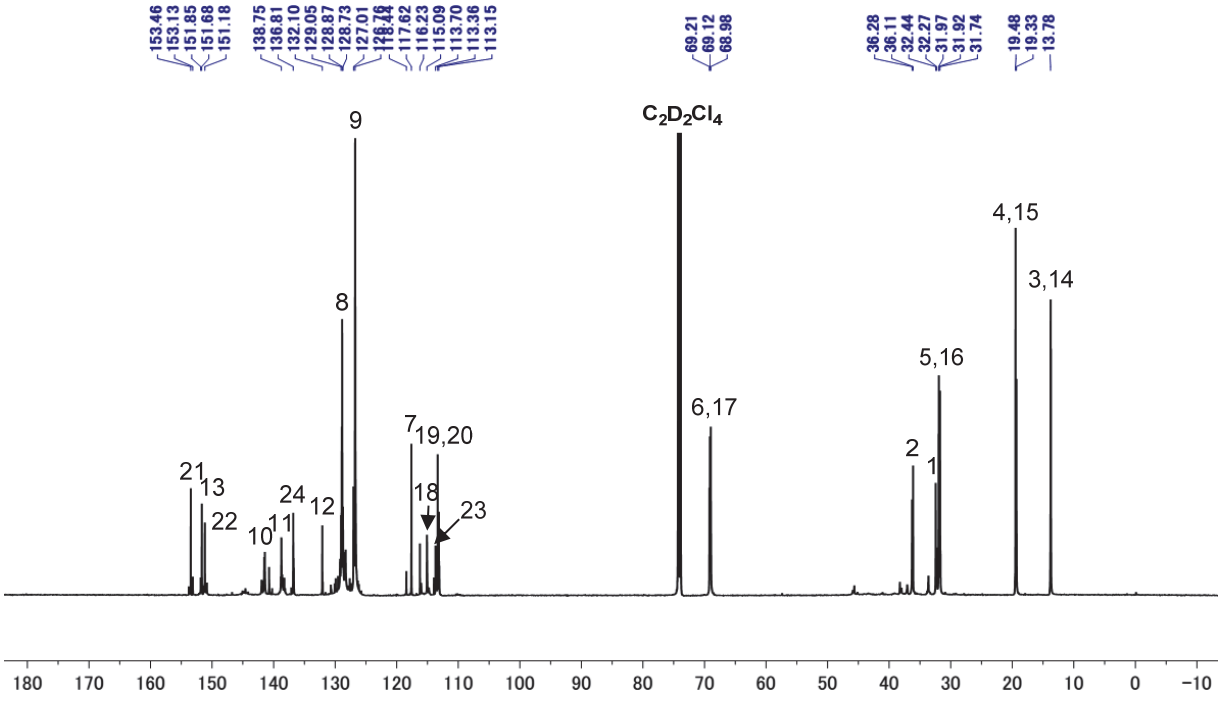


Figure S28. ^{13}C NMR spectrum (125 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(1,4-dibutoxybenzene/4,4′-divinylbiphenyl)

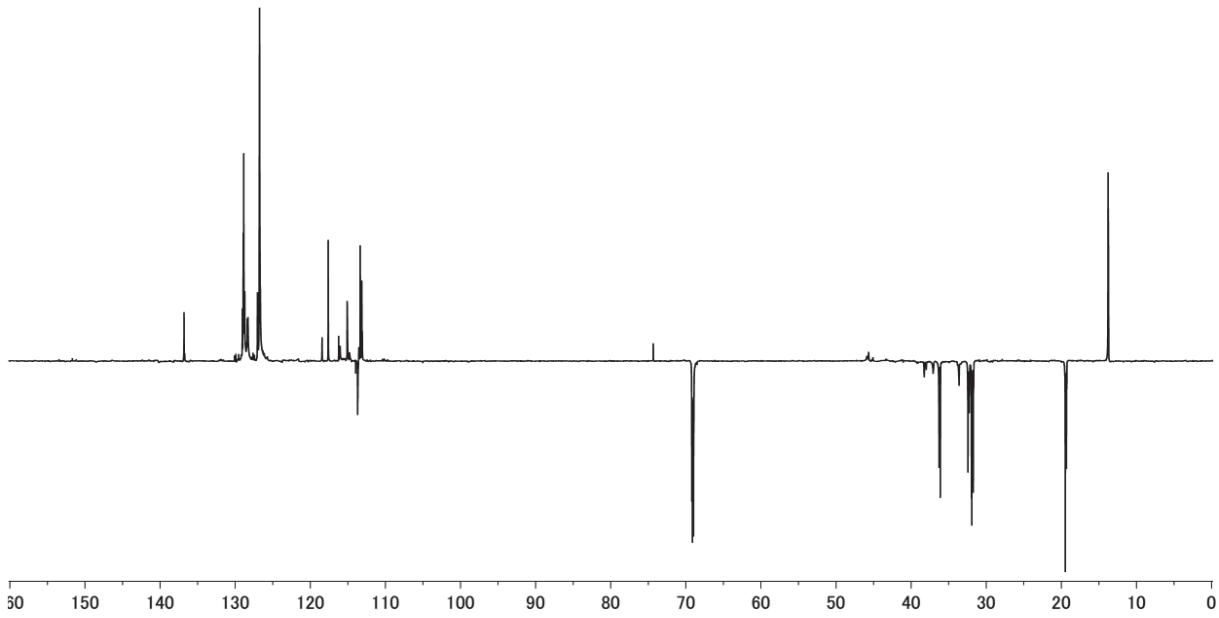


Figure S29. DEPT135-^{13}C spectrum (125 MHz, $C_2D_2Cl_4$, 120 °C) of copoly(1,4-dibutoxybenzene/4,4′-divinylbiphenyl)

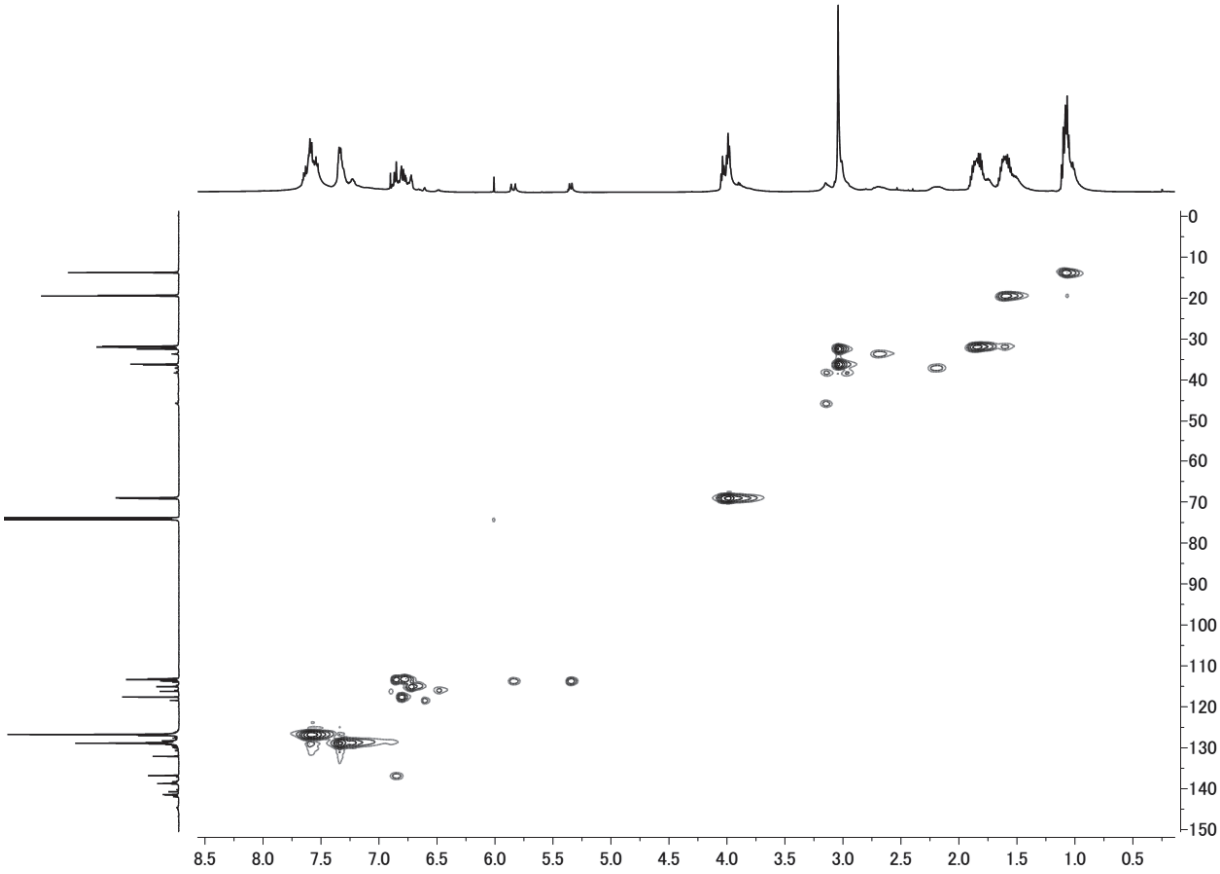


Figure S30. HSQC spectrum ($C_2D_2Cl_4$, 120 °C) of copoly(1,4-dibutoxybenzene/4,4′-divinylbiphenyl)

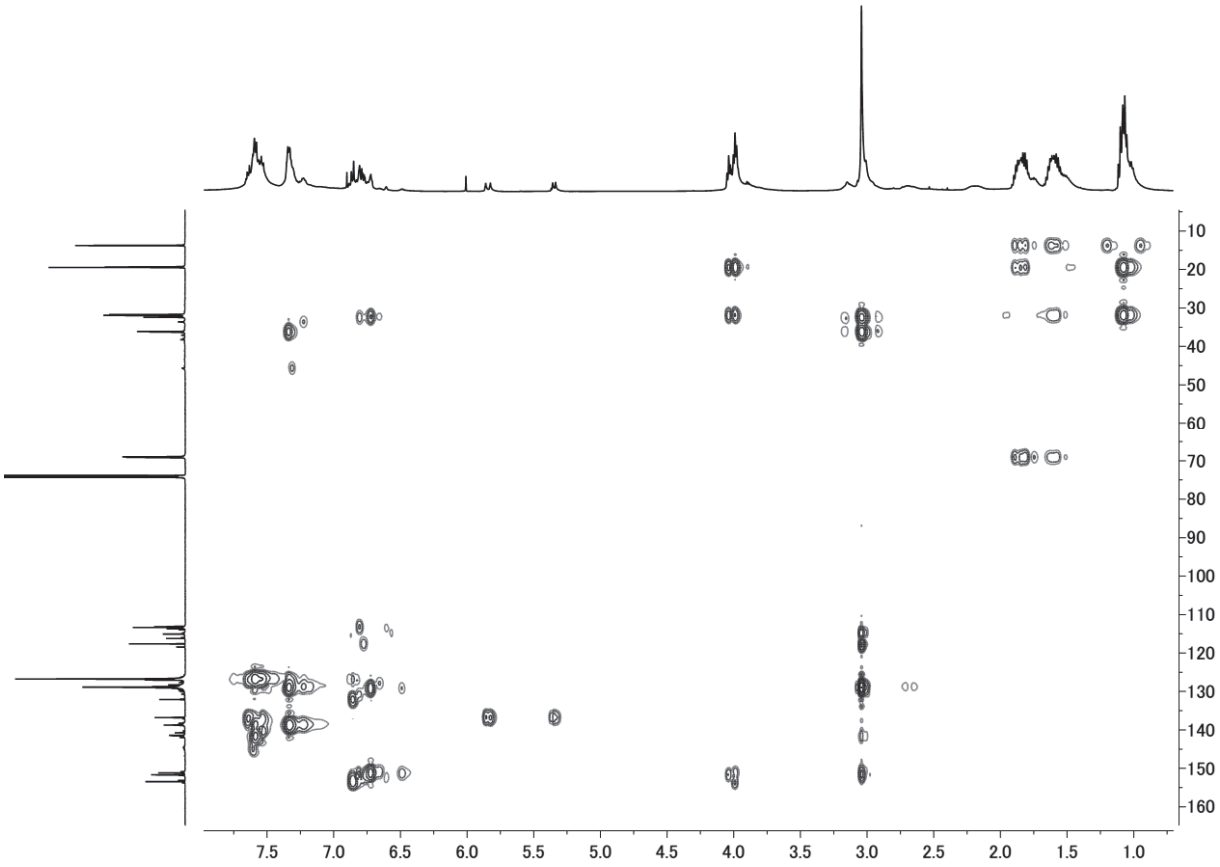


Figure S31. HMBC spectrum ($C_2D_2Cl_4$, 120 °C) of copoly(1,4-dibutoxybenzene/4,4′-divinylbiphenyl)

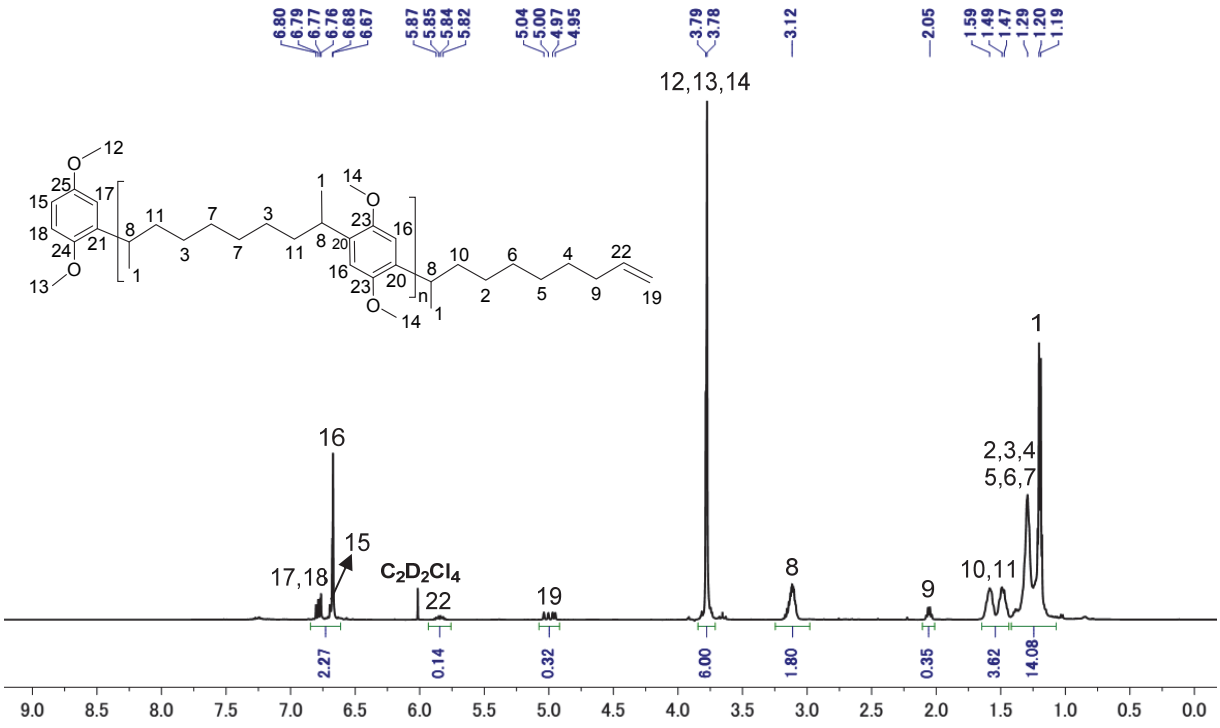


Figure S32. ^{1}H NMR spectrum (500 MHz, $C_2D_2Cl_4$, 26.8 °C) of copoly(1,4-dimethoxybenzene/1,9-decadiene)

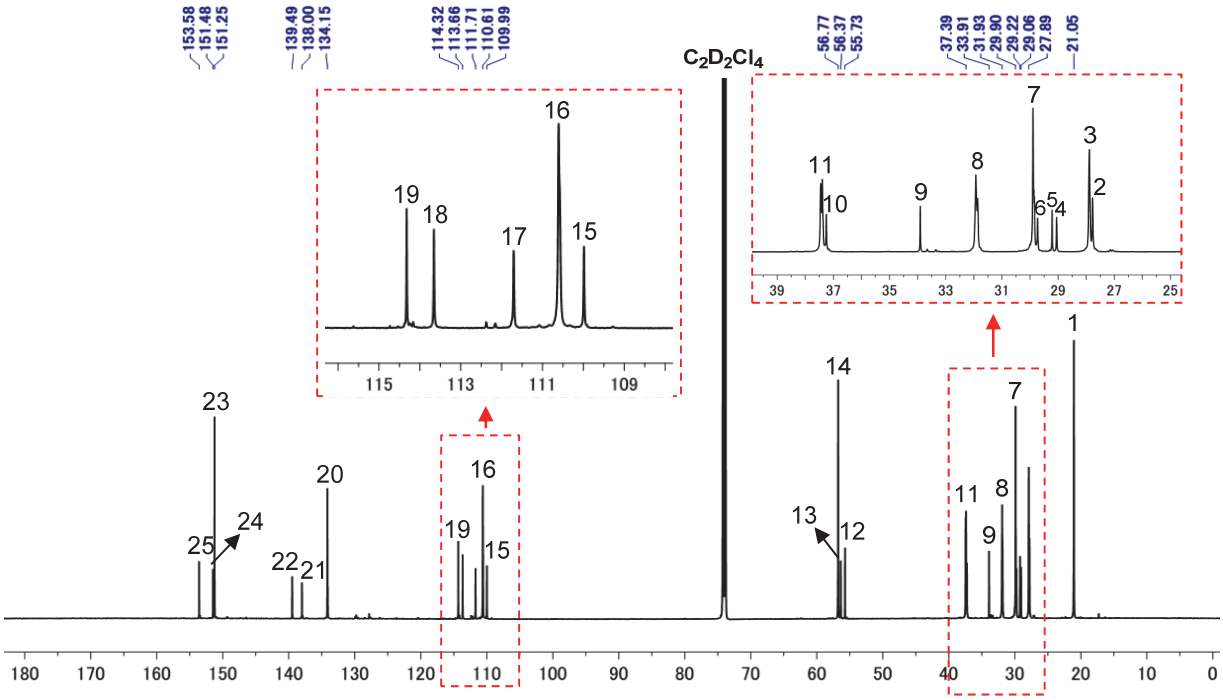


Figure S33. ^{13}C NMR spectrum (125 MHz, $C_2D_2Cl_4$, 26.8 °C) of copoly(1,4-dimethoxybenzene/1,9-decadiene)

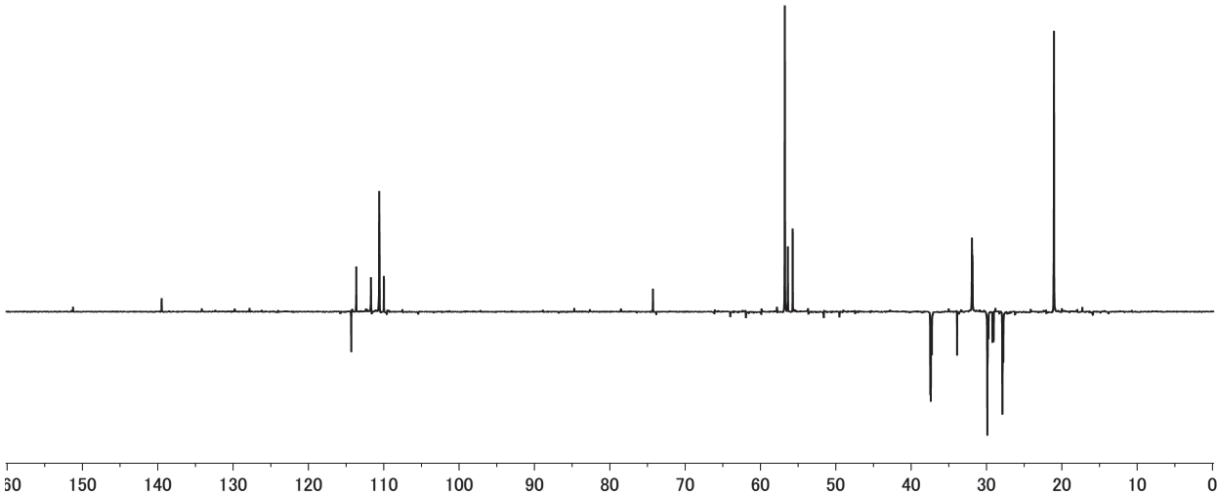


Figure S34. DEPT135-^{13}C spectrum (125 MHz, $C_2D_2Cl_4$, 26.8 °C) of copoly(1,4-dimethoxybenzene/1,9-decadiene)

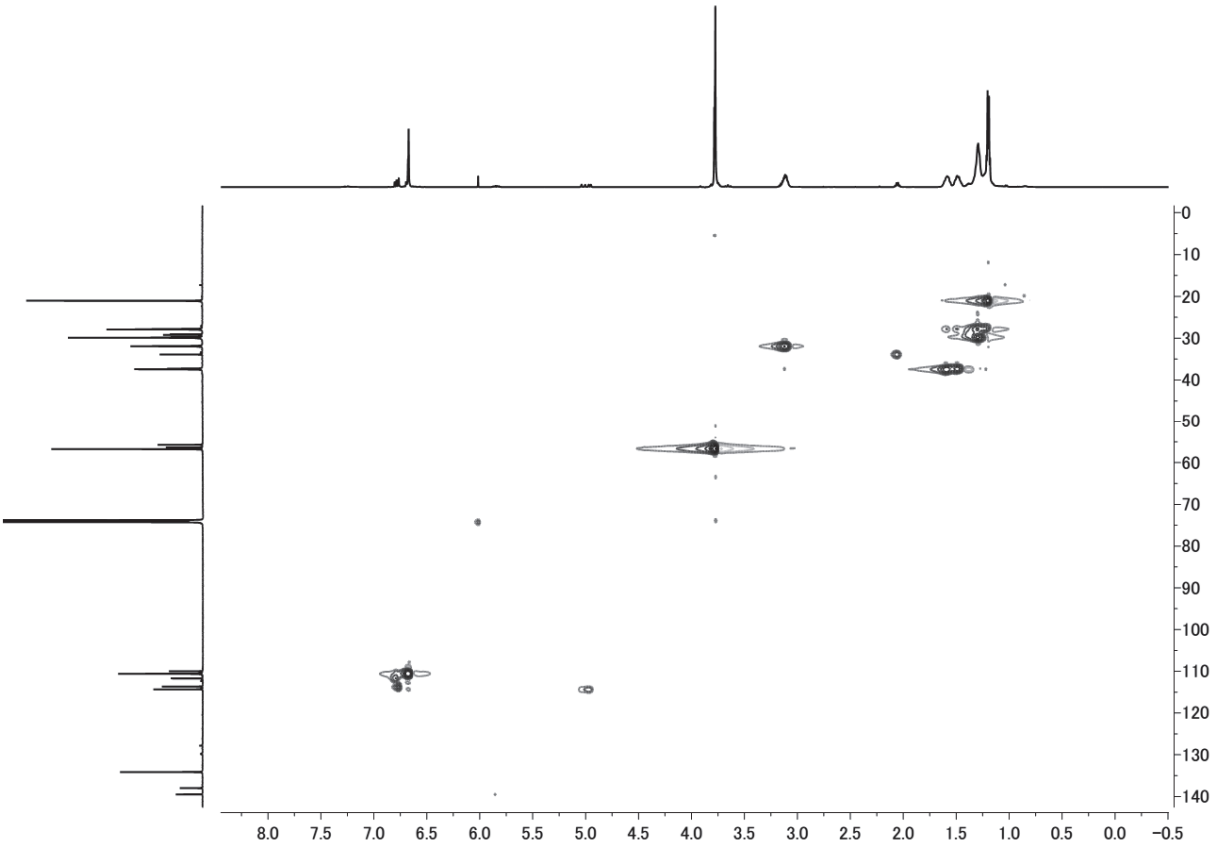


Figure S35. HSQC spectrum ($C_2D_2Cl_4$, 26.8 °C) of copoly(1,4-dimethoxybenzene/1,9-decadiene)

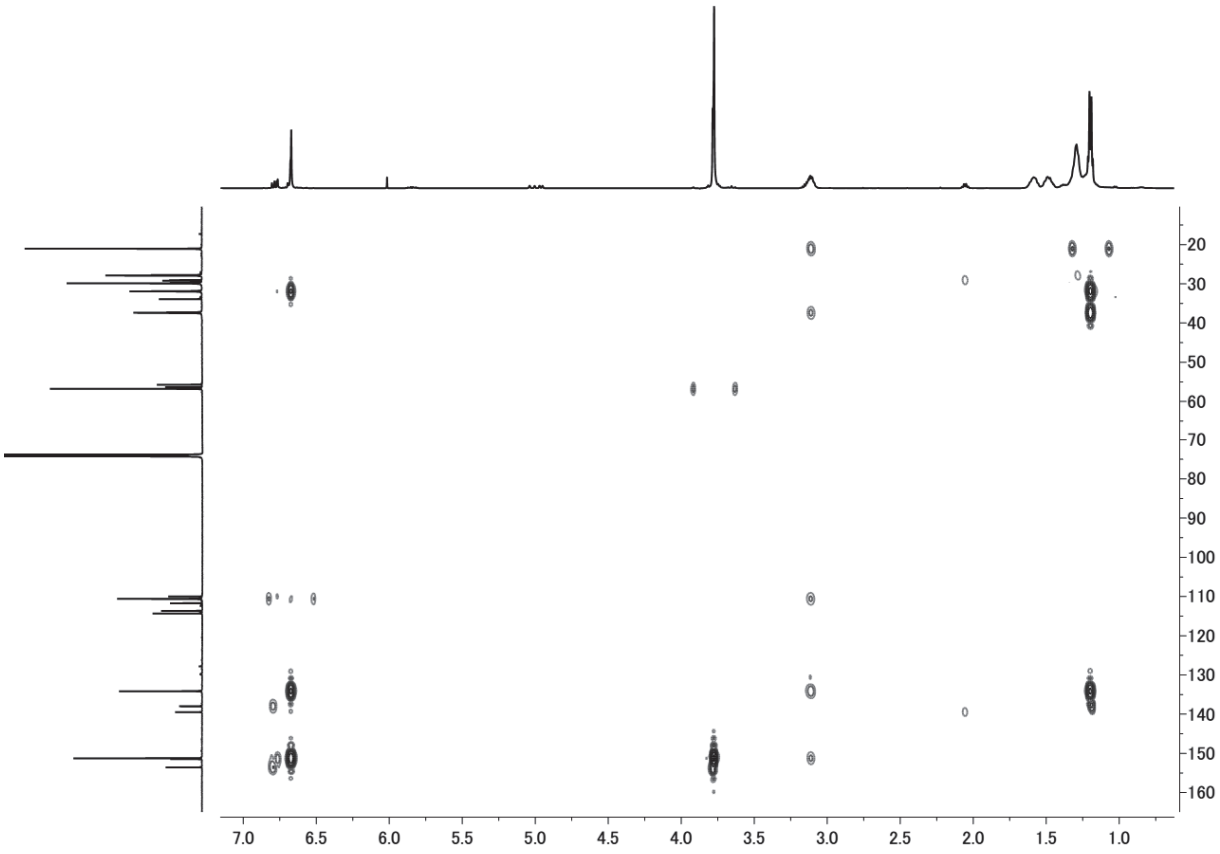


Figure S36. HMBC spectrum ($C_2D_2Cl_4$, 26.8 °C) of copoly(1,4-dimethoxybenzene/1,9-decadiene)

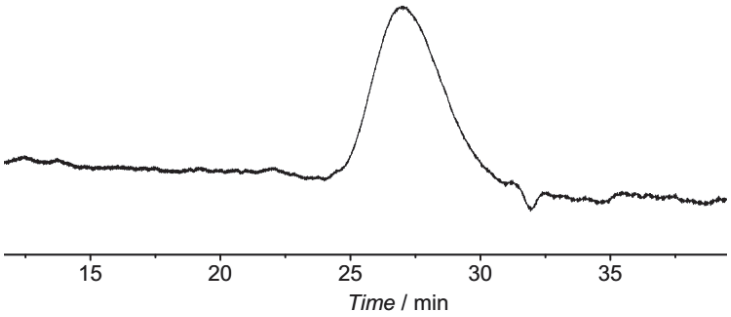


Figure S37. GPC curve of copoly(1,4-dimethoxybenzene/norbornadiene) (M_n = 9800, M_w/M_n = 2.00) in Table 1, Entry 6.

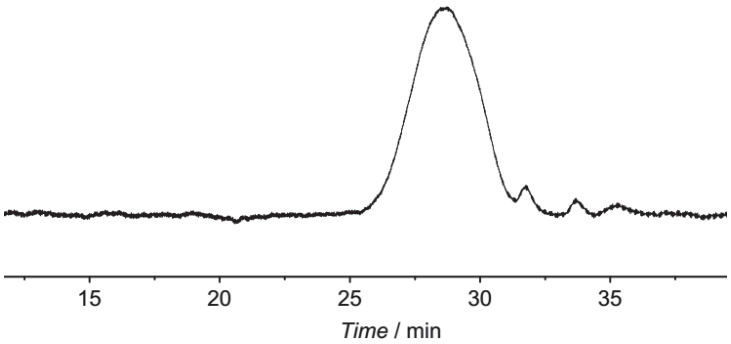


Figure S38. GPC curve of copoly(1,4-dimethoxybenzene/1,4-divinylbenzene) (M_n = 3180, M_w/M_n = 2.38) in Table 2, Entry 3.

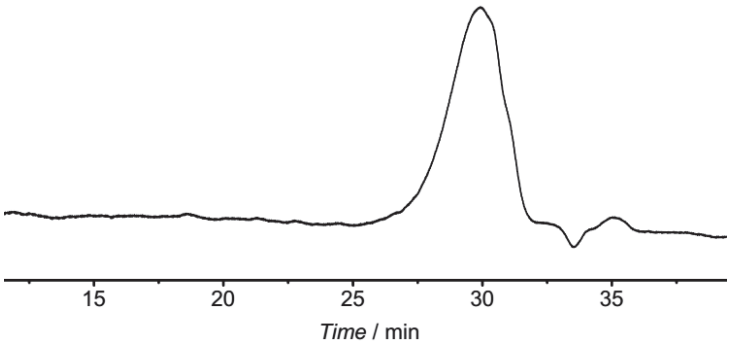


Figure S39. GPC curve of copoly(1,4-dimethoxybenzene/4,4′-divinylbiphenyl) (M_n = 1900, M_w/M_n = 1.94)

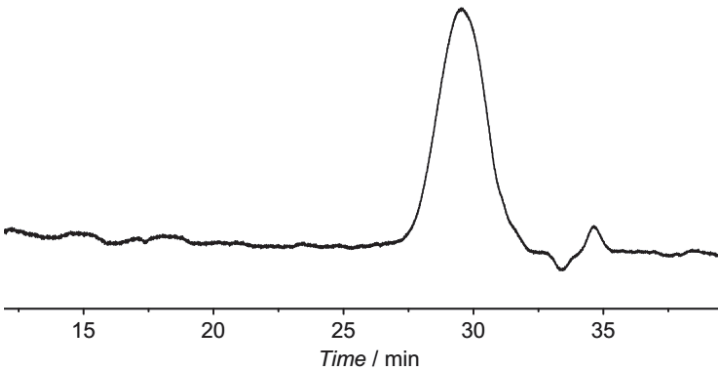


Figure S40. GPC curve of copoly(4,4′-dimethoxybiphenyl/norbornadiene) (M_n = 1330, M_w/M_n = 1.91)

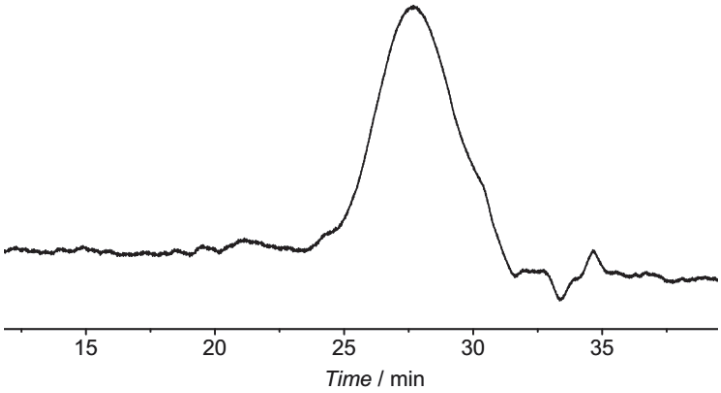


Figure S41. GPC curve of copoly(4,4′-dimethoxybiphenyl/1,4-divinylbenzene) (M_n = 4550, M_w/M_n = 2.52)

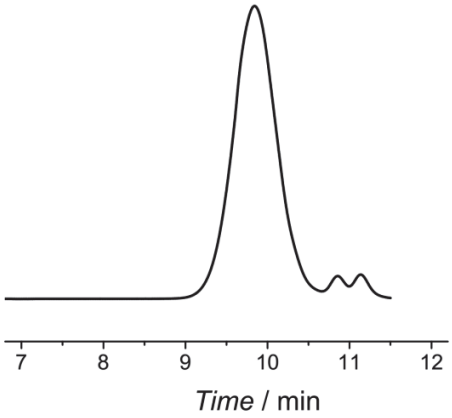


Figure S42. GPC curve of copoly(1,4-dimethoxybenzene/1,9-decadiene) (M_n = 2160, M_w/M_n = 1.23)

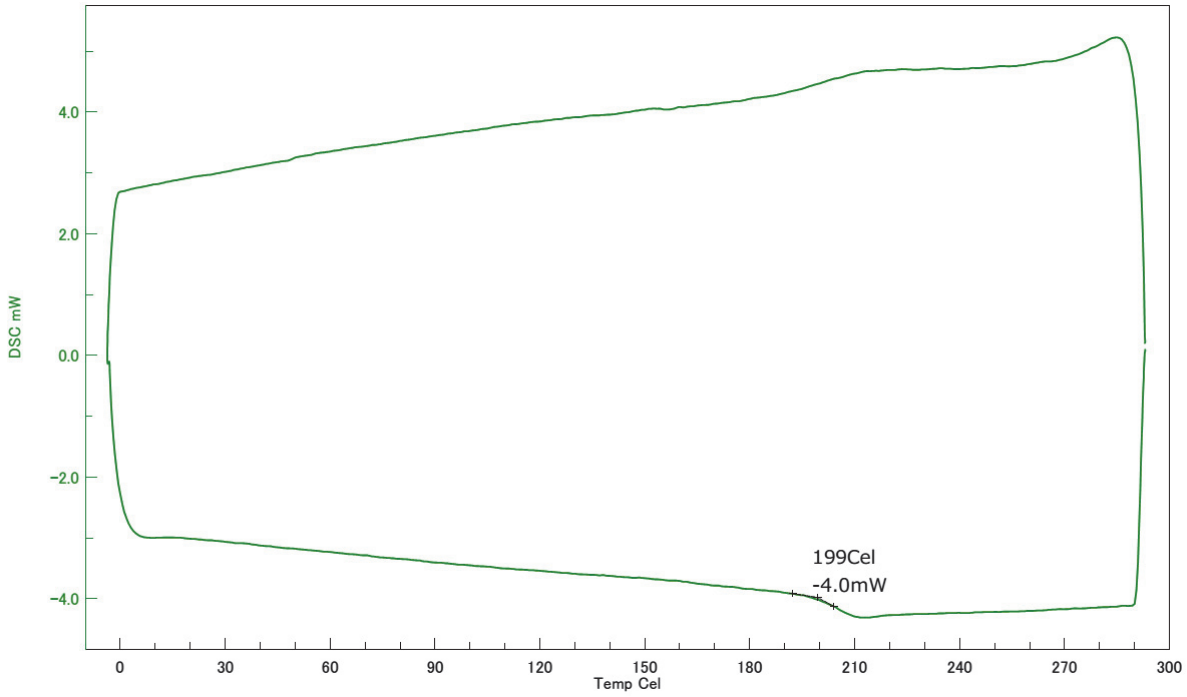


Figure S43. DSC curve of copoly(1,4-dimethoxybenzene/norbornadiene) (Table 1, Entry 6)

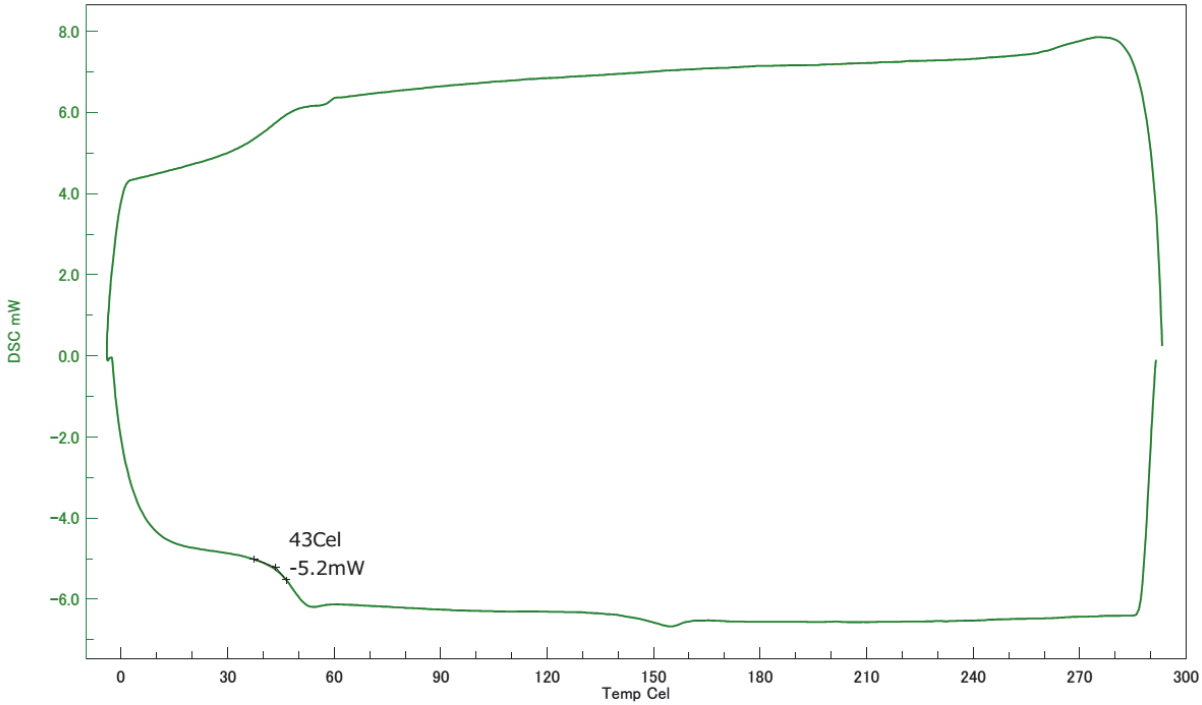


Figure S44. DSC curve of copoly(1,4-dimethoxybenzene/1,4-divinylbenzene)(Table 2, Entry 3)

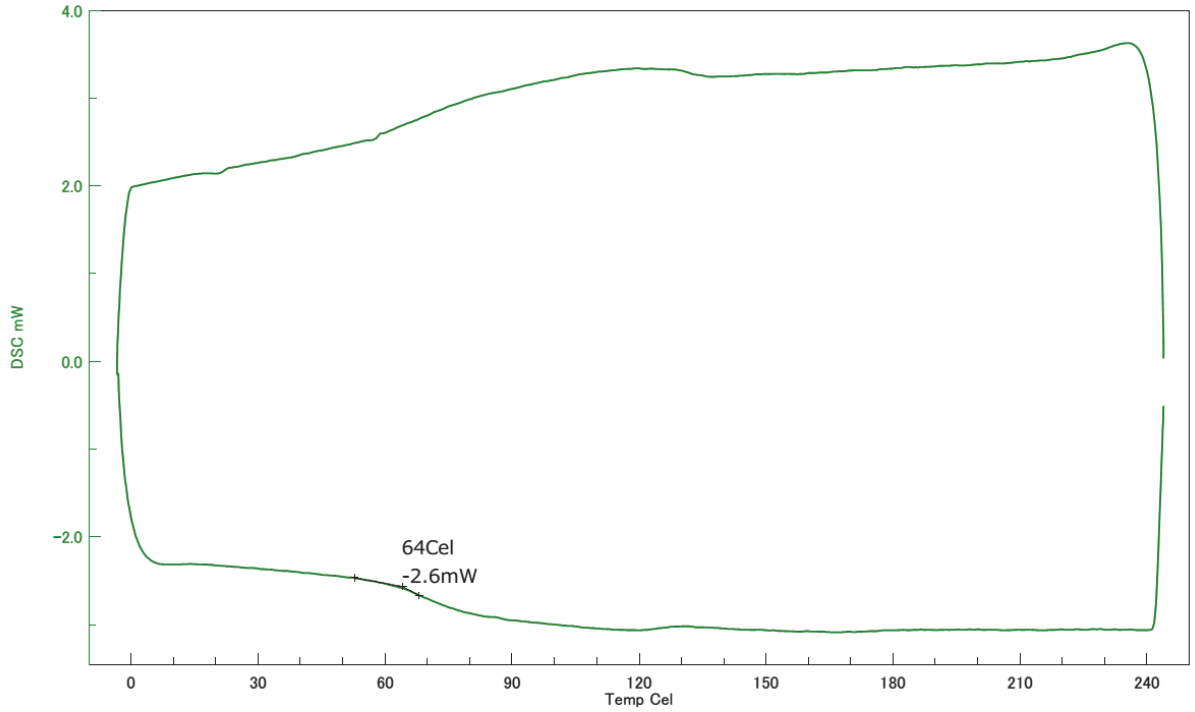


Figure S45. DSC curve of copoly(1,4-dimethoxybenzene/4,4′-divinylbiphenyl)

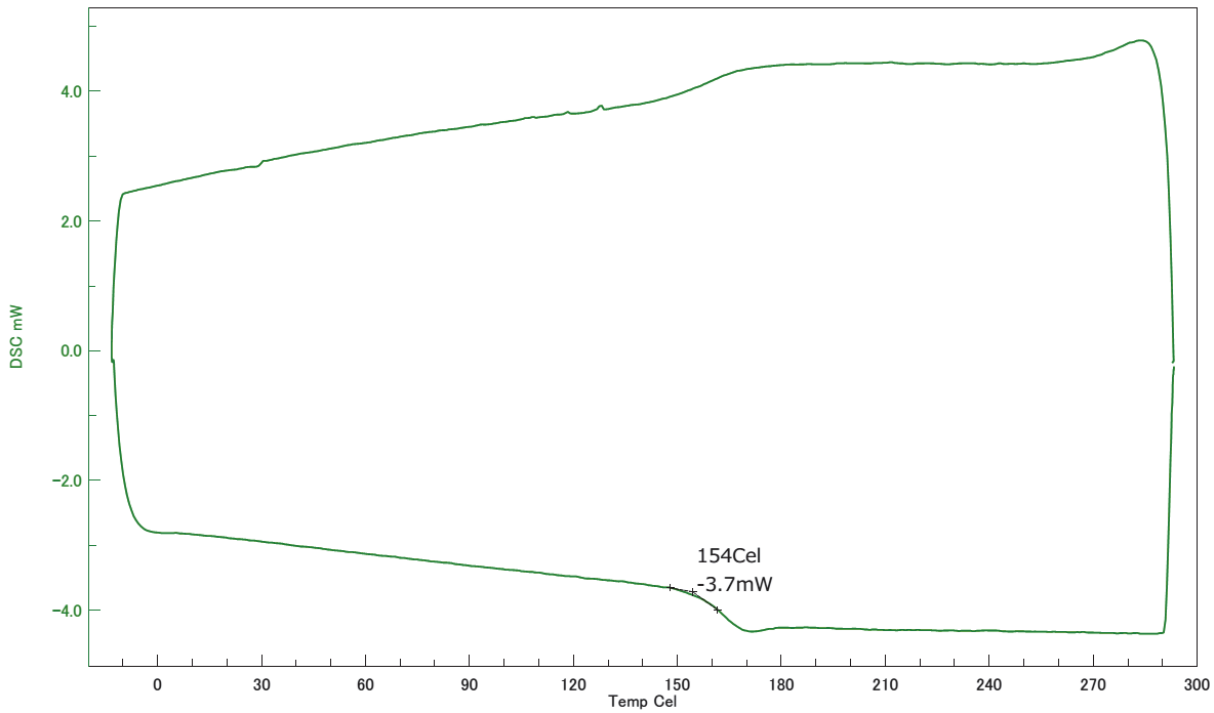


Figure S46. DSC curve of copoly(4,4′-dimethoxybiphenyl/norbornadiene)

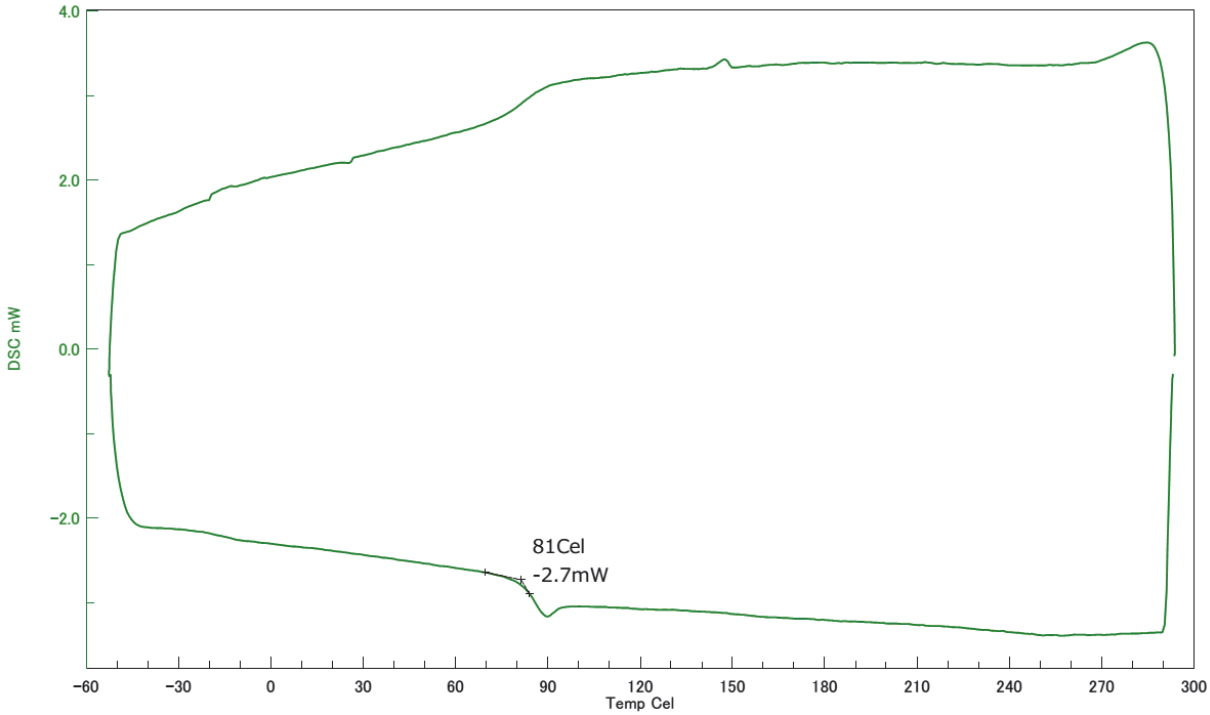


Figure S47. DSC curve of copoly(4,4′-dimethoxybiphenyl/1,4-divinylbenzene)

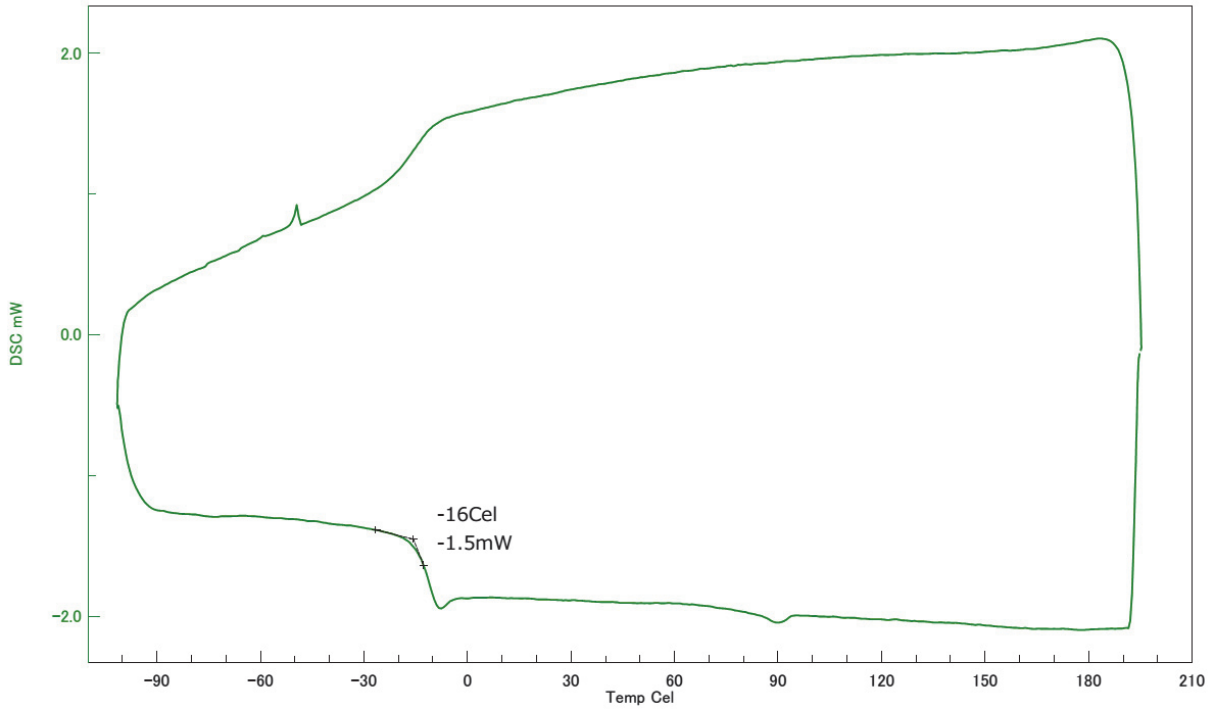


Figure S48. DSC curve of copoly(1,4-dimethoxybenzene/1,9-decadiene)