Supplementary Information (SI) for Polymer Chemistry.
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Supplementary Information

Binuclear Nickel Catalysts Enable One-Step Copolymerization of Ethylene with 2-Allylphenol to Phenol-Functionalized Branched Polyethylenes

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1. Materials and Methods

Toluene and other solvents used for catalyst synthesis and polymerization were purified using an MBraun SPS-800 system. Polymerization-grade ethylene was purified using an ethylene purification system developed by the Dalian Institute of Chemical Physics, CAS. 2-Allylphenol was dried over anhydrous $CaSO_4$ and distilled under reduced pressure. Eugenol, estragole and allylbenzene were commercially available and were verified by ^1H NMR prior to use. 4-Allylphenol[1], 2-methoxy allylbenzene[2], 2-allylphenoxy trimethylsilane[3], and 2-allylphenoxy triisopropylsilane[4] were prepared according to literature procedures and were verified by ^1H NMR.

Trimethylaluminum (TMA), triethylaluminum (TEA), triisobutylaluminium (TIBA) and diethylaluminum chloride (DEAC) were purchased from Jiangsu Yongjian Chemical Co., Ltd as neat liquids, and were diluted with toluene to 1.0 M solutions before use. Ethylaluminum dichloride (1.8 M in toluene) was purchased as a commercial reagent.

All air- and moisture-sensitive manipulations were carried out under high purity argon or nitrogen using standard Schlenk techniques or in a glovebox. ^1H NMR, ^{13}C NMR, DEPT-135, COSY, HSQC and HMBC spectra were recorded on Agilent (400 MHz, 600 MHz) or Varian (400 MHz) NMR spectrometer. Number-average molecular weight (M_n), weight-average molecular weight (M_w), and dispersity (Đ) were determined using an Agilent PL-GPC 220 high-temperature gel permeation chromatograph at 150 °C (polystyrene calibration; 1,2,4-trichlorobenzene; 150°C). Poly(E-*co*-2-allylphenol) was acetylated prior to GPC analysis. DSC measurements were performed on a TA Instruments DSC 2500. Samples were heated from -80 °C to 180 °C at 10 °C /min under a nitrogen atmosphere, cooled to -80 °C at 10 °C /min for two cycles. The reported DSC data were collected from the second heating cycle.

2. General Procedure for Olefin Copolymerizations with Polar Monomer

(a) Polar monomer pretreated with Et_2AlCl in situ.

Under 1 atm of ethylene, a flame-dried two-neck flask equipped with a stir bar was charged with the specified amounts of toluene and Et_2AlCl solution at desired temperature. After stirring for 10 min, the polar monomer was added dropwise. The resulting mixture was stirred for 10 min, and then a toluene solution of the Ni catalyst was added to initiate the polymerization. The reaction mixture was quenched by pouring into 250 mL of acidified MeOH (concentrated HCl/MeOH =

1/10, v/v) and stirring at room temperature overnight. The precipitated polymer was collected by filtration, washed with MeOH, and dried under vacuum at 60 °C to a constant weight.

(b) Polar monomer pretreated with masking reagents for 12 h.

A flame-dried Schlenk tube equipped with a stir bar was charged with the specified amount of toluene and the masking reagent at 30 °C under argon atmosphere. The polar monomer was then added dropwise, and the mixture was stirred at 30 °C for 12 h prior to use in polymerization.

Under 1 atm of ethylene, a flame-dried two-neck flask equipped with a stir bar was charged with the specified amounts of toluene and Et_2AlCl solution at 30 °C. After 10 min, the polar monomer solution pretreated with the masking reagent was added. The resulting mixture was stirred for 10 min, and then a toluene solution of the Ni catalyst was added to initiate polymerization. The reaction mixture was quenched by pouring into 250 mL of acidified MeOH (concentrated HCl/MeOH = 1/10, v/v), and the suspension was stirred at room temperature overnight. The precipitated polymer was collected, washed with MeOH, and dried under vacuum at 60 °C to a constant weight.

3. Acetylation Procedure for Poly(E-*co*-2-allylphenol)

A thick-wall sealed vessel equipped with a stir bar was charged with poly(E-*co*-2-allylphenol) (~50 mg) and 1,2-dichlorobenzene (8 mL) under argon atmosphere. The mixture was heated to 60 °C until the polymer fully dissolved and then allowed to cool to room temperature. Et_3N (2 mL) and AcCl (0.25 mL) were added, the vessel was sealed, and the mixture was reheated to 60 °C. After stirring for 30 min, the hot reaction solution was poured into MeOH (100 mL). The precipitated polymer was collected by filtration, washed with MeOH, and dried under vacuum at 60 °C to a constant weight. The polymer product was characterized by ^1H NMR, confirming complete conversion of phenol to acetate groups.

4. NMR Spectra of Comonomers

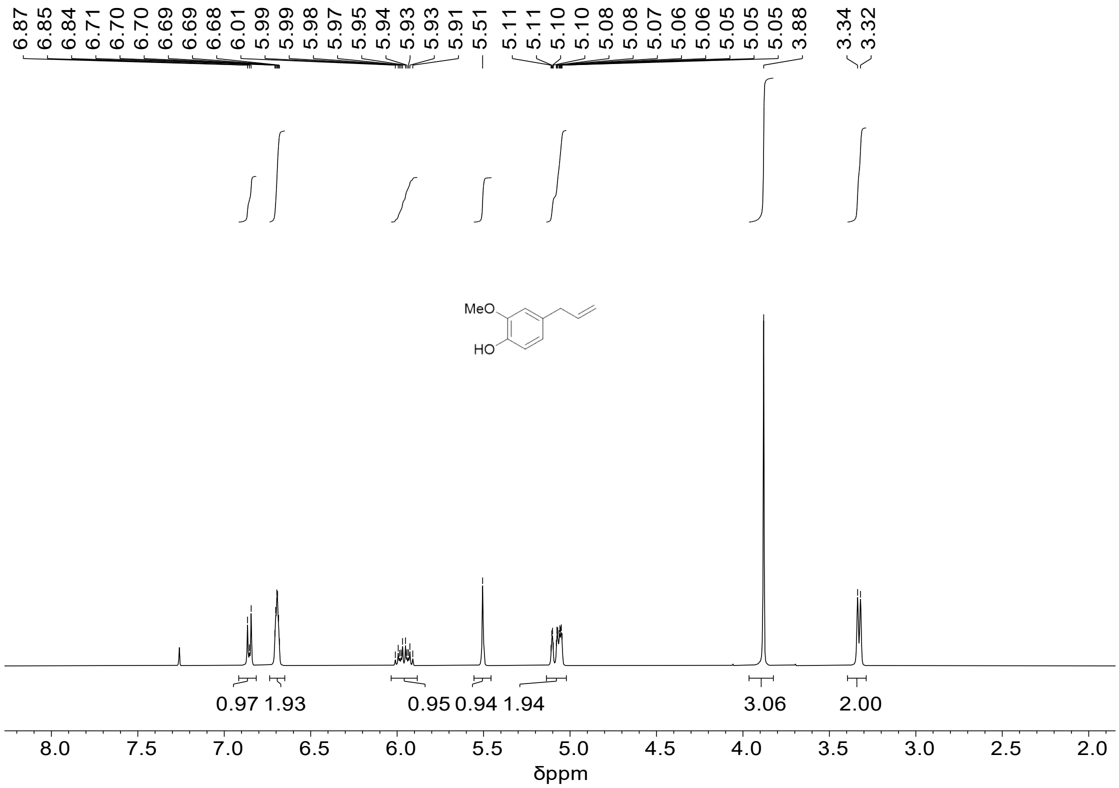


Figure S1. ^{1}H NMR spectrum (400 MHz) of eugenol in CDCl$_3$.

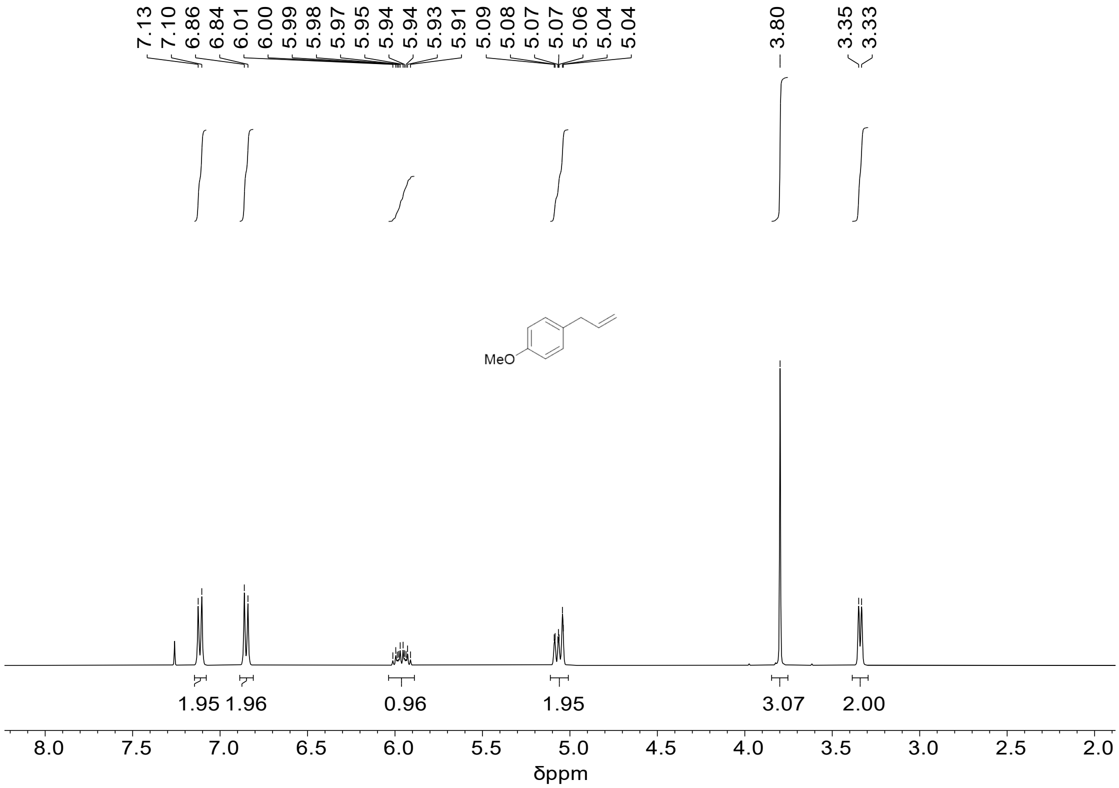


Figure S2. ^{1}H NMR spectrum (400 MHz) of estragole in CDCl$_3$.

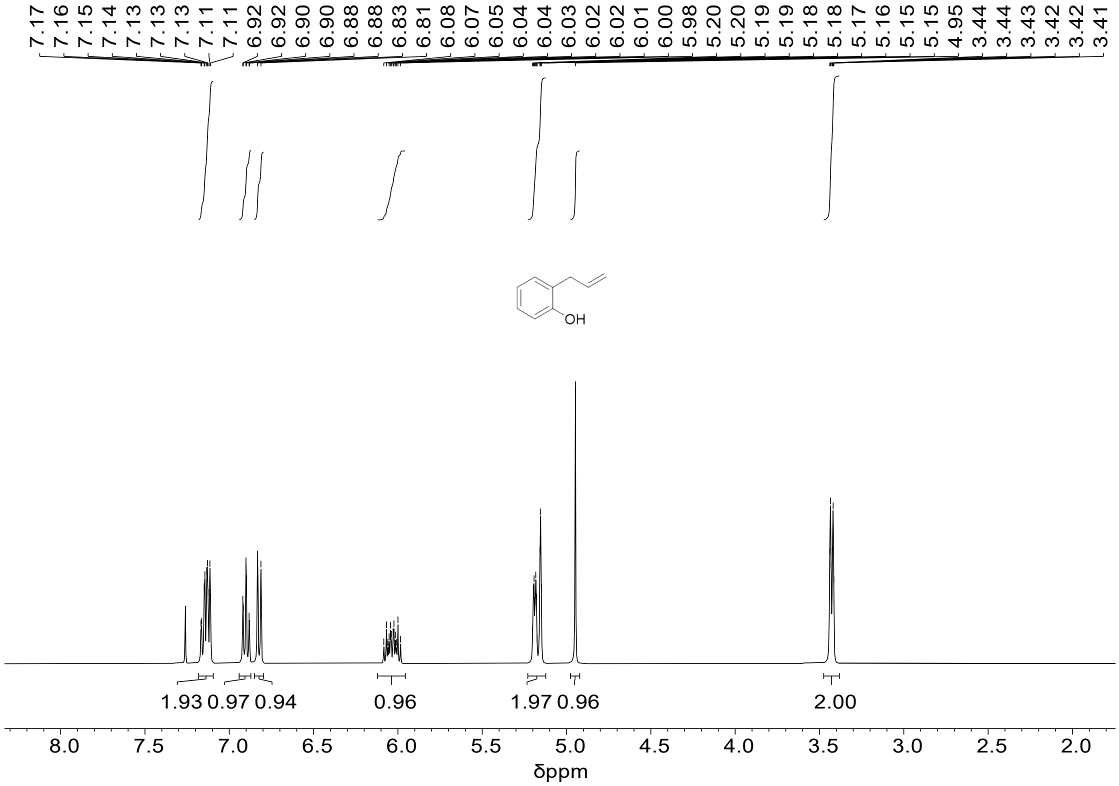


Figure S3. ^{1}H NMR spectrum (400 MHz) of 2-allylphenol in $CDCl_3$.

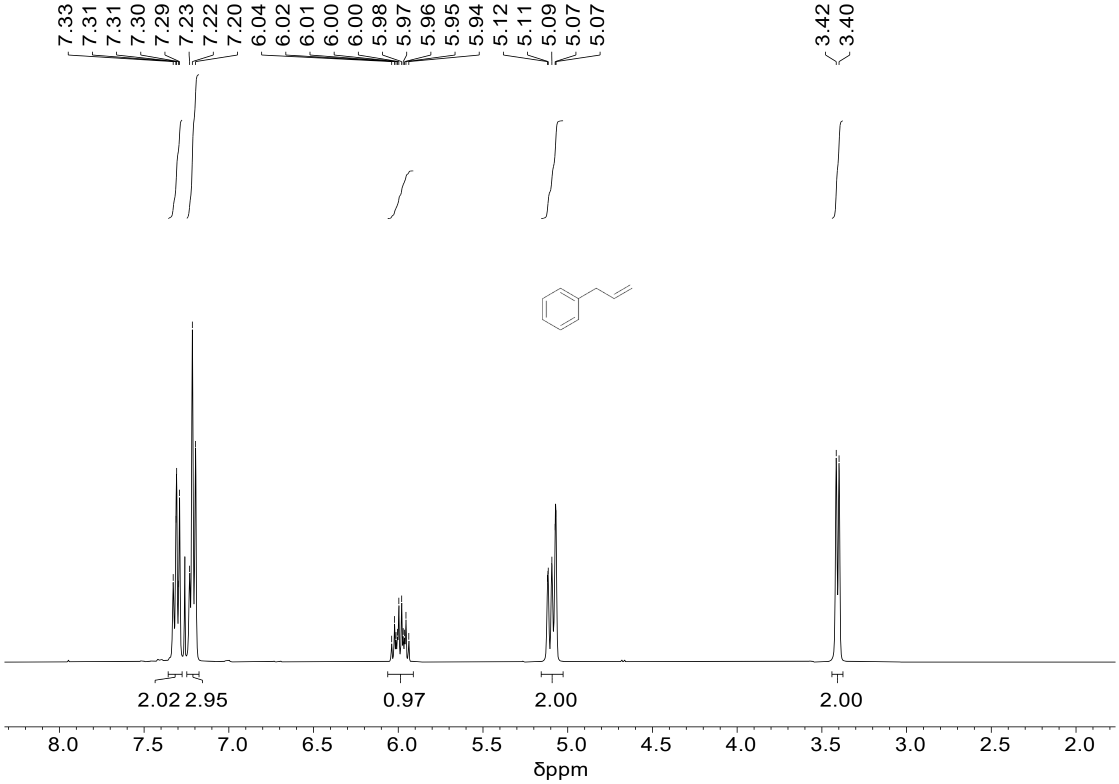


Figure S4. ^{1}H NMR spectrum (400 MHz) of allylbenzene in $CDCl_3$.

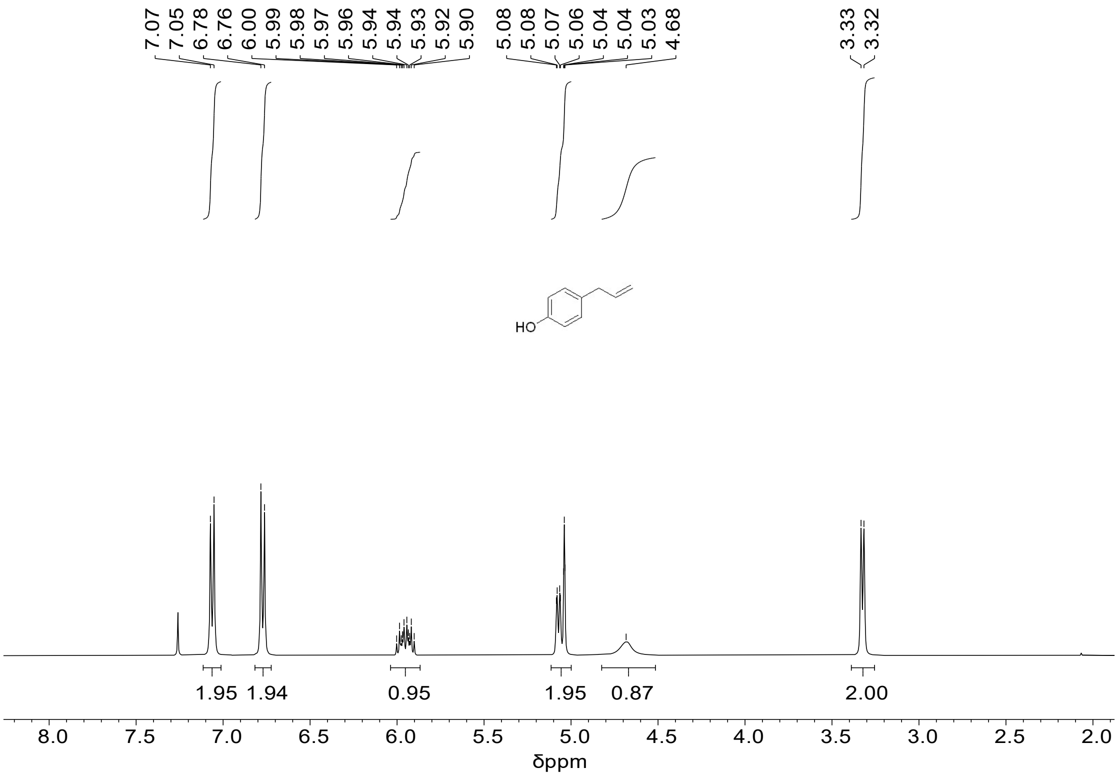


Figure S5. ^{1}H NMR spectrum (400 MHz) of 4-allylphenol in $CDCl_3$.

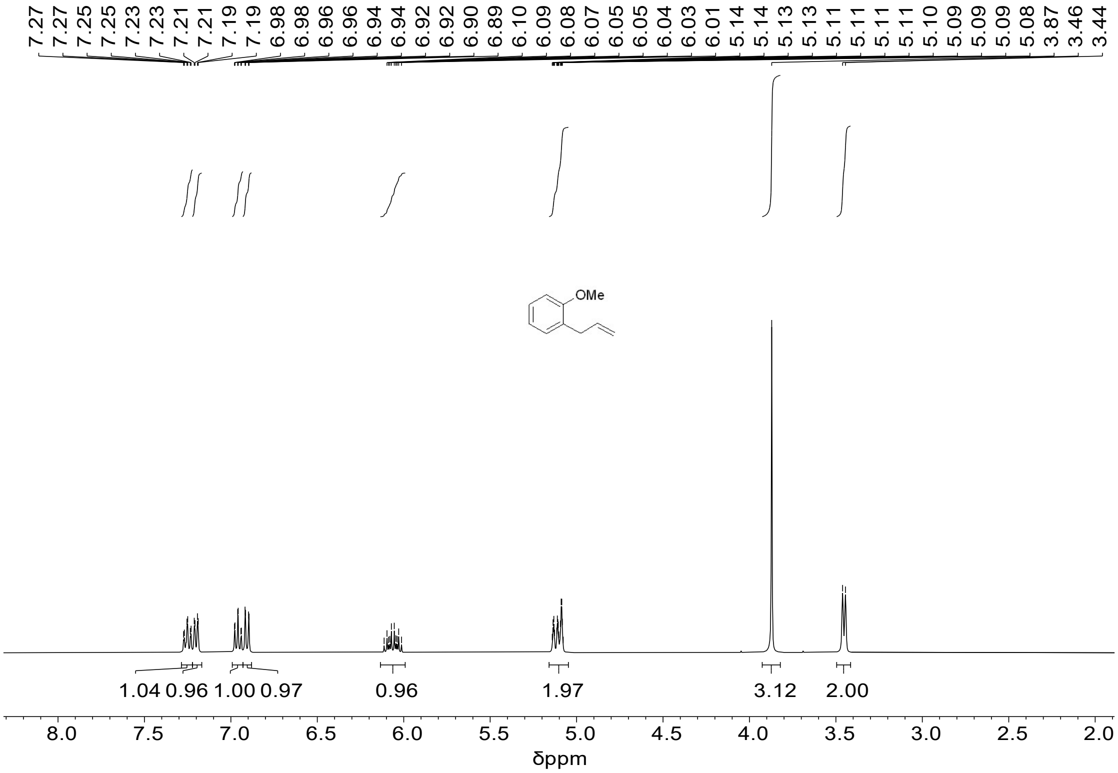


Figure S6. ^{1}H NMR spectrum (400 MHz) of 2-methoxy allylbenzene in $CDCl_3$.

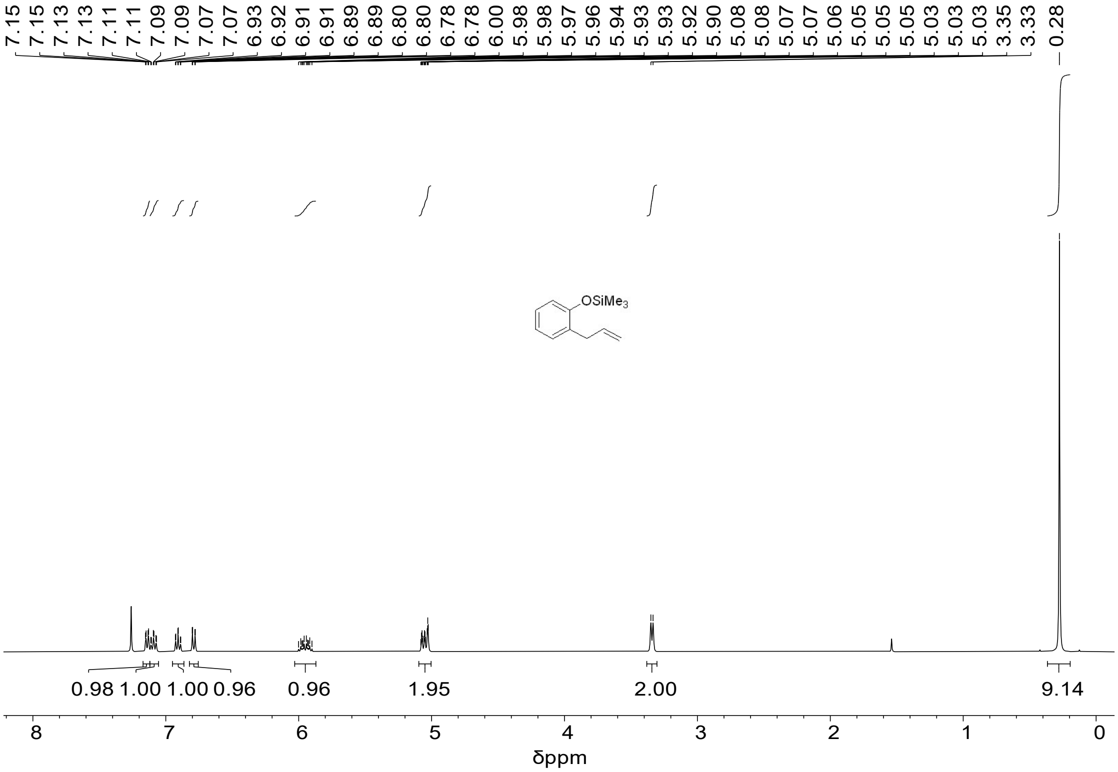


Figure S7. ^{1}H NMR spectrum (400 MHz) of 2-allylphenoxy trimethylsilane in CDCl$_3$.

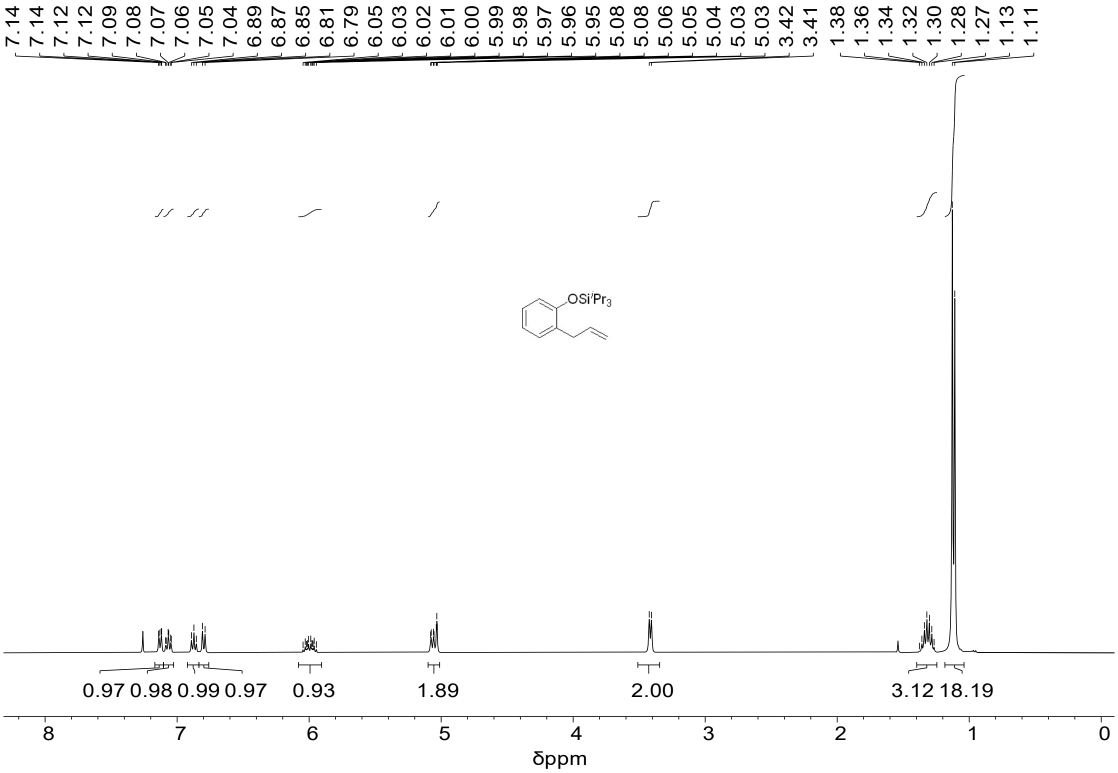


Figure S8. ^{1}H NMR spectrum (400 MHz) of 2-allylphenoxy triisopropylsilane in CDCl$_3$.

5. NMR Assignments of Poly(E-*co*-2-allylphenol)

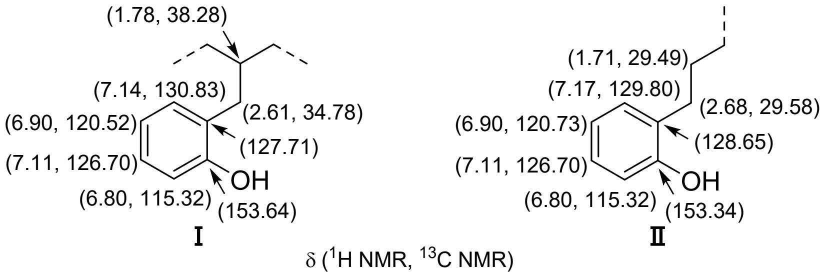


Figure S9. NMR assignments of poly(E-*co*-2-allylphenol)

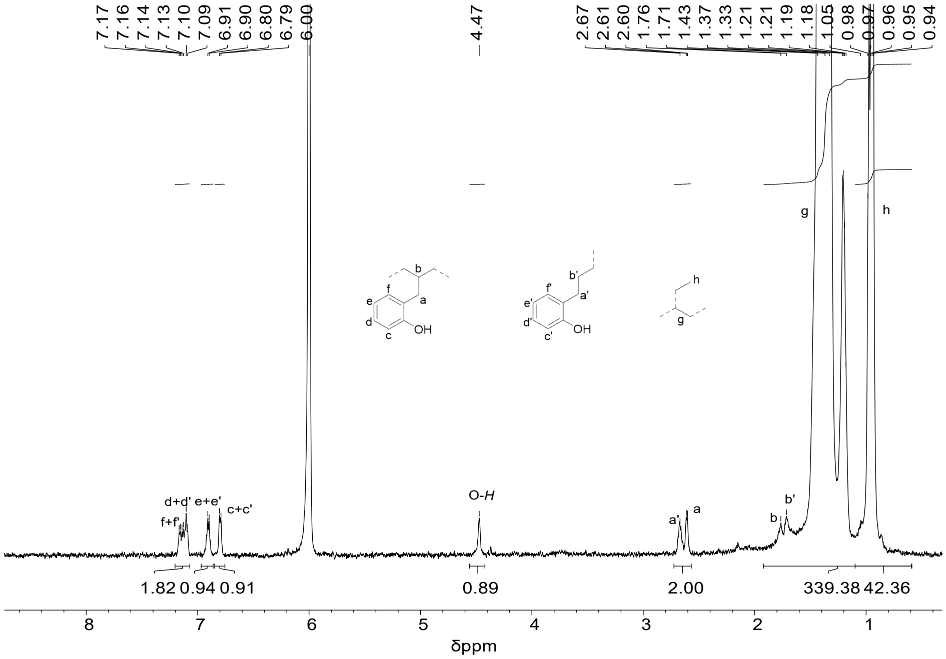


Figure S10. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 3, entry 2 & Table 2, entry 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

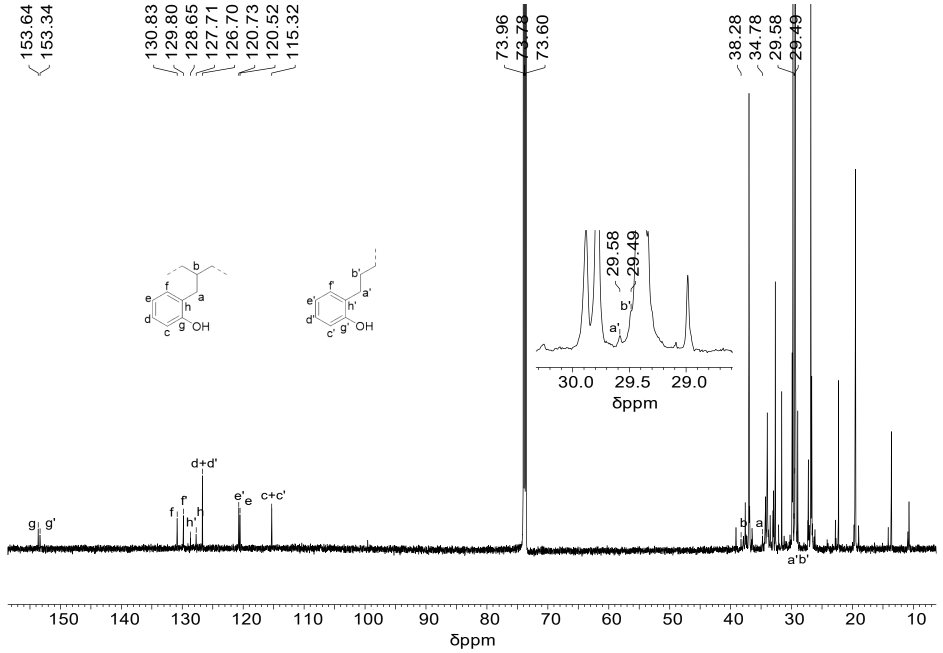


Figure S11. ^{13}C NMR spectrum (150 MHz) of poly(E-*co*-2-allylphenol) (Table 3, entry 2 & Table 2, entry 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

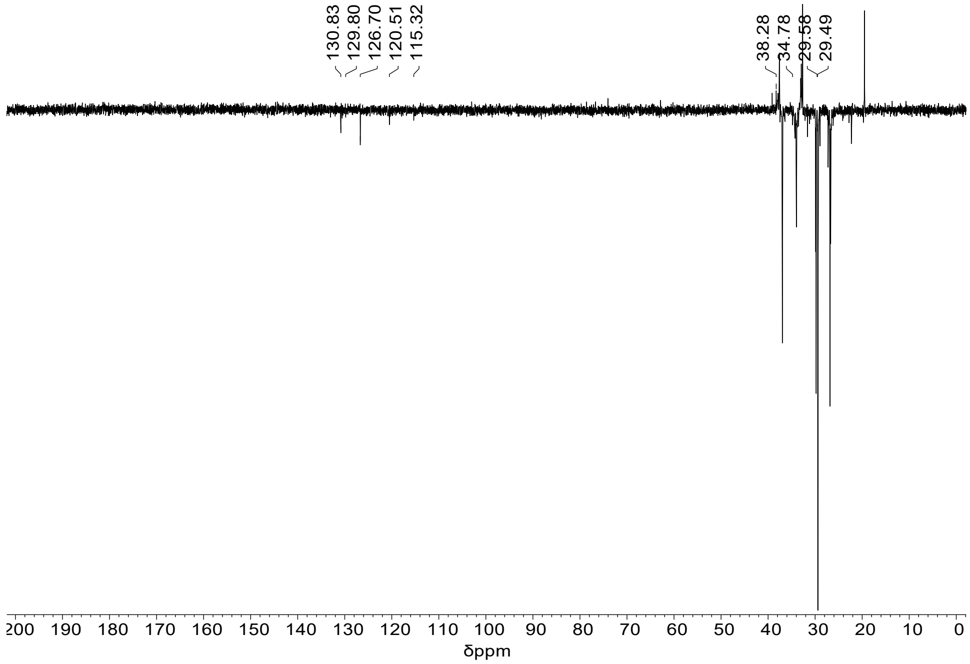


Figure S12. DEPT 135 spectrum of poly(E-*co*-2-allylphenol) (Table 3, entry 2 & Table 2, entry 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

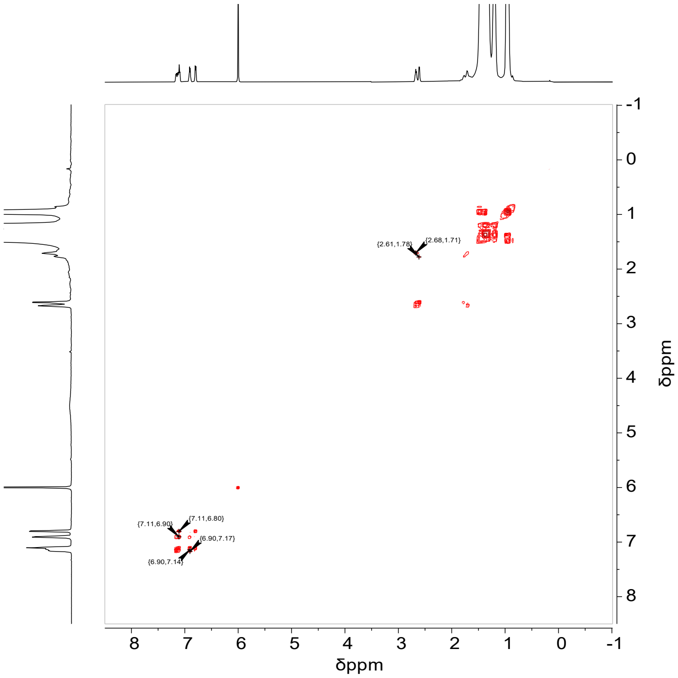


Figure S13. COSY spectrum of poly(E-*co*-2-allylphenol) (Table 3, entry 2 & Table 2, entry 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

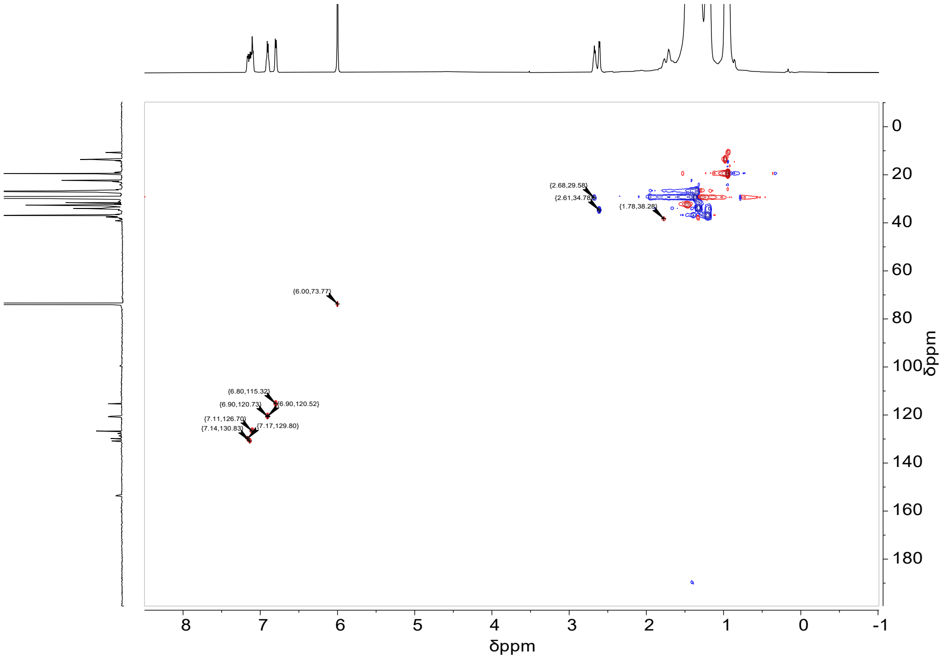


Figure S14. HSQC spectrum of poly(E-*co*-2-allylphenol) (Table 3, entry 2 & Table 2, entry 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

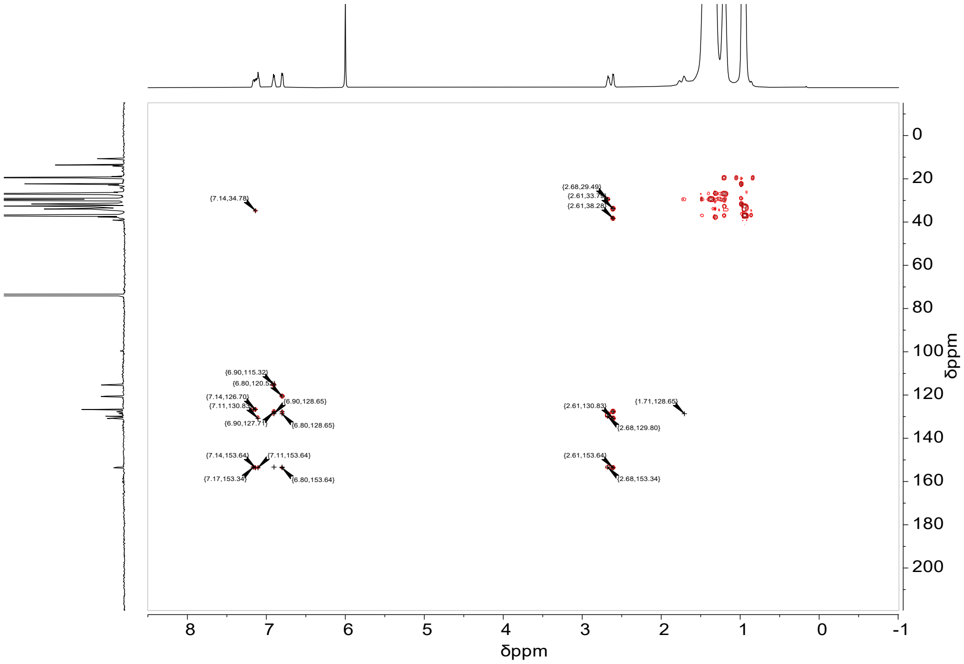


Figure S15. HMBC spectrum of poly(E-*co*-2-allylphenol) (Table 3, entry 2 & Table 2, entry 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

6. Calculations of Comonomer Incorporation and Branching.

The 2-allylphenol comonomer content was determined by quantitative ^{1}H NMR analysis. The comonomer composition is expressed as a mole fraction of 2-allylphenol (x) and ethylene (1-x). For quantification, the combined integral of signals **b**, **b'**, **c**, **c'**, **h** and **i** (denoted as $I_{b+b'+c+c'+h+i}$) was defined as **n**, and the combined integral of signals **a** and **a'** (denoted as $I_{a+a'}$) was normalized to 2.

$$\frac{2x}{3x+4(1-x)}=\frac{2}{n}$$

$$x=\frac{4}{n+1}\times 100\%$$

The comonomer contents of other copolymers, *i.e.* poly(E-*co*-eugenol), poly(E-*co*-estragole), poly(E-*co*-allylbenzene), poly(E-*co*-4-allylphenol), poly(E-*co*-2-methoxy allylbenzene), poly(E-*co*-2-allylphenoxy trimethylsilane), and poly(E-*co*-2-allylphenoxy triisopropylsilane) were determined from quantitative ^{1}H NMR analysis using the same method as described above.

The amount of methyl groups ($N_{\text{Me groups/1000C}}$) based on the ^{1}H NMR spectra was determined according to literature methods[5, 6].

$$N_{\text{Me}}\text{ groups/1000C} = 2\times I_{Me}/(3\times I_{tot})\times 1000$$

7. Representative NMR Spectrum of Poly(E-co-2-allylphenol) after Acetylation

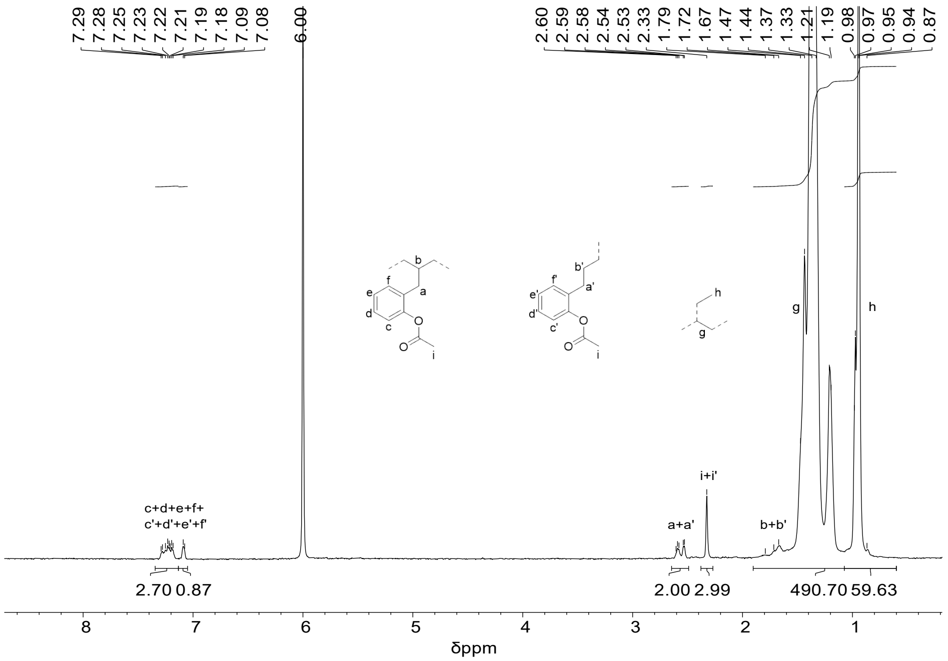


Figure S16. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 2, Entry 3) after acetylation in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

8. NMR Spectra of polymer samples from Table 1

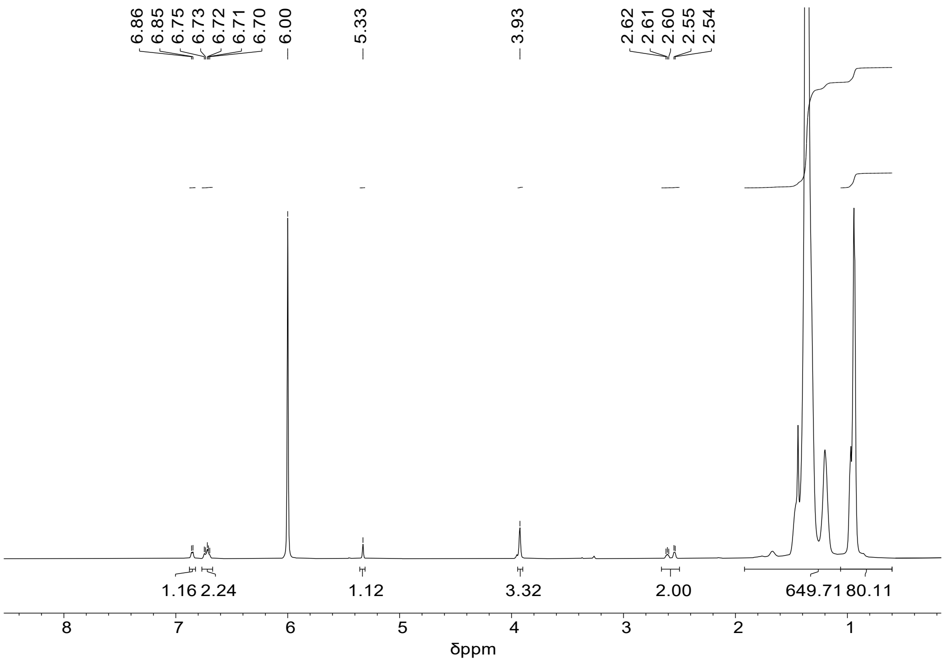


Figure S17. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-eugenol) (Table 1, Entry 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

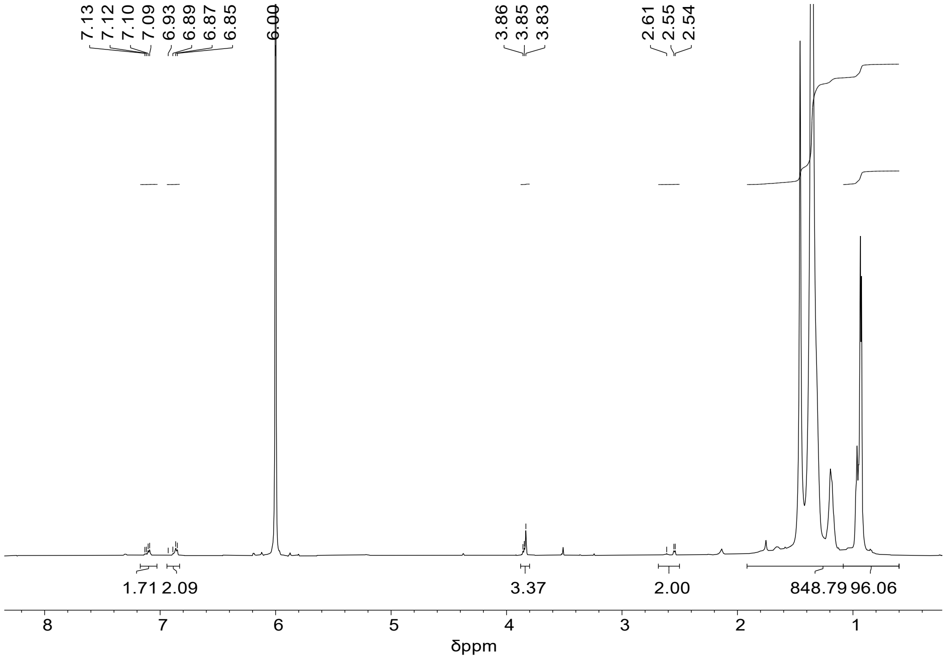


Figure S18. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-estragole) (Table 1, Entry 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

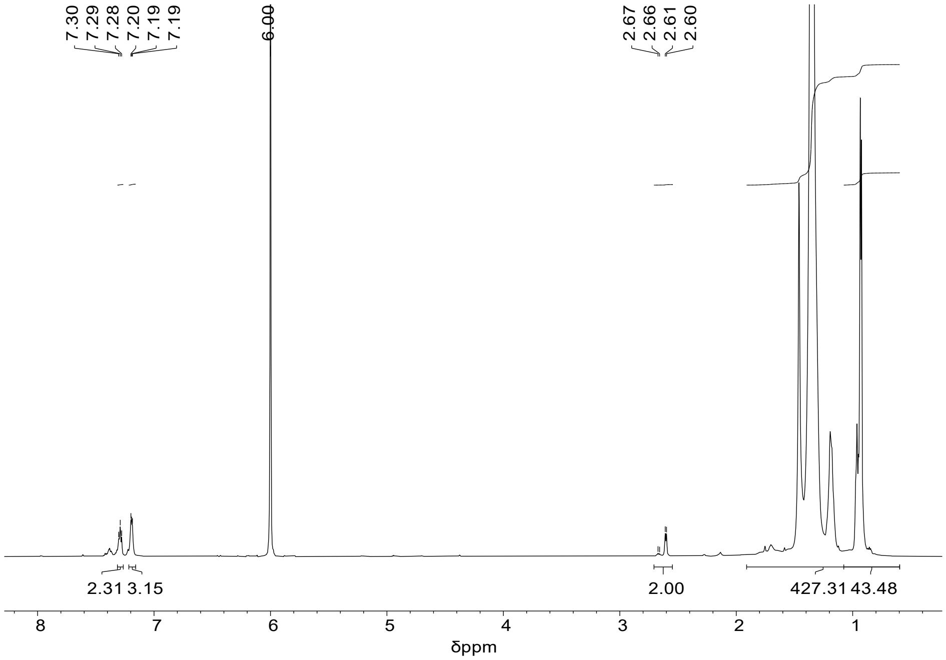


Figure S19. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-allylbenzene) (Table 1, Entry 4) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

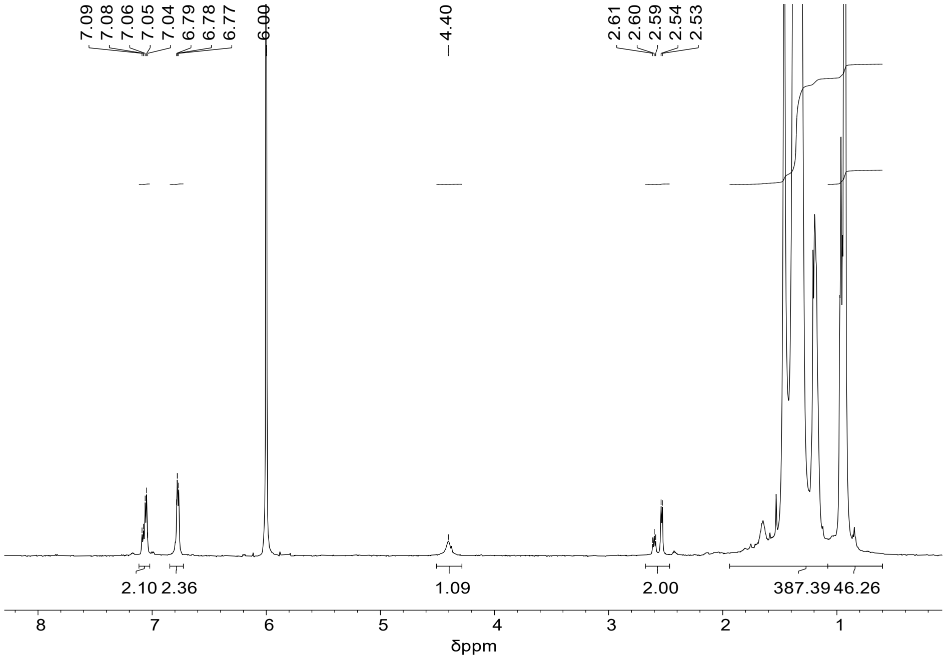


Figure S20. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-4-allylphenol) (Table 1, Entry 5) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

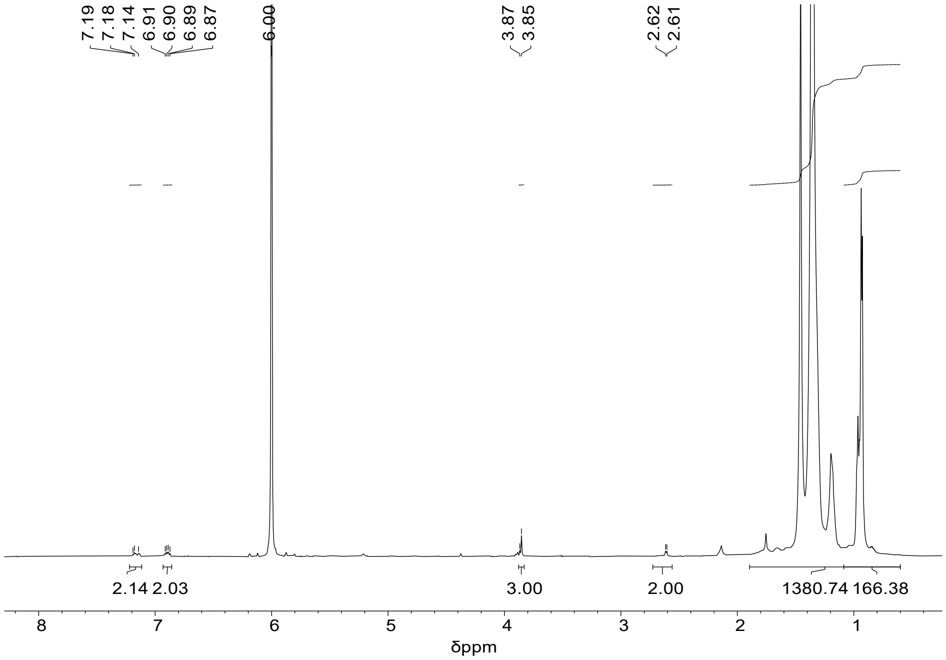


Figure S21. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-methoxy allylbenzene) (Table 1, Entry 6) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

9. NMR Spectra of polymer samples from Table 2

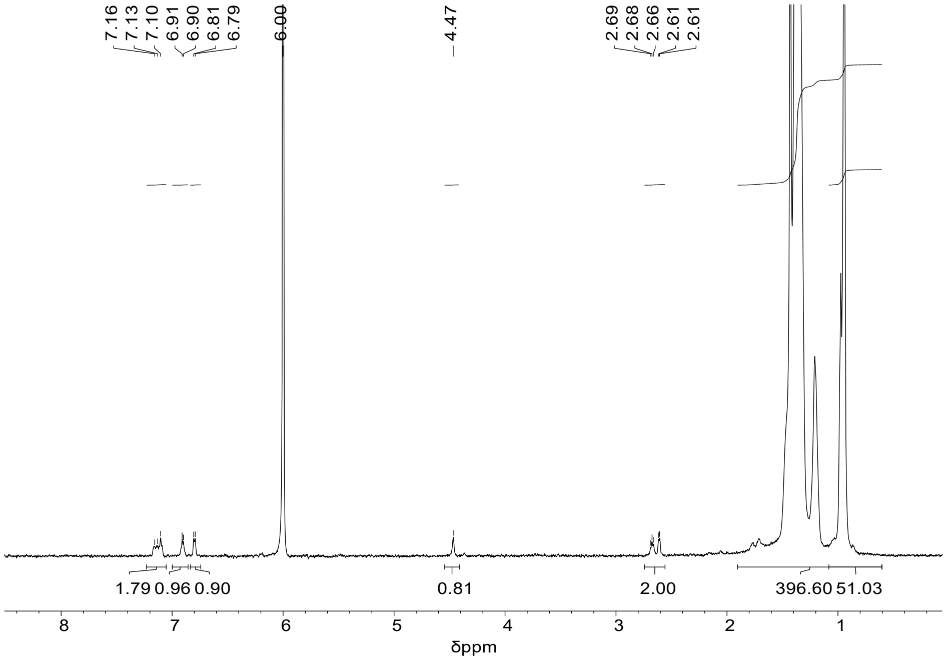


Figure S22. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 2, Entry 2 & Table 1, entry 3) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

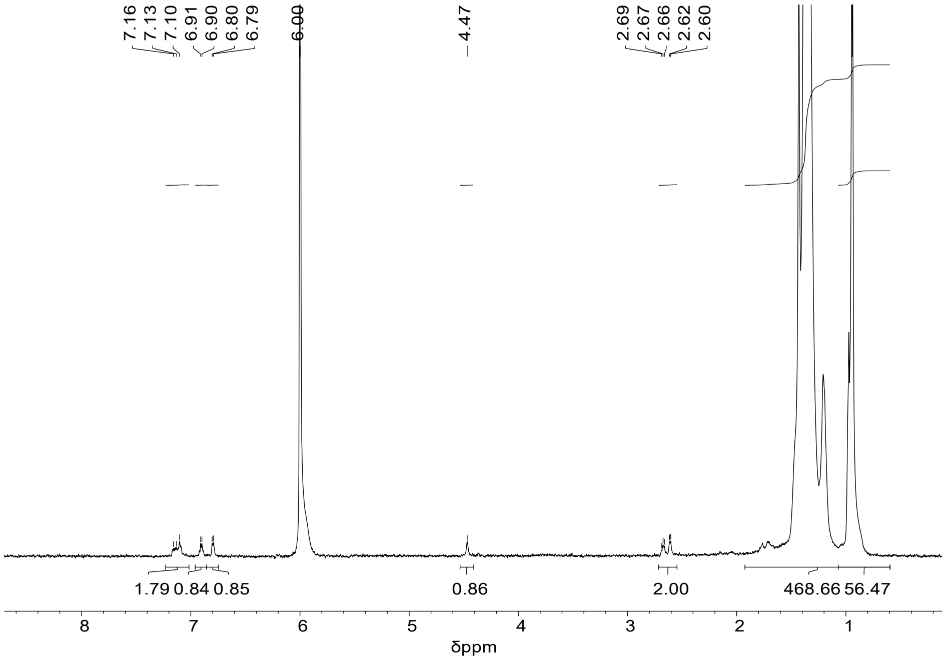


Figure S23. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 2, Entry 3) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

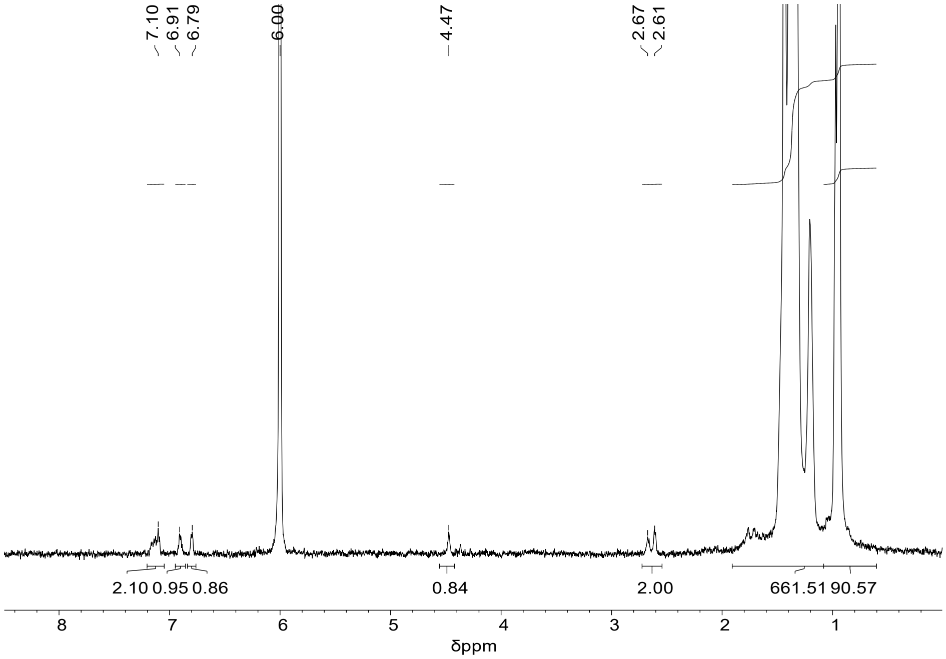


Figure S24. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 2, Entry 4) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

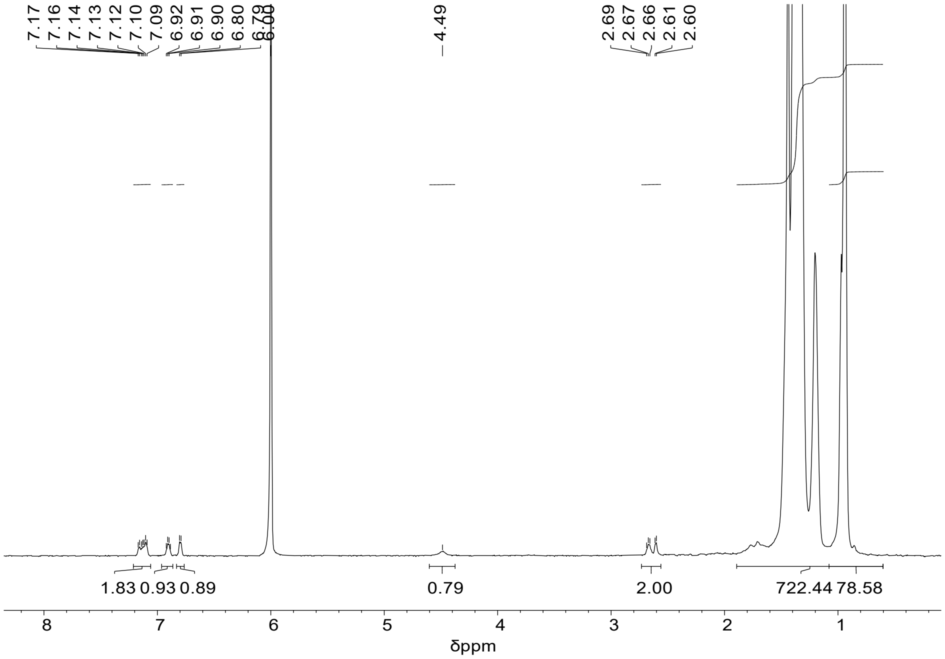


Figure S25. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 2, Entry 5) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

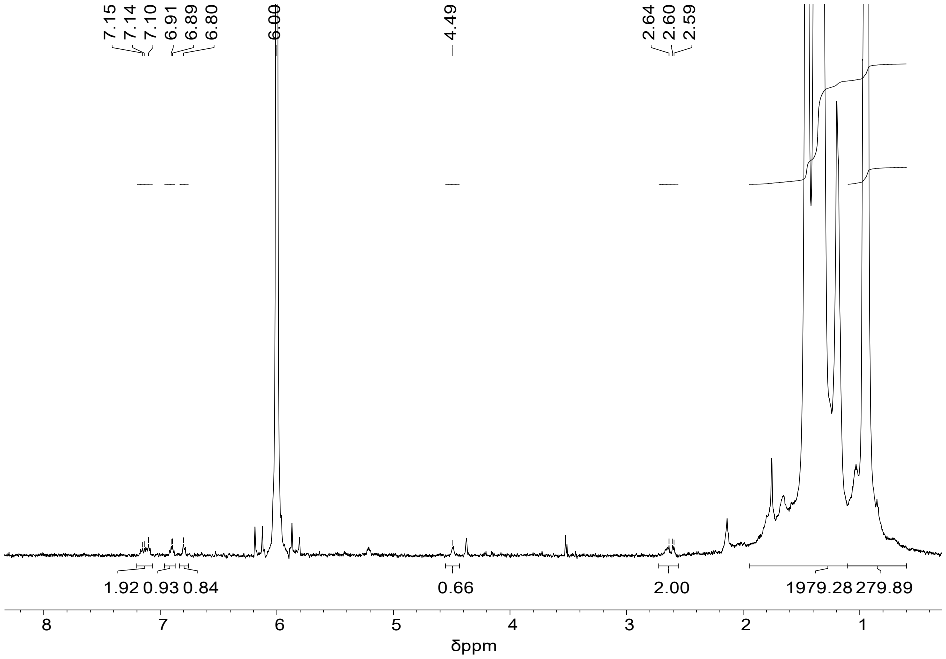


Figure S26. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 2, Entry 6) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

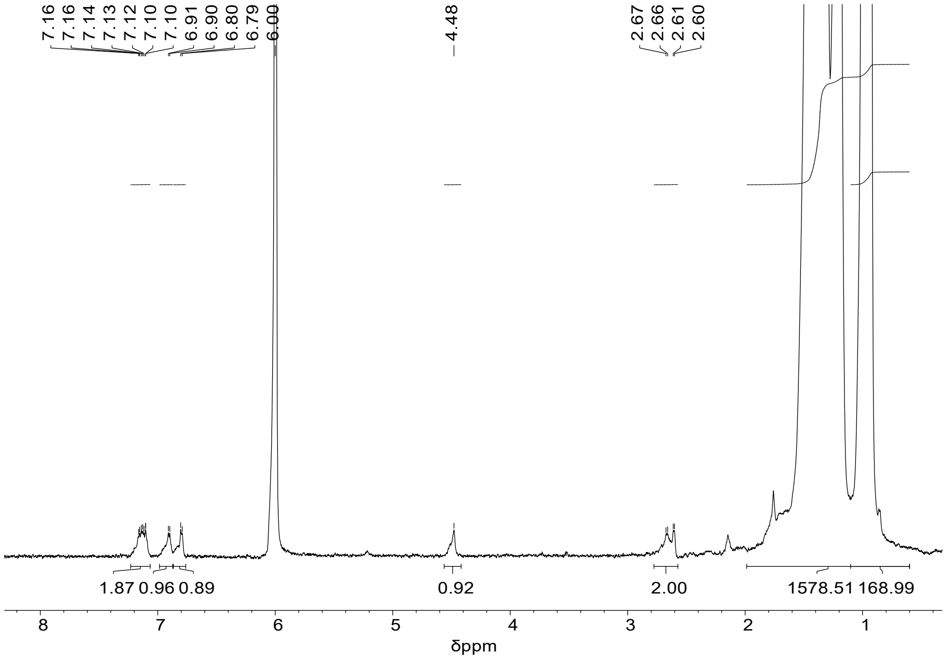


Figure S27. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 2, Entry 7) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

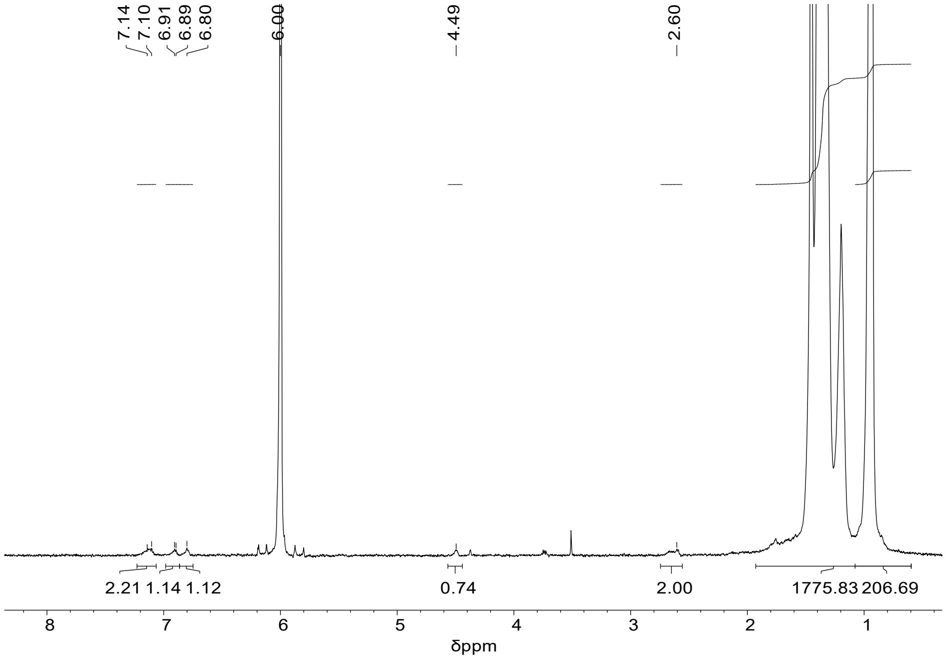


Figure S28. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 2, Entry 8) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

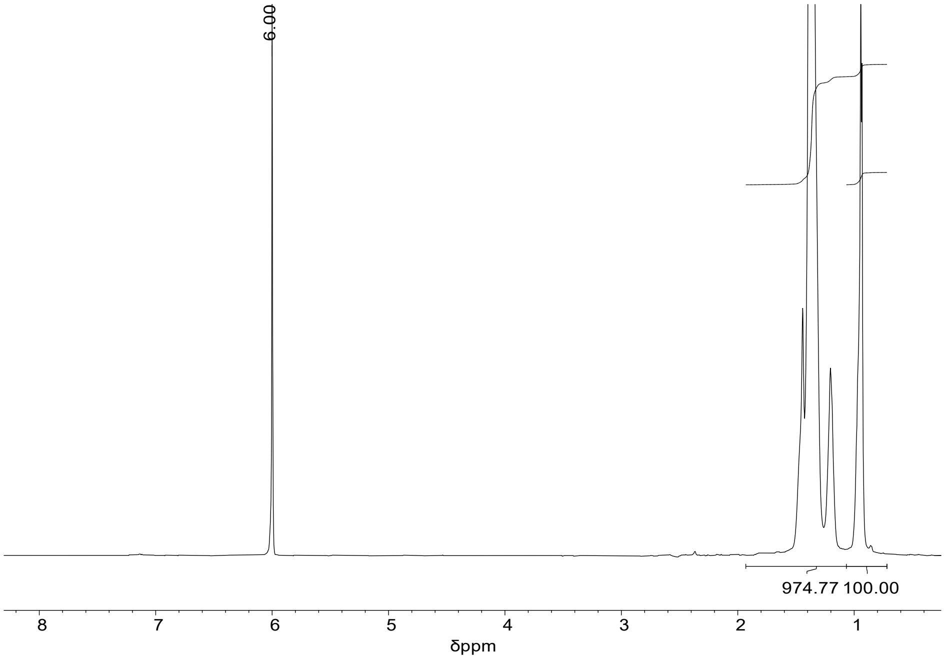


Figure S29. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 2, Entry 9) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

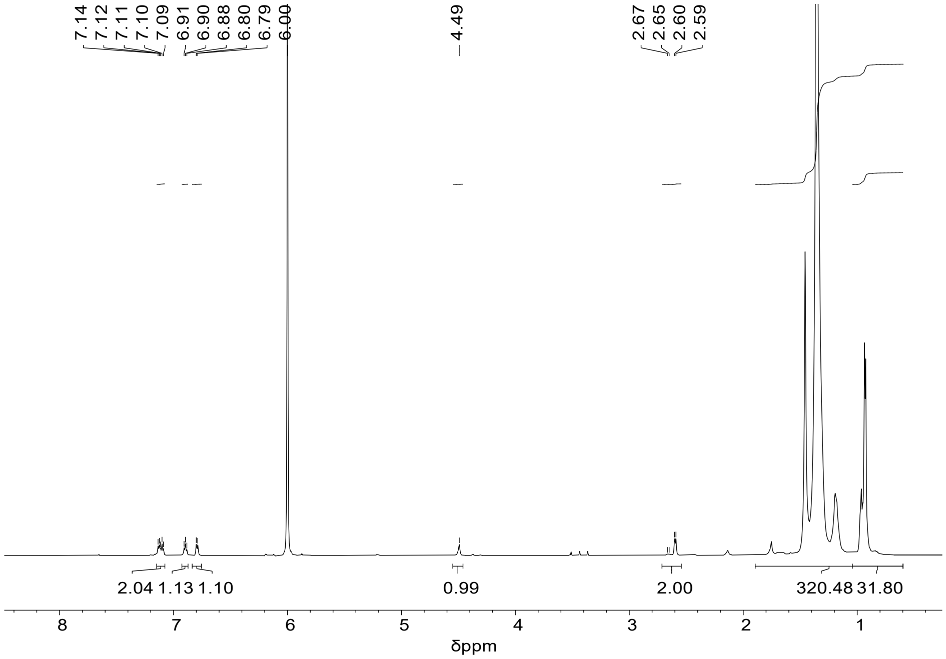


Figure S30. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenoxy trimethylsilane) (Table 2, Entry 10) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

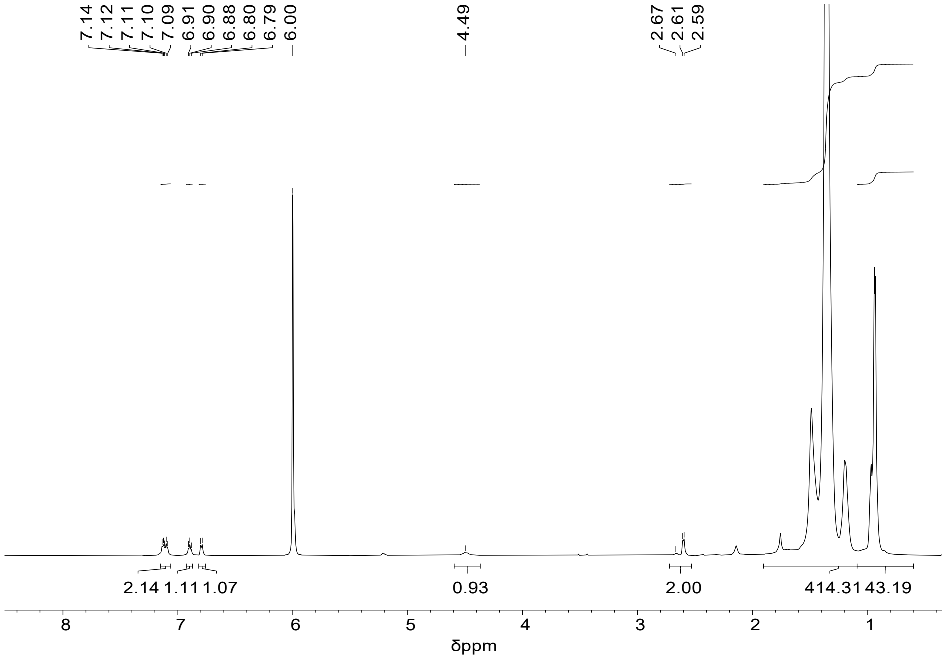


Figure S31. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenoxy trimethylsilane) (Table 2, Entry 11) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

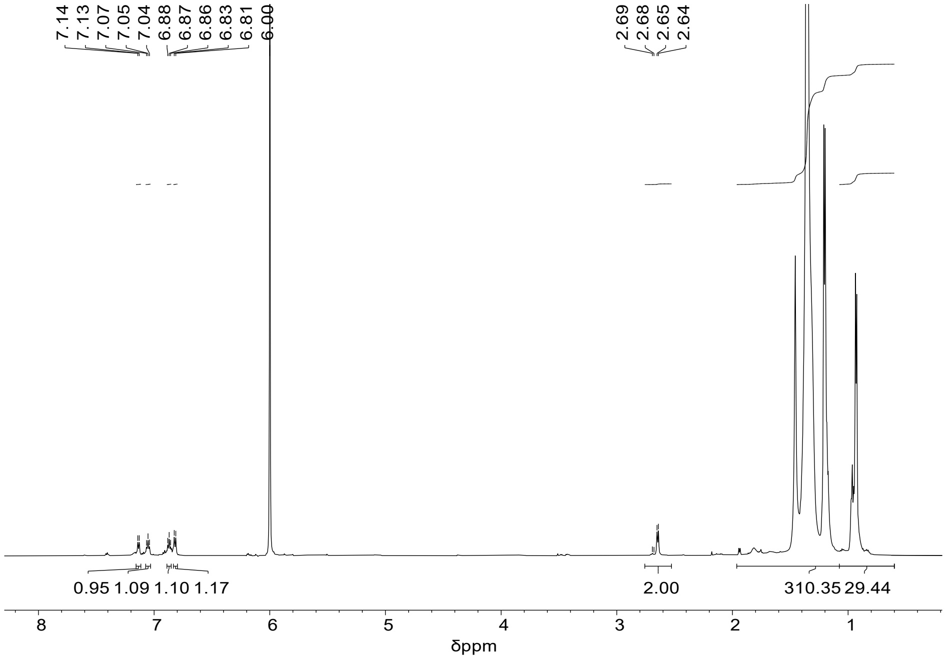


Figure S32. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenoxy triisopropylsilane) (Table 2, Entry 12) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

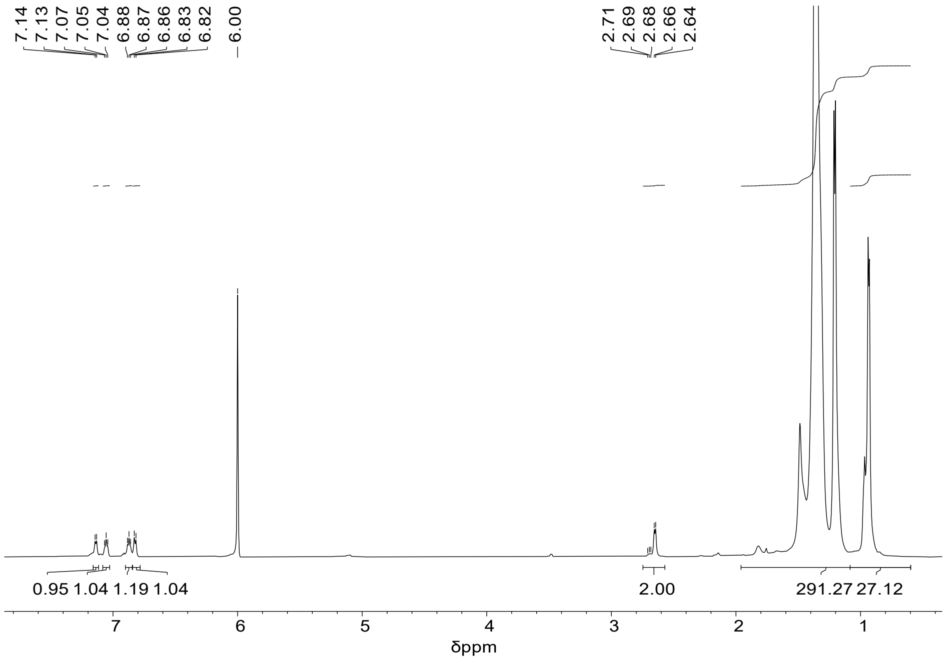


Figure S33. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenoxy triisopropylsilane) (Table 2, Entry 13) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

10. NMR Spectra of polymer samples from Table 3

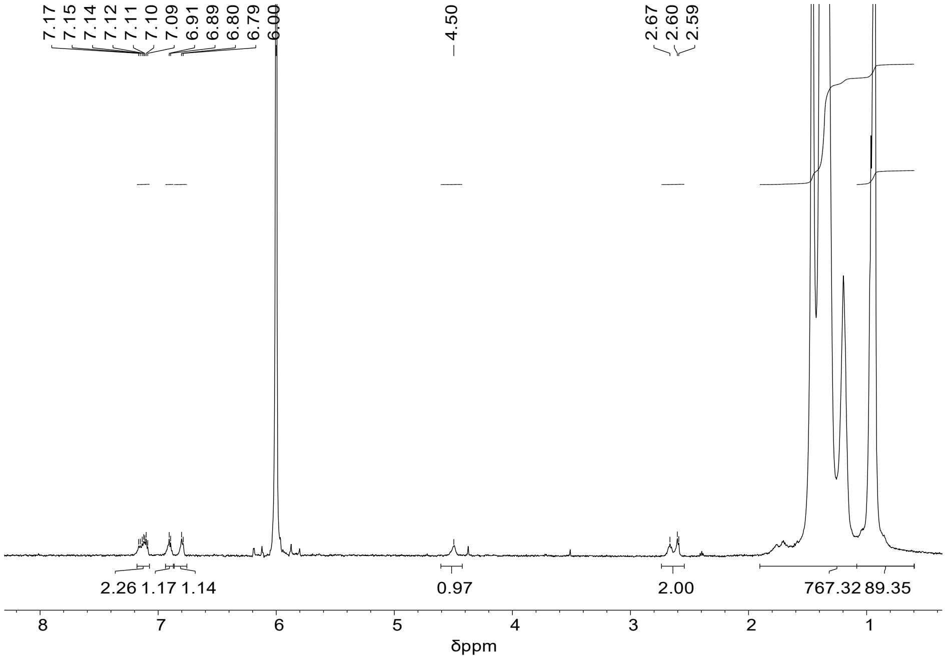


Figure S34. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 3, Entry 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

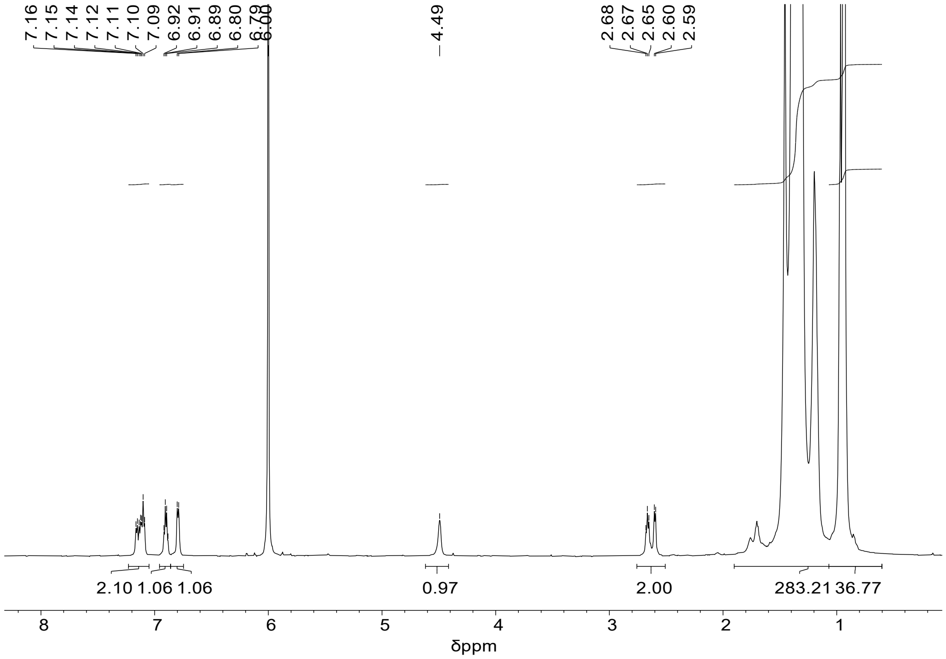


Figure S35. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 3, Entry 3) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

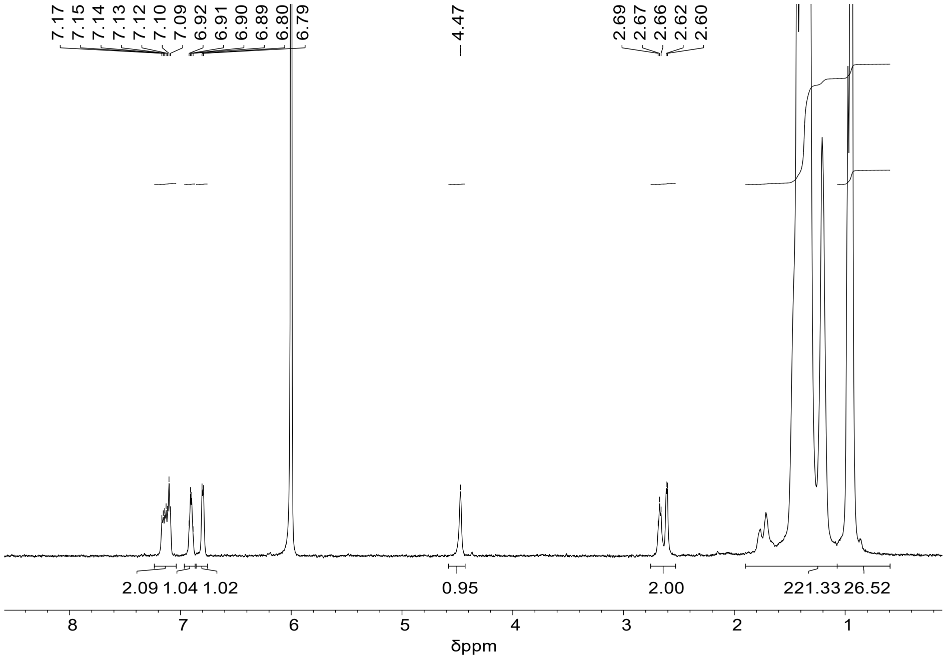


Figure S36. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 3, Entry 4) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

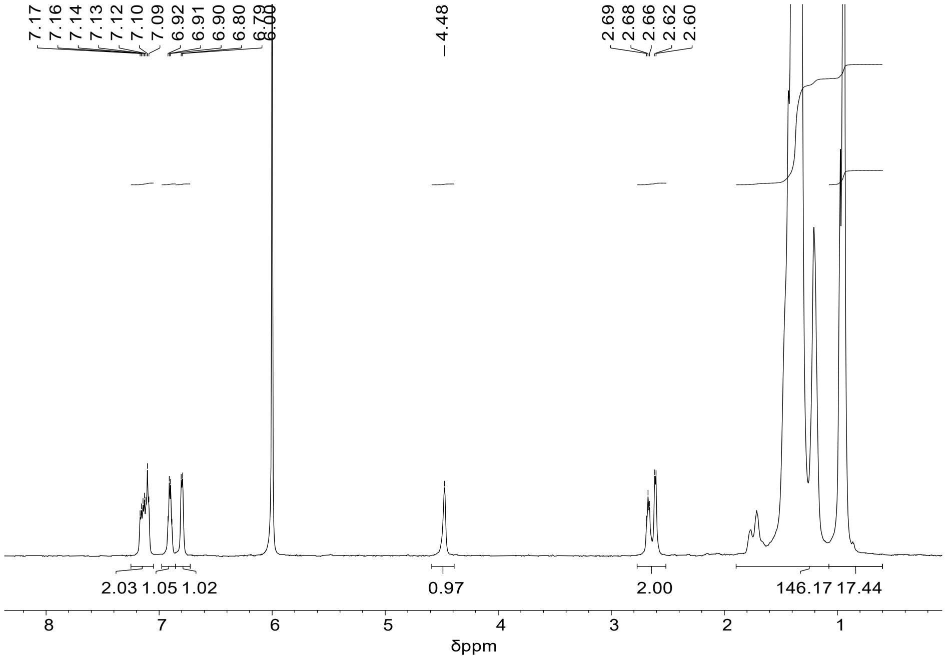


Figure S37. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 3, Entry 5) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

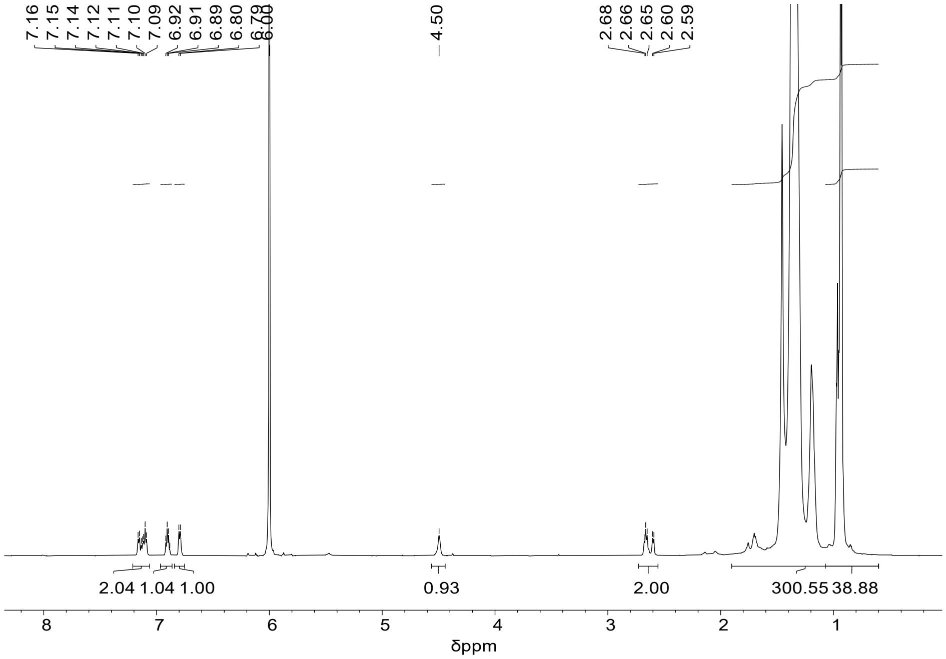


Figure S38. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 3, Entry 6) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

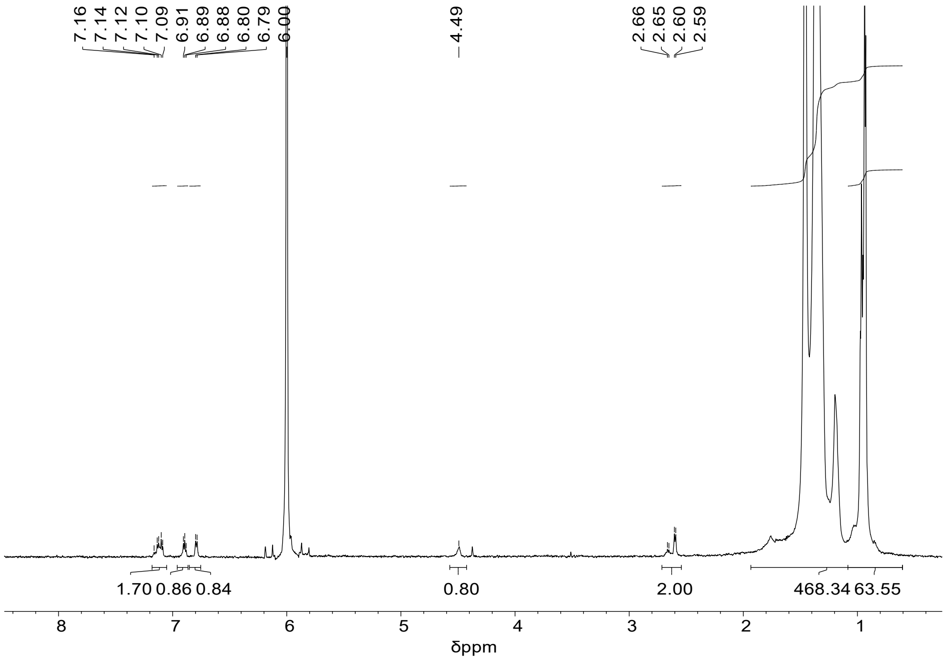


Figure S39. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 3, Entry 7) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

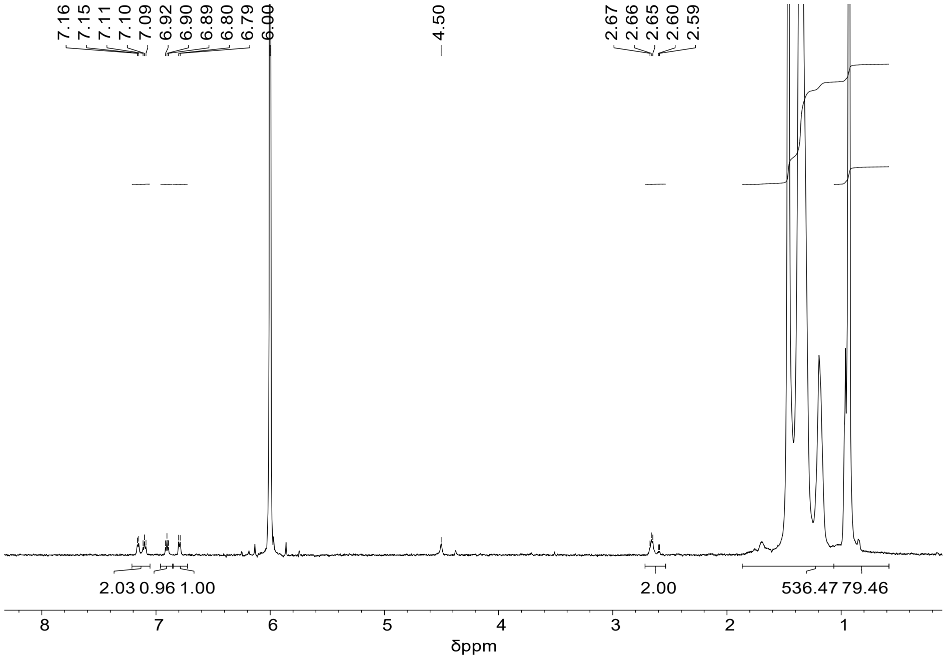


Figure S40. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 3, Entry 8) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

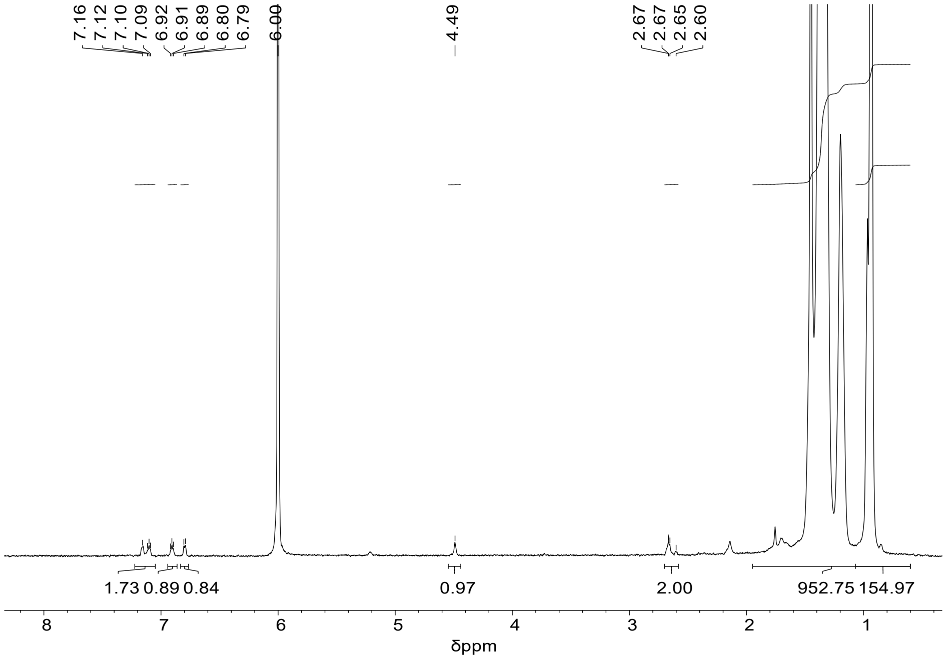


Figure S41. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 3, Entry 9) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

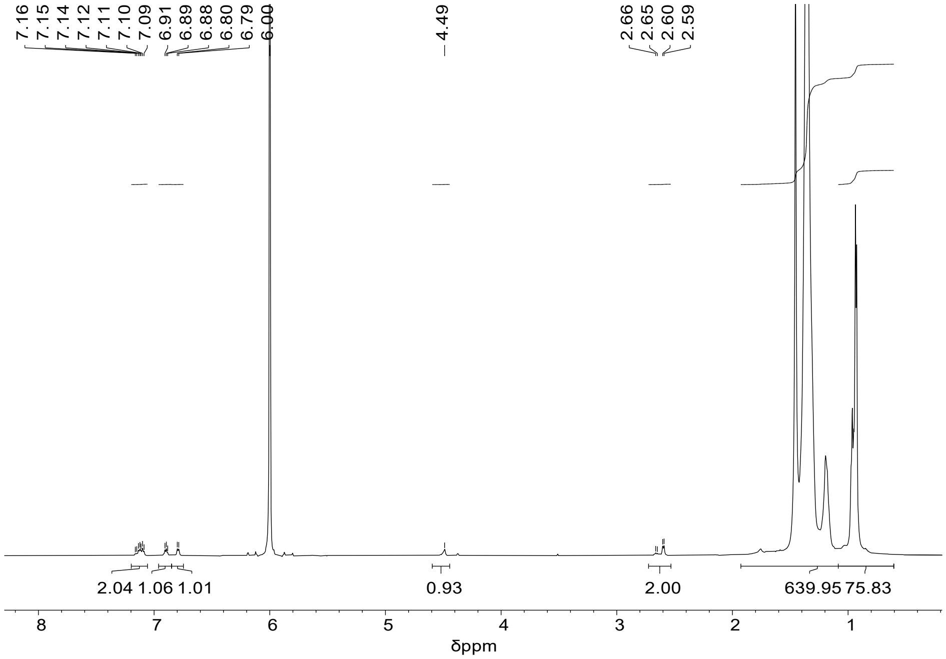
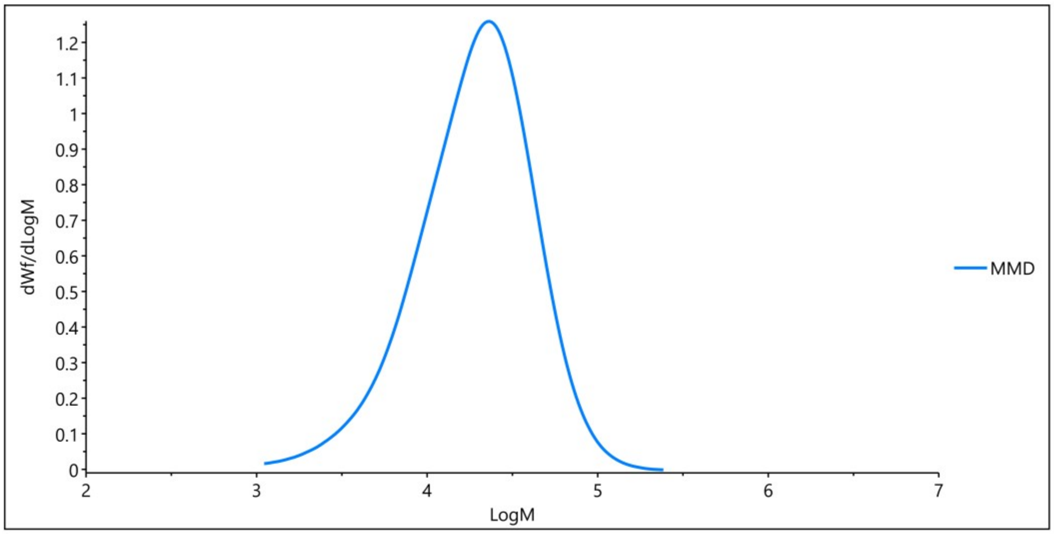


Figure S42. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-2-allylphenol) (Table 3, Entry 10) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

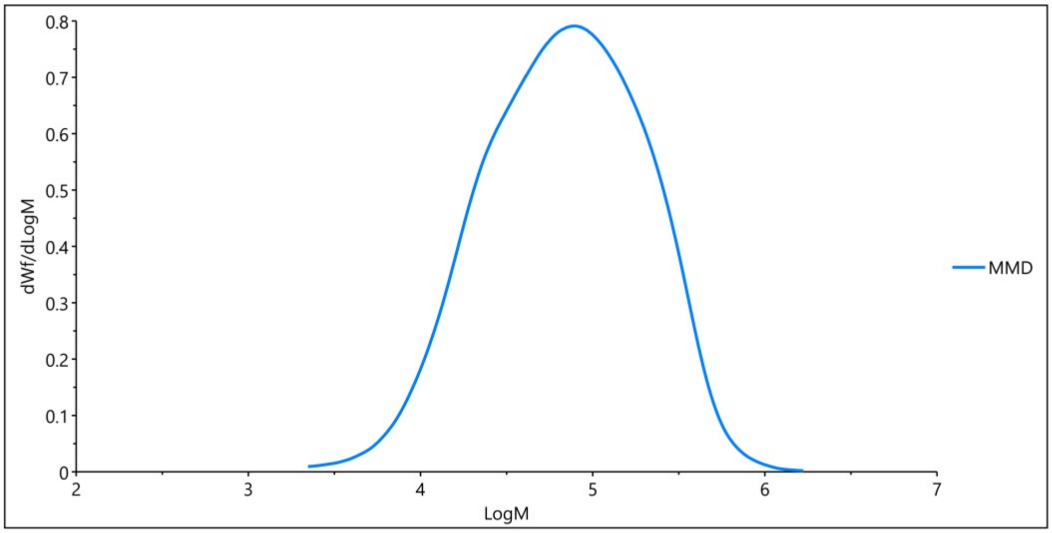
11. GPC Traces of Polymer Samples



Results

Mw	24642	g/mol
Mn	13264	g/mol
Mw / Mn	1.86	
Mz	39075	g/mol
Mp	22985	g/mol
Mv	22972	g/mol
IVmwd	0.64	dL/g

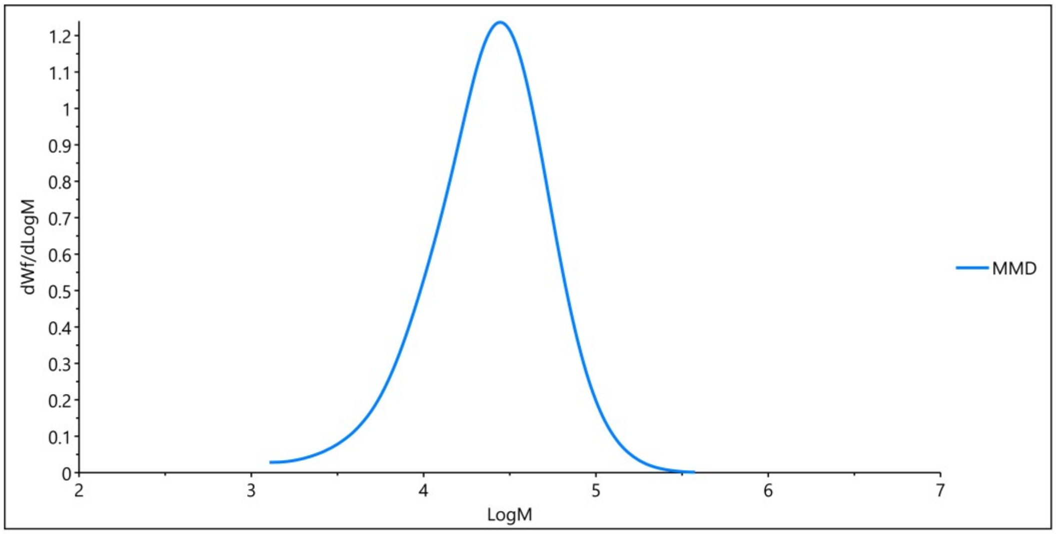
Figure S43. GPC trace of poly(E-*co*-estragole) (Table 1, Entry 2).



Results

Mw	112373	g/mol
Mn	38432	g/mol
Mw / Mn	2.92	
Mz	248308	g/mol
Mp	78191	g/mol
Mv	98817	g/mol
IVmwd	1.85	dL/g

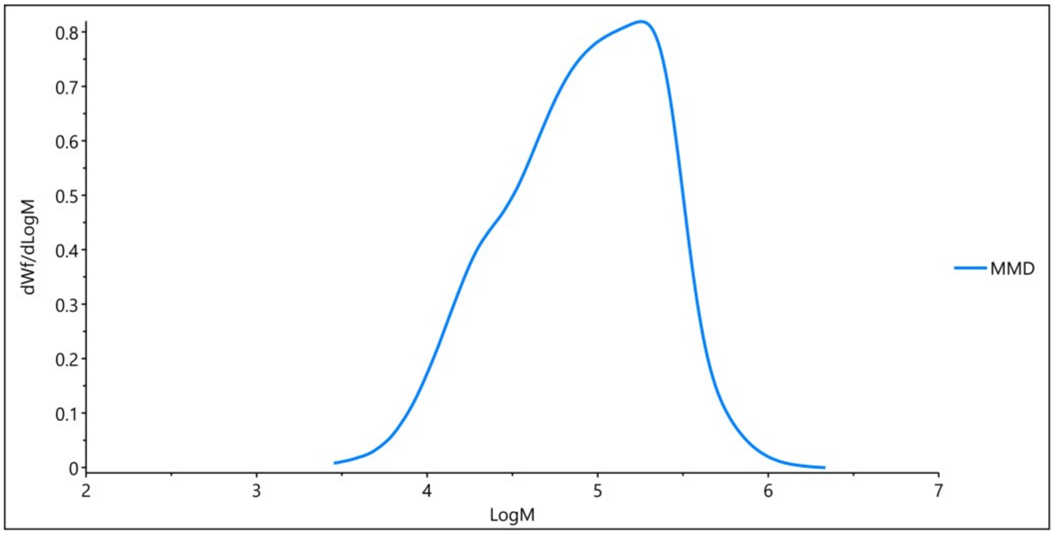
Figure S44. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 1, Entry 3).



Results

Mw	32178	g/mol
Mn	16259	g/mol
Mw / Mn	1.98	
Mz	55137	g/mol
Mp	27813	g/mol
Mv	29745	g/mol
IVmwd	0.77	dL/g

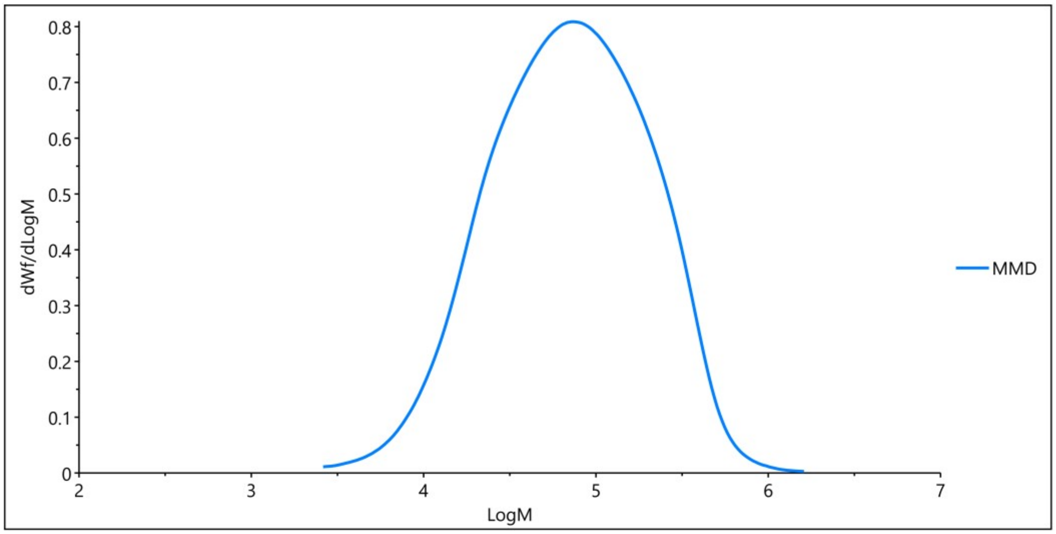
Figure S45. GPC trace of poly(E-*co*-2-methoxy allylbenzene) (Table 1, Entry 6).



Results

Mw	131290	g/mol
Mn	44139	g/mol
Mw / Mn	2.97	
Mz	272255	g/mol
Mp	178317	g/mol
Mv	116429	g/mol
IVmwd	2.08	dL/g

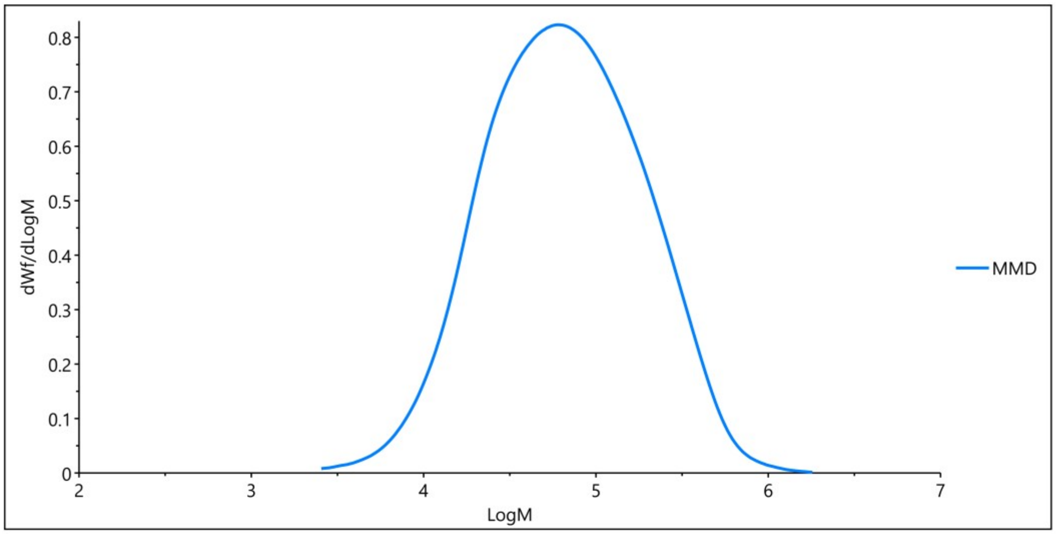
Figure S46. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 2, Entry 1).



Results

Mw	113312	g/mol
Mn	40654	g/mol
Mw / Mn	2.79	
Mz	245022	g/mol
Mp	73900	g/mol
Mv	100090	g/mol
IVmwd	1.86	dL/g

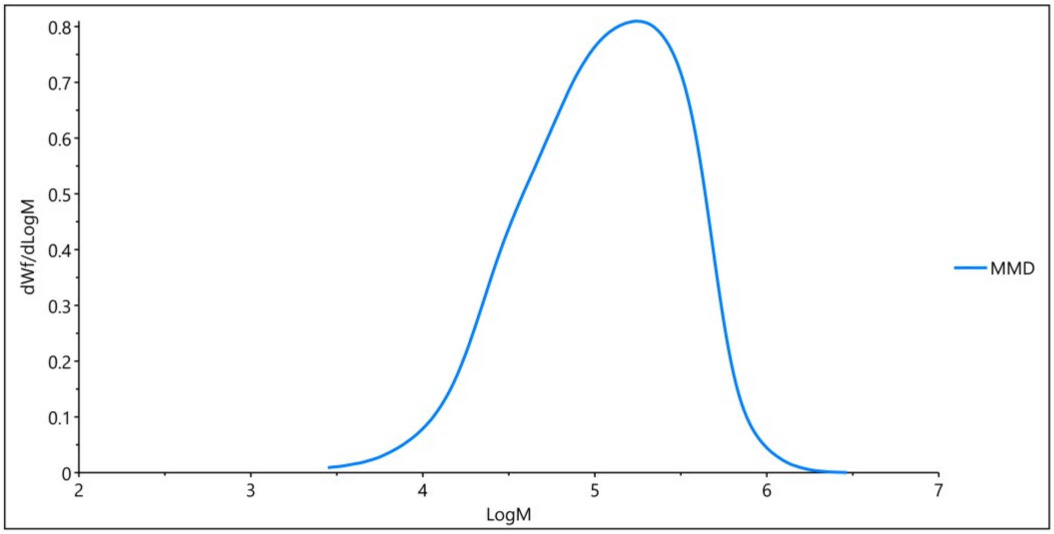
Figure S47. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 2, Entry 3).



Results

Mw	107128	g/mol
Mn	38895	g/mol
Mw / Mn	2.75	
Mz	250610	g/mol
Mp	60708	g/mol
Mv	93879	g/mol
IVmwd	1.78	dL/g

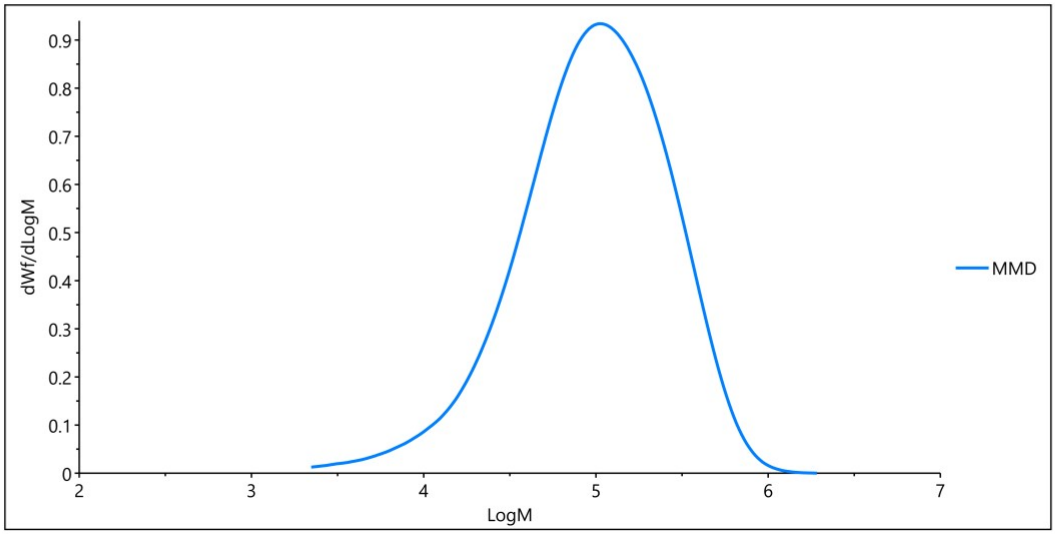
Figure S48. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 2, Entry 4).



Results

Mw	177005	g/mol
Mn	59363	g/mol
Mw / Mn	2.98	
Mz	360636	g/mol
Mp	175753	g/mol
Mv	157389	g/mol
IVmwd	2.59	dL/g

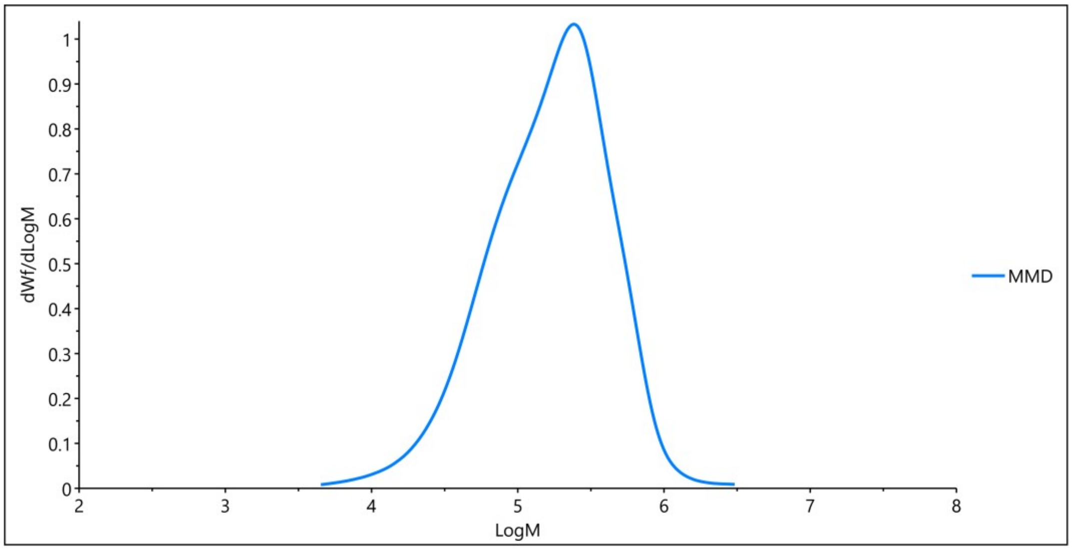
Figure S49. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 2, Entry 5).



Results

Mw	145645	g/mol
Mn	52585	g/mol
Mw / Mn	2.77	
Mz	279133	g/mol
Mp	106193	g/mol
Mv	131050	g/mol
IVmwd	2.27	dL/g

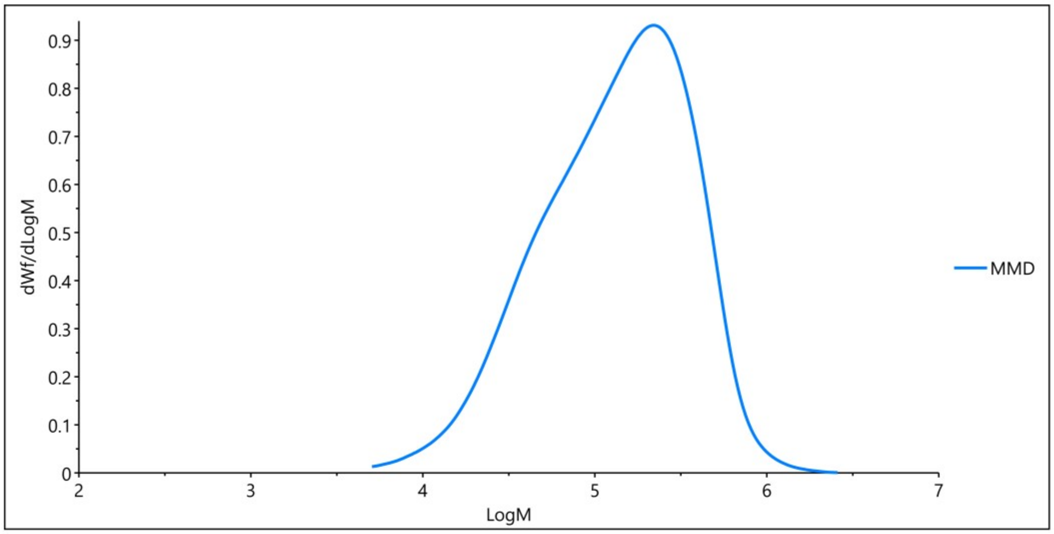
Figure S50. GPC trace of poly(E-*co*-2-allylphenol) (Table 2, Entry 6).



Results

Mw	240410	g/mol
Mn	96471	g/mol
Mw / Mn	2.49	
Mz	468651	g/mol
Mp	241216	g/mol
Mv	214861	g/mol
IVmwd	2.4783	dL/g

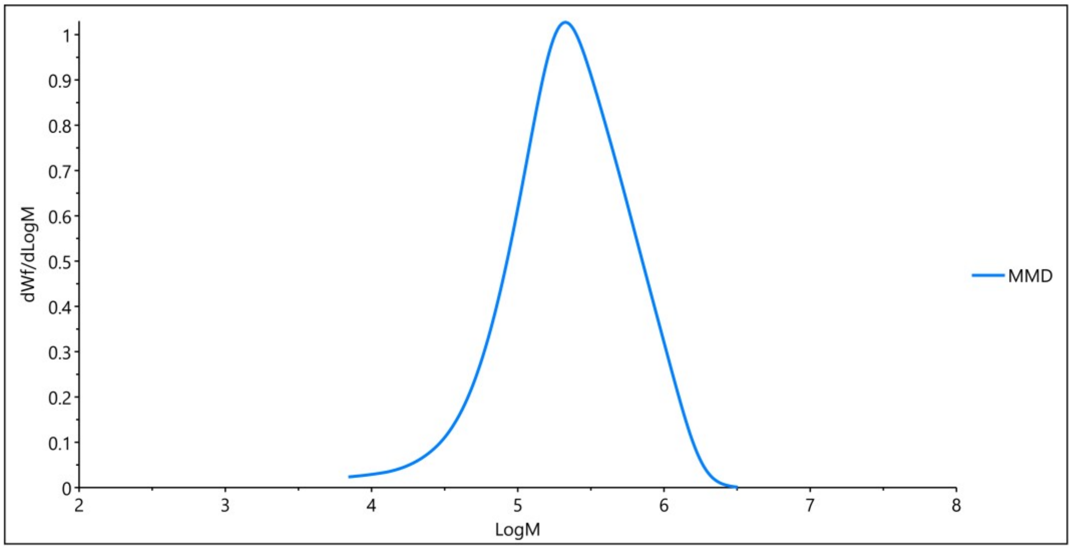
Figure S51. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 2, Entry 7).



Results

Mw	196385	g/mol
Mn	75764	g/mol
Mw / Mn	2.59	
Mz	365272	g/mol
Mp	219613	g/mol
Mv	177341	g/mol
IVmwd	2.82	dL/g

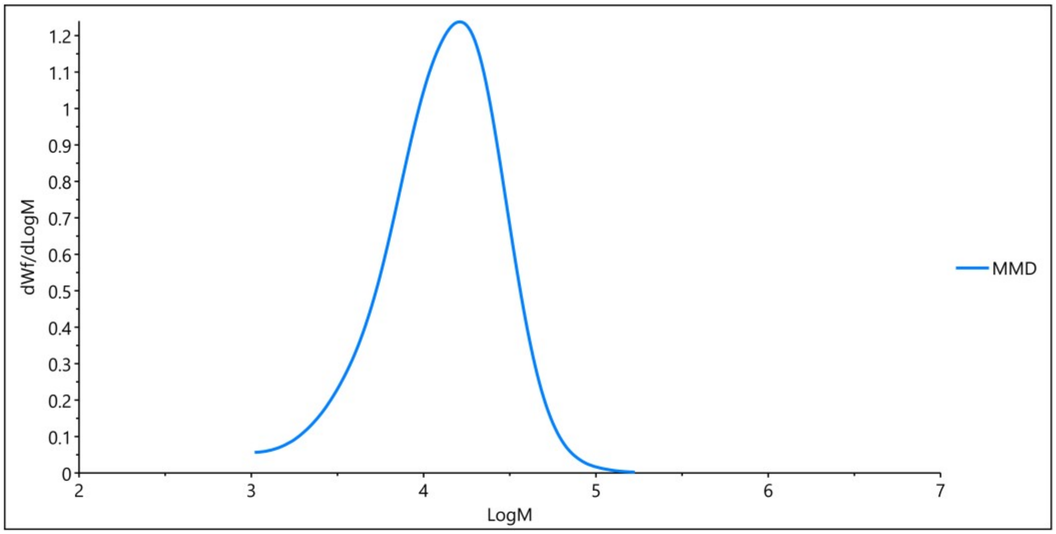
Figure S52. GPC trace of poly(E-*co*-2-allylphenol) (Table 2, Entry 8).



Results

Mw	332576	g/mol
Mn	130017	g/mol
Mw / Mn	2.56	
Mz	638402	g/mol
Mp	212026	g/mol
Mv	296110	g/mol
IVmwd	3.0952	dL/g

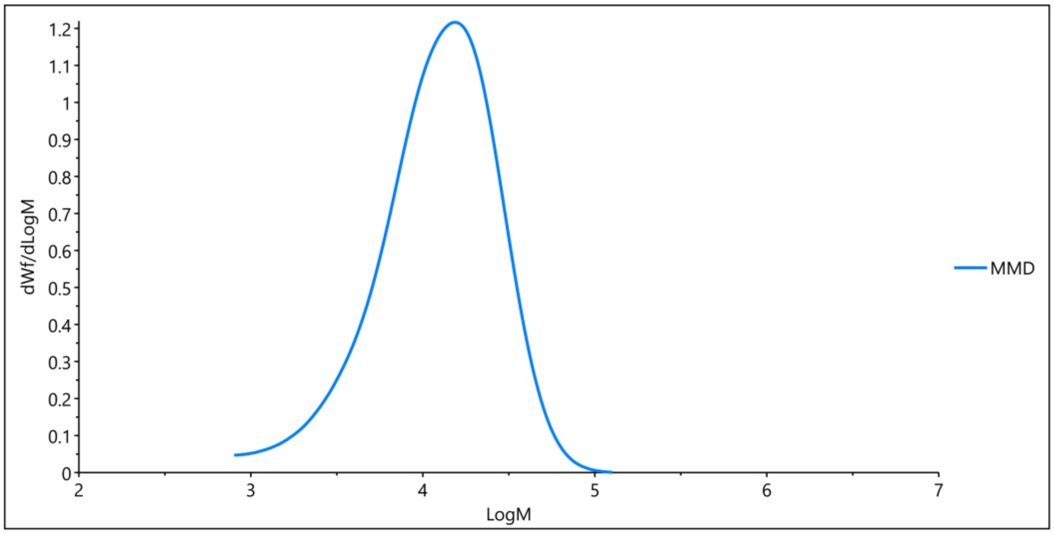
Figure S53. GPC trace of poly(E-*co*-2-allylphenol) (Table 2, Entry 9).



Results

Mw	16815	g/mol
Mn	9052	g/mol
Mw / Mn	1.86	
Mz	27032	g/mol
Mp	16178	g/mol
Mv	15665	g/mol
IVmwd	0.49	dL/g

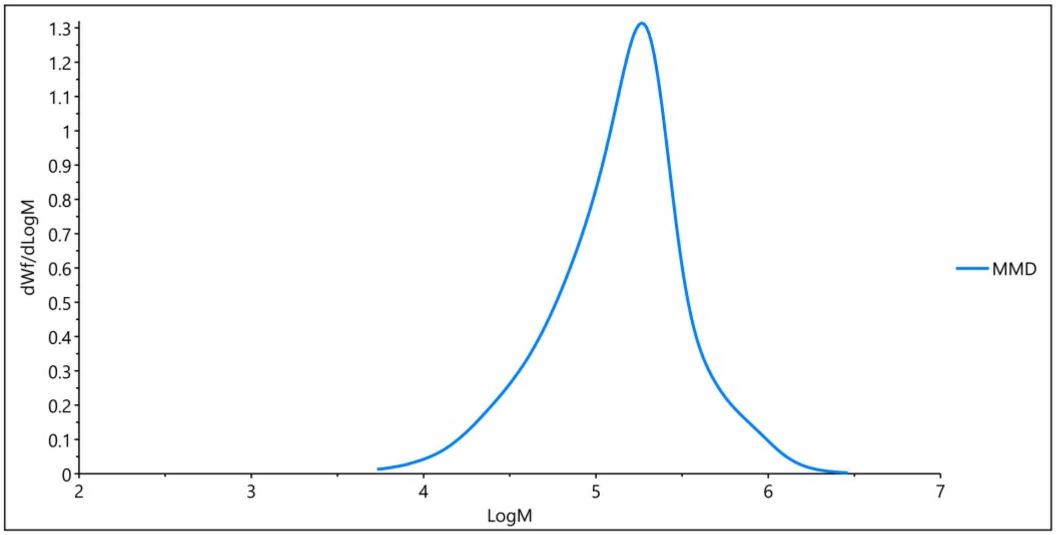
Figure S54. GPC trace of poly(E-*co*-2-allylphenoxy triisopropylsilane) (Table 2, Entry 12).



Results

Mw	15830	g/mol
Mn	8265	g/mol
Mw / Mn	1.92	
Mz	24628	g/mol
Mp	15362	g/mol
Mv	14767	g/mol
IVmwd	0.47	dL/g

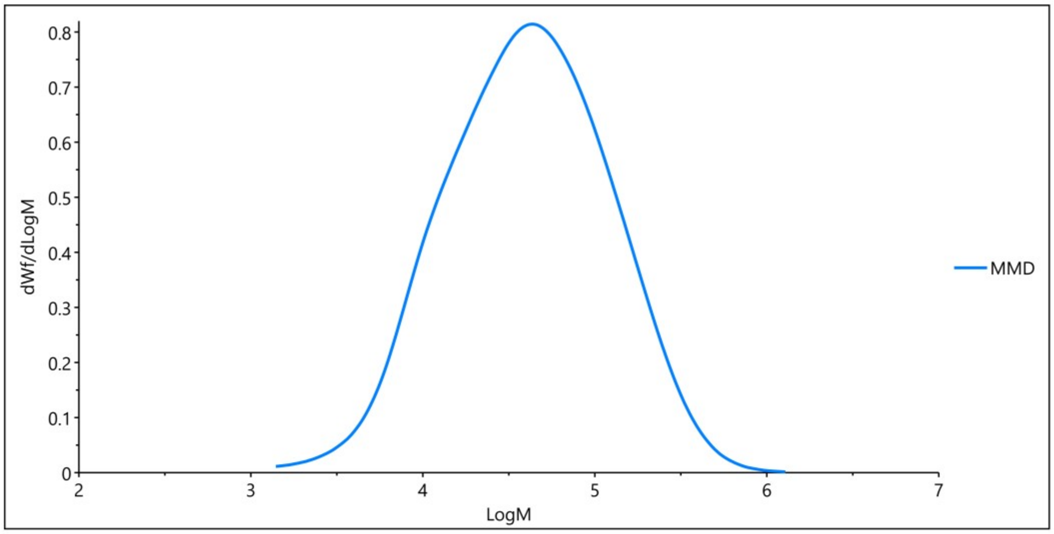
Figure S55. GPC trace of poly(E-*co*-2-allylphenoxy triisopropylsilane) (Table 2, Entry 13).



Results

Mw	200015	g/mol
Mn	84121	g/mol
Mw / Mn	2.38	
Mz	422711	g/mol
Mp	184207	g/mol
Mv	180250	g/mol
IVmwd	2.85	dL/g

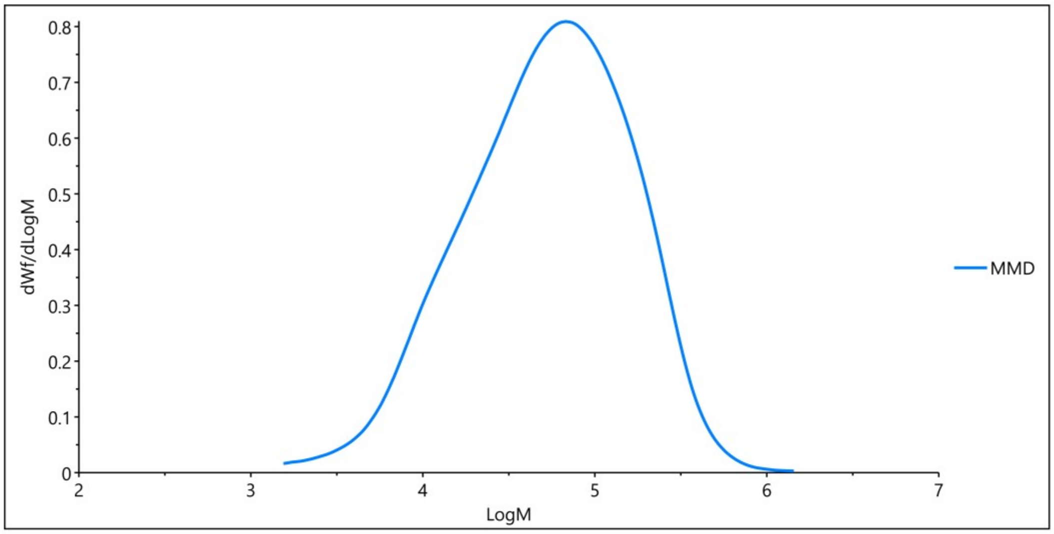
Figure S56. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 3, Entry 1).



Results

Mw	69615	g/mol
Mn	22755	g/mol
Mw / Mn	3.06	
Mz	173930	g/mol
Mp	43320	g/mol
Mv	60355	g/mol
IVmwd	1.29	dL/g

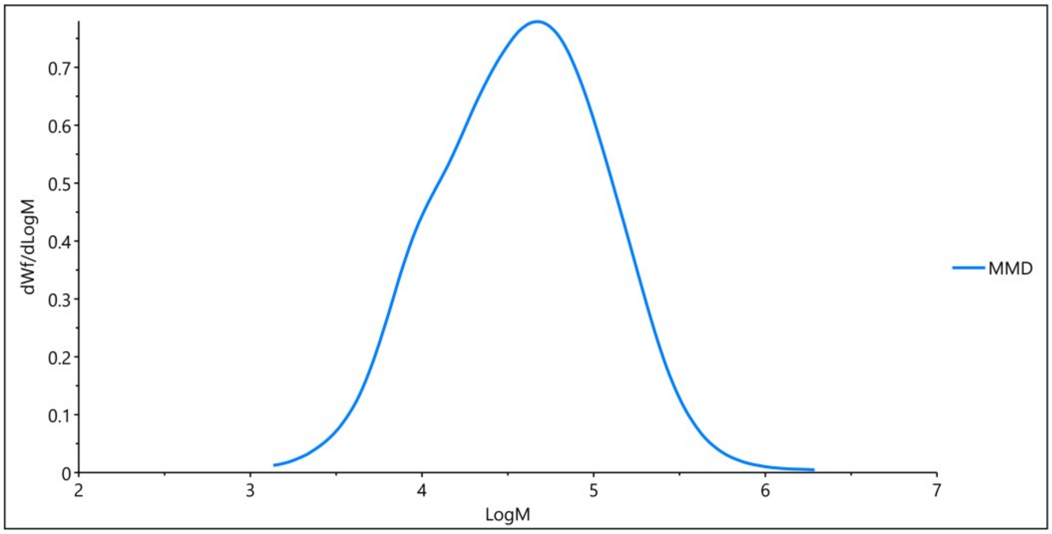
Figure S57. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 3, Entry 3).



Results

Mw	88817	g/mol
Mn	27528	g/mol
Mw / Mn	3.23	
Mz	200528	g/mol
Mp	68186	g/mol
Mv	77868	g/mol
IVmwd	1.55	dL/g

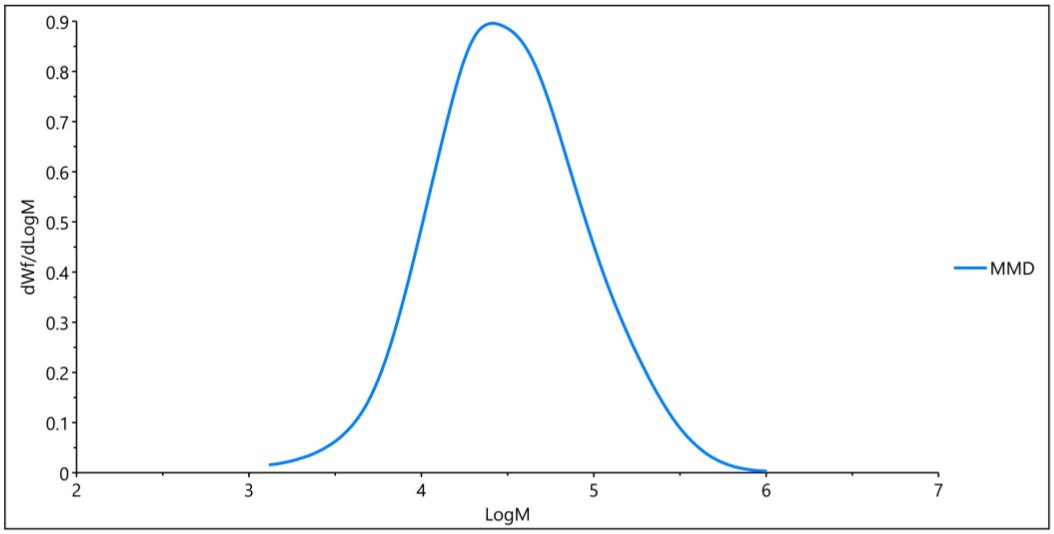
Figure S58. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 3, Entry 4).



Results

Mw	70836	g/mol
Mn	20271	g/mol
Mw / Mn	3.49	
Mz	229856	g/mol
Mp	46941	g/mol
Mv	59945	g/mol
IVmwd	1.28	dL/g

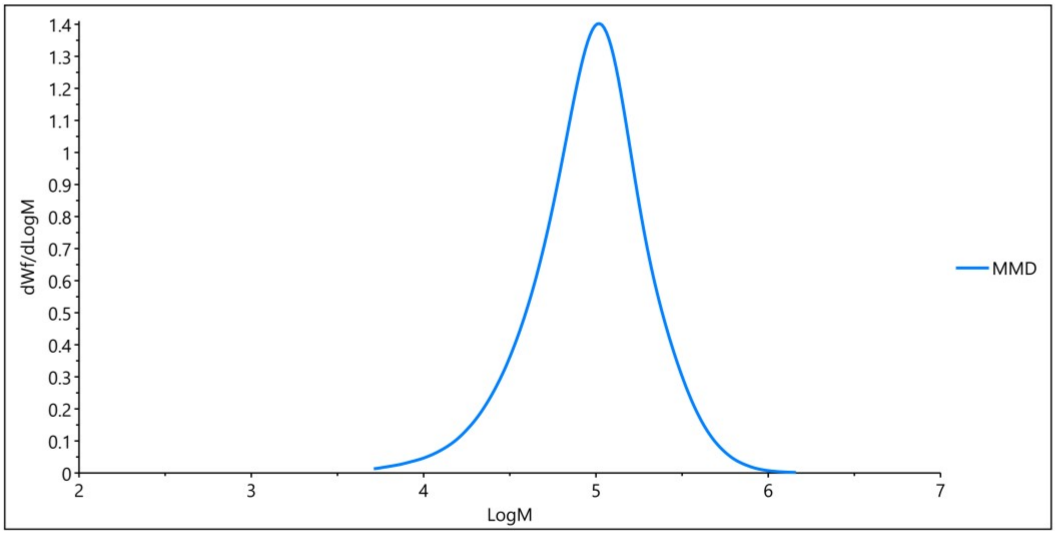
Figure S59. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 3, Entry 5).



Results

Mw	54606	g/mol
Mn	19124	g/mol
Mw / Mn	2.86	
Mz	148611	g/mol
Mp	26007	g/mol
Mv	47139	g/mol
IVmwd	1.08	dL/g

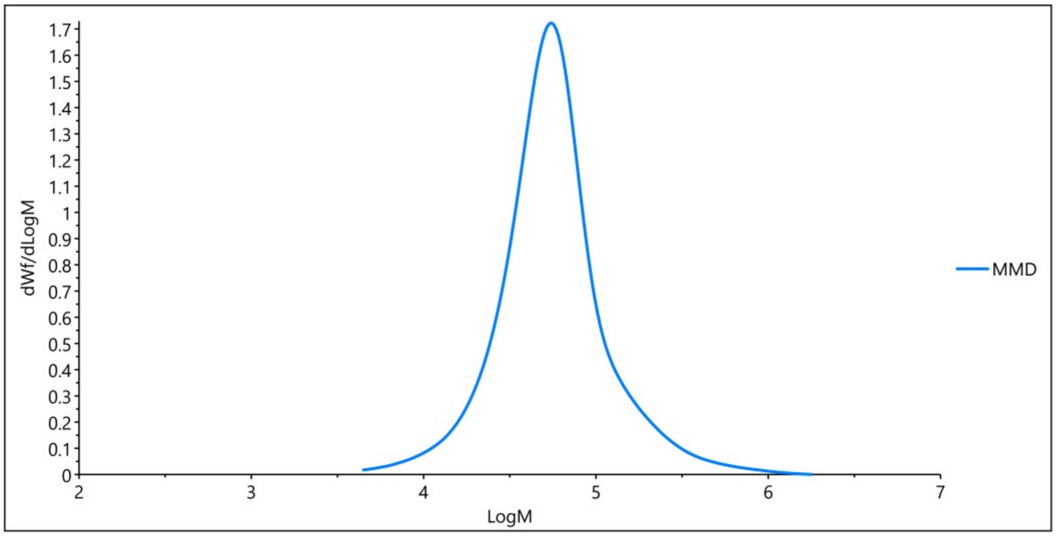
Figure S60. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 3, Entry 6).



Results

Mw	122519	g/mol
Mn	66317	g/mol
Mw / Mn	1.85	
Mz	208302	g/mol
Mp	103908	g/mol
Mv	113746	g/mol
IVmwd	2.04	dL/g

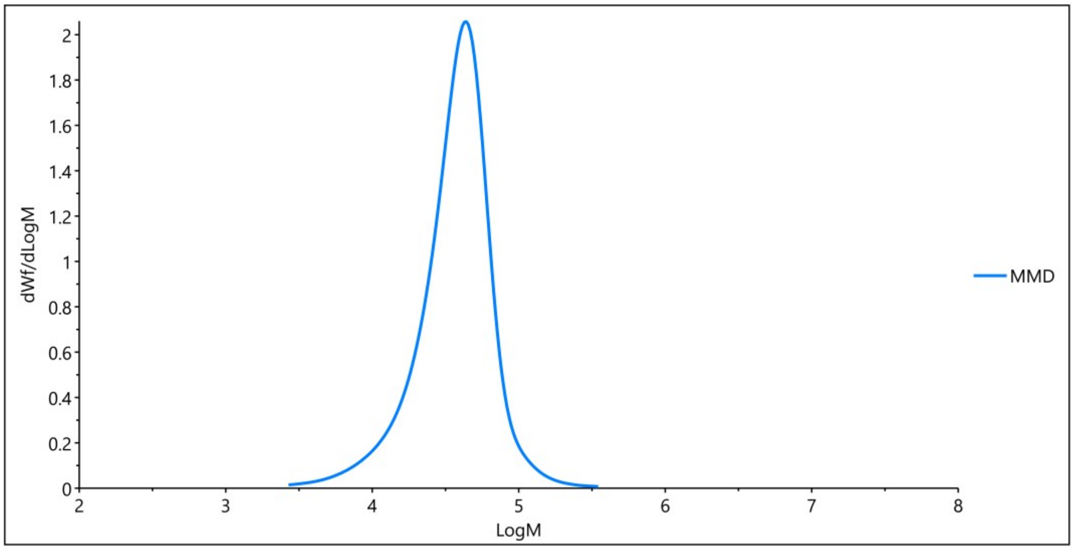
Figure S61. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 3, Entry 7).



Results

Mw	76379	g/mol
Mn	42774	g/mol
Mw / Mn	1.79	
Mz	187502	g/mol
Mp	54890	g/mol
Mv	69237	g/mol
IVmwd	1.43	dL/g

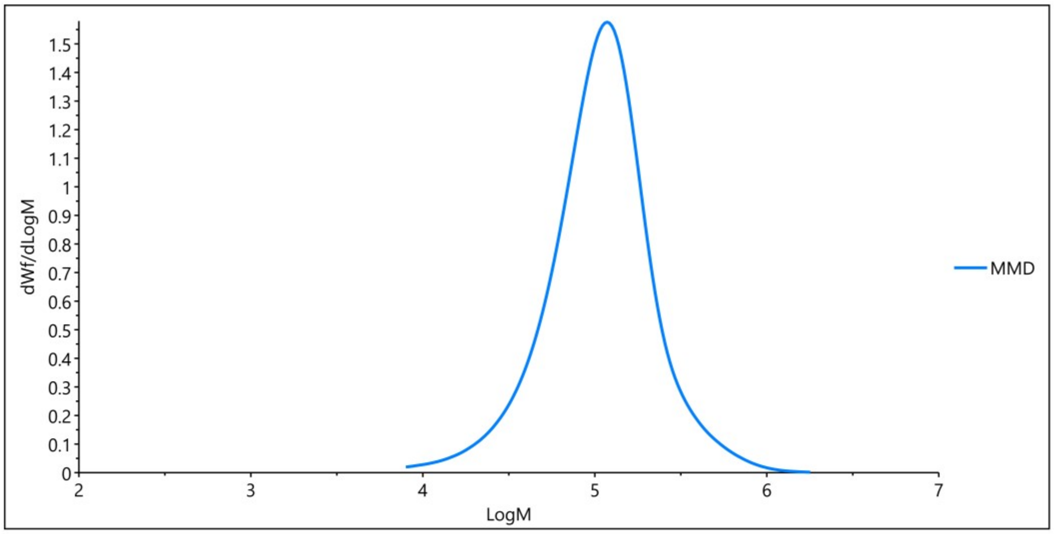
Figure S62. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 3, Entry 8).



Results

Mw	42592	g/mol
Mn	29326	g/mol
Mw / Mn	1.45	
Mz	58604	g/mol
Mp	43351	g/mol
Mv	40621	g/mol
IVmwd	0.7813	dL/g

Figure S63. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 3, Entry 9).



Results

Mw	136739	g/mol
Mn	81514	g/mol
Mw / Mn	1.68	
Mz	234857	g/mol
Mp	117752	g/mol
Mv	127640	g/mol
IVmwd	2.22	dL/g

Figure S64. GPC trace of poly(E-*co*-2-allylphenol) after acetylation (Table 3, Entry 10).

12. DSC Traces of Polymer Samples

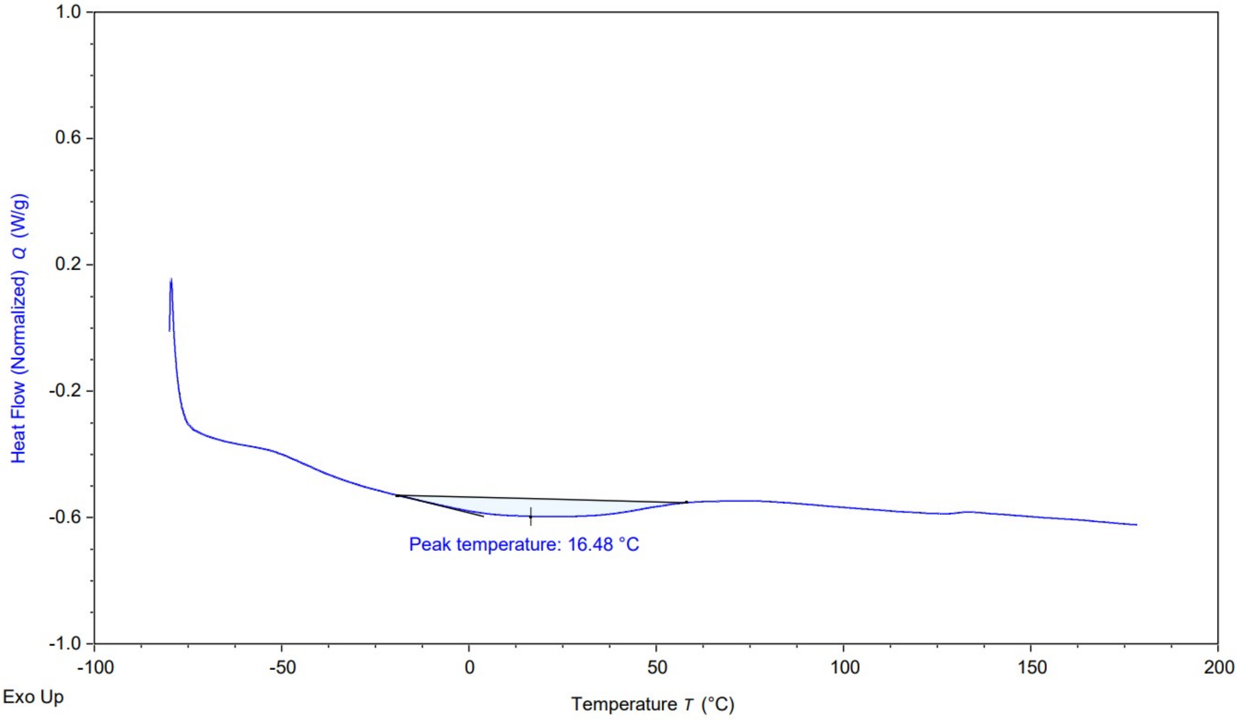


Figure S65. DSC trace of poly(E-*co*-2-allylphenol) (Table 1, Entry 3).

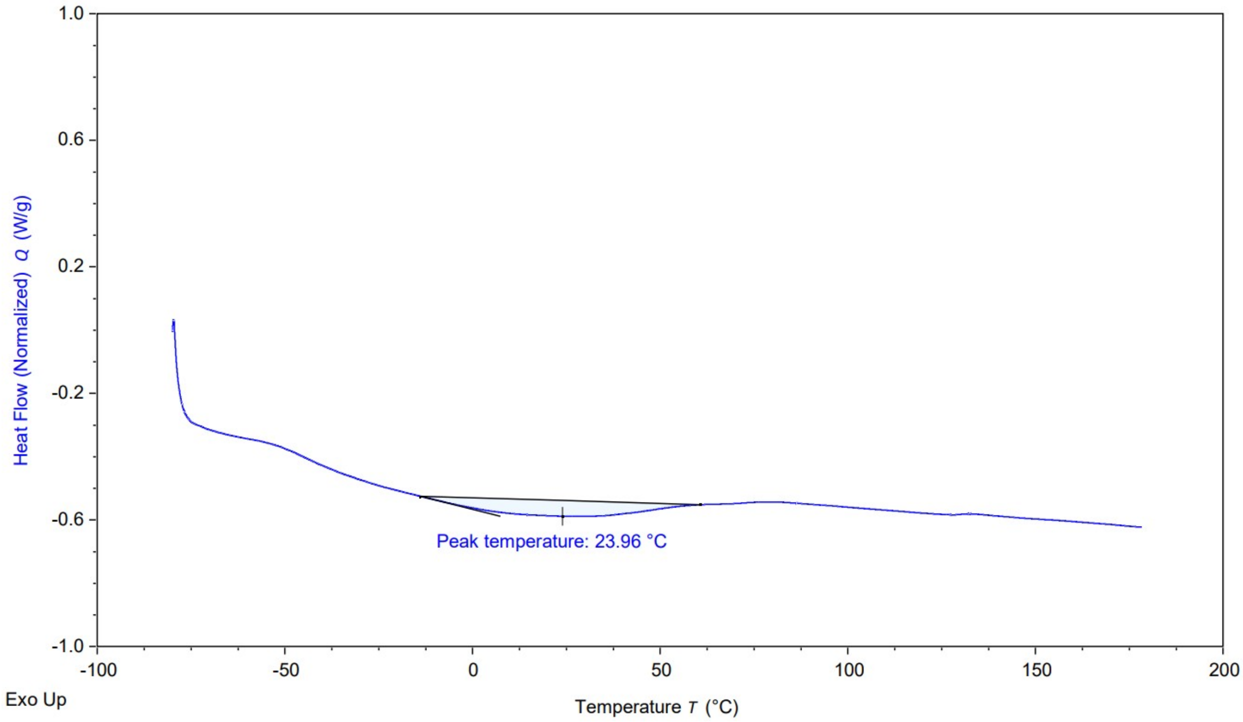


Figure S66. DSC trace of poly(E-*co*-2-allylphenol) (Table 2, Entry 1).

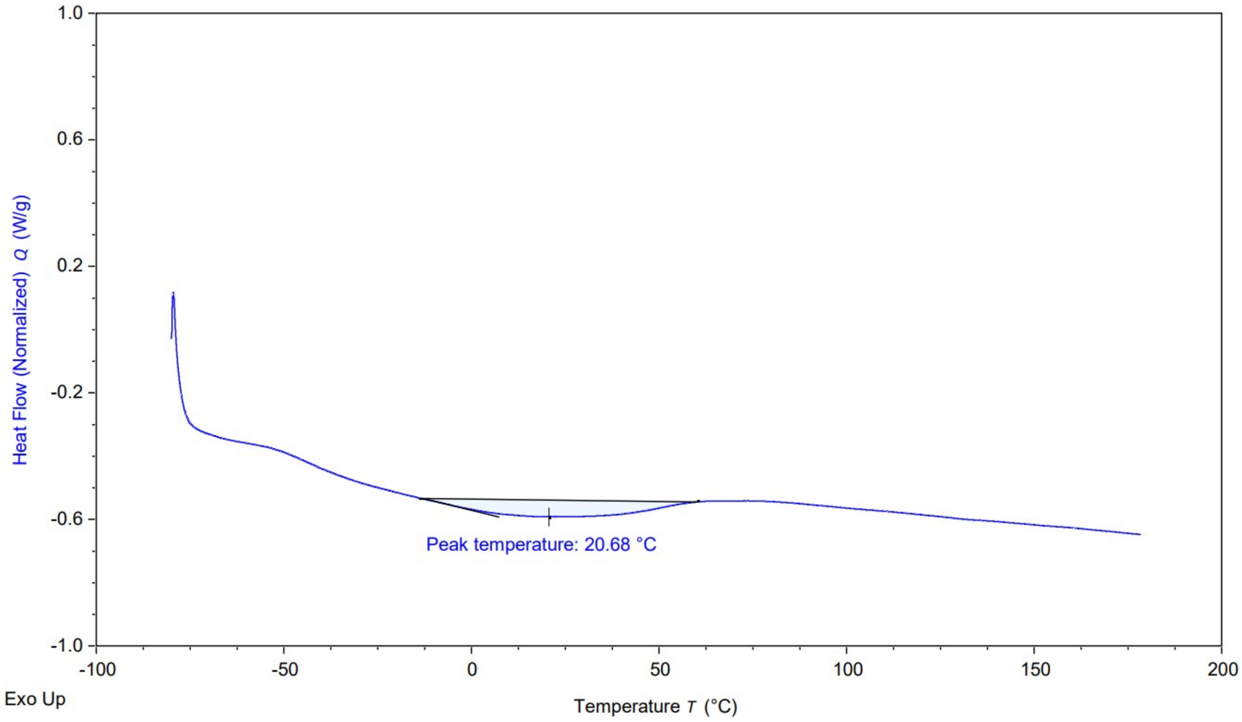


Figure S67. DSC trace of poly(E-*co*-2-allylphenol) (Table 2, Entry 3).

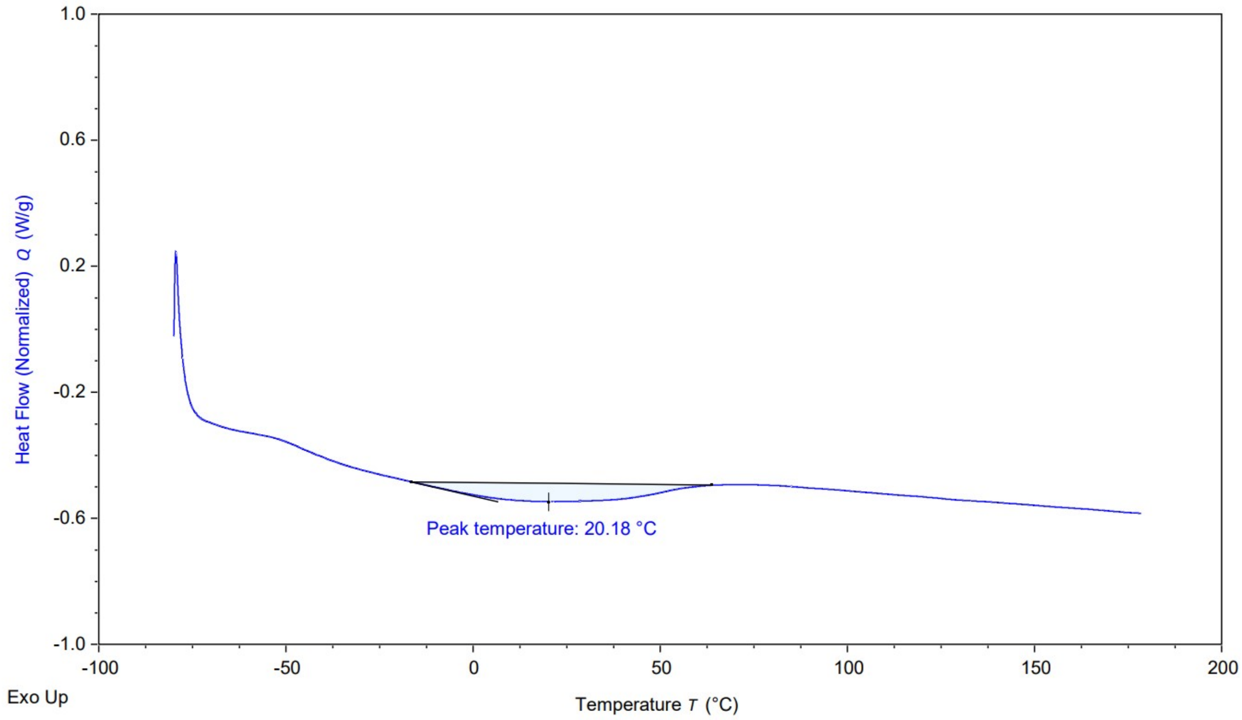


Figure S68. DSC trace of poly(E-*co*-2-allylphenol) (Table 2, Entry 4).

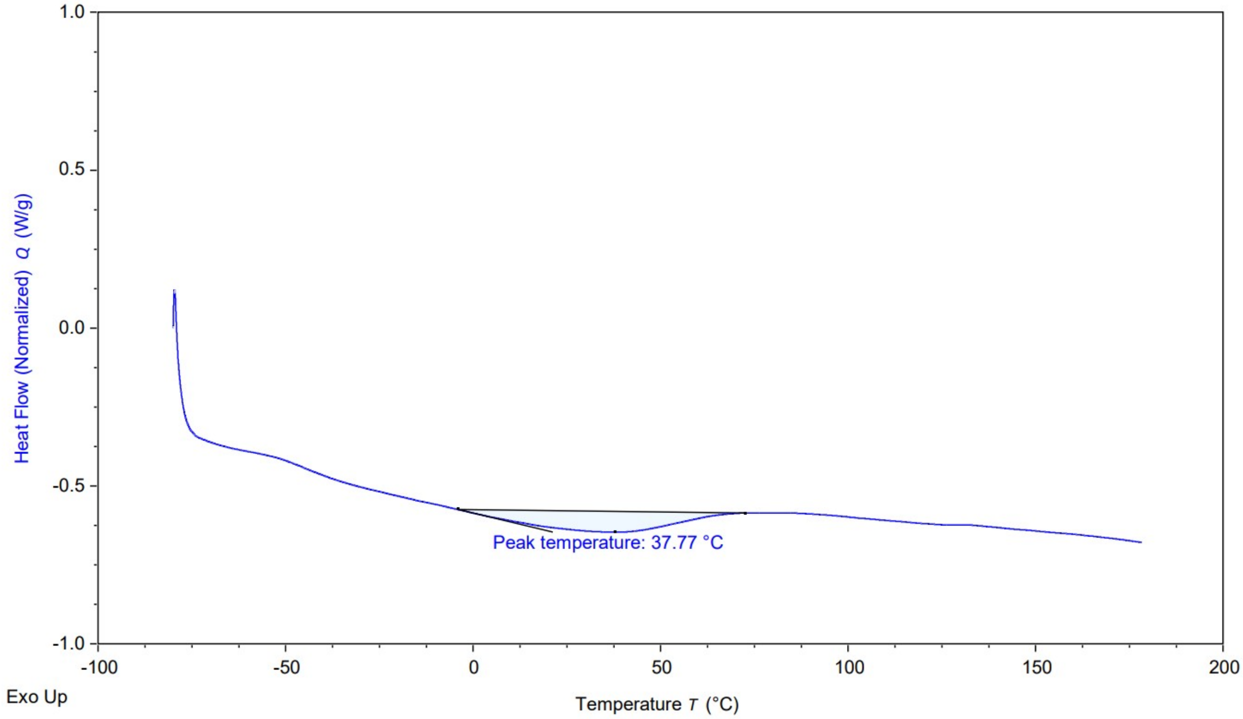


Figure S69. DSC trace of poly(E-*co*-2-allylphenol) (Table 2, Entry 5).

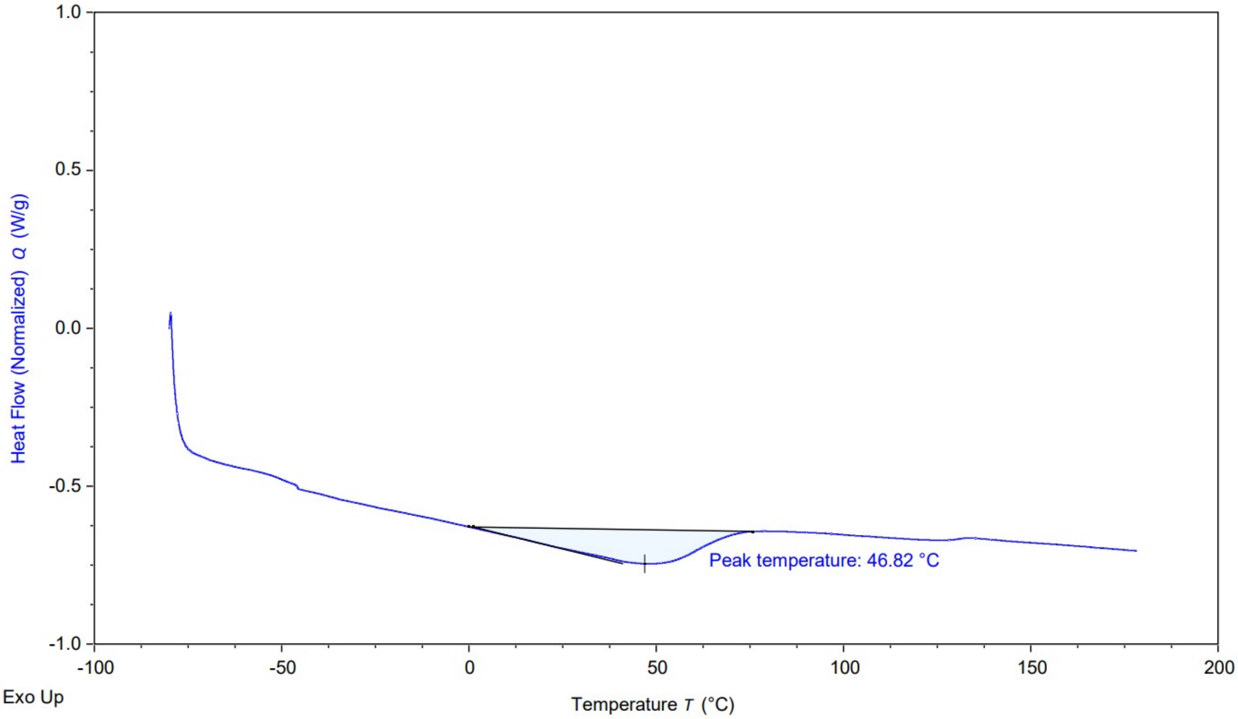


Figure S70. DSC trace of poly(E-*co*-2-allylphenol) (Table 2, Entry 6).

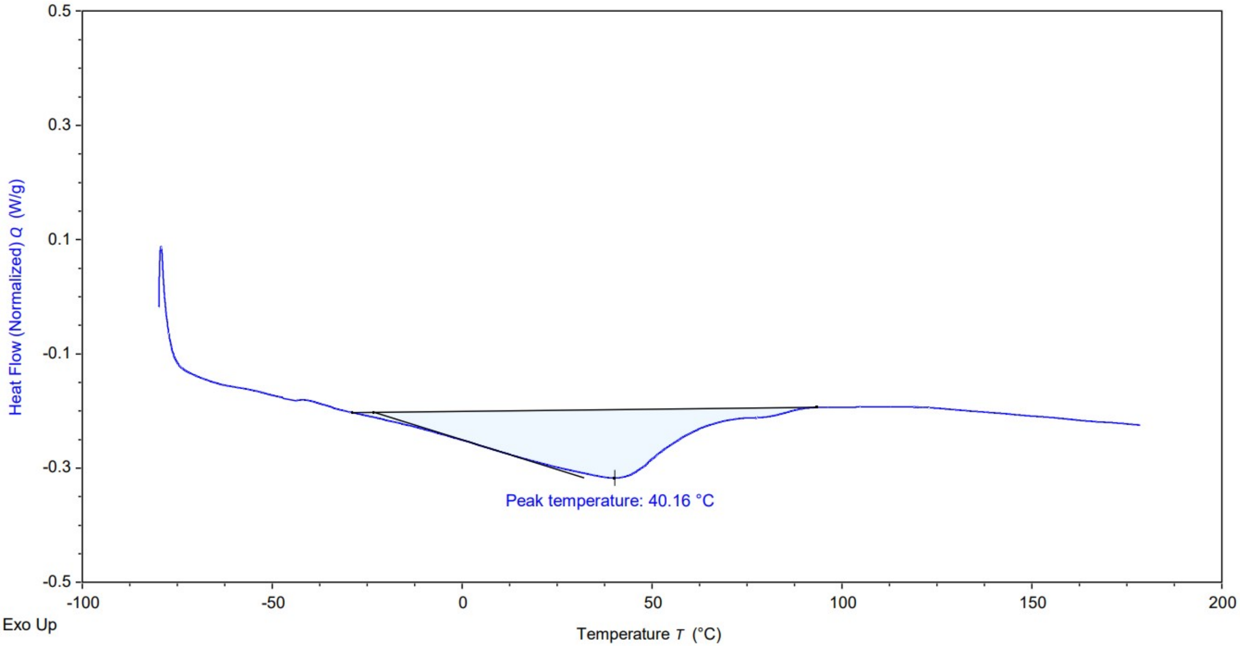


Figure S71. DSC trace of poly(E-*co*-2-allylphenol) (Table 2, Entry 7).

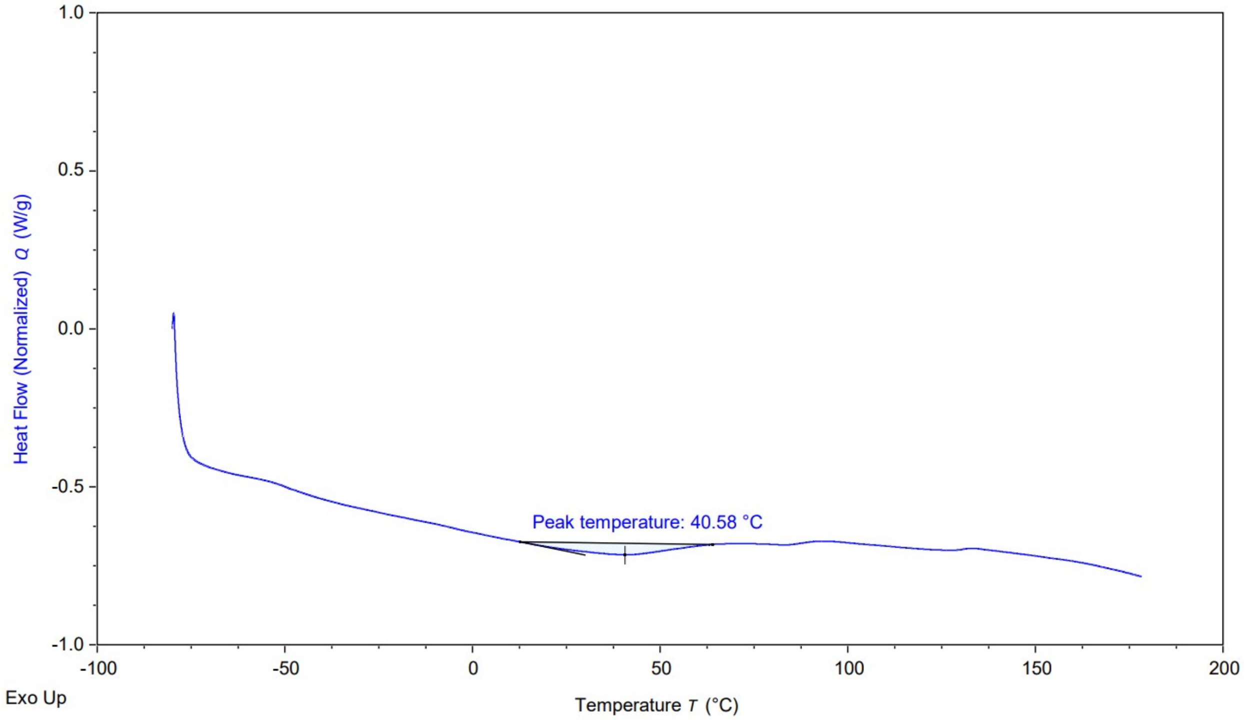


Figure S72. DSC trace of poly(E-*co*-2-allylphenol) (Table 2, Entry 8).

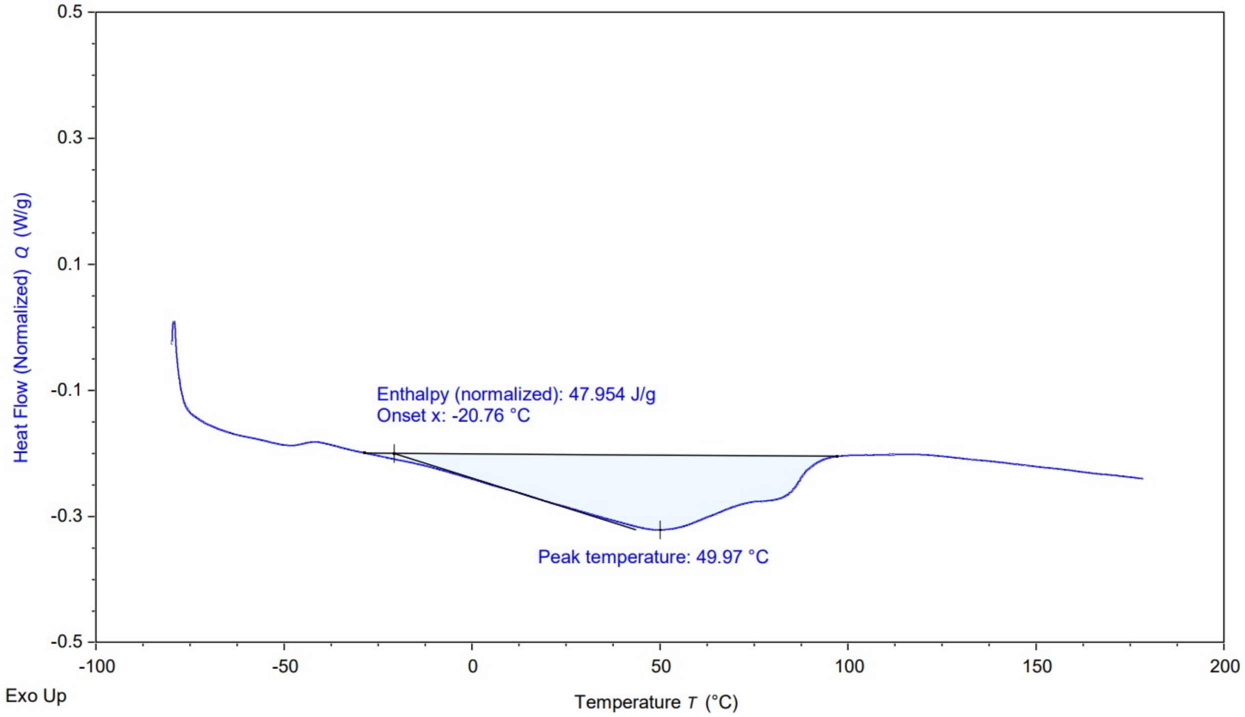


Figure S73. DSC trace of poly(E-*co*-2-allylphenol) (Table 2, Entry 9).

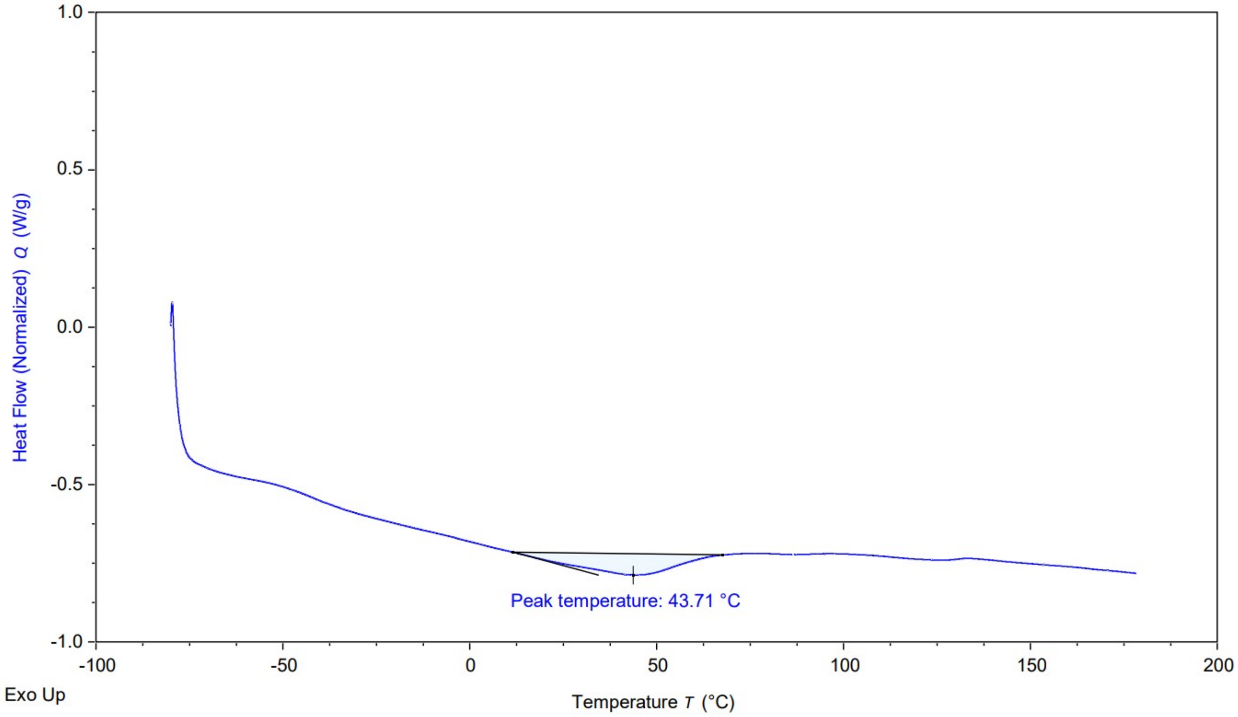


Figure S74. DSC trace of poly(E-*co*-2-allylphenol) (Table 3, Entry 1).

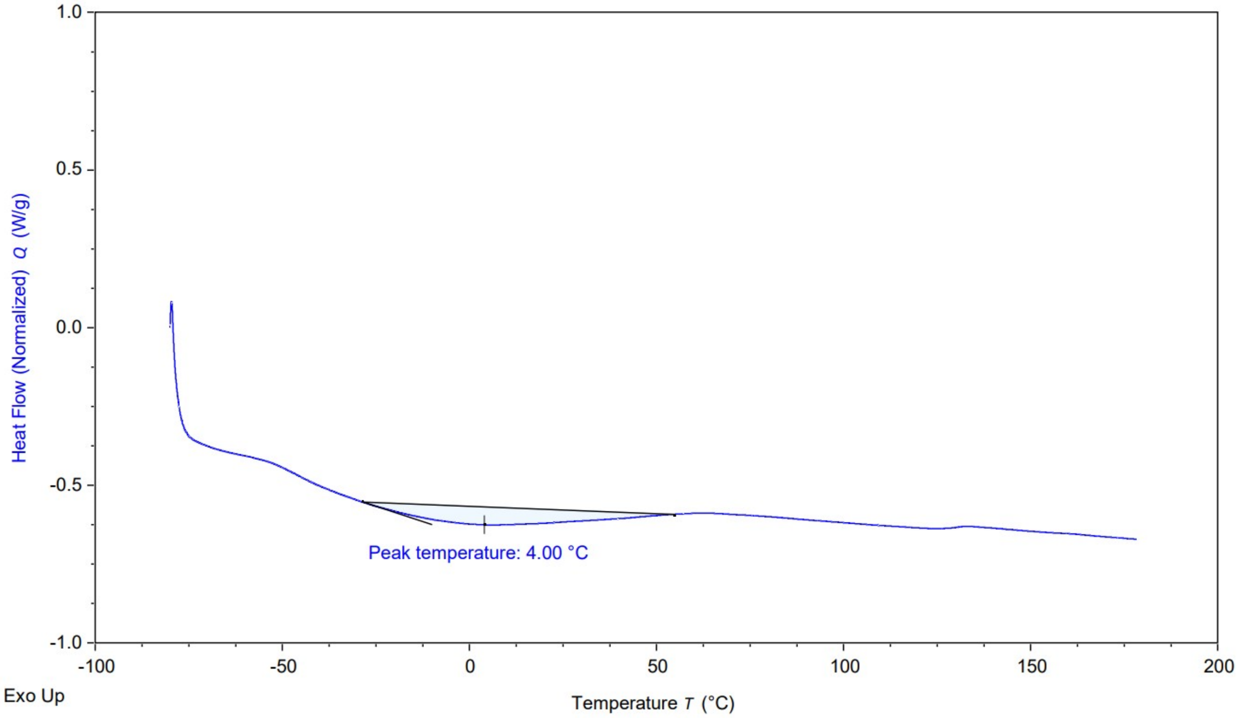


Figure S75. DSC trace of poly(E-*co*-2-allylphenol) (Table 3, Entry 3).

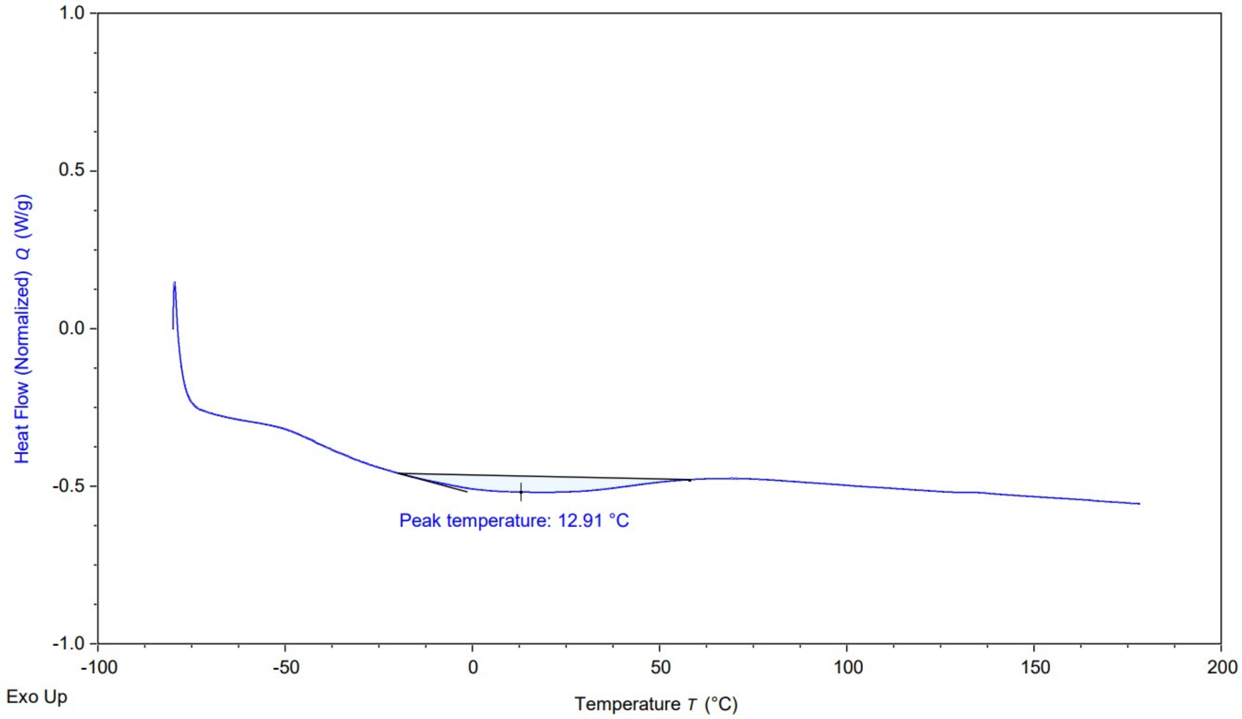


Figure S76. DSC trace of poly(E-*co*-2-allylphenol) (Table 3, Entry 4).

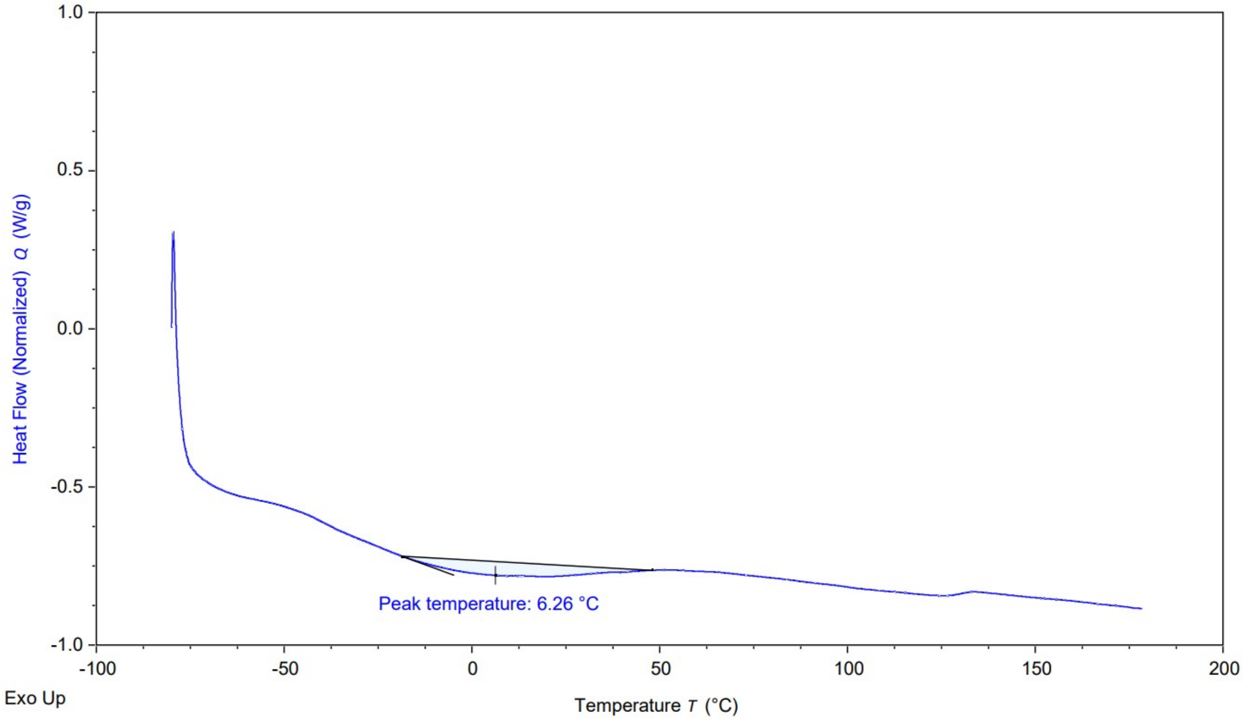


Figure S77. DSC trace of poly(E-*co*-2-allylphenol) (Table 3, Entry 5).

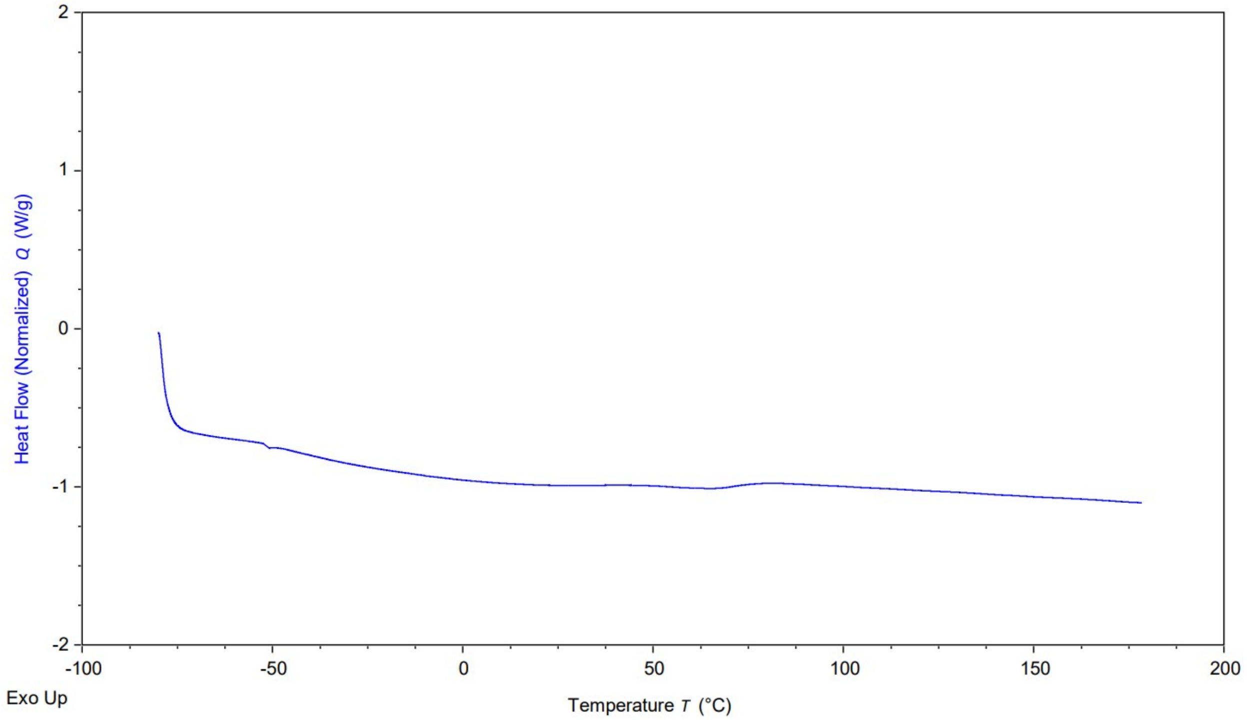


Figure S78. DSC trace of poly(E-*co*-2-allylphenol) (Table 3, Entry 6).

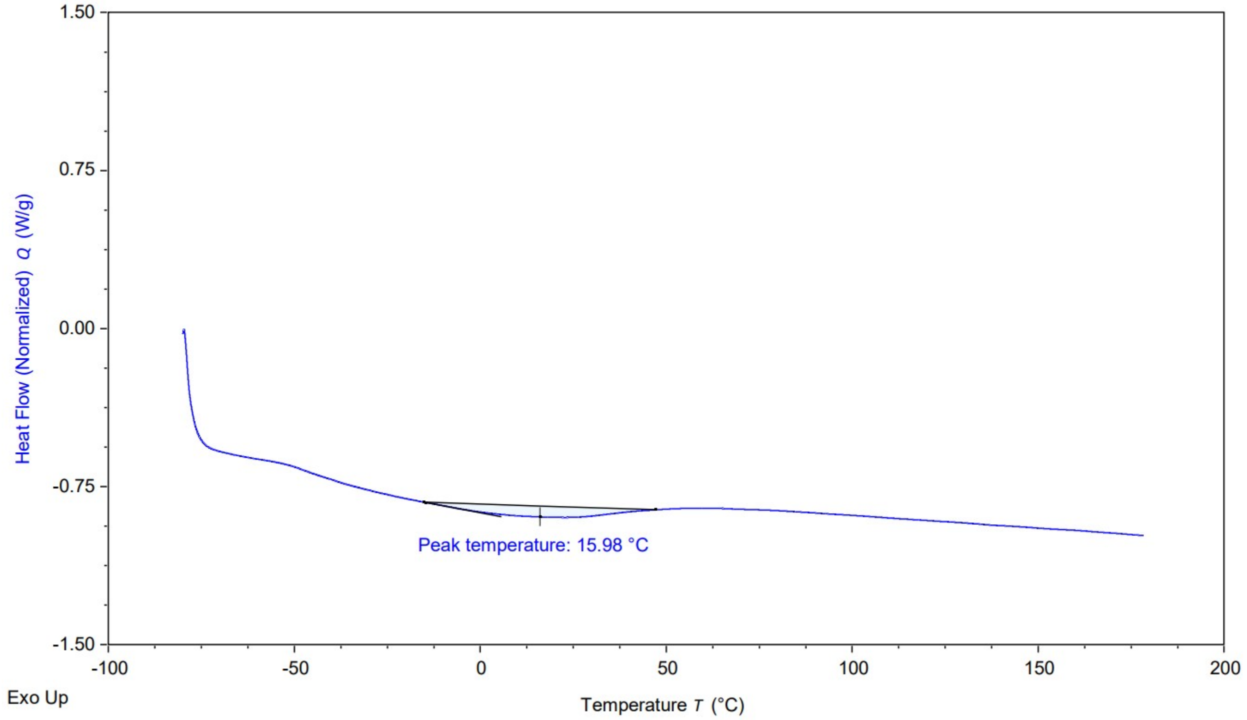


Figure S79. DSC trace of poly(E-*co*-2-allylphenol) (Table 3, Entry 7).

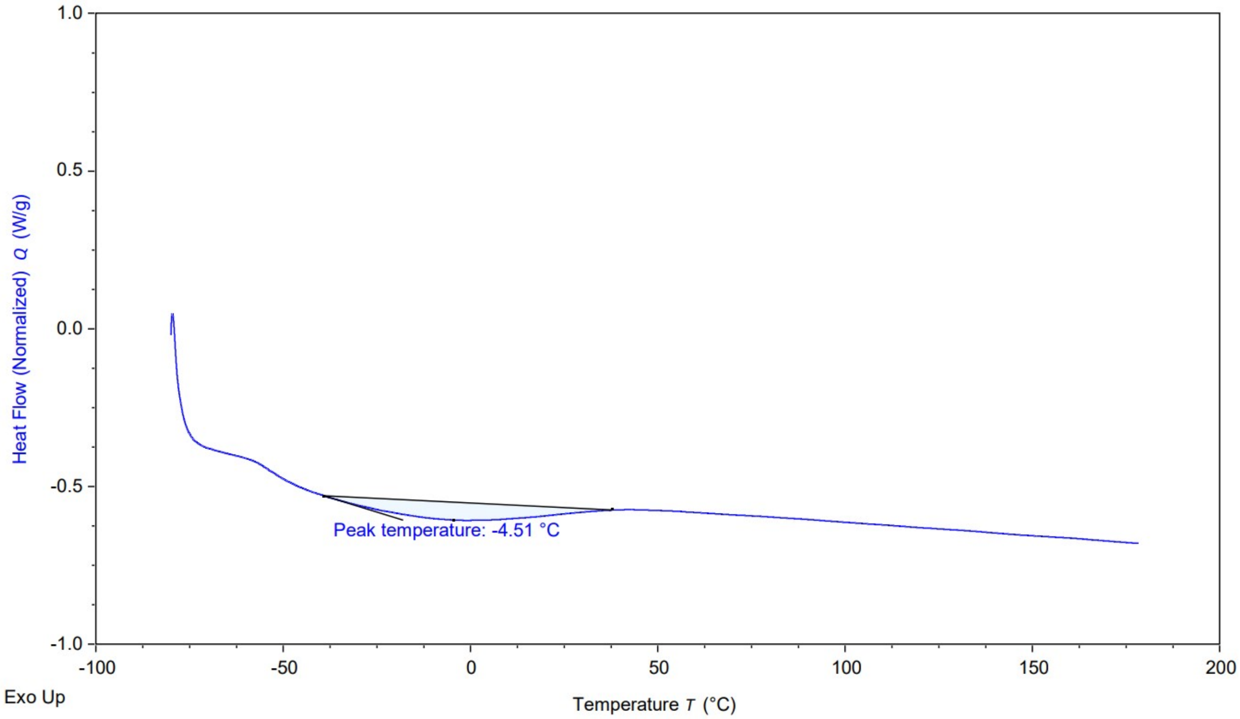


Figure S80. DSC trace of poly(E-*co*-2-allylphenol) (Table 3, Entry 8).

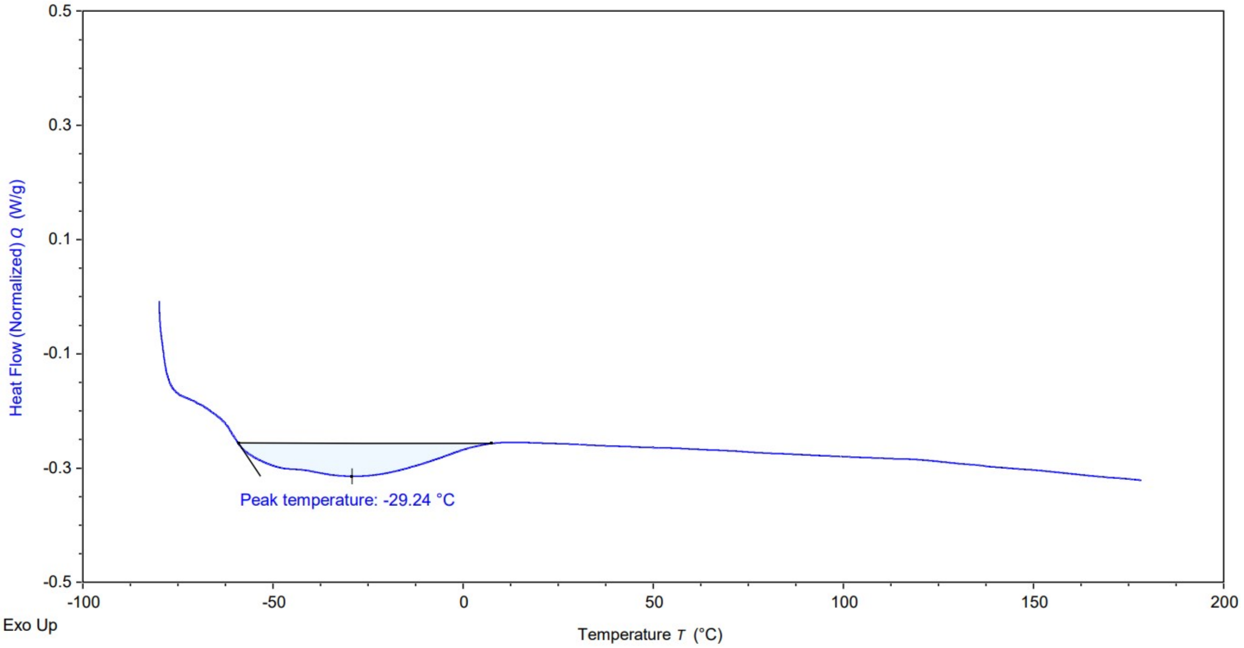


Figure S81. DSC trace of poly(E-*co*-2-allylphenol) (Table 3, Entry 9).

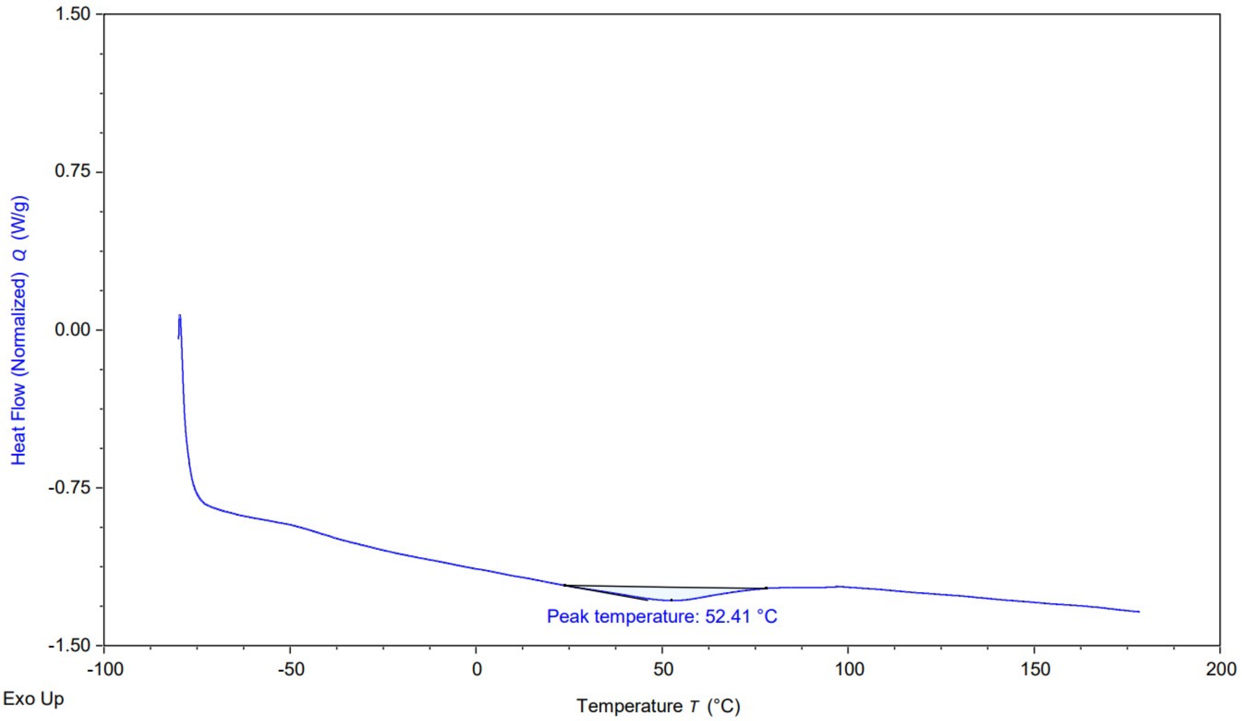


Figure S82. DSC trace of poly(E-*co*-2-allylphenol) (Table 3, Entry 10).

13. NMR Spectra of 2-allylphenol + DEAC Mixture

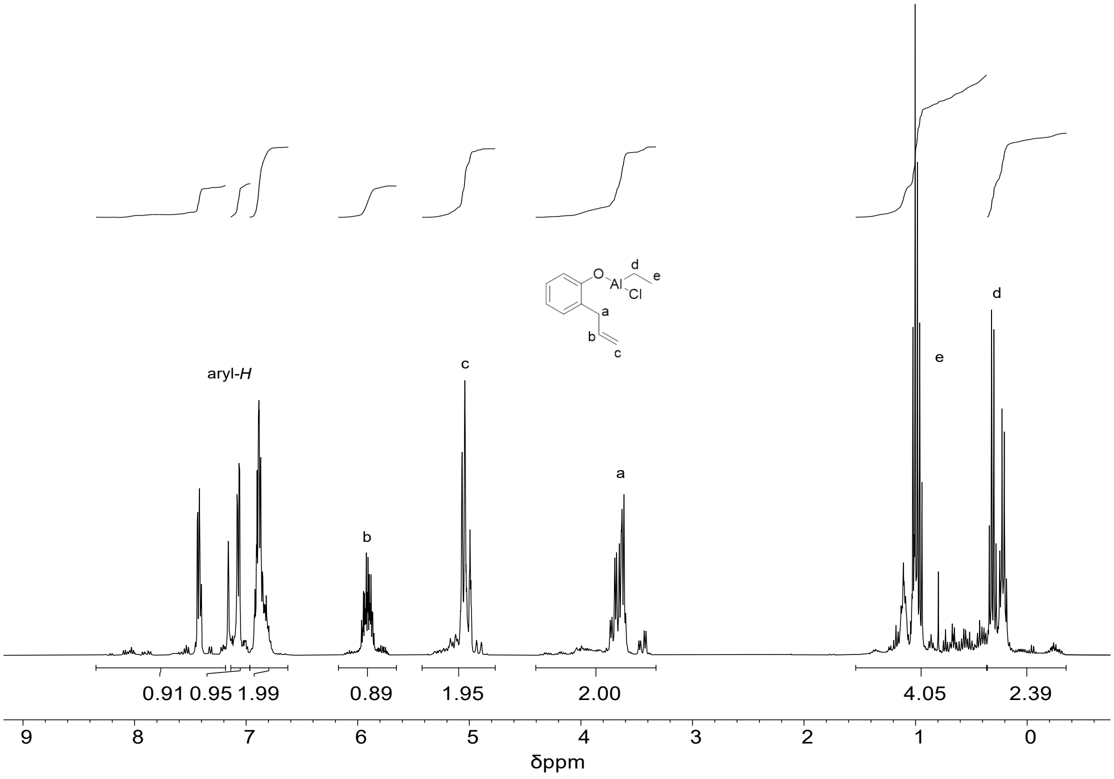


Figure S83. ^{1}H NMR spectrum (400 MHz) of 2-allylphenol + DEAC (1:1) in C_6D_6 at 30 °C for 12 h.

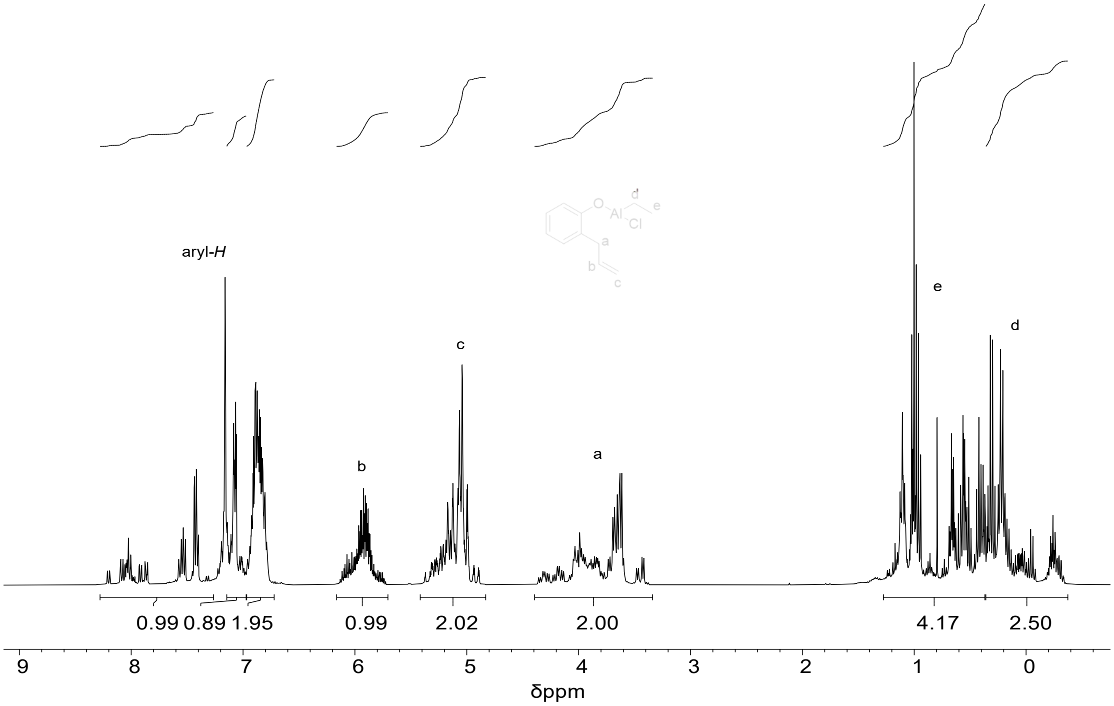


Figure S84. ^{1}H NMR spectrum (400 MHz) of 2-allylphenol + DEAC (1:1) in C_6D_6 after 1 week.

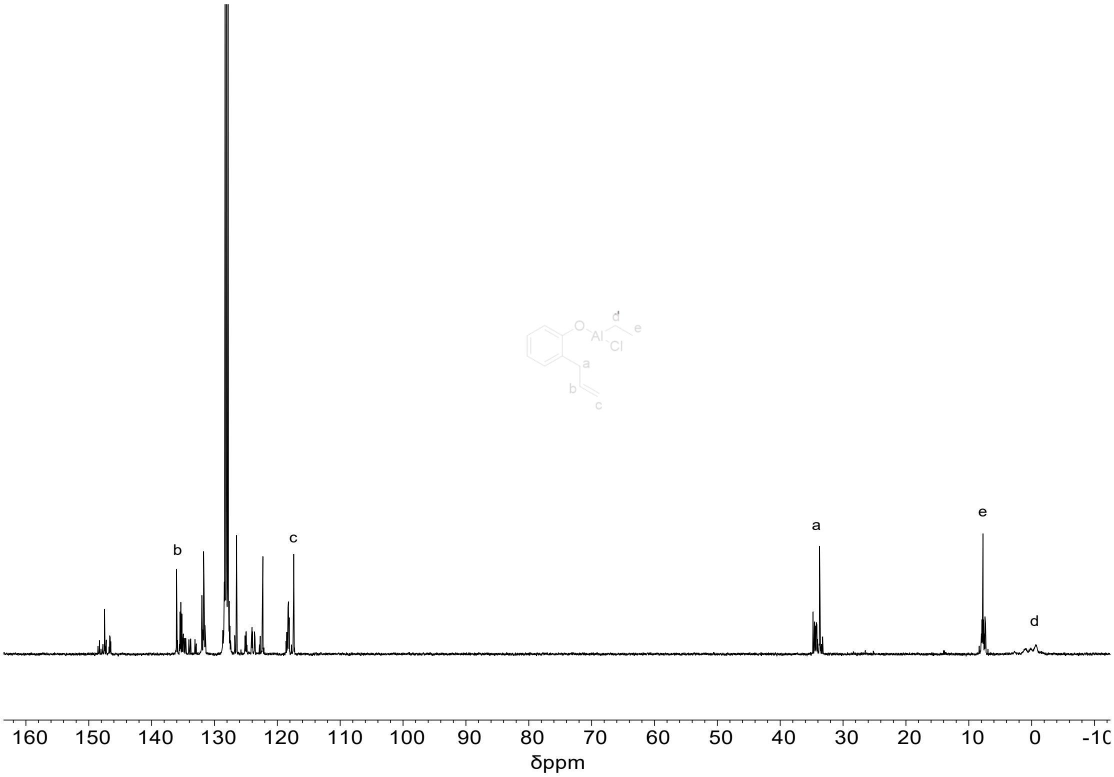


Figure S85. ^{13}C NMR spectrum (100 MHz) of 2-allylphenol + DEAC (1:1) in C_6D_6 after 1 week.

14. Water Contact Angle Measurements

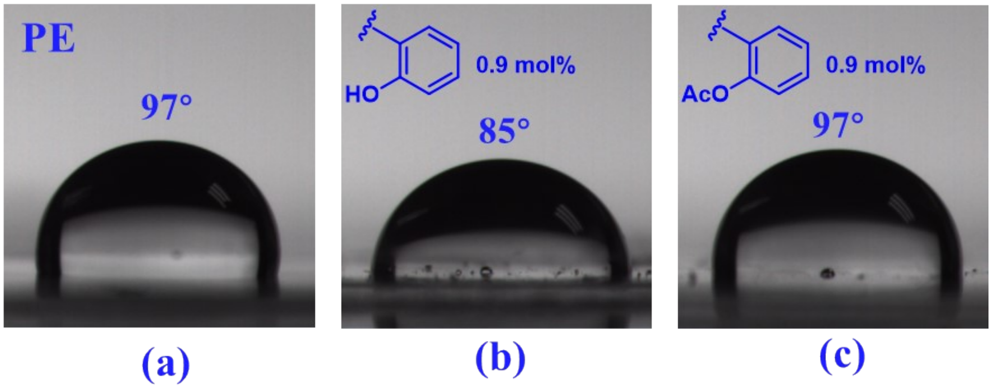


Figure S86. Water contact angle measurements on three representative samples: branched PE prepared by ethylene homopolymerization with cat. **c** (a); PE/2-allylphenol copolymer from Table 3, entry 7 (b); the corresponding acetylated copolymer (c).

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