Toward More Sustainable Elastomers: Stereoselective Copolymerization of Linear Terpenes with Butadiene

*David Hermann Lamparelli,[†] Veronica Paradiso,[†] Francesco Della Monica,[†] Antonio Proto[†], Silvia Guerra[§], Luca Giannini[§], Carmine Capacchione[†]**

[†] Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, via Giovanni Paolo II, 132 I-84084 Fisciano(SA), Italy.

[§]Pirelli Tyre S.p.A. Viale Piero e Alberto Pirelli, 25 - 20126 Milano

* e-mail: ccapacchione@unisa.it

Table of contents

1. NMR Characterization.

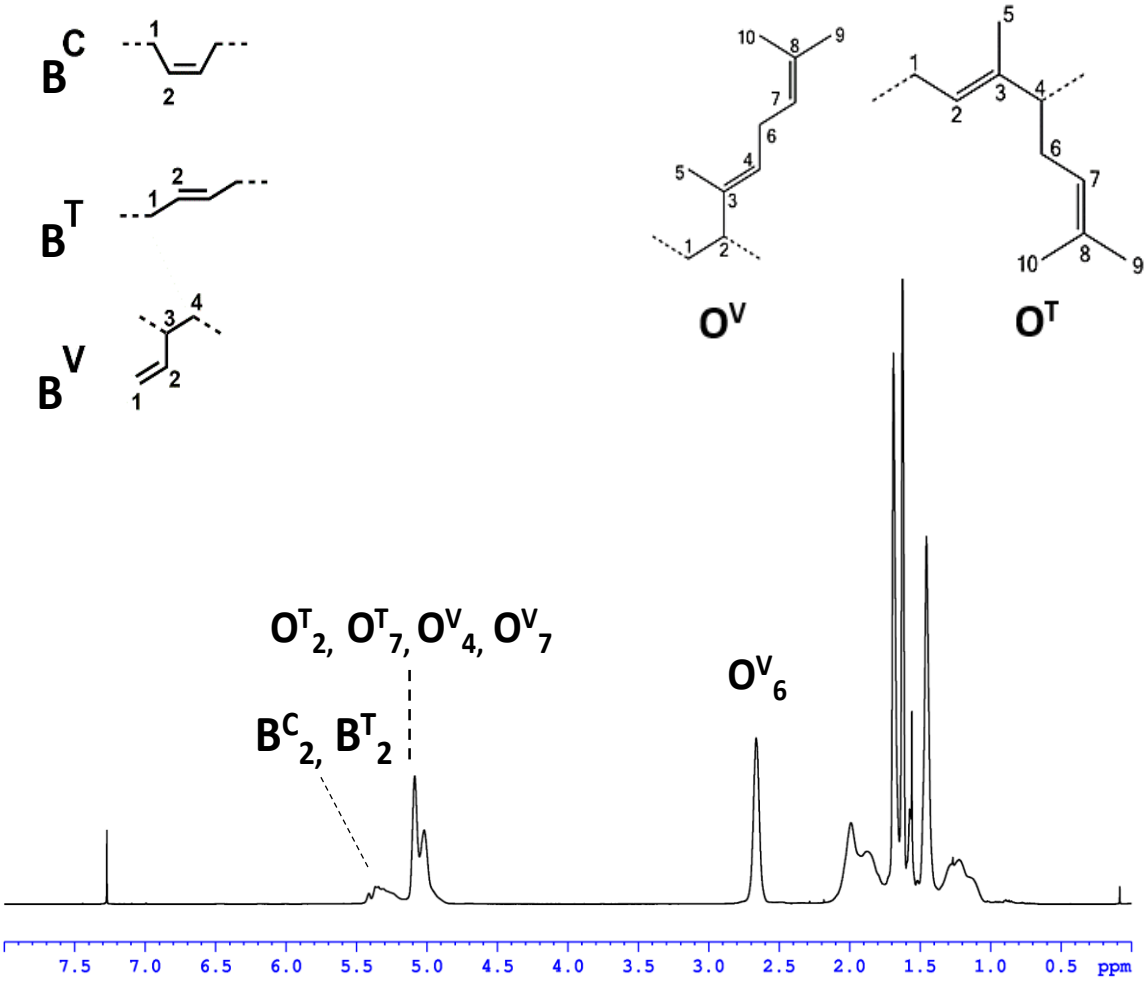


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB from run **1** of **Table 1**

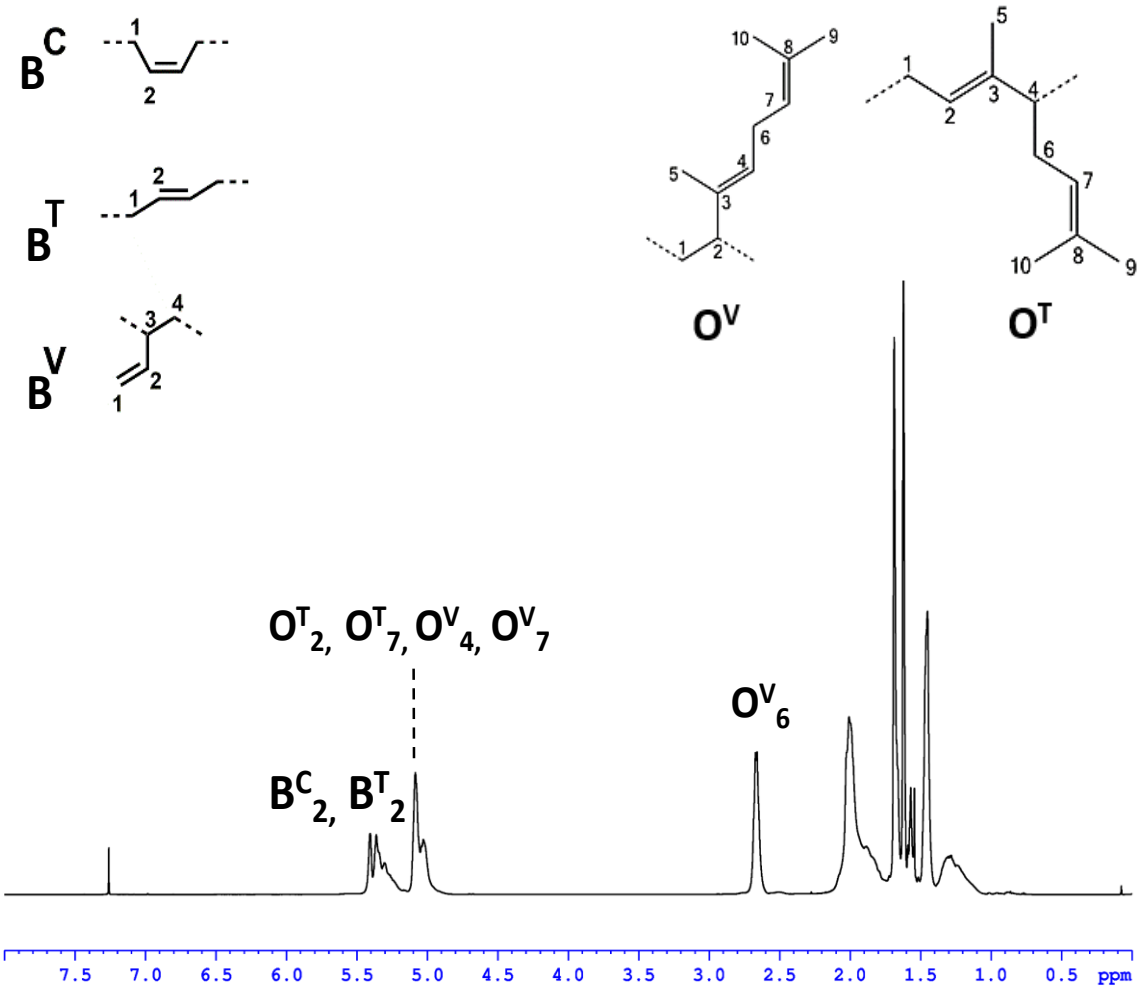


Figure S2. ^{1}H NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB from run **2** of **Table 1**

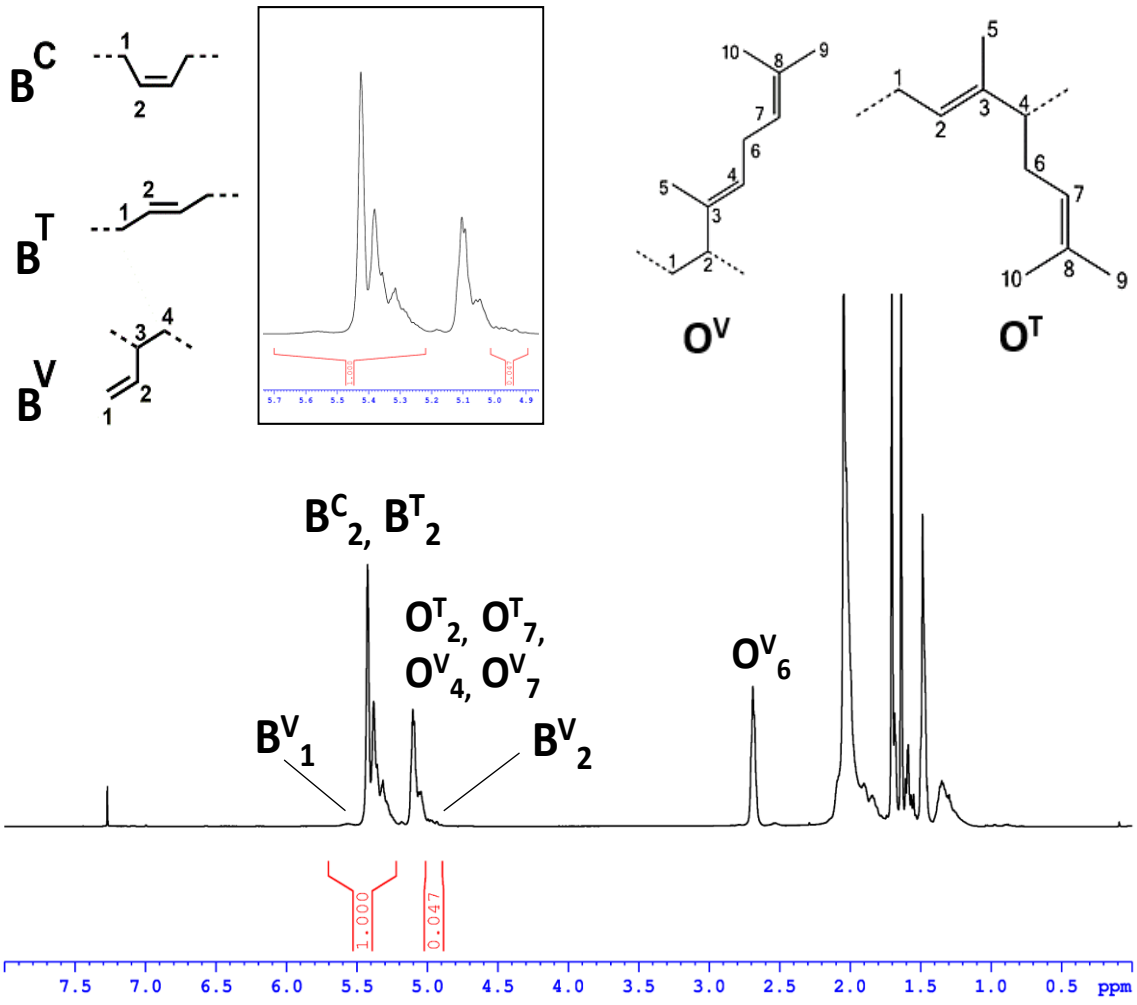


Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB from run **3** of **Table 1**

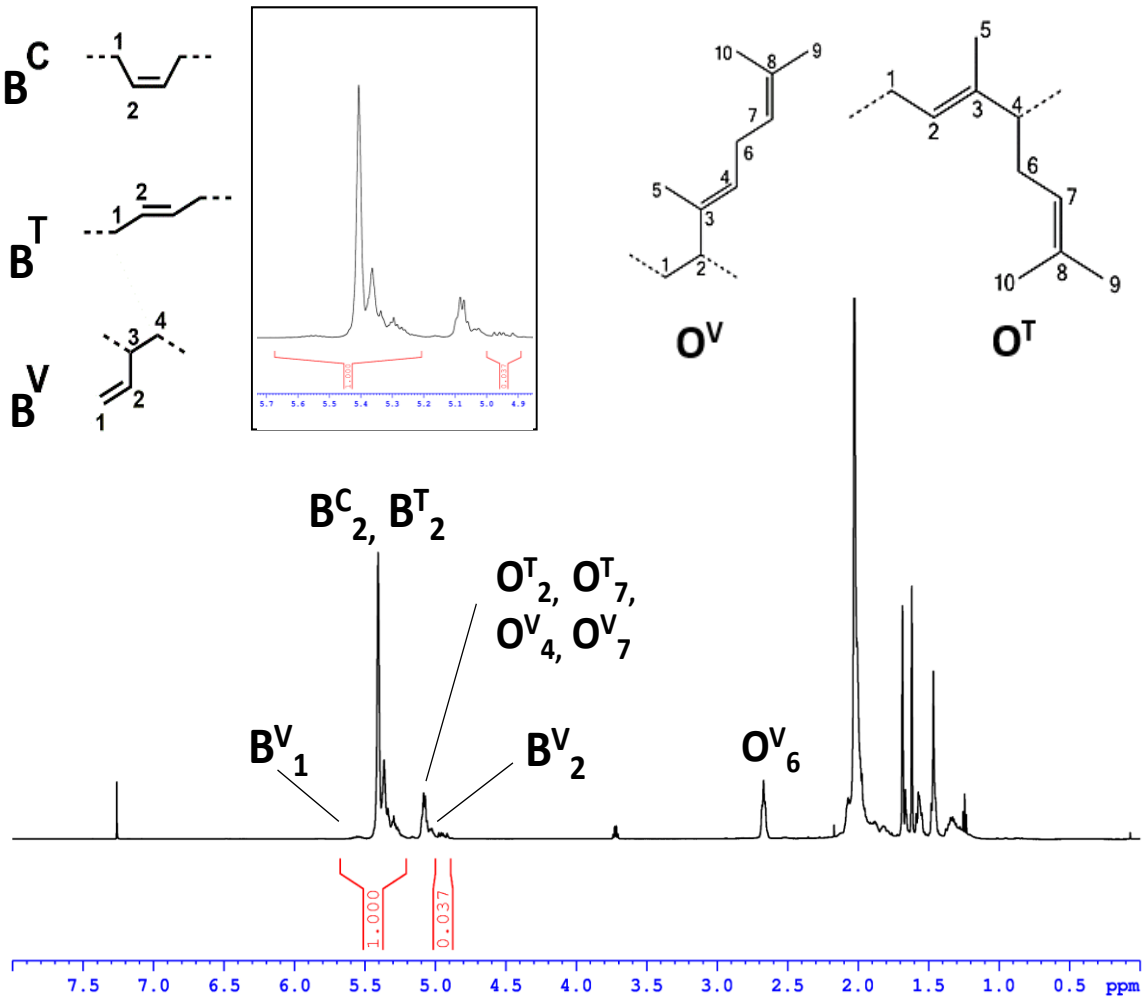


Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB from run **4** of **Table 1**

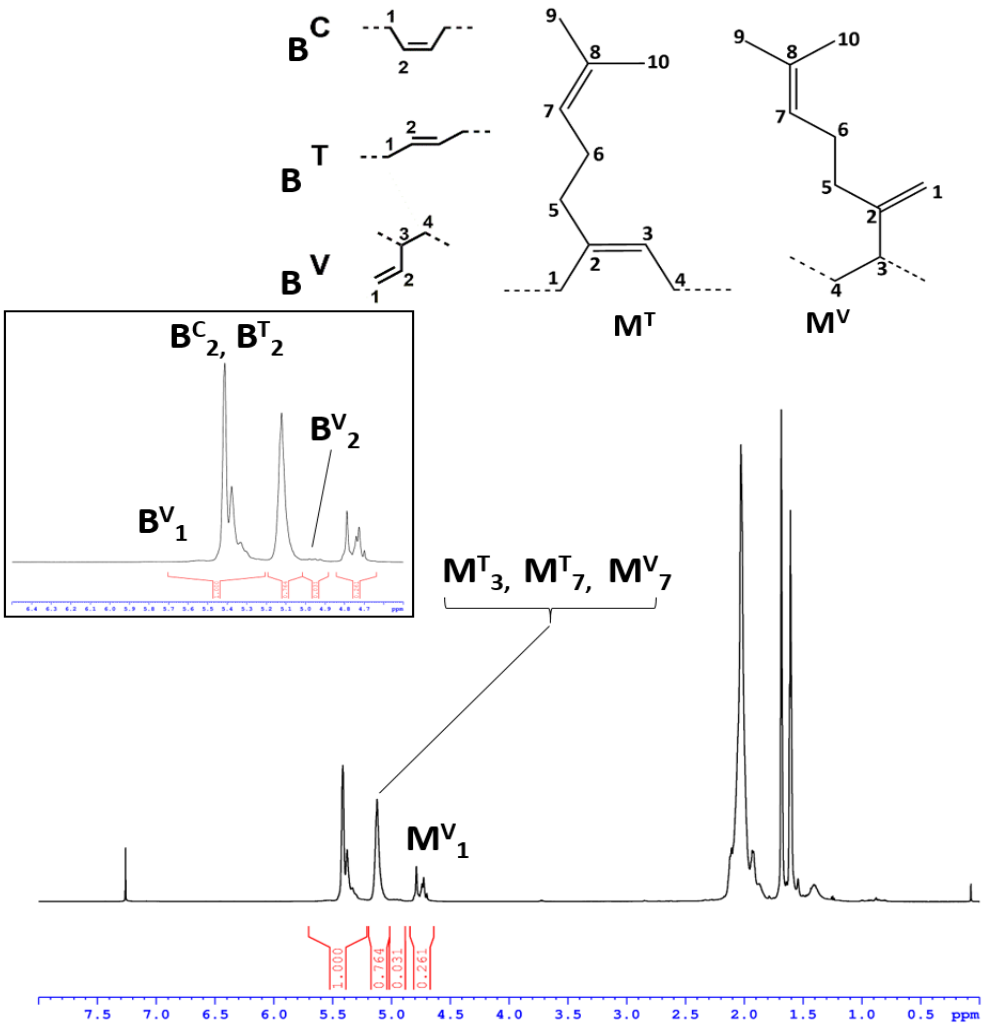


Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of PMB from run **5** of **Table 3**

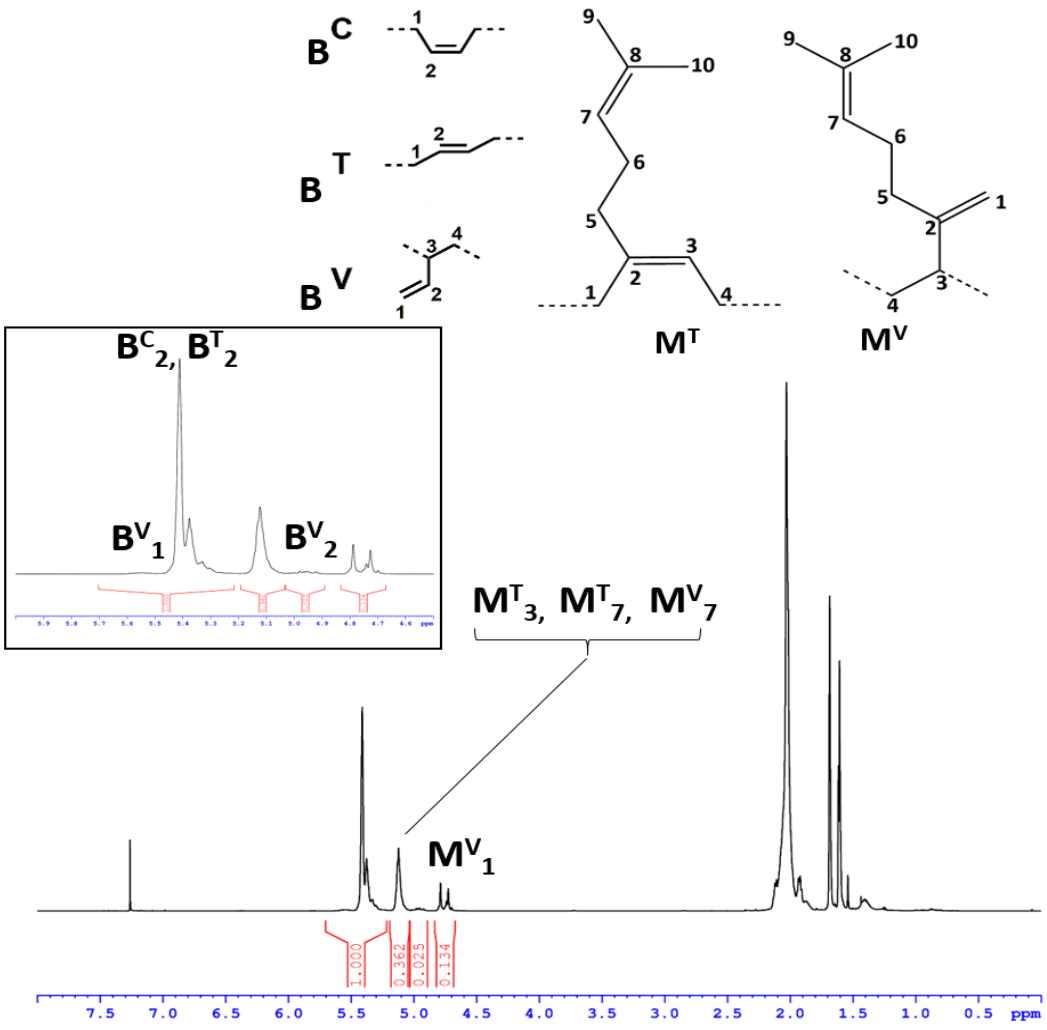


Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of PMB from run **6** of **Table 3**

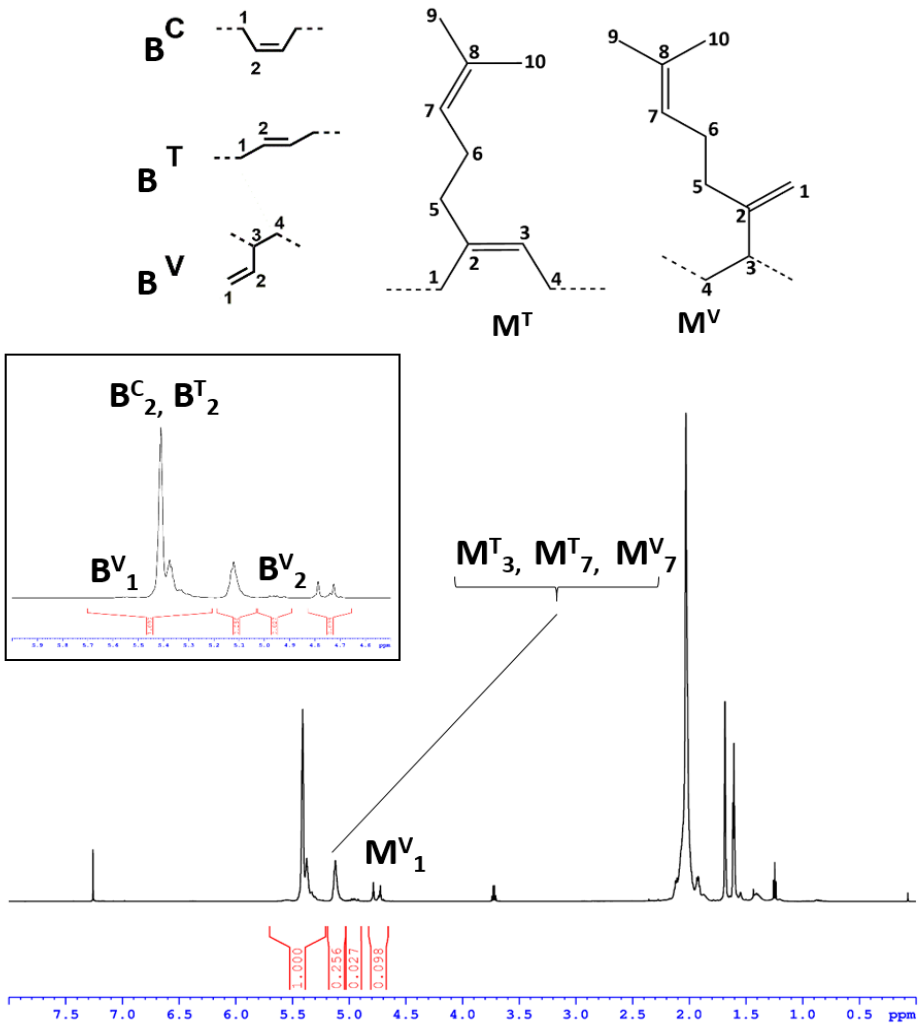


Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of PMB from run **7** of **Table 3**

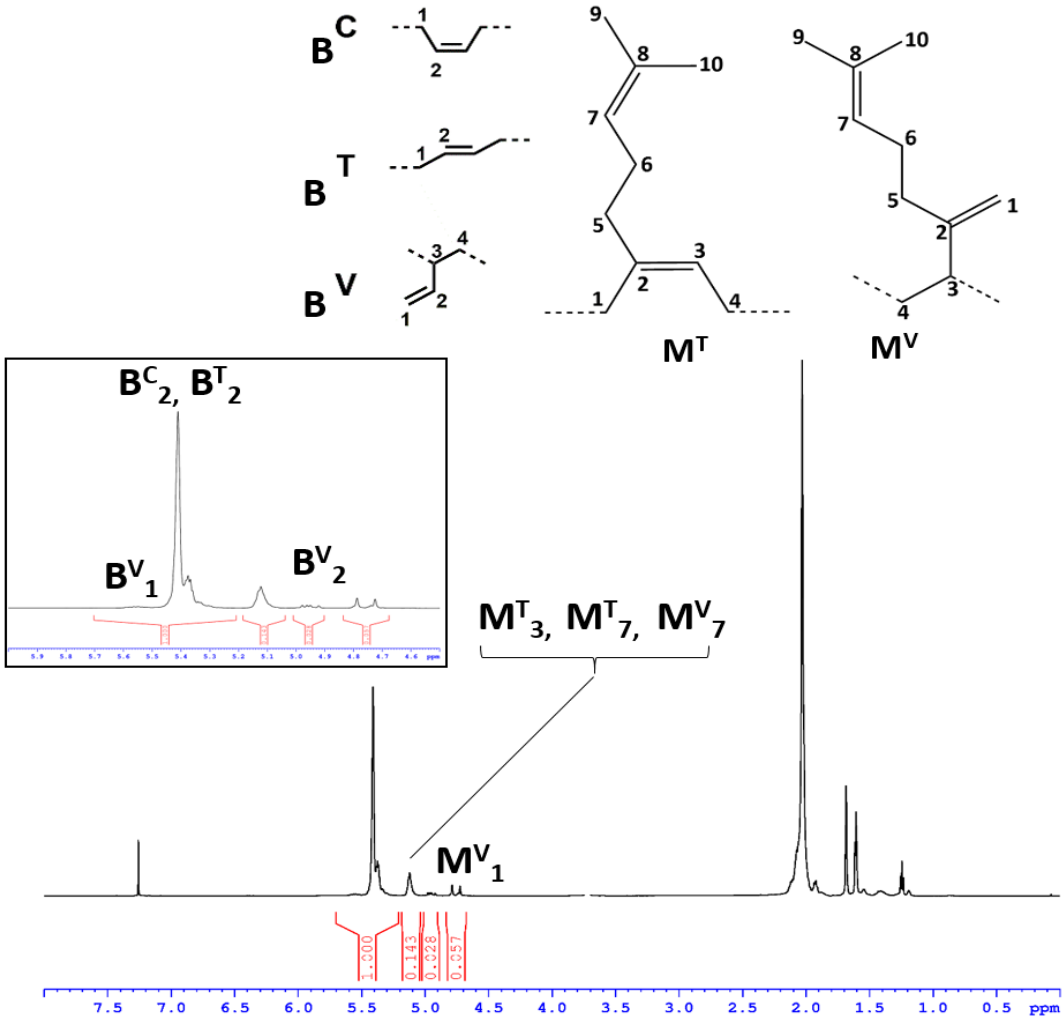


Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of PMB from run **8** of **Table 3**

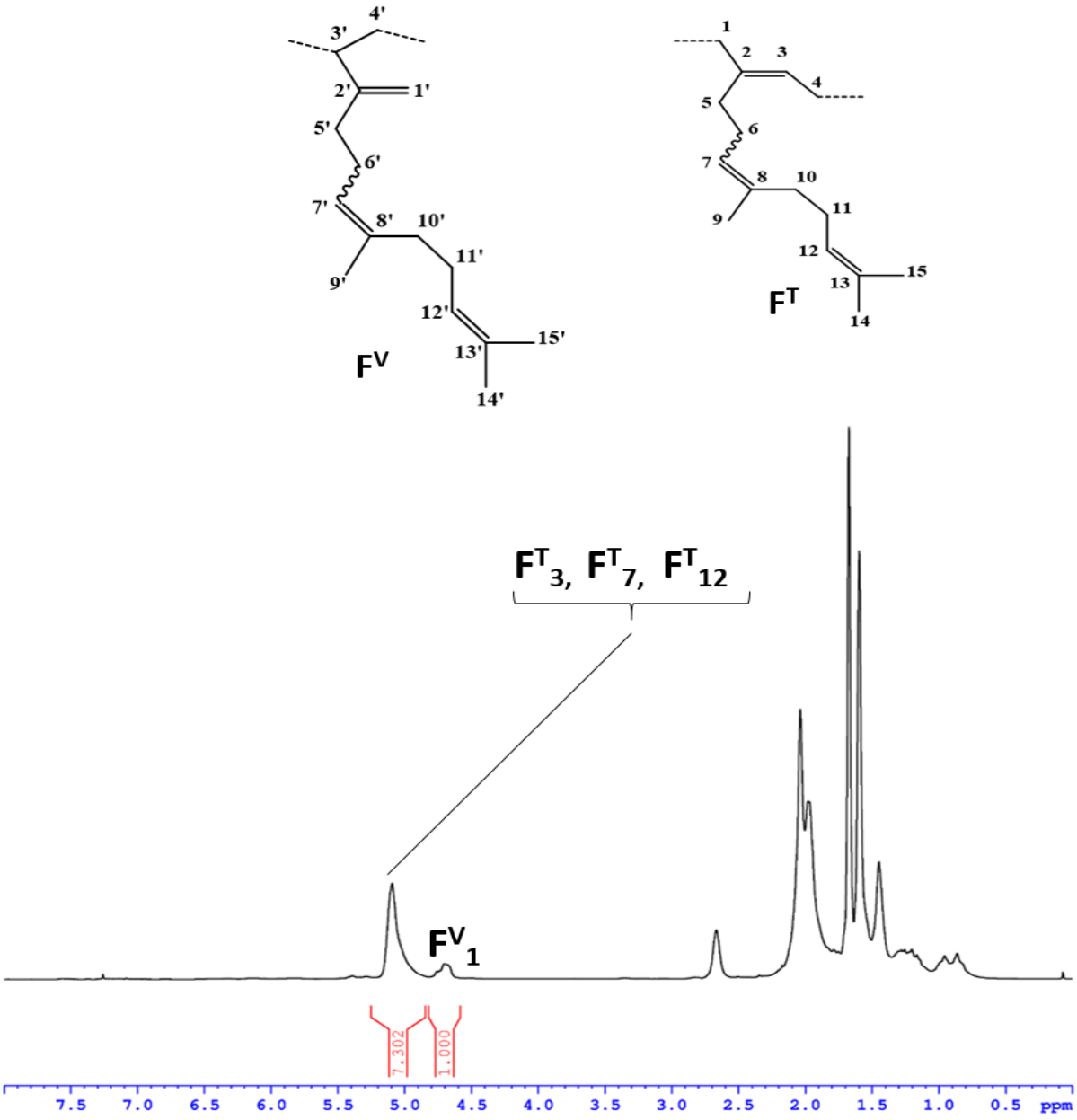


Figure S9. ^{1}H NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of PF from run **9** of **Table 5**

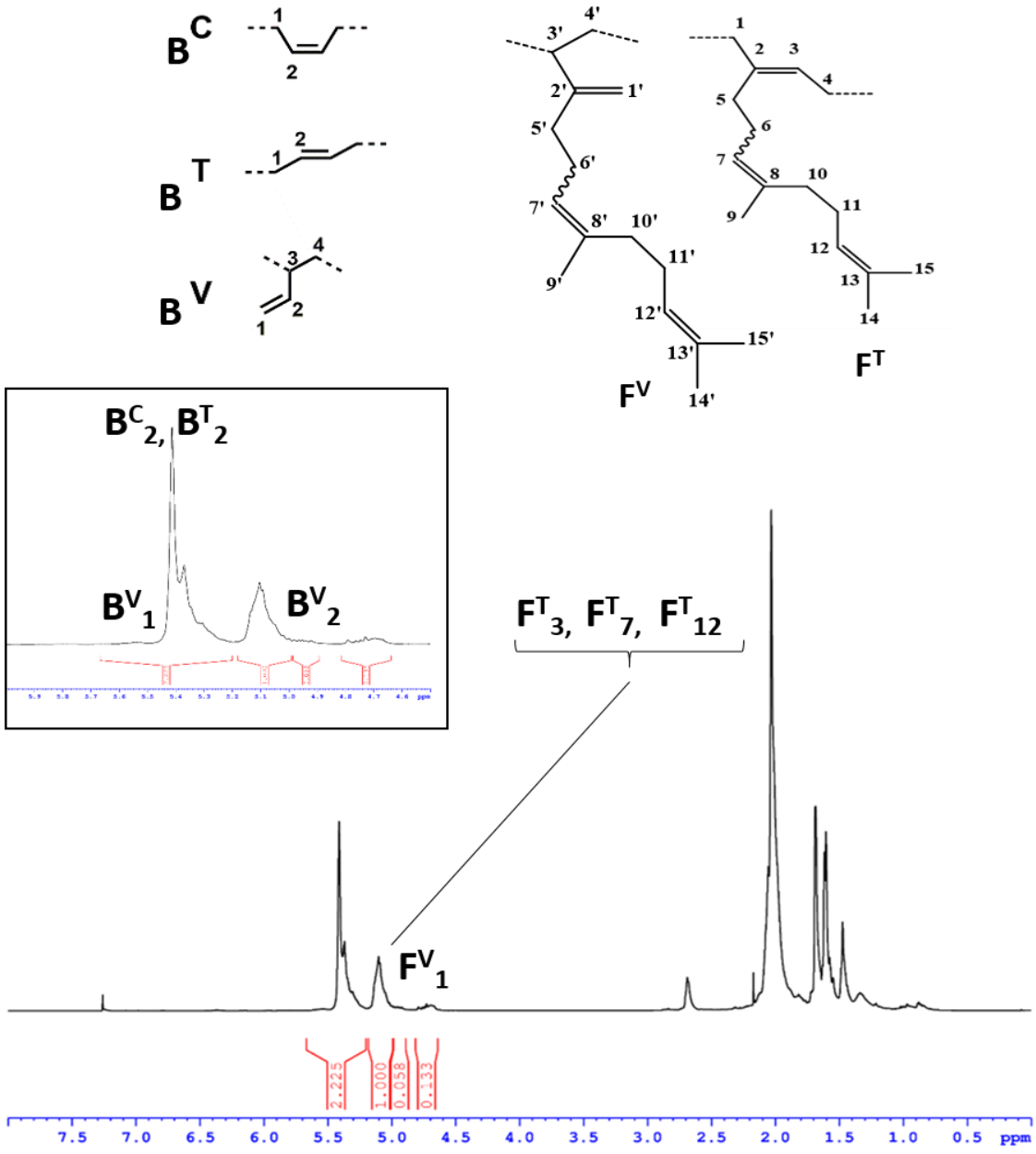


Figure S10. ^{1}H NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of PFB from run **11** of **Table 5**

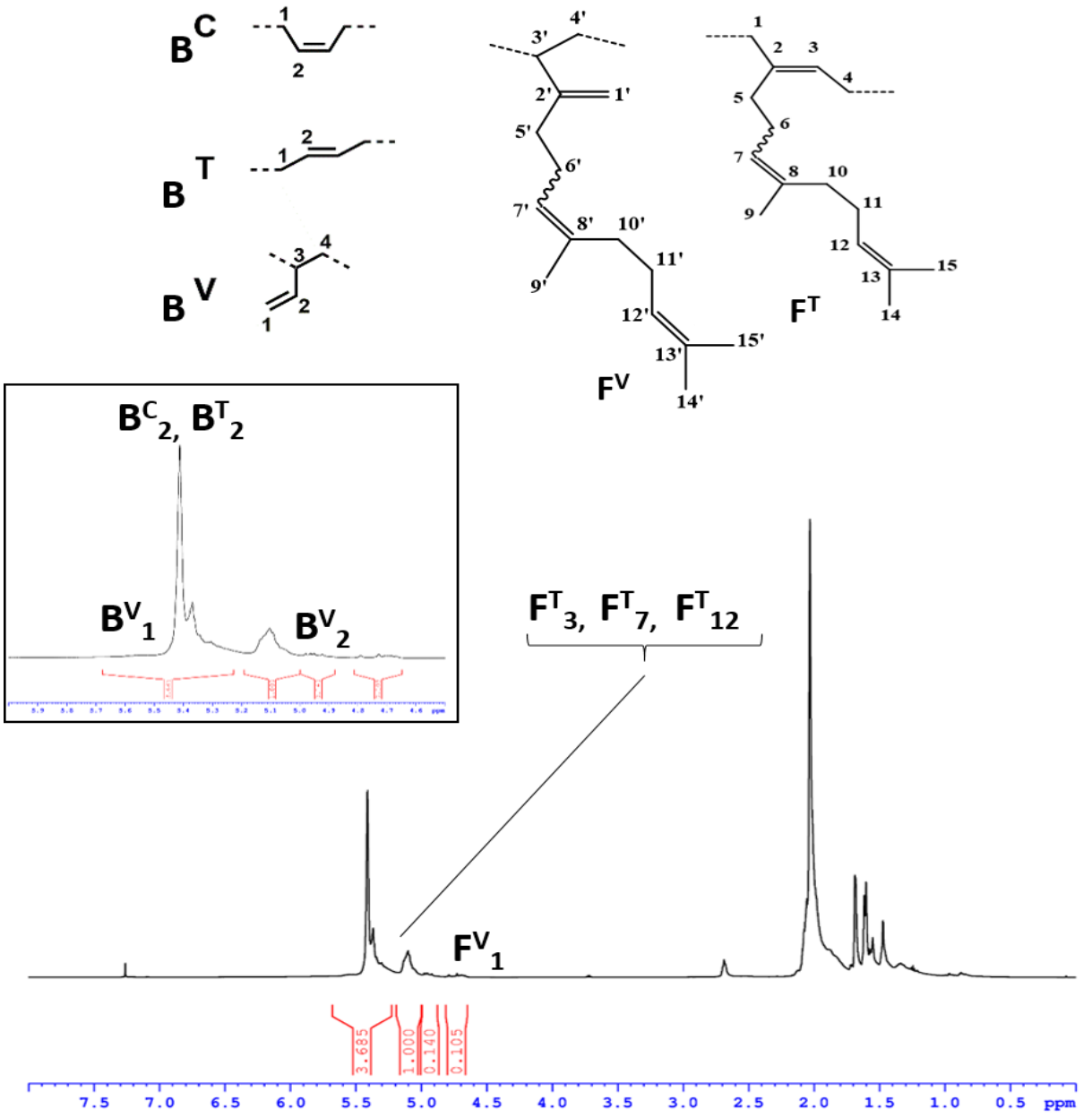


Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of PFB from run **12** of **Table 5**

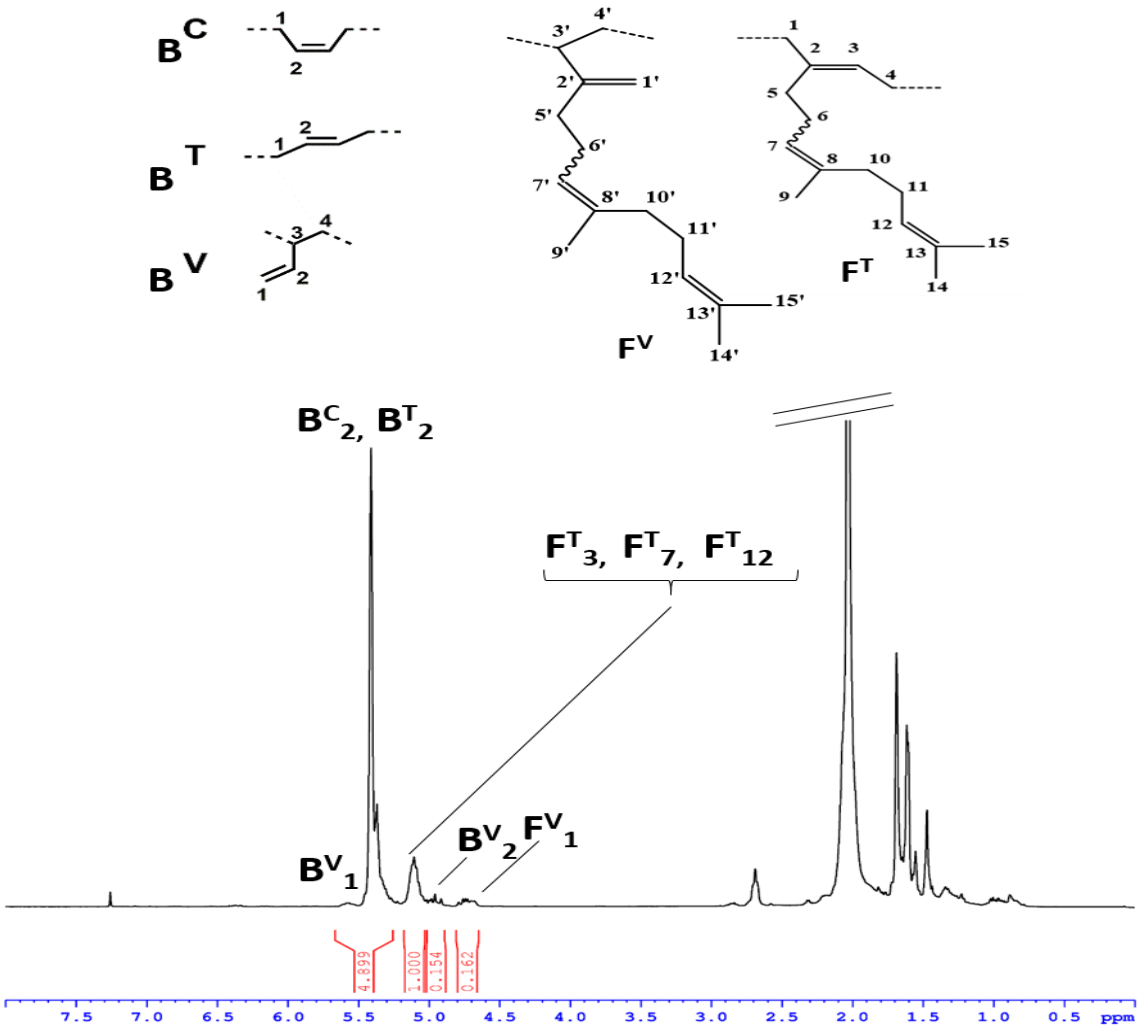


Figure S12. ^{1}H NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of PFB from run **13** of **Table 5**

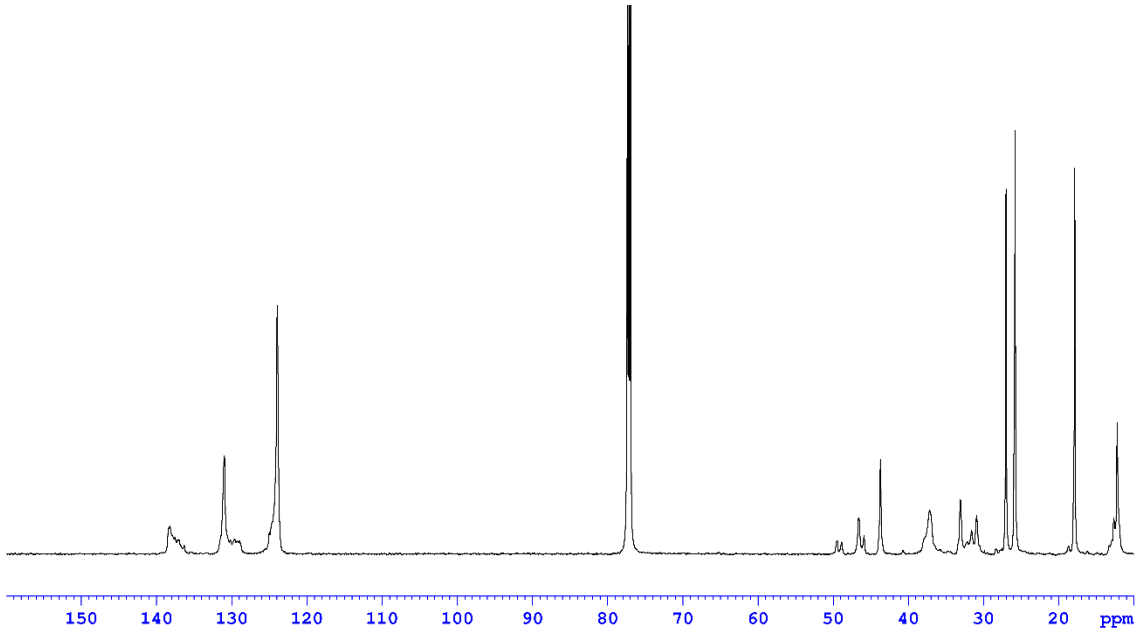


Figure S13. ^{13}C NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB copolymer from run **1** of **Table 1.**

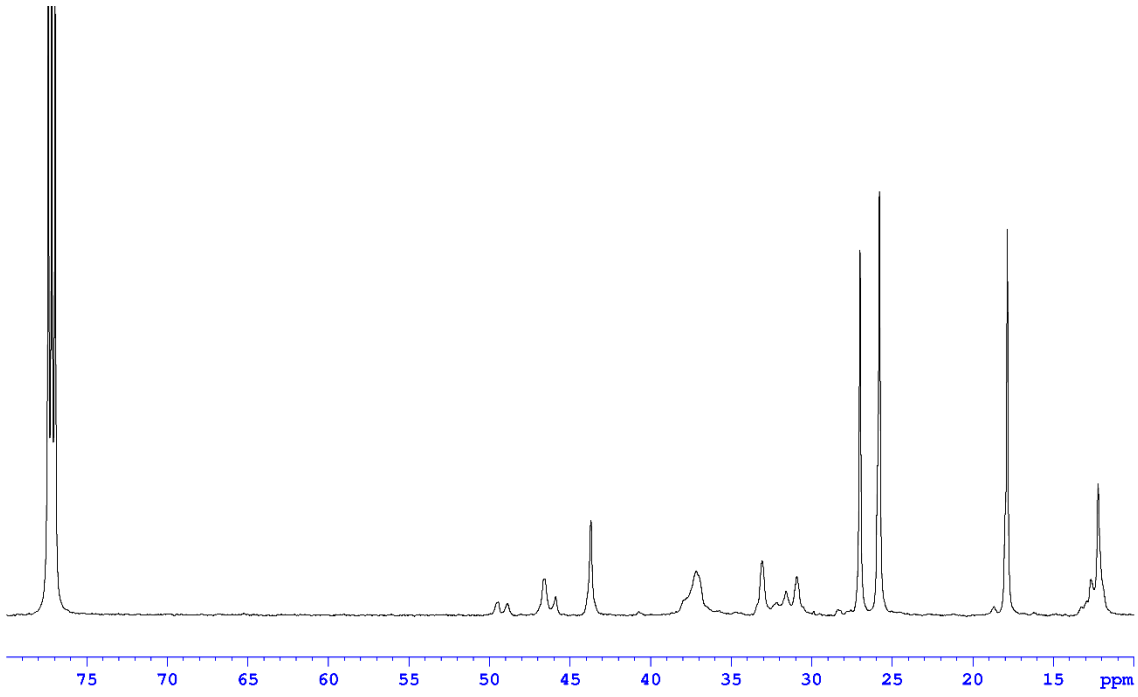


Figure S14. Enlargment of aliphatic region of ^{13}C NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB copolymer from run **1** of **Table 1.**

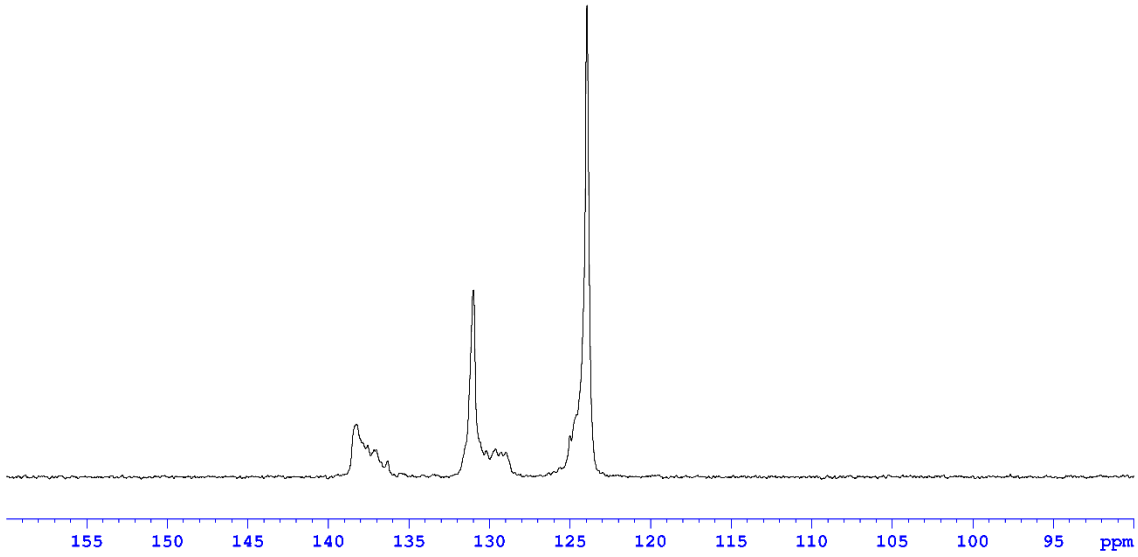


Figure S15. Enlargment of olefinic region of ^{13}C NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB copolymer from run **1** of **Table 1.**

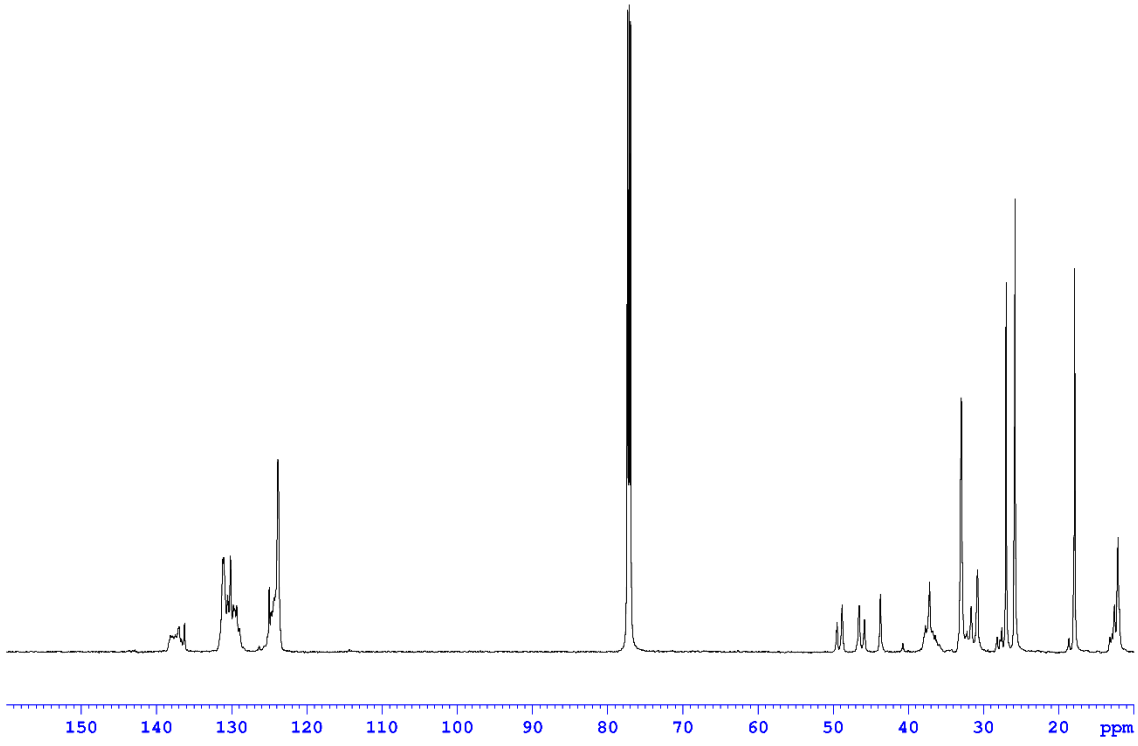


Figure S16. ^{13}C NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB copolymer from run **2** of **Table 1.**

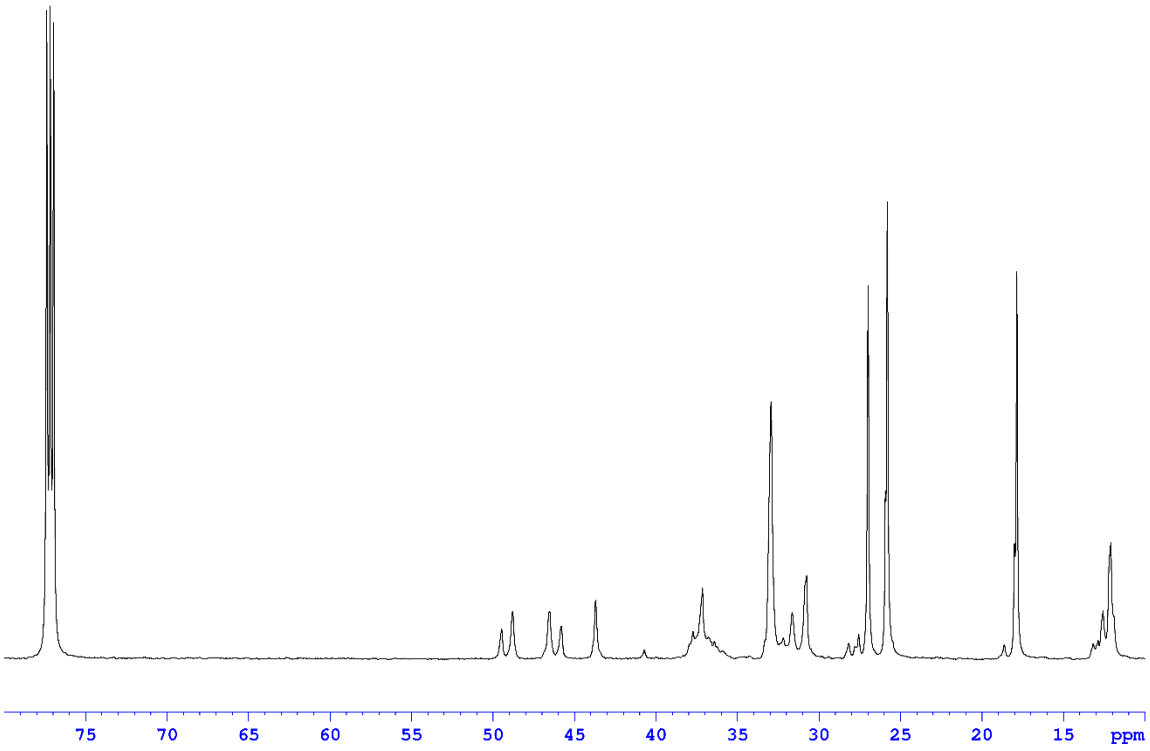


Figure S17. Enlargment of aliphatic region of 13C NMR spectrum (CDCl3, 25 °C, 600 MHz) of POB copolymer from run **2** of **Table 1**

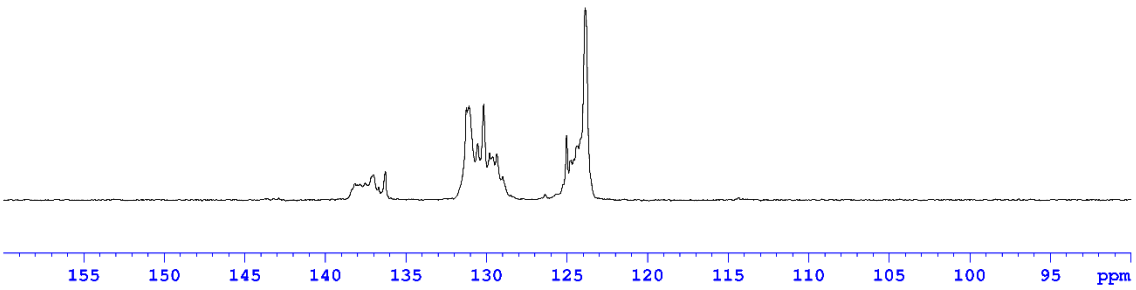


Figure S18. Enlargment of olefinic region of ^{13}C NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB copolymer from run **2** of **Table 1.**

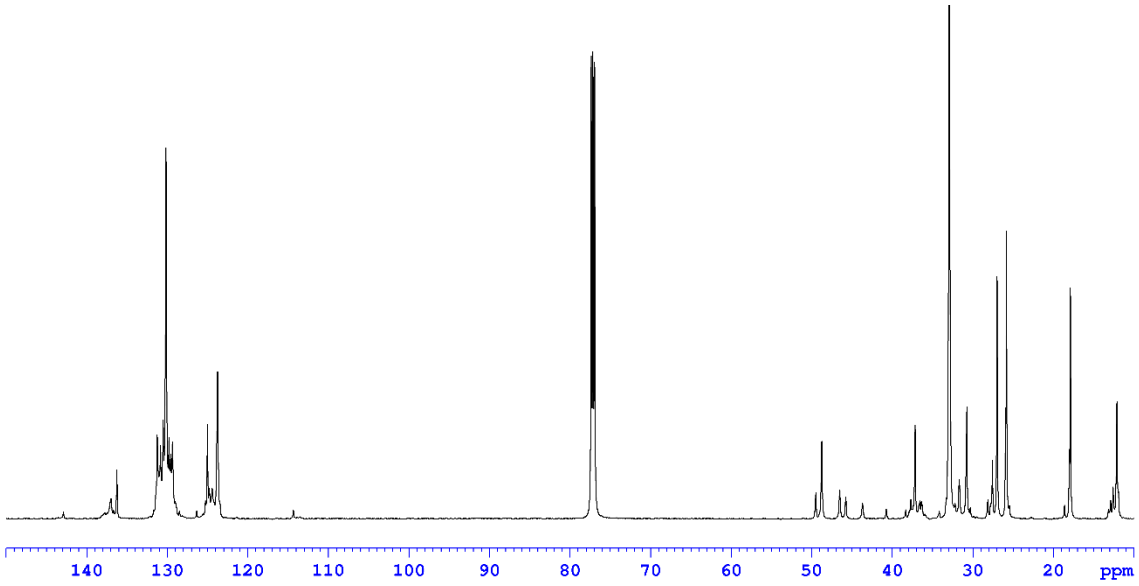


Figure S19. ^{13}C NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB copolymer from run **3** of **Table 1.**

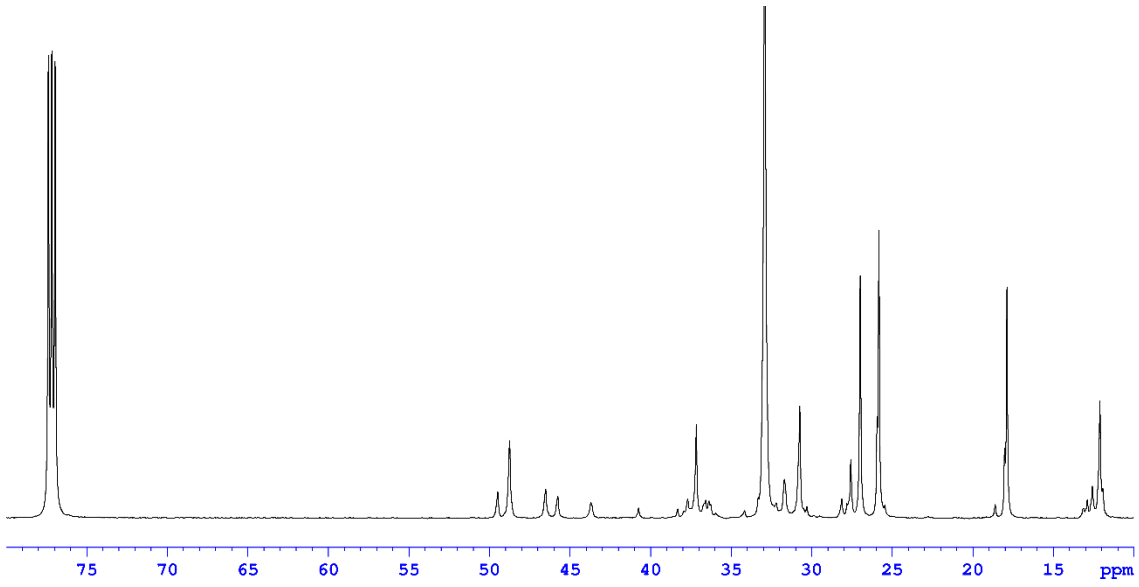


Figure S20. Enlargment of aliphatic region of ^{13}C NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB copolymer from run **3** of **Table 1.**

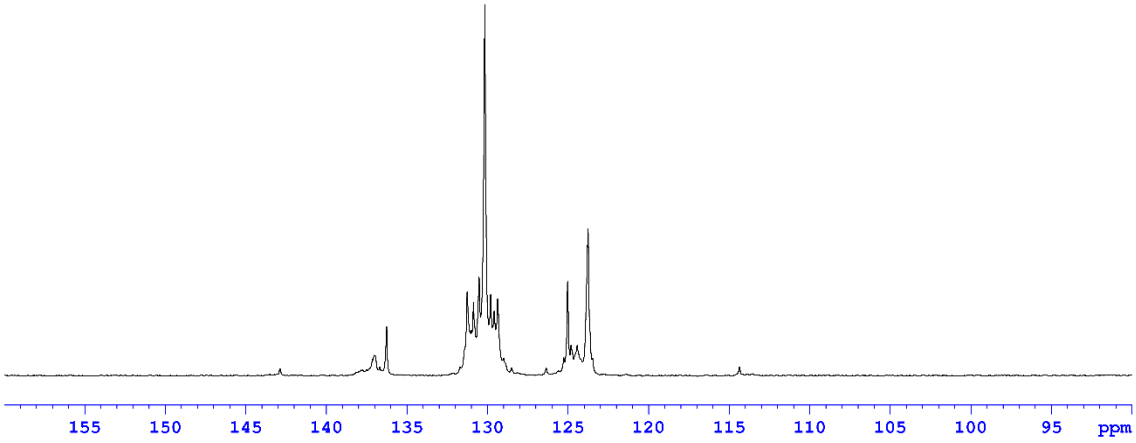


Figure S21. Enlargment of olefinic region of ^{13}C NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB copolymer from run **3** of **Table 1.**

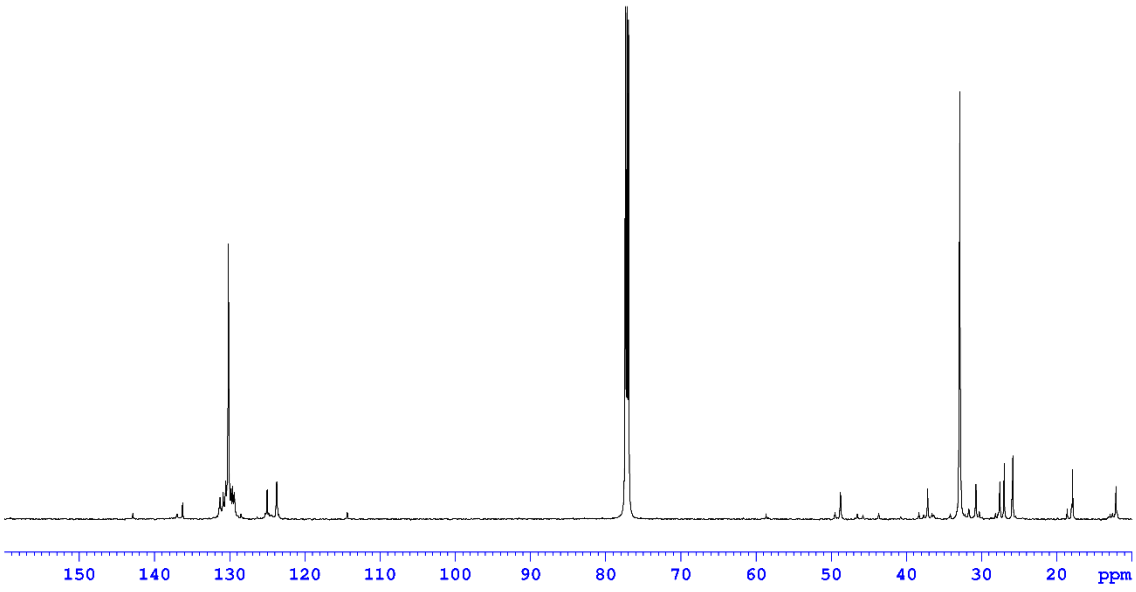


Figure S22. ^{13}C NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB copolymer from run **4** of **Table 1.**

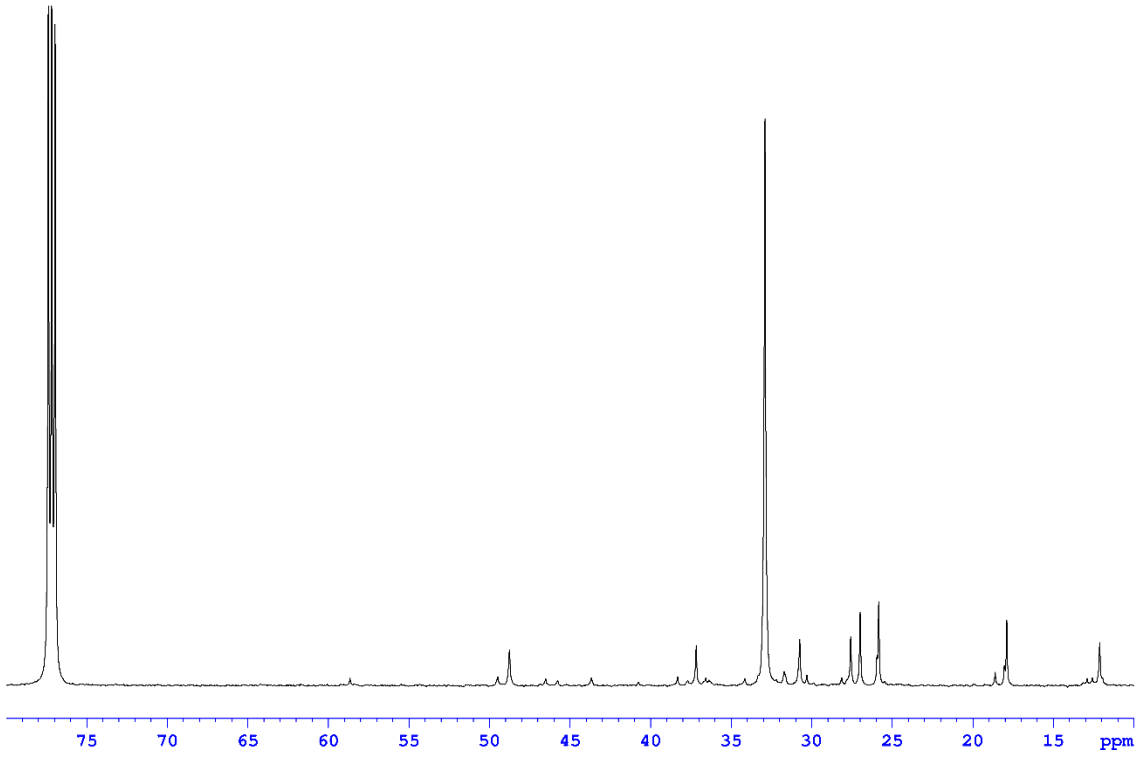


Figure S23. Enlargment of aliphatic region of ^{13}C NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB copolymer from run **4** of **Table 1.**

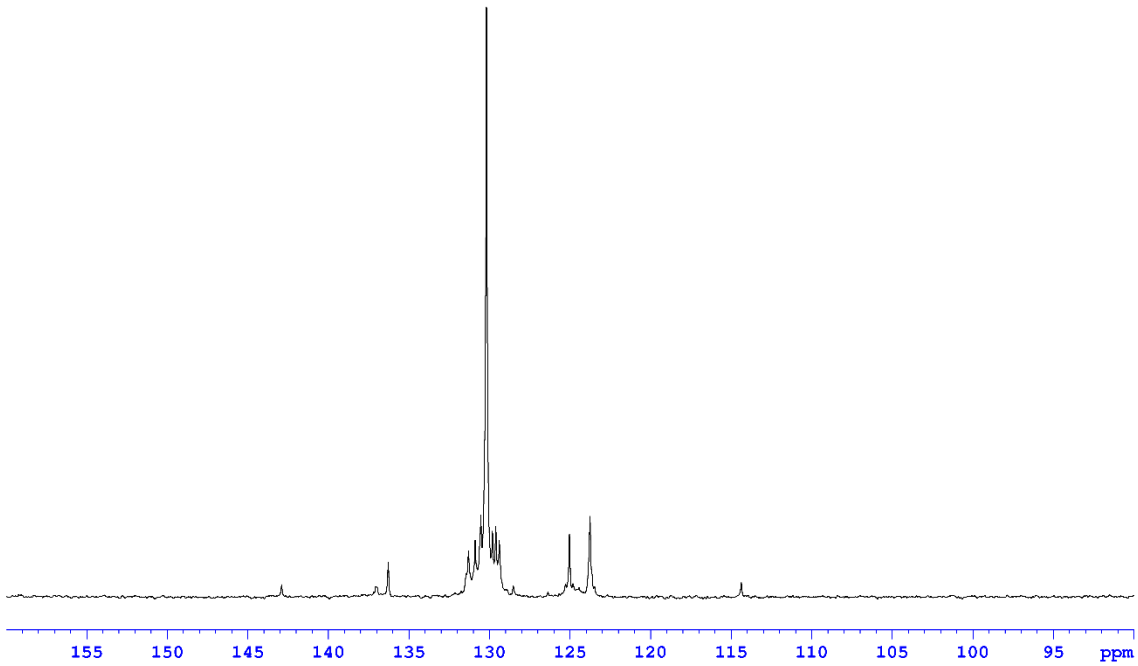


Figure S24. Enlargment of olefinic region of ^{13}C NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB copolymer from run **4** of **Table 1.**

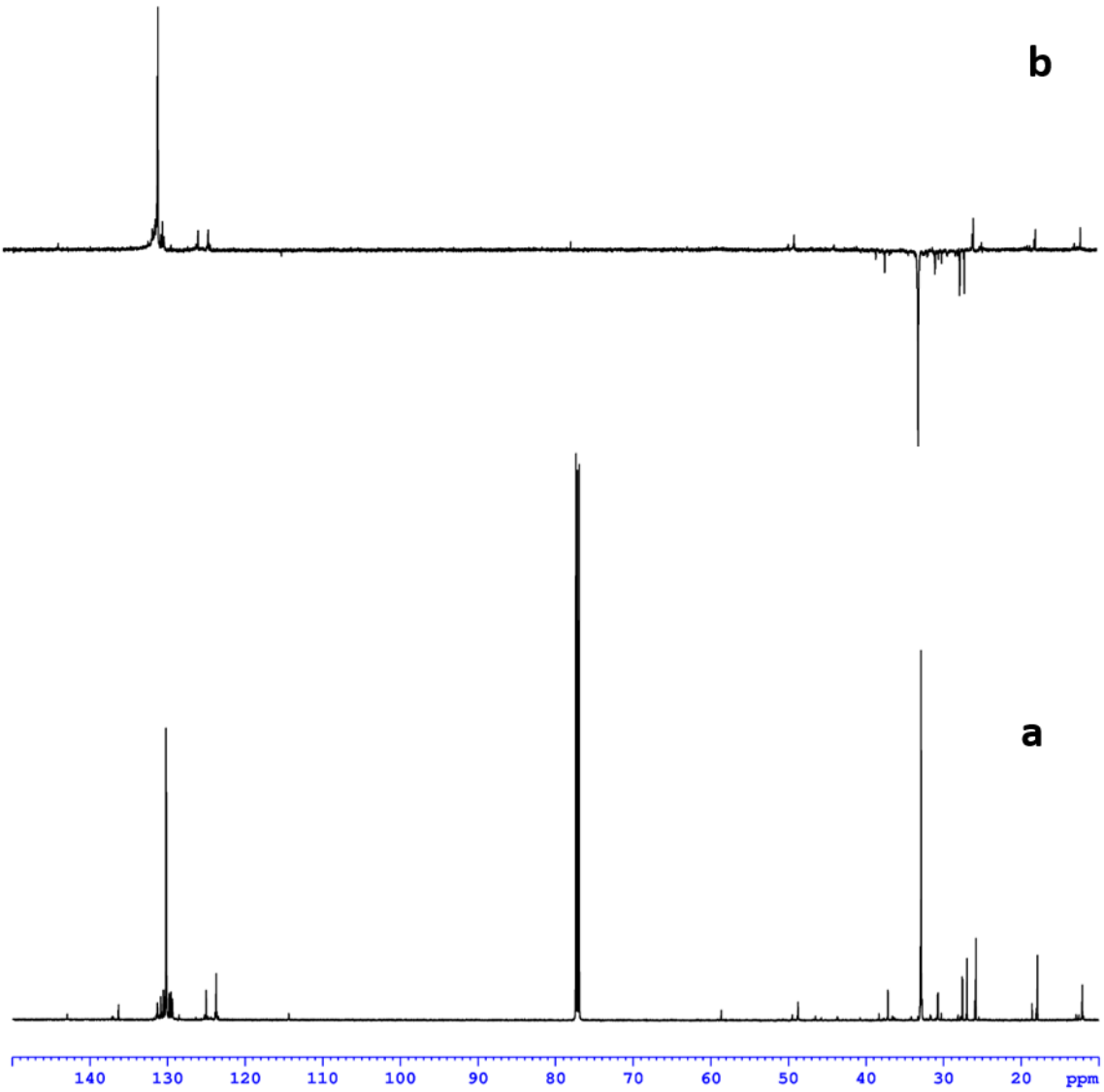


Figure S25. DEPT-135 (b) and ^{13}C NMR (a) spectra ($CDCl_3$, 25 °C, 600 MHz) of PMB copolymer from run **3** of **Table 1.**

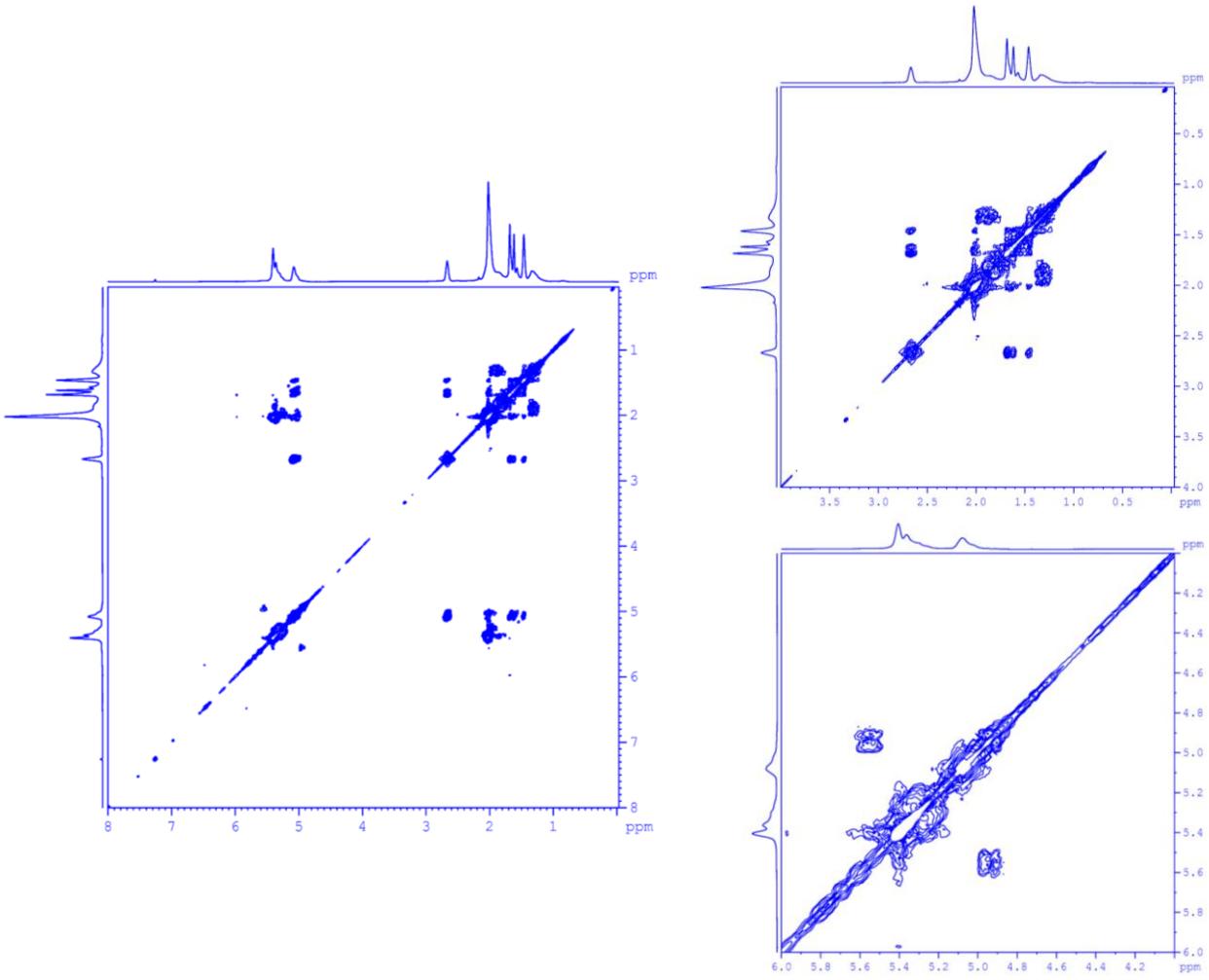


Figure S26. ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB copolymer from run **3** of **Table 1**.

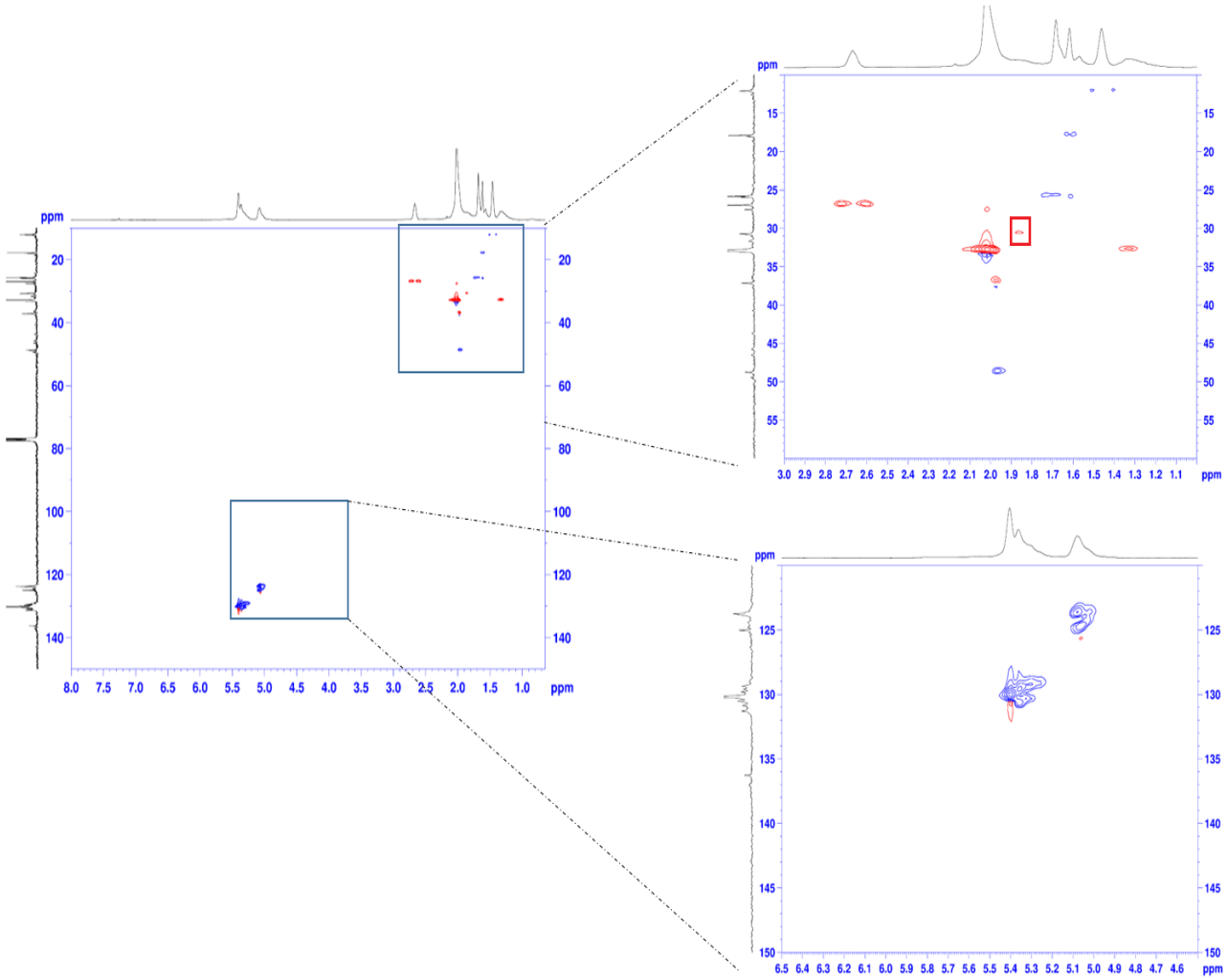


Figure S27. ^{13}C-^{1}H HSQC spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB from run **3** of **Table 1** with magnification of diagnostic regions. Methyl and methine signals are displayed in blue while methylenes in red.

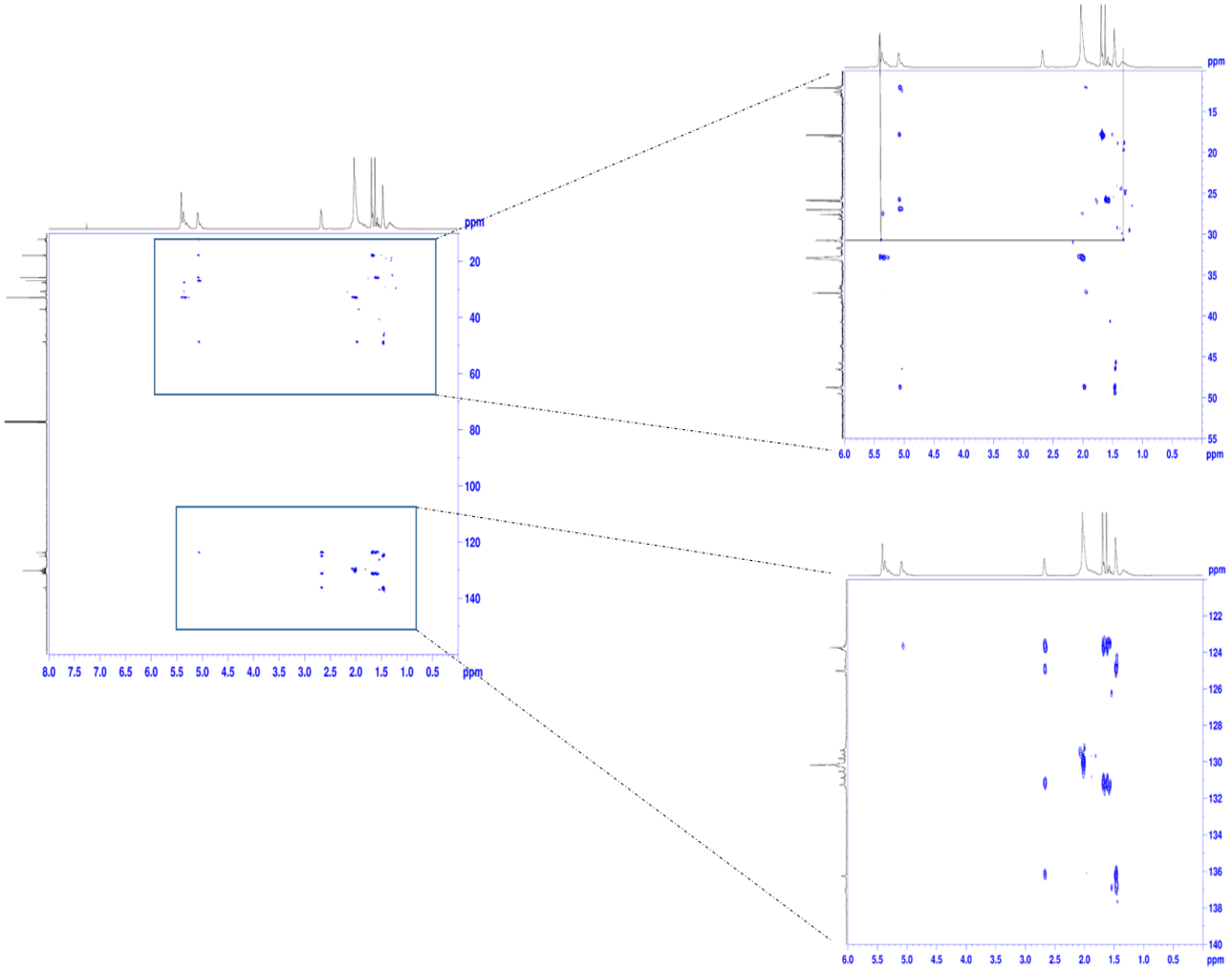


Figure S28. HMBC spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB from run **3** of **Table 1.**

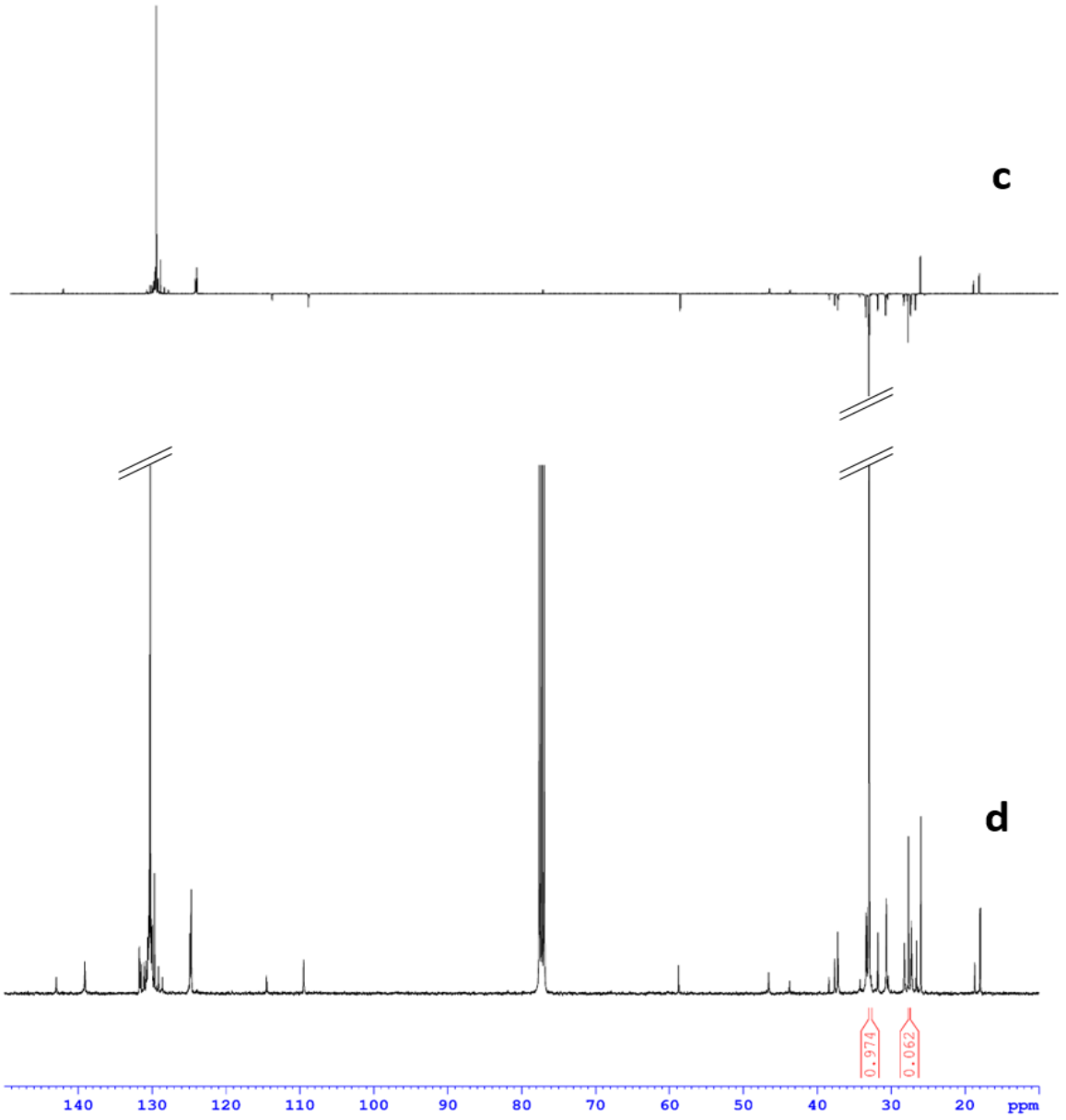


Figure S29. DEPT-135 (c) and ^{13}C NMR (d) spectra ($CDCl_3$, 25 °C, 600 MHz) of PMB copolymer from run **8** of **Table 3.**

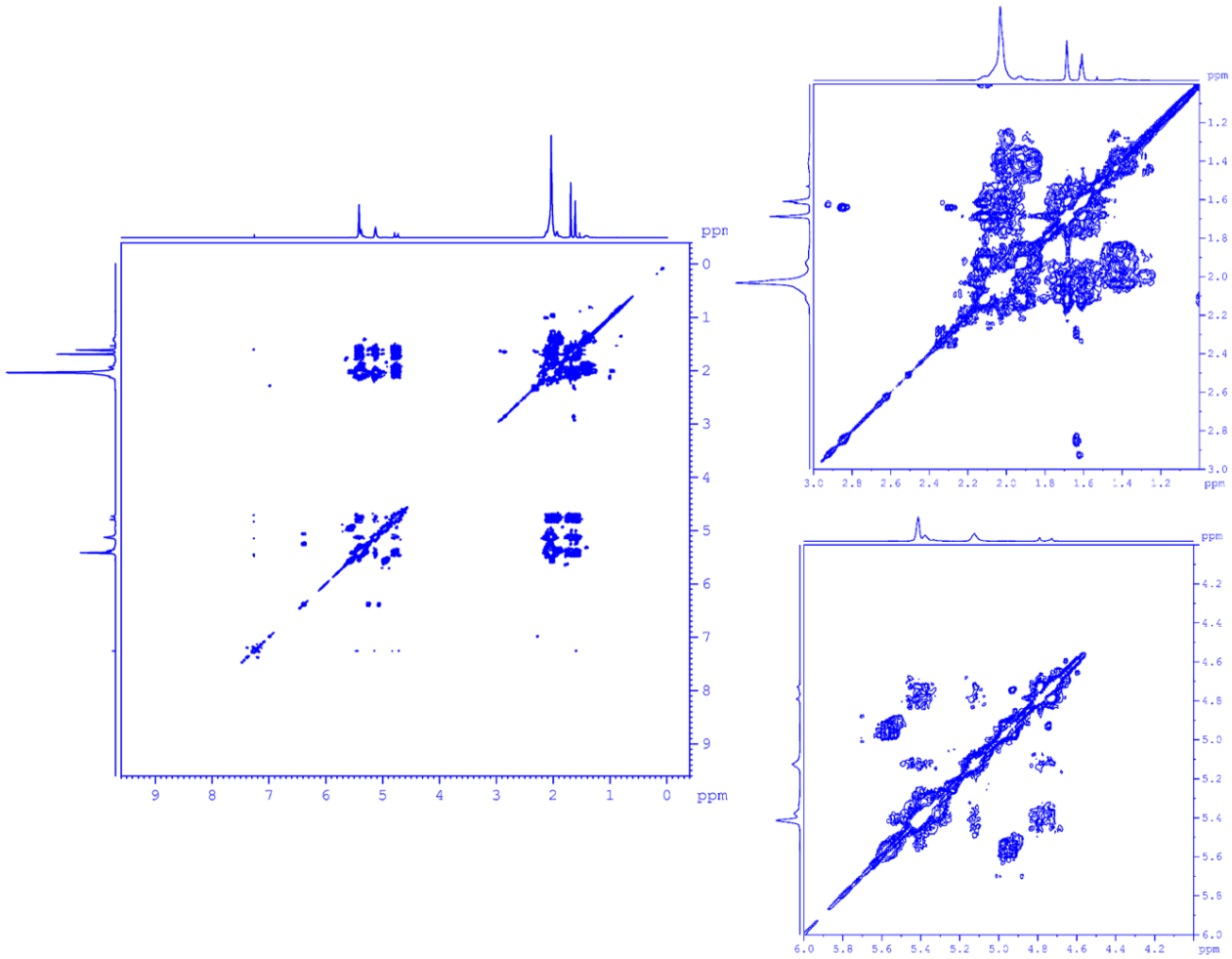


Figure S30. ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 25 °C, 400 MHz) of PMB copolymer from run 6 of Table 3

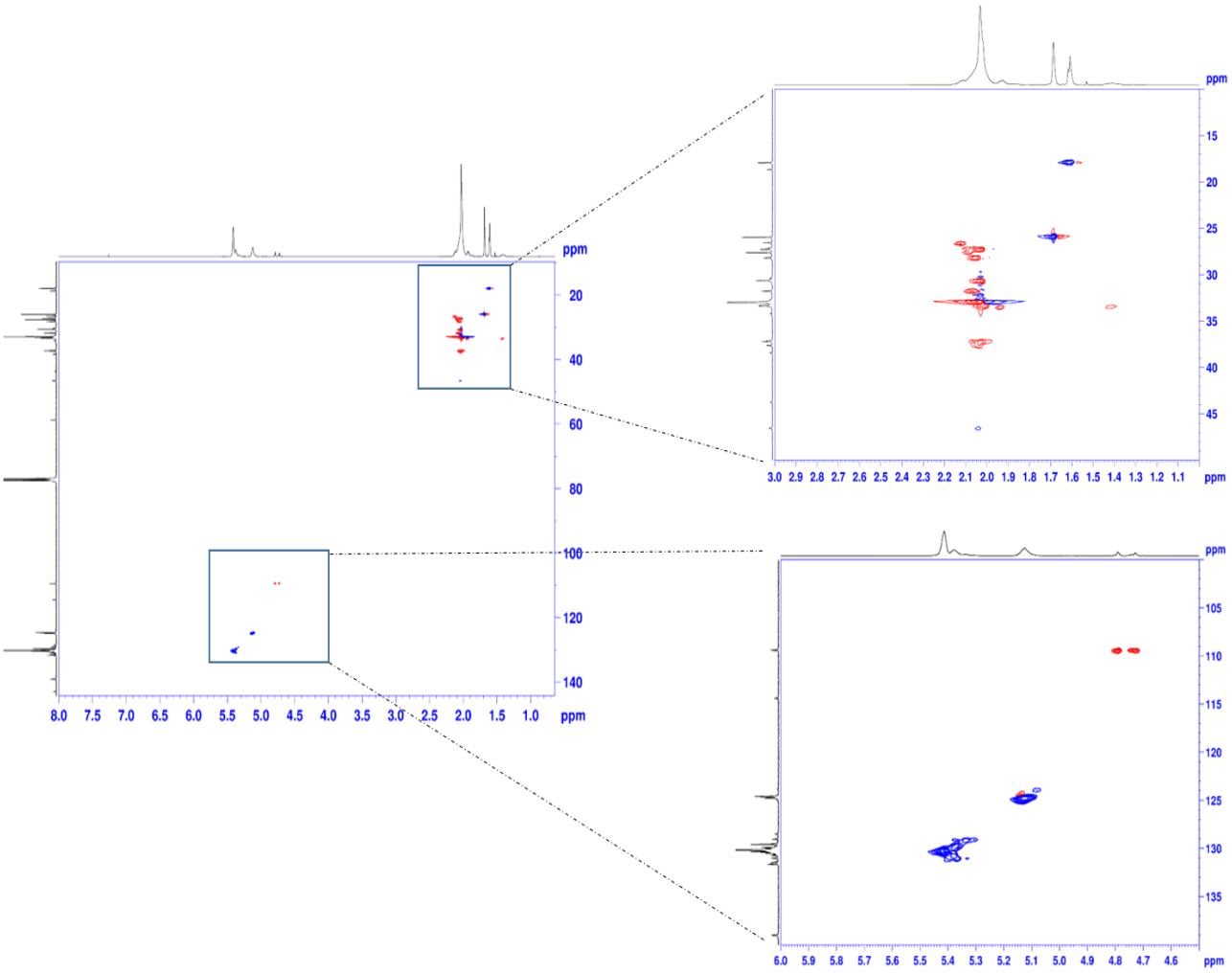


Figure S31. ^{13}C-^{1}H HSQC spectrum ($CDCl_3$, 25 °C, 400 MHz) of PMB from run **6** of **Table 3** with magnification of diagnostic regions. Methyl and methine signals are displayed in blue while methylenes in red.

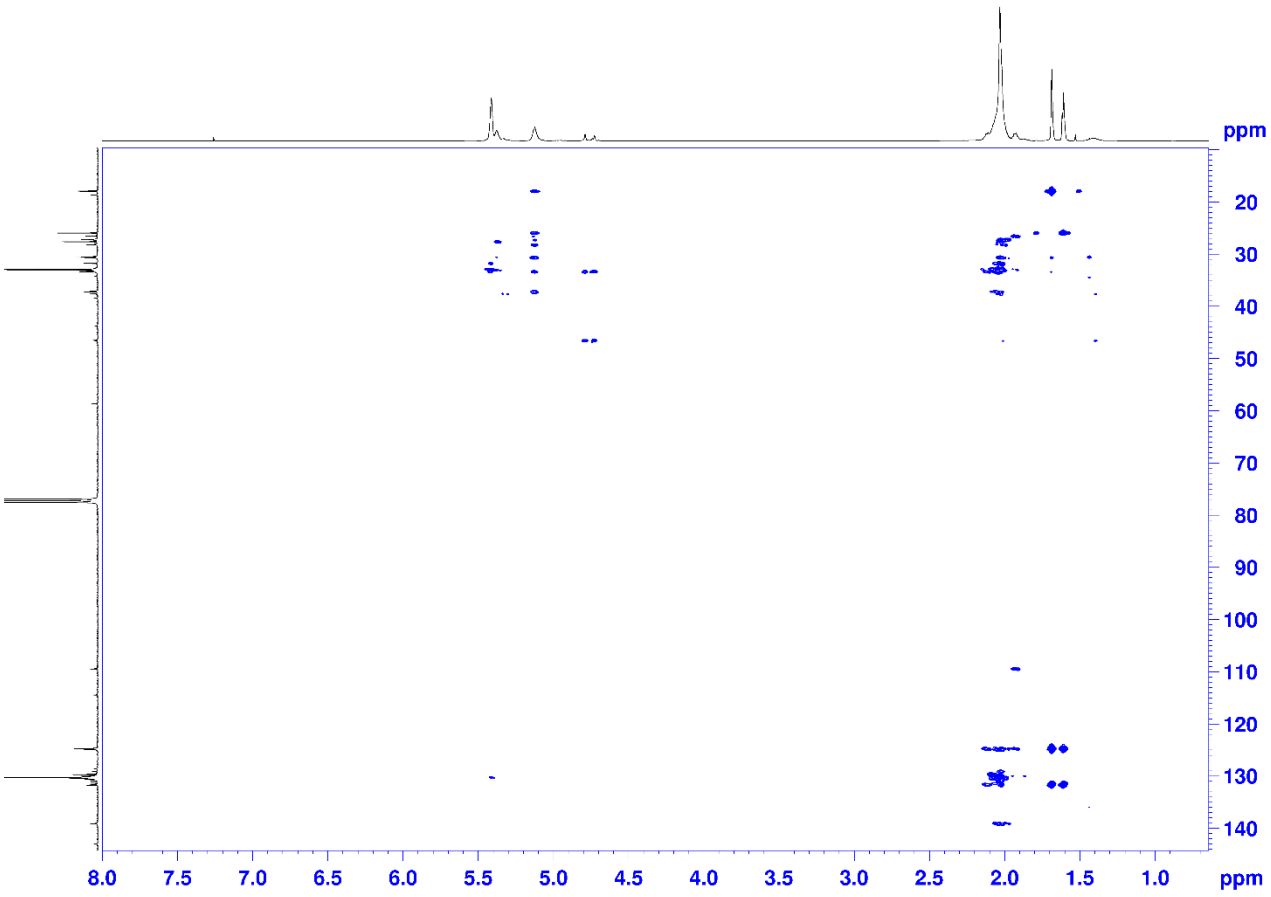


Figure S32. HMBC spectrum ($CDCl_3$, 25 °C, 400 MHz) of PMB from run **6** of **Table 3.**

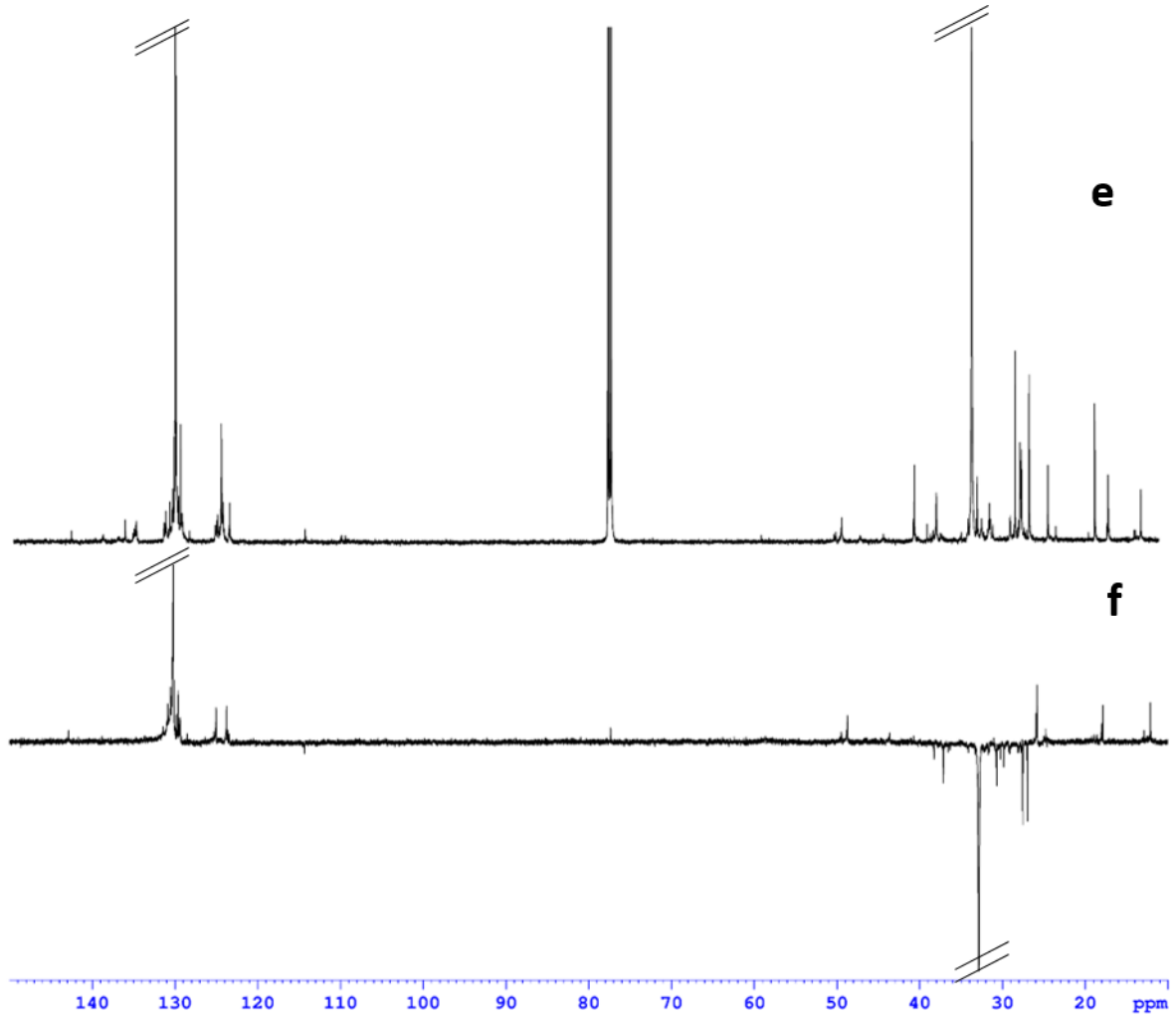


Figure S33. DEPT-135 (e) and DEPT-90 (f) spectra (CDCl3, 25 °C, 600 MHz) of PFB copolymer from run **13** of **Table 5.**

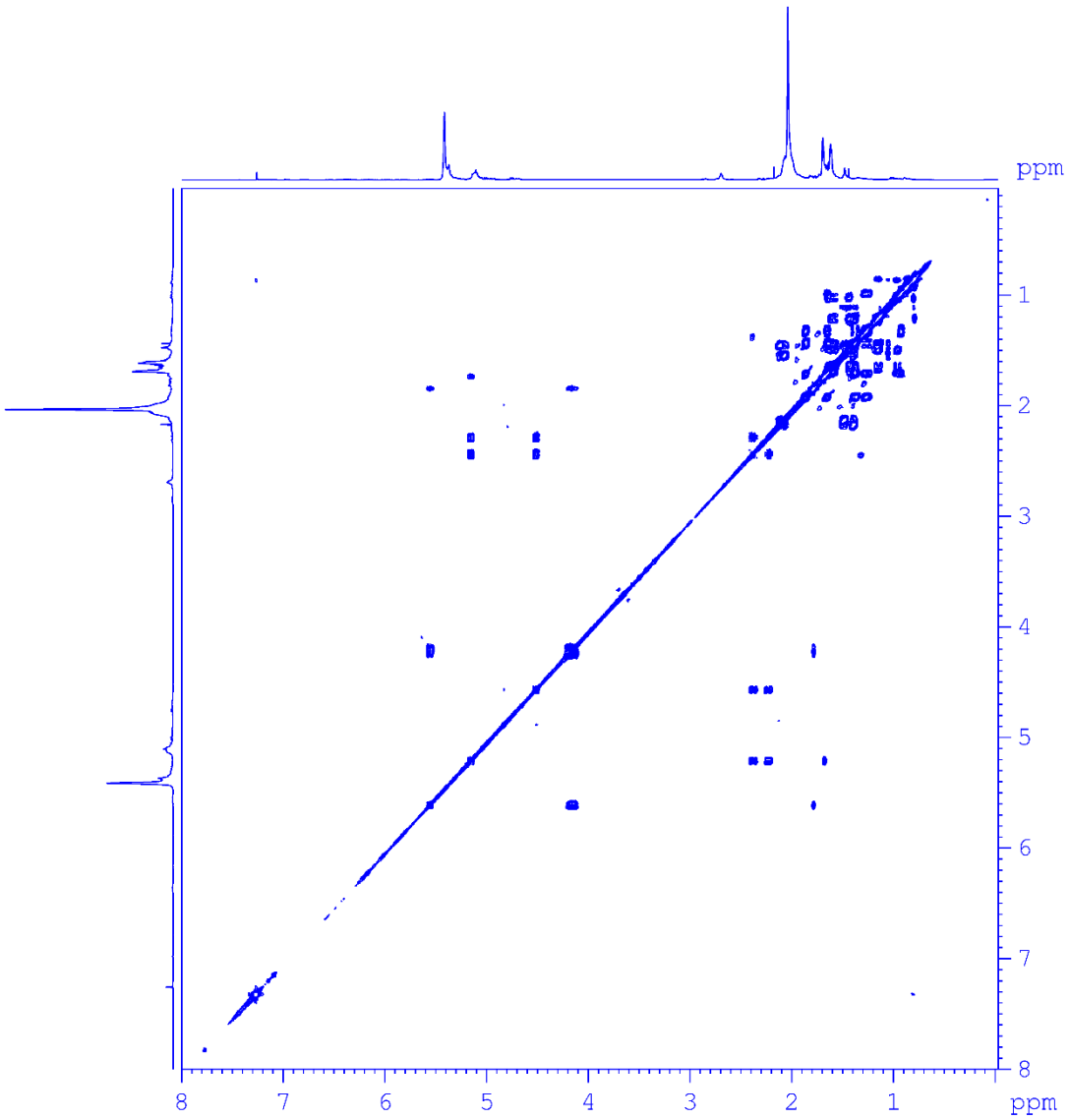


Figure S34. ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 25 °C, 600 MHz) of PFB copolymer from run **13** of Table **5**

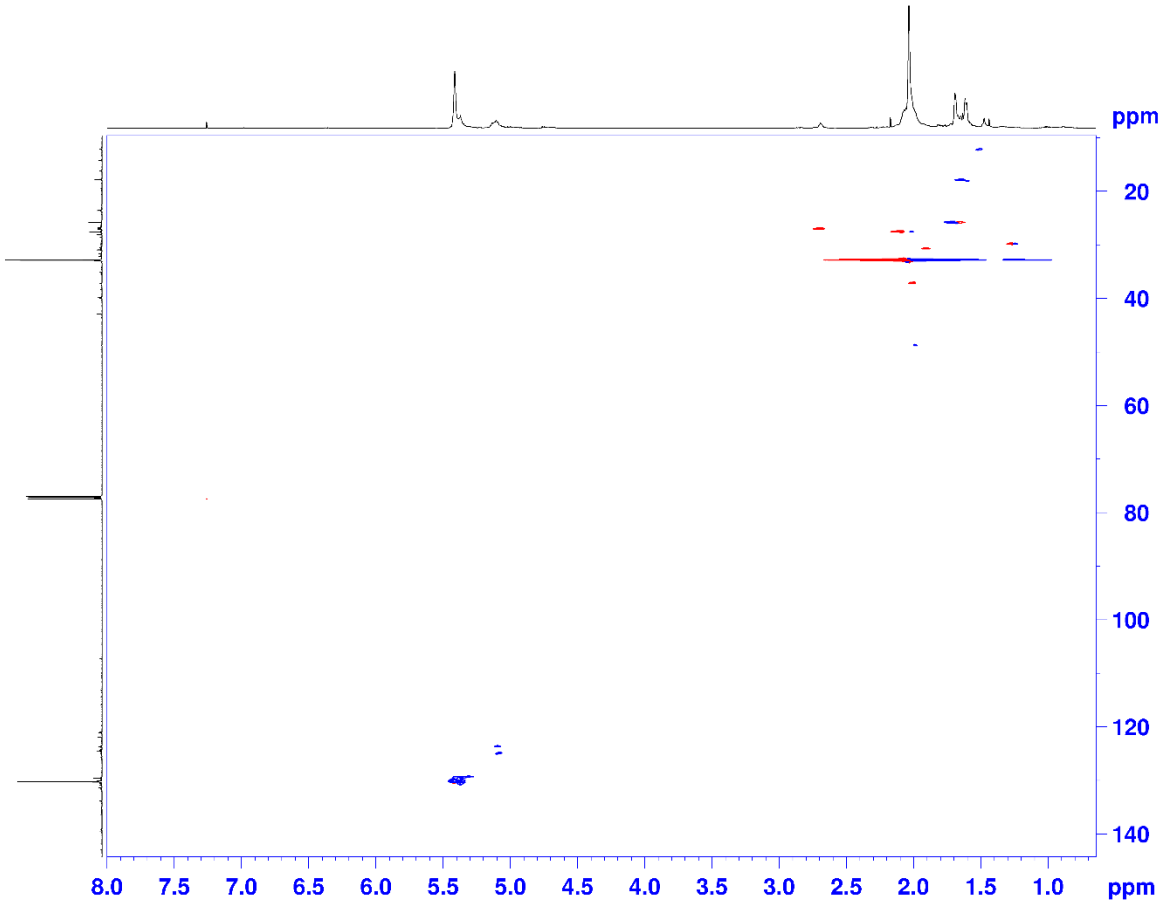


Figure S35. ^{13}C-^{1}H HSQC spectrum ($CDCl_3$, 25 °C, 600 MHz) of PFB from run **13** of **Table 5**. Methyl and methine signals are displayed in blue while methylenes in red.

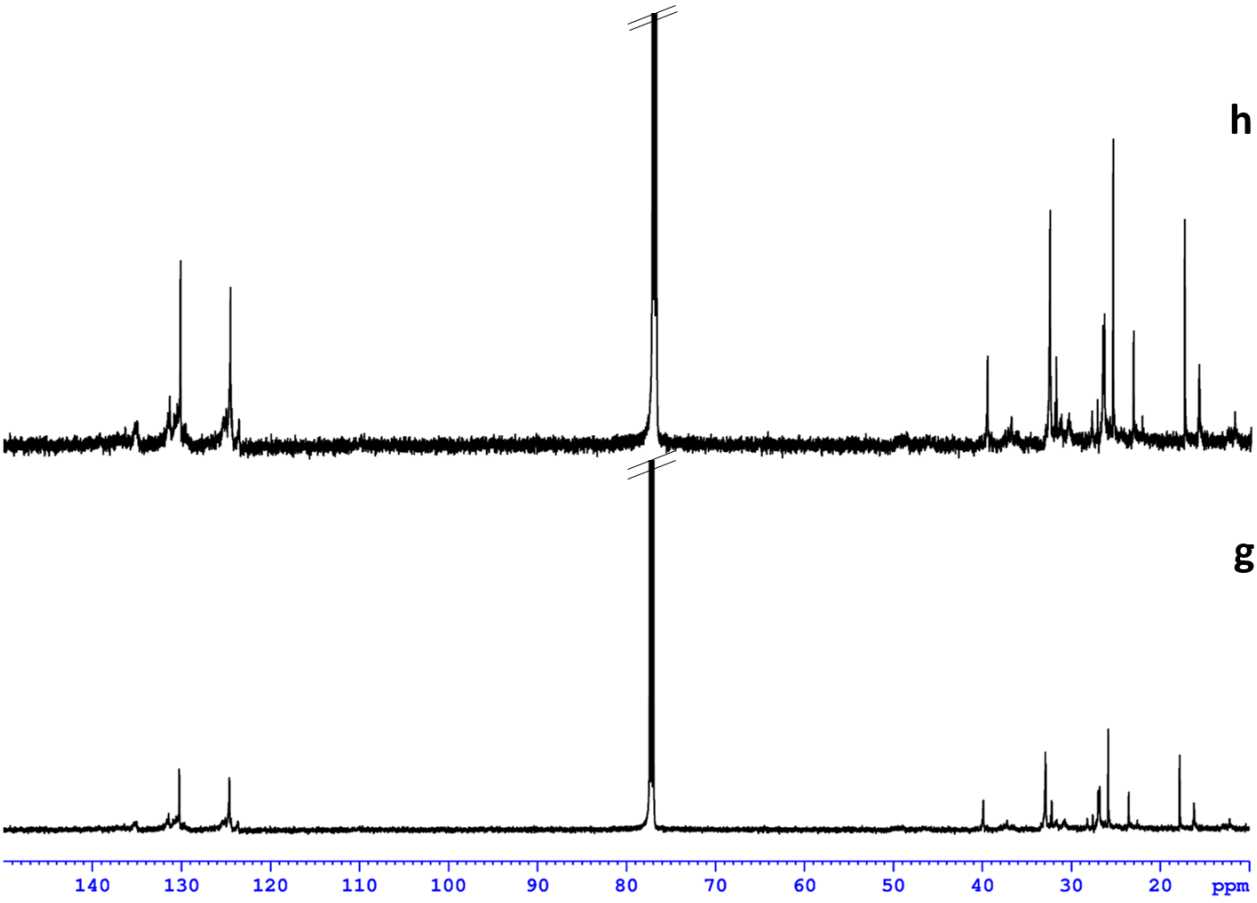


Figure S36. ^{13}C spectrum ($CDCl_3$, 25 °C, 600 MHz) of PFB from run **10 (g)** of **Table 5** and ^{13}C spectrum ($CDCl_3$, 25 °C, 600 MHz) of PFB from run **11 (h)** of **Table 5.**

1.1 Acquisition parameters of NMR (^1H and ^{13}C) experiments.

^1H and ^{13}C NMR spectra were recorded with Bruker spectrometers (300, 400 and 600 MHz) using 5 mm (o.d.) NMR tubes. 30 mg of samples were dissolved in $CDCl_3$ (0.6 mL) and were analyzed at room temperature. Chemical shifts were referenced to TMS and calculated by using the residual isotopic impurities of the deuterated solvent ($CDCl_3$: δ = 7.26 ppm in ^1H NMR and δ = 77.17 ppm in ^{13}C NMR experiments).

^1H NMR spectra were recorded using zg pulse program; pre-scan delay was 6.0 μs, and the relaxation delay between scans was 1 s; spectrum width was 12.0 ppm; 64 scans were accumulated.

^{13}C NMR spectra were recorded using zgpg30 pulse program; pre-scan delay was 6.0 μs, and relaxation delay between pulses was 2 s; spectrum width was set to 220.0 ppm; number of scans was 32000.

Exponential digital filter with the lb parameter of 2 Hz was applied prior to Fourier transformation. All the NMR spectra were integrated after baseline correction (a mean of minimum three integration values has been taken for each calculation).

2.Determination of Polymer Compositions

2.1 Determination of O^V and O^T contents in POB copolymers by ^{13}C NMR ($CDCl_3$, 25 °C)

- $O^V(mol\%) = \frac{A_B}{A_B + \frac{A_A}{2}} \cdot 100$ **Equation 1**

  Where $\boldsymbol{A_A}$ is the area of the signals $\mathbf{O^T_1}$ and $\mathbf{O^T_6}$ (δ=31.7 ppm) and $\boldsymbol{A_B}$ is the area of the signal $\mathbf{O^V_6}$ (δ=27.0 ppm).

- $O^T(mol\%) = 100 - O^V(mol\%)$ **Equation 2**

2.2 Determination of B^C and B^T contents in POB and PMB copolymers by ^{13}C NMR ($CDCl_3$, 25 °C)

- $B^C(mol\%) = \frac{\frac{A_k}{2}}{\frac{A_k}{2} + \frac{A_l}{2}} \cdot 100$ **Equation 3**

  Where $\boldsymbol{A_K}$ is the area of the $\mathbf{B^C_1}$ and $\mathbf{B^C_4}$ carbons (δ=27.5 ppm) and $\boldsymbol{A_l}$ is the area of the $\mathbf{B^T_1}$ and $\mathbf{B^T_4}$ carbons (δ=32.9 ppm).

- $B^T(mol\%) = 100 - B^C(mol\%)$ **Equation 4**

2.3 Determination of 1, 2-structure and 1, 4-structure (cis and trans) of B contents in POB, PMB e PFB copolymers by ^1H NMR ($CDCl_3$, 25 °C)

- $B^{1,2}(mol\%) = \frac{A_d/2}{\frac{A_{a+b+c} - A_d/2}{2} + A_d/2} \cdot 100$ **Equation 5**

  Where $\mathbf{A_{a+b+c}}$ represents the integrated area of $\mathbf{B^C_2}$, $\mathbf{B^T_2}$ and $\mathbf{B^V_2}$ (δ= 5.20-5.70 ppm), and $\mathbf{A_d}$ is the area of $\mathbf{B^V_1}$ (δ= 4.91-4.98 ppm).

- $B^{1,4}(mol\%) = 100 - B^{1,2}(mol\%)$ **Equation 6**

2.4 Determination of M^V and M^T contents in PMB copolymers by ^{1}H NMR (CDCl3, 25 °C)

- $M^V(mol\%) = \frac{B_B}{B_A + \frac{B_B}{2}} \cdot 100$ **Equation 7**

  Where $\boldsymbol{B_A}$ is the area of the signals $\mathbf{M^T_3}$, $\mathbf{M^T_7}$ and $\mathbf{M^V_7}$ (δ = 5.12 ppm) and $\boldsymbol{B_B}$ is the area of the signal $\mathbf{M^V_1}$ (δ = 4.72, 4.79 ppm).

- $M^T(mol\%) = 100 - M^V(mol\%)$ **Equation 8**

2.5 Determination of total B contents in POB copolymers by ^{13}C NMR(CDCl$_3$, 25 °C)

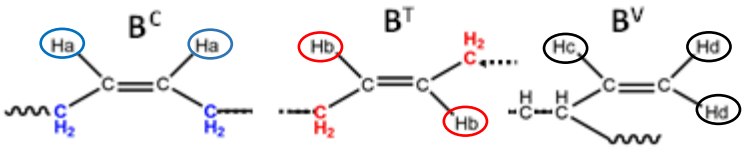
- $B(mol\%) = \frac{\frac{A_k}{2} + \frac{A_l}{2}}{\frac{A_k}{2} + \frac{A_l}{2} + A_B + \frac{A_A}{2}}$ **Equation 9**

  Where $\boldsymbol{A_K}$ is the area of the $\mathbf{B^C_1}$ and $\mathbf{B^C_4}$ carbons (δ=27.5 ppm) and $\boldsymbol{A_l}$ is the area of the $\mathbf{B^T_1}$ and $\mathbf{B^T_4}$ carbons (δ=32.9 ppm); $\boldsymbol{A_A}$ is the area of the signals $\mathbf{O^T_1}$ and $\mathbf{O^T_6}$ (δ=31.7 ppm) and $\boldsymbol{A_B}$ is the area of the signal $\mathbf{O^V_6}$ (δ=27.0 ppm).

2.6 Determination of total B contents in PMB copolymers by ^{1}H NMR (CDCl$_3$, 25 °C)

- $B(mol\%) = \frac{\frac{A_{a+b+c} - A_d/2}{2} + A_d/2}{\frac{A_{a+b+c} - A_d/2}{2} + A_d/2 + \frac{B_A + B_B/2}{2}}$ **Equation 10**

  Where $\mathbf{A_{a+b+c}}$ represents the integrated area of polybutadiene $\mathbf{H_a}$, $\mathbf{H_b}$ and $\mathbf{H_c}$ (δ= 5.20-5.70 ppm), $\mathbf{A_d}$ is the area of $\mathbf{H_d}$ (δ= 4.91-4.98 ppm); $\boldsymbol{B_A}$ is the area of the myrcene signals $\mathbf{M^T_3}$, $\mathbf{M^T_7}$ and $\mathbf{M^V_7}$ (δ = 5.12 ppm) and $\boldsymbol{B_B}$ is the area of the myrcene signal $\mathbf{M^V_1}$ (δ = 4.72, 4.79 ppm).



2.7 Determination of F^C, F^T and F^V contents in PFB copolymers by ^{1}H NMR ($CDCl_3$, 25 °C)

- $$F^{T+C}(mol\%) = \frac{\frac{C_A}{3}}{\frac{C_A}{3}+\frac{C_B}{2}} \cdot 100$$ **Equation 11**

  Where C_A is the integrated area of the signals F^T_3, F^T_7 and F^T_{12} (δ= 5.10 ppm) and C_B is the integrated area of the signal F^V_1 (δ= 4.66-4.81ppm).

- $$F^v(mol\%) = 100 - F^{T+C}(mol\%)$$ **Equation 12**

2.8 Determination of total B contents in PFB copolymers by ^{1}H NMR ($CDCl_3$, 25 °C)

- $$B(mol\%) = \frac{\frac{A_{a+b+c}-A_d/2}{2}+{A_d}/{2}}{\frac{A_{a+b+c}-A_d/2}{2}+{A_d}/{2}+\frac{C_A}{3}+\frac{C_B}{2}}$$ **Equation 13**

- $$F(mol\%) = 100 - B(mol\%)$$ **Equation 14**

Where A_{a+b+c} represents the integrated area of polybutadiene H_a, H_b and H_c (δ= 5.20-5.70 ppm), A_d is the area of H_d (δ= 4.91-4.98 ppm); C_A is the integrated area of the 1,4 polyfarnesene signals F^T_3, F^T_7 and F^T_{12} (δ= 5.10 ppm) and C_B is the integrated area of the 3,4 polyfarnesene signal F^V_1 (δ= 4.66-4.81ppm).

3. DSC Thermal Analyses

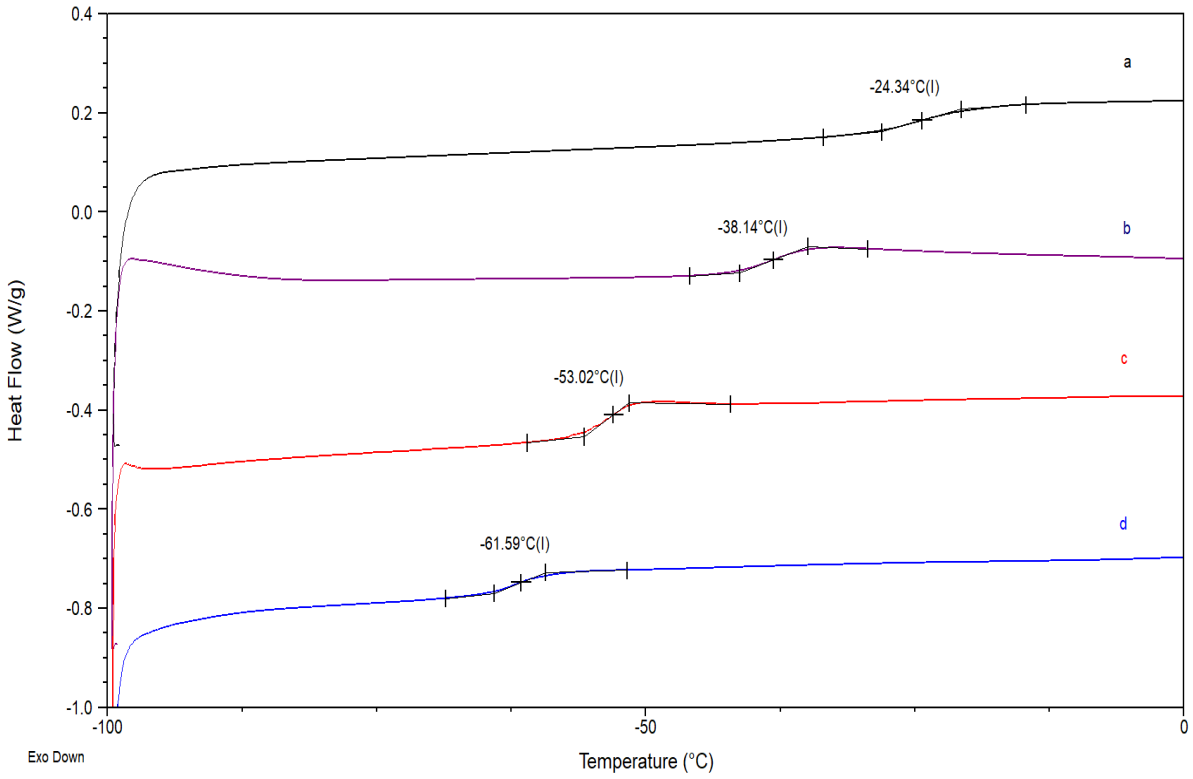


Figure S37. DSC thermograms of POB copolymer from run 1 (a), 2 (b), 3 (c) and 4 (d) of **Table 1.**

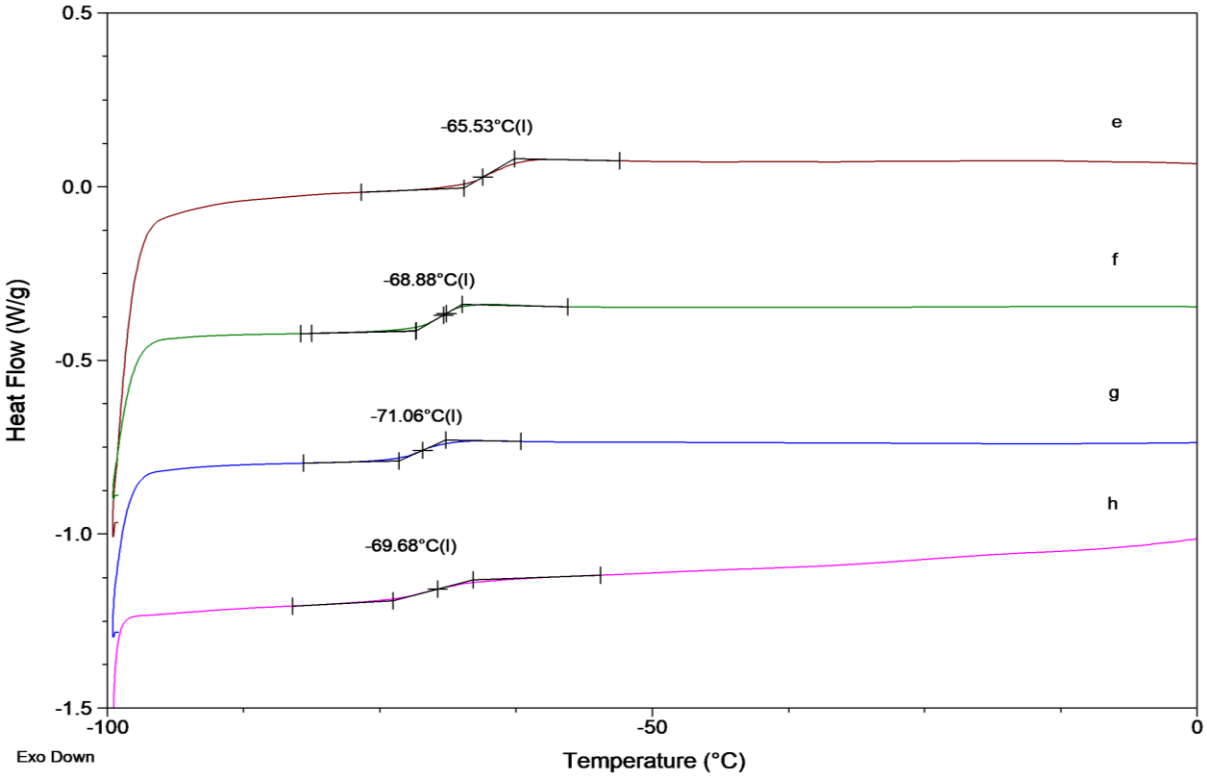


Figure S38. DSC thermograms of PMB copolymer from run 5 (e), 6 (f), 7 (g) and 8 (h) of **Table 3.**

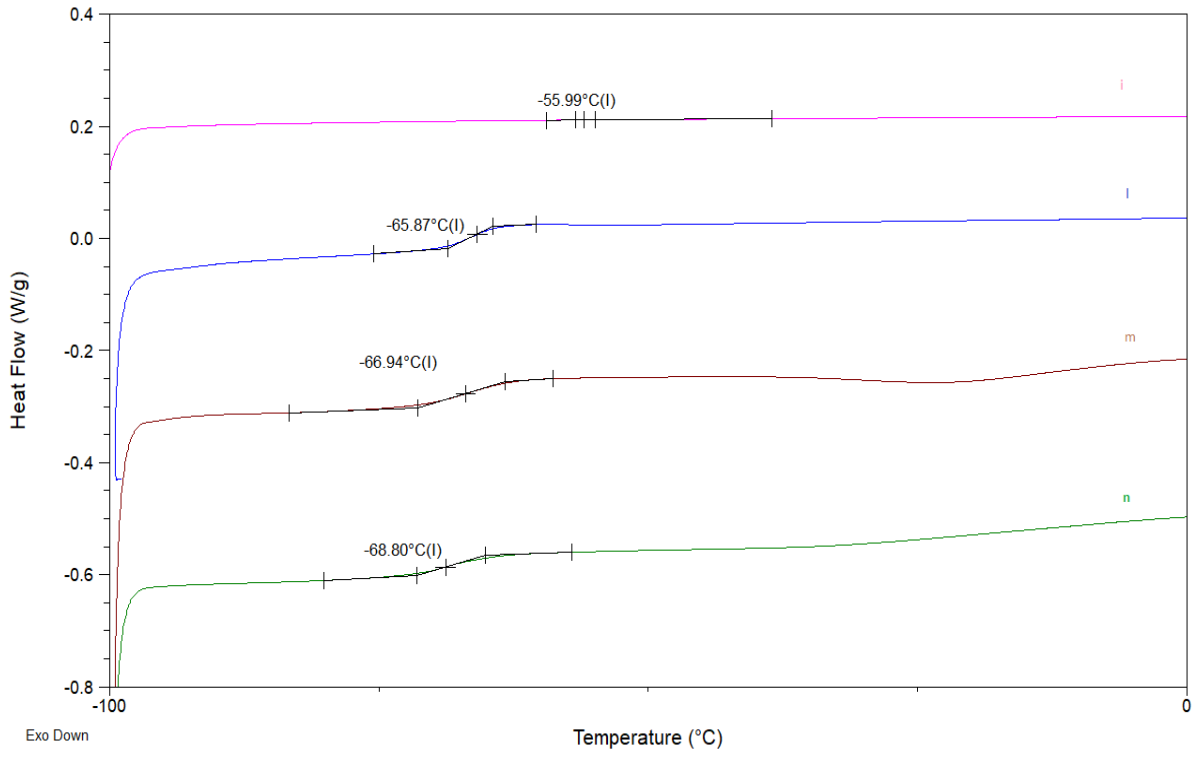


Figure S39. DSC thermograms of PFB copolymer from run 10 (i), 11 (l), 12 (m) and 13 (n) of **Table 5.**

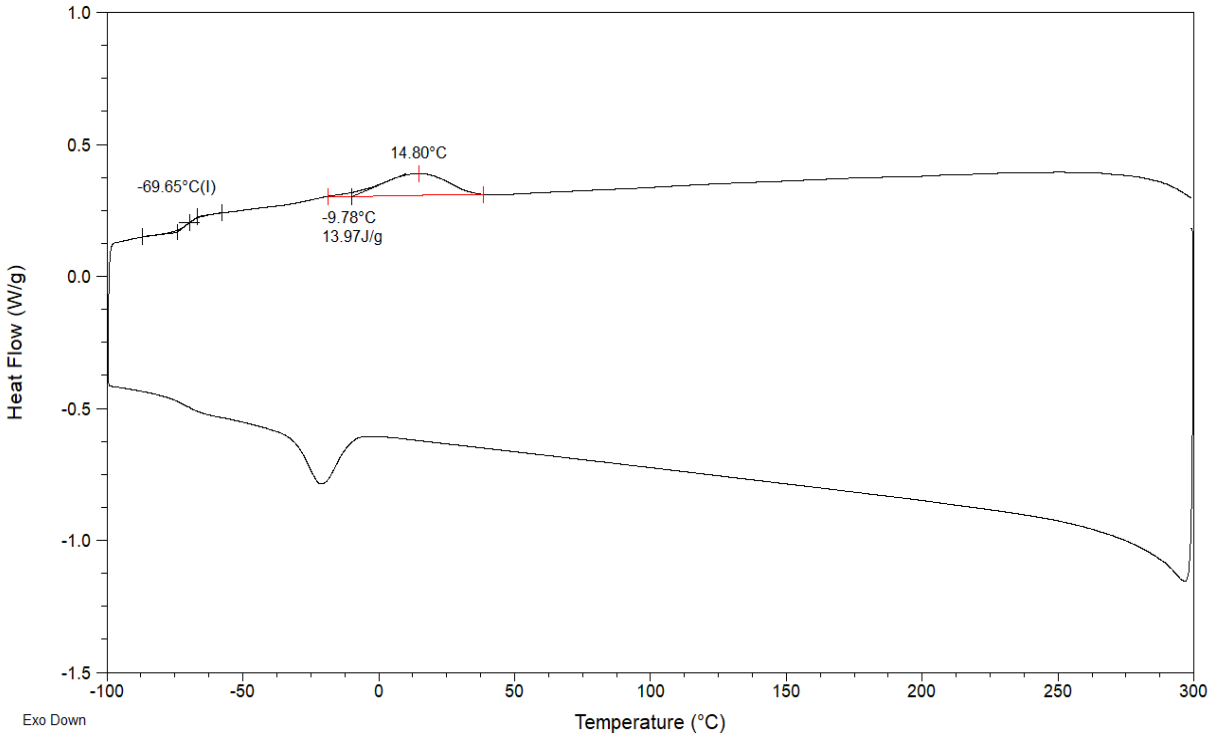


Figure S40. DSC thermograms of PFB copolymer from run 8 of **Table 3**.

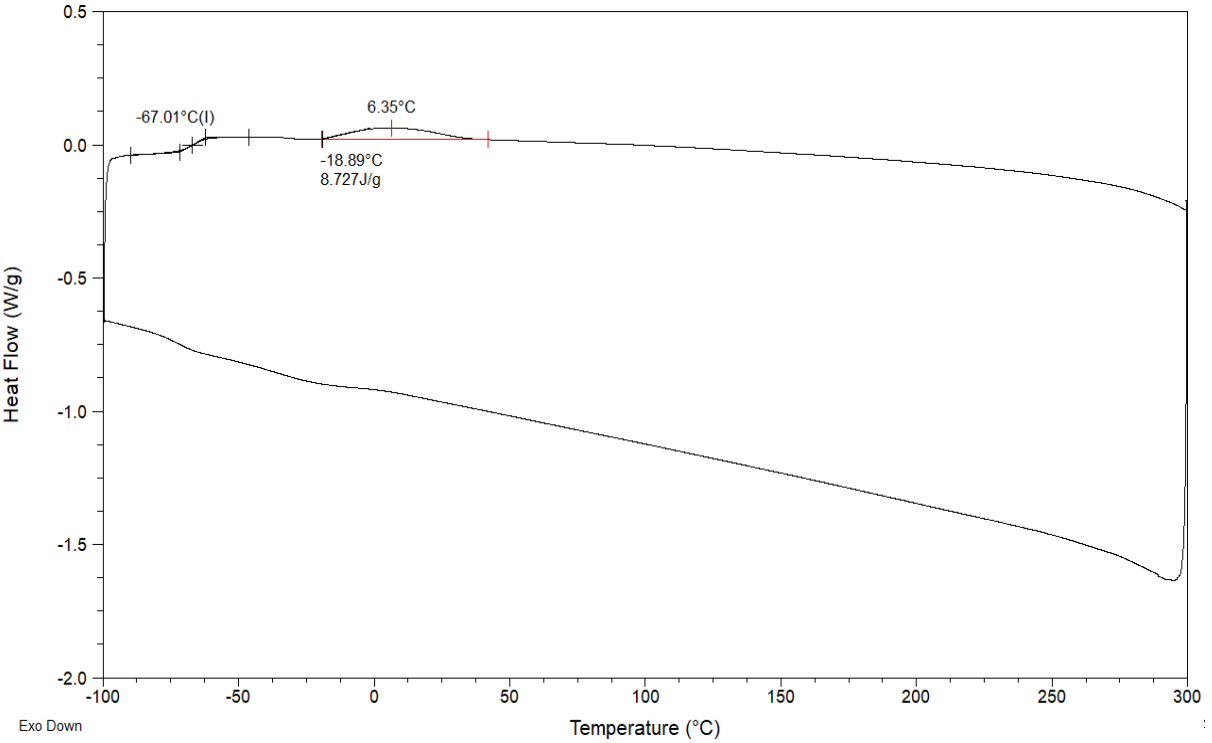


Figure S41. DSC thermograms of PFB copolymer from run 12 of **Table 5**.

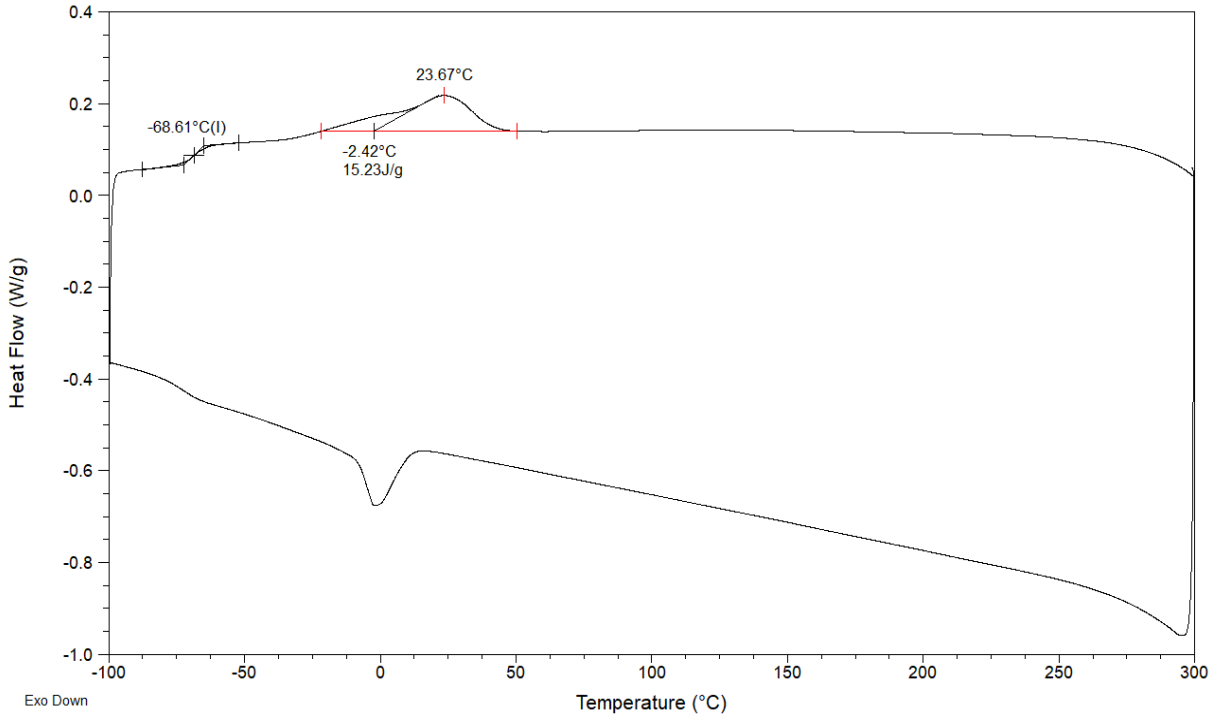


Figure S42. DSC thermograms of PFB copolymer from run 13 of **Table 5**.

4. GPC Analyses

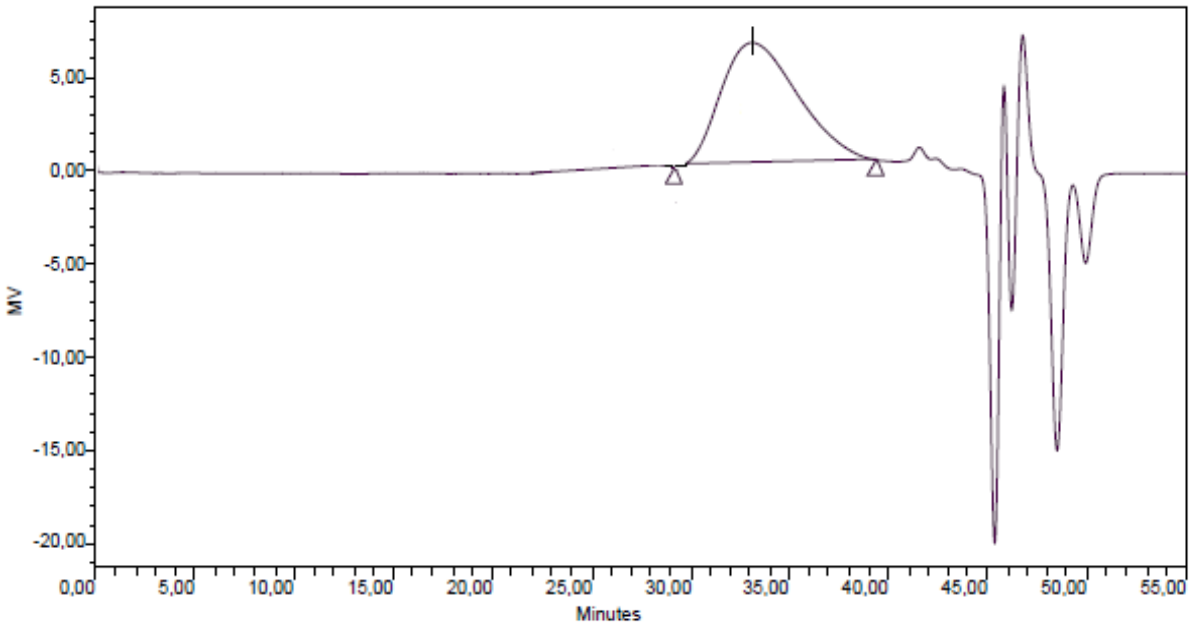


Figure S43. GPC curve of PMB copolymer from **run 5** of **Table 3**

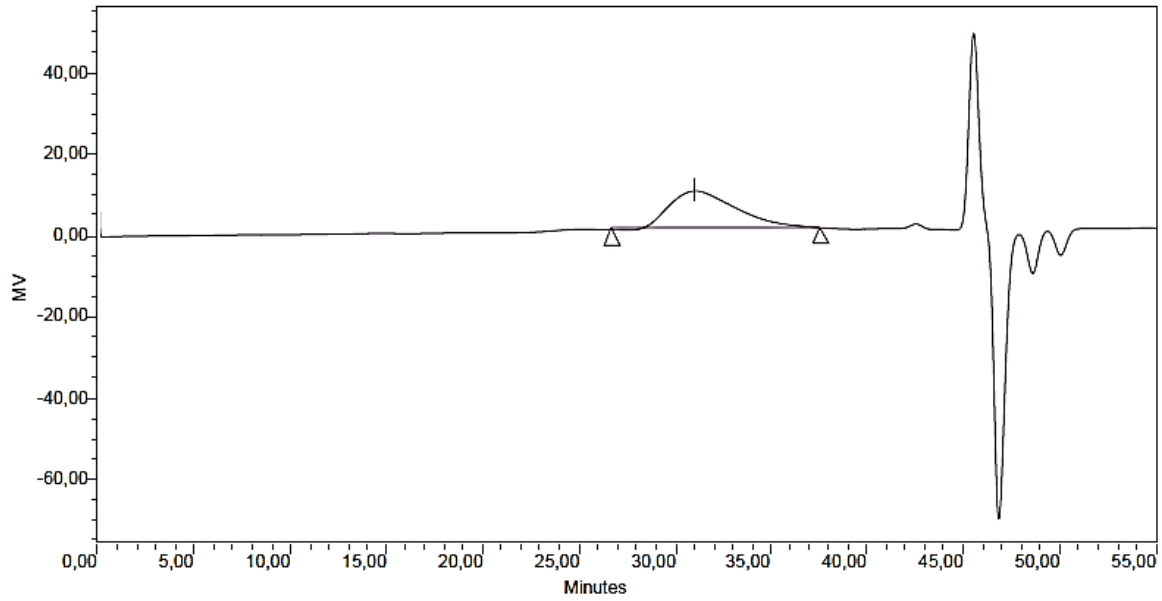


Figure S44. GPC curve of PMB copolymer from **run 6** of **Table 3**

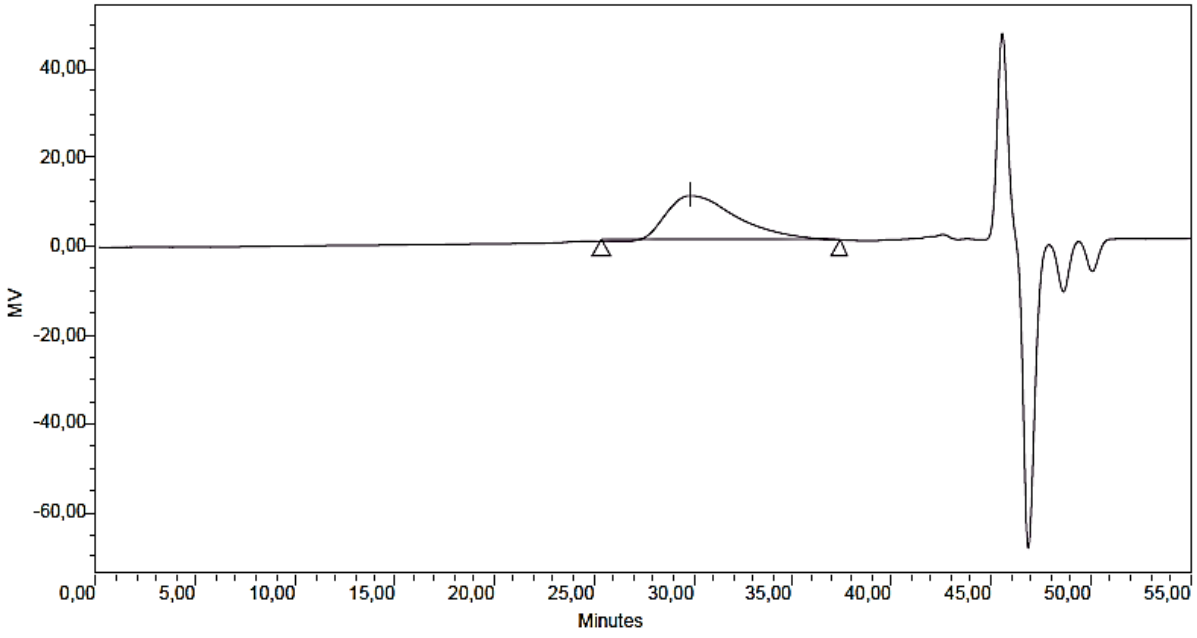


Figure S45. GPC curve of PMB copolymer from **run 7** of **Table 5**

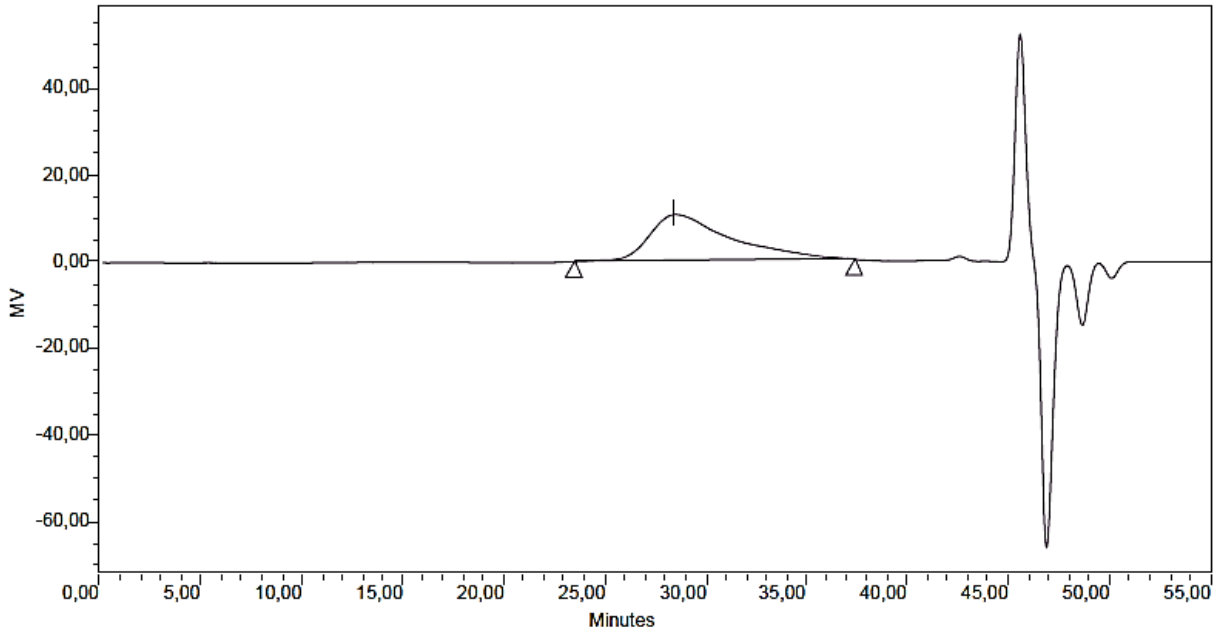


Figure S46. GPC curve of PMB copolymer from **run 8** of **Table 3**

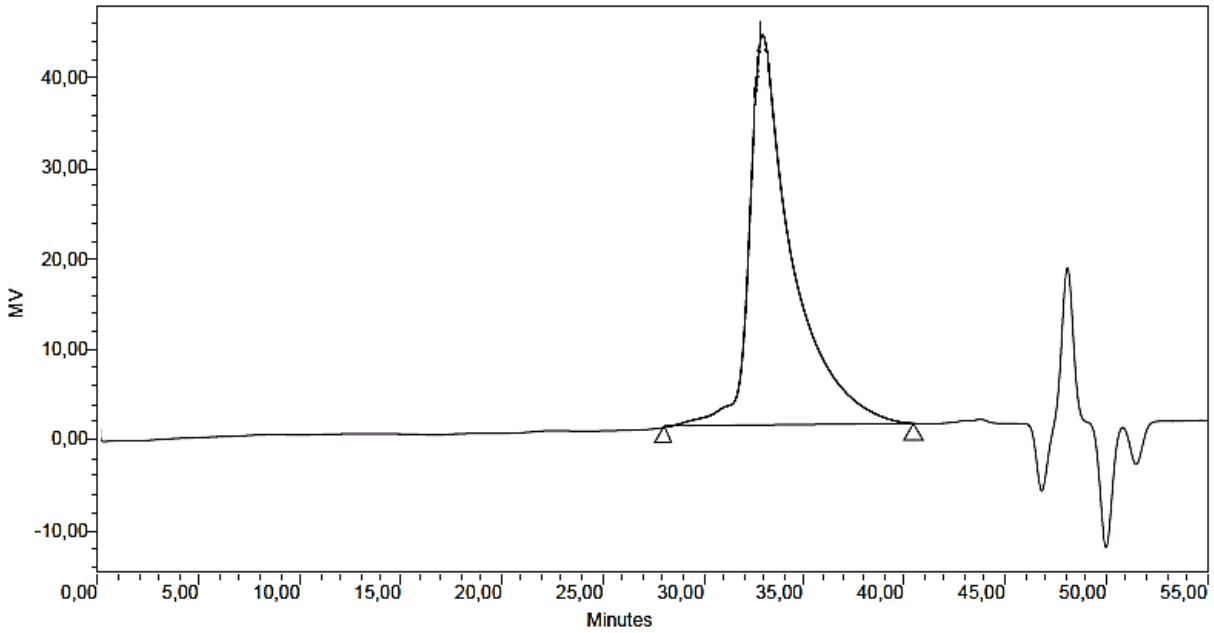


Figure S47. GPC curve of POB copolymer from **run 1** of **Table 1**

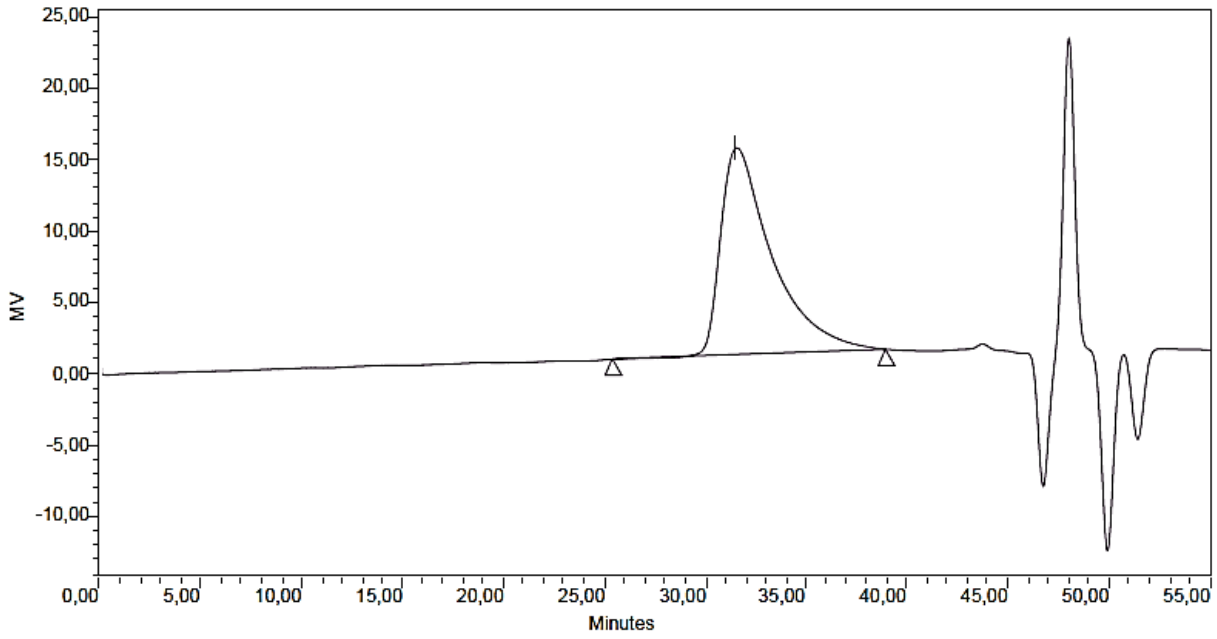


Figure S48. GPC curve of POB copolymer from **run 2** of **Table 1**

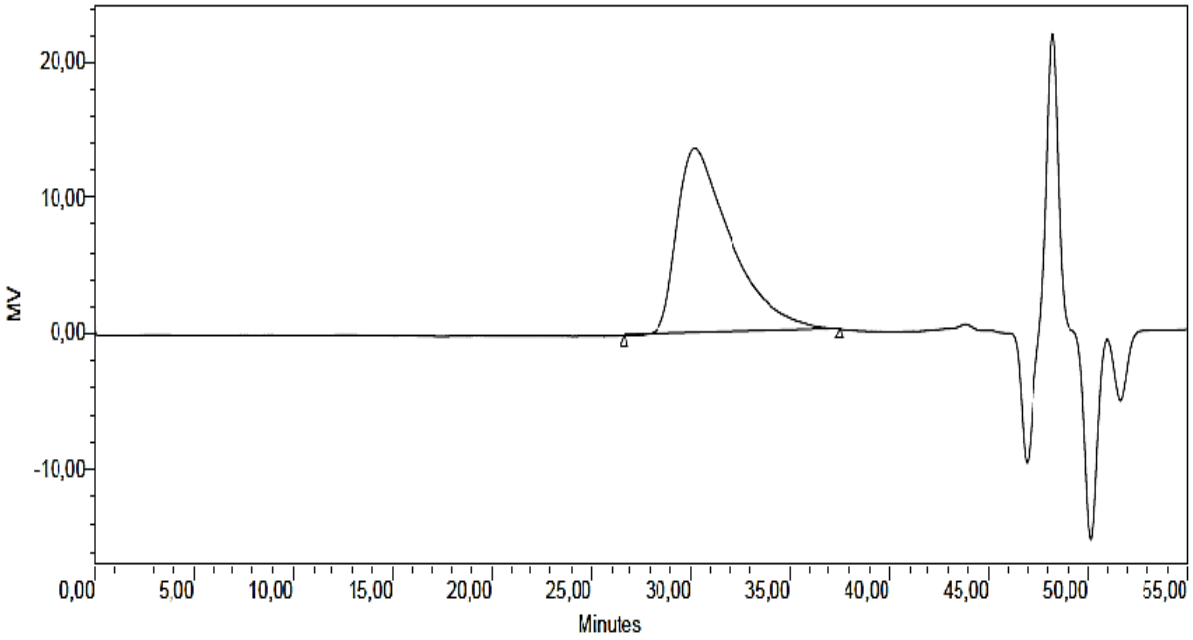


Figure S49. GPC curve of POB copolymer from **run 3** of **Table 1**

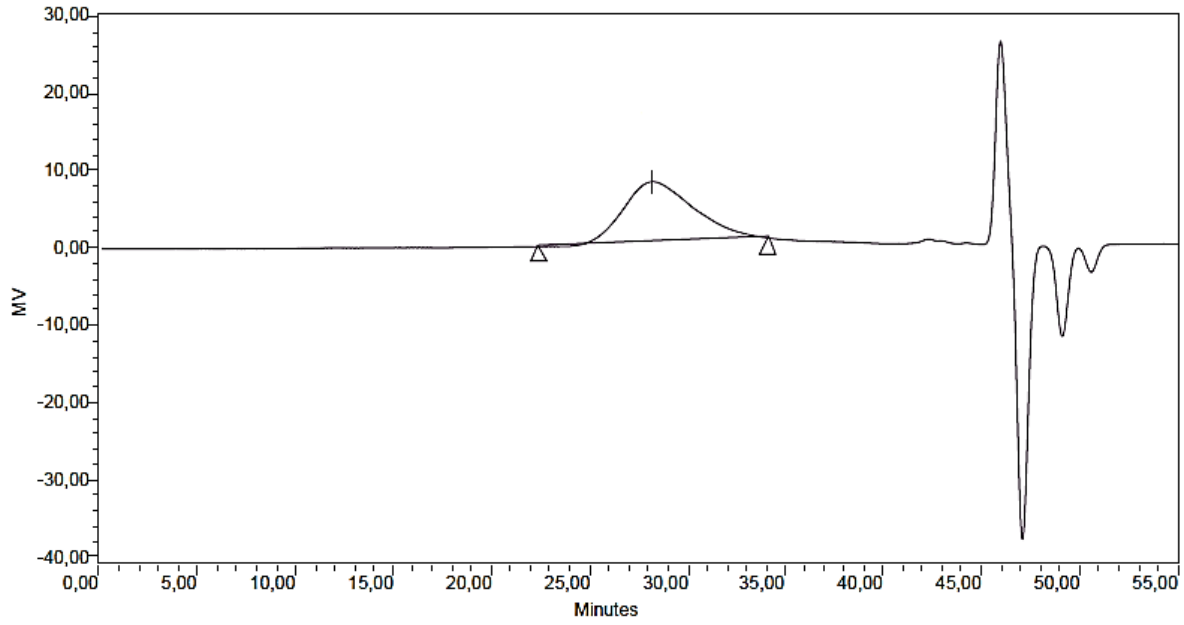


Figure S50. GPC curve of POB copolymer from **run 4** of **Table 1**

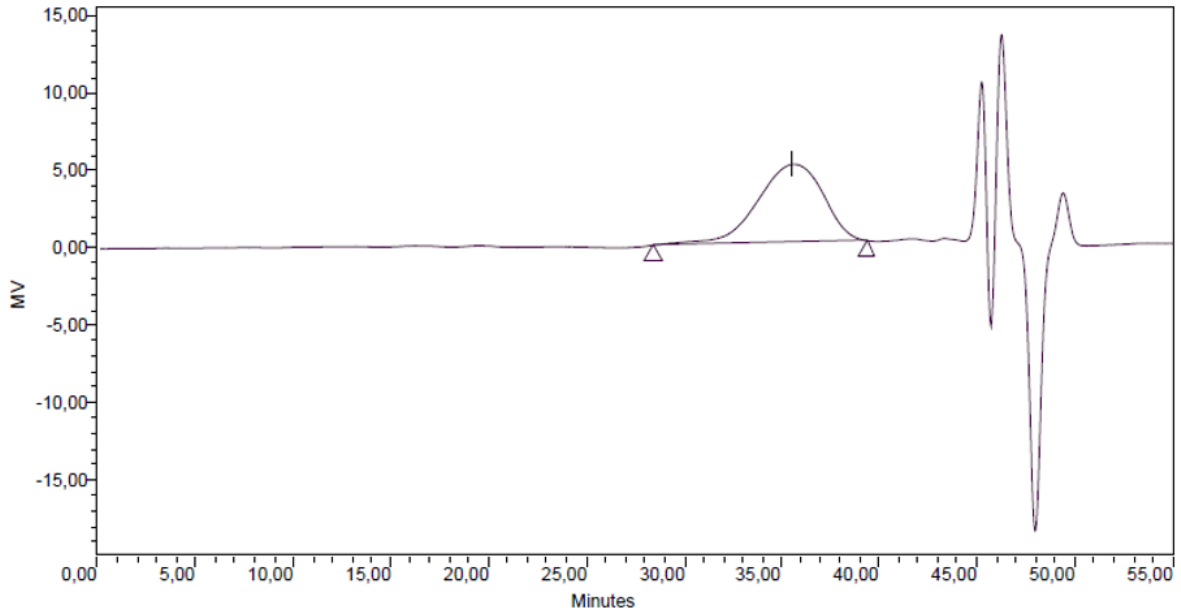


Figure S51. GPC curve of PF polymer from **run 9** of **Table 5**

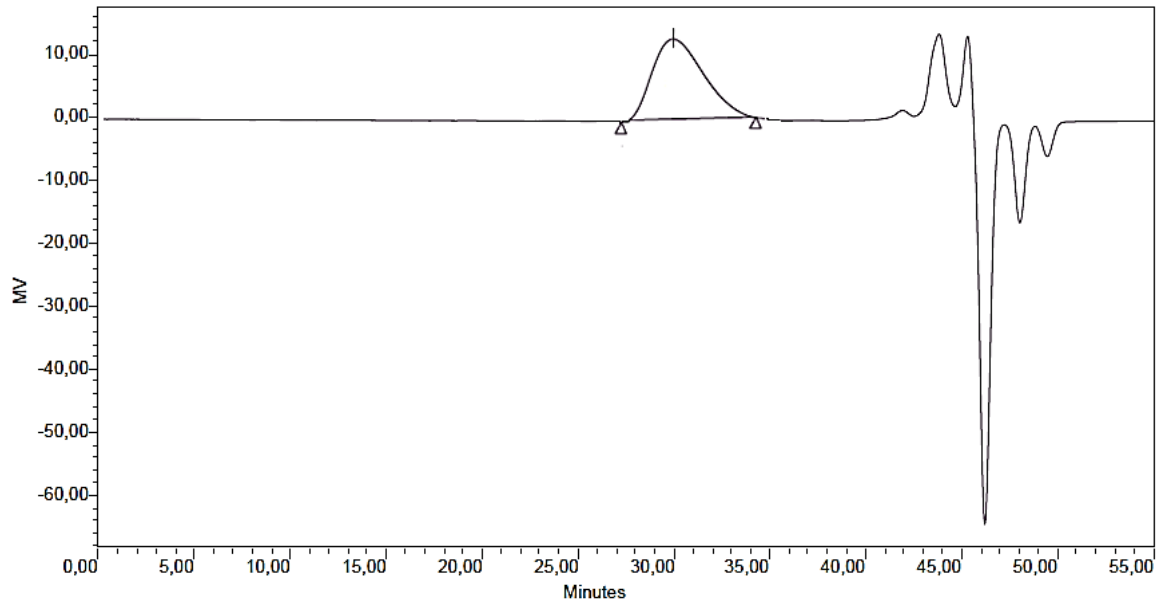


Figure S52. GPC curve of PFB copolymer from **run 10** of **Table 5**

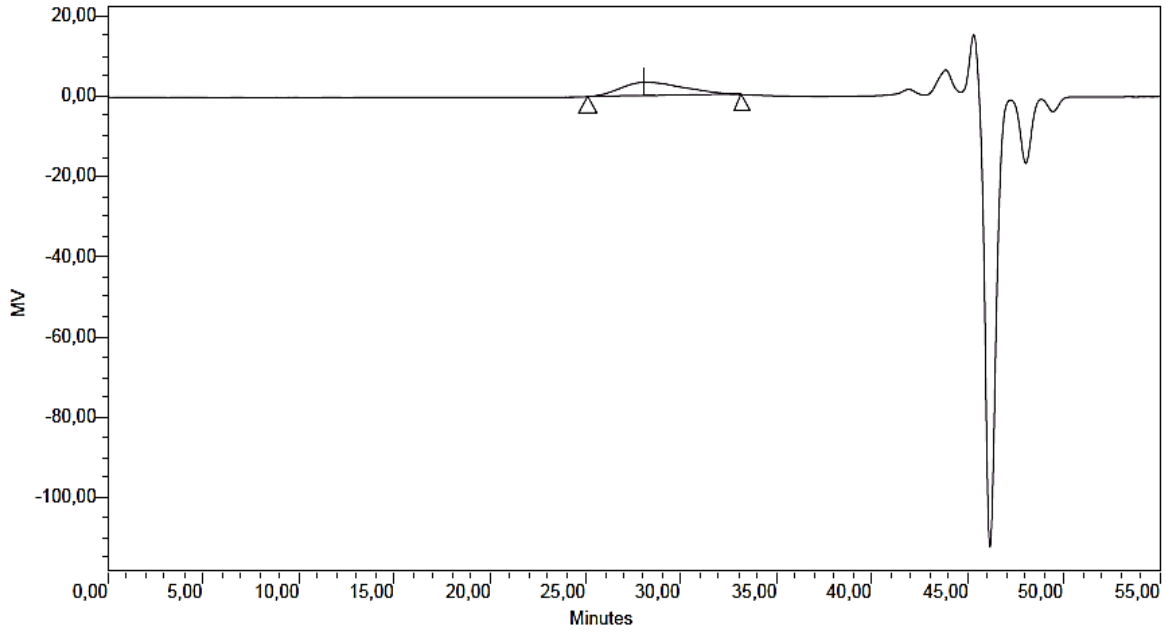


Figure S53. GPC curve of PFB copolymer from **run 11** of **Table 5**

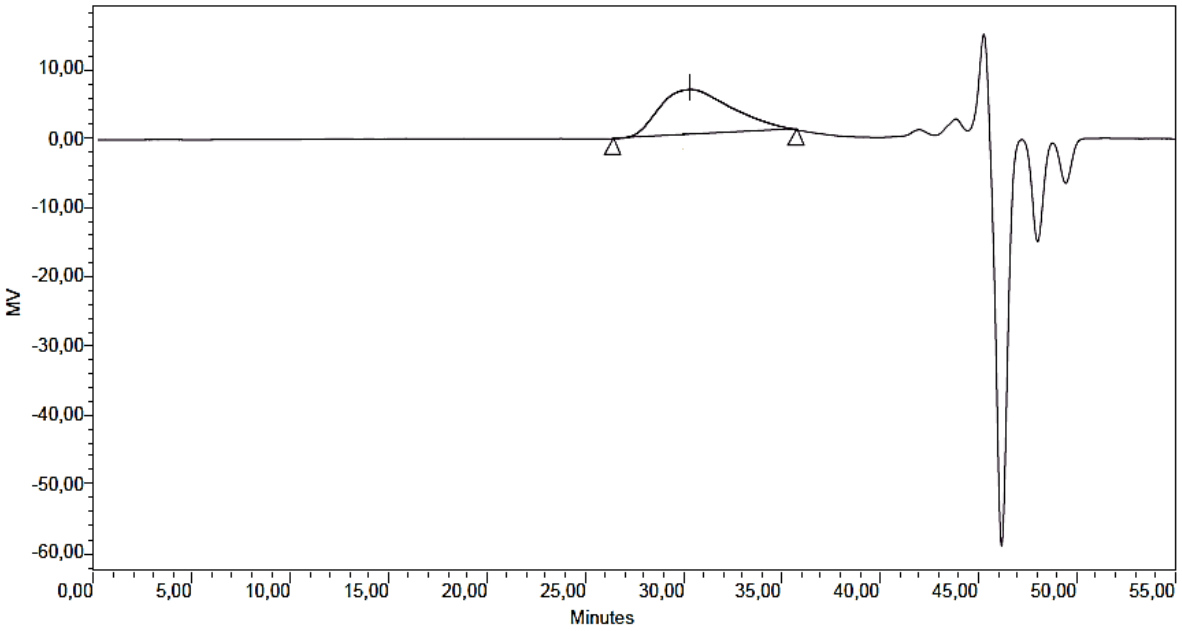


Figure S54. GPC curve of PFB copolymer from **run 12** of **Table 5**

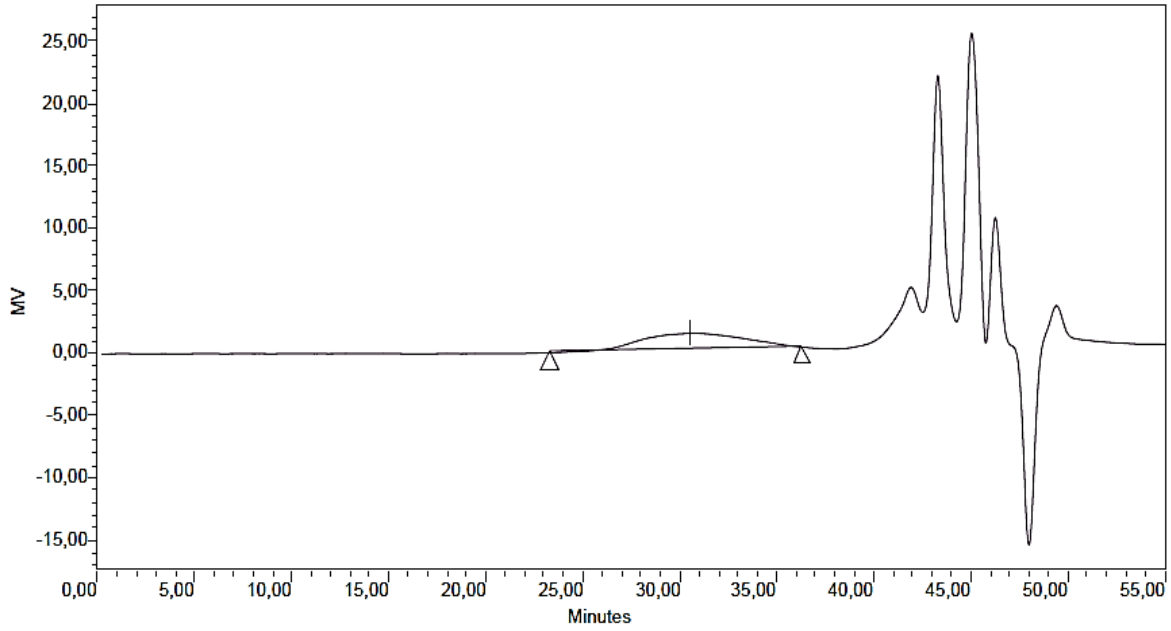


Figure S55. GPC curve of PFB copolymer from **run 13** of **Table 5**

5. Further investigations and graphs.

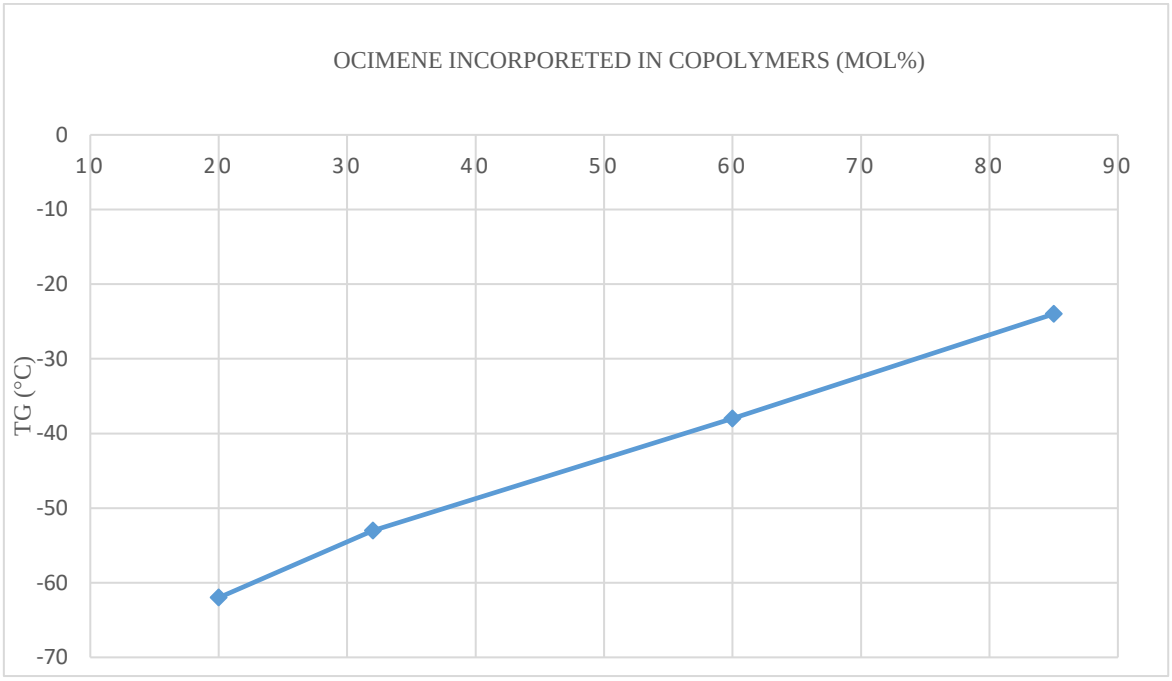
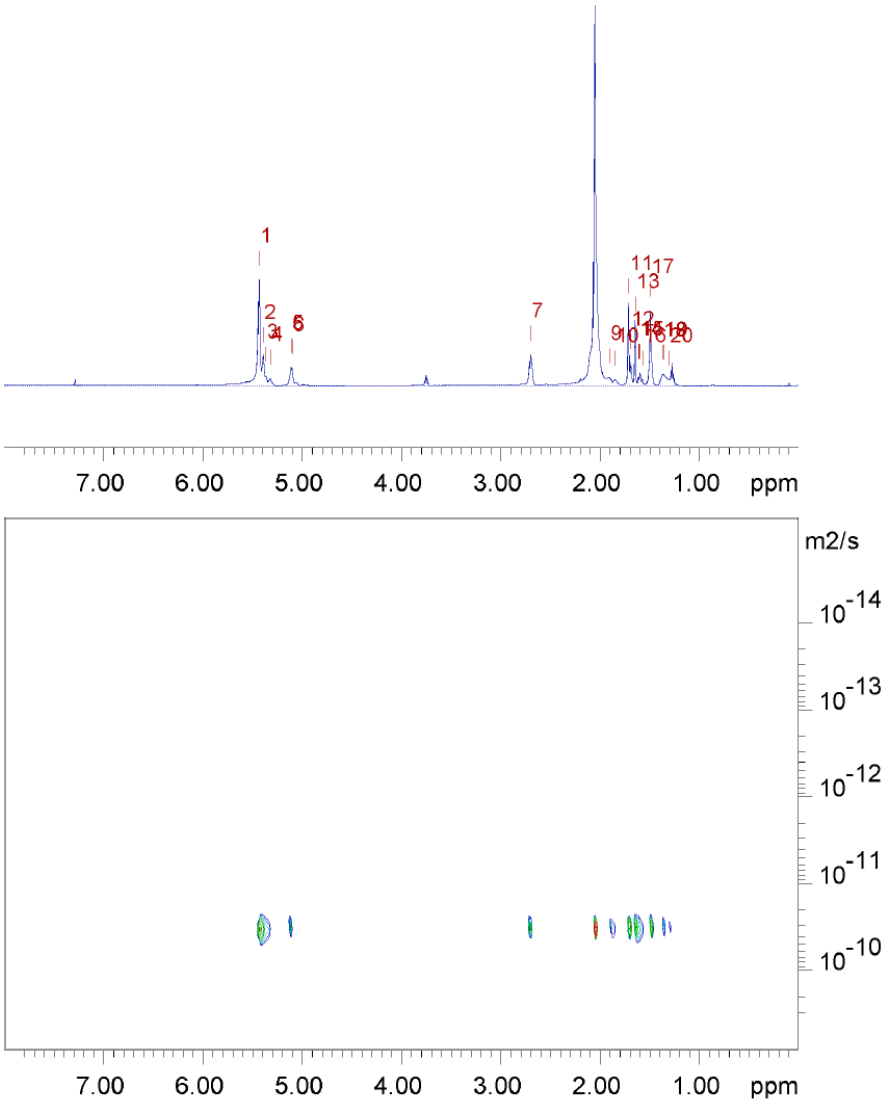
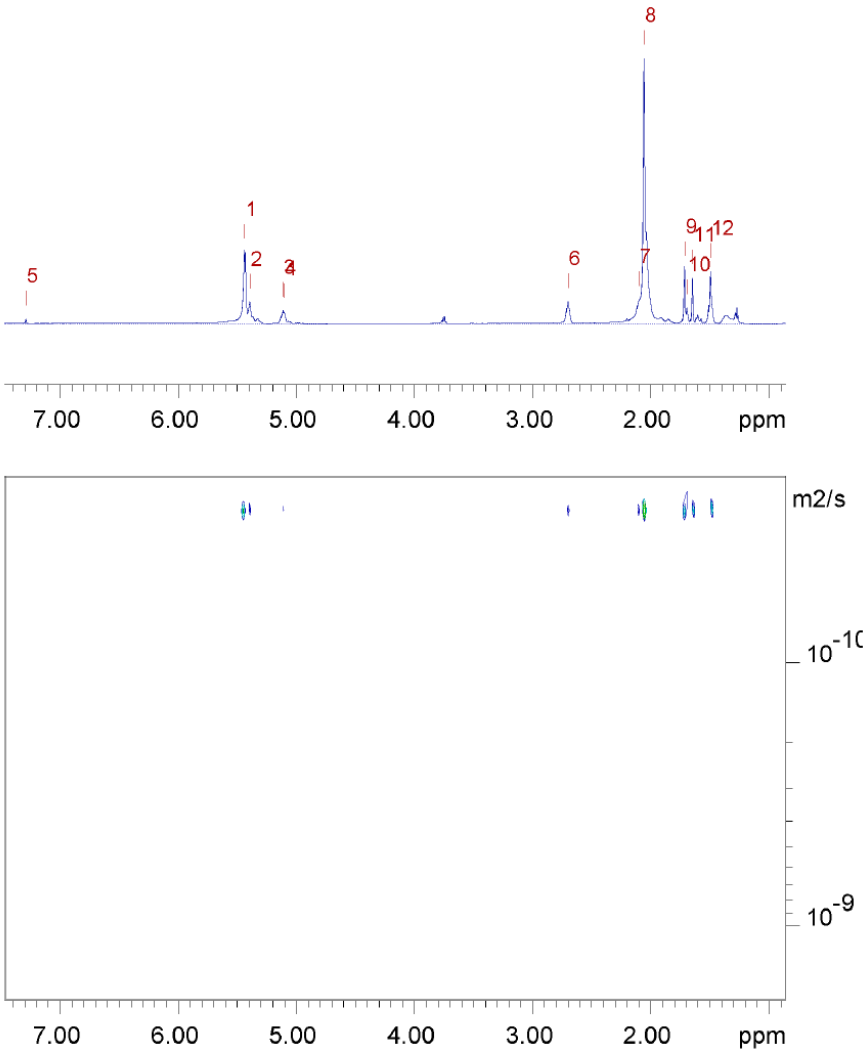


Figure S56. Variation of the glass transition temperature (Tg) of POB copolymers as a function of the ocimene content.



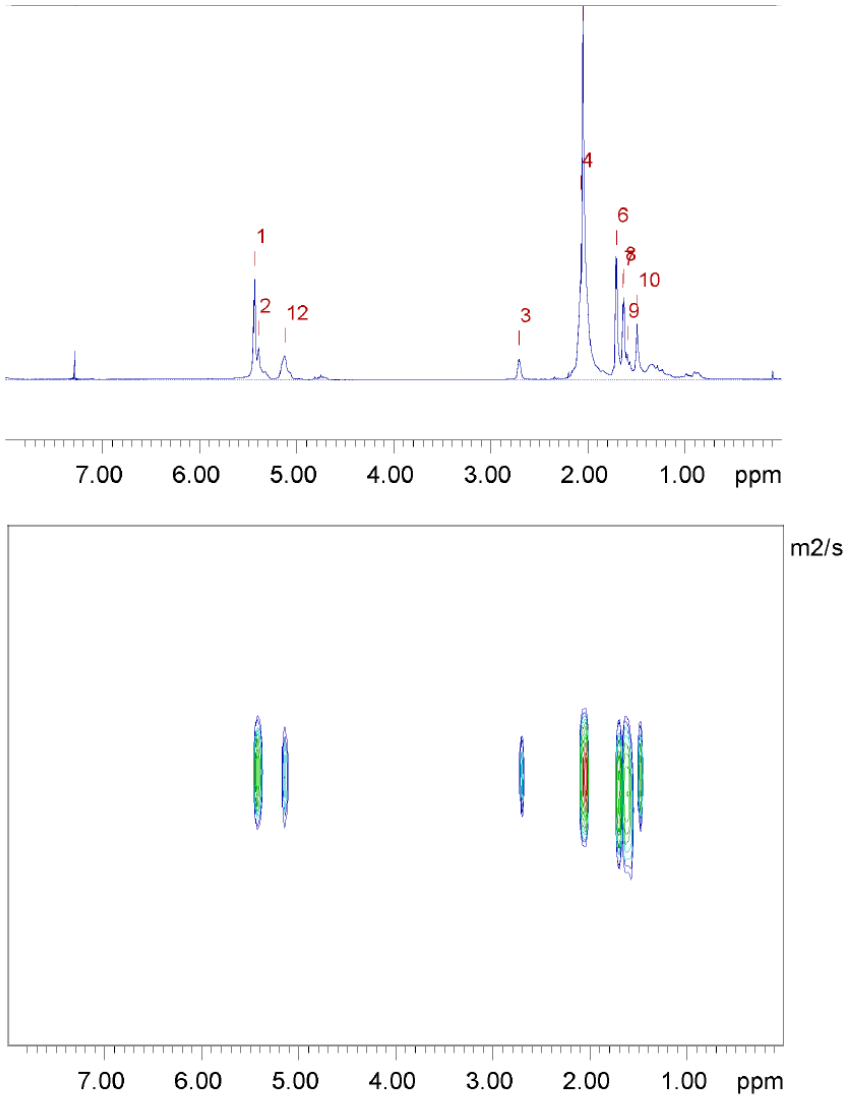
Peak name	F2 [ppm]	D [m2/s]	error
1	5.434	2.82e-11	1.736e-12
2	5.392	2.80e-11	1.738e-12
3	5.364	2.77e-11	1.808e-12
4	5.323	2.80e-11	1.770e-12
5	5.111	2.82e-11	1.784e-12
6	5.100	2.81e-11	1.713e-12
7	2.698	2.81e-11	1.711e-12
8	2.053	2.83e-11	1.754e-12
9	1.908	2.80e-11	2.362e-12
10	1.848	2.83e-11	2.042e-12
11	1.712	2.85e-11	1.794e-12
12	1.691	2.83e-11	2.013e-12
13	1.646	2.86e-11	1.795e-12
14	1.612	3.02e-11	3.826e-12
15	1.600	3.02e-11	3.031e-12
16	1.574	3.04e-11	3.498e-12
17	1.493	2.83e-11	1.756e-12
18	1.371	2.91e-11	2.693e-12
19	1.358	2.93e-11	2.708e-12
20	1.304	3.49e-11	6.889e-12

Figure S57. DOSY NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of POB copolymers from **run 4** of **Table 1**.



Peak name	F2 [ppm]	D [m2/s]	error
1	5.434	2.82e-11	1.732e-12
2	5.392	2.79e-11	1.725e-12
3	5.113	2.80e-11	1.773e-12
4	5.101	2.80e-11	1.696e-12
5	7.287	1.83e-09	2.876e-10
6	2.700	2.80e-11	1.678e-12
7	2.101	2.74e-11	2.036e-12
8	2.054	2.83e-11	1.748e-12
9	1.713	2.85e-11	1.761e-12
10	1.691	2.83e-11	2.028e-12
11	1.646	2.85e-11	1.760e-12
12	1.494	2.82e-11	1.708e-12

Figure S58. DOSY NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of PMB copolymers from **run 8** of **Table 3**.



Peak name	F2 [ppm]	D [m2/s]	error
1	5.434	3.81e-11	4.970e-12
2	5.392	3.90e-11	5.498e-12
3	2.709	4.04e-11	5.957e-12
4	2.074	4.13e-11	6.425e-12
5	2.052	3.97e-11	5.215e-12
6	1.707	4.38e-11	7.520e-12
7	1.637	4.51e-11	8.801e-12
8	1.625	4.42e-11	7.716e-12
9	1.595	4.80e-11	1.038e-11
10	1.493	4.06e-11	5.873e-12
11	0.095	5.38e-11	3.753e-12
12	5.124	4.21e-11	6.713e-12

Figure S59. DOSY NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of PFB copolymers from **run 11** of **Table 5**.