Supporting information

Yttrium-catalyzed Heteroatom-assisted Terpolymerization of *ortho*-Alkoxystyrene, Isoprene and Butadiene with High Regio- and Stereoselectivity

Legends

Table S1. Terpolymerization of *o*MOS, BD and IP with 250/500/250 in 1 min

Figure S1. ^{1}H NMR spectrum of poly(*o*MOS-IP-BD) (entry 2, Table 1) (400 MHz, $C_2D_2Cl_4$, 100 °C)

Figure S2. ^{1}H NMR spectrum of poly(*o*MOS-IP-BD) (entry 4, Table 1) (400 MHz, $C_2D_2Cl_4$, 100 °C)

Figure S3. ^{1}H NMR spectrum of poly(*o*MOS-IP-BD) (entry 5, Table 1) (400 MHz, $C_2D_2Cl_4$, 100 °C)

Figure S4. ^{1}H NMR spectrum of poly(*o*MOS-IP-BD) (entry 6, Table 1) (400 MHz, $C_2D_2Cl_4$, 100 °C)

Figure S5. ^{1}H NMR spectrum of poly(*o*EOS-IP-BD) (entry 8, Table 1) (400 MHz, $C_2D_2Cl_4$, 100 °C)

Figure S6. ^{1}H NMR spectrum of poly(*o*MOS-IP-BD) isolated in 1 min (400 MHz, $C_2D_2Cl_4$, 100 °C) (entry 1, Table S1)

Figure S7. ^{1}H NMR spectrum of poly(*o*MOS) (entry 2, Table 2) (400 MHz, $C_2D_2Cl_4$, 100 °C)

Figure S8. ^{1}H NMR spectrum of poly(*o*EOS) (entry 5, Table 2) (400 MHz, $C_2D_2Cl_4$, 100 °C)

Figure S9. ^{1}H NMR spectrum of poly(*o*EOS-IP-BD) for uniaxial extension experiments (500 MHz, $CDCl_3$, 25 °C)

Figure S10. ^{1}H NMR spectrum of PBD (500 MHz, $CDCl_3$, 25 °C)

Figure S11. ^{1}H NMR spectrum of PIP (500 MHz, $CDCl_3$, 25 °C)

Figure S12. ^{1}H NMR spectrum of poly(BD-IP) (500 MHz, $CDCl_3$, 25 °C)

Figure S13. ^{13}C NMR spectrum of poly(*o*MOS-IP-BD) (entry 2, Table 1) (100 MHz, $C_2D_2Cl_4$, 100 °C)

Figure S14. ^{13}C NMR spectrum of poly(*o*MOS-IP-BD) (entry 4, Table 1) (100 MHz, $C_2D_2Cl_4$, 100 °C)

Figure S15. ^{13}C NMR spectrum of poly(*o*MOS-IP-BD) (entry 5, Table 1) (100 MHz, $C_2D_2Cl_4$, 100 °C)

Figure S16. ^{13}C NMR spectrum of poly(*o*MOS-IP-BD) (entry 6, Table 1) (100 MHz, $C_2D_2Cl_4$, 100 °C)

Figure S17. ^{13}C NMR spectrum of poly(*o*EOS-IP-BD) (entry 8, Table 1) (100 MHz, $C_2D_2Cl_4$, 100 °C)

Figure S18. ^{13}C NMR spectrum of poly(*o*MOS-IP-BD) isolated in 1 min (100 MHz, $C_2D_2Cl_4$, 100 °C) (entry 1, Table S1)

Figure S19. ^{13}C NMR spectrum of polystyrene (entry 1, Table 2) (100 MHz, $C_6D_4Cl_2$, 100 °C)

Figure S20. ^{13}C NMR spectrum of poly(*o*MOS) (entry 2, Table 2) (100 MHz, $C_2D_2Cl_4$, 100 °C)

Figure S21. ^{13}C NMR spectrum of poly(*o*EOS) (entry 5, Table 2) (100 MHz, $C_2D_2Cl_4$, 100 °C)

Figure S22. ^{13}C NMR spectrum of poly(*o*EOS-IP-BD) for uniaxial extension experiments (500 MHz, $CDCl_3$, 25 °C)

Figure S23. ^{13}C NMR spectrum of PBD (500 MHz, $CDCl_3$, 25 °C)

Figure S24. ^{13}C NMR spectrum of PIP (500 MHz, $CDCl_3$, 25 °C)

Figure S25. DEPT 135 spectrum of PIP (500 MHz, $CDCl_3$, 25 °C)

Figure S26. HSQC spectrum of PIP (500 MHz, $CDCl_3$, 25 °C)

Figure S27. GPC curve of poly(*o*MOS-IP-BD) (entry 2, Table 1)

Figure S28. GPC curve of poly(*o*MOS-IP-BD) (entry 3, Table 1)

Figure S29. GPC curve of poly(*o*MOS-IP-BD) (entry 4, Table 1)

Figure S30. GPC curve of poly(*o*MOS-IP-BD) (entry 5, Table 1)

3, Table 1)

Calculation for activation energies of homopolymerizing *o*MOS and *o*EOS

Table S1. Terpolymerization of *o*MOS, BD and IP with 250/500/250 in 1 min

Entry	Cat	*o*AOS	*o*AOS:IP:BD	Time/ min	Conv. (%)	*o*AOS[b] (mol%)	IP[b] (mol%)	BD[b] (mol%)	M_n[c] $\times 10^{-4}$	PDI[c]	T_g[d] (°C)
1	**2**	*o*MOS	250:500:250	1	16.0	76.5	0	23.5	3.62	1.1	66.6/-

[a] Conditions: Cat 5 μmol, [*o*AOSt+IP+BD]/[Cat]/[Ph_3C][$B(C_6F_5)_4$] =1000:1:1 (mol/mol/mol), T = 13 °C, Toluene 1 mL. [b] Measured by ^1H NMR and ^{13}C NMR in $C_2D_2Cl_4$ at 100 °C. [c] Determined by GPC in THF at 40 °C against polystyrene standard. [d] Determined by DSC.

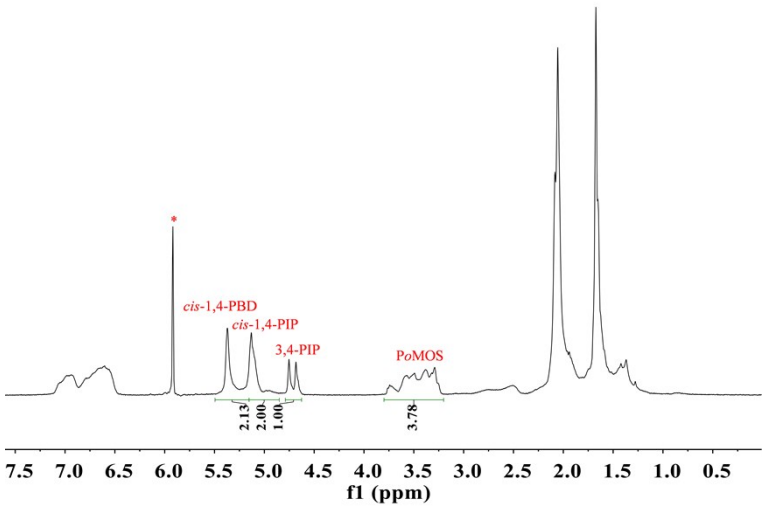

Figure S1. ^{1}H NMR spectrum of poly(*o*MOS-IP-BD) (entry 2, Table 1) (400 MHz, $C_2D_2Cl_4$, 100 °C)

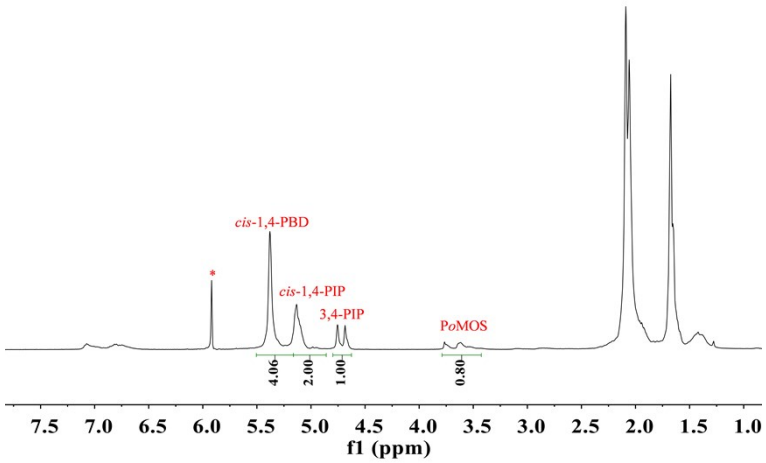

Figure S2. ^{1}H NMR spectrum of poly(*o*MOS-IP-BD) (entry 4, Table 1) (400 MHz, $C_2D_2Cl_4$, 100 °C)

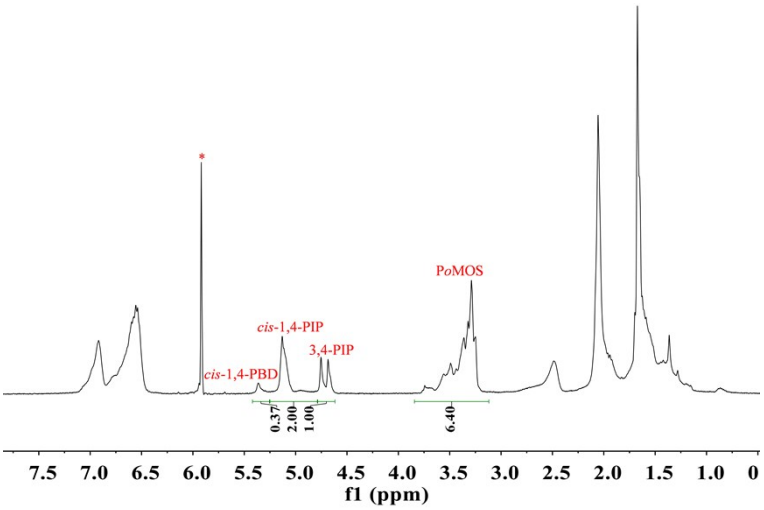

Figure S3. ^{1}H NMR spectrum of poly(*o*MOS-IP-BD) (entry 5, Table 1) (400 MHz, $C_2D_2Cl_4$, 100 °C)

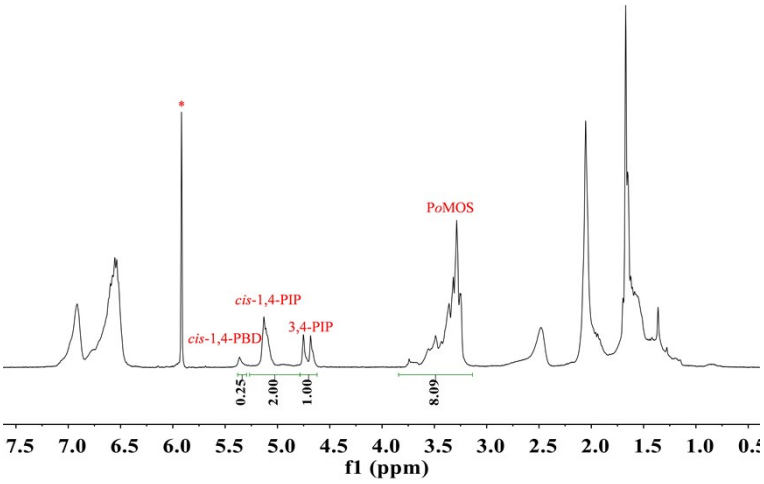

Figure S4. ^{1}H NMR spectrum of poly(*o*MOS-IP-BD) (entry 6, Table 1) (400 MHz, $C_2D_2Cl_4$, 100 °C)

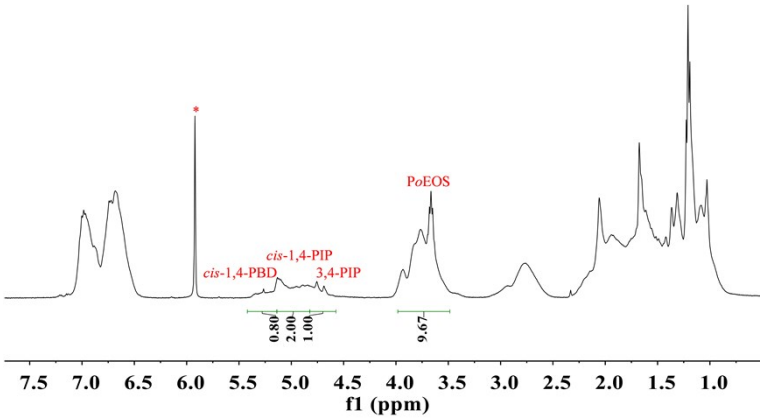

Figure S5. ^{1}H NMR spectrum of poly(*o*EOS-IP-BD) (entry 8, Table 1) (400 MHz, $C_2D_2Cl_4$, 100 ^{o}C)

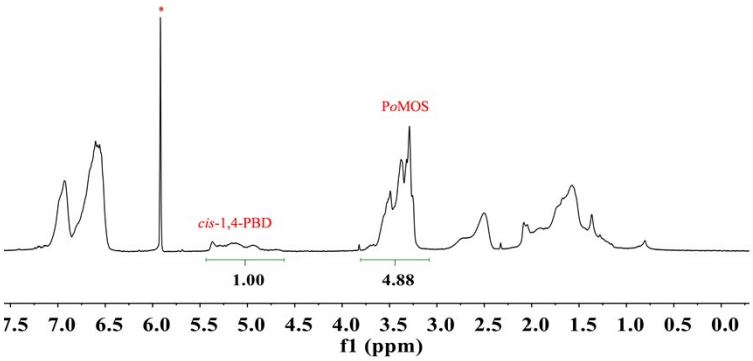

Figure S6. ^{1}H NMR spectrum of poly(*o*MOS-IP-BD) isolated in 1 min (400 MHz, $C_2D_2Cl_4$, 100 ^{o}C) (entry 1, Table S1)

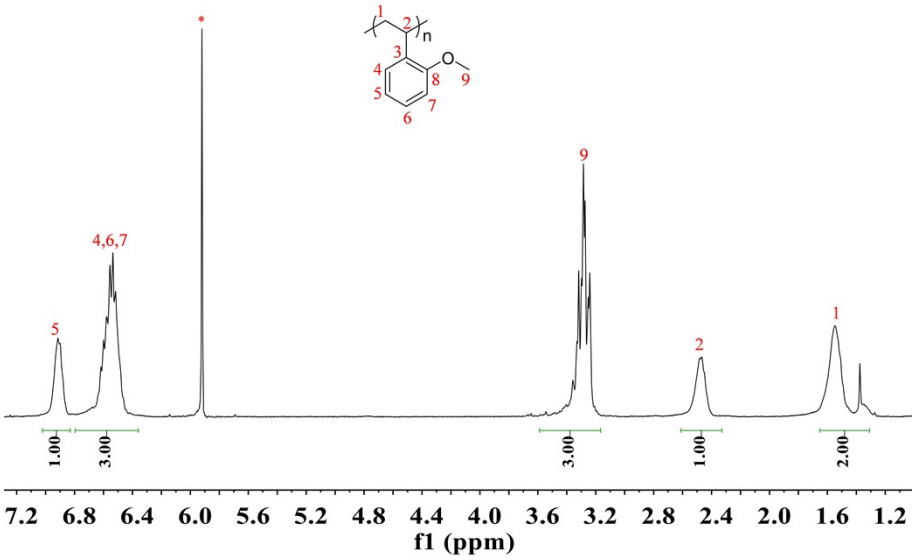

Figure S7. ^{1}H NMR spectrum of poly(*o*MOS) (entry 2, Table 2) (400 MHz, $C_2D_2Cl_4$, 100 °C)

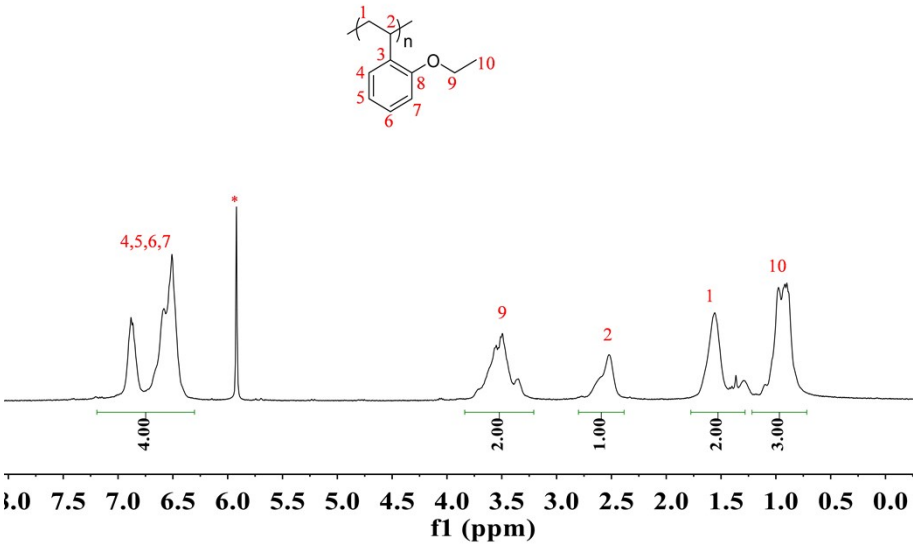

Figure S8. ^{1}H NMR spectrum of poly(*o*EOS) (entry 5, Table 2) (400 MHz, $C_2D_2Cl_4$, 100 °C)

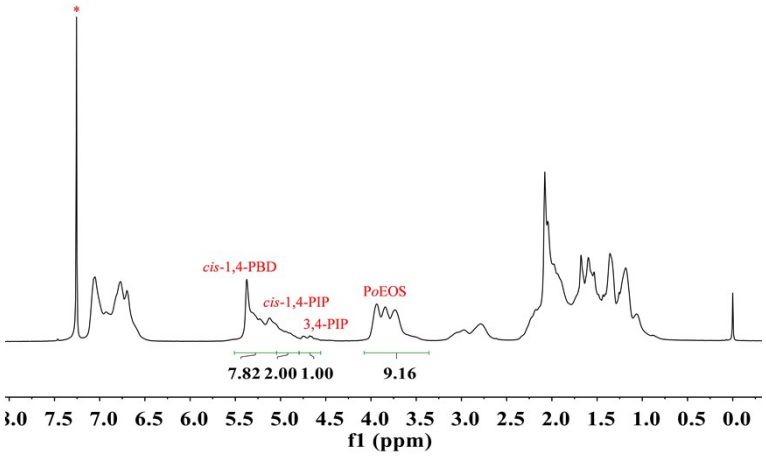

Figure S9. ^{1}H NMR spectrum of poly(*o*EOS-IP-BD) for uniaxial extension experiments (500 MHz, $CDCl_3$, 25 °C)

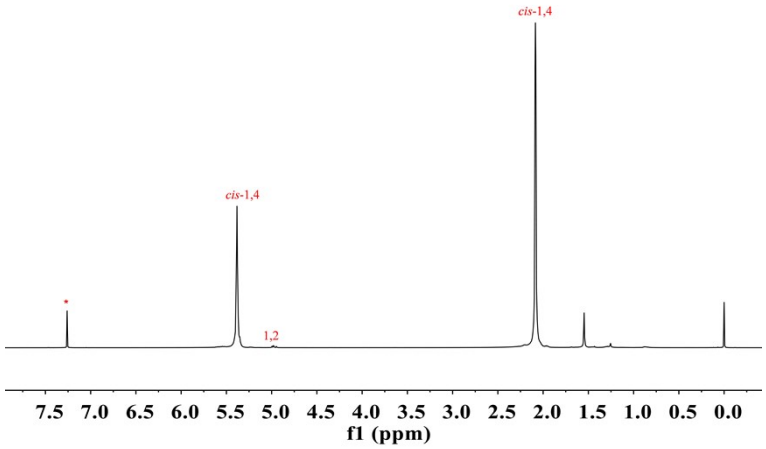

Figure S10. ^{1}H NMR spectrum of PBD (500 MHz, $CDCl_3$, 25 °C)

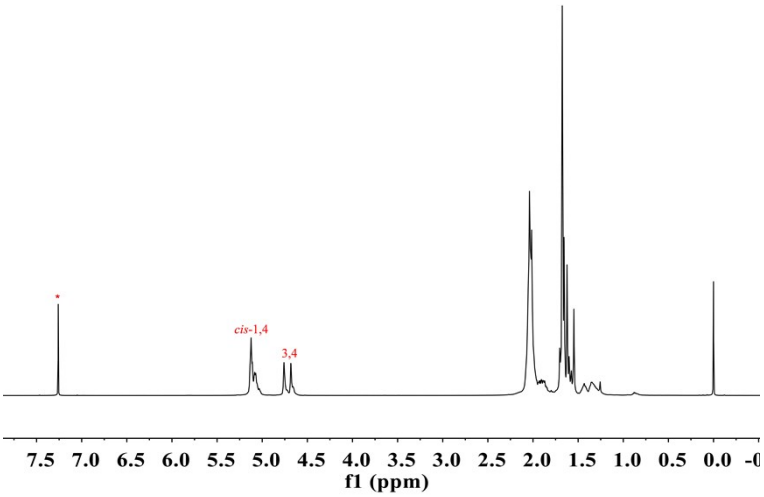

Figure S11. ^{1}H NMR spectrum of PIP (500 MHz, $CDCl_3$, 25 ^{o}C)

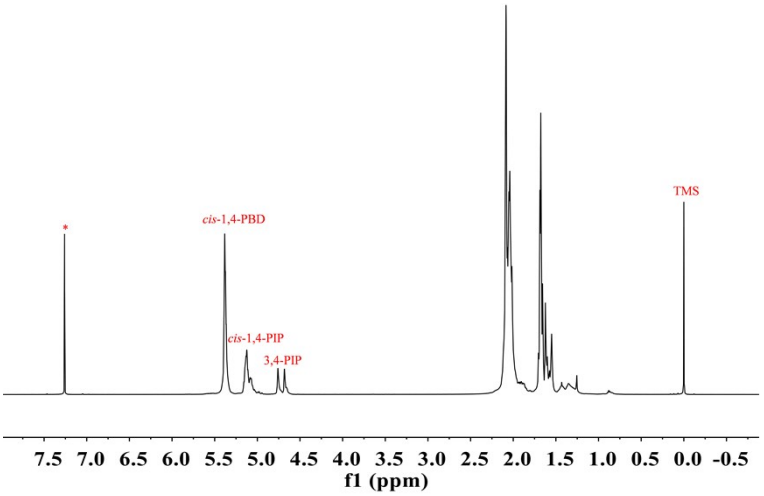

Figure S12. ^{1}H NMR spectrum of poly(BD-IP) (500 MHz, $CDCl_3$, 25 ^{o}C)

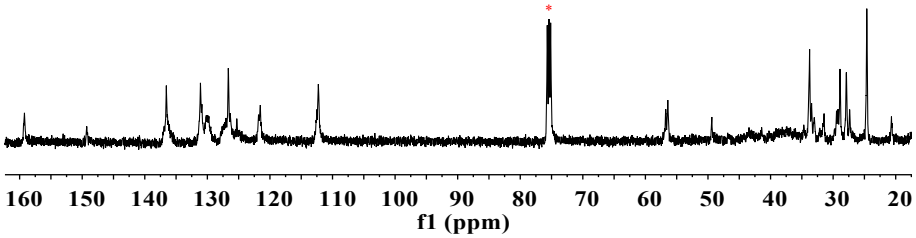

Figure S13. ^{13}C NMR spectrum of poly(*o*MOS-IP-BD) (entry 2, Table 1) (100 MHz, $C_2D_2Cl_4$, 100 °C)

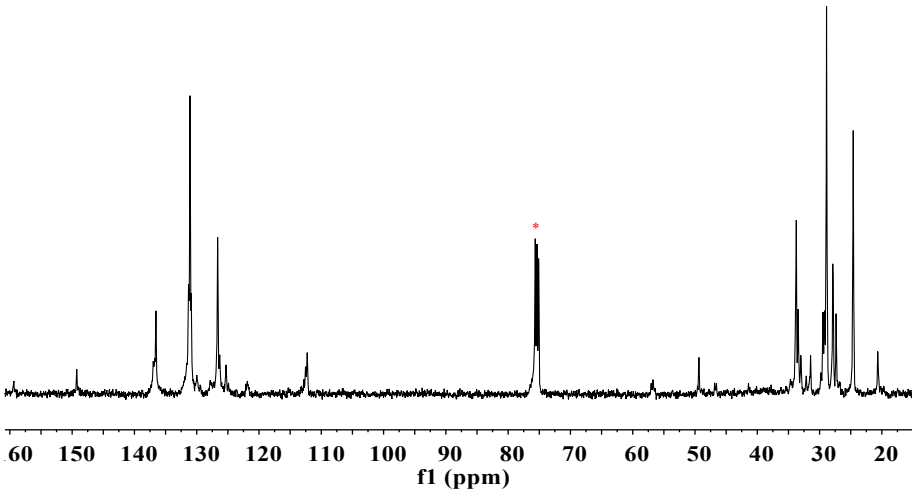

Figure S14. ^{13}C NMR spectrum of poly(*o*MOS-IP-BD) (entry 4, Table 1) (100 MHz, $C_2D_2Cl_4$, 100 °C)

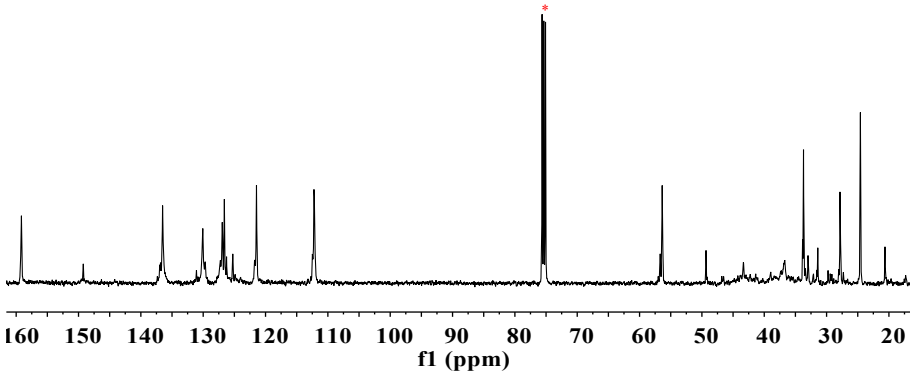

Figure S15. ^{13}C NMR spectrum of poly(*o*MOS-IP-BD) (entry 5, Table 1) (100 MHz, $C_2D_2Cl_4$, 100 °C)

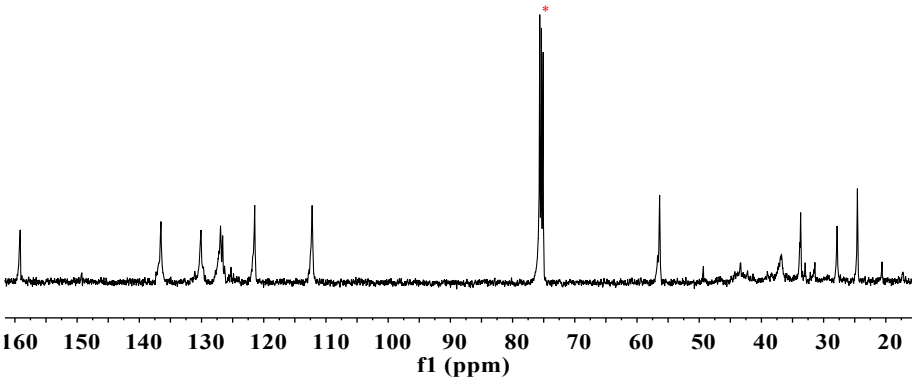

Figure S16. ^{13}C NMR spectrum of poly(*o*MOS-IP-BD) (entry 6, Table 1) (100 MHz, $C_2D_2Cl_4$, 100 °C)

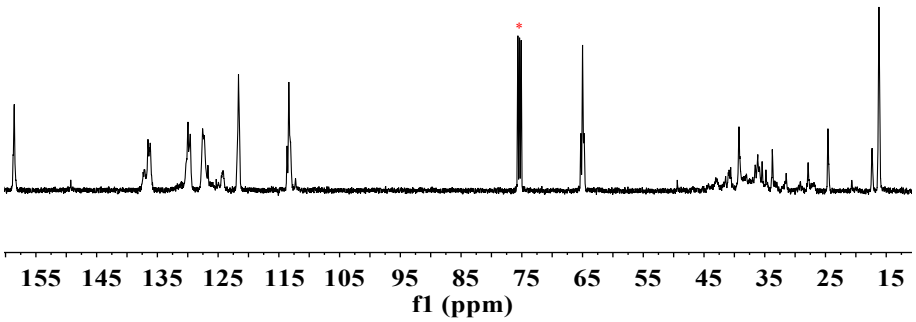

Figure S17. ^{13}C NMR spectrum of poly(*o*EOS-IP-BD) (entry 8, Table 1) (100 MHz, $C_2D_2Cl_4$, 100 °C)

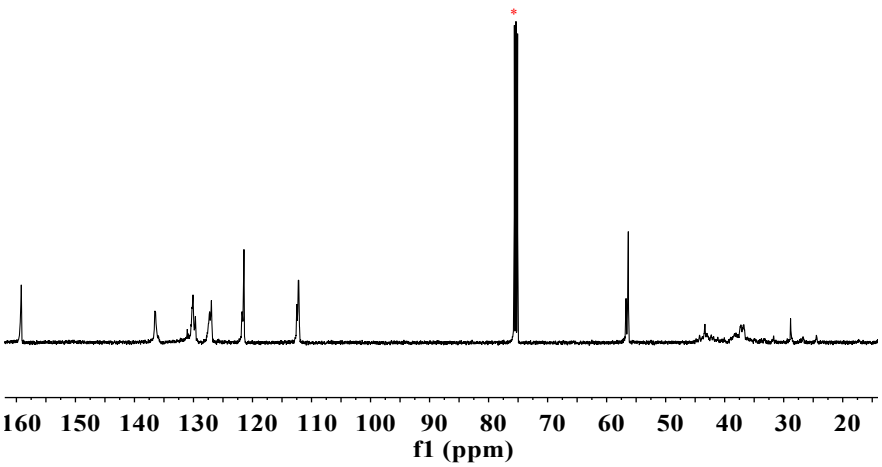

Figure S18. ^{13}C NMR spectrum of poly(*o*MOS-IP-BD) isolated in 1 min (100 MHz, $C_2D_2Cl_4$, 100 °C)

(entry 1, Table S1)

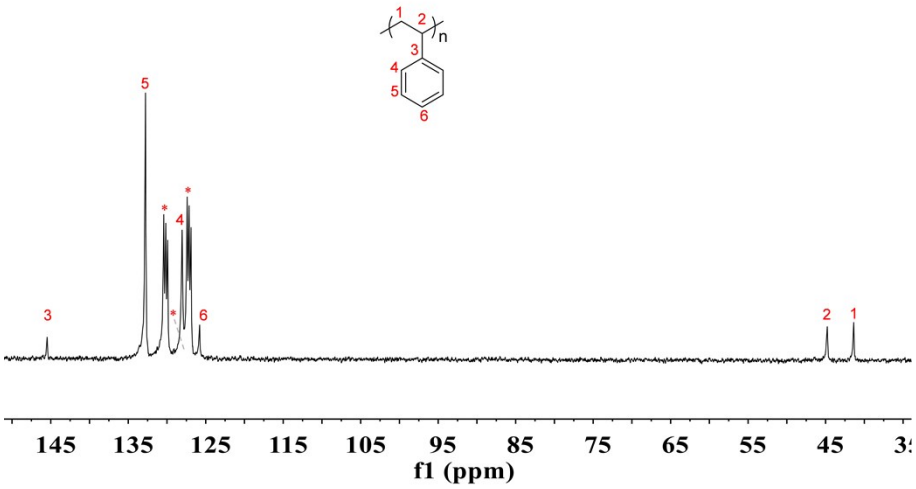

Figure S19. ^{13}C NMR spectrum of polystyrene (entry 1, Table 2) (100 MHz, $C_6D_4Cl_2$, 100 °C)

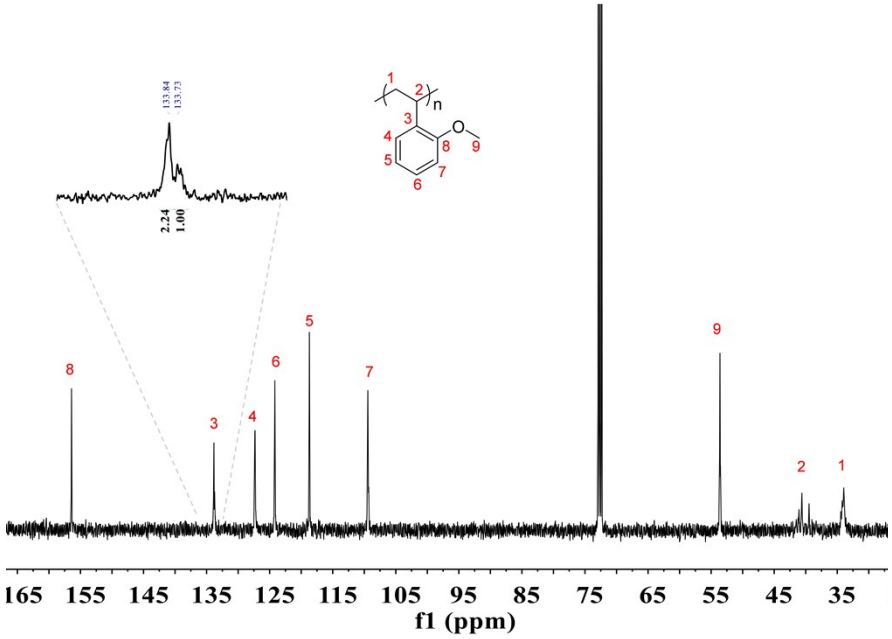

Figure S20. ^{13}C NMR spectrum of poly(*o*MOS) (entry 2, Table 2) (100 MHz, $C_2D_2Cl_4$, 100 °C)

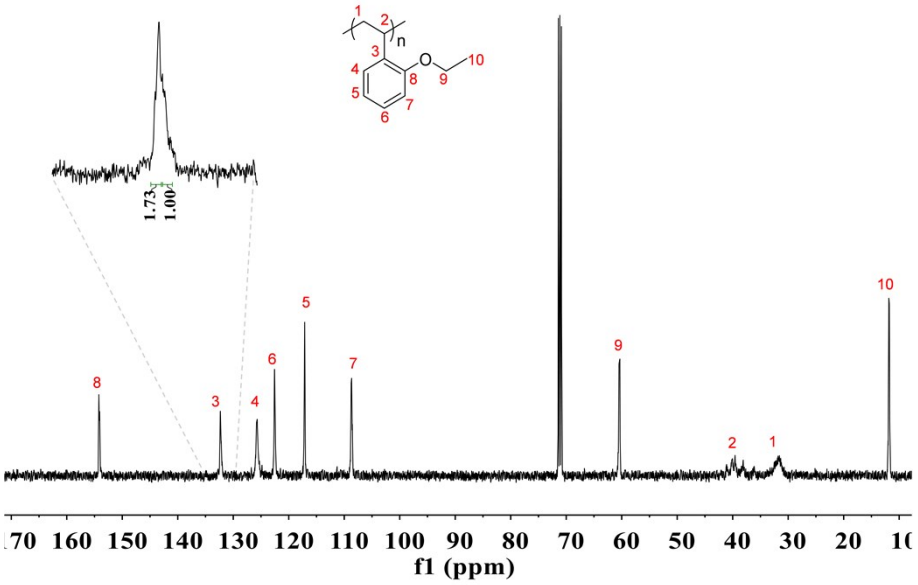

Figure S21. ^{13}C NMR spectrum of poly(*o*EOS) (entry 5, Table 2) (100 MHz, $C_2D_2Cl_4$, 100 °C)

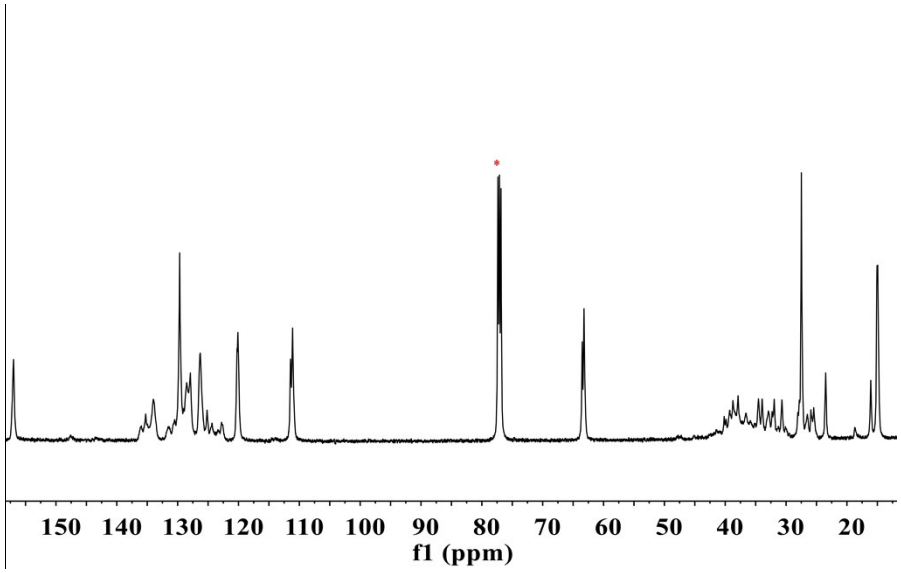

Figure S22. ^{13}C NMR spectrum of poly(*o*EOS-IP-BD) for uniaxial extension experiments (500 MHz, $CDCl_3$, 25 °C)

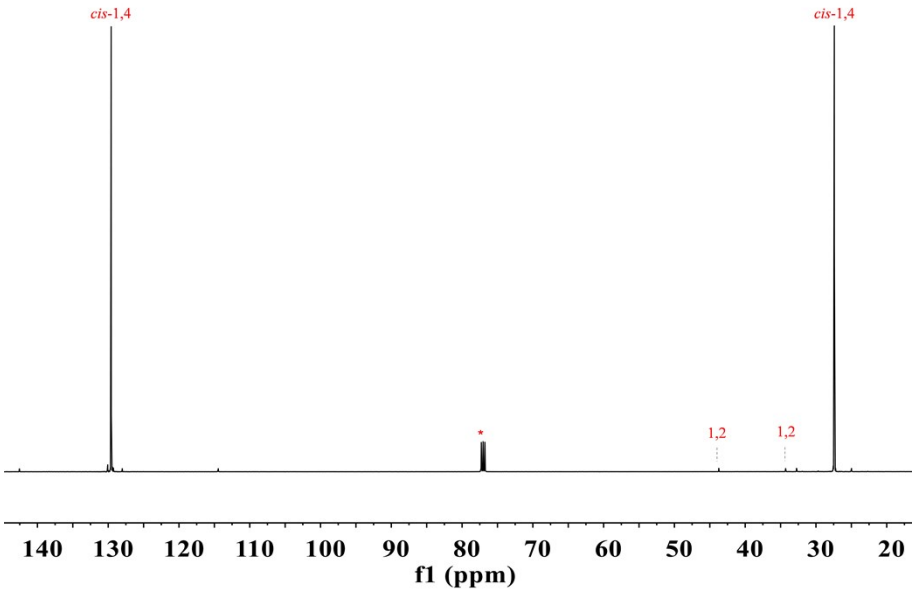

Figure S23. ^{13}C NMR spectrum of PBD (500 MHz, $CDCl_3$, 25 °C)

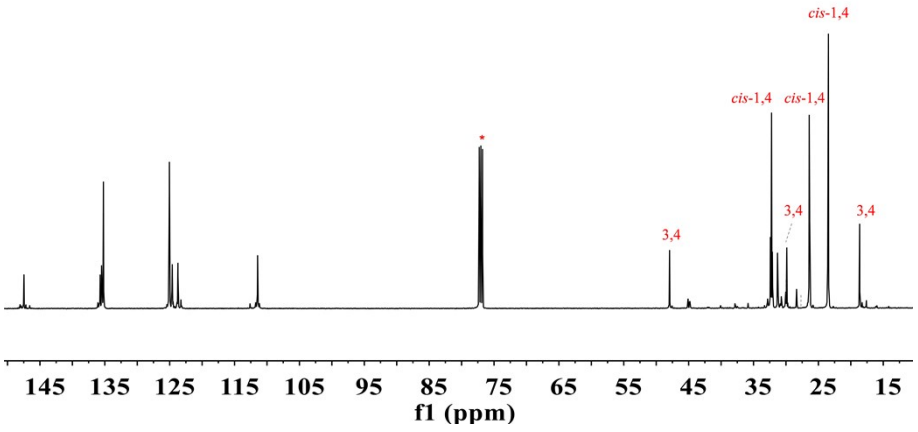

Figure S24. ^{13}C NMR spectrum of PIP (500 MHz, $CDCl_3$, 25 °C)

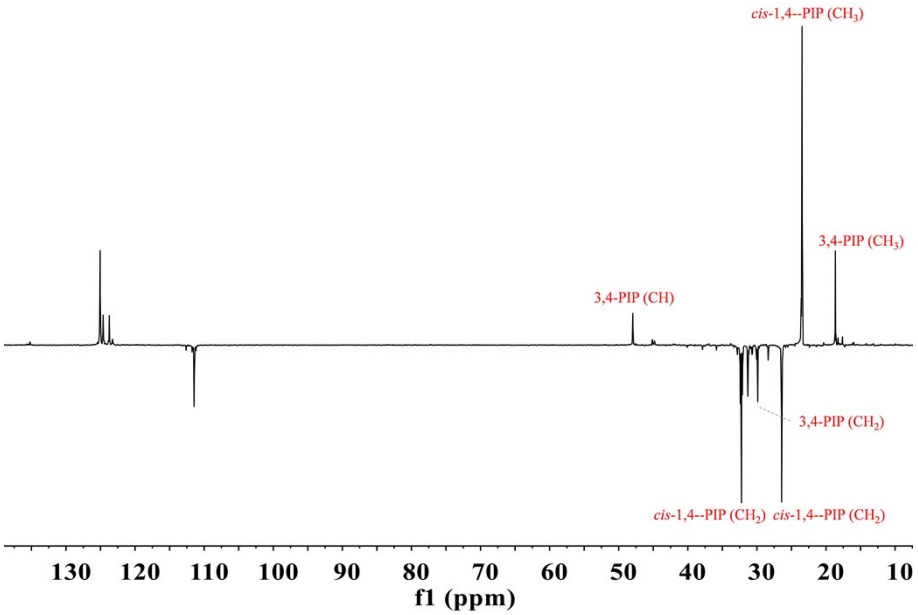

Figure S25. DEPT 135 spectrum of PIP (500 MHz, $CDCl_3$, 25 °C)

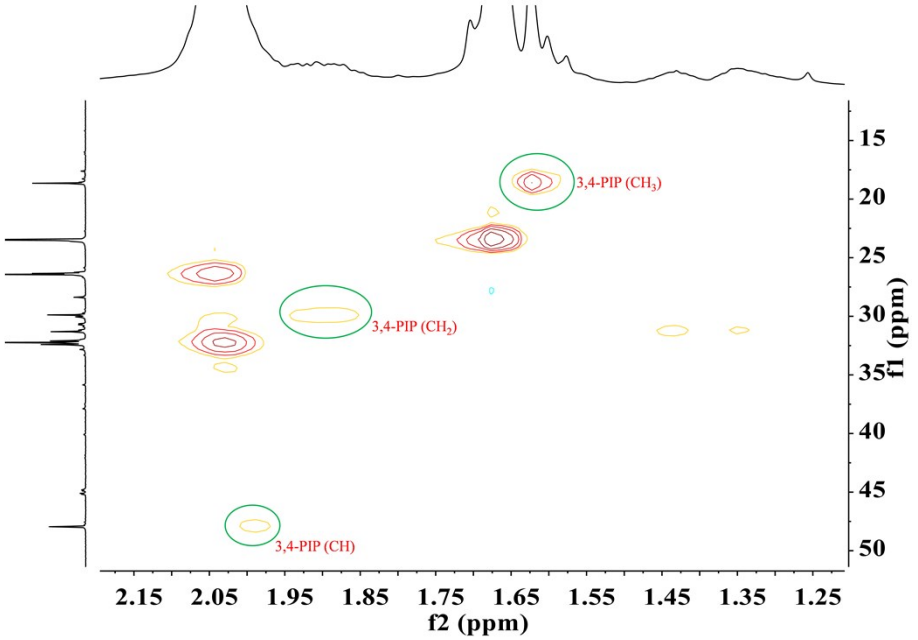

Figure S26. HSQC spectrum of PIP (500 MHz, $CDCl_3$, 25 °C)

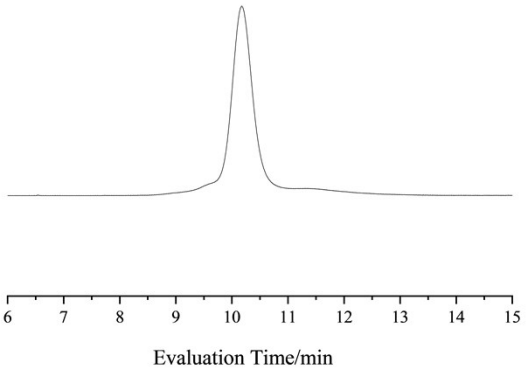

Figure S27. GPC curve of poly(*o*MOS-IP-BD) (entry 2, Table 1)

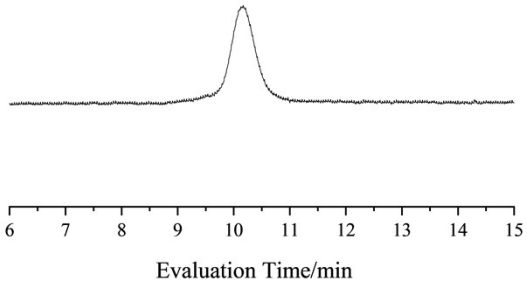

Figure S28. GPC curve of poly(*o*MOS-IP-BD) (entry 3, Table 1)

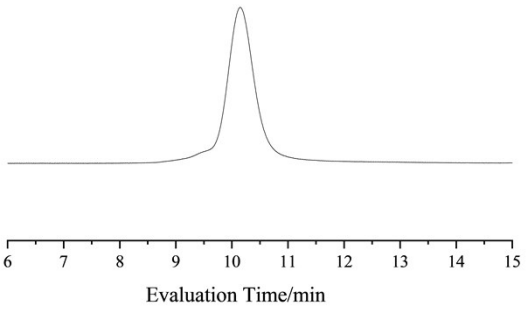

Figure S29. GPC curve of poly(*o*MOS-IP-BD) (entry 4, Table 1)

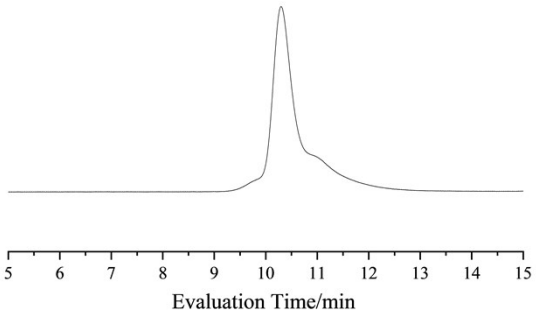

Figure S30. GPC curve of poly(*o*MOS-IP-BD) (entry 5, Table 1)

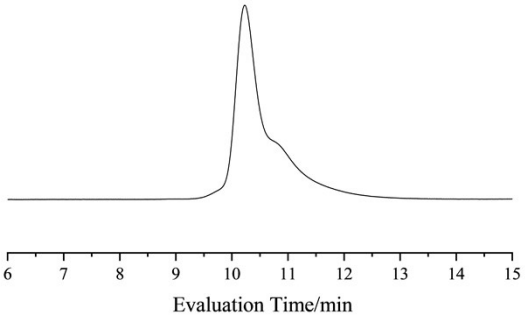

Figure S31. GPC curve of poly(*o*MOS-IP-BD) (entry 6, Table 1)

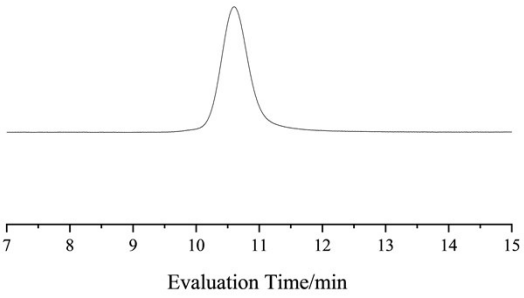

Figure S32. GPC curve of poly(*o*EOS-IP-BD) (entry 7, Table 1)

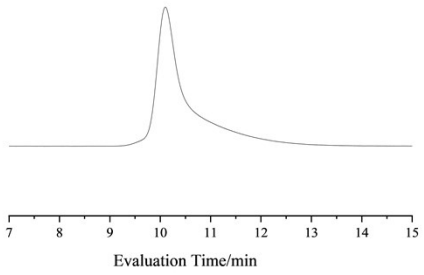

Figure S33. GPC curve of poly(*o*EOS-IP-BD) (entry 8, Table 1)

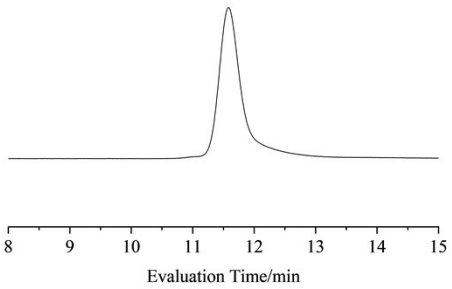

Figure S34. GPC curve of poly(*o*MOS-IP-BD) isolated in 1 min (entry 1, Table S1)

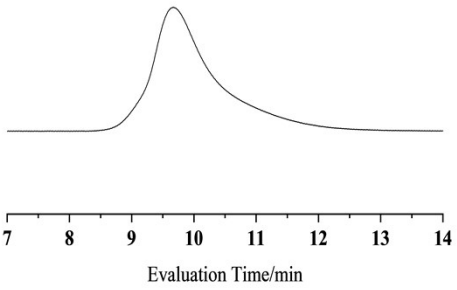

Figure S35. GPC curve of poly(*o*EOS-IP-BD) for uniaxial extension experiments

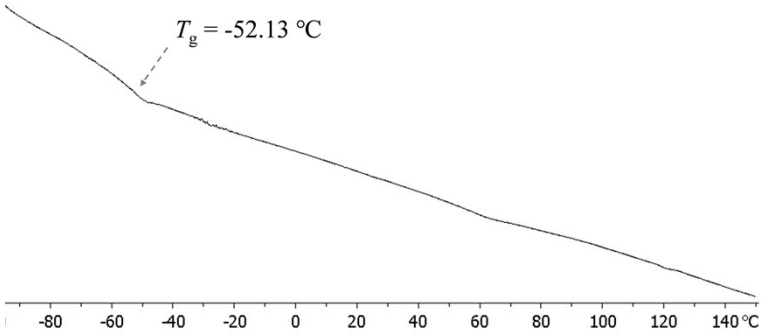

Figure S36. DSC curve of poly(*o*MOS-IP-BD) (entry 2, Table 1)

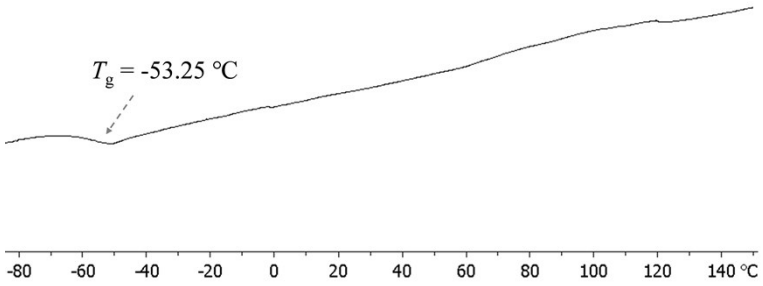

Figure S37. DSC curve of poly(*o*MOS-IP-BD) (entry 3, Table 1)

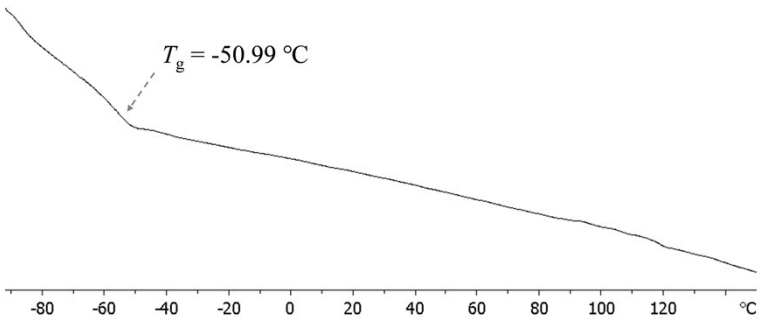

Figure S38. DSC curve of poly(*o*MOS-IP-BD) (entry 4, Table 1)

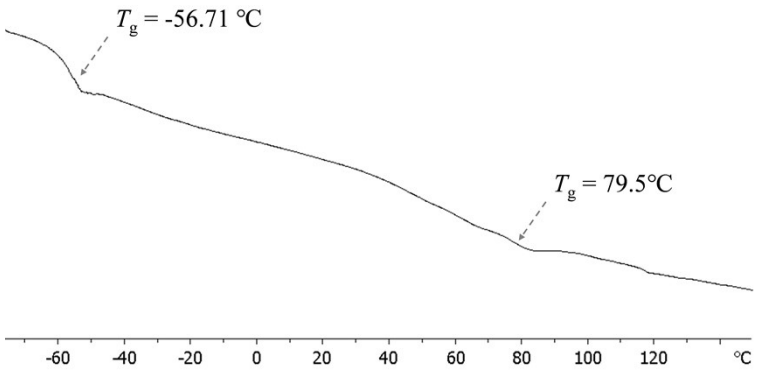

Figure S39. DSC curve of poly(*o*MOS-IP-BD) (entry 5, Table 1)

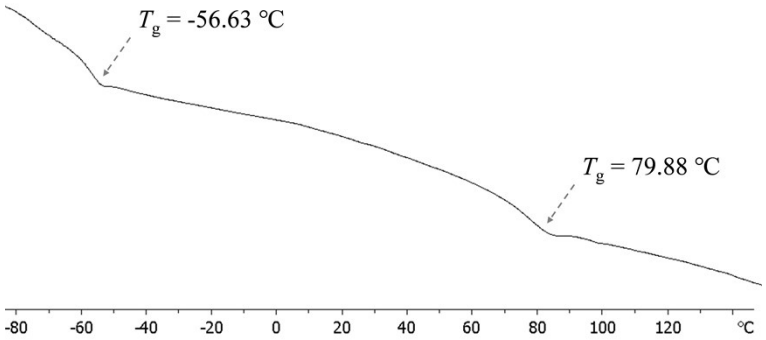

Figure S40. DSC curve of poly(*o*MOS-IP-BD) (entry 6, Table 1)

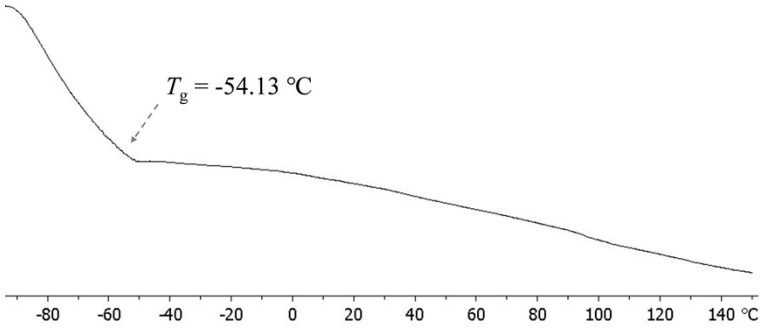

Figure S41. DSC curve of poly(*o*EOS-IP-BD) (entry 7, Table 1)

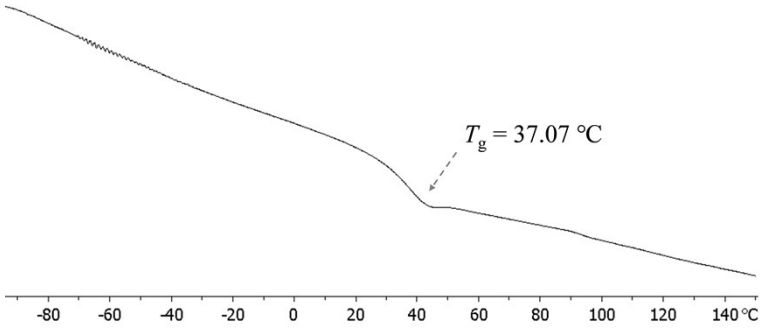

Figure S42. DSC curve of poly(*o*EOS-IP-BD) (entry 8, Table 1)

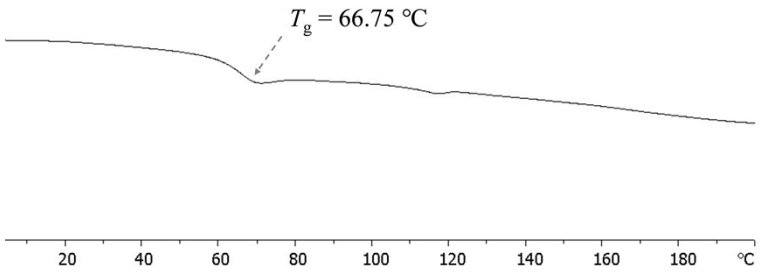

Figure S43. DSC curve of poly(*o*MOS-IP-BD) isolated in 1 min (entry 1, Table S1)

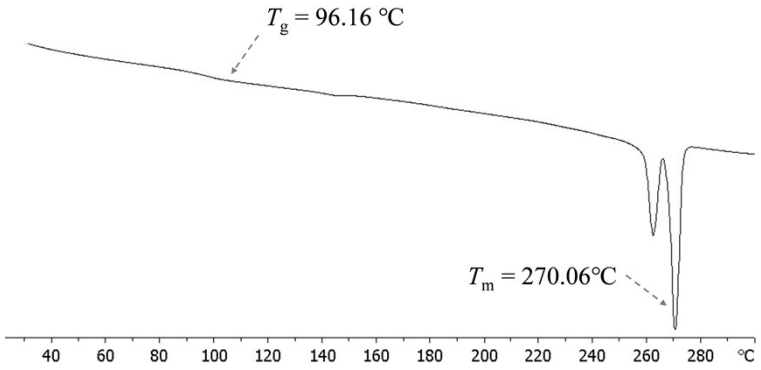

Figure S44. DSC curve of polystyrene (entry 1, Table 2)

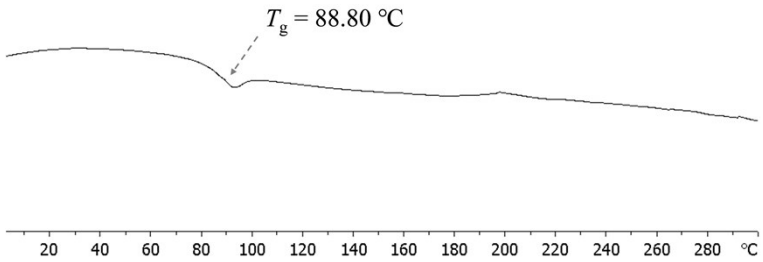

Figure S45. DSC curve of poly(*o*MOS) (entry 2, Table 2)

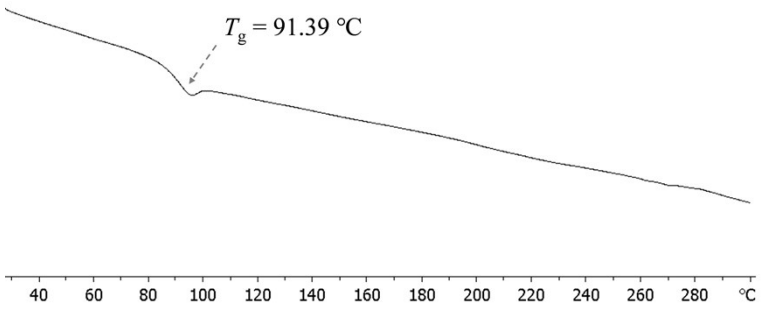

Figure S46. DSC curve of poly(*o*MOS) (entry 3, Table 2)

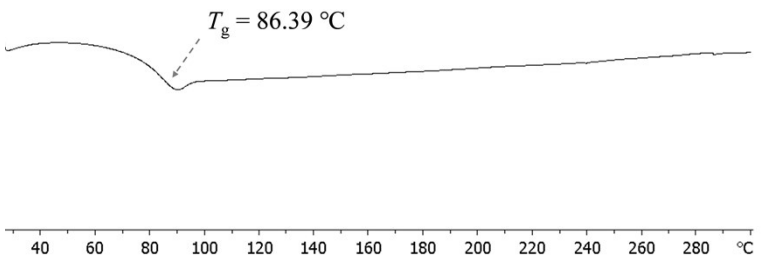

Figure S47. DSC curve of poly(*o*EOS) (entry 5, Table 2)

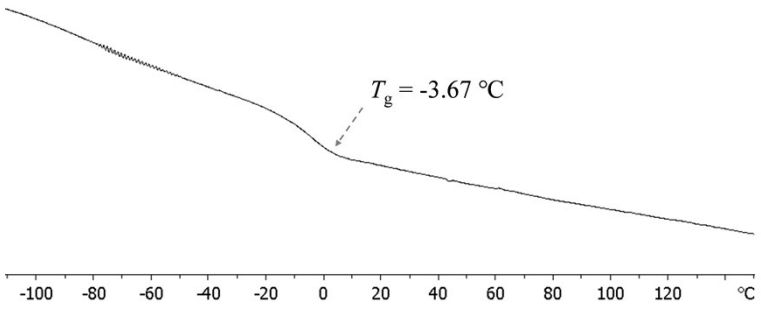

Figure S48. DSC curve of poly(*o*EOS-IP-BD) for uniaxial extension experiments

Table S2. Selected ^{13}C NMR ($CDCl_3$, 500 MHZ, 25 °C) chemical shifts of poly(*o*MOS-IP-BD) (entry 3, Table 1)

Chemical shift	Assignment	Chemical shift	Assignment
16.05/16.13	*trans*-1,4-PIP	31.28	*cis*-4,1-3,4(PIP)
17.58	PIP	31.51	*cis*-4,1-3,4(PIP)
18.62	3,4-PIP	31.89	PIP-PBD
23.45	*cis*-1,4-PIP	32.07	PIP
25.84	PIP-PBD	32.22	*cis*-1,4-PIP
26.34	*cis*-1,4-4,3(PIP)	32.38	*cis*-1,4-4,3(PIP)
26.40	*cis*-1,4-PIP	32.81/32.89	PIP
26.50	*trans*-1,4-PIP	34.30	1,2-PBD
27.41	*cis*-1,4-PBD	35.82	PIP
27.56	PIP-PBD	37.85	PIP
27.71	PIP-PBD	40.07	*trans*-1,4-PIP
27.77	PIP-PBD	43.75	1,2-PBD
27.99	PIP-PBD	44.79	PIP
28.34	PIP	45.10	PIP

29.86	3,4-PIP	47.13	PIP-PBD
30.02	PIP	47.42	PIP
30.61/30.70	PIP	47.93	3,4-PIP

Table S3. Selected ^{13}C NMR ($CDCl_3$, 500 MHZ, 25 °C) chemical shifts of poly(*o*EOS-IP-BD) (entry 3, Table 1)

Chemical shift	Assignment	Chemical shift	Assignment
15.03	P*o*EOS	31.89	PIP-PBD
16.05/16.13	*trans*-1,4-PIP	32.07	PIP
17.58	PIP	32.22	*cis*-1,4-PIP
18.62	3,4-PIP	32.38	*cis*-1,4-4,3(PIP)
23.45	*cis*-1,4-PIP	32.81/32.89	PIP
25.40	P*o*EOS-PIP/PBD	33.87	P*o*EOS-PIP/PBD
25.84	PIP-PBD	34.30	1,2-PBD
26.34	*cis*-1,4-4,3(PIP)	34.45	P*o*EOS-PIP/PBD
26.40	*cis*-1,4-PIP	35.82	PIP
26.50	*trans*-1,4-PIP	37.85	PIP
27.41	*cis*-1,4-PBD	38.64	P*o*EOS-PIP/PBD
27.56	PIP-PBD	40.07	PIP
27.71	PIP-PBD	40.61	P*o*EOS
27.77	PIP-PBD	43.75	1,2-PBD
27.99	PIP-PBD	44.79	PIP
28.34	PIP	45.10	PIP
29.86	3,4-PIP	47.13	PIP-PBD
30.02	PIP	47.42	PIP
30.61/30.70	PIP	47.93	3,4-PIP
31.28	*cis*-4,1-3,4(PIP)		
31.51	*cis*-4,1-3,4(PIP)		

Calculation for activation energies of homopolymerizing *o*MOS and *o*EOS

First of all, we carried out the homopolymerization of *o*MOS (0.268g) in 1.2 mL toluene (*V*) using complex **2** (2.5 μnol) activated with $[Ph_3C][B(C_6F_5)_4]$ (2.5 μnol) at 30 °C (T_1 = 303K) and 63 °C (T_2 = 336K) for 2 mins (Δt) respectively. The reaction was terminated by addition of a small amount methanol and poured into ethanol (50 mL) to precipitate.The polymers (m_1= 0.1177g and m_2= 0.2257g) were collected by filtration, and dried under vacuum at 40 °C to constant weights.

$v_1 = \frac{\Delta C_1}{\Delta t} = k_1[oMOS]^X[Cat]^y$, wherein v_1 is the polymerization rate; ΔC_1 is the concentration of polymer; Δt is the time for polymerization; k_1 is polymerization rate constant; $[oMOS]$and$[Cat]$ are concentrations of monomer and catalyst; x and y are orders of reaction.

For the time (Δt), volume of toluene (*V*), and $[oMOS]^X[Cat]^y$ are same in two polymerizations at different temperatures,

$ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{T_1 - T_2}{T_1 \times T_2}\right) = ln\frac{v_1}{v_2} = ln\frac{\Delta C_1}{\Delta C_2} = ln\frac{m_1/V}{m_2/V} = ln\frac{m_1}{m_2}$, wherein *R* is the gas constant, 8.314 J/(mol·k).

$$E_a = R \times \left(\frac{T_1 \times T_2}{T_1 - T_2}\right) \times ln\frac{m_1}{m_2} = 8.314 \times \left(\frac{303 \times 336}{303 - 336}\right) \times ln\frac{0.1177}{0.2257}\, kJ/mol = 16.7\ kJ/mol$$

The homopolymerizations of *o*EOS (0.296g) were carried out in toluene (*V'* = 1.4 mL) using complex **2** (2.5 μnol) activated with $[Ph_3C][B(C_6F_5)_4]$ (2.5 μnol) at 30 °C (T_1' = 303K) and 60 °C (T_2' = 333K) for 4 mins $(\Delta t')$ respectively. Finally, we obtained 0.0030g (m_1') and 0.0750g (m_2') polymers. According to the similar calculation process for homopolymerization of *o*MOS, we obtained the activation energy of homopolymerizing oEOS (E_a'= 120.7 kJ/mol).