SUPPORTING INFORMATION

Efficient One-pot Synthesis of End-functionalized *trans*-stereoregular Polydiene Macromonomers

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Figure S14. SEC traces of polymer samples (runs 9, 10)

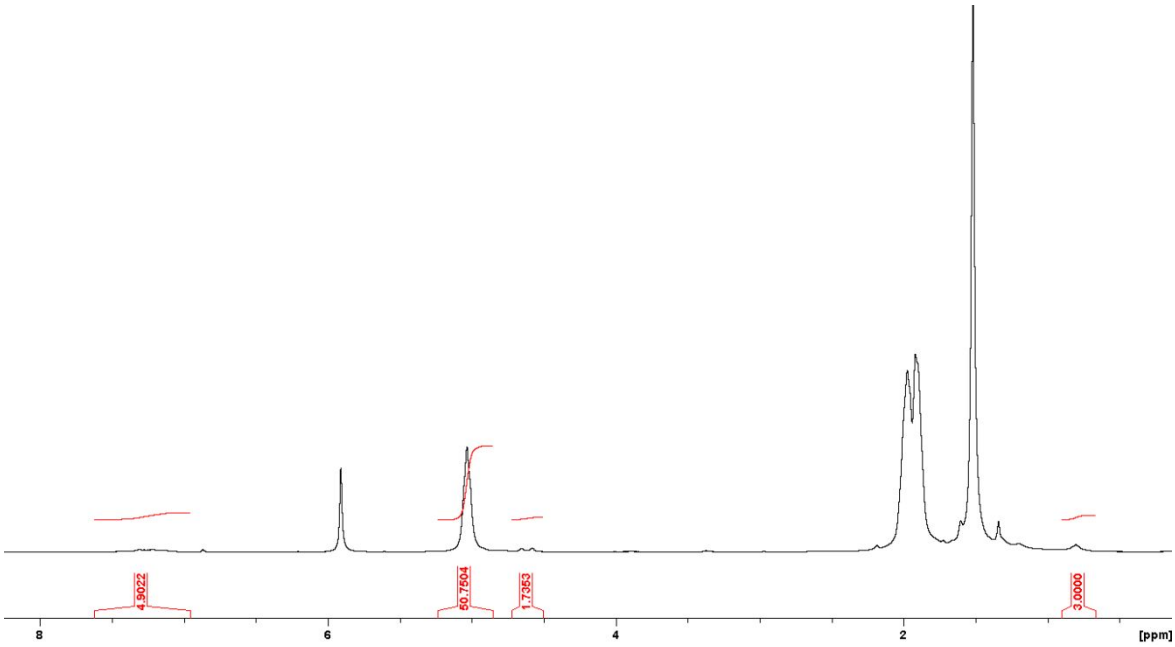


Figure S1. ^{1}H NMR spectrum of hydroxydiphenylmethylenyl-1,4-*trans*-polyisoprene (run 1, $C_2D_2Cl_4$).

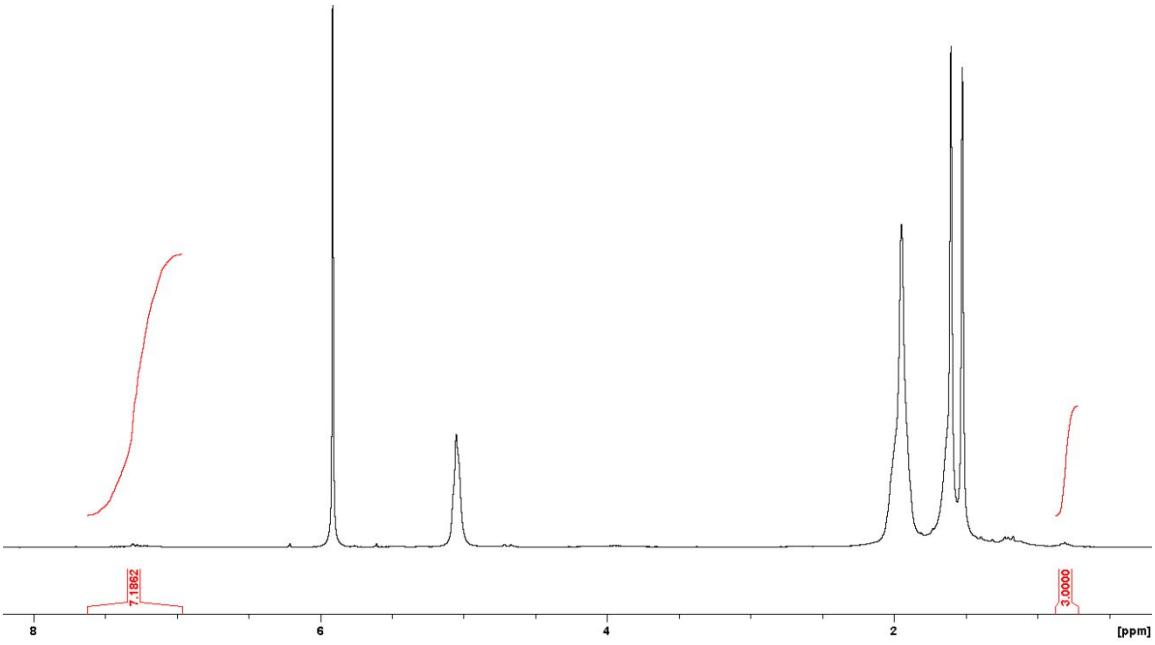


Figure S2. ^{1}H NMR spectrum of hydroxydiphenylmethylenyl-1,4-*trans*-polymyrcene (run 2, $C_2D_2Cl_4$).

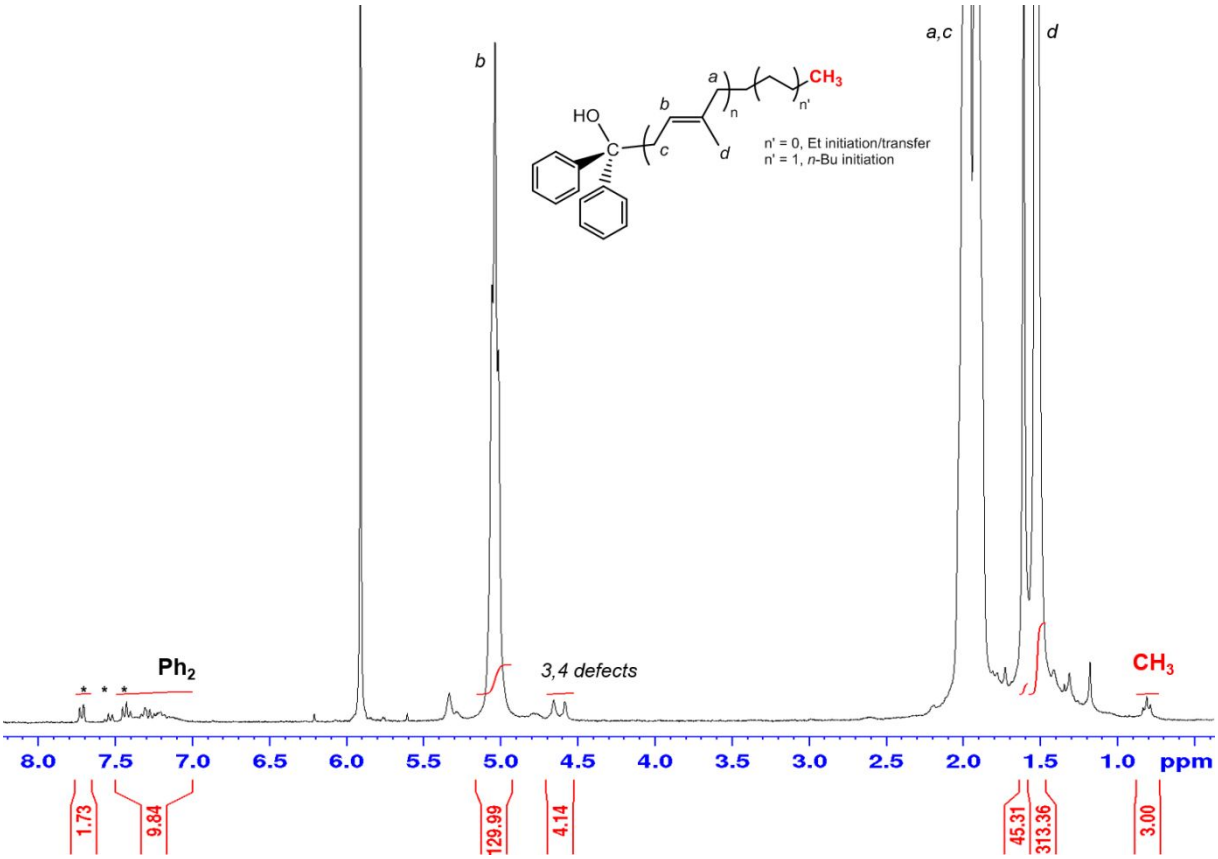


Figure S3. ^{1}H NMR spectrum of hydroxydiphenylmethylenyl-1,4-*trans*-polyisoprene (run 3, $C_2D_2Cl_4$, * residue of unreacted benzophenone).

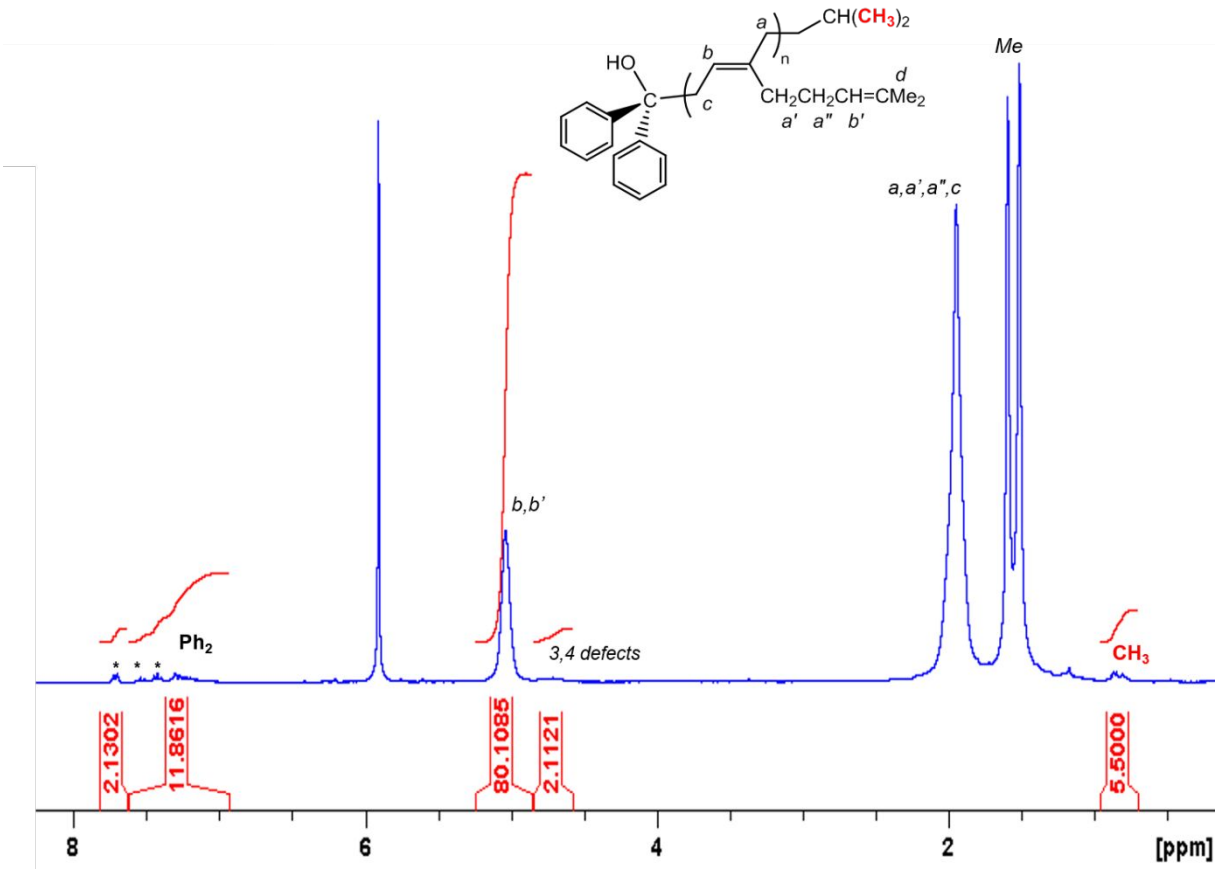


Figure S4. ^{1}H NMR spectrum of hydroxydiphenylmethylenyl-1,4-*trans*-polymyrcene (run 4, $C_2D_2Cl_4$, * residue of unreacted benzophenone)

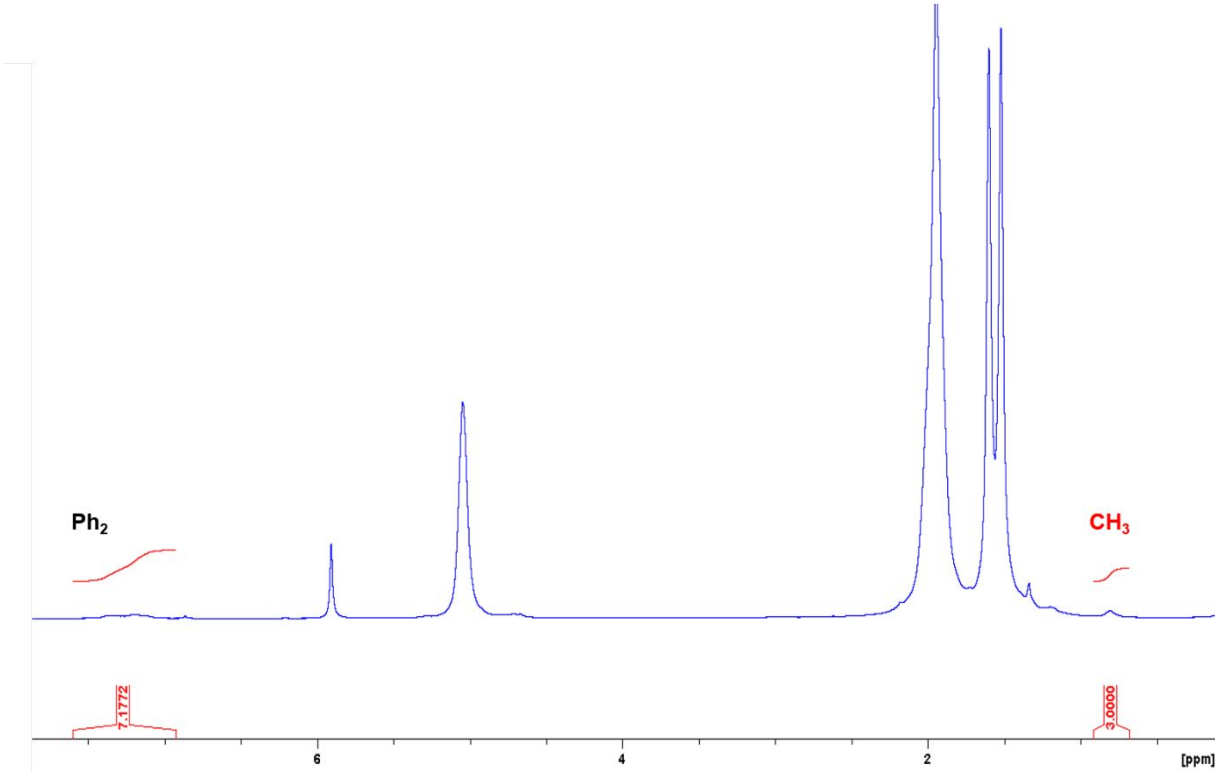


Figure S5. ^{1}H NMR spectrum of hydroxydiphenylmethylenyl-*trans*-polymyrcene (run 6, $C_2D_2Cl_4$)

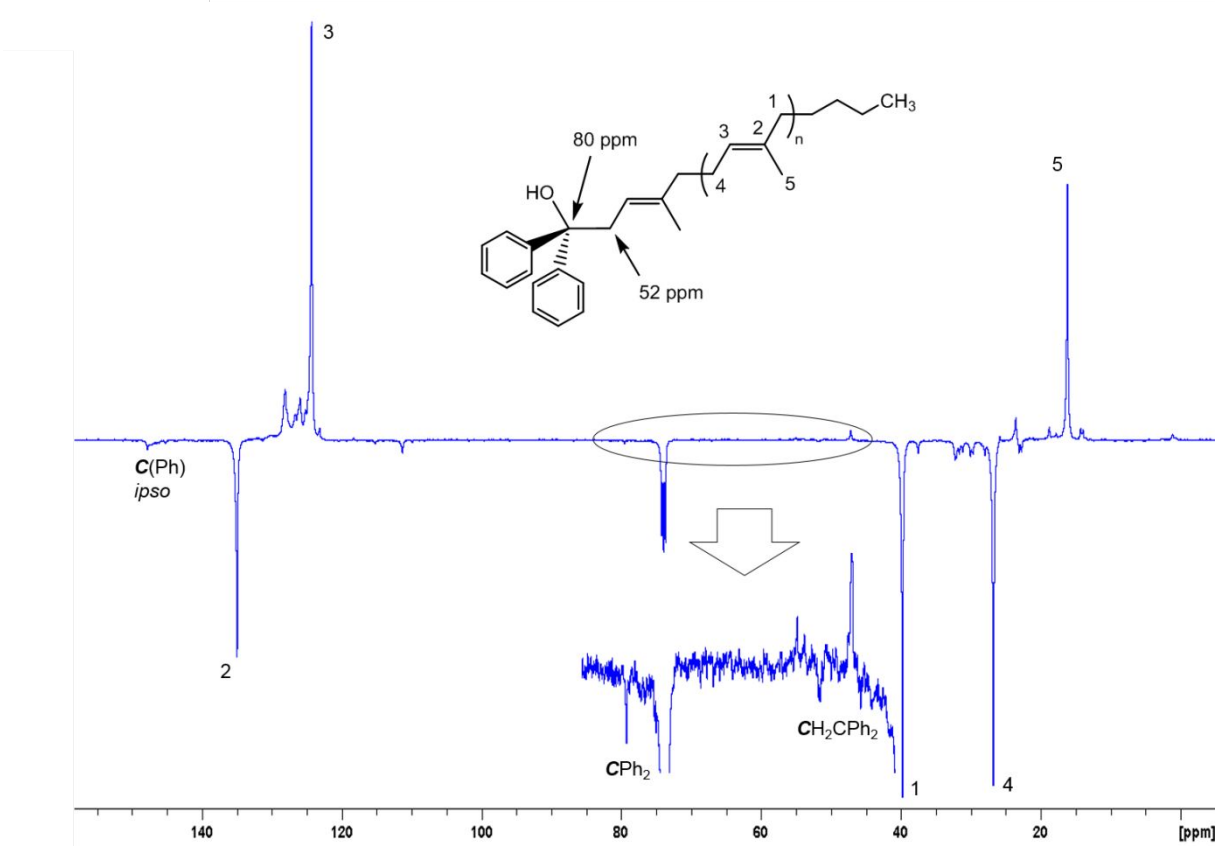


Figure S6. JMOD ^{13}C NMR spectrum of hydroxydiphenylmethylenyl-*trans*-polyisoprene (run 7, $C_2D_2Cl_4$) showing the typical CH_2-CPh_2OH resonances.

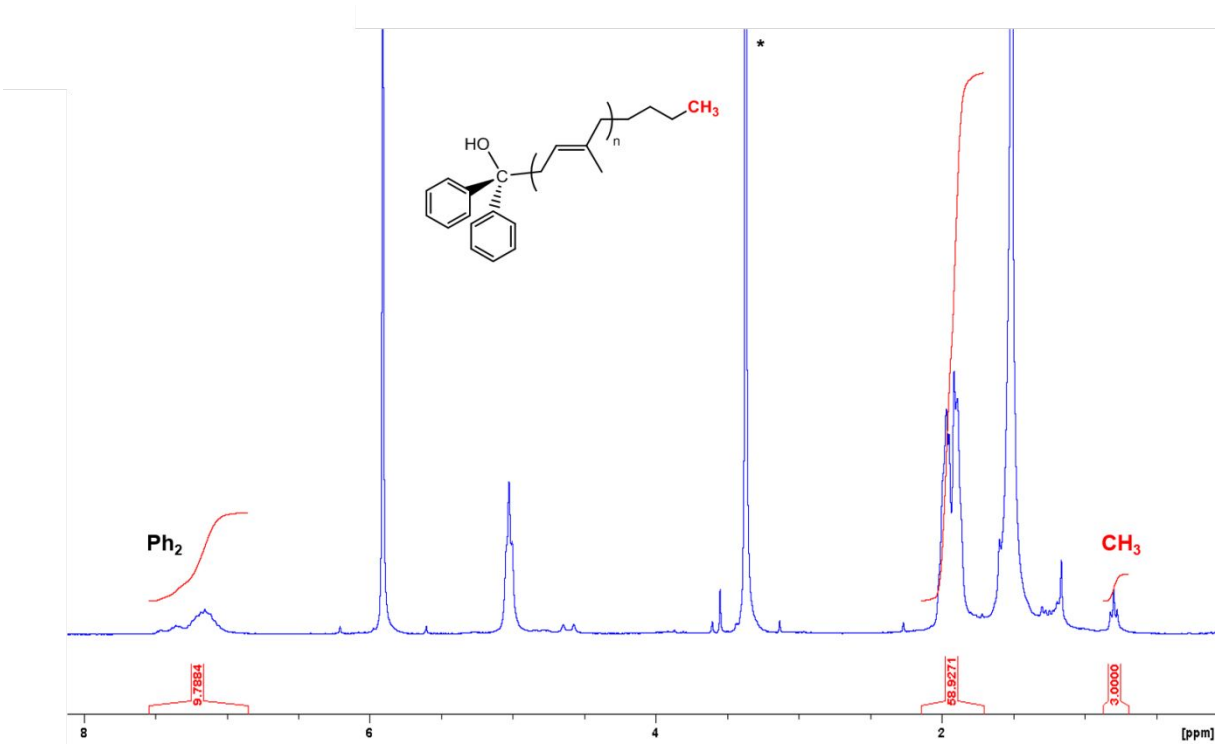
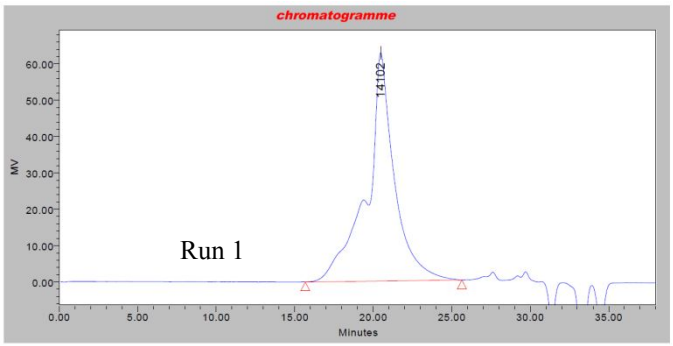
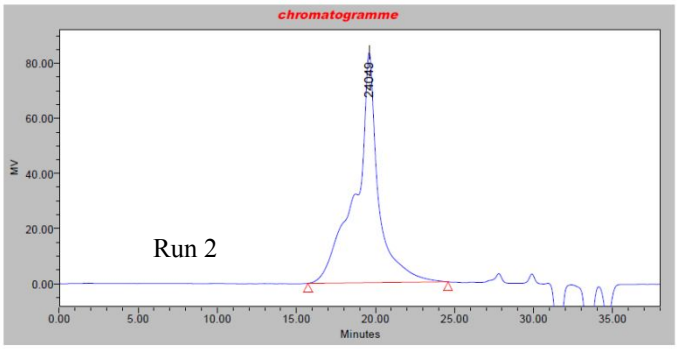


Figure S7. ^{1}H NMR spectrum of low M_n sample of hydroxydiphenylmethylenyl-*trans*-polyisoprene (run 7', $C_2D_2Cl_4$, * CH_3OH residue)



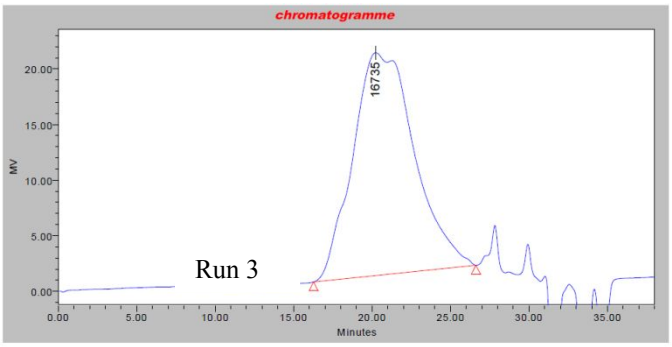
Résultats

	SampleName	Sample Type	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity
1	UCCS-SG1106	Broad Unknown	12048	22093	14102	49871	101492		1.83



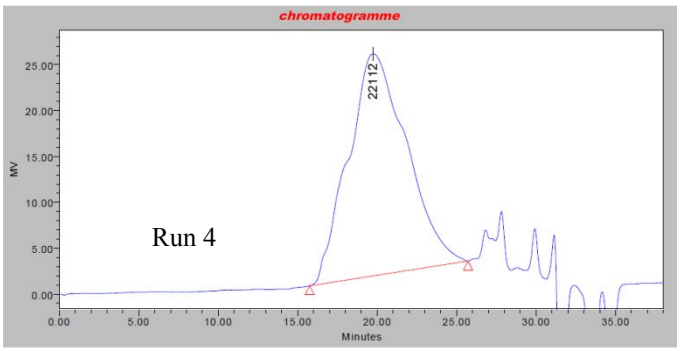
Résultats

	SampleName	Sample Type	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity
1	UCCS-SG1156	Broad Unknown	22276	39048	24049	72472	123991		1.75



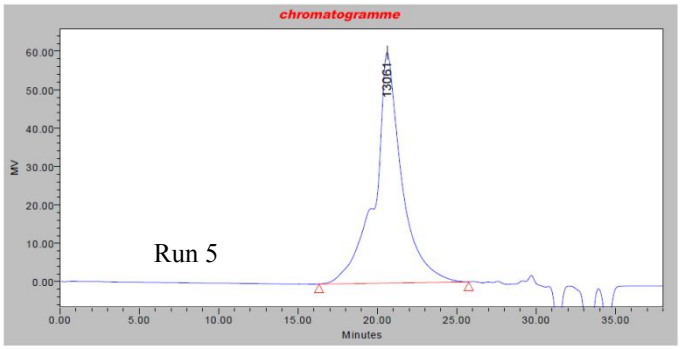
Résultats

	SampleName	Sample Type	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity
1	UCCS-SG1152	Broad Unknown	7841	19567	16735	45364	80577		2.50



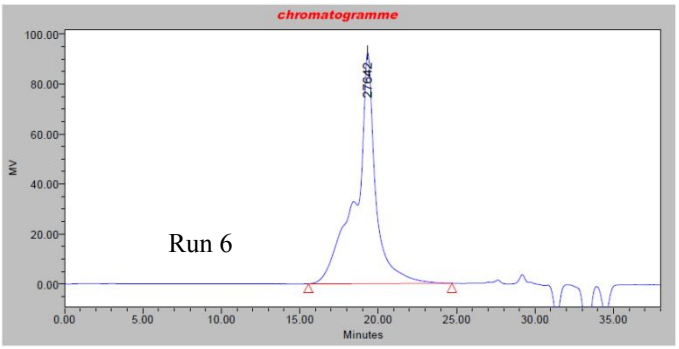
Résultats

	SampleName	Sample Type	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity
1	UCCS-SG1153	Broad Unknown	11636	31069	22112	75793	131894		2.67



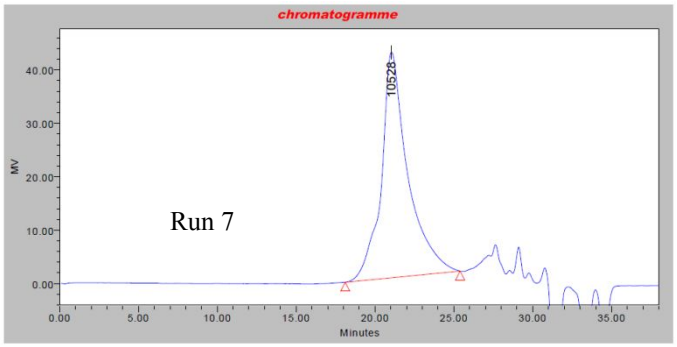
Résultats

	SampleName	Sample Type	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity
1	UCCS-SG1104	Broad Unknown	10532	16536	13061	30180	57964		1.57



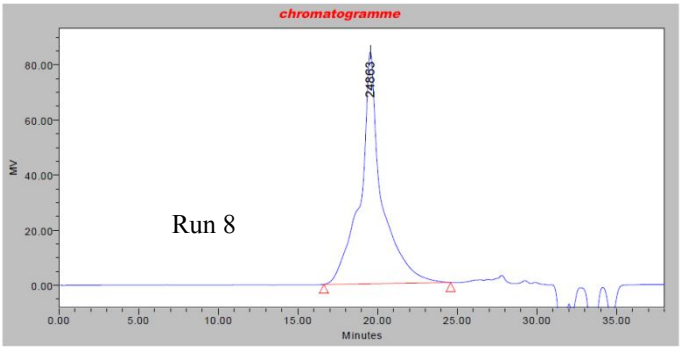
Résultats

	SampleName	Sample Type	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity
1	UCCS-SG1105	Broad Unknown	26612	44086	27642	77943	131501		1.66



Résultats

	SampleName	Sample Type	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity
1	UCCS-SG1150	Broad Unknown	7606	10169	10528	13303	17455		1.34



Résultats

	SampleName	Sample Type	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity
1	UCCS-SG1155	Broad Unknown	18817	28313	24863	41710	60427		1.50

Figure S8. SEC traces of polymers isolated from runs 1-8 (the shoulder observed at high molecular weights is classical in the case of 1,3 dienes polymerization using $Nd(BH_4)_3(THF)_3$/BEM as catalyst.[1]

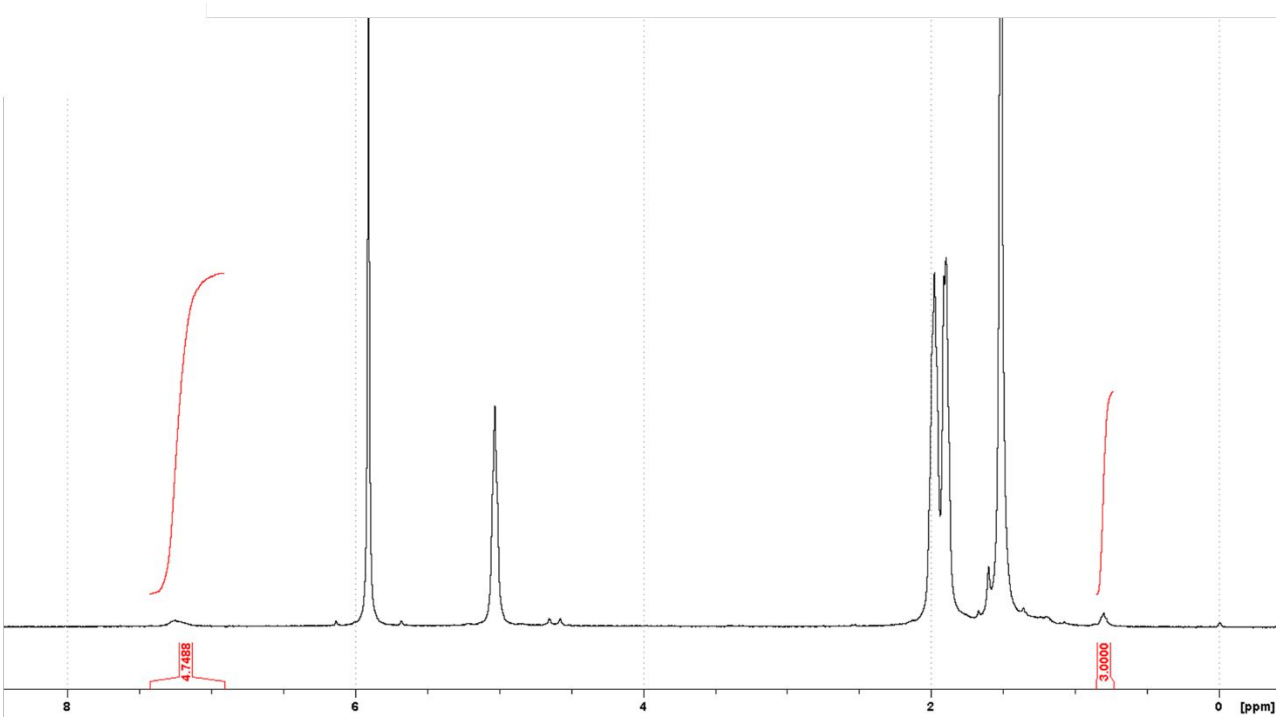


Figure S9. ^{1}H NMR spectrum of end-capped 1,4-*trans*-polyisoprene after functionalization with benzaldehyde (run 9, $C_2D_2Cl_4$)

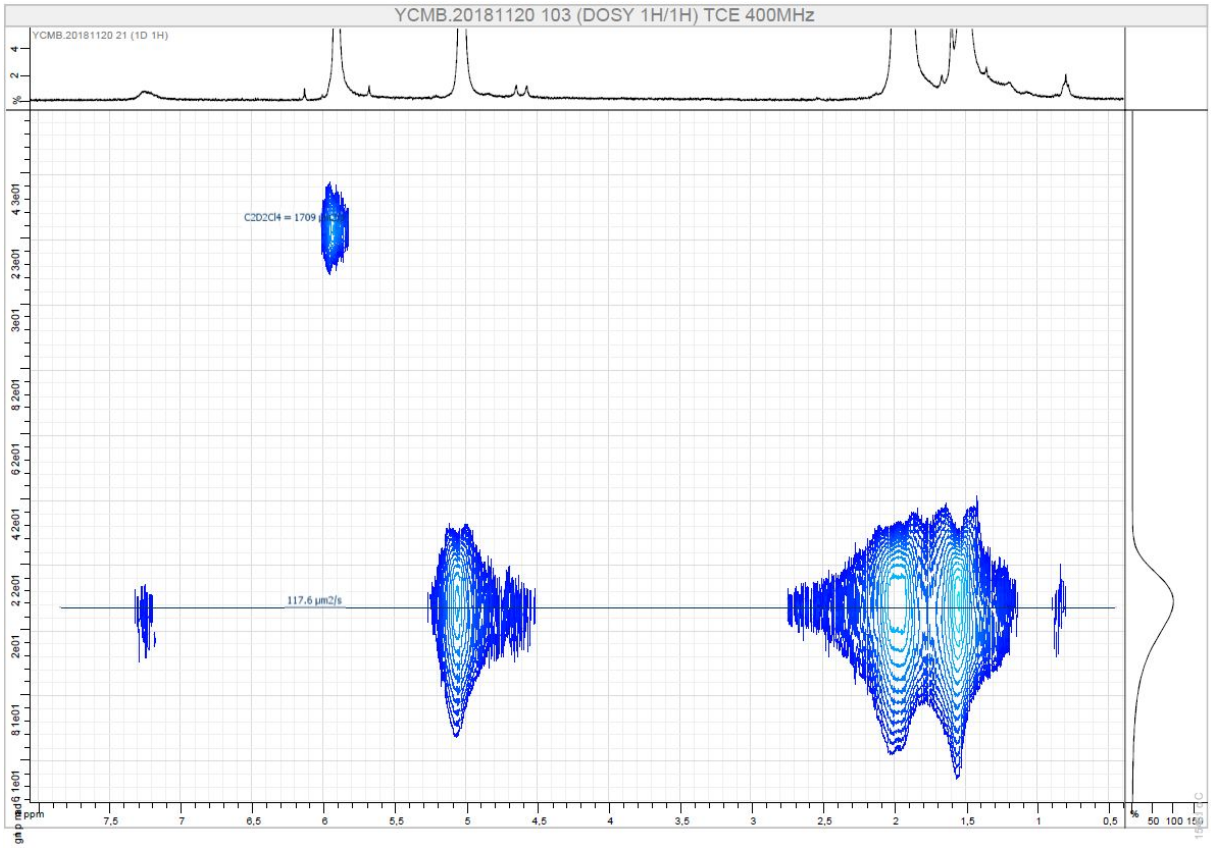


Figure S10. ^{1}H DOSY NMR spectrum of end-capped 1,4-*trans*-polyisoprene after functionalization with benzaldehyde (run 9, $C_2D_2Cl_4$)

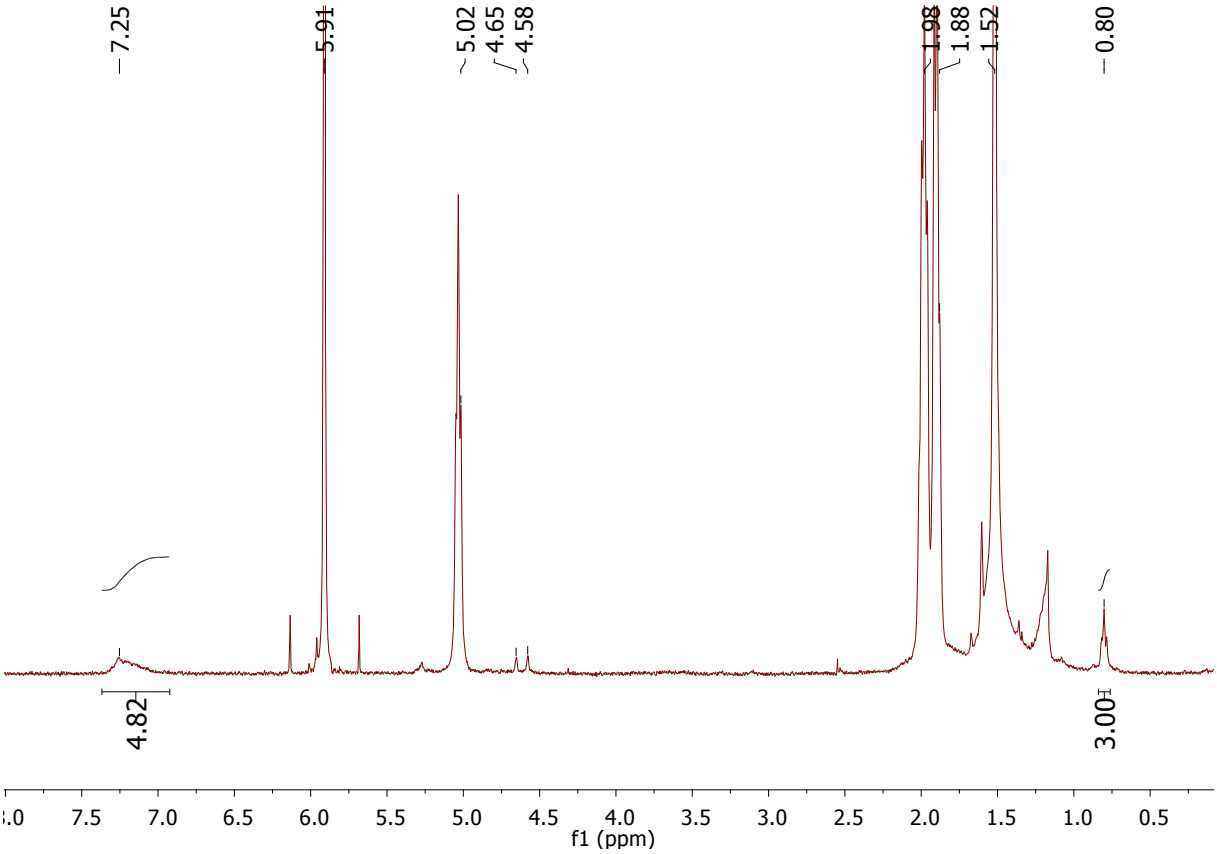


Figure S11. ^{1}H NMR spectrum of end-capped 1,4-*trans*-polyisoprene after functionalization with styrene oxide (run 10, $C_2D_2Cl_4$)

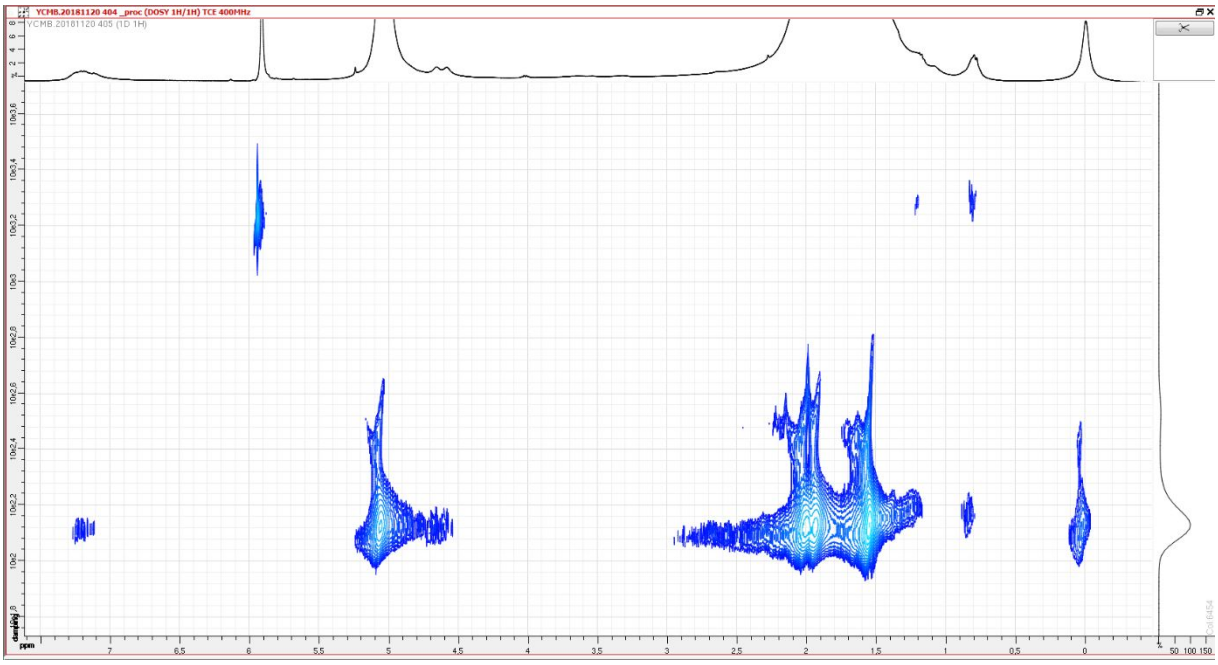


Figure S12. ^{1}H DOSY NMR spectrum of end-capped 1,4-*trans*-polyisoprene after functionalization with styrene oxide (run 10, $C_2D_2Cl_4$)

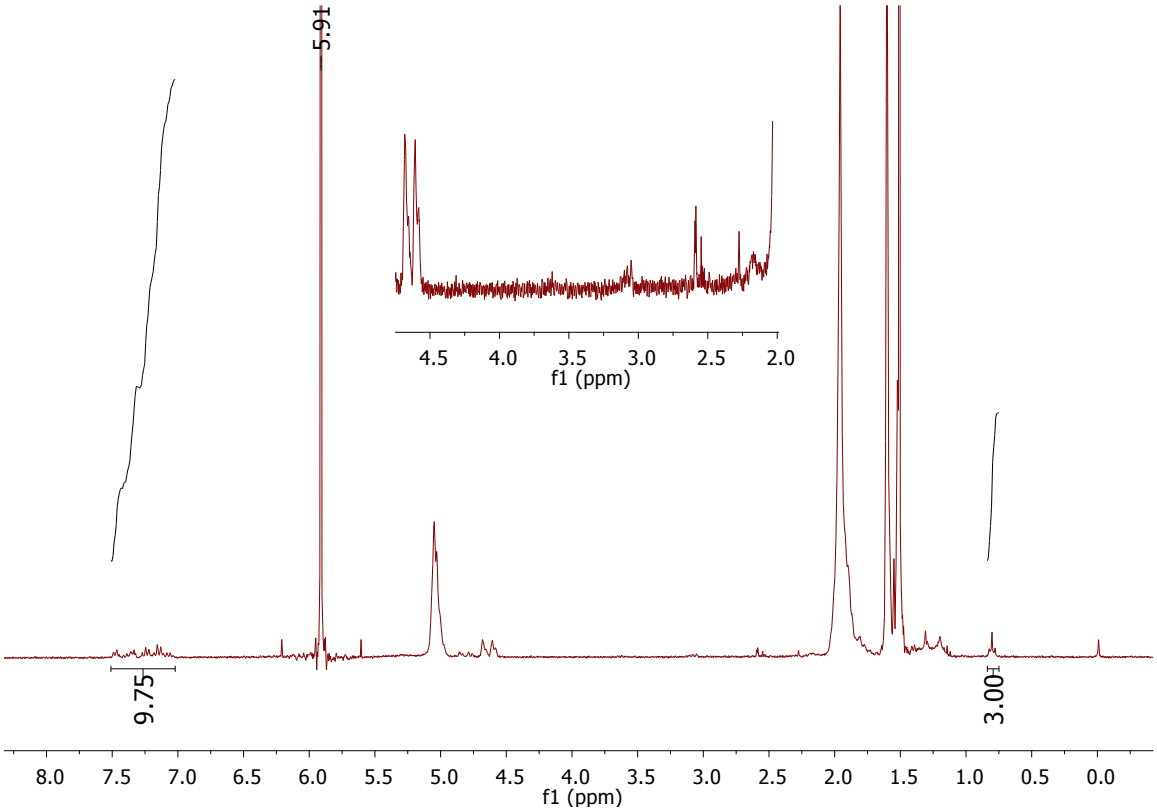
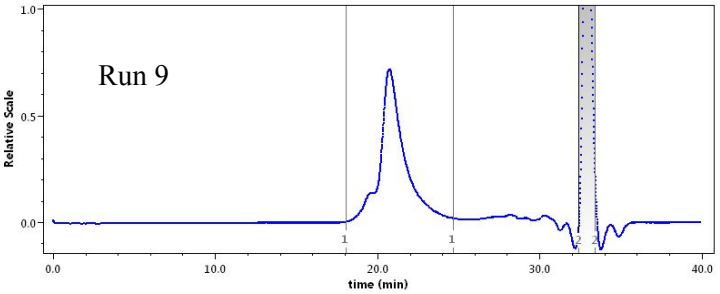
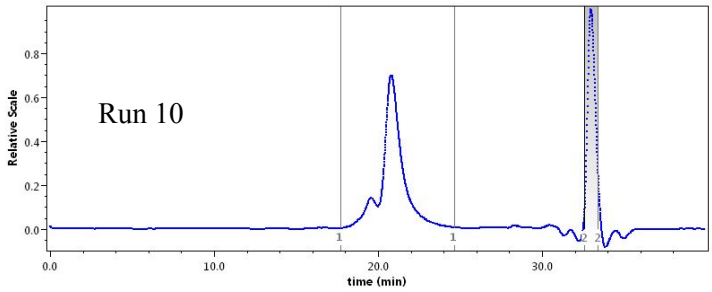


Figure S13. ^{1}H NMR spectrum of hydroxydiphenylmethylenyl-polyisoprene prepared by anionic initiation with *n*BuLi according to the method of Cramail.[2]

Conditions: ^{n}BuLi (V = 0.1 mL, n = 2.10^{-4} mol) was added to 50 equiv. of isoprene (V = 1 mL, n = 1.10^{-2} mol) in toluene (1 mL) in an Ace vial. The solution was stirred at 50 °C for 2 hours under argon. After 2 hours, 2 equiv. of benzophenone (m = 55 mg, n = $3.04.10^{-4}$ mol) in 1 mL of THF was then added dropwise and the mixture was stirred at 50 °C for 2 hours. The reaction was quenched with few drops of acidified methanol. The polymer was recovered by precipitation in large excess of EtOH containing BHT and dried under vacuum.



Peak Results	Peak 1	MARKER
Masses		
Calculated Mass (µg)	340.28	0.00
Molar mass moments (g/mol)		
Mn	1.009×10^{4} (±7.018%)	n/a
Mw	1.335×10^{4} (±7.018%)	n/a
Mz	1.744×10^{4} (±15.692%)	n/a
M(avg)	4.226×10^{3} (±0.333%)	2.171×10^{1} (±0.678%)
Polydispersity		
Mw/Mn	1.323 (±9.924%)	n/a
Mz/Mn	1.729 (±17.189%)	n/a



Results

Peak Results	Peak 1	MARKER
Masses		
Calculated Mass (µg)	346.07	0.00
Molar mass moments (g/mol)		
Mn	1.169×10^{4} (±7.018%)	n/a
Mw	1.508×10^{4} (±7.018%)	n/a
Mz	2.039×10^{4} (±15.692%)	n/a
M(avg)	4.412×10^{3} (±0.332%)	2.265×10^{1} (±0.753%)
Polydispersity		
Mw/Mn	1.290 (±9.924%)	n/a
Mz/Mn	1.744 (±17.189%)	n/a

Figure S14. SEC traces of polymer samples (runs 9, 10)

References

1. See for example: Leicht, H.; Bauer, J.; Göttker-Schnetmann, I.; Mecking, S. Heterotelechelic and In-Chain Polar Functionalized Stereoregular Poly(dienes), *Macromolecules*, **2018**, *51*, 763-770.
2. Heurtefeu, B.; Merna, J.; Ibarboure, E.; Cloutet, E.; Cramail, H. Organic support for ethylene polymerization based on the self-assembly in heptane of end-functionalized polyisoprene. *Polym. Chem.* **2010**, *1*, 1078-1085.