Supporting informations for

Isoprene chain shuttling polymerization between *cis* and *trans* regulating catalysts: straightforward access to a new material

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Experimental section

Materials

All operations were performed under dry argon by using Schlenk techniques. Toluene was purified through alumina column (Mbraun SPS). Isoprene (99% from Aldrich) were dried over calcium hydride, distilled twice over molecular sieves and once just before use. *n*-butylethylmagnesium (BEM, 20 wt%. in heptane from Texas Alkyl) and aluminiumtriisobutyl (Al^iBu_3), pure, Aldrich), aluminiumtriethyl ($AlEt_3$, pure, Aldrich), were used as received. The complexes $Cp^*La(BH_4)_2(THF)_2$ (**1**) was synthesized according to literature procedures[1] and $NdCl_3(THF)_2$ (**2**) was obtained by treatment of anhydrous $NdCl_3$ (99%, Strem) in THF under reflux for 3 days.

Polymerization

In a glove box, the complexes were weighed into different vessels and dissolved in toluene. 1 equivalent of BEM was added to complex **1** and 20 equivalents of AlR_3 to complex **2** using microsyringes. The mixtures were magnetically stirred for some minutes, before being mixed for the chain shuttling experiments. The resulting solution was heated at 50°C for a given time, quenched with methanol, diluted in toluene and poured into methanol, leading to the precipitation of the polymer. Solvents were evaporated under partial vacuum, and the products were dried under vacuum until constant weight.

[1] A. Valente, P. Zinck, A. Mortreux, M. Visseaux, *Macromol. Rapid Commun*, 2009, **30**, 528–531.

Measurements

^{1}H, ^{13}C and HMBC NMR spectra were recorded on a AV II 400MHz (9.4T) with TBI probe at room temperature in $CDCl_3$. Quantitative ^{13}C NMR analyses were realized using the zgig sequence (Bruker library). The chemical shifts were calibrated using the residual resonances of the solvent. Size exclusion chromatography was performed in THF as eluent at 40°C using a Waters SIS HPLC-pump, a Waters 410 refractometer and Waters styragel columns (HR2, HR3, HR4, HR5E) calibrated with polystyrene standards. DSC measurements were conducted under nitrogen on a DSC Q20 apparatus at a heating and cooling rates of 10°C.min-1 from -90°C to 100°C using around 10 mg samples in aluminium crucibles. The temperature range and the heat flow scale were calibrated from the recording of the melting of high purity indium sample at the same scanning rate. WAXS experiments were performed using a Genix microsource (XENOCS) equipment operating at 50 kV and 1 mA. The Cu-K_α radiation used was selected with a curved mirror monochromator and the 2D patterns were recorded on a CCD camera from Photonic Science. Sample to detector distances of 8cm were used. Standard corrections were applied to the patterns before their integration using the FIT2D® software. Tensile testing was conducted on an Instron machine under ambient conditions using specimens with L_0= 15mm and l_0= 3mm gauge length and width, respectively. The tensile tests were carried out at a constant crosshead speed of 9 $mm.min^{-1}$, corresponding to an initial strain rate of 1.10^{-2} s^{-1}. The nominal stress σ (MPa) and strain ε (%) are defined conventionally as the ratio $F/(l_0*e_0)$ and $(L-L_o)/L_o$, respectively, where F is the force (N) and e_0 (mm) the sample thickness. 100 μm thick films were prepared for the tensile test using the solution casting method consisting in dissolving the polymer in THF and putting the solution in a crystallizer before evaporation during 2 days under ambient conditions.

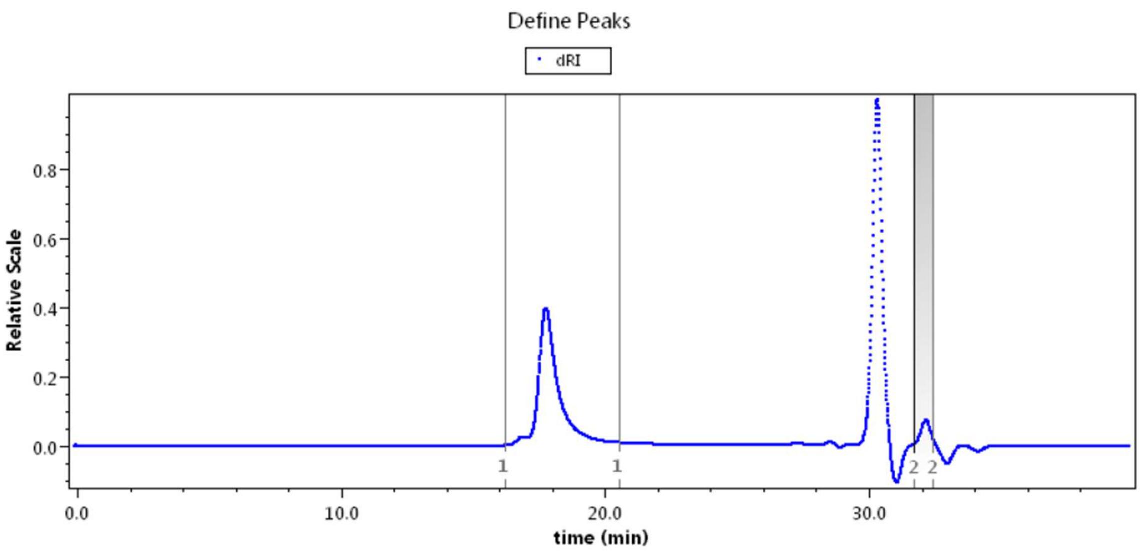


Figure SI1. SEC (Size Exclusion Chromatography) chromatograms of poly(1,4-*trans* isoprene) obtained using **1** combined to 1 equiv. $Mg^{n}BuEt$ (entry 1).

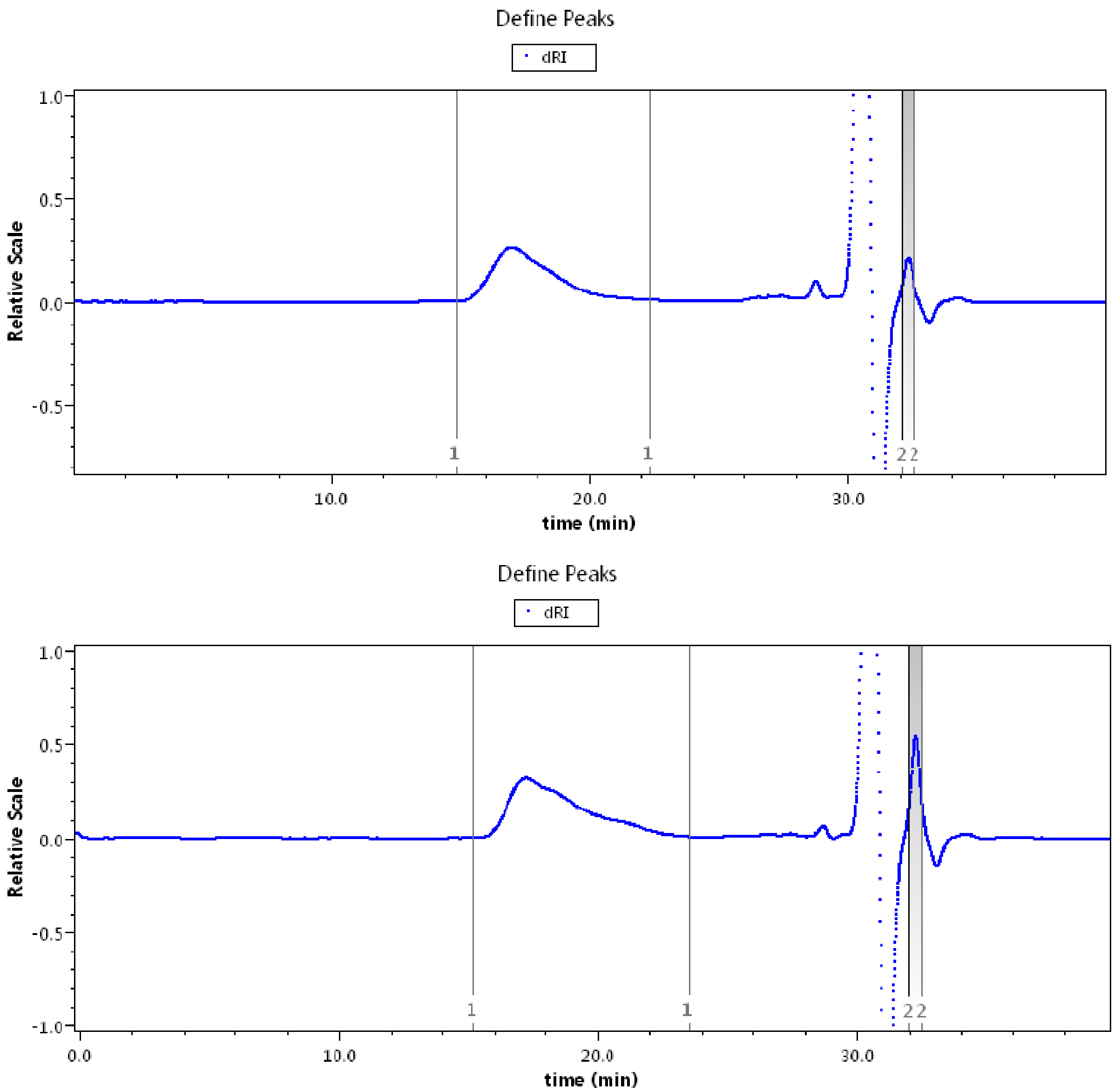


Figure SI2. SEC chromatograms of poly(1,4-*cis* isoprene) obtained using **2** combined to 20 equiv. $AlEt_3$ (entry 2, top) and 20 equiv. Al^iBu_3 (entry 3, bottom).

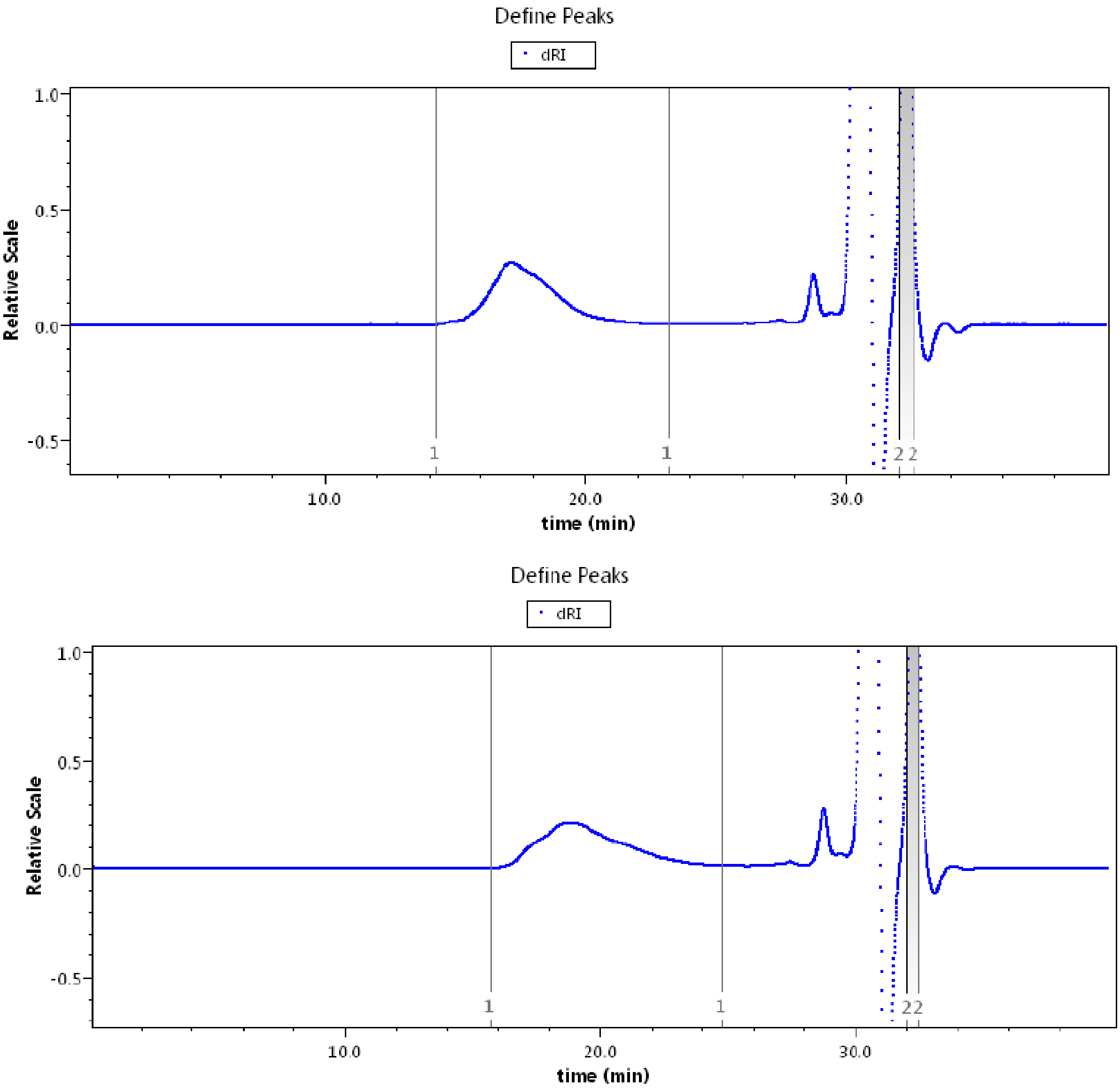


Figure SI3. SEC chromatograms of polyisoprene obtained using a 50/50 mixture of **1** and **2** combined to 1 equiv. $Mg^{n}BuEt$ and 20 equiv. $AlEt_3$ (entry 4, top) and 20 equiv. $AliBu_3$ (entry 5, bottom) respectively.

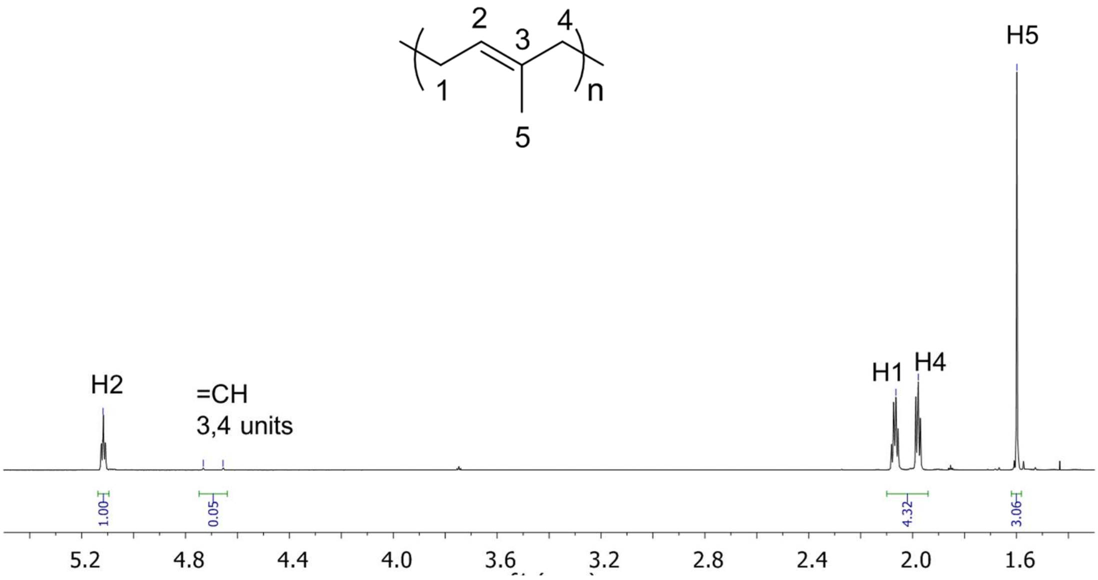


Figure SI4. ^{1}H-NMR spectrum of poly(1,4-*trans* isoprene) (entry 1)

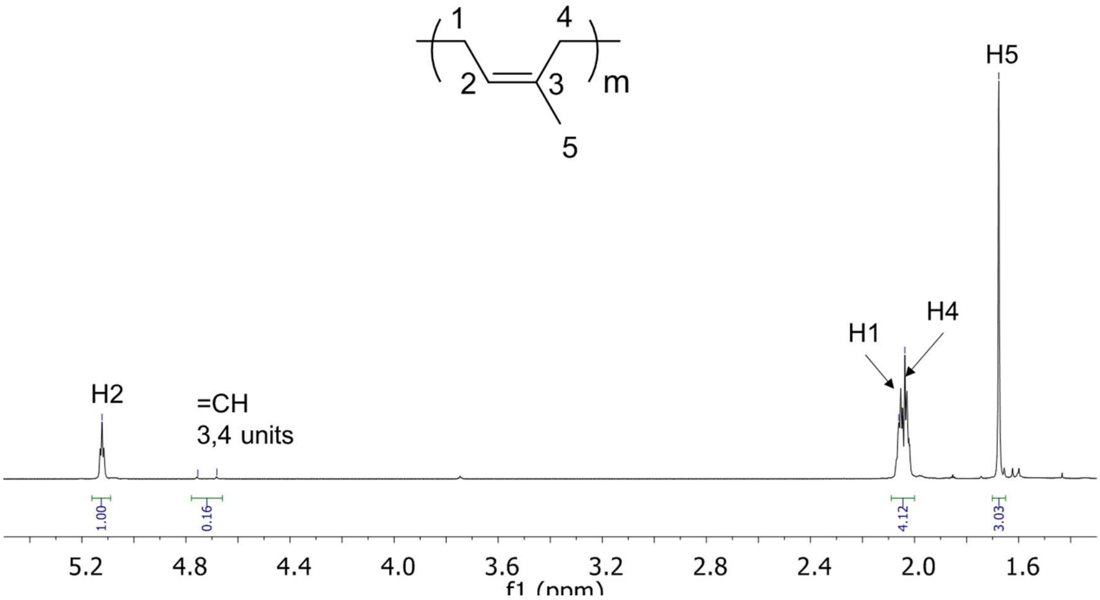


Figure SI5. ^{1}H-NMR spectrum of poly(1,4-*cis* isoprene) (entry 2)

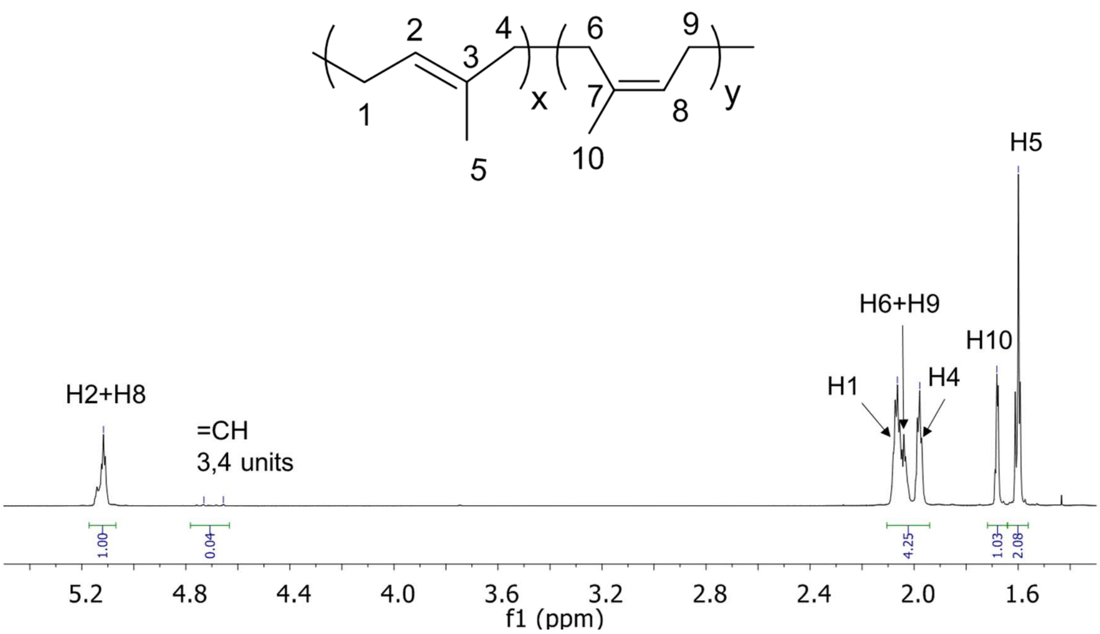


Figure SI6. [1]H-NMR spectrum of chain shuttled polyisoprene (entry 4) obtained using $AlEt_3$ as cocatalyst.

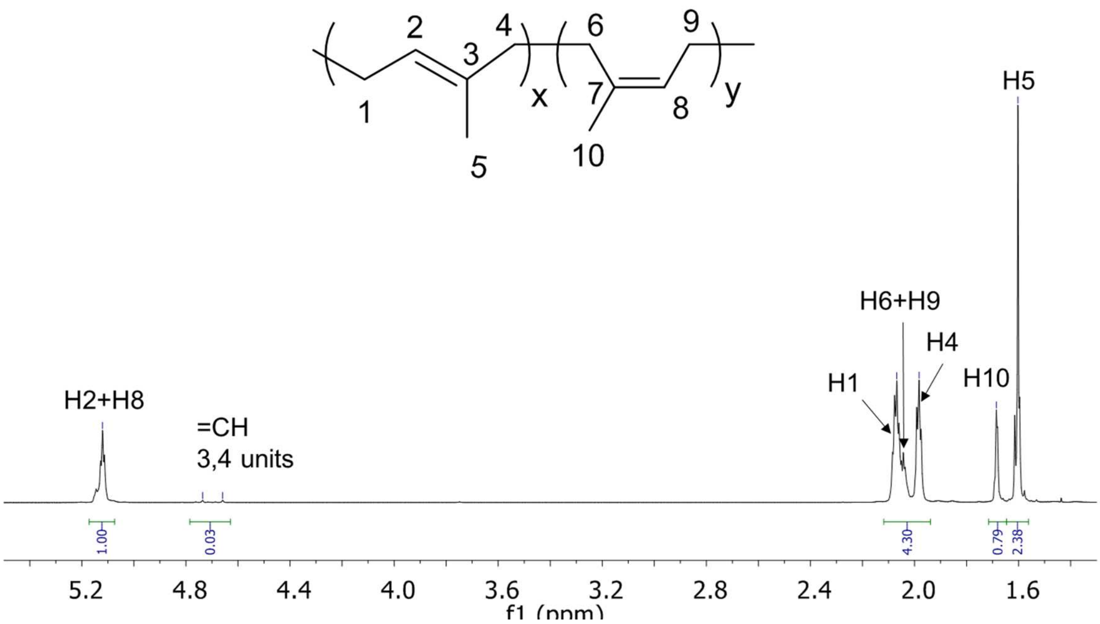


Figure SI7. [1]H-NMR spectrum of chain shuttled polyisoprene (entry 5) obtained using $Al^{i}Bu_3$ as cocatalyst.

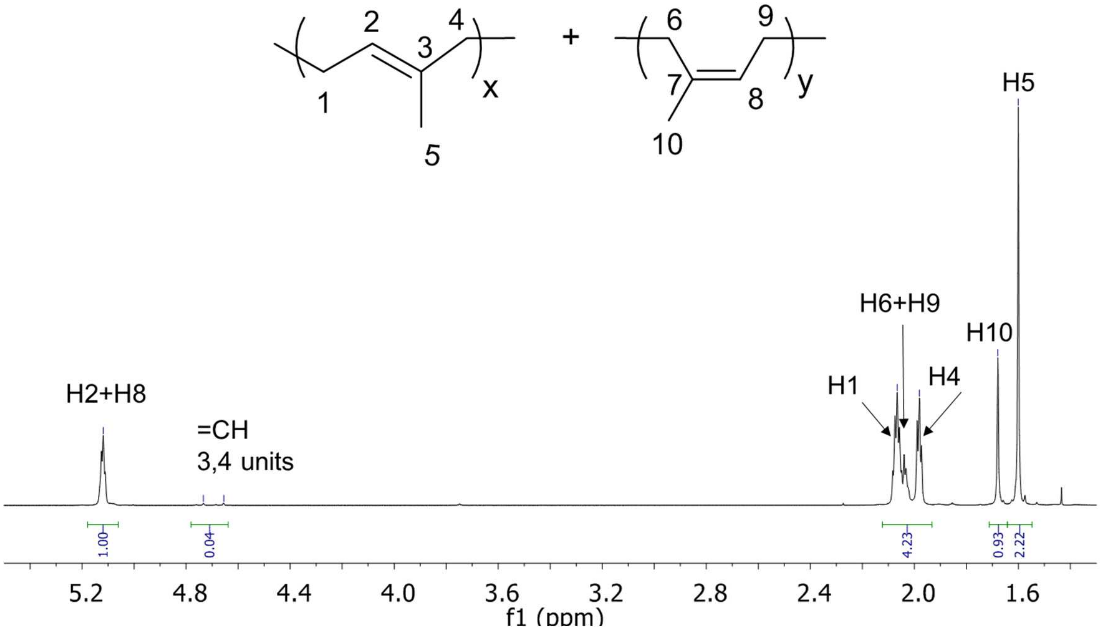


Figure SI8. ^{1}H-NMR spectrum of a physical mixture of poly(1,4-*cis* isoprene) and poly(1,4-*trans* isoprene) (entries 1 + 2) with a weight ratio *cis*/*trans* = 1/3.

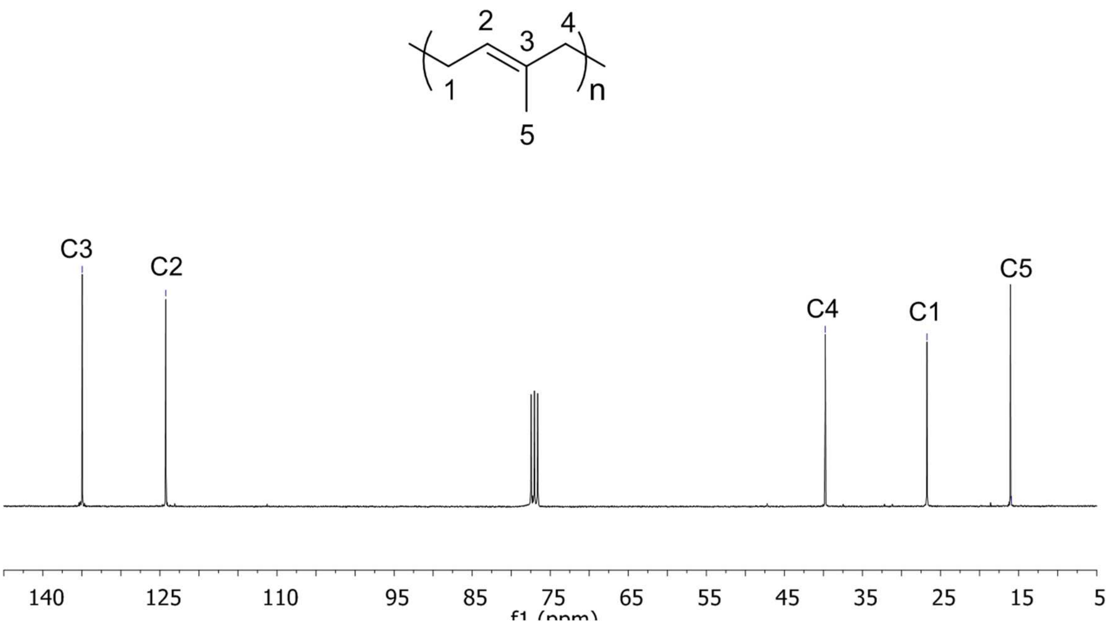


Figure SI9. ^{13}C-NMR spectrum of poly(1,4-*trans* isoprene) (entry 1)

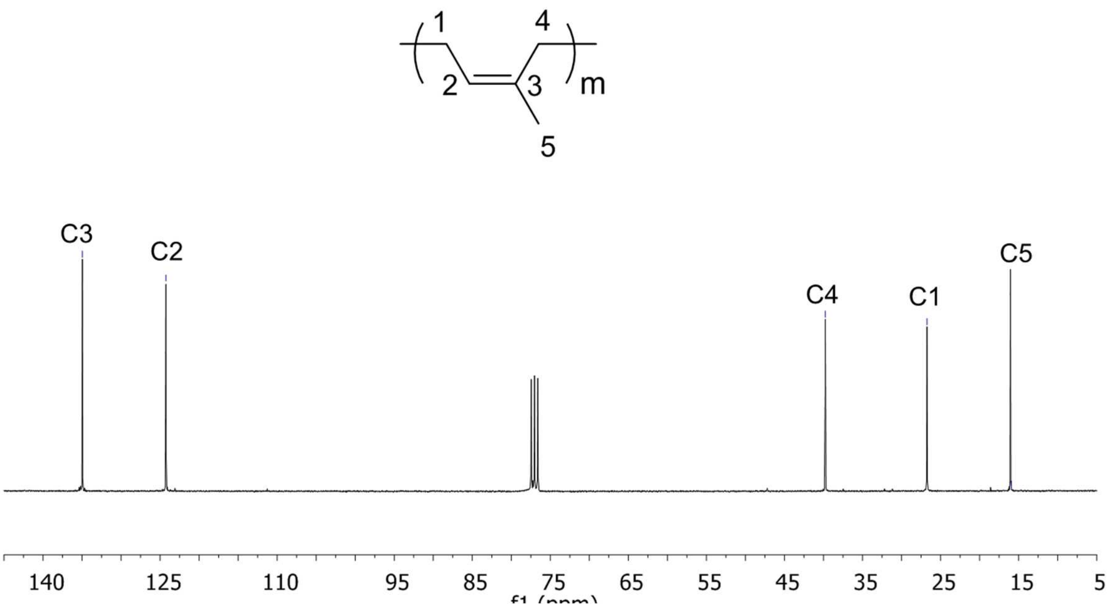


Figure SI10. ^{13}C-NMR spectrum of poly(1,4-*cis* isoprene) (entry 2)

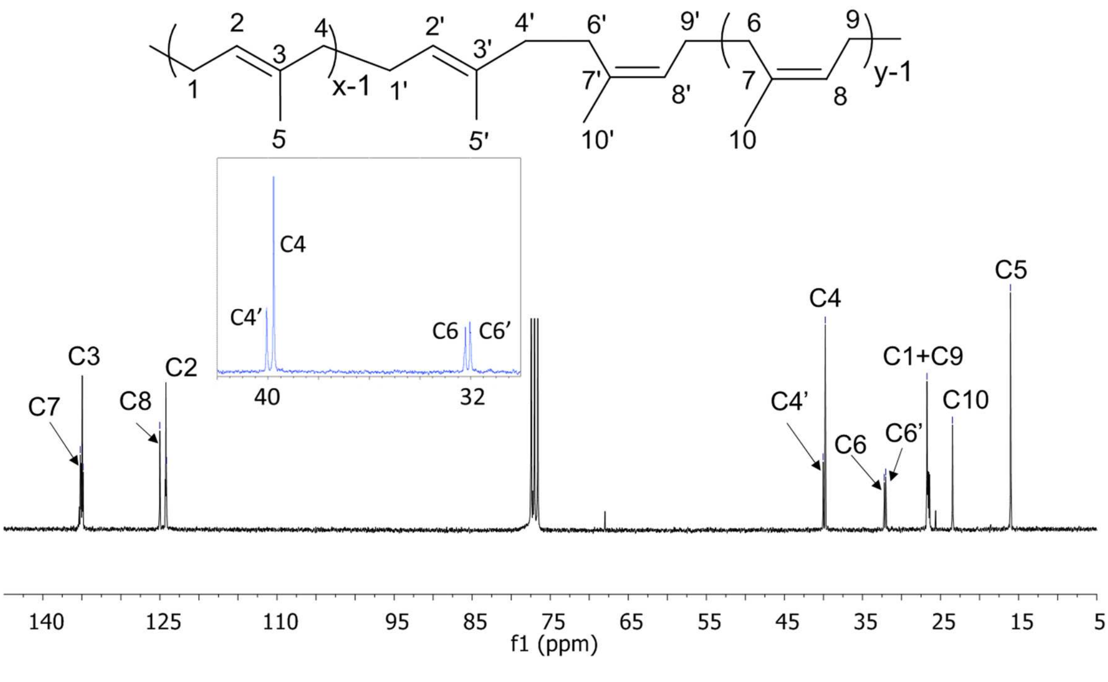


Figure SI11. ^{13}C -NMR spectrum of chain shuttled polyisoprene (entry 4) obtained using $AlEt_3$ as cocatalyst. Inlet : 32 – 40 ppm zone

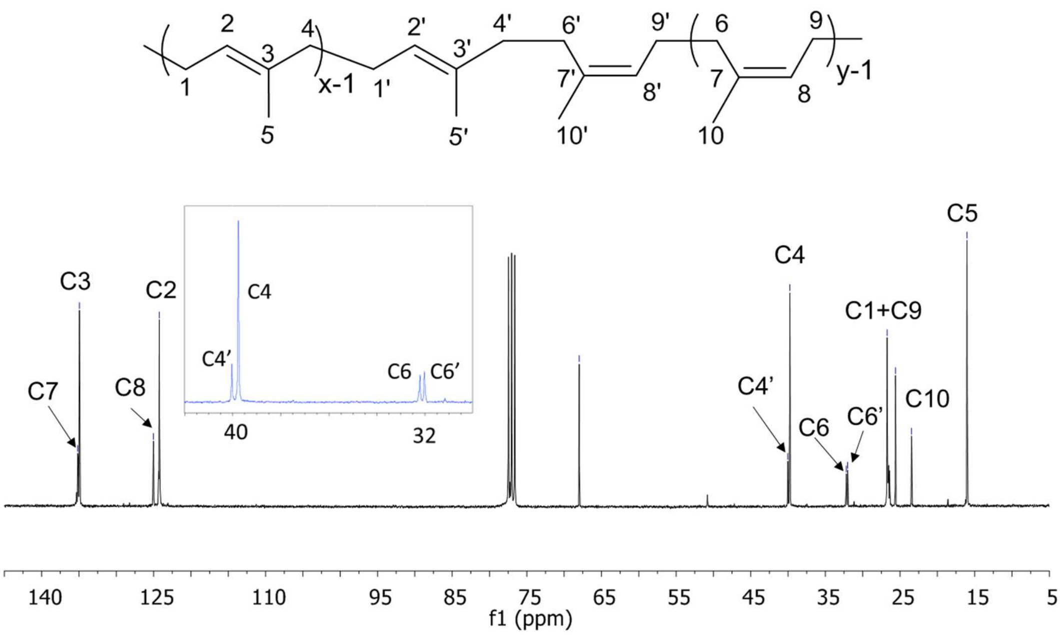


Figure SI12. ^{13}C -NMR spectrum of chain shuttled polyisoprene (entry 5) obtained using Al^iBu_3 as cocatalyst. Inlet : 32 – 40 ppm zone

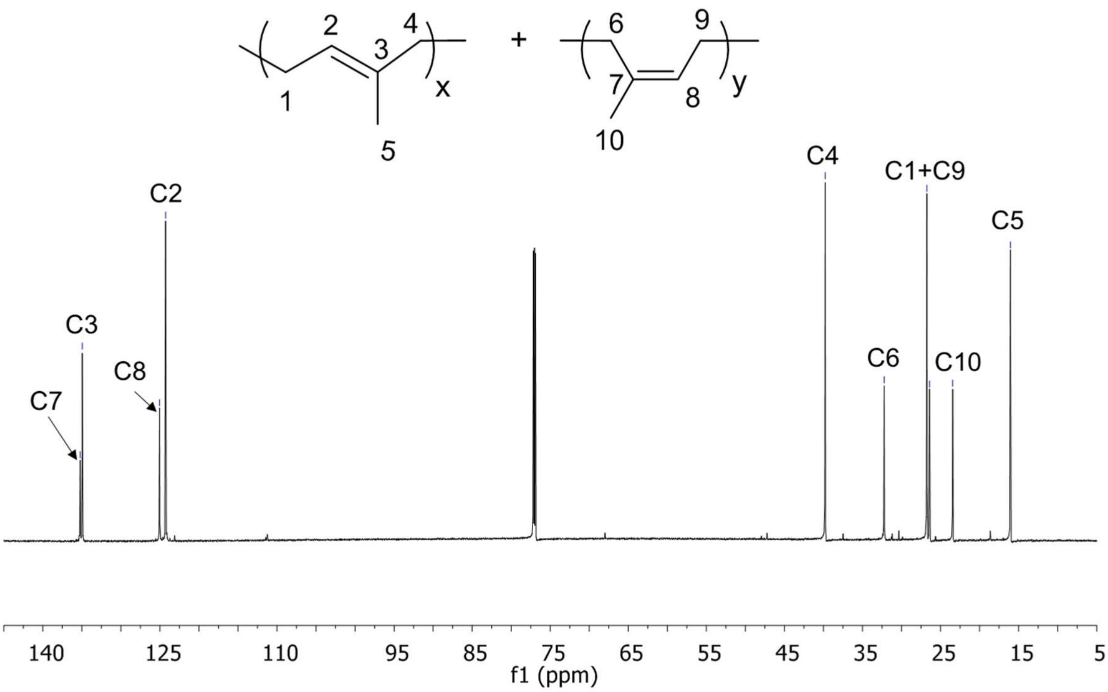


Figure SI13. ^{13}C-NMR spectrum of a mixture of poly(1,4-*cis* isoprene) and poly(1,4-*trans* isoprene) (entries 1 + 2) with a weight ratio cis/trans = 1/3.

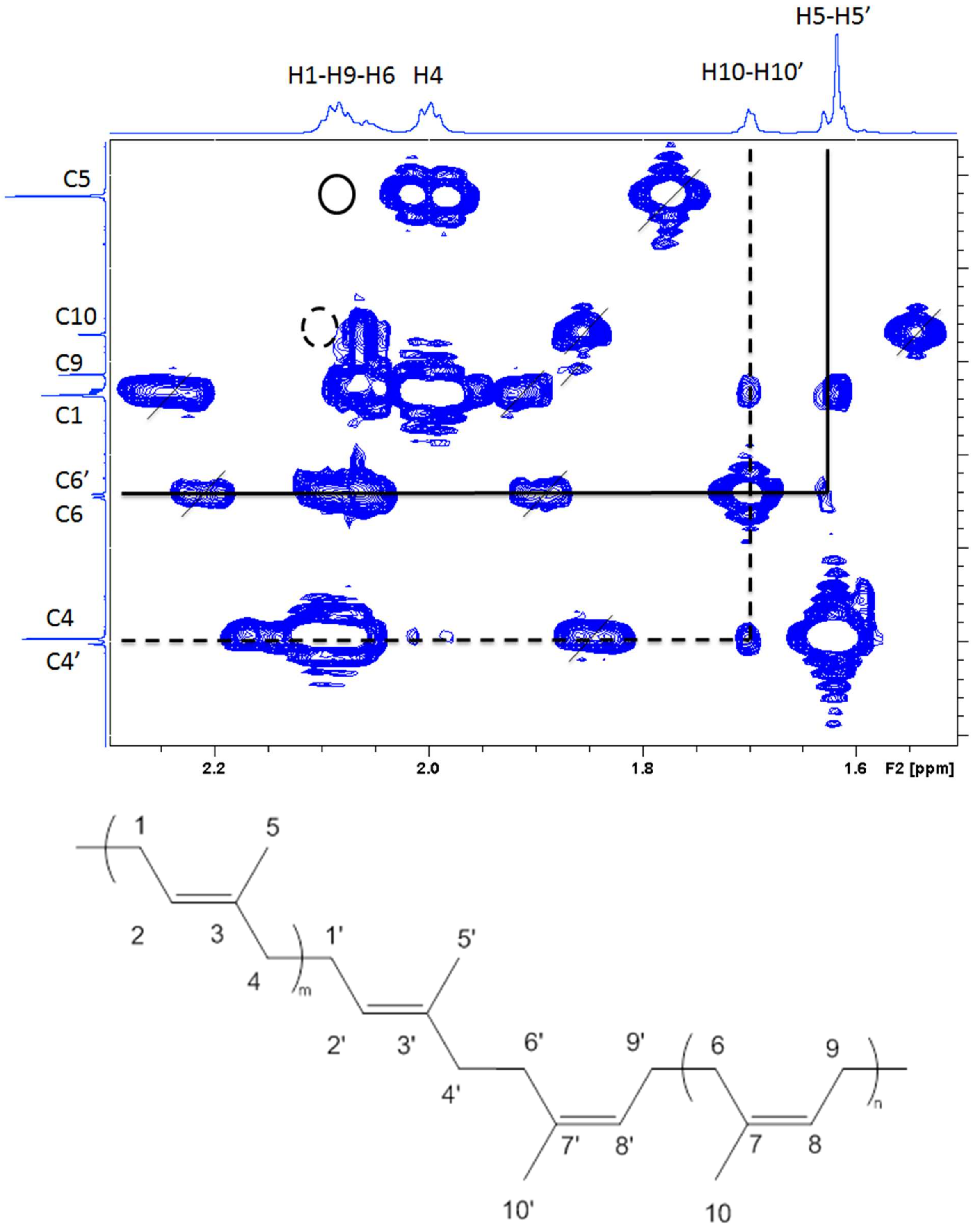


Figure SI14. 2D HMBC spectrum of chain shuttled polyisoprene (entry 5) obtained using $Al^{i}Bu_3$ as cocatalyst.

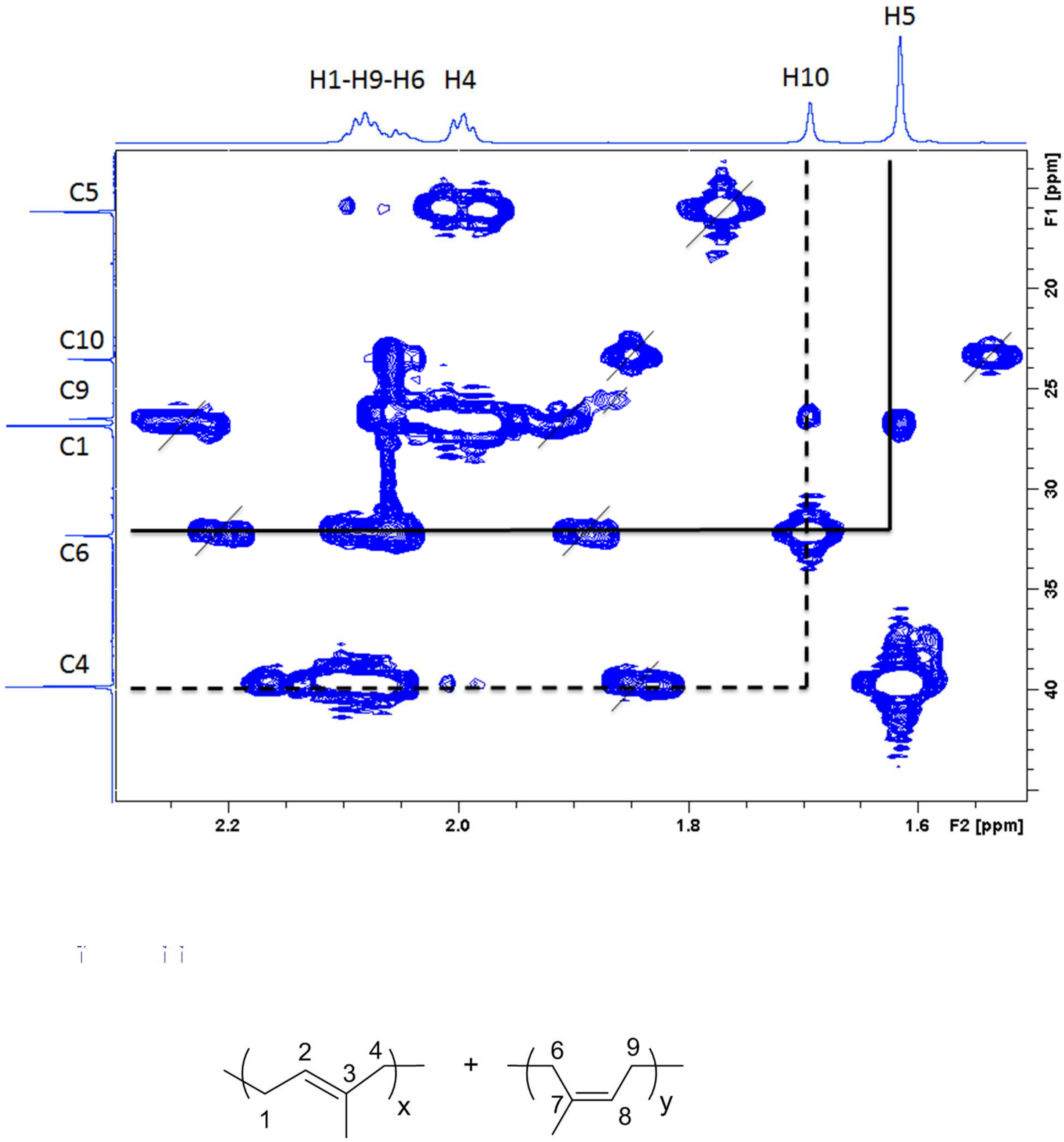


Figure SI15. 2D HMBC spectrum of a physical mixture of poly(1,4-*cis* isoprene) and poly(1,4-*trans* isoprene) (entries 1 + 2) with a weight ratio *cis*/*trans* = 1/3

Entry	Cata 1/2	AlR_3	Yield (%)	% *Trans*	% *Cis*[b]	1st heating			2nd heating		
						T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)
1	100/0	-	82	98	0	-64.7	58.0	65.3	-65.3	48.4	50
2	0/100	$AlEt_3$	61	0	97	-63.2	-	-	-63.2	-	-
3	0/100	$Al(^iBu)_3$	68	0	99	-63.0	-	-	-63.0	-	-
4	50/50	$AlEt_3$	76	68	30	-67.4	-	-	-67.4	-	-
5	50/50	$Al(^iBu)_3$	87	75	24	-66.8	38.6	7.5	-67.0	31.2	0.4
70/30 *trans/cis*	-	-	-	69	29	-64.7	43	3.2	-64.7	-	-

Table SI1. DSC (Differential Scanning Calorimetry) results including a second heating

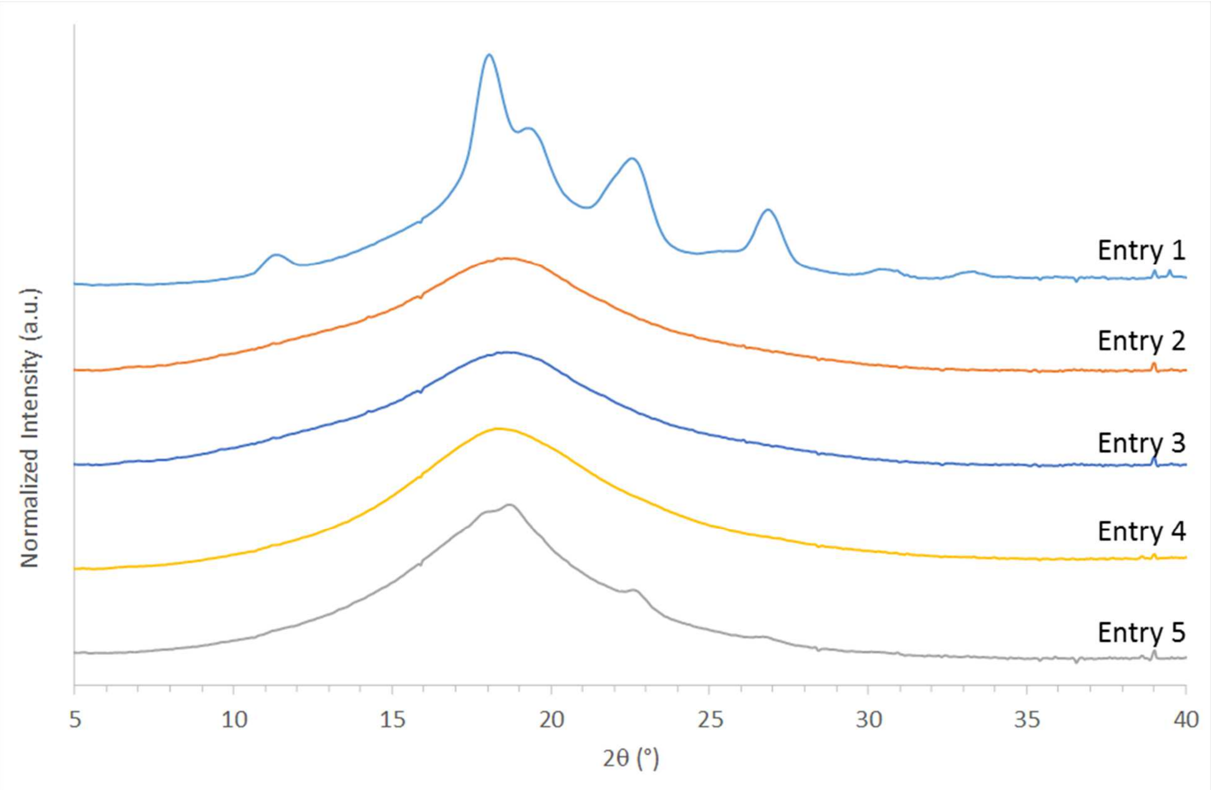


Figure SI16 WAXS analysis of entries 1-5

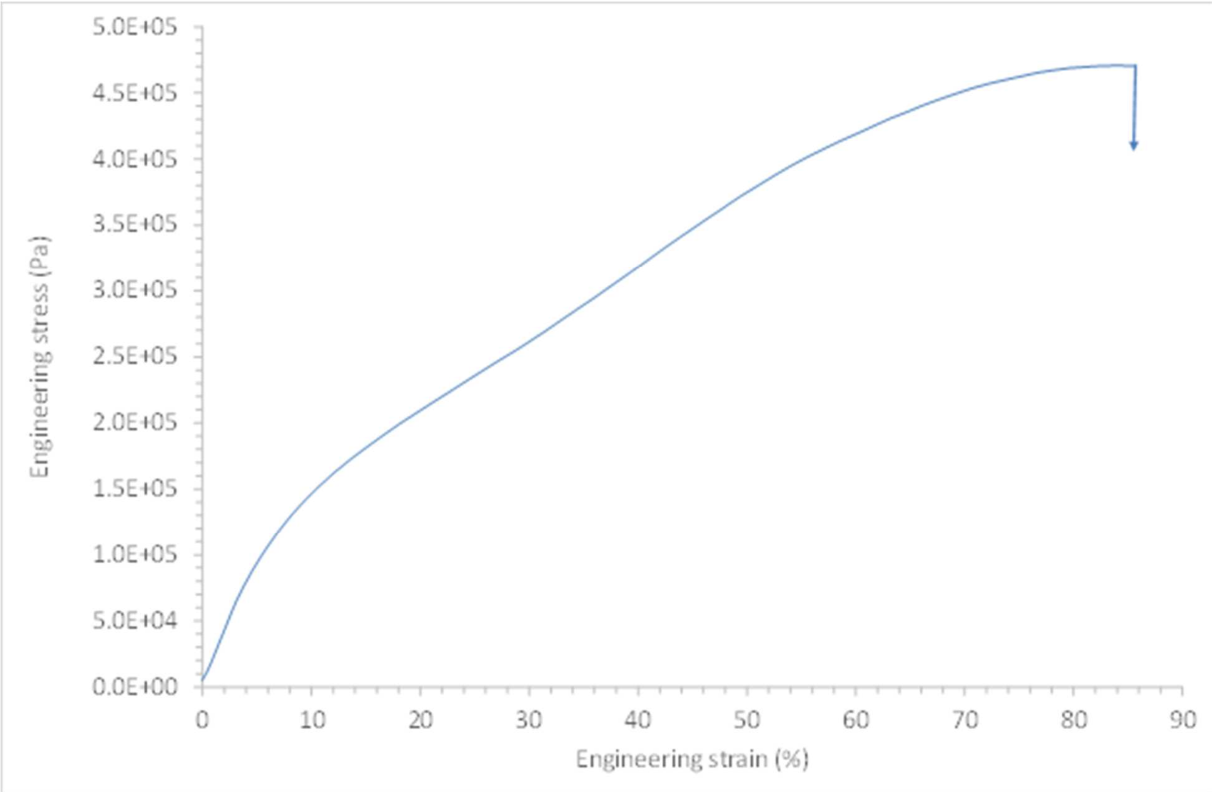
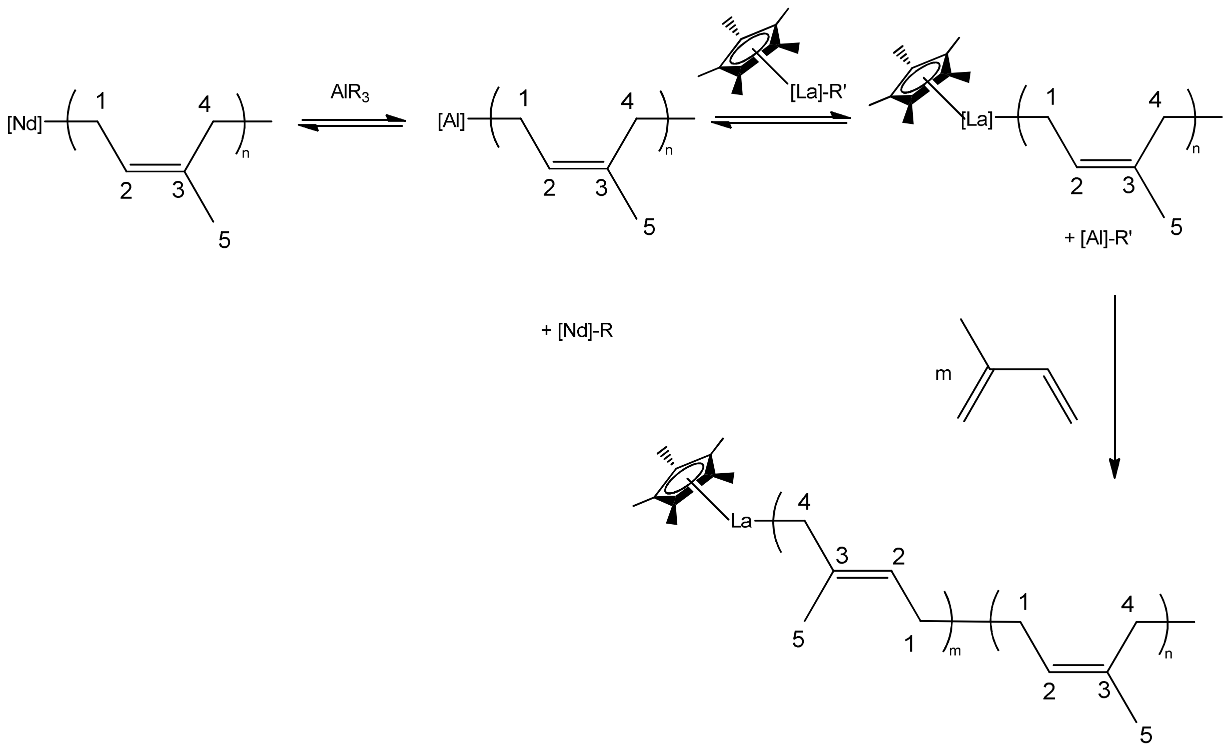


Figure SI17 Mechanical behaviour upon uniaxial stretching - entry 5



Scheme SI1. Proposed mechanism for the formation of c*is-trans* head-to-head enchainments under the hypothesis of a 4,1 polymerization of isoprene on the **2** / AlR_3 catalytic system.

AlR_3	**Time (h)**	**Yield (%)**	**%** ***Trans*** [b]	**%** ***Cis*** [b]	**% 3,4** [b]	M_n **g/mol** [c]	$Ð_m$ [c]
Et	1	13	0	98	2	189300	1.37
iBu	0.33	30	0	97	3	56500	2.65

Table SI2. Polymerization experiments using the $NdCl_3$ / 20 equiv. AlR_3 / 1 equiv . Mg^nBuEt. Experimental conditions similar to entries 4 and 5, Table 1, main manuscript. The reaction was stopped in both cases when the magnetic stirrer was blocked.