

## Supporting informations

### Experimental

#### Materials

All operations were performed under dry argon by using Schlenk techniques. Toluene was purified through alumina column (Mbraun SPS). Styrene and 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) was used as received. The complexes  $\text{Cp}^*\text{La}(\text{BH}_4)_2(\text{THF})_2$  (**1**)<sup>[SI1]</sup> and  $[(\text{C}_5\text{H}_4\text{CMe})_2\text{Nd}(\text{BH}_4)_2]_2\text{Mg}(\text{THF})_3$  (**2**)<sup>[SI2]</sup> were synthesized according to literature procedures.

#### Polymerization

In a glove box, the borohydrido complex(es) was (were) weighed into a vessel. Toluene, the monomers and BEM were added in the flask in this order using syringes. The mixture was magnetically stirred at the reaction temperature for a given time, quenched with methanol, eventually 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.

A blank experiment was made with BEM alone (without lanthanide catalysts) in the standards conditions (24h, ratio monomers/BEM 2000, *e.g.* entry 7). This led to 0.2% yield, probably due to the well-known initiation of a radical polymerization via a Diels-Alder dimerization of styrene (Mayo dimer).

#### Measurements

NMR spectra of the copolymers were recorded on a Bruker Avance 300 Instrument at room temperature in tetrachloroethane-*d*<sub>2</sub>. The chemical shifts were calibrated using the residual resonances of the solvent. Approximately 5 and 40 mg of sample were directly dissolved into the NMR tube in 0.6 mL of solvent for <sup>1</sup>H and <sup>13</sup>C NMR, respectively. 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 Diamond DSC apparatus at a heating rate of 20°C.min<sup>-1</sup> from -80°C to 120°C using around 10 mg samples in aluminum 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. Atomic Force Microscopy (AFM) analyses were performed on a Dimension 3100 apparatus from Digital Instruments operated in Tapping mode. The Nanoworld silicon SPM sensors (type NCL) has a tip radius less than 10 nm, the nominal spring constant and resonance frequency of the cantilever being, respectively, 48 N.m<sup>-1</sup> and 190 kHz. Observations were carried out on spin-coated samples. Samples were prepared by dissolving the copolymers in toluene at a concentration of 0.5 wt%. Thin films for AFM measurements were spin-coated from the solution onto silicon wafers at 2000 rpm during 60s at room temperature. The samples were let overnight in order to remove solvent traces. Small-Angle X-ray scattering (SAXS) analyses were carried out using a Genix microsource equipment (Xenocs) operating at 50 kV and 1 mA. The Cu K $\alpha$  radiation ( $\lambda$ = 1.54 Å) was selected with Fox2D curved mirror. The SAXS patterns were recorded on a VHR CCD camera (Photonic Sciences) in the transmission mode. The incoming and transmitted intensities were measured in order to perform blank corrections. Standard patterns corrections were also applied. Integrated intensity profiles were computed from the SAXS patterns using the FIT2D software. The SAXS intensity profiles were treated using the Irena Package.<sup>[SI3]</sup>

#### Fractionation

It is not easy to find a solvent combination selective for the two blocks, as both blocks are composed of both isoprene and styrene. A solvent combination selective for the polyisoprene / polystyrene combination is dimethylformamide (DMF) / heptane. Polystyrene is soluble in DMF, but not in heptane, while polyisoprene is soluble in heptane, but not DMF. The extractions were performed for 3 days at room temperature. The copolymers obtained with **1** containing 12% styrene, typically entry 1, were found to be soluble in heptane, but not in DMF, a behavior similar to polyisoprene. The copolymers obtained with **2**, comprising 50% of each monomer, were found to be neither soluble in hexane, nor in DMF. No polymer could be extracted from the block copolymers made by chain shuttling using DMF. The results of the extractions conducted using heptane are presented in the table hereafter. As one can see, the styrene content of the extract fraction is close but slightly lower than that of the copolymer (36 vs. 38% and 40 vs. 42% for entries 14 and 15 respectively), and different from that of the copolymer obtained using **1** alone (12%). The solubility of the extracted fraction can be explained on the basis of a lower number-average molecular weight combined to a slightly lower styrene content. This shows clearly the absence of copolymers formed using **1** alone.

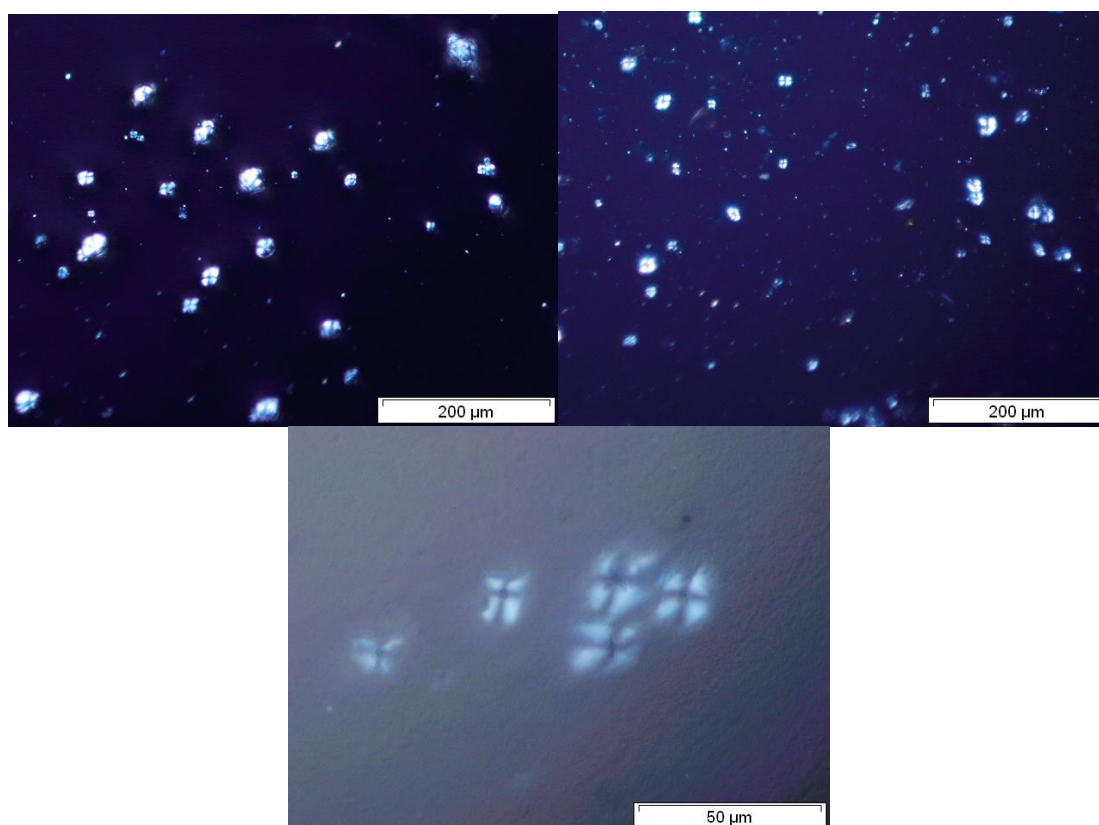
**Table SI1.** Typical fractionation results

Entry	St in copolymer <sup>[a]</sup> (%)	$M_n^{[b]}$ (g/mol)	$\bar{D}_M^{[b]}$	Hexane soluble part			
				Fraction extracted wt%	St (%) <sup>[a]</sup>	$M_n$ (g/mol) <sup>[b]</sup>	$\bar{D}_M^{[b]}$
14	38	80400	1.7	18	36	31000	2.1
15	42	85900	1.8	5	40	17100	1.8

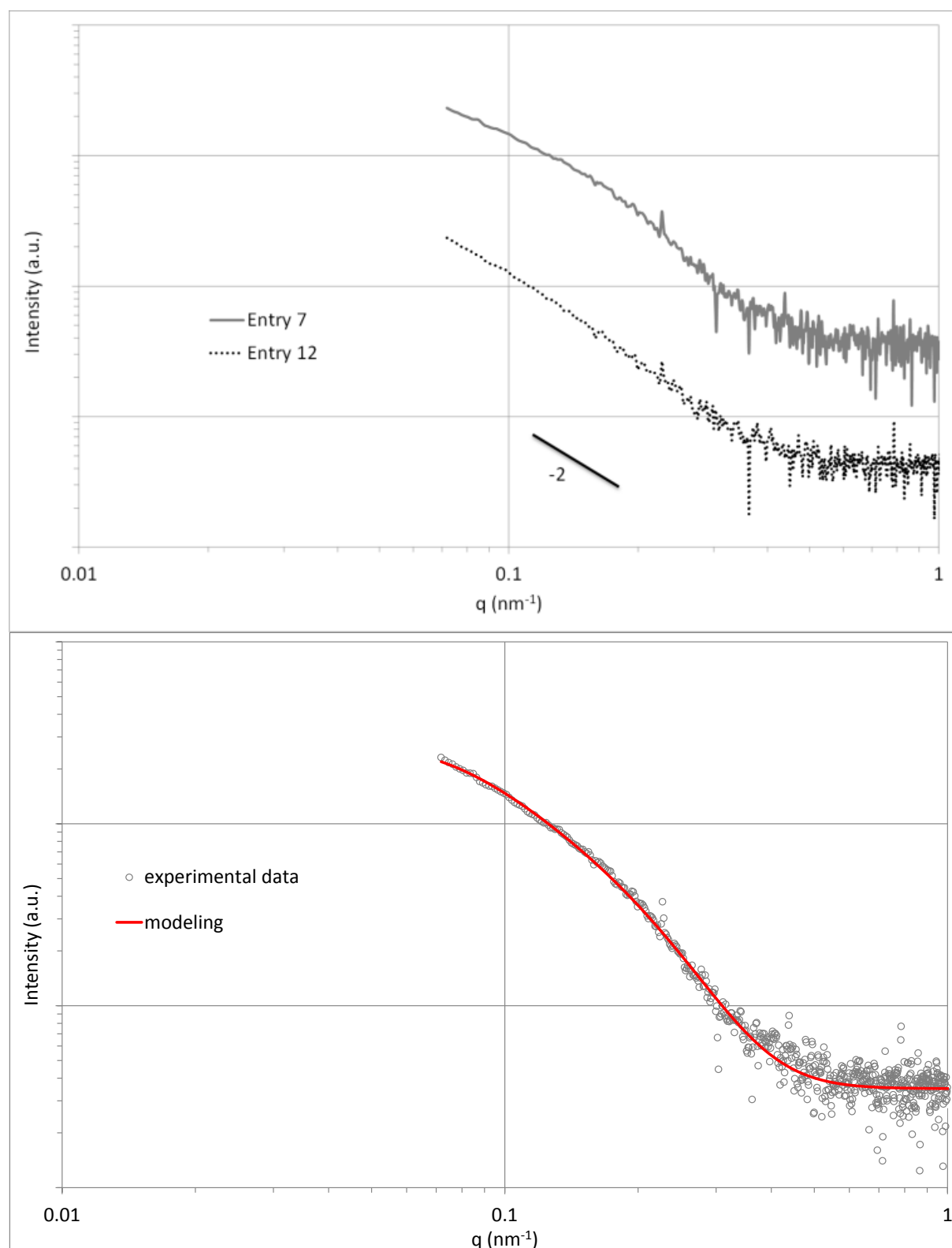
[a] Determined by  $^1\text{H}$  NMR; [b] Number-average molecular weight and dispersity determined by size exclusion chromatography using polystyrene standards.

#### *Blends of copolymers obtained using 1 and 2 separately*

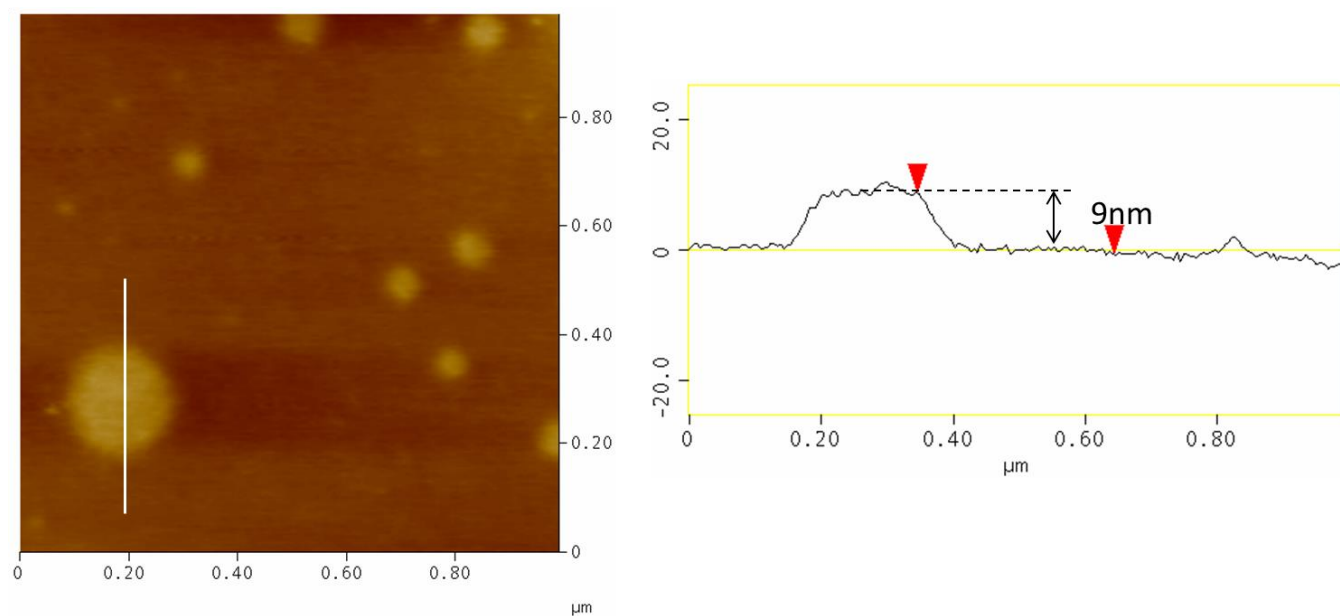
Spherulite formation can be observed by polarized light microscopy for the blend of the copolymers made separately (fig SI1) indicating phase separation, while the copolymers made by chain shuttling are perfectly transparent (see figure 2 in the manuscript). This confirms further the formation of multiblocks by chain shuttling.



**Figure SI1.** Polarized light microscopy analysis of a blend of the copolymers obtained using 1 and 2.



**Figure SI2.** Top: Log plot of SAXS integrated intensity profiles of entry 7 and 12.  
Bottom: Modeling of entry 7 scattering profile



**Figure SI3.** Line profile analysis of a hard nanodomain (entry 7).

## References

- [SI1] A. Valente, P. Zinck, A. Mortreux, M. Visseaux, *Macromol. Rapid. Commun.*, **2009**, *30*, 528-531.
- [SI2] M. Visseaux, M. Terrier, A. Mortreux, P. Roussel, *Eur. J. Inor. Chem.*, **2010**, *18*, 2867-2876.
- [SI3] J. Ilavsky, P. R. Jemian, *J. Appl. Cryst.*, **2009**, *42*(2), 347-353.