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Block Copolymerization

Isoprene–Styrene Chain Shuttling Copolymerization Mediated by a Lanthanide Half-Sandwich Complex and a Lanthanidocene: Straightforward Access to a New Type of Thermoplastic Elastomers**

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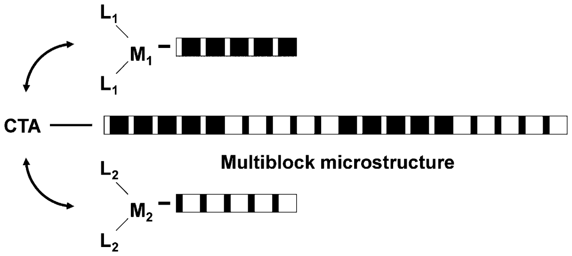
Abstract: *A lanthanide half-sandwich complex and a ansa lanthanidocene have been assessed for isoprene–styrene chain shuttling copolymerization with n-butylethylmagnesium (BEM). In the presence of 1 equiv BEM, a fully amorphous multiblock microstructure of soft and hard segments is achieved. The microstructure consists of poly(isoprene-co-styrene) blocks, with hard blocks rich in styrene and soft blocks rich in isoprene. The composition of the blocks and the resulting glass transition temperatures (T_g) can be easily modified by changing the feed and/or the relative amount of the catalysts, highlighting a new class of thermoplastic elastomers (TPEs) with tunable transition temperatures. The materials self-organize into nanostructures in the solid state.*

Thermoplastic elastomers (TPEs) are materials that exhibit an elastic behavior similar to that of vulcanized rubber.[1] In contrast to thermosets elastomers, they possess thermoreversible cross-links and can be processed as thermoplastics. TPEs are widely used to improve the properties of rigid thermoplastics, notably their impact strength. TPEs in the form of block copolymers can furthermore self-assemble in the solid state or in solution, leading to nanostructures with a variety of properties and potential functions.[2] Poly(styrene-*co*-butadiene-*co*-styrene) triblock copolymers have been commercialized and are used as bitumen additives and viscosity modifiers.[2,3] The polybutadiene block shows a glass transition temperature below room temperature, providing the elastomeric character or soft block, while polystyrene with a T_g above room temperature acts as the cross-link or hard block. Di- and triblock copolymers are formed by anionic polymerization,[1] while multiblock microstructures of homopolymers can be obtained by chain shuttling copolymerization (see below).[4d] These blocky structures show well-defined transition temperatures (T_g or melting temperature of the homopolymers) that cannot be tuned, which restricts their fields of application. An approach that is able to tune the transition temperatures of the blocks may widen the applications of these materials to other fields including for example shape memory polymers. The synthesis of such adjustable structures is not an easy task and requires the use of advanced synthetic methods.

Chain shuttling polymerization[4] is a process based on coordinative chain transfer polymerization[5,6] that gives access to multiblock microstructures (Scheme 1). The growing macromolecular chain is allowed to "shuttle" between two catalysts presenting a difference in monomer selectivity via a chain transfer agent. Our objective in this study was to extend the potentialities of chain shuttling copolymerization to the synthesis of a new class of thermoplastic elastomers with variable transition temperatures. As the T_g of statistical copolymers can be easily varied by a change of their composition, a fully amorphous multiblock microstructure consisting of hard and soft statistical copolymers was targeted. Over the last few years, we have developed catalytic systems based on lanthanide half-sandwich complexes for the coordinative chain transfer polymerization and copolymerization of conjugated dienes, styrene, and 1-alkenes.[6] We elaborated our strategy based on this knowledge. Borohydrido half-lanthanidocenes are known to lead to isoprene-rich poly(isoprene-*co*-styrene) copolymers with a high 1,4-*trans* stereoselectivity when combined to magnesium dialkyls. We envisioned the use of a sterically hindered complex as second precatalyst to obtain styrene-rich poly(isoprene-*co*-styrene)



Scheme 1. Chain shuttling copolymerization. M_i represents transition metals or lanthanides allowing propagation, L_i ligands, and CTA the chain transfer or chain shuttling agent.

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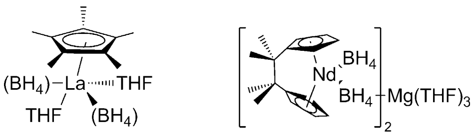
blocks. Lanthanum- and neodymium-based pre-catalysts were found to be particularly well-suited for the reversible transmetalation of a growing polymeric chain with magnesium dialkyls. Herein we present the first example of a chain shuttling copolymerization leading to a fully amorphous multiblock microstructure of soft and hard statistical copolymers, providing a straightforward access to a new class of thermoplastic elastomers with variable transition temperatures. Isoprene and styrene were selected as monomers, the lanthanum half-sandwich complex [Cp*La$(BH_4)_2(THF)_2$] (**1**) (Cp* = C_5Me_5), and the *ansa*-neodymocene [$(C_5H_4CMe)_2Nd(BH_4)_2]_2Mg(THF)_3$ (**2**) as pre-catalysts (Scheme 2) and *n*-butylethylmagnesium as the chain-transfer agent.



Scheme 2. The pre-catalysts used in this study.

Experiments that are representative of the statistical copolymerization of isoprene and styrene (50:50 molar ratio) conducted in the presence of either **1** or **2** combined to 1 and 10 equiv BEM are presented in Table 1, entries 1–5. The decrease of the number-average molecular weight observed for 10 equiv BEM vs. 1 equiv shows that the transmetalation is occurring efficiently with both pre-catalysts. Statistical copolymers with a unique T_g and monomodal molecular weight distributions are obtained. Compound **1** leads to isoprene-rich statistical copolymers exhibiting a low T_g, while the copolymers obtained with **2** show higher styrene content and higher T_g. The chromatograms reveal a monomodal distribution of the molecular weight in all cases.

Chain shuttling experiments were first conducted with a 50:50 molar ratio of the monomers and a 50:50 molar ratio of the catalysts (entries 6–10, Table 1). NMR investigations of possible ligand exchange were conducted prior to polymerization, and no ligand exchange between the two complexes was observed in [D_6]benzene after several hours at 50 °C before and after introduction of 10 equiv BEM. The decrease of the number-average molecular weight with increasing quantities of BEM shows that the transmetalation is occurring efficiently. The copolymer obtained using **1** + **2** and 1 equiv BEM exhibits an overall composition comprised between those obtained using **1** and **2** alone (39 % styrene inserted in the copolymer vs. 12 and 50 %, respectively) and a highly 1,4-*trans* microstructure of the polyisoprene part. The occurrence of chain shuttling between the two catalysts was assessed from the chromatograms obtained after 2 h reaction (Figure 1). The molecular-weight distribution of the copolymer obtained by chain shuttling is monomodal, and located between those obtained using **1** and **2** alone. The resulting polymer is characterized by two T_g, the lower one being ascribed to the glass transition of isoprene rich blocks and the higher one to styrene-rich blocks. Such characteristics are typical of thermoplastic elastomers. Endothermic peak resulting from the melting of polyisoprene crystalline phase could not be observed, confirming the amorphous nature of the materials. The formation of the multiblock microstructure was confirmed by fractionation experiments showing that the reaction product is not a mixture of the copolymers made by **1** and **2** separately (see the Supporting Information). Additionally, the blend of the copolymers made by **1** and **2** separately shows a phase separation (Supporting Information, Figure S1), while the copolymers formed by chain shuttling are fully transparent (see a typical example in Figure 2).

Chain shuttling copolymerizations were further conducted in the presence of increasing amounts of BEM

Table 1: Isoprene–styrene statistical and chain shuttling copolymerizations using **1** and **2** in combination with BEM.

Entry[a]	Pre-catalysts **1**/**2**	Ip/St	Mg [equiv]	*t* [h]	Yield [%]	M_n[b] [g mol^{-1}]	$Đ_M$[b]	Ip[c] [%]	St[c] [%]	Polyisoprene microstructure[c] 1,4-*trans* [%]	1,4-*cis* [%]	3,4 [%]	T_g [°C]
1	100:0	50:50	1	2	48	45 200	1.3	88	12	98	–	2	−50
2	100:0	50:50	10	40	58	8100	1.8	68	32	84	–	16	−26
3	0:100	50:50	1	2	5	9400	1.3	50	50	100	–	–	nd
4	0:100	50:50	1	24	26	45 300	1.6	50	50	100	–	–	5
5	0:100	50:50	10	30	79	10 700	1.8	48	52	100	–	–	2
6	50:50	50:50	1	2	8	23 200	1.4	70	30	100	–	–	nd
7	50:50	50:50	1	24	68	62 300	2.1	61	39	100	–	–	−15, 41
8	50:50	50:50	3	24	76	33 800	2.3	55	45	100	–	–	0
9	50:50	50:50	5	24	75	19 800	2.0	52	48	100	–	–	−2
10	50:50	50:50	10	26	72	10 000	1.8	62	38	92	–	8	−10
11	50:50	30:70	1	2	11	25 700	1.2	60	40	96	4	–	−10, 34
12	50:50	30:70	1	24	61	60 600	2.3	56	44	94	6	–	−3, 31
13	50:50	70:30	1	18	84	82 700	1.6	76	24	99	1	–	−35, 36
14	30:70	50:50	1	24	74	80 400	1.7	62	38	100	–	–	−10, 40
15	10:90	50:50	1	24	62	85 900	1.8	58	42	100	–	–	−2, 36
16	70:30	50:50	1	24	67	80 200	1.6	69	31	100	–	–	−27

[a] Reactions conducted at 50 °C in toluene for a monomers/pre-catalyst(s) ratio of 2000 (for example, 1.1 mL styrene (10^{-2} mol) and 1 mL isoprene (10^{-2} mol) in 1.5 mL toluene for a 50:50 molar ratio of the monomers). [b] Number-average molecular weight and dispersity determined by size-exclusion chromatography using polystyrene standards. [c] From ^{1}H and ^{13}C NMR spectroscopy measurements.

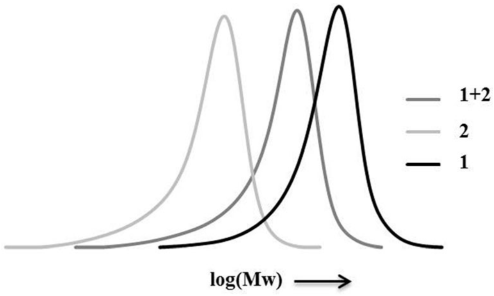


Figure 1. Molecular weight distributions obtained by size-exclusion chromatography after 2 h reaction (Table 1, entries 1, 3, and 6).

Figure 2. An image of the sample from Table 1, entry 7 cast onto a glass slide.

(Table 1, entries 8–10). A unique T_g was observed for these copolymers, showing that the microstructure has shifted from a thermoplastic elastomer material to a more conventional statistical copolymer. In the presence of excess BEM, the transmetalation does not allow sufficient chain growth on each of the catalysts to afford the multiblock microstructure. Keeping in mind that substantial quantities of chain shuttling agent are usually required for the formation of the multiblock microstructure by chain shuttling polymerization, it is noteworthy that we achieve this goal with only 1 equiv. Chain shuttling copolymerization experiments conducted in the presence of 1 equiv BEM with excess styrene (entries 11 and 12) and excess isoprene (entry 13) in the feed are presented in Table 1. Two T_g values are also observed for these materials, highlighting again the formation of the multiblock microstructure. The influence of the catalyst ratio was further assessed (entries 14–16). If an excess of **2** leads to the desired multiblock microstructure, the copolymer resulting from the reaction conducted with 70 % of **1** shows only one T_g value. It is noteworthy that both the modification of the feed and that of the relative amount of the catalysts lead to a variation of both T_g.

The nanostructure of the copolymers was investigated by means of small-angle X-ray scattering (SAXS). A scattering contrast could be observed only for samples exhibiting the multiblock microstructure (see typical examples in the Supporting Information, Figure S2). The scattering curves could be modeled by a dispersion of dilute disks having an average thickness of 6 ± 1 nm. From a structural point of view, this can be interpreted by the self-assembly of one of the blocks into lamellas. The dilute term of the model indicates furthermore that the lamellas are non-interacting, or in other words that there is no nanostructuration of the lamellas at a large scale.

Atomic force microscopy (AFM) analyses were performed to pursue the investigation of the nanostructure (Figure 3). In the presence of **1** or **2** alone, when a random copolymer is formed, a uniform structure is observed (entry 4 in Figure 3). The nanostructuration of the samples resulting from chain shuttling copolymerization in the presence of 1 equiv BEM can be seen Figure 3, entries 7 and 11. Assuming that bright domains are assigned to hard domains, the nanodomains correspond to a self-assembly of the rigid blocks. AFM line profile analysis (Supporting Information, Figure S3) shows that the top of the hard domains is flat, indicating a disk-like shape. The height of the disks (about 9 nm) is in good agreement with the values obtained from SAXS. Finally, the examination of a sample synthesized by chain shuttling with a higher amount of BEM (entry 10 in Figure 3) does not show the presence of disk-like nanodomains. This is in agreement with the thermal properties of this material for which only one T_g was detected as expected for a random copolymer structure.

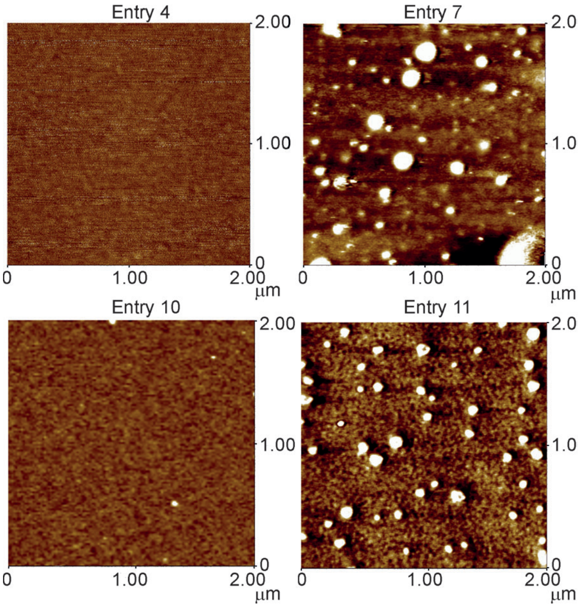


Figure 3. AFM phase contrast images of samples from Table 1, entries 4, 7, 10, and 11 (*z* scale = 20°).

In summary, we report a synthetic approach affording a straightforward access to an unprecedented fully amorphous multiblock microstructure of soft and hard statistical copolymers. The microstructure consists of blocks of poly(isoprene-*co*-styrene) copolymers, with hard blocks rich in styrene and soft blocks rich in isoprene. The T_g of the blocks can be varied simply by changing the feed or the relative amount of the catalysts, and the resulting copolymers self-organize into nanostructures. Additional work is currently in progress to explore the potential applications of these new block copolymers.

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Keywords: block copolymers · chain shuttling · coordinative chain transfer polymerization · copolymerization · lanthanides

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