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Stereocontrolled styrene–isoprene copolymerization and styrene–ethylene–isoprene terpolymerization with a single-component allyl *ansa*-neodymocene catalyst

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ABSTRACT

The *ansa*-metallocene complex (CpCMe$_2$Flu)Nd(C$_3$H$_5$)(THF) (**1**) is an effective single-component catalyst for the production of syndiotactic styrene-rich polymer materials modified by isoprene and/or ethylene. The recovered copolymers have high molecular weights ($M_n = 12{,}000$–$91{,}000$ g/mol) and unimodal, relatively narrow molecular weight distributions ($M_w/M_n = 1.3$–2.8). The comonomer feeds can be easily manipulated to tune the respective amounts of monomers incorporated in the copolymer and eventually modify the final properties (T_m, T_g) of the obtained materials.

1. Introduction

Copolymerization is the most commonly used method to tune the polymer characteristics. Many efforts have been paid accordingly to improve syndiotactic polystyrene (sPS) brittleness and high melting temperature, which constitute major limitations for processability of this material. However, only a few catalytic systems are able to efficiently copolymerize styrene with ethylene (or an α-olefin) to give stereocontrolled styrene-rich copolymers without homopolymers' contamination [1]. Cationic scandium half-metallocenes give multiblock styrene-rich (up to 87 mol%) styrene–ethylene copolymers presenting long, highly syndiotactic polystyrene sequences alternated with polyethylene sequences [2]. We also recently reported on single-component neutral allyl *ansa*-neodymocene catalysts, e.g. (CpCMe$_2$Flu)Nd(C$_3$H$_5$)(THF) (**1**) [3] (Cp = C$_5$H$_4$, Flu = 9-fluorenyl), that allow the preparation of styrene-rich (up to 98 mol%) copolymers with a different microstructure, *i.e.* isolated ethylene units are incorporated into highly syndiotactic polystyrene chains [4,5]. Compared to pure sPS, these materials feature quite different thermo-mechanical properties (lower T_m, T_g, and elasticity modulus).

The styrene-1,3-diene copolymerization field has been much more explored than the styrene–ethylene copolymerization, in particular for the synthesis of styrene–butadiene rubbers (SBRs). This kind of copolymers is usually obtained with radical [6,7] or anionic [8,9] processes that do not allow precise regio- and stereocontrol. Some transition metal-based catalyst systems have been also reported to copolymerize styrene with 1,3-dienes. Systems based on group 4 and late transition metals were generally found to be poorly stereoselective, giving prevailingly 1,4-*cis* microstructure regardless of the ancillary ligand used [10–13]. Ternary systems lanthanide tricarboxylate/Al(iBu)$_3$/AlEt$_2$Cl are active for styrene–butadiene and styrene–isoprene copolymerizations, giving copolymers with up to 60 mol% styrene and a predominant 1,4-*cis* microstructure of the diene units [14–16]. Random and block copolymerizations of styrene and butadiene were also achieved with the bimetallic complex Cp$^*_2$Sm(μ-Me)$_2$AlMe$_2$ [17] and other binary systems based on an alkylating agent and homoleptic lanthanide pre-catalysts such as Nd(acac)$_3$ [18], Nd(phosphonate)$_3$ [19] or Nd(amide)$_3$ [20]. For all these catalyst systems, a decrease in the *cis* stereoselectivity of the diene incorporation was observed with increasing styrene content, which was attributed to a disturbance of the back-biting coordination and inhibition of the terminal butadiene unit control; also, the polystyrene blocks were not stereocontrolled. Very recently, Grassi and co-workers reported the copolymerization of styrene with isoprene or butadiene in the presence of a Ti(Cp)(phenolate)Cl/MAO binary catalyst to yield

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block copolymers containing segments of *cis*-1,4-polydiene and crystalline syndiotactic polystyrene (up to 73 mol%) [21]. On the other hand, catalysts able to copolymerize styrene with diene affording 1,4-*trans* selectivity remain rare. Stereoselective 1,4-*trans* diene–styrene copolymerization, with up to 30 mol% inserted styrene, was reported with lanthanide borohydrides/MgR_2 [22]. Quite recently also, a Ti-bis(phenolate)/MAO system was found to produce highly isotactic polystyrene-*co*-*trans*-1,4-polybutadiene with a wide range of compositions (15–97 mol% of styrene) [23].

Furthermore, there are very few examples of styrene–ethylene–diene terpolymerization in the academic and patent literature [1]. The introduction of vinyl aromatic comonomers was found to be problematic with most of the classical catalyst systems. Using “constrained geometry” Ti catalysts, DSM [24] and Mülhaupt and Sernetz [25] achieved to terpolymerize styrene, ethylene and a *non-conjugated* diene (1,7-octadiene and 1,5-hexadiene, respectively). In the first case, however, both styrene and diene contents were very low (≤3 and 0.6 mol%, respectively) [24]. Since 1,5-hexadiene cyclizes during its insertion, its incorporation led to original cycloolefin terpolymer containing styrenic units, but with a very broad polydispersity ($M_w/M_n = 14.5$) [25]. Styrene–ethylene–dicyclopentadiene terpolymerization with an Sc half-metallocene catalyst affords random cyclic olefin terpolymers with styrene contents ranging from 4 to 57 mol% and diene contents of 5–26 mol% [26]. As far as we are aware, there is, to date, no example of terpolymers of styrene, ethylene and a *conjugated* diene.

Herein, we report on the use of allyl *ansa*-neodymocene complex **1** as a single-component catalyst for the copolymerization of styrene with isoprene, affording copolymers with 1,4-*trans* diene units and syndiotactic polystyrene sequences, as well as styrene–ethylene–isoprene terpolymerization, giving brand new polymers. Preliminary analyses indicate that these materials feature different thermo-mechanical properties compared to sPS.

2. Results and discussion

2.1. Isoprene homopolymerization

A preliminary investigation showed that (CpCMe$_2$-Flu)Nd(C_3H_5)(THF) (**1**) [3] is able to homopolymerize isoprene with a moderate activity (122 kg PI/(mol(Nd) h) at 60 °C in bulk) (Table 1, entry 2). The recovered polymer material was fully soluble in chloroform but partly soluble (ca. 95 wt%) in THF at room temperature, while regular polyisoprenes (1,4-*trans*, 1,4-*cis*, 3,4- and 1,2-) are usually highly soluble in the latter solvent. This observation strongly suggests the presence of cyclized polyisoprene sequences [27–30].

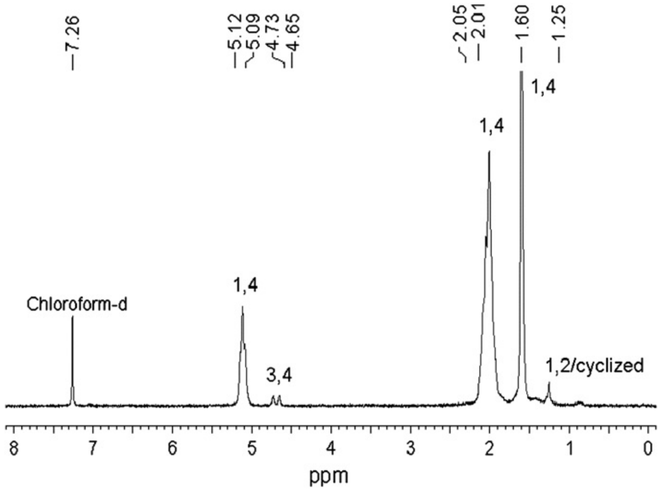


Fig. 1. ^1H NMR spectrum (200 MHz, 25 °C, $CDCl_3$) of 1,4-*trans*-enriched polyisoprene prepared with complex **1**.

The ^1H NMR spectrum (Fig. 1) of the polyisoprene in $CDCl_3$ indicates a predominant (ca. 95%) 1,4-microstructure and the ^{13}C NMR spectrum (Fig. 2) showed diagnostic signals for a *trans* configuration [31] (δ 16.20, 26.91, 39.92, 124.42 and 135.12 ppm). Minor resonances were also observed and assigned to 3,4-isoprene units [32–34] (δ 18.76, 37.64, 111.41 and 147.85 ppm), and 1,2- and/or cyclized units (δ 31.33, 68.15 and 123.26 ppm). Thus, the regiocontrol for the polymerization of a conjugated diene with complex **1**, though quite significant, is not as high as that observed for styrene [3–5].

The T_m value of 49 °C determined by DSC differs significantly from the values observed for regular (non-cyclized) 1,4-*trans* ($T_m = 60$–67 °C) and 1,4-*cis* ($T_m = 28$–42 °C) isomers [35]. The latter observation might be consistent with the presence of a few 3,4- and 1,2-unit as well as fused-ring sequences. It might also reflect a rather low molecular weight [36].

In fact, the THF soluble fraction was analyzed by GPC and shown to have $M_n = 27{,}000$ g/mol and $M_w/M_n = 1.09$. The very narrow molecular weight distribution and the good agreement between the experimental and calculated M_n values ($M_{n,calc} = 35{,}000$ g/mol, considering the 29 mol% conversion of the monomer) demonstrate the “living-controlled” behavior of this polymerization.

Table 1
Styrene–isoprene copolymerization catalyzed by complex **1**[a]

Entry	[St]/[Nd]	[St][b]	[Ip][b]	T (°C)	Time (min)	Yield[c] (g)	Activity[d] (kg/(mol h))	St[e] (mol%)	M_n[f] × 10^3 (g/mol)	M_w/M_n[f]	T_m[g] (°C)	T_g[g] (°C)	T_g[h] (°C)
1	600	8.7	–	60	5	2.3	1710	100	54	1.73	264	–	nd
2	–[i]	0	10	60	35	2.0	122	0	27	1.09	49	–	nd
3	600	4.7	4.0	60	6	2.4	550	70	55	1.54	–	–	63
4	600	6.0	3.0	60	15	3.8	165	85	91	1.25	–	62	67
5	600	7.9	0.9	60	10	9.6	380	94	63	1.62	218	77	nd
6	600	8.3	0.5	60	4	9.2	957	97 ± 2	12	3.25	228	77	84
7	600	8.3	0.5	80	3.5	8.8	1025	97 ± 2	20	2.95	227	83	91
8	1700	8.3	0.5	60	7	1.8	309	97 ± 2	73	1.33	245	–	112

[a] General conditions: 0.05–0.15 mmol Ln; total volume 10 mL; reactions were conducted in neat monomers.

[b] Styrene and isoprene concentration in mol/L.

[c] Mass of copolymer recovered.

[d] Catalytic activity in kg/(mol(Ln) h).

[e] Amount of styrene incorporated in the copolymer, as determined by ^1H NMR; “±2” refers to the experimental uncertainty in determining the isoprene content in styrene-rich copolymers.

[f] Number average molecular weight and polydispersity determined by GPC in 1,3,6-trichlorobenzene at 135 °C vs. PS standards.

[g] Melting and glass transition temperatures determined by DSC.

[h] Glass transition determined by DMA.

[i] [Ip]/[Nd] = 1800.

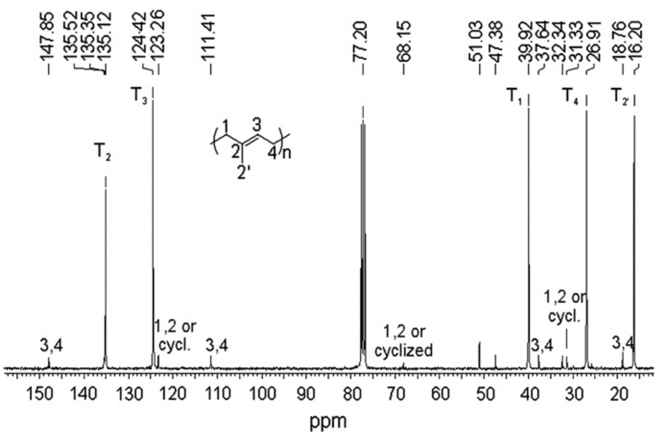


Fig. 2. $^{13}C\{^1H\}$ NMR spectrum (75 MHz, 25 °C, $CDCl_3$) of 1,4-*trans*-enriched polyisoprene prepared with complex **1**.

2.2. Styrene–isoprene copolymerization

Complex **1** is highly active for styrene–isoprene copolymerization (Scheme 1, Table 1). Although somewhat lower than that observed for styrene homopolymerization (1710 kg sPS/(mol(Nd) h) at 60 °C, entry 1), the copolymerization activity reaches up to 1025 kg P(S-*co*-I)/(mol(Nd) h) at 80 °C (entry 7). Consistent with the aforementioned lower reactivity of isoprene, higher overall activities were observed for styrene-rich feeds. Also as expected, the copolymerization activity increased slightly with the polymerization temperature (entries 6 and 7) but the latter did not exert a major influence on the copolymer molecular weights.[1] Relatively high molecular weights and unimodal narrow polydispersities, consistent with a single-site catalytic behavior and the formation of true copolymers, were observed, provided there was no precipitation of the polymer during the reaction course.[1] This could be achieved either using a minimal amount (>10 mol%) of isoprene in the feed to obtain copolymers with at most 94 mol% of styrene (entries 3–5) (vide infra) or using a larger styrene-to-catalyst ratio to maintain in solution copolymers from styrene-rich feeds (entry 8). However, in the latter case, a decrease of activity was noticed (entries 6 and 8), which was not observed in both styrene homopolymerization and styrene–ethylene copolymerization [3–5].

The respective amounts of styrene and isoprene incorporated in the copolymers were easily controlled by the initial concentration of each monomer in the feed (Fig. 3). The fraction of styrene (F_{sty}) in the copolymer was determined by ^1H NMR with the following equation:

$$F_{sty} = \frac{7A_{Ph}}{4A_{Ph} + 5A_{Me}}$$

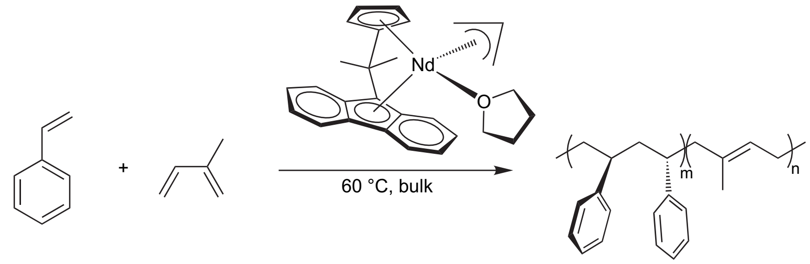
where A_{Ph} is the area of the aromatic styrene proton resonances (δ 7.5–6.2 ppm) and A_{Me} is the area of methylene and methine proton resonances of styrene and isoprene (δ 1.2–2.2 ppm). Significant integration uncertainties exist for styrene-rich copolymers (entries 5–8), as the aliphatic resonances are of quite low intensity compared to the aromatic ones.

Styrene–isoprene copolymers were all found completely insoluble in THF, except for entry 3 that features the highest isoprene content (30 mol%) and which was fully soluble in THF. These observations confirm the true copolymer nature of those materials (as the PI produced with **1** is soluble in THF; vide supra) and indicate that a quite significant amount (>15 mol%) of isoprene is needed to overturn sPS insolubility (vide supra).

Microstructural characterization of these styrene-*co*-isoprene copolymers was attempted by ^{13}C NMR spectroscopy. The typical $^{13}C\{^1H\}$ NMR spectrum of a copolymer containing 70 mol% of styrene (Fig. 4) reveals intense resonances diagnostic for syndiotactic polystyrene (δ 40.9 ppm, $T_{\beta\beta}$; δ 44.2 ppm, $S_{\alpha\alpha}$; δ 145.4 ppm, *ipso* carbon) [21] and 1,4-*trans* polyisoprene sequences (δ 16.1, 27.0, 40.0 ppm) [22,31]; no resonances for 1,4-*cis* or 3,4-isoprene units were detected. Other resonances were also observed, some of which correspond well with those recently calculated by Grassi and co-workers for styrene-*co*-isoprene polymers [21], in particular the intense resonance at δ 37.6 ppm (calculated 37.8) for the styrene-1,4-*trans*-PI junction. The complexity of this spectrum is consistent with a statistical copolymer having isolated and/or a few isoprene units inserted in sPS sequences[2] rather than a blocky sPS–PI microstructure. The $^{13}C\{^1H\}$ NMR spectra of styrene-rich (>94 mol%) copolymers were simpler and contained essentially sPS resonances, the resonances for 1,4-PI being hardly discernable.

As far as we know, such microstructure (sPS with 1,4-*trans*-isoprene units) has not been described in the literature: random incorporation giving 1,4-*cis* isoprene units was reported by Shen et al. [18], Jin et al. [37] and Naga and Imanishi [38], and isolated styrene units incorporated into 1,4-*trans* PI chains were observed by Visseaux et al. [22]. Grassi et al. [21] and Zambelli et al. [39] obtained a blocky microstructure with a 1,4-*cis* stereoselectivity.

The high melting temperatures ($T_m = 218$–245 °C) associated to endothermic peaks in the DSC profiles for styrene-rich copolymers (≥94 mol%), as well as the glass transition temperature ($T_g = 77$–112 °C), confirmed the syndiotacticity of the polystyrene sequences.



Scheme 1. Styrene–isoprene copolymerization catalyzed by complex **1**.

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[1] Polymers from entries 6 and 7 featured somewhat lower molecular weights and broader (but still unimodal) polydispersities, illustrated in the GPC traces by a tail in the low molecular weight region. This fact can be related to the precipitation of the polymer after ca. 2 min under these conditions (not observed in other polymerization tests – see text), which is likely to perturb the catalyst control.

[2] In the $^{13}C\{^1H\}$ NMR spectrum of the styrene-*co*-isoprene copolymer (70 mol% styrene; Table 1, entry 3; Fig. 4), the signals corresponding to comonomer junctions (δ 37.6 ppm) and the resonances corresponding to the methylene groups of 1,4-*trans* polyisoprene sequences (δ 27.0, 40.0 ppm) have a relative intensity of 79, 21 and 20, respectively. These data allow a rough estimate of ca. 1/5 of isoprene units involved in homo-polyisoprene sequences and 4/5 of isoprene units isolated in between sPS sequences.

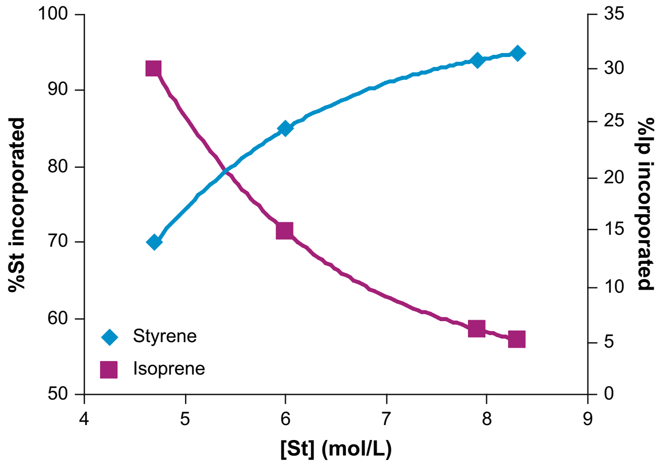


Fig. 3. Influence of styrene concentration on styrene and isoprene incorporation in styrene–isoprene copolymerization catalyzed by complex **1** (Table 1, entries 3–6).

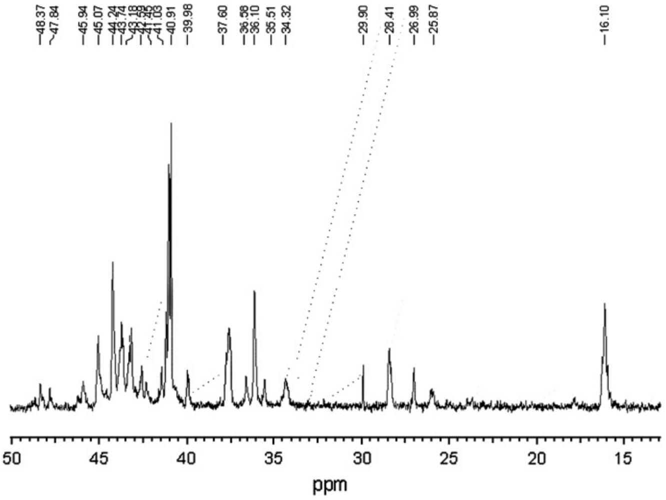


Fig. 4. Aliphatic region of the $^{13}C\{^1H\}$ NMR solution spectrum (75 MHz, 25 °C, $CDCl_3$) of a styrene-*co*-isoprene copolymer (70 mol% styrene) prepared with complex **1** (Table 1, entry 3).

Similar to the observations made in the case of styrene-*co*-ethylene copolymers [4,5], the melting temperature increases with incorporated styrene amounts, as expected from the increasing crystallinity of the copolymers. Thus, we are now able to modify sPS properties by introducing a minimal amount of a diene comonomer.

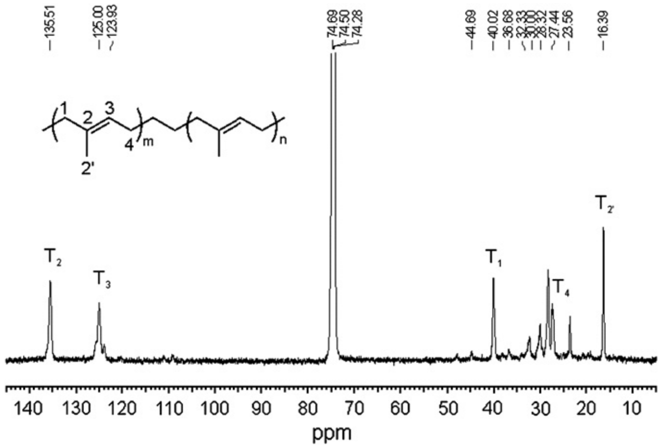


Fig. 5. $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 135 °C, tetrachloroethane-d_2) of an ethylene-*co*-isoprene copolymer (76 mol% isoprene) prepared with complex **1**.

2.3. Styrene–ethylene–isoprene terpolymerization

Styrene–ethylene–isoprene terpolymerization was also briefly investigated. In order to evaluate the performances of catalyst **1**, a preliminary ethylene–isoprene copolymerization was first carried out in neat isoprene at 60 °C, under 4 bar of ethylene (Table 2, entry 1). A moderate activity of 138 kg/(mol(Nd) h) was observed and a gummy material, fully soluble in THF, was recovered. ^1H NMR spectroscopy revealed that this copolymer contained 76 mol% of isoprene, and no melting or glass transition temperature were detected by DSC. These solubility and thermic data argue against the formation of blends of homopolymers. The high molecular weight and unimodal, relatively narrow polydispersity determined by GPC ($M_n = 111{,}700$ g/mol, $M_w/M_n = 1.61$) are consistent with a single-site behavior of the catalyst and confirm the true copolymer nature of this material.

Microstructural characterization of this copolymer was attempted by ^{13}C NMR spectroscopy. It is worth noting that no ^{13}C NMR data are currently available in the literature for isoprene-*co*-ethylene polymers, contrary to *trans*-butadiene-*co*-ethylene polymers [40]. The $^{13}C\{^1H\}$ NMR spectrum (in $C_2D_2Cl_4$ at 135 °C) of this isoprene-rich copolymer showed resonances characteristic for 1,4-*trans* PI sequences (δ 16.4, 27.4, 40.0, 125.0 and 135.5 ppm) (Fig. 5) [22,31]. Beside these, only four principal resonances, of similar intensity, were observed in the aliphatic region at δ 23.6, 28.3,

Table 2

Styrene–ethylene–isoprene terpolymerization catalyzed by complex **1**[a]

Entry	[St]/[Nd]	[St][b]	[Ip][b]	*P* (bar)	*T* (°C)	Time (min)	Yield[c] (g)	Activity[d]	St[e] (mol%)	Ip (mol%)	Et (mol%)	M_n[f] × 10^3 (g/mol)	M_w/M_n[f]	T_m[g] (°C)	T_g[g] (°C)	T_g[h] (°C)
1	1800	–	10	4	60	15	11.4	138	–	76	24	112	1.61	–	–	nd
2	600	2.2	2.2	5	60	60	7.2	33	41	34	25	73	2.41	–	–	35
3	600	7.9	0.9	1	60	15	8.9	244	96 ± 2	3	<1	41	2.84	204	76	nd
4	600	4.1	0.5	4	60	15	25.6	235	71	6	23	83	1.18	219	56	55
5	600	4.1	0.5	4	80	15	40.5	375	71	6	23	nd	nd	nd	nd	nd
6	600	4.1	0.5	1	60	30	18.7	86	81	3	16	nd	nd	–	60	84

[a] General conditions: 0.02–0.35 mmol Ln; total volume 1–60 mL.

[b] Styrene and isoprene concentration in mol/L.

[c] Mass of copolymer recovered.

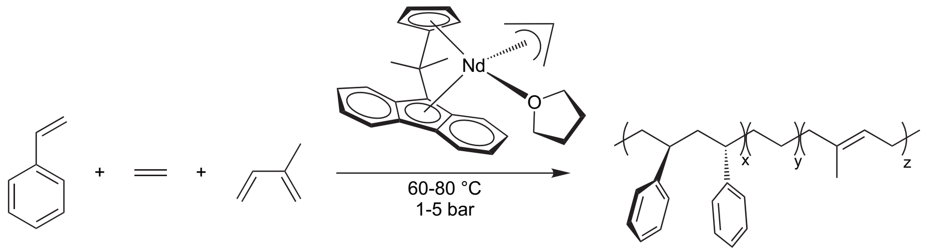
[d] Catalytic activity in kg/(mol(Nd) h).

[e] Amount of styrene incorporated in the copolymer, as determined by ^1H NMR; "±2" refers to the experimental uncertainty in determining the isoprene and ethylene contents in styrene-rich terpolymers.

[f] Number average molecular weight and polydispersity determined by GPC in 1,3,6-trichlorobenzene at 135 °C vs. PS standards.

[g] Melting and glass transition temperature determined by DSC.

[h] Glass transition determined by DMA.



Scheme 2. Styrene-*co*-ethylene-*co*-isoprene terpolymerization catalyzed by complex **1**.

30.0, 32.3 ppm. Since the signal at δ 30.0 ppm was not significantly more intense than that of the other three, the presence of long PE sequences is highly unlikely. Therefore, we tentatively assigned those four extra resonances to isolated ethylene units distributed in PI chains (chemical shift for the ethylene CH_2 group of an I–*E*–I sequence calculated using reported additive factors [21,40]: δ 32.34 ppm; the chemical shifts of the isoprene 1,4-methylene units in an *I*–E–*I* sequence could not be calculated with the additive factors available).

Since allyl *ansa*-neodymocene **1** showed rather good catalytic performances for styrene–ethylene [4,5], styrene–isoprene and ethylene–isoprene copolymerizations, we were expecting this catalyst to be also active for styrene–ethylene–isoprene terpolymerization (Scheme 2). Indeed, we observed activities up to 375 kg/(mol(Nd) h) (Table 2) and recovered gummy-like to soft materials.

The relative amounts of incorporated monomers could be easily controlled by the initial concentrations of the three monomers in the feed. The relative reactivities of each monomer were not significantly perturbed by the presence of another monomer: when the styrene and isoprene concentrations in the feed were equal, isoprene was less incorporated than styrene (Table 2, entry 2). Likewise, for a styrene concentration of 4.1 mol/L and 4 bar of ethylene, the incorporated ethylene amount was ca. 23 mol% (entries 4 and 5), which is very similar to the value (ca. 25 mol%) that we previously observed for styrene–ethylene copolymerization under the same conditions [4,5]. Expectedly, increase of the polymerization temperature led to an increase of the activity (Table 2, entries 4 and 5) but, as we observed for styrene–isoprene polymerization (Table 1, vide supra), no influence on the composition was detected. Thus, we could readily prepare a range of original polymers, both with high styrene (41–97 mol%) and diene (3–34 mol%) contents.

The terpolymer composition was determined using a similar method as previously reported for styrene-*co*-isoprene polymers; *i.e.* the fraction of styrene (F_{sty}) was determined by ^{1}H NMR with the following equation:

$$F_{\mathrm{sty}} = \frac{4A_{\mathrm{Ph}}}{A_{\mathrm{Ph}} + 5A_{\mathrm{Me}} + 13A_{\mathrm{diene}}}$$

where A_{Ph} is the area of the aromatic styrene proton resonances (δ 6.2–7.5 ppm), A_{Me} is the area of methylene and methine proton resonances of styrene, ethylene and isoprene (δ 1.2–2.1 ppm) and A_{diene} is the area of isoprene olefinic proton resonances (δ 4.6–5.2 ppm). As previously mentioned, integration uncertainty for styrene-rich terpolymers is significant.

The recovered terpolymers were fully soluble in styrene and THF, except for entry 2 that features a very high styrene content (ca. 97 mol%) and which was not soluble in any of these solvents. The GPC analyses indicate that the recovered terpolymers have moderate molecular weights ($M_n = 41{,}000$–$83{,}000$ g/mol) with unimodal and relatively narrow polydispersities ($M_w/M_n = 1.18$–2.84).[3] These data are in agreement with the formation of true copolymers and negligible (if any) contamination by homopolymers.

The microstructure of those styrene-*co*-ethylene-*co*-isoprene polymers was analyzed by ^{13}C NMR spectroscopy. A representative $^{13}C\{^1H\}$ NMR spectrum of a terpolymer with a balanced composition is shown in Fig. 6. As anticipated, this spectrum is rather complicated and a preliminary interpretation was attempted using the previous copolymers' assignments. As observed for styrene-*co*-isoprene copolymers, the ^{13}C NMR spectrum contains predominant signals attributed to syndiotactic PS sequences (δ 41.4, 43.6 and 145.8–146.0 ppm) [21] and 1,4-*trans* isoprene units (δ 16.1, 27.8, 39.9, 124.8 and 135.1 ppm) [22,31]; no resonances for 1,4-*cis* or 3,4-isoprene units were detected. The other resonances are assigned to ethylene units and corresponding junctions with styrene and isoprene. The low intensity of the signal at δ 30.0 ppm indicates that long PE sequences are not predominant (if any), and suggests a statistical insertion of isolated or few ethylene units.

The thermo-mechanical properties of these terpolymers were briefly evaluated by DSC and DMA (Table 2). As expected, these new materials display different melting and glass transition temperatures, depending on the incorporated styrene and isoprene contents.

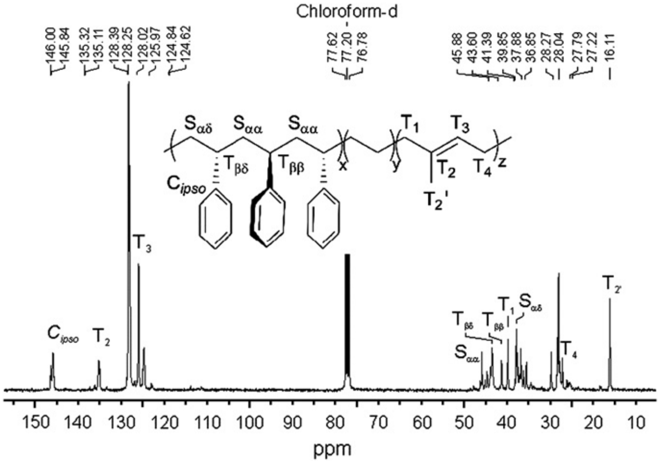


Fig. 6. $^{13}C\{^1H\}$ NMR spectrum (75 MHz, 25 °C, $CDCl_3$) of styrene-*co*-ethylene-*co*-isoprene terpolymer (41 mol% styrene) prepared with complex **1** (Table 2, entry 2).

3. Conclusions

In summary, we have synthesized new polymers by taking advantage of the high reactivity and stereospecificity of an original single-component catalyst towards a wide range of different monomers. The allyl *ansa*-neodymocene complex **1** is able to copolymerize styrene not only with ethylene but also with isoprene to give crystalline styrene-*co*-isoprene polymers that showed tunable melting and glass transition temperatures. This constitutes a second efficient way to prepare "modified sPS" with improved processability properties. We were also able to simultaneously

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[3] Polymer from entry 3 precipitated during the polymerization course, possibly accounting for the larger (but still unimodal) polydispersity observed.

incorporate in a controlled manner ethylene and isoprene in significant amounts into a highly syndiotactic polystyrene chain. Further studies will be aimed at a more complete characterization of such materials and determination of potential applications.

4. Experimental part

4.1. General

All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were distilled from appropriate agents under argon and degassed thoroughly prior to use. $(CpCMe_2Flu)Nd(C_3H_5)(THF)$ (**1**) was prepared following a reported procedure [3,4]. Styrene (99%, Acros) and isoprene (99%, Acros) were dried over CaH_2 and distilled under reduced pressure prior to polymerization experiments or stored at −30 °C under argon in the glovebox. Ethylene (N35, Air Liquide) was used without purification.

NMR spectra were recorded on Bruker AC-200, AC-300 and AM-500 spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm vs. $SiMe_4$ and were determined by reference to the residual solvent resonances. GPC analyses of the polymers were carried out in 1,3,6-trichlorobenzene at 135 °C in the Research Center of Total Petrochemicals in Feluy, using PS standards for calibration and a refractometer detector. DSC measurements were performed on a TA Instrument DSC 2920, at a heating rate of 10 °C/min under a nitrogen flow; first and second runs were recorded after cooling down to ca. 20 °C; the melting and glass transition temperatures reported in the tables correspond to second runs. DMA was carried out on a TA Instruments DMA 2980 apparatus, at a heating rate of 38 °C/min in the tension film mode with a deformation amplitude of 10 mm and 1 Hz frequency.

4.2. Typical procedure for styrene and isoprene homopolymerizations

In the glovebox, a pre-weighed amount of allyl *ansa*-lanthanidocene **1** (ca. 15 mg) was added to styrene (2.00 mL, 17.4 mmol). The Schlenk flask was then placed in an oil bath at the appropriate temperature and vigorous stirring was immediately started. After a given time period, the Schlenk flask was opened to air and a 10 vol% solution of HCl in methanol (ca. 1 mL) was added to quench the reaction. The precipitated polymer was washed repeatedly with methanol (ca. 500 mL), filtered and dried in vacuo overnight at room temperature.

4.3. Typical procedure for styrene–isoprene copolymerization

In the glovebox, a pre-weighed amount of allyl *ansa*-lanthanidocene **1** (25–80 mg, 47.4–152 μmol) was added to styrene (3.0–10.0 mL, 26.1–86.9 mmol) and isoprene (0.50–3.0 mL, 5.0–29.9 mmol). The Schlenk flask was then placed in an oil bath at the appropriate temperature and vigorous stirring was immediately started. After a given time period, the Schlenk flask was opened to air and a 10 vol% solution of HCl in methanol (ca. 1 mL) was added to quench the reaction. The precipitated polymer was washed repeatedly with methanol (ca. 500 mL), filtered and dried in vacuo overnight at room temperature.

4.4. Typical procedure for styrene–isoprene–ethylene terpolymerization at low pressure (1 bar)

In the glovebox, a pre-weighed amount of allyl *ansa*-lanthanidocene **1** (10–80 mg, 19–152 μmol) was introduced in a Schlenk flask. The latter was then connected to the vacuum/argon line and to an ethylene cylinder equipped with a pressure regulator. The whole system was purged under vacuum and swept with 1 bar of ethylene (constant bubbling). Styrene and isoprene were injected by syringe under ethylene pressure and vigorous magnetic stirring at the appropriate temperature was immediately started. After a given time period, the Schlenk tube was opened to air and a 10 vol% solution of HCl in methanol (ca. 1 mL) was added to quench the reaction. The precipitated polymer was washed repeatedly with methanol (ca. 500 mL), filtered and dried in vacuo overnight at room temperature.

4.5. Typical procedure for styrene–isoprene–ethylene terpolymerization at high pressure (>1 bar)

A 300 mL glass high-pressure reactor (TOP-Industrie) was charged with 30 mL of freshly distilled solvent (if needed) under argon flash. The reactor was then purged with ethylene and loaded with styrene and isoprene (15–60 mL) at atmospheric pressure, and then kept at the desired temperature by circulating water in a double wall. A solution of the catalyst in 2 mL of toluene was injected by syringe. Mechanical stirring (Pelton turbine, 1000 rpm) was started immediately and the gas pressure in the reactor was maintained constant with a back regulator throughout the experiment. The ethylene consumption was monitored *via* an Aalborg flowmeter. After a given time period, the reactor was depressurized and the reaction was quenched by adding ca. 5 mL of 10 vol% solution of HCl in methanol. The polymer was further precipitated by adding 500 mL of methanol, washed and dried in vacuo overnight at room temperature.

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