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Copolymerization of Isoprene with Nonconjugated α,ω−Dienes Using a Single Component Samarocene Catalyst

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Introduction. The copolymerization of olefins with functionalized monomers is of particular importance to many industrial fields: adhesives, dyeing agents, compatibilizers, and elastomers.[1] Functional copolymers may be sequenced by successive polymerization of two different monomers[2] or by random copolymerization of the olefin with a α,*ω*-diene.[3] In addition to the change of mechanical properties resulting of the insertion of the new monomer, the latter offers the opportunity to functionalize the pendant unsaturation.[4] The copolymerization of conjugated dienes with small olefins, using essentially group 4 metallocene catalysts, has been widely investigated since Kaminsky reported the copolymerization of butadiene with ethylene.[5] Random or alternating copolymers of ethylene, propylene, or isobutene with butadiene or isoprene could be obtained; however, both the catalytic activity and the incorporation of the conjugated diene remained low.[6] Lanthanide derivatives were used successfully to produce polyisoprene[7] and polybutadiene[8] in high yield. This research continues to be covered by patents.[9] Very recently, a lanthanocene catalyst reportedly produced a butadiene−ethylene copolymer containing up to 40% of inserted butadiene.[10] However, despite numerous efforts to copolymerize conjugated dienes with longer olefins, only one example of such a copolymer has been reported.[11]

We described previously[12,13] the synthesis and properties of some bridged allyllanthanocenes, acting as single component catalysts, which are able to produce copolymers whith ca. 6−10% of C_6−C_{18} α-olefin randomly incorporated in a *trans*-polyisoprene chain. We report here the copolymerization of isoprene with hexa-1,5-diene and octa-1,7-diene α,*ω*-dienes, the latter leading to a functionalizable polymeric material. The molecular structure of the macromolecular chain is established on the basis of NMR analysis. The thermal properties of the copolymers are discussed. The alternate (*block*-isoprene−comonomer-*block*-isoprene) microstructure is related to the constrained geometry of the ansasamarocene catalyst. Isoprene/α-olefin/α,*ω*-diene terpolymers are also obtained.

Results and Discussion. Hexa-1,5-diene and octa-1,7-diene copolymerize with isoprene in different ways. The former inserts with cyclization; the latter inserts preferentially only one double bond. In every case, the polyisoprene backbone keeps a 1,4-trans configuration (see NMR discussion below). The inserted comonomer is in the range 4−10%, depending on the experimental conditions.[14]

Table 1. Isoprene/α,*ω*-Diene Co- (and Ter-) Polymerization Results

run	monomers[a]	toluene (mL)	Sm (*μ*mol)	$[M]_0$/ [Sm][b]	time (h)	yield (%)	comonomer content (%)[c]
1	1/1/0		6.9	720	20	73	8.2
2	1/0.5/0		7.4	900	20	98	4.5
3	0.5/1/0		6.9	480	40	99	5.4
4	1/1/0	4	1.4	720	27	80	4
5	0.5/0.5/0.5		6.5	520	17	28	4.6;[d] 6.3[e]
1′	1/1/0		6.9	720	19	93[f]	*f*
2′	0.9/0.9/0	1.8	3.8	650	20	97[f]	*f*
3′	0.5/0.5/0	1	5.5	450	63	64	6.5
4′	0.5/0.5/0	2	4.6	360	17	79	4.3
5′	0.5/1/0	2	4.7	300	21	24	10
6′	0.25/0.5/0.25		11.1	450	16	58[f]	*f*
7′	0.5/0.4/0.1		11.1	450	5	87[f]	*f*
8′	0.5/0.1/0.4		11.1	450	17	82	4;[g] 4.8[e]

[a] Isoprene/hexa-1,5-diene (runs 1−5) or octa-1,7-diene (runs 1′-8′)/hex-1-ene, volumes in mL. [b] Initial concentration of isoprene. [c] On the basis of ^{1}H NMR integration. [d] Hexa-1,5-diene. [e] Hex-1-ene. [f]Cross-linked: does not take octa-1,7-diene into account. [g] Octa-1,7-diene.

Scheme 1. Copolymers A, Poly-1,4-trans(isoprene-*co*-methylenecyclopentane), and B, Poly-1,4-trans(isoprene-*co*-octadiene)

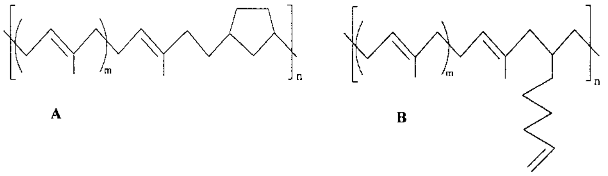

Table 1 summarizes the results. Hexa-1,5-diene: the highest comonomer content (8.2%, run 1) is obtained in the absence of solvent with one volume equivalent of each monomer; it is in the range of the insertion of α-olefins into polyisoprene with the same catalyst.[13] With half as much hexa-1,5-diene (run 2), the yield is better but the copolymer contains only 4.5% of the inserted comonomer, while an excess of nonconjugated diene slows the reaction (run 3). In the presence of solvent (run 4), the amount of insertion falls to 4%. Octa-1,7-diene: the copolymerization performed without a solvent (run 1′), or in toluene with a high [isoprene]/[Sm] ratio (run 2′), afforded an insoluble cross-linked material. A [isoprene]/[Sm] ratio < 500 and toluene as solvent (runs 3′, 4′) produced soluble materials (at higher dilution, the catalyst loses its activity). The comonomer content can reach 10% (run 5′), but the total yield of copolymer is then low.

When a third comonomer (hex-1-ene) is added to the reaction medium, it competes with the α,*ω*-diene, leading to terpolymers of poly(isoprene-*co*-hexene-*co*-methylenecyclopentane) (run 5) and poly(isoprene-*co*-hexene-*co*-octadiene) (runs 6′−8′). In the latter case, the termonomer plays the role of solvent,which had to be added to the system to minimize the cross-linking.

The copolymers were characterized by ^{13}C NMR{^{1}H}. For isoprene−hexadiene, there were no vinyl signals in the range 110−150 ppm in addition to the signals of the *trans*-polyisoprene units, whereas at least 11 well-defined signals appear in the range of aliphatic carbons (20−50 ppm).[15] This indicates that methylene−*cis*- and −*trans*-cyclopentane rings (trans selectivity 70%) are incorporated in the polymeric chain (Scheme 1, copolymer **A**).[16]

The soluble samples of isoprene−octadiene copolymers show the expected spectrum for a copolymer containing pendant vinyl groups (Scheme 1, copolymer **B**), including well-defined vinyl signals at 139.4 (=CH)

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Scheme 2. (a) Insertion of an Olefin Leading to an Undercoordinated Species and (b) Second Olefin Insertion in the Case of a Nonconjugated Diene

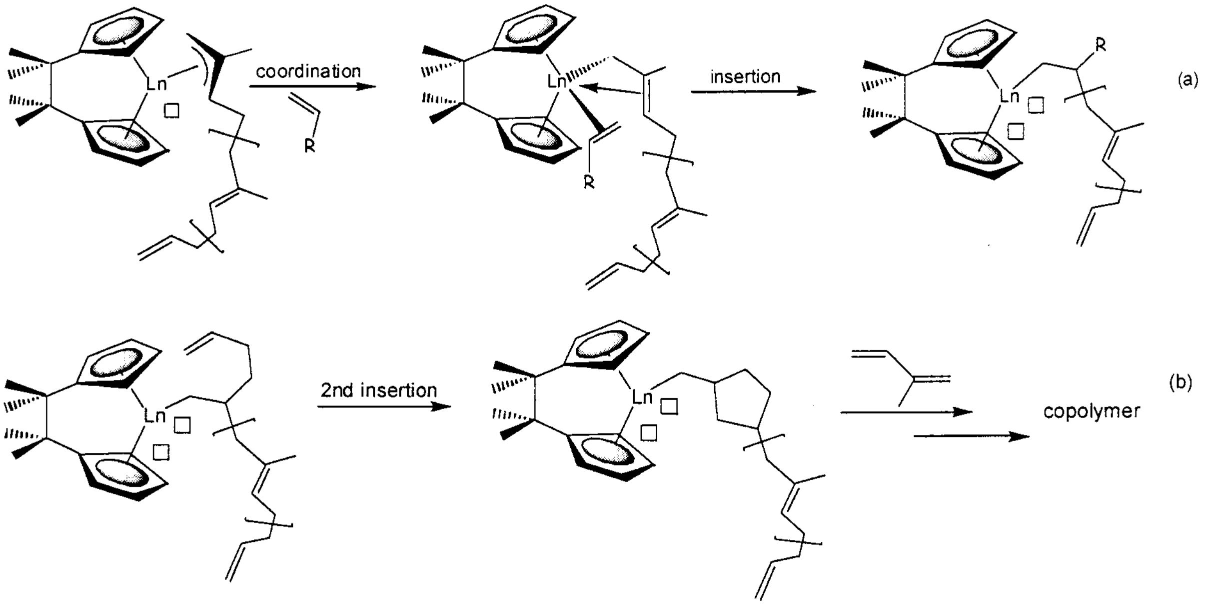

Table 2. Characteristic Data of a Selection of Co- and Terpolymers Isoprene/α,ω-Diene

run	$[M]_0/[Sm]$	$M_n \times 10^{-3\,a}$	PDI[b]	comonomer content (%)[c]	T_g (°C)[d]	solubility in toluene
1	720	50	1.3	8.2	−60	soluble
3	480	38	1.6	5.4	−58	soluble
5	520	39.5	1.5	10.9	−62	soluble
1′	720				−45	insoluble[e]
3′	450	50	1.8	6.5	−69	soluble
8′	450	41.4	2.0	8.8	−66	soluble

[a] Determined by SEC analysis at room temperature against polystyrene standards. [b] Polydispersity index $\bar{M}_w/\bar{M}_n$. [c] Total monomer, on the basis of ^{1}H NMR integration. [d] Determined by modulated DSC. [e] Cross-linked.

and 114.8 (=CH$_2$) ppm.[17] In addition, at least 15 signals for the aliphatic carbons appear in the range 46−18 ppm,[18] instead of the 8 signals normally expected for the monoinserted chain.[19] The presence of cross-linking or of methylenecycloheptane moieties thus cannot be excluded.

^{1}H NMR data were used to evaluate the rate of inserted comonomer in the copolymer (hexa-1,5-diene, $\delta = 5.83$, 1 H, $\delta = 5.05$, 2 H; octa-1,7-diene, $\delta = 1.89$, 2 H, $\delta = 0.80$, 1 H).

The ^{1}H and ^{13}C NMR spectra of the terpolymers are the exact superposition of those of the two copolymers isoprene−hexene and isoprene−α,ω-diene.

Physicochemical data are reported in Table 2. The molecular weights are comparable to those already obtained from isoprene/α-olefin copolymerizations[13,19] and are close to the expected theoretical values calculated from the [isoprene]/[Sm] ratios. The polydispersity indexes are typical of a single-site catalyst mechanism.[20] Concerning copolymerizations involving octadiene, the molecular weights of the soluble material (runs 3′, 8′) are twice the expected (ca 50 000 vs 26 000) values and polydispersity values (run 3′, 1.8; run 8′, 2.0) are slightly higher, which indicates that the material is sparingly cross-linked. Such a cross-linking cannot be avoided. DSC measurements: the presence of an inserted comonomer in the poly(1,4-*trans*-isoprene) chain (homopolymer: mp 48 °C, Δ*H* 60 J g^{-1}, T_g −65 °C[13]) prevents crystallization (a low crystallinity—mp 34.5 °C, ΔH 1.2 J g^{-1}—was detected for run 8′ only). The T_g value (vs homopolymer) increases in the presence of methylenecyclopentane motives (runs 1, 3, 5) while the amorphous phase is slightly plasticized in the presence of alkyl arms (runs 3′, 8′). Cross-linked materials show the expected increase of T_g value (run 1′). As a consequence, all of the soluble octadiene-based copolymers synthesized are sticky, while cross-linked materials behave as typical elastomers.

Terpolymer 8′ is by far the stickiest material. SEC indicates that it is also the least cross-linked, which is consistent with its adhesive properties.[21] This suggests that the two comonomers are randomly distributed along the polyisoprene backbone rather than as blocks, which would have the same behavior as a mixture of the two copolymers.

The catalyst is an ansasamarocene allylic compound, which was used without any cocatalyst. It is obtained by reaction of two equivalents of allyllithium(dioxane) adduct with the bimetallic precursor $[(CMe_2C_5H_4)_2SmCl(THF)MgCl_2(THF)_2{\cdot}THF]$.[22] The exact structure of the catalyst and the nature of the active species involved in such copolymerizations has been studied in detail elsewhere.[12,23] The microstructure of the described copolymers (one inserted comonomer between two blocks of *trans*-1,4-polyisoprene) is consistent with the mechanism described in Scheme 2a; i.e., the allyl species in the growing polyisoprene chain offers only one vacant site for coordination to isoprene or the olefin. After the olefin insertion, an alkyl species is formed, producing two vacant sites. At that time, the competition between isoprene and the monoolefin favors isoprene, which is a better ligand. Such a behavior may also occur for α,ω-dienes: after one olefinic extremity of a molecule of diene is integrated in the polymeric chain, the other unsaturation may react to give cyclic moieties. This happens with hexa-1,5-diene, which leads quantitatively and for entropic reasons, to methylenecyclopentane rings (Scheme 2b). With octa-1,7-diene, cross-linking could occur, but also cyclization, as recently reported.[3,16,24] However, most of the pendant unsaturations remain unreacted, since the cross-linking was nearly completely impeded by maintaining the [monomer]/[catalyst] ratio lower than 500 and by dilution.

Polymerization experiments involving polar monomers with the same catalysts are in progress.

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(14) A typical polymerization experiment is conducted as follows: in a glovebox, the catalyst (10 mg, 6.9×10^{-6} mol) is weighed in a 20 mL flask. The solvent (toluene, 0−4 mL) and the monomer(s) (isoprene, 1 mL, 9.9×10^{-3} mol; hexadiene, 1 mL, 8.4×10^{-3} mol) are added via syringes into the flask. The mixture is magnetically stirred at 50 °C during 20 h. The medium has become viscous, it is diluted with toluene (5 mL) and the resulting solution poured in ethanol. The off-white polymer is filtered out, washed with ethanol, and dried for 24 h under vacuum. Copolymer yield (for 8.2% hexadiene inserted): 73% (0.54 g). ^{1}H and ^{13}C NMR were recorded on Bruker DRX 500 and Avance 300 (C_6D_6, 300 K). SEC analyses were carried out in THF solutions at 20 °C (1 mL/min) using a Gynkotek P580A apparatus equipped with 2 JORDI divinylbenzene mixed B columns and a RI detector. Absolute values of molecular weights were obtained against polystyrene standards with Mark−Houwink corrections. DSC analyses were performed on a modulated TA Instruments apparatus under nitrogen (range −100 to +100 °C, rate 5 °C/min, modulation ±0.5 °C/40 s).

(15) Aliphatic signals: 47.43, 40.96, 38.93, 38.67, 37.53, 37.20, 33.40, 33.11, 32.15, 31.95, 27.74 ppm (C_6D_6 = 128 ppm).

(16) Polymerization or copolymerization of hexa-1,5-diene leads to *cis*- or *trans*-cyclopentane rings: (a) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953. (b) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223.

(17) These signals cannot be confused with those of the terminal allylic group of the *trans*-polyisoprene chain at 139.1 and 118.4 ppm because, for polymeric chains containing more than 500 monomeric units, it is not possible to obtain any information on the nature of the chain termination. Such information can only be obtained for low molecular weight polymers.[13]

(18) Aliphatic signals: 45.56, 35.43, 34.42, 34.14, 33.76, 33.63, 31.20, 29.99, 28.89, 27.84, 26.58, 25.73, 19.84, 18.94, 16.50 ppm (C_6D_6 = 128 ppm).

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