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Article

# Stereoselective Copolymerization of Butadiene and Functionalized 1,3-Dienes with Neodymium-Based Catalysts

Hannes Leicht,<sup>®</sup> Inigo Göttker-Schnetmann,<sup>®</sup> and Stefan Mecking<sup>\*®</sup>

Chair of Chemical Materials Science, Department of Chemistry, University of Konstanz, 78464 Konstanz, Germany

#### **S** Supporting Information

**ABSTRACT:** Neodymium based Ziegler–Natta systems catalyze the 1,4-*cis* selective copolymerization of isoprene and 1,3-butadiene with different R<sub>2</sub>N- and RS-functionalized 1,3-dienes. Incorporation of the functionalized 1,3-diene occurs very efficiently with high comonomer conversions, to yield polymers with typical  $M_n = 5 \times 10^4$  to  $2 \times 10^5$  g mol<sup>-1</sup>. High (>10 mol %) to very high (45 mol %) incorporation ratios and even homopolymerizations of the functionalized dienes can be achieved readily as observed for e.g. TMS<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>C(= CH<sub>2</sub>)CH=CH<sub>2</sub> or PhS(CH<sub>2</sub>)<sub>3</sub>C(=CH<sub>2</sub>)CH=CH<sub>2</sub>. Compar-



ison of turnover numbers, microstructure, and molecular weights of the obtain copolymers show little to no adverse impact of the comonomer when compared to butadiene homopolymerizations. Additionally, cleavage of TMS groups in copolymers of 1,3-butadiene or isoprene with  $TMS_2N(CH_2)_3C(=CH_2)CH=CH_2$  results in copolymers bearing primary  $-NH_2$  amine groups as functional groups.

## INTRODUCTION

Stereoregular polymers like polypropylene and polydienes are produced on a large scale by catalytic insertion polymerization. The production of synthetic rubbers like poly(butadiene) (PBD) and poly(isoprene) (PIP) traditionally employs Ziegler-Natta catalysis based on, e.g., Ti, Co, or Ni. These were later extended by neodymium catalysts.<sup>1,2</sup> Nd-based systems are known to yield butadiene rubber with the highest 1,4-cis content. This is important, as microstructure control is paramount in the synthesis of synthetic rubber because it translates directly to different polymer properties like glass transition temperature, crystallinity, or strain-induced crystallization.<sup>3</sup> These properties are significant for tire manufacturing, the main application of synthetic rubber. Besides microstructure control, the functionalization with polar groups can give access to improved properties of such materials. In particular, for tire applications, enhanced interactions with the filler materials used (e.g., silica or carbon black) are desired. However, copolymerizations of 1,3-butadiene (BD) or isoprene (IP) with polar functionalized dienes were exclusively accomplished by free-radical methods<sup>4-9</sup> that do not allow control over the polymer's microstructure. Recently, we reported on the stereoselective insertion copolymerization of BD and IP with various polar functionalized dienes using cationic (allyl)Ni complexes.<sup>10</sup> The copolymerization of IP and 2-(4-methoxyphenyl)-1,3-butadiene catalyzed by a  $\beta$ -diketiminato yttrium bis(alkyl) complex was also recently reported by Cui and co-workers.<sup>11</sup> In view of industrial applications, these advances raise the question of the functional group tolerance of simple in situ catalyst systems that are preferred by industry. We

now report on the (co)polymerization of functionalized dienes by such systems.

### RESULTS AND DISCUSSION

Comonomers 1–3 were synthesized by Kumada-coupling of  $R_2N-(CH_2)_n-MgX$  (n = 3, 4; X = Cl, Br) with chloroprene catalyzed by (dppp)NiCl<sub>2</sub>. **4**, **6**, and 7 were obtained by a Li<sub>2</sub>CuCl<sub>4</sub>-mediated coupling reaction of PhS-(CH<sub>2</sub>)<sub>3</sub>-Cl, PhSO<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-I or (EtO)<sub>3</sub>Si-(CH<sub>2</sub>)<sub>3</sub>-I and buta-1,3-dien-2-ylmagnesium chloride. Comonomers **5** and **8** were synthesized by the Pd-catalyzed hydrosulfuration of 2-methylbut-1-en-3-yne with thiophenol or the Cu-catalyzed hydroboration of 2-methylbut-1-en-3-yne with pinacolborane (for detailed procedures cf. Supporting Information).

The synthesized N- or S-functionalized 1,3-diene comonomers (comonomers 1–4, Chart 1) were copolymerized with 1,3-butadiene and isoprene using different Nd-based catalyst systems. These catalyst systems are based on the widely employed Nd-precursors Nd(versatate)<sub>3</sub> (NdV),<sup>3</sup> Nd-(O<sup>i</sup>Pr)<sub>3</sub>,<sup>12,13</sup> and Nd(allyl)<sub>3</sub>·dioxane<sup>14</sup> and activated with Alalkyls diisobutylaluminum hydride (DIBALH) or triisobutylaluminum (TIBA) and a Cl-source ethylaluminum sesquichloride (EASC) or [PhNMe<sub>2</sub>H]<sup>+</sup> [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>. The polymerizations were conducted at elevated temperatures (50–60 °C) in aromatic solvents (benzene or toluene).

The principal feasibility and limits of such direct copolymerizations were probed in polymerizations in NMR-tubes

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Chart 1. Functionalized Diene Comonomers Used in Copolymerizations with 1,3-Butadiene and Isoprene



Table 1. NMR Scale (Co)Polymerizations of Butadiene or Isoprene with Polar Functionalized Comonomers<sup>4</sup>

entry	cat.	time [h]	diene [mmol]	funct diene comon. [µmol]	funct diene:Al ratio [x:1]	comon. content in polymer <sup>i</sup> [mol %]	$[10^3 \text{ g mol}^{-1}]$	$M_{ m w}/M_{ m n}^{~j}$	1,4-cis content <sup>k</sup> [%]	1,4- <i>trans</i> content <sup>k</sup> [%]	vinyl content <sup>k</sup> [%]
1-1	A <sup>b</sup>	30	BD: 1.2	1 (51)	5	4.2	59	3.5	96.7	3.0	0.2
1-2	B <sup>c</sup>	19	BD: 0.5	1 (76)	7	13.1	40	1.9	94.0	5.8	0.2
1-3	B <sup>c</sup>	19	BD: 1.2	1 (430)	41	45	77	2.8	97.4	2.5	0.1
1-4	B <sup><i>c</i>,<i>l</i>,<i>m</i></sup>	8	-	1 (509)	24	100	n.d.	n.d.	88	8	4
1-5	$C^{d,l,m}$	8	-	1 (705)	23	100	21	5	90	6	4
1-6	B <sup>c</sup>	19	IP: 0.8	1 (98)	9	11.3	105	2.4	97	1	2
1-7	$C^d$	12	IP: 0.4	1 (400)	26	42.8	49	5.7	92	5	3
1-8	D <sup>e</sup>	14	IP: 0.8	1 (98)	20	11.2	36	6.2	91	3	6
$1 - 9^{l}$	Ef	8	BD: 0.8	1 (200)	32	20.8	15	3.9	94.5	5.4	0.1
$1 - 10^{l}$	F <sup>g</sup>	1	IP: 1.2	1 (50)	10	4.4	n.d.	n.d.	90	9	1
1-11	B <sup>c</sup>	15	BD: 0.5	2 (65)	6	11.1	23	2.2	86.3	13.5	0.2
1-12	A <sup>b</sup>	19	BD: 2.6	3 (110)	10	4.3	84	2.8	96.0	4.0	_
1-13	$B^{c}$	19	BD: 2.6	3 (110)	10	3.8	70	3.7	95.7	4.1	0.2
1-14	$G^{h}$	20	IP: 1.0	3 (100)	18	10.2	52	7	95	2	3
1-15	$C^{d,l,n}$	16	-	3 (500)	16	100	16	4.7	91	5	4
1-16	A <sup>b</sup>	15	BD: 1.1	4 (25)	2	2.4	199	1.9	96	3.8	0.2
1-17	$B^{c}$	19	BD: 2.7	4 (60)	6	2.0	83	2.2	92.0	7.8	0.2
1-18	D <sup>e</sup>	19	BD: 1.2	4 (65)	13	5.9	n.d.	n.d.	88	11	1
1-19	$B^{c}$	19	BD: 0.5	4 (80)	8	16.2	9.4	3.2	92.4	7.5	0.1
1-20	$G^{h}$	19	IP: 2.0	4 (47)	9	2.5	n.d.	n.d.	98	-	2
1-21	$G^{h}$	12	IP: 1.0	4 (100)	18	9.5	73	3.1	96.8	0.7	2.5
1-22	$C^{d,l,m}$	68	-	4 (500)	16	100	15	5.8	n.d.	n.d.	4

<sup>*a*</sup>All reactions performed with 0.5  $\mu$ mol of Nd at 333 K (until otherwise noted) in NMR-tubes in C<sub>6</sub>D<sub>6</sub> until ca. >90–95% diene conversion was reached. <sup>*b*</sup>A: Nd(versatate)<sub>3</sub>:TIBA:EASC (1:20:1). <sup>*c*</sup>B: NdV:DIBALH:EASC (1:20:1). <sup>*d*</sup>C: NdV:TIBA:EASC: DIBALH (1:20:1:10). <sup>*e*</sup>D: Nd(O<sup>i</sup>Pr)<sub>3</sub>:DIBALH:[PhNMe<sub>2</sub>H<sup>+</sup>][(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B<sup>-</sup>] (1:10:3). <sup>*f*</sup>E: Nd(O<sup>i</sup>Pr)<sub>3</sub>:DIBALH:EASC (1:10:2.5) <sup>*g*</sup>F: Nd(allyl)<sub>3</sub>\*(dioxane):DIBALH: [PhNMe<sub>2</sub>H<sup>+</sup>][(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B<sup>-</sup>] (1:10:3). <sup>*h*</sup>G: Nd(allyl)<sub>3</sub>\*(dioxane):TIBA:EASC (1:10:1). <sup>*i*</sup>Determined by <sup>1</sup>H NMR spectroscopy of crude reaction mixture and/or isolated polymer. <sup>*i*</sup>Determined by GPC in THF vs PS standards. <sup>*k*</sup>Determined by <sup>13</sup>C NMR spectroscopy of crude reaction mixture and/or isolated polymer. <sup>*i*</sup>1  $\mu$ mol Nd. <sup>*m*</sup>Reaction at 353 K. <sup>*n*</sup>Reaction at 343 K. <sup>*o*</sup>Reaction at 323 K.



Figure 1. <sup>1</sup>H NMR spectrum of a BD-1 copolymer after isolation and before cleavage of the TMS-groups (Table 1, entry 1–1, recorded at 27 °C in  $C_6D_6$ ).

with different catalyst systems A (NdV/TIBA/EASC), B (NdV/DIBALH/EASC), C (NdV/TIBA/DIBALH/EASC), D (Nd(O<sup>i</sup>Pr)<sub>3</sub>/DIBALH/[PhNMe<sub>2</sub>H<sup>+</sup>][(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B<sup>-</sup>]), E (Nd-(O<sup>i</sup>Pr)<sub>3</sub>/DIBALH/EASC), F (Nd(allyl)<sub>3</sub>·(dioxane)/DIBALH/[PhNMe<sub>2</sub>H<sup>+</sup>][(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B<sup>-</sup>]), and G (Nd(allyl)<sub>3</sub>·(dioxane)/TIBA/EASC) and different comonomers (Table 1).

Consumption of the nonfunctionalized diene was observed for all combinations of different catalyst systems and comonomers studied. Further, the formation of typical polybutadiene or polyisoprene signals were observed in these reactions by means of <sup>1</sup>H NMR spectroscopy, showing that the attempted polymerizations are productive. <sup>13</sup>C NMR analyses of the obtained polymers reveal differences in stereoregularity depending on the catalyst system used. Systems C, D, and F give the polymers with the lowest 1,4-*cis* content of ca. 90%, followed by system E with 94% 1,4-*cis* units. Systems A, B and



Figure 2. <sup>1</sup>H NMR spectra of butadiene copolymers in  $C_6D_6$  containing 4 and 45 mol % comonomer 1 (entries 1–1 and 1–3) as well as poly-1 homopolymer (entry 1–4).



Figure 3. <sup>13</sup>C NMR spectra of butadiene copolymers in  $C_6D_6$  containing 4 and 45 mol % comonomer 1 (entries 1–1 and 1–3) as well as poly-1 homopolymer exhibiting distinct backbone resonances for carbons labeled 1 and 4 (entry 1–4), as compared to 1' and 4' in the copolymers.

G are capable of synthesizing polymers with a highly defined microstructure with 1,4-*cis* contents >94%. In addition, polymers obtained with systems A and B typically exhibit very low vinyl contents (ca. 0.2 mol %).

The materials obtained are true copolymers, as concluded from extensive NMR analysis. For example, <sup>1</sup>H NMR spectra of the copolymers obtained from the copolymerization of BD or IP and comonomer 1 display the presence of both  $-CH_2-$ N(TMS)<sub>2</sub> groups at  $\delta = 2.84$  ppm and trimethylsilyl groups at  $\delta$ = 0.20 ppm (Figure 1) for all different incorporation ratios (Table 1, entries 1–1 to 1–10). Additionally, extensive <sup>13</sup>C, 2D, and DOSY NMR spectroscopy verifies the incorporation of 1 into the polydiene backbone.

The formation of true copolymers through insertion polymerization in these copolymerizations was further established for a BD-3 copolymer by means of  ${}^{13}C{-}$ 

All copolymerizations in NMR tubes with comonomers 1, 2, 3, and 4 (diene:comonomer ratios are between 45:1 and 1:1, e.g. entries 1–17 and 1–7) yielded the desired copolymers with a defined microstructure (typically 92–97% 1,4-*cis* units for catalyst systems A or B). Note that molecular weights are not very high in most examples due to higher catalyst:monomers ratios, deliberately applied in order to keep the viscosities of the samples in a suitable range for solution NMR spectroscopy (for examples of stirred polymerizations in glass vials, yielding polymers consistent with  $M_n > 1 \times 10^5$  g mol<sup>-1</sup>, please cf. Supporting Information, Table S1).

A shielding of the comonomer's polar functionality by an excess of Al–alkyls cannot be accountable for the unprecedented copolymerization behavior as Al:comonomer ratios are between 1:2 and 1:41 (cf. Table 1, column 6), proving a true functional group tolerance of the catalyst systems studied.

The excellent consumption and incorporation of the comonomers suggests comparable incorporation rates of butadiene and the comonomers used. To gain more insight into this advantageous behavior, we followed such copolymerization by means of <sup>1</sup>H NMR spectroscopy and subjected the obtained data to kinetic evaluations. Polymerization rate constants of copolymerizations are ca. 1 order of magnitude decreased when compared to rate constants of butadiene homopolymerizations under comparable conditions. The ratio of the rate constants for comonomer and butadiene consumption gives the comonomer reactivity ratio r (for kinetic plots and further information cf. Supporting Information). Comonomer reactivity ratios for comonomers 1, 2, and 4 are between r = 0.8 and 1.1, indicating the formation of random copolymers.

Such favorable comonomer reactivity ratios allow very efficient comonomer incorporation even for high diene:comonomer ratios (cf. Supporting Information, Table S1). Incorporation ratios between 4 and 45 mol % are achieved without difficulty for copolymerizations of BD with comonomer 1 (Figure 2 and Table 1, e.g., entries 1-1 and 1-3). High incorporation ratios (>10 mol %) are not only easily reached for other nitrogen functionalized comonomer **2** and **3**, but also for sulfur functionalized comonomer **4** (Table 1, entries 1-11, 1-14, and 1-19).

Remarkably, not only high incorporation ratios are easily reached, but also homopolymerizations of comonomers 1, 3, and 4 are catalyzed by catalyst systems B or C (Table 1, entries 1-4, 1-5, 1-15, and 1-24). Moreover, these functionalized diene homopolymers are also stereoregular and exhibit a high content of 1,4-cis units. In detail, stereoregularity of e.g. poly-1 is somewhat decreased when compared to copolymerizations of

Chart 2. Functionalized Diene Comonomers Not Amenable to Copolymerizations with the Nd-Based in Situ Catalyst Systems Studied



Figure 4. <sup>1</sup>H NMR (topmost spectrum) and 1D-TOCSY spectra of a BD-1 copolymer after cleavage of the TMS-groups with MeOH (Table 1, entry 1–1, recorded at 27 °C in  $C_6D_6$ ). Residual solvent is marked with an \*.

the same monomer with nonfunctionalized dienes (88% - 91% for polar diene homopolymerizations vs >94% 1,4-*cis* units for polar diene copolymerizations with BD or IP). The comparison of <sup>13</sup>C NMR backbone signals of poly-1 with BD-1 copolymers indicates the presence of consecutively incorporated comonomer units for a copolymer with very high incorporation (45 mol %) while such units are virtually not present in comonomers with lower incorporation ratios (Figure 3). Note that these copolymerizations can also be extended to analogues of 1, 2, and 4 with other lengths of the spacer between the diene moiety and the functional group (cf. Supporting Information, Table S2).

In contrast to the aforementioned copolymerizations, copolymerizations with functionalized dienes 5, 6, 7, and 8 were not successful (Chart 2). A polymerization in the presence of 5 showed that BD was converted over time into polybutadiene, however, 5 was not incorporated into the formed polymer. This lack of incorporation may be due to the 1,3-disubstituted structure of 5. A detrimental effect on the polymerization is observed in attempted copolymerizations in the presence of oxygen-containing comonomers 6, 7, and 8. In all cases, no polymerization activity was observed. This can probably be attributed to an interaction of the oxygen atoms in the comonomers with the active Nd-species. Additionally, we observed in NMR experiments that these monomers can react with aluminum alkyls, especially EASC, which is an additional issue contributing to the detrimental effect on the polymerization. For example, the formation of additional - Si-O-CH<sub>2</sub>-CH<sub>3</sub> signals was observed in copolymerizations with 7, most likely due to the formation of different alkoxysilane species by reaction with the aluminum alkyls present.

Although these Nd-based catalyst systems are not able to copolymerize the oxygen containing comonomers studied, a comparison with cationic (allyl)Ni systems is instructive: While the aforementioned oxygen containing comonomers can be readily copolymerized stereoselectively with the Ni-catalyst, it is observed that some nitrogen and sulfur based comonomers, like 1 or 4, are more challenging, resulting in a certain retardation of the polymerization. For the Nd-based systems studied here, the opposite is the case. N- and S-based comonomers are copolymerized readily while O-based comonomers are detrimental for the polymerization. Thus, the complementary behavior of Nd- and Ni-based catalyst systems provides the opportunity to choose the best-suited catalyst systems for every class of comonomers.

While the incorporation of comonomers 1-4 via direct insertion polymerization to stereoregular polar functionalized dienes was successful, there are still functional groups that cannot be directly incorporated. For example, primary amine groups RNH<sub>2</sub> still remain incompatible with the catalyst systems used. Protecting groups<sup>15-17</sup> could resolve this issue. In our case, the trimethylsilyl groups present in copolymers of comonomer 1 can be cleaved readily by the reaction with MeOH<sup>18</sup> to give polydienes functionalized with primary amine groups. The presence of these  $-NH_2$  groups drastically changes the polymer's solubility properties. Dissolution now requires heating of the sample to 60 °C in a suitable solvent for several days vs a few hours for other (protected) copolymers.

<sup>1</sup>H and 1D TOCSY NMR spectra of the dissolved polymer are shown in Figure 4. The  $-NH_2$  groups 9 present in the polymer resonate at 0.54 ppm and 1D-TOCSY spectroscopy reveals the connectivity along the propyl side chain to the PBD backbone: Excitation of nitrogen bound  $-CH_2$ - group 7 (spectrum 2, Figure 4), results in magnetization transfer through coupling to  $CH_2$  groups 6 and 5 as well as to  $-NH_2$ group 9. Additionally, responses of olefinic -CH= group 3 and even of the polybutadiene backbone are observed. Irradiation at 0.54 ppm ( $NH_2$  group 9, spectrum 1, Figure 4) shows the inverted responses of  $CH_2$  groups 7, 6, and 5 clearly corroborating the functionalization with RNH<sub>2</sub> groups.

In conclusion, various simple *in situ* generated Nd-based catalyst systems of industrial relevance are able to produce copolymers of isoprene or 1,3-butadiene with heteroatom functionalized dienes bearing polar groups based on nitrogen

and sulfur. A shielding of the functional groups by an excess of aluminum alkyls is not required to observe productive copolymerization. The obtained copolymers are stereoregular and exhibit a high content of 1,4-*cis* units. Even stereoregular homopolymerizations of the functionalized dienes are feasible. In contrast, we observed no polymerization activity in the presence of several oxygen functionalized dienes studied.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.7b02007.

NMR spectra, GPC and DSC data, kinetic experiments, and synthetic procedures (PDF)

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*(S.M.) E-mail: stefan.mecking@uni-konstanz.de.

#### ORCID <sup>©</sup>

Hannes Leicht: 0000-0002-4694-9399

Inigo Göttker-Schnetmann: 0000-0003-1059-9689 Stefan Mecking: 0000-0002-6618-6659

#### Notes

The authors declare no competing financial interest.

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(18) The addition of defined amounts of MeOH to a copolymer solution followed by stirring for a sufficient amount of times ensures the complete deprotection of the amine groups. Precipitation in MeOH of the copolymer can lead to only partially deprotected amine groups.