Ethylene–Butadiene Copolymers

Alternating Copolymerization of Ethylene and Butadiene with a Neodymocene Catalyst**

*Julien Thuilliez, Vincent Monteil, Roger Spitz, and Christophe Boisson**

The introduction of unsaturated groups into the backbone of polyolefins is of interest for many applications, including the production of vulcanizable materials for the tire industry. The ideal would be to copolymerize conjugated dienes (butadiene, isoprene) with olefins, which are all cheap and readily available monomers. Since the discovery of Ziegler–Natta catalysts, research efforts have focused on the copolymerization of these two families of monomers. However, as the two classes of monomers polymerize according to different mechanisms, only a very limited number of catalysts are able to copolymerize them successfully.

Methods for producing alternating olefin–butadiene copolymers have been discussed in the literature for over 40 years. For instance, Natta et al. isolated this type of copolymer by extraction from a polymer mixture prepared at −25 °C using a vanadium-based system.[1] The disadvantage is that the catalysts must be prepared at very low temperature (−70 °C), and polymerization must be performed at low temperature (0 °C). Almost ten years later, Furukawa prepared similar polymers with a $TiCl_4/AlR_3$ catalyst system.[2] The polymerization temperature was slightly higher in this case (25 °C). $VO(OR)_2Cl/AlR_3$ catalysts, developed in the 1970s, can also be used to make alternating poly(ethylene-*co*-butadiene), as confirmed by Arnold et al. in 1991.[3] However, low polymerization temperatures are again required, since the proportion of 1,2-units increases with temperature and cross-linking reactions occur.[4] More recently, advances in the field of single-site catalysts have made possible the copolymerization of ethylene with butadiene by using Group 4 metallocene catalysts.[5] The difficulty here is that butadiene acts as a poison for the catalysts. Experimental studies have shown that activity decreases dramatically as the butadiene content increases.[6]

It appears that there are no Group 4 or vanadium-based catalysts that can be used for the copolymerization of conjugated dienes with olefins under acceptable conditions. Given this limitation, most industrial research groups have chosen an alternative route for the production of polyolefinic elastomers, namely, the terpolymerization of ethylene (E), propylene (P), and a diene monomer (DM) such as ethylenenorbornene, which is much more expensive than mainstream α olefins. However, compatibility problems, not expected with copolymers of olefins and conjugated dienes, have been observed during covulcanization of EPDM polymers with styrene–butadiene or natural rubbers. The copolymerization of olefins and conjugated dienes is therefore of significant interest from both scientific and economic points of view.

We have studied this reaction using organolanthanide catalysts. Previous studies have already resulted in efficient systems for the copolymerization of ethylene with butadiene, both in terms of activity and diene incorporation.[7] Recently, we described a new elastomer containing cyclohexane units obtained by intramolecular cyclization.[8] Since the ligand has a strong influence on the polymer microstructure, we extended our investigations to the silylene-bridged cyclopentadienyl fluorenyl neodymium complex $[\{Me_2Si(C_5H_4)(C_{13}H_8)\}NdCl]$ (**1**).

This complex was used in combination with butyloctylmagnesium (Bomag), an alkylating and transfer agent. To moderate the drift of polymer composition, copolymerization experiments were stopped at low conversion. Results are reported in Table 1. It is well known that the polymerization of ethylene is controlled by a reversible chain-transfer reaction between the dialkylmagnesium compound and the lanthanide complex until polymer precipitation.[9] After the precipitation of di(polyethenyl)magnesium, the molecular weight distribution generally broadens. As expected, the system **1**/Bomag leads to a high polydispersity index (PDI) in homopolymerization of ethylene (run 1). On the contrary, polymers with narrow molecular weight distribution were obtained in the presence of butadiene (Bd). Moreover, higher productivity was accompanied by an increase in molecular weight (compare runs 6 and 9). This interesting result can be simply explained by the fact that the copolymers remain soluble in the polymerization medium. Whereas only polymers of low molecular weight are accessible in the homopolymerization of ethylene, high-molecular-weight poly(ethylene-*co*-butadiene) can easily be prepared.

Table 1: Polymerization results.[a]

Run	Bd in feed [mol %]	n(Nd) [μmol]	Yield [g]	Reaction time [min]	M_n [g mol^{-1}] (PDI)
1	0	41	1.95	60	2700 (3.61)
2	5	41	1.20	20	2740 (1.36)
3	10	45	1.60	12	4230 (1.40)
4	20	43	2.50	12	5855 (1.62)
5	30	41	1.70	12	6695 (1.41)
6	50	41	1.95	20	7580 (1.52)
7	75	45	7.60	120	17660 (1.90)
8	100	43	1.50	720	6185 (2.30)
9	50	41	7.00	90	32500 (1.90)

[a] Polymerization conditions: $T = 80$ °C, toluene (200 mL), ratio [Mg]/[Nd] = 5.

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[*] J. Thuilliez, Dr. V. Monteil, Dr. R. Spitz, Dr. C. Boisson
LCPP-CNRS/CPE Lyon UMR 140
Bât. 308F-B.P. 2077
43 Bd du 11 Novembre 1918, 69616 Villeurbanne (France)
Fax: (+33) 4-7243-1768
E-mail: boisson@lcpp.cpe.fr

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In the homopolymerization of ethylene or butadiene, the catalyst **1**/Bomag shows poor activities. In run 1, the activity was close to 50 kg mol^{-1} h^{-1}, which is lower than the activity of similar systems (for example, typical activities for $[(C_5Me_5)_2NdCl_2Li(OEt_2)_2]$/Bomag are close to 800 kg mol^{-1} h^{-1}).[10] Similarly, run 8 shows that only 1.50 g of polybutadiene was obtained after 12 h. Therefore, while the present system is not suitable for the preparation of homopolymers, it exhibits a novel and unexpected behavior in copolymerization reactions.

Mean activities were calculated for runs 1–8 (Figure 1). Activity increases considerably in the presence of butadiene, even at relatively high concentrations. The maximum value (around 300 kg mol^{-1} h^{-1}) was observed with a butadiene feed content of 20 mol %. To our knowledge, a system that is significantly more active in copolymerization than in homopolymerization has never before been observed with these kinds of catalysts; increasing the amount of butadiene usually decreases the activity.[5b]

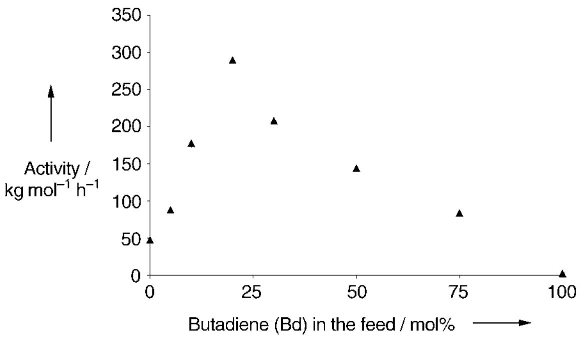


Figure 1. Average activity of **1**/Bomag in the copolymerization of ethylene and butadiene.

Detailed stereochemistry of the polymers (determined by NMR spectroscopy) is reported in Table 2. Butadiene is mainly inserted in *trans*-1,4 configuration. ^{13}C NMR spectra also provide some important information on the sequence of the two monomers (Figure 2). The different copolymers have a strongly alternating character, as confirmed by run 6: TET triads are predominant, few TEE triads are observed, and no TEEE units are detected (T and E stand for *trans*-1,4-butadiene and ethylene units, respectively). The ability of the system to copolymerize ethylene with butadiene is confirmed, since the polymer prepared in run 9 shows the same alternating structure and has a molecular weight higher than 30000 g mol^{-1}. Differential scanning calorimetry revealed the typical thermal properties of poly(ethylene-*alt*-*trans*-1,4-butadiene) ($T_g = -70$ °C, $T_m = 54$ °C).[11] Furthermore, activity remains stable for long polymerization times.

Table 2: Polymer microstructure.

Run	Bd in feed [mol %]	Bd in polymer [mol %][a]	1,4-units (*trans*[b]) [mol %][a]	1,2-units [mol %][a]
2	5	24.5	96.3 (94.7)	3.7
3	10	34.3	97.6 (96.2)	2.4
4	20	41.5	96.9 (97.6)	3.1
5	30	45.2	96.6 (98.2)	3.4
6	50	48.3	95.6 (98.9)	4.4
7	75	52.4	93.8 (99.6)	6.2
8	100	100	84.1 (94.6)	15.9
9	50	49.4	94.5 (97.5)	5.5

[a] According to ^{1}H NMR spectroscopic data. [b] According to ^{13}C NMR spectroscopic data.

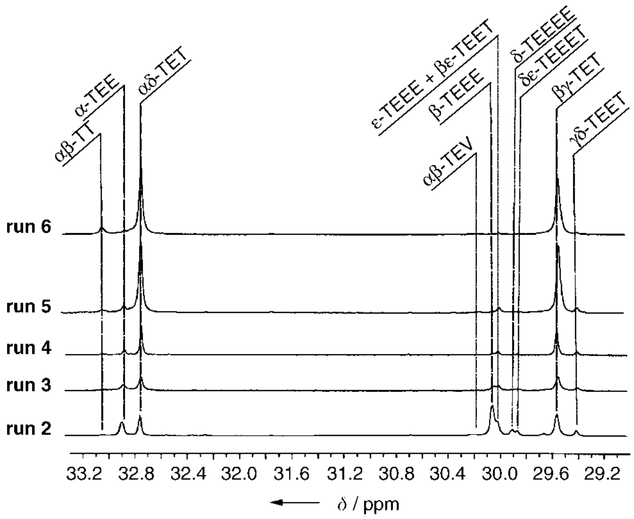


Figure 2. Comparison of the ^{13}C NMR spectra of ethylene–butadiene copolymers.

Using the different ^{13}C NMR spectra, and assuming that butadiene units are mainly in *trans*-1,4 configuration, we calculated the reactivity ratio as $R_{Bd} = 0.07$ and $R_E = 0.09$ ($R_{Bd}R_E = 0.063$).[7b] Experimental data fit the theoretical composition diagram (Figure 3).

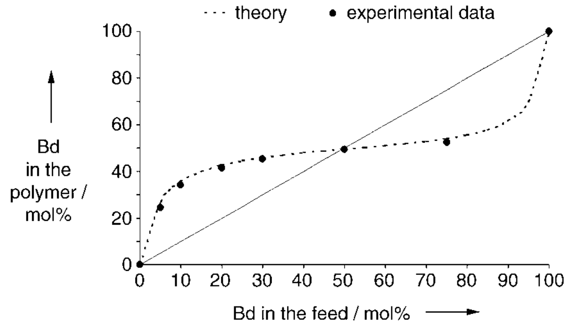
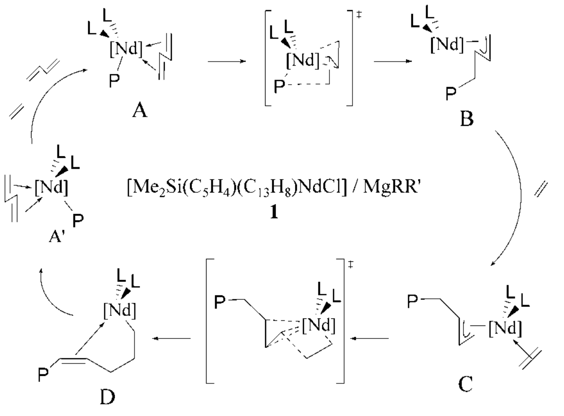


Figure 3. Composition diagram for the ethylene–butadiene copolymerization.

Copolymers prepared with **1**/Bomag exhibit the same alternating character as those obtained from vanadium-based catalysts.[1,3] The advantage of the neodymocene catalyst is that the polymerization is performed at high temperature (80 °C). In addition, high activities (one to two orders of magnitude higher than those of vanadium-based catalysts) are reached and there is no molecular-weight limitation with temperature.

The catalyst **1**/Bomag leads to good insertion of butadiene in *trans*-1,4 configuration. The mechanism for this positive result can be explained in the light of some of the more relevant theoretical studies presented in the literature. It has been reported that *cis*-1,4 stereoselectivity in the polymerization of butadiene is obtained by *s*-η^4-*cis*-butadiene insertion into a η^3-π-allylic metal–carbon bond.[12,13] Conversely, *trans*-1,4 units are commonly attributed to an *anti–syn* isomerization or to insertion of a η^2-coordinated *trans*-butadiene.[13] In a recent paper,[14] Wakatsuki and co-workers performed an interesting theoretical study on the coordination and insertion of butadiene into the Sm−H bond of the complex $[(C_5Me_5)_2SmH]$. It appears that η^2 coordination is widely favored because of steric effects.

Nevertheless, experimental evidence shows that bis(pentamethylcyclopentadienyl)lanthanide complexes give small amounts of butadiene insertion,[7a] an observation that is completely opposite to the efficiency of the catalyst **1**/Bomag ($R_E = k_{EE}/k_{EB} = 0.09$). Furthermore, Erker et al. isolated stable zirconocene and tantalocene complexes which involve *s-trans*-η^4-butadiene.[15] They suggested that *s-trans*-η^4-diene complexes can be postulated as intermediates responsible for the stereoselectivity in the polymerization of conjugated dienes.[15a] The experimental results reported herein can be explained by the existence of such an intermediate **A** (Scheme 1). In the case of the bridged complex **1**, the metal is less hindered than in the structures "$(C_5Me_5)_2LnR$", and therefore more accessible. This then leads to the favorable reactivity of the diene in an *s-trans*-η^4 coordination mode. This hypothesis is also in agreement with a very low rate of subsequent diene insertion into the η^3-π-allylic metal–carbon bond ($R_B = k_{BB}/k_{BE} = 0.09$) and very low activity in the homopolymerization of butadiene. In fact, formation of an η^3-butenyl neodymocene complex impedes η^4 coordination of butadiene in the plane between the two Cp rings. For this reason the insertion of ethylene is preferred. This emphasizes another unexpected characteristic of the new catalyst for the alternating copolymerization of ethylene with butadiene: the system leads to a better insertion of ethylene into an η^3-π-allylic metal–carbon bond than into a σ metal–carbon bond ($k_{BE} > k_{EE}$). Assuming that insertions of monomers are first-order reactions, calculations based on kinetics using the slope of the curve in Figure 1 show that k_{BE}/k_{EE} is close to 10. This is illustrated by the unique activity increase observed in the presence of butadiene. We suggest that the formation of a η^3-allyl intermediate (**C**) modifies the electronic environment of the metal atom and assists the insertion of ethylene.



Scheme 1. Polymerization mechanism based on *s-trans*-η^4 coordination of butadiene. MgRR′ = butyloctylmagnesium.

For the first time, alternating copolymerization of ethylene with butadiene has been performed with a metallocene-based single-site catalyst. The diene is mainly inserted in *trans*-1,4 configuration. In contrast with conventional systems which lead to similar polymers, the catalyst **1**/Bomag can be used at high temperature, and no gel formation is observed. The complex has useful activities in the range of 100–300 $kg\,mol^{-1}\,h^{-1}$, and high molecular weights were obtained. Furthermore, the catalyst shows an unprecedented behavior. In comparison with the homopolymerization of ethylene, a significant activity increase is observed when butadiene is added to the polymerization medium. With regard to the experimental results obtained with this bridged lanthanidocene-containing catalyst, it seems reasonable to assume an *s*-η^4-*trans* coordination mode of butadiene.

Experimental Section

All syntheses were performed under pure and dry argon by using standard Schlenk techniques or a glove box. Tetrahydrofuran was dried with sodium and distilled prior to use. Toluene and heptane were dried over 3-Å molecular sieves. Other reagents were purchased from commercial sources and used without any further purification. Complex **1** was prepared by reaction of $[\{Me_2Si(C_5H_4)(C_{13}H_8)\}Li_2(thf)_2]$ with $NdCl_3$ in THF, according to the procedure described by Qian et al.[16] No signal was observed by NMR spectroscopy because of the paramagnetism of neodymium.

Analytical techniques and polymerization procedures (250-mL glass reactor) are available in the Supporting Information.

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[1] G. Natta, A. Zambelli, I. Pasquon, F. Ciampelli, *Makromol. Chem.* **1964**, *79*, 161.

[2] J. Furukawa, *J. Polym. Sci.* **1972**, *10*, 3027.

[3] M. Arnold, L. Wohlfahrt, W. Frank, G. Reinhold, *Makromol. Chem.* **1991**, *192*, 1017.

[4] M. Arnold, J. Reussner, L. Wohlfahrt, *Angew. Makromol. Chem.* **1992**, *196*, 37.

[5] a) S. Pragliola, G. Milano, G. Guerra, P. Longo, *J. Am. Chem. Soc.* **2002**, *124*, 3502; b) T. N. Choo, R. M. Waymouth, *J. Am. Chem. Soc.* **2003**, *125*, 8970.

[6] a) W. Kaminsky, M. Schlobohm, *Makromol. Chem. Macromol. Symp.* **1986**, *4*, 130; b) M. Marques, F. Coutinho, *Eur. Polym. J.* **1994**, *30*, 1055.

[7] a) F. Barbotin, V. Monteil, M.-F. Llauro, C. Boisson, R. Spitz, *Macromolecules* **2000**, *33*, 8521; b) M.-F. Llauro, C. Monnet, F. Barbotin, V. Monteil, R. Spitz, C. Boisson, *Macromolecules* **2001**, *34*, 3604.

[8] V. Monteil, R. Spitz, F. Barbotin, C. Boisson, *Macromol. Chem. Phys.* **2004**, *205*, 737.

[9] S. Bogaert, T. Chenal, A. Mortreux, J.-F. Carpentier, *J. Mol. Catal. A* **2002**, *190*, 207.

[10] C. Boisson, V. Monteil, D. Ribour, R. Spitz, F. Barbotin, *Macromol. Chem. Phys.* **2003**, *204*, 1747.

[11] a) H. Utschick, J. Reussner, T. Wegner, G. Höhne, H. Fischer, M. Arnold, *J. Therm. Anal.* **1993**, *39*, 643; b) W. Gerum, G. Höhne, W. Wilke, M. Arnold, T. Wegner, *Macromol. Chem. Phys.* **1995**, *196*, 3797.

[12] a) S. Tobisch, *Acc. Chem. Res.* **2002**, *35*, 96; b) S. Tobisch, T. Nowak, H. Bögel, *J. Organomet. Chem.* **2001**, *619*, 24.

[13] a) S. Maiwald, H. Weissenborn, C. Sommer, G. Müller, R. Taube, *J. Organomet. Chem.* **2001**, *640*, 1; b) S. Maiwald, C. Sommer, G. Müller, R. Taube, *Macromol. Chem. Phys.* **2002**, *203*, 1029.

[14] S. Kaita, N. Koga, Z. Hou, Y. Doi, Y. Wakatsuki, *Organometallics* **2003**, *22*, 3077.

[15] a) G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich, *J. Am. Chem. Soc.* **1980**, *102*, 6344; b) H. C. Strauch, G. Erker, R. Fröhlich, *Organometallics* **1998**, *17*, 5746; c) M. Dahlmann, G. Erker, R. Fröhlich, O. Meyer, *Organometallics* **1999**, *18*, 4459.

[16] C. Qian, W. Nie, J. Sun, *Organometallics* **2000**, *19*, 4134.