Macromolecules

Volume 33, Number 23 November 14, 2000

Communications to the Editor

First Synthesis of Poly(ethene-*co*-1,3-butadiene) with Neodymocene Catalysts

Fanny Barbotin, Vincent Monteil, Marie-France Llauro, Christophe Boisson,* and Roger Spitz

Laboratoire de Chimie et Procédés de Polymérisation,
CNRS-CPE Lyon - Bât. 308 F - 43,
Bd du 11 Novembre 1918 - B.P. 2077,
69616 Villeurbanne Cedex, France

Received July 11, 2000
Revised Manuscript Received October 2, 2000

The copolymerization of conjugated dienes and olefins is of particular importance but is considered very difficult because the two classes of monomers behave differently on polymerization catalysts.

The most widely studied catalysts are vanadium- or titanium-based. Early studies showed that alternating copolymers have been obtained at very low temperature.[1] At higher temperatures, homogeneous vanadium[2] or heterogeneous titanium[3] systems have been reported to copolymerize dienes and olefins. The resulting copolymers have a rather multiblock structure and tend to form gels.[2c,d,3e] In addition, the amount of butadiene inserted into the chains remained low. With group IV metallocene catalysts, a significant decrease of olefin polymerization activity has been observed in the presence of butadiene. Butadiene−ethylene copolymers containing small amounts of 1,4-trans inserted butadiene were nevertheless obtained.[4] However, in some recent patents, more efficient catalytic systems for conjugated diene−olefin copolymerization based on ansa-cyclopentadienyl-amido or phenoxy complexes have been reported.[5]

Coordination catalysts based on lanthanides are known to homopolymerize both conjugated dienes and olefins. They appear to be promising catalysts for diene−olefin copolymerization. Some recent studies showed that some diene polymerization catalysts[6] were able to insert α-olefins to produce diene−olefin copolymers. However, the reported activities were very low, and the quantity of olefin inserted into the copolymer remains limited (up to 10 mol %) because of the inhibiting effect of the olefin.

We report herein efficient catalysts based on nonbulky neodymocenes which can lead to butadiene−ethylene copolymers with up to 40 mol % of inserted butadiene.

Recently, we developed a catalyst based on a neutral base-free neodymocene complex and an equimolar mixture of BuLi/(^{i}Bu)$_2$AlH as alkylating agent.[7] This catalyst led to high and stable activity in ethylene polymerization. In this paper, we studied the ability of such ternary systems Cp′$_2$NdX (Cp′ = η^5-C$_5$H$_x$R$_{5-x}$, R = alkyl or SiMe$_3$)/BuLi/(^{i}Bu)$_2$AlH to copolymerize ethylene and butadiene. The experimental conditions[8] and results are summarized in Table 1.

Lanthanocene catalysts based on the bulky C_5Me_5 ligand have been used intensively in ethylene polymerization.[9] We therefore investigated the behavior of the $(C_5Me_5)_2NdCl(LiCl)(OEt_2)_2$(**1**)[10]/BuLi/(^{i}Bu)$_2$AlH (ratio 1/10/10) catalyst system. As shown in Table 1 (runs 1 and 2), this catalyst was active in ethylene polymerization, but in the presence of 5 mol % of butadiene an important drop in activity was observed. The resulting copolymer contained very small amounts of inserted butadiene (0.6 mol %) with a 1,2 (24%) and 1,4-trans (76%) microstructure. The low activity can be explained by the better coordination of butadiene, which is more basic than ethylene, on the metal. The resulting coordinated butadiene cannot easily be inserted into the metal carbon bond and impedes new coordination and insertion of ethylene.

The less bulky complex $(tBuC_5H_4)_2NdCl$ (**2**)[7] associated with a BuLi/(^{i}Bu)$_2$AlH mixture was inactive in the presence of 2 mol % of butadiene. This lack of activity might be due to the formation of a stable η^3-allyl bond after butadiene insertion, which impedes any new insertion. To investigate this possibility, we added hydrogen and the polymerization resumed immediately. After a short period the activity began to decay slowly but was once again increased with a new addition of

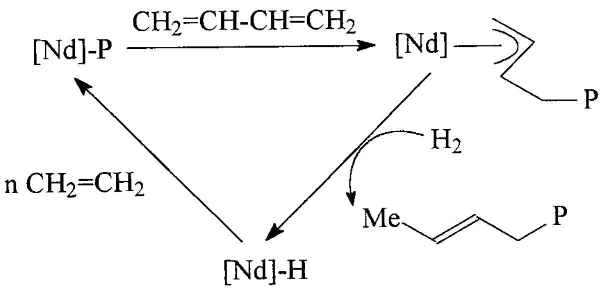
10.1021/ma0012043 CCC: $19.00 © 2000 American Chemical Society
Published on Web 10/27/2000

Table 1. Ethylene Polymerization and Butadiene−Ethylene Copolymerization with Neodymocene/BuLi/(^{i}Bu)$_2$AlH[a]

run	complex ([Nd] μM)	yield (g)	time (min)	butadiene (mol %) feed	polymer[d]	microstructure[d] 1,4-cis	1,4-trans	1,2	M_n (PDI)[e]	T_m[f] (°C)
1	**1** (31)	6.4	30						15700 (12)	132
2	**1** (75)	1.4	60	5	0.6	<1	76	24	12950 (5.3)	127
3	**2** (213)	13	30						7030 (1.9)	125
4	**3** (212)	20	30						12450 (2.6)	130
5	**3** (235)	3.7	80	3.9	3.5	<1	96	4	4030 (1.5)	80−114
6	**3** (264)	2.0	270	21	16.4	<1	97	3	1810 (1.9)	40−90
7	**4** (90)	19.1	30						14680 (2.2)	132
8	**4** (202)	13.5	30	5.4	6.6	<1	98	2	7080 (2.5)	70−116, 121
9[b]	**4** (196)	4.8	120	41	42	<1	97.5	2.5	6900 (2.2)	40−80
10[c]	**4** (183)	2.2	1380	100	100	6	88.5	6.5	7700 (1.8)	

[a] Polymerization conditions: 300 mL of toluene; ratio Nd/Li/Al = 1/10/10; $T = 80$ °C, $P = 4$ bar. [b] Pressure was not kept constant. [c] 30 mL of butadiene was condensed in the reactor. [d] Determined by ^{1}H and ^{13}C NMR analysis. [e] Determined by GPC analysis against polystyrene standard. [f] Temperature at peak maximum and temperature range are given respectively for sharp and broad melt transitions.

Scheme 1



hydrogen. ^{13}C NMR oligomers analysis showed that butadiene inserted at the chain ends with a 1,4-trans configuration. This means that ethylene is not able to insert itself into the highly stable metal allylic bond after a butadiene insertion. Hydrogenation of this metal carbon bond leads to an hydride complex which is able to polymerize ethylene until the insertion of a new butadiene monomer (Scheme 1).

To verify the influence of ligand's electronic effects, we synthesized the $(Me_3SiC_5H_4)_2NdCl$[11] (**3**) complex. Actually, the $Me_3SiC_5H_4$ and $tBuC_5H_4$ ligands have the same steric environment, but the former is less of an electron donor due to the withdrawing effect of $SiMe_3$.[12] For the first time, with the $(Me_3SiC_5H_4)_2NdCl$ (**3**)/BuLi/(^{i}Bu)$_2$AlH (ratio 1/10/10) catalyst system, a significant activity with efficient butadiene insertion was observed (run 5). Copolymers containing 3.5 mol % of inserted butadiene were obtained. In this case, butadiene units are isolated in the polyethylene chain[2b] and have a high 1,4-trans microstructure (96%) (Figure 1). It was also possible to synthesize copolymers containing 16 mol % of inserted butadiene (run 6). Nevertheless, we noted that the copolymerization activity of complex **3** as well as the polymer molecular weight decreased in comparison with ethylene polymerization. This means that the insertion of ethylene into the metal allylic bond does occur but is not easily done.

We also synthesized the bridged complex $[Me_2Si(3\text{-}Me_3SiC_5H_3)_2]NdCl$[13] (**4**). With this compound high activities were measured in ethylene polymerization, and in the presence of 5 mol % of butadiene the activity was not much affected (runs 7 and 8). A butadiene−ethylene copolymer containing 6.6 mol % of butadiene with a high 1,4-trans microstructure (98%) was thus obtained. Moreover, when the amount of butadiene fed to the reaction was increased from 5 to 40 mol %, we observed a drop in activity, but a copolymer with a high butadiene content (42 mol %) was obtained (run 9). Butadiene units are mostly alternating with ethylene (Figure 2).

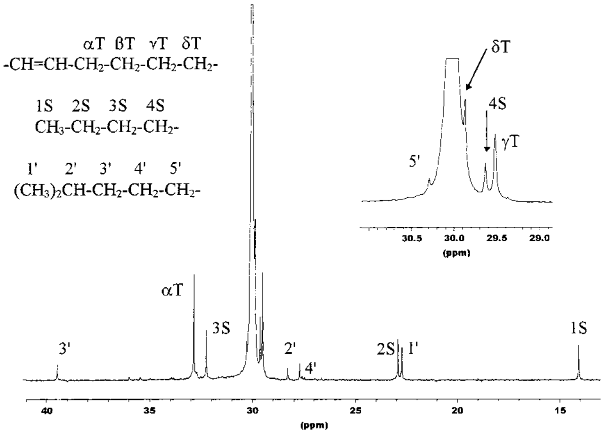


Figure 1. ^{13}C NMR spectrum of butadiene−ethylene copolymer (run 5). T: 1,4-trans butadiene unit.

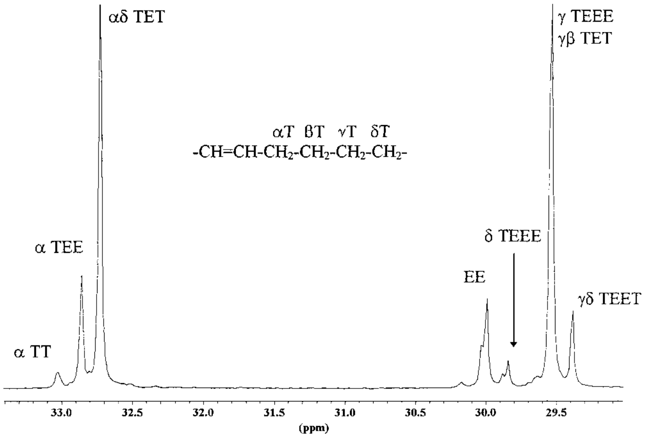


Figure 2. ^{13}C NMR spectrum of copolymer containing 42 mol % of inserted butadiene (run 9).

The system based on the silylene-bridged complex **4** was also active for the homopolymerization of butadiene (run 10). It is noteworthy that the butadiene was essentially 1,4-trans inserted. This trans selectivity can be attributed to a η^2-trans coordination of butadiene due to the steric hindrance of the ligands.[14]

DSC analysis of copolymers was performed, and the results are shown in Table 1. In contrast to the sharp melt transition observed for polyethylene, incorporation of butadiene in the copolymer caused a broadening of the thermal transition.

In summary, an original synthesis of butadiene−ethylene copolymers with a neodymium-based system was achieved. By working on ligands structure it was possible to efficiently produce copolymers with high butadiene content (up to 40 mol %). Further studies on the influence of the ligands on butadiene insertion and on copolymer microstructure are under progress and will be discussed in further publications.

Acknowledgment. The authors thank Michelin for support and in particular Dr. P. Robert for useful discussions.

References and Notes

(1) For examples, see: (a) Natta, G.; Zambelli, A.; Pasquon, I.; Ciampelli, F. *Makromol. Chem.* **1964**, *79*, 161. (b) Furukawa, J. *Rubber Chem. Technol.* **1978**, *51*, 600. (c) Arnold, M.; Wohlfahrt, L.; Frank, W.; Reinhold, G. *Makromol. Chem.* **1991**, *192*, 1017.

(2) For examples, see: (a) Cucinella, S.; De Chirico, A.; Mazzei, A. *Eur. Polym. J.* **1976**, *12*, 65. (b) Bruzzone, M.; Carbonaro, A.; Corno, C. *Makromol. Chem.* **1978**, *179*, 2173. (c) Bruzzone, M.; Guilani, G.; Paiella, R. *Makromol. Chem.* **1978**, *179*, 2187. (d) Cesca, S. In *Transition Metal Catalyzed Polymerizations*; Quirk, R. P., Ed.; MMI Press: New York, 1981; Vol. 4, Part B, p 569.

(3) For examples, see: (a) Soga, K.; Chen, S. I.; Ohnishi, R. *Polym. Bull.* **1982**, *8*, 473. (b) Sun, L.; Lu, Z.; Lin, S. *J. Polym. Sci., Part B* **1988**, *26*, 2113. (c) Müllhaupt, R.; Ovenall, D. W.; Ittel, S. D. *J. Polym. Sci., Part A* **1988**, *26*, 2487. (d) Kudashev, R. K.; Glukhov, E. A.; Mauslukhov, R. R.; Monakov, Y. B.; Rafikov, S. R. *Dokl. Phys. Chem.* **1989**, *308*, 1398. (e) Robert, P.; Spitz, R. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 261.

(4) (a) Kaminsky, W.; Schobohm, M. *Makromol. Chem., Macromol. Symp.* **1986**, *4*, 103. (b) Galimberti, M.; Albizzati, E. *Makromol. Chem.* **1991**, *192*, 2591.

(5) (a) Igai, S.; Mitani, N.; Imaoka, K. JP 9316118, 1997. (b) Nishiyama, T.; Ogawa, A. DE 19909721, 1999.

(6) (a) Kaulbach, R.; Gebauer, U.; Gehrke, K.; Lechner, M. D.; Hummel, K. *Angew. Makromol. Chem.* **1995**, *226*, 101. (b) Desmurs, P.; Dormond, A.; Barbier-Baudry, D. *C. R. Acad. Sci. Paris II-C* **1999**, *2*, 375.

(7) Boisson, C.; Barbotin, F.; Spitz, R. In *Progress and Development of Catalytic Olefin Polymerization*; Sano, T., Uozumi, T., Nakatani, H., Terano, M., Eds.; Technology and Education Publishers: Tokyo, 2000; p 75.

(8) Polymerizations were performed in a 0.5 L glass reactor, equipped with a stainless steel blade. Butyllithium, diisobutylaluminum hydride, and the neodymium complex were introduced respectively in a flask containing 300 mL of toluene. The mixture was stirred for 15 min and then transferred into the reactor under a stream of argon. The argon was then pumped out, and the reactor was charged with ethylene, butadiene, or a butadiene−ethylene mixture. The pressure was kept constant (4 bar) during the entire reaction. The polymer was then precipitated in 800 mL of methanol, washed, and dried under vacuum. ^{1}H and ^{13}C NMR were recorded on a Bruker DRX 400 (tetrachloroethylene/C_6D_6-363 K). Gel permeation chromatography data were obtained in 1,2,4-trichlorobenzene solutions at 145 °C using a Waters apparatus except for homopolybutadiene (45 °C in THF). The system was calibrated with polystyrene standard. The melting points were determined by differential scanning calorimetry (Perkin-Elmer Pyris 1). The samples were heated from 35 to 180 °C at 5 °C/min.

(9) For examples, see: (a) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471. (b) Geske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (c) Yasuda, H.; Ihara, E. *Macromol. Chem. Phys.* **1995**, *196*, 2417. (d) Pelletier, J. F.; Mortreux, A.; Olonde, X.; Bujadoux, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1854.

(10) Tiley, T. D.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3267.

(11) Synthesis: A Schlenk tube was charged with $NdCl_3$ (1.0 g, 4.0 mmol) and THF (80 mL). The suspension was heated at 70 °C for 15 h, and then [Li][$Me_3SiC_5H_4$] (1.15 g, 8.0 mmol) in THF (20 mL) was slowly added at room temperature. The resulting solution was heated for 48 h at 70 °C. After evaporation of THF, the residue was extracted with toluene (50 mL) and LiCl was filtered off. The solution was concentrated to 10 mL and was kept at −30 °C for 15 h. Blue crystals were obtained. These crystals were washed with cold toluene (2 × 10 mL) and dried under vacuum (0.95 g, 52%). ^{1}H NMR (C_6D_6): δ 26.55 (C_5H_4, 4H); 11.4 (C_5H_4, 4H); −12.38 ($SiMe_3$, 18H). Anal. Calcd for $C_{16}H_{26}Si_2NdCl$: C, 42.31; H, 5.77. Found: C, 42.05; H, 5.90.

(12) See electrochemical measurements on close complexes such as $(RC_5H_4)_3UCl$ or $(RC_5H_4)_2ZrCl_2$: (a) Berthet, J. C. Thesis, Université Paris Sud-Orsay, 1992; p 257. (b) Lappert, M. F.; Pickett, C. J.; Riley, P. L.; Yarrow, P. I. W. *J. Chem. Soc., Dalton Trans.* **1981**, 805.

(13) Synthesis: A Schlenk tube was charged with $NdCl_3$ (2.5 g, 10.0 mmol) and THF (100 mL). The suspension was heated at 70 °C for 15 h, and then a THF solution of $[Li]_2[Me_2Si(Me_3SiC_5H_3)_2]$ (3.44 g, 10.0 mmol) was slowly added. The mixture was stirred 36 h at room temperature, and THF was then evaporated. Addition of toluene (100 mL) precipitated a blue solid. This solid was filtered off and then extracted with hot toluene. The toluene was then removed in vacuo to yield a blue solid which was washed with cold heptane (2 × 10 mL) and dried under vacuum (1.0 g, 20%). According to ^{1}H NMR analysis, the meso isomeric form was isolated. ^{1}H NMR (C_6D_6): δ 2.13 ($SiMe_2$, 3H); −2.99 ($SiMe_3$, 18H); −8.97 ($SiMe_2$, 3H); C_5H_3 very wide signals are not detected. Anal. Calcd for $C_{18}H_{30}Si_3NdCl$: C, 42.36; H, 5.92. Found: C, 42.88; H, 5.87.

(14) Taube, R.; Windisch, H.; Maiwald, S. *Macromol. Symp.* **1995**, *89*, 393.

MA0012043