Macromolecules **2008**, *41*, 4573−4575

Ethylene−Butadiene Copolymerization Promoted by Titanium Complex Containing a Tetradentate [OSSO]-Type Bis(phenolato) Ligand

Carmine Capacchione, Antonietta Avagliano, and Antonio Proto*

Dipartimento di Chimica, Università di Salerno,
84084 Fisciano, Salerno, Italy

Received April 18, 2008
Revised Manuscript Received May 12, 2008

The copolymerization of conjugated dienes monomers and olefin is of particular interest since the resulting copolymers containing double bonds into the chain backbone are suitable of many practical applications. In spite of this interest, these materials are difficult to obtain because of the completely different behavior of the two class of monomers for a given catalytic system.

Titanium and vanadium compounds activated by aluminum alkyls produce a mixture of polymers containing alternating olefin−butadiene copolymers that can be separated by extraction.[1] Indeed, these systems should be prepared at very low temperature to avoid reductive processes that lead to the catalyst deactivation and the polymerization which are usually performed at subambient temperatures.

Recently, the development of single-site catalysts has renewed the interest for these polymers in both academic and industrial environments. Despite the good performance in the polymerization of α-olefin, group 4 metallocenes provided poor results in terms of catalytic activity and incorporation of the diene monomer.[2] Intriguingly, Galimberti et al.[3] and Longo et al.[4] have reported respectively the formation of cyclopentane and cyclopropane rings which may be obtained after 1,2-insertion of butadiene. Following these results, Waymouth et al. realized the alternating cyclopolymerization of butadiene with ethylene by using an asymmetric metallocene system.[5] Notwithstanding these materials are potentially interesting, all the catalytic systems based on metallocene compounds display very low activity and poor efficiency to incorporate butadiene since an increase of butadiene concentration acts as poison of the catalytic system.

It appears that the only efficient catalytic systems for the synthesis of poly(ethene-*co*-1,3-butadiene) under reasonable experimental conditions are those developed by Boisson et al. based on neodymium complexes.[6] In this case an alternating structure with butadiene mainly inserted in the *trans*-1,4 configuration was observed.

More recently, the efforts to expand the variety of group 4 complexes able to efficiently polymerize olefins has resulted in a mushrooming of catalytic systems based on noncyclopentadienyl ligands. In particular, we became interested in a new class of group 4 metal catalyst precursors which incorporate a tetradentate ligand having two phenolate units linked through a 1,*ω*-dithiaalkanediyl bridge $S(CH_2)_nS$ (n = 2 and 3).[7] Namely, the dichloro{1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butylphenoxy)}titanium complex (**1**) having 1,4-dithiabutanediyl bridge (Figure 1) possesses C_2 symmetry and was shown to be highly active, after proper activation, in isospecific styrene and 4-methyl-1,3-pentadiene polymerization.[8] Notably this system has shown to homopolymerize butadiene and efficiently copolymerize styrene with butadiene selectively.[9]

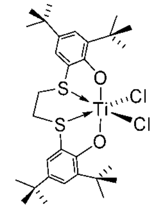

Figure 1. Dichloro{1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butylphenoxy)}titanium (**1**).

We report herein his ability to efficiently copolymerize ethylene with butadiene giving, under acceptable experimental conditions, a polymer with alternating microstructure.

The performances of **1**/MAO in ethylene−butadiene polymerization were explored under different experimental conditions: the main results are summarized in Table 1.

The catalyst shows the highest so far reported activity under the polymerization conditions used, and notably no dramatic lowering of the catalyst activity by increasing the butadiene concentration in the feed is observed. In particular, the activity is more than 4 times higher that those reported in the case of neodymocene systems.[6] The activity does not vary significantly in the range of temperatures explored and is appreciably higher than those observed in the butadiene homopolymerization. The maximum values were obtained with a butadiene feed content between 30% and 60% while lower or higher butadiene contents cause a decrease of the catalytic activity. A similar trend was observed also in the case of the neodymocene-based catalytic system. In our case the incorporation of butadiene in the polymer backbone is less efficient, but it is possible to obtain a wide variety of copolymers with butadiene content ranging from 9% to 65% by regulating the feed composition. The molecular weight distributions are monomodal ranging between 1.9 and 3.4, indicating a single-site catalyst. The molecular weights increase by increasing the butadiene content in the polymer backbone and are of the same order of magnitude as that reported in the literature for other catalytic systems under similar reaction conditions.[6d]

A detailed insight into the microstructural features of the polymers was achieved by using ^{13}C NMR spectroscopy. Butadiene is mainly inserted in the 1,4-*trans* configuration with a minor amount of 1,4-*cis* units, and notably neither 1,2-units nor the formation of cycle by butadiene cyclopolymerization was detected.

In Figure 2, the spectra of the copolymers obtained in runs 3 and 7 containing respectively 23 and 51 mol % of butadiene are shown. The peaks have been assigned accordingly to Boisson et al.,[10] and one can observe a strong tendency to the alternating microstructure. Even at low butadiene content the TET triads are predominant over the TEE, and in sample 7 no TEEE units are detected (T and E stand for *trans*-1,4 butadiene and ethylene units, respectively). The presence of 1,4-*cis* units is easily visible by the presence of the signal at 27.41 ppm, notably the presence of *cis* units (cc) is sensibly higher in the copolymers compared to the butadiene homopolymer. This different behavior of the catalyst in ethylene−butadiene copolymerization can be explained on the basis of the well-established polymerization mechanism proposed for conjugated dienes.[11] *trans*-1,4-Buta-

---

* To whom correspondence should be addressed: e-mail aproto@unisa.it.

10.1021/ma800864y CCC: $40.75

Table 1. Ethylene−Butadiene Polymerization Results

run[a]	temp [°C]	BD in feed [mol %]	yield [g]	activity[b]	BD in the polymer [mol %]	trans-1,4 [%]	cis-1,4 [%]	T_g [°C]	$M_n \times 10^3$	M_w/M_n
1	0	30	1.05	1260	30	84	16	−76.0	3.0	2.7
2	20	10	0.27	326	9	82	18	−50.0[c]	1.7	2.2
3	20	30	0.92	1104	23	82	18	−55.0	2.8	2.1
4	20	40	0.93	1116	20	81	19	n.d	1.6	2.7
5	20	50	0.79	948	46	85	15	−81.0	4.2	3.4
6	20	60	0.90	1080	45	81	19	−84.0	3.8	3.2
7	20	70	0.08	96	51	84	16	n.d	3.0	2.3
8	20	80	0.14	168	65	90	10	−88.0	6.4	1.9
9	50	30	0.46	552	23	83	17	−59.0	1.7	2.4
10	50	50	1.11	1332	24	77	23	−54.0	2.2	2.2
11	50	80	0.47	564	58	89	11	−89.0	4.7	2.4

[a] Polymerization conditions: Ti complex (10.0 μmol), Al/Ti = 1000, toluene (26 mL), ethylene pressure = 1 atm, polymerization time: 5 min. [b] Activity = kg/(mol of Ti h). [c] T_m = 102.0 °C.

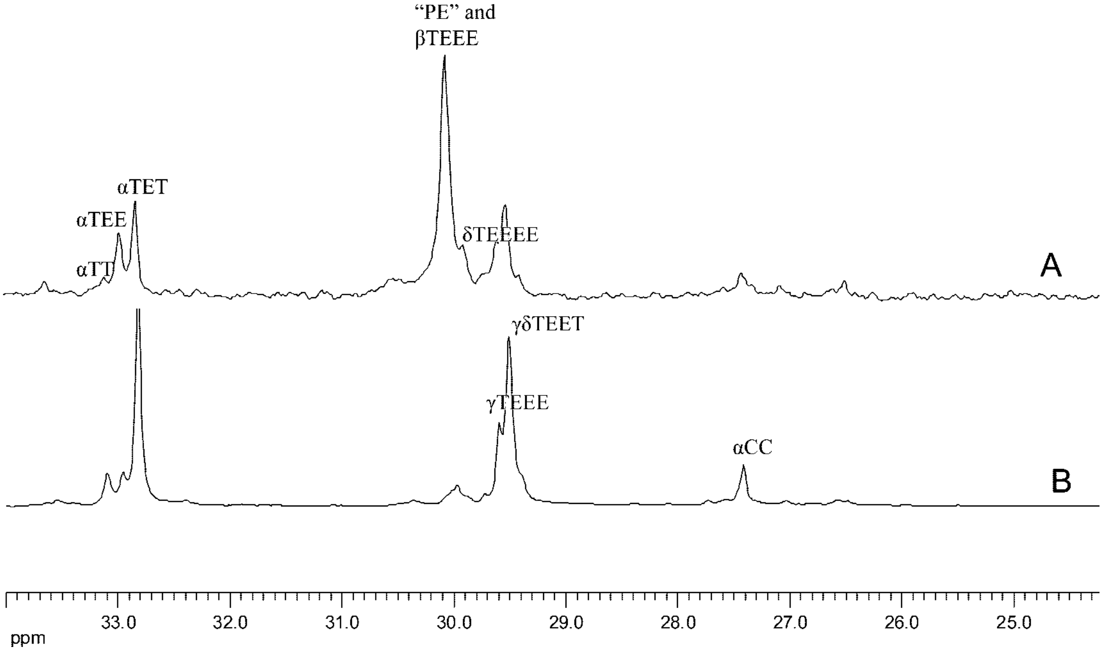

Figure 2. Aliphatic region of the ^{13}C NMR spectra of ethylene−butadiene copolymers prepared with catalyst **1**/MAO 23% butadiene (entry 3, Table 1) (A) and 51% butadiene (entry 7, Table 1) (B).

diene insertion arises from the *s-trans*-η^4 or η^2 monomer coordination to the metal center, producing the intermediate η^3 coordinated allyl complex in the *syn* configuration while the η^4-*cis* coordination of the monomer produces both 1,2-butadiene insertion and the η^3-intermediate π-allyl complex in the *anti*-configuration: the latter leads to the *cis*-1,4 insertion of the butadiene or *trans*-1,4 through *syn*−*anti* isomerization of the π-allyl complex. In the case of ethylene−butadiene copolymerization when the last inserted monomer is an ethylene unit, the polymer chain is bound to the metal through a $\eta^1-\sigma$ bond that renders the metal center less hindered and, thus, less disfavored than the η^4-*cis* coordination of butadiene which leads to *cis*-1,4 insertion.

Differential scanning calorimetry revealed the T_g values for these polymers variable in the range −89 to −50 °C depending on the butadiene content and on the relative amount of *cis* units present in the polymer. No melting temperature was observed, except for the polymer presenting very low butadiene content, probably due to the presence of the *ci*s units that disturb the crystallinity of the polymer.

The reactivity ratios $r_1 = k_{EE}/k_{EB}$ and $r_2 = k_{BB}/k_{BE}$ for ethylene−butadiene copolymerization catalyzed by **1**/MAO were evaluated.[12] As the butadiene insertion is mainly *trans*-1,4 specific, a binary copolymerization scheme and the terminal model in which only the last inserted monomer units at the active catalyst site influence the propagation reaction were assumed.

To minimize the composition drift, the copolymerization reactions were stopped after 5 min, corresponding to a monomer conversion of 5−7%. The reactivity ratios obtained from the Fineman−Ross plot are $r_1 = 1.43$ and $r_2 = 0.07$. These values indicate a preference for insertion of ethylene vs butadiene when the last inserted monomer unit in the growing polymer chain is ethylene. On the other hand, both monomers have comparable reactivity after a butadiene insertion.

This behavior could be ascribed to the higher stability of the η^3-allyl intermediate formed between the growing polymeric chain and the metal center when the last inserted monomer is a butadiene compared to that formed with ethylene. The product of the reactivity ratios ($r_1r_2 = 0.1$) indicates a tendency of the monomers to form alternating copolymers in agreement with the microstructure determined by ^{13}C NMR analysis.

To the best of our knowledge, **1**/MAO is the first homogeneous titanium catalyst active in the ethylene−butadiene copolymerization under reasonable experimental conditions affording prevailingly alternating copolymers. These results show that this catalysts has unique features in the copolymerization of conjugated diene with olefins due to the electronic and steric characteristic of the ancillary ligand present on the metal center.

Acknowledgment. We gratefully acknowledge the Ministero dell'Università e della Ricerca Scientifica (MURST, Roma, Italy) for financial support. Dr. P. Oliva is gratefully acknowledged for NMR analyses.

Supporting Information Available: Experimental preparations and polymerization procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Natta, G.; Zambelli, A.; Pasquon, I.; Ciampelli, F. *Makromol. Chem.* **1964**, *79*, 161. (b) Furukawa, J. *J. Polym. Sci.* **1972**, *10*, 3027.

(2) Kaminsky, W.; Schlobohm, M. *Makromol. Chem., Macromol. Symp.* **1986**, *4*, 103.

(3) Galimberti, M.; Albizzati, E.; Abis, L.; Bacchilega, G. *Makromol. Chem.* **1991**, *192*, 2591.

(4) (a) Pragliola, S.; Milano, G.; Guerra, G.; Longo, P. *J. Am. Chem. Soc.* **2002**, *124*, 3502. (b) Longo, P.; Pragliola, S.; Milano, G.; Guerra, G. *J. Am. Chem. Soc.* **2003**, *125*, 4799. (c) Longo, P.; Napoli, M.; Pragliola, S.; Costabile, C.; Milano, G.; Guerra, G. *Macromolecules* **2003**, *36*, 9067.

(5) Choo, T. N.; Waymouth, R. M. *J. Am. Chem. Soc.* **2003**, *125*, 8970.

(6) (a) Barbotin, F.; Monteil, V.; Llauro, M. F.; Boisson, C.; Spitz, R. *Macromolecules* **2000**, *33*, 8521. (b) Boisson, C.; Monteil, V.; Ribour, D.; Spitz, R.; Barbotin, F. *Macromol. Chem. Phys.* **2003**, *204*, 1747. (c) Boisson, C.; Monteil, V.; Thuilliez, J.; Spitz, R.; Monnet, C.; Llauro, M. F.; Barbotin, F.; Robert, P. *Macromol. Symp.* **2005**, *226*, 17. (d) Thuilliez, J.; Monteil, V.; Spitz, R.; Boisson, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 2593.

(7) (a) Capacchione, C.; Proto, A.; Ebeling, H.; Mülhaupt, R.; Spaniol, T. P.; Möller, V.; Okuda, J. *J. Am. Chem. Soc.* **2003**, *125*, 4964–4965. (b) Capacchione, C.; Proto, A.; Ebeling, H.; Mülhaupt, R.; Manivannan, R.; Möller, K.; Spaniol, T. P.; Okuda, J. *J. Mol. Cat. A: Chem.* **2004**, *213*, 137. (c) Beckerle, K.; Capacchione, C.; Ebeling, H.; Manivannan, R.; Mülhaupt, R.; Proto, A.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2004**, *689*, 4636. (d) Capacchione, C.; Manivannan, R.; Barone, M.; Beckerle, K.; Centore, R.; Oliva, L.; Proto, A.; Tuzi, A.; Spaniol, T. P.; Okuda, J. *Organometallics* **2005**, *24*, 2971. (e) De Carlo, F.; Capacchione, C.; Schiavo, V.; Proto, A. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1486.

(8) Proto, A.; Capacchione, C.; Venditto, V.; Okuda, J. *Macromolecules* **2003**, *36*, 9249.

(9) Milione, S.; Cuomo, C.; Capacchione, C.; Zannoni, C.; Grassi, A.; Proto, A. *Macromolecules* **2007**, *40*, 5638.

(10) Llauro, M. F.; Monnet, C.; Barbotin, F.; Monteil, V.; Spitz, R.; Boisson, C. *Macromolecules* **2001**, *34*, 6304.

(11) (a) Porri, L.; Giarrusso, A. In *Comprehensive Polymer Science*; Pergamon Press: Oxford, UK, 1989; Vol. *4*, p 53. (b) Costabile, C.; Milano, G.; Cavallo, L.; Guerra, G. *Macromolecules* **2001**, *34*, 7952. (c) Proto, A.; Capacchione, C. In *Stereoselective Polymerization with Single-Site Catalysts*; Baugh, L. S., Canich, J. A. M., Eds.; CRC Press: Boca Raton, FL; pp 445−473.

(12) Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 259.

MA800864Y