

Stereoselective Cyclopropanation by Cyclocopolymerization of Butadiene

Stefania Pragliola, Giuseppe Milano, Gaetano Guerra, and Pasquale Longo*

Dipartimento di Chimica, Università di Salerno, I-84081 Baronissi (SA), Italy

Received October 29, 2001

The highly strained three-member carbocycle is common in nature and sometimes occurs in multiply cyclopropanated compounds.¹ Linear as well as more complex multiply cyclopropanated architectures have been also obtained by several synthetic routes.¹ Transition-metal catalysts have provided relevant opportunities for selective cyclopropanation reactions, generally involving cycloaddition between a double bond and a metal carbene.²

Efficient transition-metal-catalyzed cyclocopolymerization processes have been described for α,ω -dienes,^{3–10} which lead to formation of homopolymers and copolymers containing methylene-1,3-cycloalkane units, where the cycles involve from five to seven carbon atoms. Moreover, 1,2-cyclopentane ring units have been obtained by cyclocopolymerization of 1,3-butadiene with ethene, by suitable metallocene-based catalytic systems.^{11,12} However, cyclopropane rings have never been obtained by cyclocopolymerization reactions.³ In fact (substituted and unsubstituted) dienes with double bonds that are linked by less than two (as well as by more than four atoms) generally do not undergo efficient cyclization and result in cross-linked materials.⁴

In this note, an unprecedented cyclopropanation reaction through cyclocopolymerization is described. In particular, ethene copolymers containing controlled amounts of methylene-1,2-cyclopropane units are produced in high yields and with high *trans* selectivity, by cyclocopolymerization of butadiene with ethene, catalyzed by the highly sterically hindered metallocene *rac*-[CH₂(3-*tert*-butyl)-1-indenyl]₂ZrCl₂ (**1**).

The homogeneous catalytic system consisting of (**1**) and methylaluminoxane (MAO) is highly active as well as isospecific and highly regiospecific for propene polymerization, leading to high-molecular weight polymers.¹³ The same catalytic system is also able to promote, although in poor yields, 1,4-polymerization (substantially equimolar *cis/trans*) of 1,3-butadiene.¹⁴

Copolymerization runs of 1,3-butadiene and ethene in the presence of catalyst (**1**) are described in rows 1–2 of Table 1.

For polymer samples obtained by catalyst (**1**), the ¹³C NMR spectra (shown for sample 2 in Figure 1) do not show any signal in the region of the unsaturated carbons, while the aliphatic region includes, beside the intense peak placed at 27.8 ppm related to methylene sequences, three resonances placed at 10.1, 17.1, and 32.5 ppm which can be attributed to *trans* 1,2-disubstituted cyclopropane rings as well as five resonances of *trans* 1,2-disubstituted cyclopentane rings¹¹ and minor resonances which can be attributed to *cis* 1,2-disubstituted rings (primed numbers in Figure 1).

These assignments have been made on the basis of the data reported in the literature for carbon in similar environments,¹⁵ by distortionless enhancement by polarization transfer 90 and 135 (DEPT-90 and DEPT-135) ¹³C NMR experiments.¹⁶ The presence of cyclopropane rings was further confirmed by the presence of a

Table 1. Copolymerizations of Ethene (E) and butadiene (B) Performed in the Presence of Zirconocene-Based Catalytic Systems

cat.	run ^a	[E] ^e (mol/L)	[B] ^e (mol/L)	X _B ^f	f _Δ ^g	f _○ ^g	f _{1,4} ^g
1	1 ^b	1.65	0.55	0.003	0.70	0.30	—
1	2 ^c	0.24	0.62	0.04	0.67	0.33	—
2	3 ^d	0.27	1.62	0.21	—	0.22	0.78

^a Polymerizations were carried out using 1×10^{-5} mol of zirconocene and 1×10^{-2} mol of MAO (based on Al). ^b Time 3 min, yield 2.00 g. ^c Time 18 h, yield 0.80 g. ^d Time 15 h, yield 0.35 g. ^e Concentration in the feed. ^f Molar fraction of butadiene units in the copolymer chains. ^g Fraction of butadiene leading to cyclopropane ring units (f_Δ), cyclopentane ring units (f_○) and 1,4 units (f_{1,4}); for cycloalkane rings, *trans/cis* ratio is always >5.

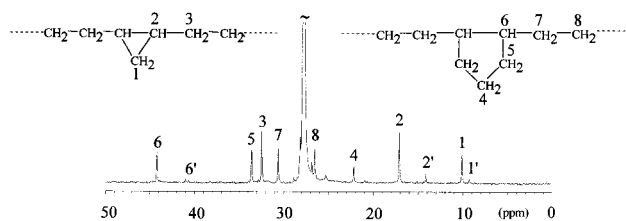


Figure 1. Aliphatic region of the ¹³C NMR spectrum of sample 2 of Table 1 (hexamethyldisiloxane scale). The peak placed at 27.8 ppm due to methylene sequences is out of scale to point out resonances due to the cyclopropane and cyclopentane rings. The minor peaks relative to carbons of cycloalkane rings in the *cis* configuration are labeled with primed numbers.

signal at 0.02₁ ppm (*J* = 5.7 Hz) due to the protons of the methines of *trans* 1,2-disubstituted cyclopropanes, and by verifying the characteristic coupling constant *J*_{C–H} of the methylene of cyclopropane ring at 10.1 ppm, and of cyclopentane ring at 22.3 ppm (160 and 130 Hz, respectively).^{15,17} All the main sequences of chemical structures of copolymers, recognized by NMR analysis, are also shown in Figure 1.

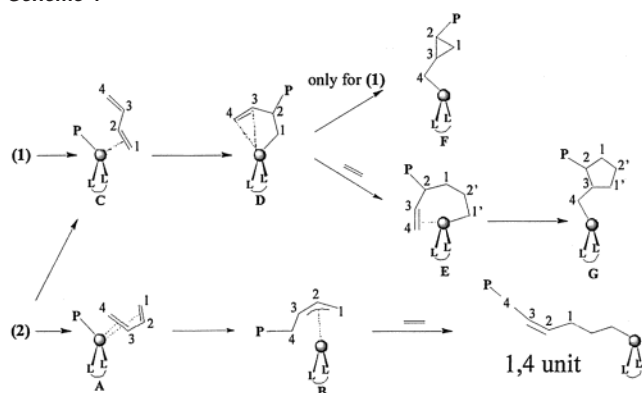
For the sake of comparison, the results of a copolymerization test effected in the presence of *rac*-(CH₂(1-indenyl)₂)ZrCl₂/MAO (**2**) (that is, the *ansa*-metallocene, similar to **1** but not presenting *tert*-butyl substituents on the indenyl groups) are reported in the third row of Table 1. Butadiene is prevalingly 1,4-inserted, and substantial fractions of 1,2-cyclopentane rings are also produced, as already observed for copolymerizations in the presence of bis-(η^5 -cyclopentadienyl)zirconium dichloride or (*rac*)-ethene-bis[1-3a,7a- η -(4,4,6,7-tetrahydro)-1-indenyl] zirconium dichloride.^{11,12}

Also on the basis of preliminary DFT calculations, it is suggested that the *s-cis*- η^4 coordination (A in Scheme 1), typical of the allyl mechanism of 1,3-butadiene polymerization (A \rightarrow B in Scheme 1) which would be prevailing for catalyst **2**, would not occur in the presence of the highly hindered *ansa*-metallocene catalyst **1**.

In the presence of **1**, butadiene would prefer a *primary* η^2 coordination (model C of Scheme 1), that is the coordinated double bond, being nearly parallel to the σ metal–polymeryl (Mt–P) bond,

* To whom correspondence should be addressed. E-mail: longo@chem.unisa.it.

Scheme 1



would present the noncoordinated double bond on the same side of the growing polymer chain (P). This primary butadiene coordination would give rise, through a 1,2-insertion into the σ metal–polymeryl bond, to a *primary* growing chain, that is a growing chain bound to the metal by a methylene group (model D of Scheme 1). Hence, the high steric hindrance of metallocene (**1**), which determines its high regioselectivity in favor of primary propene insertion,^{13a} would force butadiene to the primary 1,2-insertion typical of α -olefins. The resulting 1,2-inserted butadiene unit would be bonded to the metal also by a back-biting coordination of the closest double bond of the chain (D in Scheme 1). This four-carbon back-biting chain could give rise to a six-carbon back-biting chain (E in Scheme 1), through ethene insertion.¹¹ Both kinds of back-biting chains D and E could give rise to cyclization reactions leading to formation of cyclopropane and cyclopentane rings, respectively, through intramolecular insertion of the coordinated double bond into the metal– σ alkyl bond (F and G in Scheme 1, respectively), analogous to that one proposed for cyclopolymerizations of nonconjugated dienes.^{5,7c}

The route C \rightarrow D \rightarrow E \rightarrow G would also be a minor butadiene insertion pathway, in the presence of less hindered metallocenes, such as **2**, leading to minor fractions of 1,2-cyclopentane rings together with major fractions of 1,4-units.

At the moment it is not clear why the cyclopropanation route (D \rightarrow F in Scheme 1) would be available only for catalyst (**1**). A possible hypothesis, which we are verifying by computational methods, is that the formation of the cyclopropane rings would be related to the high steric hindrance of metallocene **1**.

As for stereochemistry, the ratio between the resonances of *trans* and *cis* isomers of 1,2-cyclopropane and 1,2-cyclopentane units is always higher than 5:1, that is larger than for most metal-catalyzed cyclopropanation reactions.²

The molecular origin of the *trans* stereoselectivity of the cyclopropanation reaction has been investigated by recently developed hybrid quantum mechanics (density functional theory) molecular mechanics approach (see Supporting Information). In particular, minimum-energy intermediates of kind D of Scheme 1, leading to *trans* and *cis* cyclopropane units, have been compared in Figure 2 A and B, respectively.

The minimum-energy conformation for the five-membered ring (four carbon atoms + metal) is essentially the same (envelope, with the dihedral 2-1-Zr-4 \approx 0) for both models, while the growing chain (CH₂P in Figure 2) is in equatorial or axial (more hindered) position

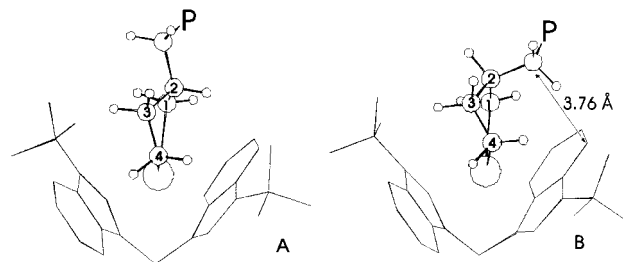


Figure 2. Minimum-energy intermediates (D of Scheme 1) possibly leading to *trans* (A) and *cis* (B) cyclopropane units. Lower steric hindrances correspond to the model for *trans* cyclization.

for intermediates leading to *trans* and *cis* cyclopropane rings, respectively. This results in a calculated energy difference in favor of the intermediate for *trans* cyclization of nearly 2.5 kcal/mol.

To our knowledge, this is the first case of complete cyclopropanation of butadiene as well as the first case of cyclopropanation by cyclopolymerization. This result seems particularly relevant since refers to basic monomers leading to reactive ethene-based copolymers of potential industrial relevance. In fact, the insertion of a controlled number of reactive cyclopropane rings, and of possible derived functional groups, into polyolefin chains can be important to several applications.

Acknowledgment. This paper is dedicated to the memory of Professor Dr. Guido Sodano. This work was supported by the MIUR of Italy, Grant PRIN-2000 and Cluster 26. We thank Dr. Luigi Resconi of Basell and Dr. Luigi Cavallo of the University of Naples for useful discussions.

Supporting Information Available: Details about experimental procedures and computational method (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>

References

- (1) Faust, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 2251.
- (2) (a) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 819. (b) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 493.
- (3) Butler, G. B. *Acc. Chem. Res.* **1982**, *15*, 370.
- (4) Coates, W. C. *Chem. Rev.* **2000**, *100*, 1223.
- (5) Marvel, G. S., Jr.; Garrison, W. E. *J. Am. Chem. Soc.* **1959**, *81*, 4737.
- (6) Cheng, H. N.; Khasat, N. P. *J. Appl. Polym. Sci.* **1988**, *35*, 825.
- (7) (a) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953. (b) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91. (c) Cavallo, L.; Guerra, G.; Corradini, P.; Resconi, L.; Waymouth, R. M. *Macromolecules* **1993**, *26*, 260.
- (8) Schaverien, C. J. *Organometallics* **1994**, *13*, 69.
- (9) Jeremic, D.; Wang, Q. Y.; Quyoum, R.; Baird, M. C. *J. Organomet. Chem.* **1995**, *497*, 143.
- (10) Mitani, M.; Oouchi, K.; Hayakawa, M.; Yamada, T.; Mukaiyama, T. *Chem. Lett.* **1995**, 905.
- (11) Galimberti, M.; Albizzati, E.; Abis, L.; Bacchilega, G. *Makromol. Chem.* **1991**, *192*, 2591.
- (12) Welborn, H. C., Jr. Eur. Pat. EP0275676, 1988; *Chem. Abstr.* **1988**, *109*, 150259z.
- (13) (a) Resconi, L.; Balboni, D.; Baruzzi, G.; Fiori, C.; Guidotti, S.; Mercandelli, P.; Sironi, A. *Organometallics* **2000**, *19*, 420. (b) Toto, M.; Cavallo, L.; Corradini, P.; Moscardi, G.; Resconi, L.; Guerra, G. *Macromolecules* **1998**, *31*, 3431.
- (14) Pragliola, S.; Forlenza, E.; Longo, P. *Macromol. Rapid Commun.* **2001**, *22*, 783.
- (15) O'Connor, E. J.; Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1987**, *109*, 3739.
- (16) (a) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Res.* **1982**, *48*, 323. (b) Aubert, P.; Sledz, J.; Schue, F.; Brevard, C. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 955. (c) Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984.
- (17) Burke, J. J.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1964**, *86*, 1870.

JA017416C