



Ethylene/1,3-butadiene cyclocopolymerization catalyzed by zirconocene systems



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ARTICLE INFO

Article history:

Received 23 January 2014

Received in revised form 3 June 2014

Accepted 23 June 2014

Available online 1 July 2014

Dedicated to Prof. Adolfo Zambelli on the occasion of his 80th birthday.

Keywords:

Cyclopolymerization

Metallocene catalysts

1,3-Butadiene

DFT

ABSTRACT

Copolymerizations of ethylene with 1,3-butadiene in the presence of catalytic systems based on C_2 -symmetric zirconocenes $rac-(CH_3)_2Si(2-R-4-R'-1-indenyl)_2ZrCl_2$ (where $R = CH_3$ – or H and $R' = C_6H_5$ – or H) are compared. The chemical nature and the relative amount of constitutional comonomer units from butadiene (1,4-*trans*, methylene-1,2-cyclopentane and methylene-1,2-cyclopropane) are strongly affected by the bulkiness of the substituent on the indenyl ligands. The unsubstituted indenyl zirconocene system $rac-(CH_3)_2Si(indenyl)_2ZrCl_2$ /methylalumoxane (MAO) inserts 1,3-butadiene leading to both cyclopentane and 1,4-*trans* units, whereas exclusively cyclopentane constitutional units are obtained from $rac-(CH_3)_2Si(2-methyl-1-indenyl)_2ZrCl_2$ /MAO. The catalytic system $rac-(CH_3)_2Si(2-methyl-4-phenyl-1-indenyl)_2ZrCl_2$ /(MAO) is able to incorporate about 30% of butadiene units into polymer chains and to form up to 10% of cyclopropane units. An unusual insertion mechanism for conjugated diolefins, that involves a butadiene η^2 primary coordination and insertion leading to formation of cycloalkane units, is largely predominant for all used catalytic systems. Mechanistic studies and DFT calculations indicate that the chemoselectivity of the reaction depends on the bulkiness of the substituents on the indenyl ligands of catalyst.

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1. Introduction

Cyclic olefin copolymers (COCs) form a class of thermoplastic materials of growing interest [1,2]; they are useful materials due to solvent and chemical resistance, stiffness, and excellent transparency and, therefore, they are suitable for optical applications.

COCs can be produced by copolymerization of α -olefins, like ethylene or propylene, with cycloalkenes; a drawback of this method is, however, the low reactivity of cyclic alkenes with respect to that of linear olefins [2–5].

Polyolefins containing cycles and structurally similar to COCs can be also obtained by copolymerization of α -olefins with α,ω -nonconjugated dienes involving intramolecular cyclization [6–9]. Nevertheless, this last polymerization

process allows obtaining only COCs with cycles involving from five to seven carbon atoms. Cross-linked materials are, instead, obtained by using α,ω -nonconjugated dienes with double bonds, that are connected by more than four carbon atoms [10,11].

In the last decade, several articles focused on COCs obtained by copolymerization of α -olefins and conjugated dienes in the presence of group IV metal [12–21] or rare earth [22–24] based catalysts, were reported. In particular, Longo et al. recorded an unprecedented cyclopropanation reaction by copolymerization of 1,3-butadiene with α -olefins (ethylene and propylene) [12–15], catalyzed by the highly sterically hindered metallocene $rac-[CH_2(3-tert-butyl-1-indenyl)_2]ZrCl_2$ [25], activated by methylalumoxane (MAO).

It was found that, in suitable copolymerization conditions, all butadiene can be inserted as cyclic monomeric units, methylene-1,2-cyclopropane units and methylene-

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1,2-cyclopentane units, in a ratio generally not far from 2:1 and both with high *trans* selectivity [12–15]. As widely clarified, the cyclopolymerization of 1,3-butadiene occurs with a mechanism involving an intramolecular insertion of the double bond added to the polymeryl chain after an unusual primary vinyl insertion of 1,3-butadiene (see Scheme 1). The primary insertion of 1,3-butadiene unusual in the generally well accepted diene homopolymerization mechanism [26–32], which involves the secondary coordination and insertion of a monomer unit, can be ascribed to the butadiene insertion on a metal – polymeryl σ bond [33,34], associated to the bulkiness of the substituent in positions 3 and 3' of the catalytic precursor [12–15]. In particular, it was found that the steric hindrance of ligand substituents is responsible for the formation of cyclopropane rings. In fact, by using metallocenes which include, in the C_2 symmetry related positions 3 and 3', methyl and ethyl substituents instead of *tert*-butyl groups, only methylene-1,2-cyclopentane constitutional units from butadiene are obtained with high selectivity, whereas zirconocenes, which includes an unsubstituted bis(indenyl) ligand, gives rise together to methylene-1,2-cyclopentane, 1,4-*trans* constitutional units from butadiene [13].

It is worth noting that, these peculiar COCs containing a controlled number of reactive cyclopropane rings could be industrially relevant, if obtained with high yields from basic monomers. As an example, it was shown that it is possible to produce crosslinked polyethylene by simple thermal treatments of such copolymers [35,36]. Moreover, by using a similar procedure, polyethylene-*graft*-polystyrene copolymers were prepared by thermal treatment at 200 °C of polyethylene samples containing cyclopropane rings in the presence of a high excess of styrene [37]. Both processes were generated by radicals formed at high temperature from the breaking of the constrained cyclopropane rings. It is worth underlining that these processes do not pollute the natural environment because both crosslinking polyolefins and graft copolymers are obtained without solvent and initiators and only require thermal treatments of reagents.

However, one of the limits of the catalytic system *rac*-[CH₂(3-*tert*-butyl-1-indenyl)]₂ZrCl₂/MAO is the low activity shown towards 1,3-butadiene. In fact, the amount of cyclopropane rings in the copolymer chains is never higher than 3% of all inserted units.

In this paper, an investigation on bis-indenyl-ZrCl₂ catalysts presenting a $-(CH_3)_2Si-$ bridge and different substituents on indenyl ligands (see Scheme 2) was conducted an attempt to increase incorporation of cyclopropane ring units along the copolymer chains.

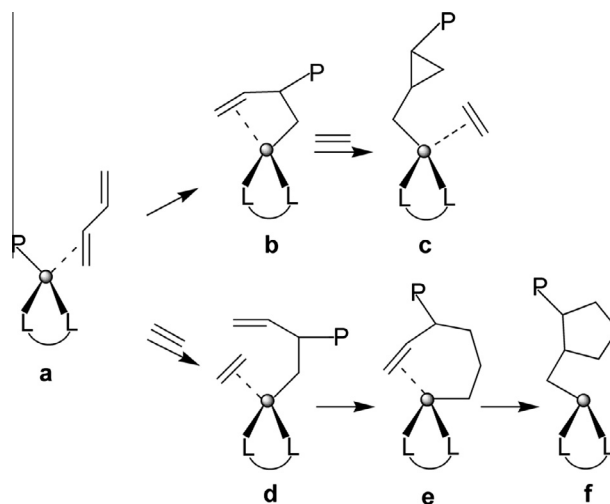
2. Experimental section

2.1. General polymerization procedure

All the operations were performed under nitrogen atmosphere by using conventional Schlenk-line techniques. Toluene was refluxed over sodium for 48 h and distilled before use. 1,3-butadiene and ethylene were purchased from Sigma–Aldrich and used without further purification. Methylalumoxane was purchased by Witco and used as a solid after distillation of solvent (toluene). The catalytic precursors, *rac*-(CH₃)₂Si(2-methyl-1-indenyl)₂ZrCl₂ **2** and *rac*-(CH₃)₂Si(2-methyl-4-phenyl-1-indenyl)₂ZrCl₂ **3**, were synthesized using the procedure reported in literature [38]. The catalytic precursor, *rac*-(CH₃)₂Si(1-indenyl)₂ZrCl₂ **1** was purchased by Strem Chemicals.

2.2. Ethylene-1,3-butadiene copolymerizations

In a typical copolymerization procedure, a constant ethylene overpressure was applied to a solution of 1,3-butadiene (330 mg, 6.1 mmol for runs **A**, **B**, **C** of Table 1; 1.48 g, 27.4 mmol for runs **D**, **F**, **G** of Table 1) and 290 mg of MAO in 10 mL of dry toluene. After thermostatisation at reaction temperature (20 °C), 1.5×10^{-5} mol of metallocene in 2 mL of dry toluene were added to the solution. All the copolymers were recovered by precipitation with



Scheme 1.

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