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Advances and Limits in Copolymerization of Olefins with Conjugated Dienes

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Summary: The field of the copolymerization of olefins with conjugated dienes has been investigated. While the insertion of butadiene is often limited with most catalyst systems designed for olefin polymerization, lanthanide metallocene catalysts insert butadiene with good efficiency. In the present paper, the preparation of a vast range of products including new polymers is reviewed.

Keywords: copolymerization; metallocene; neodymium; poly(ethylene-*co*-butadiene)

Introduction

The copolymerization of olefins and conjugated dienes is of particular importance since the resulting unsaturated copolymers may exhibit interesting properties (crosslinking efficiency, rubber compatibility...). However, this reaction is considered as to be very difficult to perform since the two classes of monomers polymerize according to different mechanisms. In most cases, homopolymers are obtained and/or a polymerization inhibition is observed.

Early studies with Ziegler-Natta catalysts have not allowed to develop these polymers on industrial scale. Two families of polymers have been prepared. Alternating olefins/butadiene copolymers have been obtained with titanium and vanadium based catalysts.[1] Nevertheless, these catalysts have to be prepared at very low temperature (ca -70°C) and the polymerizations are performed at temperatures under 0°C. Copolymers with a multiblock structure have been obtained with vanadium catalysts and conventional Ziegler-Natta catalysts at higher temperatures. These polymers tend to form gels when increasing the butadiene content.

Recently, a new interest appeared for these polymers in both academic and industrial research.

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Advances in organometallic chemistry have allowed the synthesis of tailor-made catalysts which can be used to synthesize new polymers.

First investigation with group 4 metallocenes provided poor results. Actually, a high decrease in activity has been observed in the presence of conjugated dienes and the butadiene insertion was low.[2] Interestingly, Galimberti et al have reported the formation of cyclopentane rings which may be obtained after a 1,2-insertion of butadiene.[3] More recently, Longo et al. have studied in details the mechanisms of cyclocopolymerization of butadiene with ethylene and have discovered the formation of cyclopropane rings in addition of cyclopentane rings.[4] The alternating cyclocopolymerization of butadiene with ethylene have been elegantly described by Waymouth et al. using metallocene catalysts.[5] Nevertheless, in all the aforementioned works the activity was very low and the insertion of butadiene was not efficient. In order to obtained significant amount of diene in the polymer, high concentration of butadiene were required. Interestingly, the synthesis of poly(olefin-*co*-butadiene) have also been reported in several patents from Ube Industry,[6] Sumimoto Chemical Company[7] and Mitsui Chemicals.[8] Catalysts based on *ansa*-cyclopentadienyl-amido and ansa-cyclopentadienyl-phenoxy compounds have been used.

Coordination catalysts based on lanthanides are known to homopolymerize both conjugated dienes and olefins. While the insertion of butadiene is often limited with most catalyst systems designed for olefin polymerization, lanthanide metallocene catalysts insert butadiene with good efficiency.[9-12] The authors have prepared a vast range of products including new polymers, the main results are summarized in this paper.

Experimental

Materials. The syntheses of complexes $(Me_3SiC_5H_4)_2NdCl$ **1**, $[Me_2Si(3\text{-}Me_3SiC_5H_3)_2]NdCl$ **2** and $[Me_2Si(C_{13}H_8)_2]NdCl$ **3** have been reported previously by the authors.[9, 11]

Polymerization procedure. Copolymerizations of ethylene with butadiene were performed in a 500 mL glass reactor according to the procedure described previously.[10] Copolymerization of α-olefin with butadiene were performed in a 250 mL glass reactor equipped with a stainless steel blade stirrer and an external water jacket for temperature control. Alkylating agents (Li/Al or Mg compounds) and the neodymium complex in 10 mL of toluene were introduced respectively in a flask containing 100 mL of α-olefin. The mixture was stirred for 5 min and then transferred into the reactor under a stream of argon.

The argon was then pumped out and the reactor was charged with 25 mL of butadiene and heated at 80°C. In the case of propylene, the polymerization was performed in a 1 L stainless steel reactor at 7 bar (450 mL of toluene, 80°C).

Analytical techniques. Molecular weight of the polymers were measured at 45 °C by means of gel permeation chromatography (Waters apparatus) using THF as solvent and calibrated with polystyrene standards. ^{1}H and ^{13}C NMR were recorded on a Bruker DRX 400 operating at 400 MHz for ^{1}H and 100.6 MHz for ^{13}C by using a mixture of tetrachloroethylene (TCE) and perdeuterobenzene (C_6D_6) as solvent. Melting points were determined by differential scanning calorimetry (Perkin Elmer Pyris 1). Samples were heated from 35 °C to 180 °C at 5°C/min. Glass-transition temperatures were measured on a Setaram DSC 131 apparatus. Samples were heated from -120 °C to 150 °C at 10 °C/min.

Results and Discussion

Lanthanidocene chloride precursors can be transformed to neutral active species for olefin polymerization with alkylating agents such as BuLi, MgR_2, and mixture of BuLi and $AlH(i\text{Bu})_2$. The activity in ethylene polymerization is high (10^6-10^7 g/mol.h) but significantly lower than in the case of group 4 metallocenes. However, they present an original behavior in the presence of butadiene.

Copolymerization of ethylene with butadiene. Neodymocene complexes with very simple structures such as $(Me_3SiC_5H_4)_2NdCl$ **1** allowed the synthesis of poly(ethylene-*co*-butadiene). It is the first successful copolymerization of ethylene with butadiene using lanthanide catalysts. The microstructure of butadiene units was highly *trans*-1,4 and the insertion of butadiene was efficient (Table 1). As in the case of group 4 metallocenes a decrease in activity was observed since the insertion of monomer was slow after the insertion of a butadiene unit. This problem can be overcome by introducing a bridging group (silylene bridge) between the two cyclopentadienyl ligands. High activity and efficient butadiene insertion were obtained with catalyst systems based on the complex $[Me_2Si(3\text{-}Me_3SiC_5H_3)_2]NdCl$ **2** (runs 2, 3).

DSC thermograms of copolymers (Figure 1) showed the absence of homopolyethylene in copolymers. Copolymers have a strong alternating character as demonstrated by the reactivity ratios (r_E = 0.25 and r_B = 0.08) obtained from ^{13}C NMR analyses.[13] The polymers were obtained at convenient temperature (80°C) which was not the case with vanadium catalysts.

Table 1. Copolymerization of ethylene with butadiene using neodymocene catalysts (300 mL toluene, 4 bar, 80°C).

run	catalyst	[Nd]	butadiene[b)]		yield	microstructure[b)]		
		μM	feed	pol.	g/h	1,2	*trans*-1,4	rings
1	**1**/Li/Al[a)]	235	3.9	3.5	3.7/1.3	4	96	-
2	**2**/Li/Al	202	5.4	6.6	13.5/0.5	2	98	-
3	**2**/Li/Al	196	41	42	4.8/2	2.5	97.5	-
4	**3**/Mg[a)]	195	30	19.3	8.5/4	28.4	27.6	44

[a)] Li/Al and Mg stand for respectively BuLi+AlH(iBu)$_2$ and Mg(Bu)(Oct).

[b)] Determined by ^{1}H and ^{13}C NMR.

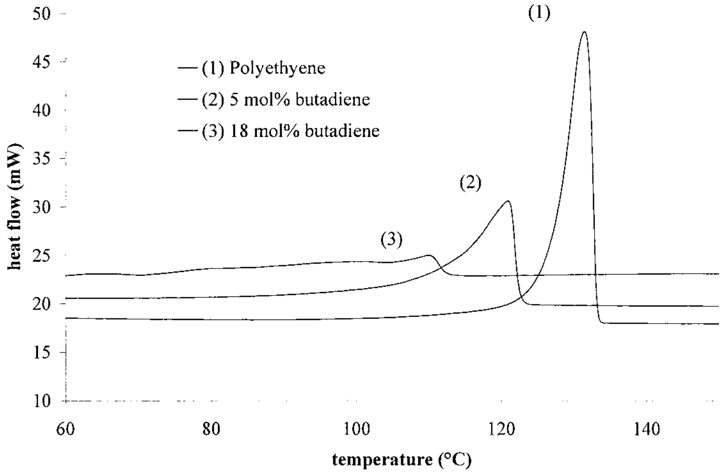

Figure 1. DSC thermograms at various compositions of poly(ethylene-*co*-butadiene) obtained with a catalyst system based on complex **2** (80°C, 4 bar).

More interestingly, a new family of polymers was obtained with catalyst systems based on the silylene-bridged bis(fluorenyl) complex [Me$_2$Si(C$_{13}$H$_8$)$_2$]NdCl **3** (run 4). Actually, NMR analyses of copolymers showed the presence of classical 1,2- and *trans*-1,4-butadiene units but also an original structure.[13] Unlike group 4 catalysts which provide polymers containing cyclopropane or cyclopentane rings, here cyclohexane rings were obtained. This result sheds lights on the unique behavior of lanthanide catalysts. A high percentage of butadiene units are involved in this ring formation depending on both butadiene content in the feed and the concentration of monomers. Copolymers containing ~ 20 mol% of inserted butadiene were prepared at various increasing concentration of monomers (ethylene + butadiene) in the reactor. *trans*-1,4-insertion was almost constant (25-29 % of butadiene units) but the cyclization selectivity decreased (from 58.6 % at low concentration to 20.3 % at high concentration) while 1,2-units increased (from 12.8 % to 54.7 %). These observations are in agreement with an intramolecular mechanism which involves 1,2-butadiene units (Figure 2).

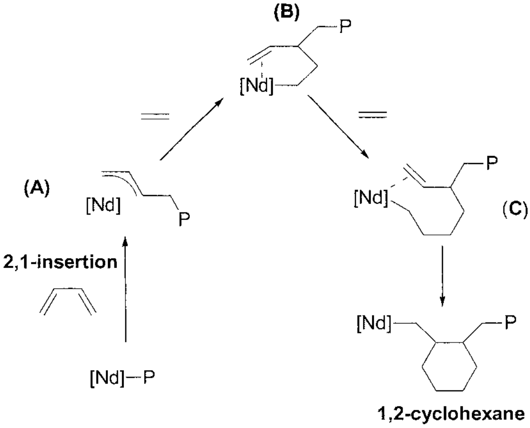

Figure 2. Mechanism of cyclization

The cyclization occurs after a classical 2,1-insertion of butadiene (via an η^3-butenyl intermediate) since in the case of group 4 catalyst butadiene is 1,2-inserted like an olefin (cyclopentane rings are then formed).

The new poly(ethylene-*co*-butadiene) have high molecular weight (run 4, Mw = 270000 g/mol – PDI = 2.7) and presents relatively high *Tg* values compared to polyethylene. DSC analyses of amorphous poly(ethylene-*co*-butadiene) with various microstructure (change of the ratio rings/1,2/*trans*-1,4) and the same butadiene content (20 mol%) showed the strong influence of the amount of cyclic structures along the polymer chain on *Tg* values. *Tg* increased from -44°C to -30 °C while the cyclization selectivity increases from 20.3% to 58.6% of butadiene units (ie 4.1 to 11.4 mol% of rings in the polymer).[11]

Copolymerization of α-olefin with butadiene. Lanthanide catalysts are efficient in polymerization of ethylene but the polymerization of α-olefin is more difficult. In the course of our studies on polymerization of olefins with butadiene, we have investigated the ability of complex **1**, **2** and **3** in copolymerization of an α-olefin with butadiene. Poor results were obtained but a modification of the catalyst structure allowed to copolymerize these monomers. The new catalyst is based on the complex $[Me_2Si(C_5H_3)(C_{13}H_8)]NdCl$ **4** which was prepared by reacting $[Li(thf)]_2[Me_2Si(C_5H_3)(C_{13}H_8)]$ with $NdCl_3$ in thf. Some of the significant results are presented in Table 2.

Table 2. Copolymerization of α-olefins with butadiene[a)]

olefin	yield	Mn[f)] (PDI)	olefin[g)]	microstructure[g)]			Tg
	g/h	g/mol	mol%	1,2	*cis*-1,4	*trans-1,4*	°C
propylene[b),c)]	7.3/15	9100 (2.0)	35.8	6.1	2.4	91.5	-75.3
hexene[c)]	18.9/17	17500 (1.9)	29.8	7.5	4.6	87.9	-68.7
octene[c)]	11.4/7	11500 (1.7)	32.0	7.0	3.7	89.3	-71.5
octene[d)]	13.3/15	8960 (1.8)	29.4	16.3	2.1	81.6	-65.4
octene[e)]	13.1/15	30650 (2.3)	28.8	10.3	3.1	86.6	-69.0

[a)] Polymerization condition: [Nd]= 0.56-0.62 mM, T = 80°C, toluene = 10 mL, α-olefin = 100 mL, butadiene = 25 mL. [b)] Toluene = 450 mL, butadiene = 25 mL, P_T = 7 bar. [c)] 4/Li/Al (1/10/10). [d)] 4/Mg (1/20). [e)] 4/Mg (1/5). [f)] Determined by GPC in thf against polystyrene standards . [g)] Determined by ^1H and ^{13}C NMR.

Copolymers containing about 30 mol% of α-olefin were obtained. The microstructure analysis of these copolymers showed that the α-olefin was isolated between butadiene units (no sequence olefin-olefin). The microstructure of butadiene units was highly *trans*-1,4. DSC thermograms showed that these polymers are amorphous and present a glass-transition temperature around –70°C. Another important remark concerns the increase of molecular weights by decreasing the amount of alkylating agent Mg(Bu)(Oct). The same observation has been done by the authors in copolymerization of ethylene with butadiene. This result is explained by a decrease of the reactions of chain transfer to magnesium.[14]

Conclusion

The ability of lanthanidocene catalysts in copolymerization of olefin with conjugated dienes was shown. The fine modification of the structure of the catalyst allowed the synthesis of original polymers.

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