Activation by the Grignard reagent of the bis(2-phenylindenyl)zirconium dichloride—triisobutylaluminum catalytic system for propene polymerization

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Polymerization of propylene with the three-component catalytic system bis(2-phenylindenyl)zirconium dichloride—alkyl magnesium chloride—triisobutylaluminum is studied. The annelated zirconocene is alkylated by the Grignard reagent. The three-component system is as good in activity as two-component systems with polymethylalumoxane as a cocatalyst. Stereoblock elastomeric polypropylene with a high molecular weight is formed.

Key words: bis(2-phenylindenyl)zirconium dichloride, alkylmagnesium chloride, propylene, elastomeric polypropylene, polymerization catalysts.

Thermoplastic elastomeric polypropylene (PP) has been found in the products of propylene polymerization more than forty years ago.[1] An interest in new catalysts for propylene polymerization remains high up to now due to a great significance of the product.[2—5] However, since the consumption of the cocatalyst (methylalumoxane) is relatively high, its use in catalytic systems affects noticeably the cost of the target product.[5] Therefore, the replacement of methylalumoxane by other cocatalysts is an urgent problem.

This work is aimed at studying propylene polymerization in the new three-component catalytic system $(2\text{-PhInd})_2ZrCl_2$—AlkMgCl—$AlBu^i{}_3$, where Alk = Me or Bu.

Experimental

Preliminarily purified and refrozen above $LiAlH_4$ hexane, heptane, toluene, and THF were used for the synthesis of the catalysts and Grignard reagents. All procedures were carried out in dry pure argon. The Grignard reagents Bu^nMgCl and MeMgCl were prepared in THF using known procedures.[6] To prepare $(2\text{-PhInd})_2ZrCl_2$, Bu^nLi (1.77 mol L^{-1}, 6.7 mmol, 3.78 mL) in heptane was added dropwise with continuous stirring at −60 °C to a suspension of 2-phenylindene (1.29 g, 6.7 mmol) in toluene (10 mL) with a minor content of THF. The resulting orange-yellow solution of 2-PhIndLi was slowly heated to 25 °C and stored for 3 h. After this the solution was slowly added to $ZrCl_4$ (Aldrich, 0.78 g, 3.35 mmol) in toluene at −20 °C. Then the mixture was heated to 25 °C and stirred for 10 h. The solvent was removed, and $(2\text{-PhInd})_2ZrCl_2$ was multiply extracted with toluene combining the extracts and concentrating the solution by the removal of a portion of the solvent, and cooled to −30 °C. The crystals were washed with hexane, dried, and isolated in 71% yield (1.15 g). Found (%): C, 66.2; H, 4.1; Cl, 13.0; Zr, 16.7. $C_{30}H_{22}Cl_2Zr$. Calculated (%): C, 66.16; H, 4.07; Cl, 13.02; Zr, 16.75. Compounds $(2\text{-}cyclo\text{-HexylInd})_2ZrCl_2$ and $(2\text{-}p\text{-TolylInd})_2ZrCl_2$ were synthesized by known procedures.[7,8]

The kinetics of propylene polymerization was studied on a UVD-60 high-pressure setup in a 0.2-L reactor. The solvent and triisobutylaluminum were successively introduced with stirring into the reactor. The reaction began from the moment of destruction in the reactor of two sealed ampules filled with $(2\text{-PhInd})_2ZrCl_2$ and the Grignard reagent. Polymerization was performed at a constant propylene pressure. The reaction was terminated by ethanol containing 10% HCl. The product was washed with water and ethanol and dried at 60 °C *in vacuo* to a constant weight. The macrotacticity index of PP (D_{998}/D_{973}) was determined on a Perkin Elmer FT-IR 1720X instrument.[9] ^{13}C NMR spectra of solutions of polymers were recorded at 75 MHz on a Bruker AM-250 instrument in tetrachloroethane at 100 °C. The molecular weight of the obtained polymer was determined from the viscosity of a solution of PP in decalin at 135 °C and by GLC on a Waters 150-C instrument.

Results and Discussion

A double excess (with respect to $(2\text{-PhInd})_2ZrCl_2$) of Bu^nMgCl or MeMgCl was introduced directly into the reaction mixture to replace the chlorine ions in $(2\text{-PhInd})_2ZrCl_2$ by the alkyl groups. However, active sites of polymerization are not formed in the two-component L_2ZrCl_2—RMgCl systems. The addition of the third component ($AlBu^i{}_3$) to them gives an active catalytic system (Fig. 1). Triisobutylaluminum itself is an efficient alkylating reagent, however, active sites of polymerization are not formed either in the two-component $(2\text{-PhInd})_2ZrCl_2$—$AlBu^i{}_3$ system (without RMgCl).

In the presence of the $(2\text{-PhInd})_2ZrCl_2$—Bu^nMgCl—$AlBu^i{}_3$ catalytic system, the rate of propylene polymerization is maximum in the very beginning of the reaction. Then it decreases during the process (Fig. 1), and the rate of deactivation of the active sites

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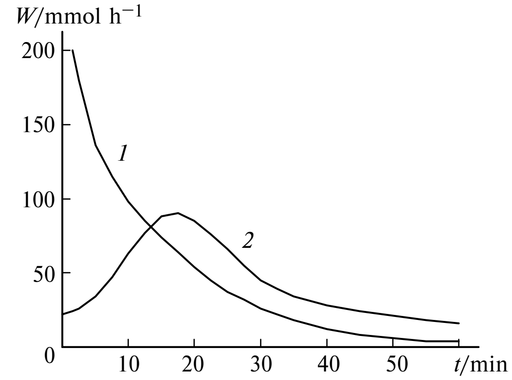

Fig. 1. Rate of propylene polymerization in the three-component systems with *n*-butyl- (*1*) and methylmagnesium chloride (*2*). Reaction conditions: −2 °C; $[(2\text{-PhInd})_2ZrCl_2] = 2.7 \cdot 10^{-5}$ mol L^{-1}, molar ratios Al/Zr = 150, Mg/Zr = 2; volume of a solution 100 cm^3 (of them 60 cm^3 toluene); partial pressure of propylene 5.0 atm.

depends on the experimental conditions. The process rate in the three-component system involving MeMgCl differs from that in the system with Bu^nMgCl (Fig. 1). In this case, the initial polymerization rate is ~20-fold lower, however, further it increases gradually, and the maximum rate, which is achieved in 17 min, becomes comparable with the polymerization rate in the system with Bu^nMgCl (Fig. 1, curve *2*).

The main experimental results of the work are presented in Table 1. The efficiencies of two systems containing Bu^nMgCl and MeMgCl, unlike their initial rates, are approximately equal (2528 and 2147 kg PP (mole Zr h)$^{-1}$, see Table 1, entries 4 and 12). As can be seen in Table 1, the efficiency increases with an increase in the propylene pressure and a decrease in the reaction temperature. When the partial pressure of propylene increases from 3 to 7 atm, the efficiency increases by ~3 times (entries 1—4), whereas the initial rate increases by ~30 times. The molecular weights of PP are rather high and range from 155000 to 590000 (entries 1—11). Polydispersity of the polymers obtained (M_w/M_n) is somewhat lower than that of similar samples obtained previously in the presence of the $(2\text{-PhInd})_2ZrCl_2$—methylalumoxane system (M_w/M_n = 3.5—4.0)[3] and is virtually independent of the propylene concentration and temperature of the process.

Analysis of the structure of the PP samples by IR and ^{13}C NMR spectroscopy indicates the formation of stereoblock PP. The polymers possess a low stereoregularity. The isotacticity index of the polymer (D_{998}/D_{973}) changes from 0.15 to 0.32 (entries 1—9). It is seen that a decrease in the reaction temperature and molar ratio Al/Zr increases the stereoregularity and molecular weight of the polymer. The pentad composition (*mmmm*) of our PP (entry 6) agrees with the stereocomposition of the elastomer obtained previously.[2] The 36% content of isotactic pentads can be achieved (entry 9) by changing the Al/Zr ratio. For comparison Table 1 contains the properties of PP obtained in the presence of $(2\text{-}cyclo\text{-HexylInd})_2Cl_2$ and $(2\text{-}p\text{-TolylInd})_2ZrCl_2$ with other ligands (entries 15 and 16).

Table 1. Influence of polymerization conditions on the catalyst efficiency and properties of polypropylene obtained in the presence of $(2\text{-PhInd})_2ZrCl_2$ and $AlBu^i_3$ (molar ratio Mg/Zr = 2, solvent toluene, 60 cm^3, reaction duration 1 h)

Entry	$(2\text{-PhInd})_2ZrCl_2$ /μmol	Al/Zr	RMgCl	p /atm	T /°C	A^a	$M_w \cdot 10^{-3}$	M_w/M_n [b]	*mmmm* [c] (%)	*m* [d] (%)
1	2.35	200	Bu	3.1	−3	808	155		22	65
2	2.61	200	Bu	5.0	−3	1037	255		24	66
3	2.65	200	Bu	6.0	−3	1780	320		26	68
4	2.69	200	Bu	7.1	−3	2528	389		27	70
5	2.44	150	Bu	5.0	25	602	139	3.0		
6	2.46	150	Bu	5.0	−2	1057	425	2.51	32	73
7	2.78	150	Me	5.0	−2	849	194	2.58		
8	2.7	150	Me	5.0	25	474	109	2.45		
9	2.81	100	Bu	7.1	−3	2341	416	2.63	36	69
10	3.13	200	Bu	7.1	25	1757	207	2.5		
11	2.69	200	Bu	7.1	−3	2528 [e]	590	2.45		
12	3.05	200	Me	7.1	−3	2147	317	2.95		
13	3.0	200	Me	7.1	25	1663	228	2.95		
14	3.4	300	Bu	7.25	18	1782	290	2.72	24	66
15	3.6 [f]	300	Bu	7.25	18	770	132	2.9	13	59
16	3.1 [g]	300	Bu	7.25	18	1219	231	3.35	25	74

[a] Efficiency A in kg PP/(mole Zr h).

[b] M_w is the weighted-mean molecular weight, and M_n is the numerical-mean molecular weight.

[c] *mmmm* is the content of isotactic pentads.

[d] *m* is the content of isotactic diads.

[e] Reaction duration 2 h.

[f] $(2\text{-}cyclo\text{-HexylInd})_2ZrCl_2$.

[g] $(2\text{-}p\text{-TolylInd})_2ZrCl_2$.

Thus, elastomeric PP can be obtained in the presence of the new three-component Ziegler—Natta system containing no methylalumoxane. Desired alkyl groups, including labile groups, can be introduced into zirconocenes using the Grignard reagent. Changing the conditions of the process allows the purposeful influence on the properties of the polymeric product (molecular-weight distribution, stereoregularity, and others, see Table 1), which makes it possible to vary the physicomechanical parameters of PP.

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