Nature of Activating Effect of Two-Step Polymerization of Propylene

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Received 9 March 1998; accepted 4 August 1998

ABSTRACT: The prepolymerization effect on propylene polymerization in the presence of a TiCl₃-based catalyst, modified by di-n-buthyl ether, was studied. The influence of prepolymerization on the electron spin resonance spectra and morphology of the catalyst, as well as the properties and the morphology of both prepolymer and regular polymerization products, was investigated. The polymer morphology was evaluated through scanning electron microscopy, polymer bulk density, and particle size distribution. Some evidence of the enhancement effect of prepolymerization on the catalyst activity and stereospecificity was obtained. No influence from prepolymerization was observed on molecular weight and its distribution, melting point, and crystallinity of polypropylene. These findings, when discussed in connection with the morphology results of the catalyst and prepolymer, showed that the prepolymerization performed at mild reaction conditions prevents fast and extensive "fragmentation" of the original catalyst agglomerates. The more controlled breakup of the catalyst particles in the course of slowed growth of prepolymer exposes the occluded catalyst fragments with uniform size and prevents their reagglomeration. Resulting from the above, catalyst homogeneity, catalyst activity, and polymer morphology are improved. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 353-359, 1999

Key words: propylene polymerization; prepolymerization; catalyst; prepolymer; polymer characterizations

INTRODUCTION

The catalysts used in the industrial production of polyethylene and polypropylene are frequently preactivated by prepolymerization of a small amount of olefin.^{1–13} Although the activating effect of this prepolymerization has been known from the literature for nearly two decades, the true nature and mechanism of the prepolymerization step still have not been understood very well and explained, and they require further attention. The comparison of literature data suggests that the extent of the rate-enhancing effect of prepolymerization is dependent on the type of the catalytic system and the type of monomer used for prepolymerization, as well as on the prepolymerization conditions.

The available literature provides various hypotheses that try to explain the reasons for the observed rate-enhancement effect of prepolymerization:

- formation of new active sites at the prepolymerization step^{2,3,5,6,9}
- activation of dormant sites as the result of creation of the more suitable ligand environment^{1,6,10}

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Journal of Applied Polymer Science, Vol. 71, 353–359 (1999)

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- reduction of diffusional mass transfer resistance of the co-catalyst and monomer through the polymeric layer surrounding the active sites 5
- \bullet controlled fragmentation of catalyst at the prepolymerization ${\rm stage}^{1,10}$ and
- structural change (i.e., increased porosities of the growing particles²).

It is difficult to determine which one of the previously described mechanisms is responsible for the increase in the polymerization rate when using the prepolymerized catalyst. Moreover, due to the complex nature of heterogeneous Ziegler– Natta catalysts, the effect of prepolymerization on the morphology of the catalyst particles cannot be neglected in the study searching for the reasons of the activating effect of a two-step polymerization.

Our earlier investigations of the two-step propylene polymerization over nonsupported titanium catalyst^{11,12} and MgCl₂-supported catalyst¹³ revealed the increased concentration of active sites in the systems subjected to preliminary polymerization, compared with their unmodified equivalents.

For a better understanding of the nature of the activating effect of prepolymerization, the influence of the two-step polymerization of propylene on the electron spin resonance (ESR) spectra and morphology of the nonsupported titanium catalyst used, as well as the properties and morphology of both prepolymer and regular polymerization products, was investigated.

EXPERIMENTAL

All of the operations connected with the synthesis and investigation of the catalysts, as well as polymerization processes, were conducted in dry and oxygen-free argon.

Materials

Polymerization-grade propylene (Petrochemia SA, Plock, Poland) and pure argon (Liquid Carbonic, Poland) were purified by passing through beds of 4 Å molecular sieves. Pure-grade hexane (Petrochemia SA, Plock, Poland) was refined with sulfuric acid, dyed by refluxing in argon over so-dium metal, and stored over 4 Å molecular sieves. The catalyst named *cat* (second generation TiCl₃ catalyst), modified with di-*n*-butyl ether, was pre-

pared as described in ref. 14. The co-catalyst (diethyl aluminum chloride) (Witco, Germany) was used without further purification.

Prepolymerization

The predetermined amounts of hexane, *cat*, and Et_2AlCl were added into a 250-mL glass reactor equipped with a magnetic stirrer, and then propylene was bubbled through the stirred solvent. Prepolymerization conditions: Al/Ti molar ratio = 5; temperature of 25°C, atmospheric pressure; and propylene/Ti molar ratio = 10. In the end, the solvent was removed, and the prepolymerized catalyst in the form of dry powder was preserved under argon. It was named *precat*.

Polymerization

The polymerization reaction was conducted for 1 h in a swinging design 400-mL steel reactor at 70°C and under constant pressure of monomer (0.6 MPa). The required amounts of hexane (250 mL), Et₂AlCl, and *cat* or *precat* (Al/Ti molar ratio = 7) were charged into the reactor. Polymerization was initiated by introducing propylene. The reaction was then terminated by adding methanol, which contained 5 wt % HCl. The resultant polymer was filtered off, washed with methanol, and dried.

Measurements

The ESR spectra of catalyst samples were recorded at ambient temperature, with the use of SE/X28 model spectrophotometer, produced by the Technical University of Wrocław (Poland). The values for Lande factor, g, were determined against the 2,2-diphenyl-1-picrylhydrazyl (DPPH) standard.

The distribution of grain size was determined by use of the laser diffraction technique (laser particle sizer, type PAR-TEC) and by sieving (Frisch particle sizer).

The molecular weights and molecular weight distributions (MWDs) of the produced polymers were measured with a Waters instrument, model 150-C. The following operating conditions were used—(1) four columns: μ -Styragel HT (7.8 mm \times 300 mm) 10³, 10⁵, 10⁶, 4 Å, and HMW-7; particle size: 10 μ m; (2) solvent: 1,2,4-trichlorobenzene, flow rate: 1.0 mL/min; (3) antioxidant: Santanox-R, 0.25 g dm⁻³_{TCB}; (4) concentration of samples: 0.1% (w/v); (5) injection volume: 200 mL; and

	Polymerization Rate in kg _{PP} /(mol _{Ti} · min) at Time						
Catalyst	$t \rightarrow 0$	t = 60	$10^{-3}\cdotar{M}_v$	Bulk Density $(g \text{ cm}^{-3})$	Melting Point (°C)	Crystallinity (%)	
cat precat	2.59 2.87	$\begin{array}{c} 1.13\\ 1.78\end{array}$	1,780 1,660	$\begin{array}{c} 0.40\\ 0.45\end{array}$	$163.2 \\ 163.2$	48.0 49.8	

Table I Effect of Prepolymerization of Catalyst on Its Activity and Characteristics of Polypropylene

(6) temperature measured: 142°C. Calibration was made with a broad MWD standard method on two polypropylene standards, $M_w = 348,000$ and $M_w = 47,500$ (Polymer Standards Lab., USA), with the use of the universal calibration procedure.

The isotacticity specifications for polymers are given as weight percent of polymers insoluble in boiling heptane. Polymer melting points were measured on samples that had been previously melted and recrystallized with the use of the Mettler calorimeter, at a heating rate of 6 K min⁻¹. The crystallinities of polymers were calculated from the heat of fusion values determined from the differential scanning calorimetric curve.

The morphologies of polypropylene were examined in a scanning electron microscope (SEM) with a BS-350 Tesla apparatus at vacuum of 10^{-5} mm Hg and at an accelerating voltage of 25 kV. Samples were prepared by coating them with gold. This technique is close to that generally used in SEM work.

RESULTS

Polymerization and Polymer Properties

The findings from propylene polymerization using a nonsupported heterogeneous titanium catalysts (*cat*) and its equivalent, modified by prepolymerization of propylene at mild conditions (*precat*) (Table I), reveal that prepolymerization increases the rate of regular polymerization and improves resistance of the catalyst to deactivation (increase of $R_{p,60}/R_{p,0}$). After that, the prepolymerized catalyst produced polypropylene with the higher bulk density. On the other hand, a two-step polymerization process has in practice no effect on the polypropylene molecular weight and its distribution, nor on the melting point and crystallinity of the product obtained (Table I, Fig. 1). It can be concluded from these findings that prepolymerization increases the number of catalyst active sites, whereas their chemical nature undergoes no significant change.

ESR Spectra of Catalysts

In Figure 2, ESR spectra were compared for nonsupported titanium catalyst samples before and after prepolymerization, activated with diethylchloroaluminum in the amounts usually used in polymerization studies. As can be seen, the spectra are clearly different as regards the shape, number, and size of bands. The ESR spectrum for *cat* is a superposition of three signals: intensive signals A, C, and a weak signal B (Fig. 2, spectrum 1). The interaction of the prepolymerized catalyst with the same organoaluminum compound produces only one type of signal in the ESR spectra (Fig. 2, spectrum 2): the same signal A as in *cat* is observed.



Figure 1 Gel permeation chromatography (GPC) distribution plots for polypropylenes obtained over *cat* (1) and *precat* (2).



Figure 2 ESR spectra of *cat* (1) and *precat* (2) reduced by Et_2AlCl ; molar ratio Al/Ti = 8.

Total and relative intensities of ESR signals depend on the Al/Ti mole ratio in the catalytic systems (Fig. 3). As can be seen (Fig. 3, spectrum 1), at a low concentration of the co-catalyst (Al/Ti = 3), the content of titanium(III) ions of various types observed in the ESR spectra is rather low. In the case of *cat*, the signal B reaches its maximum at this mole ratio. As the Al/Ti mole ratio increases, the relative intensity of signal B considerably increases, too, whereas that of signal A reaches its maximum at the mole ratio of Al/Ti = 5 and then considerably decreases. In the ESR spectra of this catalyst after its prepolymerization [precat; Fig. 3(b)], in the range of the Al/Ti mole ratio of 3-15, only the intensive signal A is observed; its intensity gradually increases with the increase of concentration of titanium(III). It should, however, be kept in mind that any dramatic increase of the catalyst concentration (Al/Ti = 30) produces the spectrum with the suppressed signal A and the emerging and poorly developed band C.

The symmetrical signal A with a *g*-factor of 1.970 represents titanium(III) ions in the tetrahedral chlorine environment.^{15,16} This signal was

observed earlier in the ESR spectrum of the reaction product of TiCl_4 and triethylaluminum,¹⁷ and it was found to be generated by isolated titanium(III) ions.¹⁶

The weak signal B, with g = 1.945, is attributed to isolated titanium(III) ions in the distorted octahedral environment of chlorine anions.^{18,19} This signal was noted earlier in the ESR spectra of various samples of titanium trichloride with the composition TiCl₃ · nAlCl₃.¹⁷⁻¹⁹

The signal C at g = 1.920, which was observed earlier in the ESR spectra of the catalysts produced by the reduction of TiCl₄ with aluminum or organoaluminum compounds,^{18,19} is said to result from titanium(III) ions in the distorted octahedral chlorine environment. These titanium ions are associated or they form TiCl₃ agglomerates; this is supported by the lack of anisotropy, the broadening of this signal with increasing titanium content in the catalyst, and the disappearance of this signal with increasing temperature of the spectrum measurement.

These findings suggest that there are at least two forms of titanium(III) ions (isolated and ag-



Figure 3 ESR spectra of *cat* (a) and *precat* (b) as a function of the Al/Ti mole ratio: (1) -3; (2) -5; (3) -8; (4) -15; (5) -30.

Polymer	$M_n \cdot 10^{-3}$	$M_w~\cdot~10^{-3}$	$M_v~\cdot~10^{-3}$	M_w/M_n	η	II (%)
Prepolymer	48	340	280	7.14	1.72	50.0
Polypropylene— <i>cat</i> Polypropylene— <i>precat</i>	622 625	2,000 1,880	1,780 1,660	3.22 3.00	$\begin{array}{c} 6.55\\ 6.24\end{array}$	95.3 98.1

Table II Molecular Weights and Isotacticity Indexes of Prepolymer and Polypropylene Samples

glomerates) present in the discussed system of *cat*, under conditions applied in the polymerization (Al/Ti = 8), whereas the same catalyst after its prepolymerization (i.e., *precat*) is more homogeneous.

Molecular Specifications for Prepolymers and Polymers

To provide explanation(s) for the findings previously described, the molecular specification and isotacticity factor were determined for the polymer obtained in the prepolymerization stage (*prepolymer*). Results were compared with those obtained for the regular polymers produced with the use of *cat* and *precat* (Table II).

The prepolymer is a polymer obtained over a short period of time and at low conversion of monomer; thus, its molecular weight is clearly lower than molecular weights for regular polymerization products. It can, moreover, be noted that the MWD for the prepolymer is more than twice as wide as distributions for both polymerization products; this suggests the initial lack of homogeneity in the catalyst. Additionally, about one-half of the prepolymer is an atactic material, whereas regular polymers have the isotacticity index of >95%. From Figure 4, one can note that



Figure 4 Isotacticity index (II) of polypropylenes obtained on *cat* (1) and *precat* (2) as a function of polymerization time t.

the concentration of the isotactic fraction in the polymerization product increases with polymerization time. Thus, aspecific sites must be predominantly used to form macromolecules at the initial step of the process, and then they undergo deactivation.

Morphology of Polymers

The polymer granules that are formed on the surface of heterogeneous catalyst particles are reported²⁰ to be in practice replicas of the catalyst structure(s) and to grow in the course of the polymerization process. When granulometric distribution specifications are compared for the catalyst and polymer produced (Table III), they are very well consistent when the growth of polypropylene granules is considered.

Figure 5 shows that the main fraction of polypropylene samples obtained over both catalysts under comparison contain particles with a diameter of $\sim 200 \ \mu\text{m}$. However, attention should be focused on the polymer produced over *precat* is more uniform (its main fraction makes $\sim 90\%$ of the total polymer) than polypropylene produced over the non-modified equivalent [*cat* (50% polypropylene is particles with a diameter of $\sim 200 \ \mu\text{m}$)]. In addition, this supports our hypothesis of a higher uniformity of the prepolymerized catalyst.

DISCUSSION

Particles of heterogeneous catalysts are known to form crystallite agglomerates. $^{20-22}$ Resulting

Table IIIParticle Size Distribution of Catalystand Polypropylene Obtained on It

Particle Size of cat (µm)	Wt %	Particle Size of Polypropylene (µm)	Wt %
$\begin{array}{c} 4.5 - 10 \\ 10 - 26 \\ 26 - 40 \\ > 40 \end{array}$	$7.0 \\ 22.0 \\ 63.3 \\ 7.7$	$\begin{array}{c} 45 - 100 \\ 100 - 200 \\ 200 - 400 \\ > 400 \end{array}$	4.6 24.3 60.3 10.8





Figure 6 SEM micrography of the *prepolymer* $(440 \times$ original magnification).

Figure 5 Particle size distribution of polypropylenes obtained on *cat* (1) and *precat* (2).

from their porous structures, the catalysts are breakable, and the fragmentation process occurs due to the polymer growth, particularly at the initial stages of the polymerization. Too-fast and extensive fragmentation of the catalyst, which is typical for the initial stage of polymerization, may cause the catalyst "explosion" and prevent a regular replication. On the other hand, the more controlled breakup of the catalyst particles in the course of slowed growth of prepolymer can expose occluded catalyst microparticles with the uniform size and prevent their reagglomeration. Thus, the rate-enhancement effect is observed. This hypothesis has been confirmed by the comparative study on morphology of the catalysts, prepolymer, and polymerization products.

As noted in the SEM diagram for prepolymerization product (Fig. 6), the diameters of prepolymer granules fall between 20 and 30 μ m, and they are comparable with grain size for the original catalyst (i.e., 25–45 μ m) (Table III). On the other hand, the prepolymer granules are much smaller than the polymer granules produced over both *cat* and *precat* (i.e., ~ 200 μ m) (Fig. 5).

At higher magnification (Fig. 7), it is seen that the whole surface of a prepolymer granule is covered with tiny and uniform catalyst microparticles with the diameter of $0.1-0.2 \ \mu m$. Additionally, it should be emphasized that such catalyst microparticles cannot be found—even at much higher magnifications—on the surface of regular polymer granules, regardless on the catalyst type used in the synthesis.

The findings herein prove that the initial prepolymerization conducted under mild conditions leads to gentle fragmentation of catalyst agglomerates into microparticles, and the prepolymer coat seems to expose the occluded catalyst centers. This results in the increase of concentration of the active sites and their homogeneity. Moreover, it is possible to obtain the polymer material with desired morphology (i.e., regular shape and narrow distribution of grain size). This makes an important property considered for commercial catalysts, just after the demand for their high activity and stereoselectivity. Hence, prepolymerization seems to be the advantageous method for catalyst modification, which is capable of impart-



Figure 7 SEM micrography of the *prepolymer* $(9,000 \times \text{ original magnification})$.

ing all of the three elements to the catalyst performance at the same time.

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