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Reversible and irreversible deactivation of propene polymerization using homogeneous Cp_2ZrCl_2/methylaluminoxane Ziegler–Natta catalysts *

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Abstract

The kinetics of propene polymerization in the presence of homogeneous Cp_2ZrCl_2/methylaluminoxane catalysts in toluene at 2 bar have been investigated at 0, 20, 40 and 60 °C. The narrow polypropylene molecular weight distributions, $M_w/M_n < 2.4$, indicate the presence of uniform catalytically active sites ($C^\star$). By assuming the existence of a reversible followed by an irreversible reaction, both of second order, which lead to formation of the catalytically inactive complexes I_1 and I_2, respectively, we propose the kinetic scheme $2\ C^\star \rightleftharpoons I_1 \rightarrow I_2$ to predict the decay of the polymerization rate as a function of time. At low temperatures there is predominantly reversible deactivation.

Novel highly active homogeneous Ziegler–Natta catalysts comprise metallocenes of titanium, hafnium, and zirconium, activated with a large excess of methylaluminoxanes (MAO). In recent years, some chiral *ansa*-metallocenes, pioneered by Brintzinger, have been used to control the regioselectivity and stereospecificity of the polymerization of 1-olefins [1–3]. In numerous publications the main correlations between metallocene structure, steric control mechanism, and polymer microstructure have been defined, leading to a broad range of commercially available 1-olefin and cycloolefin homo- and co-polymers as well as novel stereoblock polymers [4–6]. However, the role of MAO activators and the origin of catalyst deactivation are not fully understood. A few papers describe the kinetics of polymerization in the presence of soluble metallocene-based Ziegler–Natta catalysts [8–10]. In order to study propene polymerization kinetics and interactions at catalytically active sites we decided to use the non-stereospecific Cp_2ZrCl_2/MAO catalyst to produce stereo-irregular polypropylenes, which remain in solution during polymerization and can be readily characterized by ^1H and ^{13}C NMR spectroscopy and size exclusion chromatography. With a propene pressure of 2 bar, 5×10^{-5} mol/l Cp_2ZrCl_2 catalyst concentration, and an Al/Zr molar ratio of 1000, the

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* Dedicated to the memory of Professor Piero Pino.

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reaction temperature was varied from 0 to 60 ° C in order to determine the influence of temperature on propene conversion, polymerization rate, and polypropylene molecular weight and molecular weight distribution. The results are summarized in Table 1 and Fig. 1 [7].

When the temperature is increased, the polypropylene molecular weight decreases from 5310 to less than 500 g/mol. Analysis of the olefinic end-group by ^1H and ^{13}C NMR spectroscopy reveals the presence of exclusively vinylidene-terminated polypropylenes. Molecular weight determinations by end-group analysis and vapor pressure osmometry are in good agreement. The total catalyst productivity increases with increasing polymerization temperature after account is taken of the higher propene concentrations at lower temperatures. In Fig. 1 the catalyst productivity, measured as kilograms polypropylene per mole Zr, bar and h is plotted against time for various reaction temperatures. Even at 0 ° C the very high maximum catalyst productivities are reached within few seconds, and so we conclude that the activation of Cp_2ZrCl_2 complex, e.g., by alkylation with MAO, involves a very fast reaction yielding the catalytically active sites. At 0 ° C the catalyst productivities slowly decreases over a prolonged period. At a reaction temperature of 40 ° C there is a very rapid decay within a few minutes and subsequently almost constant catalyst productivity during several hours. However, when the reaction temperature is raised further to 60 ° C, there is very rapid initial productivity decay, complete within a few minutes, followed by a second slow deactivation of the catalyst.

Similar catalyst productivity time dependence has been observed in ethylene polymerization involving homogeneous metallocene catalysts. Since the polyethylene molecular weight distributions are very broad, with polydispersities $M_w/M_n >$ 2.0, Chien [8] proposed the presence of two different catalytically active sites which are deactivated in processes first order with respect to the individual catalytically active site concentrations. In our experiments polypropylene remains in solution during polymerization. Moreover, as shown in Table 1, the polypropylene molecular weight distribution is narrow and corresponds to Schulz–Flory molecular weight distributions. In low molecular weight ranges, polydispersities M_w/M_n of < 2.0 are obtained, because propene monomers, dimers, trimers, and tetramers are removed from the polypropylenes during the drying procedures. Thus, in agreement with observations by other groups [11,12], we conclude that the catalytically active sites are uniform over the entire temperature range.

Table 1

Propene polymerization at 2 bar [a]

Sample	Temperature (° C)	Time (min)	Propene concentration (mol/l)	Yield (g)	Productivity [kg PP/(mol Zr h mol/l)]	M_n [b] (g/mol)	M_w/M_n [c]
PP061	0	449	3.16	165	226	5310	2.4
PP058	20	364	1.53	89	310	1190	1.9
PP035	40	189	0.88	57	668	530	1.4
PP062	60	191	0.53	64	1242	n.d. [d]	n.d. [d]

[a] Total pressure. [b] Determined by endgroup analysis and vapor pressure osmometry. [c] Determined by size exclusion chromatography in toluene solvent. [d] n.d.: not determined.

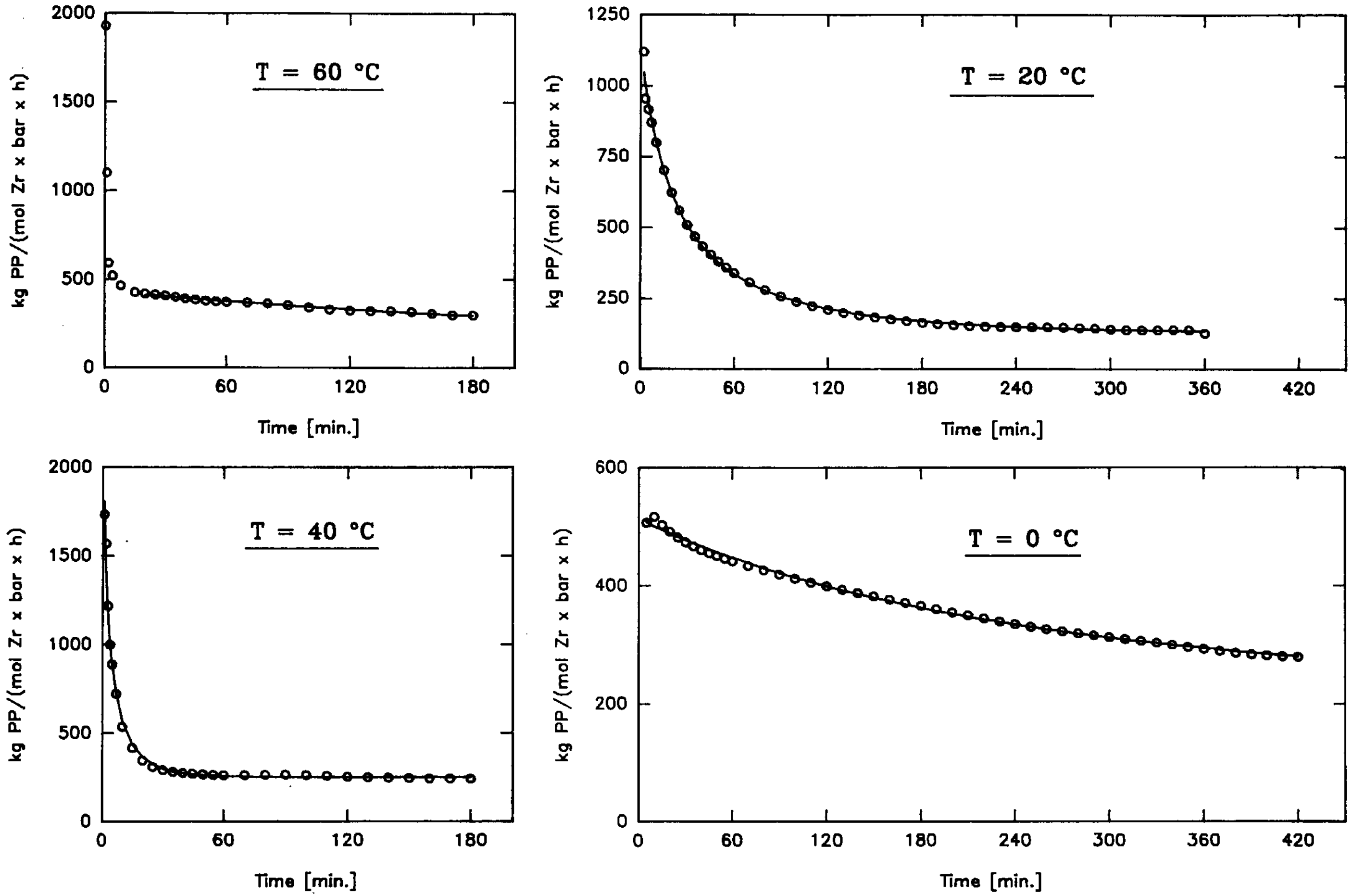

Fig. 1. Catalyst productivity as a function of time for propene polymerization in presence of Cp_2ZrCl_2/MAO at various temperatures. Solid line: calculated on the basis of the kinetic scheme. Dots: experimental data for the corresponding polymerization run.

At a given propene concentration the actual polymerization rate R_p is proportional to the concentration of the catalytically active sites $N^\star$ [13]:

$$R_p \sim N^\star \tag{1}$$

In a two-step deactivation process, the catalytically active complexes $C^\star$ are deactivated by a reversible followed by an irreversible process to form inactive species I_1 and I_2. Only I_1 can recover and again take part in propene polymerization.

$$2\,C^\star \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_1 \xrightarrow{k_2} I_2 \tag{2}$$

In the initial phase of the polymerization reaction only active centers $C^\star$ are present, and these form I_1 and I_2. Below 40 °C the rate constant k_2 is very small. Therefore, in an approximation, the simplified equilibrium 3 is responsible for the decay of the catalytically active center concentration $N^\star(t)$, which was calculated by Mauser's method [14]:

$$2\,C^\star \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_1 \tag{3}$$

$$N^\star(t) = N^\star_\infty + \frac{(N^\star_0 - N^\star_\infty) r \exp(-rt)}{r + 2k_1(N^\star_0 - N^\star_\infty)(1 - \exp(-rt))} \tag{4}$$

$$N^\star_0 \equiv N^\star_{t=0} \tag{5}$$

$$N^\star_\infty \equiv N^\star_{t\to\infty} = \tfrac{1}{2}\left[\sqrt{\left(\frac{k_{-1}}{2k}\right)^2 + 2\frac{k_{-1}}{k_1}N^\star_0} - \tfrac{1}{2}\frac{k_{-1}}{k_1}\right] \tag{6}$$

$$r \equiv \sqrt{k_{-1} + 8k_1k_{-1}N^\star_0} \tag{7}$$

It is apparent from Fig. 1 that our calculated catalyst productivity/time relationships are in good agreement with the experimental data. At 60 °C, the irreversible deactivation is introduced to account for the slow productivity decay. Also the irreversible deactivation is a second order reaction with respect to the catalytically active metallocene complexes. At present, since both processes are second order with respect to the catalytically active sites, our kinetic scheme does not permit us to differentiate between a second order irreversible deactivation of two catalytically active sites and an irreversible deactivation of the inactive complex I_1. On the basis of our model, however, we are able to quantify the influence of catalyst components, polymerization conditions such as Zr/Al molar ratios, and Lewis acid/Lewis base interactions at the catalytically active complexes to provide understanding of elementary reactions occurring at catalytically active sites which correlate with changes in catalyst performance, especially in respect of the properties of the formed polyolefin.

Experimental

Propene polymerization was carried out in a 2 l Büchi glass autoclave in a feed- and temperature-control reactor system devised by Pino and coworkers [15,16]. Catalyst components were handled under dry argon. The toluene solvent, p.a. grade, purchased from Roth, was twice refluxed over and distilled from $LiAlH_4$. The 30% by weight methylaluminoxane solution in toluene was obtained from Schering AG ($M_n = 800$ g/mol, 14.6% by weight Al) and used without further purification. Polymerization grade propene monomer was supplied by BASF AG, Ludwigshafen. In a typical polymerization run the reactor was flushed with toluene containing 1.7 g MAO. After the reactor had been dried at 60 ° C under oil pump vacuum, 600 ml of dry toluene containing 1.716 g (30.75 mmol Al) of MAO as 30% by weight solution in toluene was placed in the reactor and propene was added to saturate the toluene at the selected polymerization temperature until a total pressure of 2 bar was reached. The polymerization was initiated by injection of 8.99 mg (3.075×10^{-5} mol) Cp_2ZrCl_2, (Aldrich) in 15 ml of anhydrous toluene. An automated cooling and feed system provided constant pressure and temperature. Propene was fed in to maintain the pressure and propene consumption recorded to allow calculation of the catalyst productivity as a function of time. The polymerization was terminated by venting off the residual propene monomer. The polymer was precipitated by addition of 1.5 l methanol containing 15 ml conc. HCl, the mixture was stirred overnight and the volatile components evaporated off at 50–60 ° C under aspirator vacuum. The residue was diluted with petroleum ether (40–60 °) and extracted with 500 ml water containing 10 ml conc. HCl to remove catalyst residues. The petroleum ether was then evaporated and the residual polypropylene dried for 48 h at 60 ° C under oil pump vacuum. The molecular weight distributions were measured by size exclusion chromatography on Physical Laboratories PL-Gel columns. Microstructure analysis involved ^1H and ^{13}C NMR spectroscopy (Bruker WH 90 and AM 400 spectrometers).

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