Influence of Ziegler−Natta Catalyst Regioselectivity on Polypropylene Molecular Weight Distribution and Rheological and Crystallization Behavior

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ABSTRACT: Fundamental implications of occasional secondary (2,1-) insertions in propene polymerization with different $MgCl_2$-supported Ziegler−Natta catalysts are discussed, with reference to the properties of the polymers obtained. The relatively narrow molecular weight distribution of polypropylene prepared using catalysts of type $MgCl_2/TiCl_4$/diether−AlR_3 is ascribed to the fact that the active species in this system are relatively uniform, in the sense that significant 2,1-insertion takes place at both highly isospecific and weakly isospecific active species. In contrast, the *isospecific* species in the catalyst system $MgCl_2/TiCl_4$/diisobutyl phthalate−$AlEt_3$−alkoxysilane undergo less 2,1-insertion and are therefore less responsive to chain transfer with hydrogen. The presence of (some) highly regiospecific active sites in such catalysts will therefore lead to the formation of a high molecular weight polymer fraction and, overall, a broad molecular weight distribution. The presence of high molecular weight chains leads to relatively slow molecular relaxation and a more rapid onset of crystallization of the polymer from the melt, as evidenced by rheological studies of polypropylenes prepared using different catalysts and having different molecular weight distributions.

Introduction

Ziegler−Natta catalysts occupy a dominant position in the manufacture of polypropylene (PP) and account for more than 99% of the total PP market, which now exceeds 30 million t/a. High-activity Ziegler−Natta catalysts comprise $MgCl_2$, $TiCl_4$, and an "internal" electron donor and are typically used in combination with an aluminum alkyl cocatalyst such as $AlEt_3$ and an "external" electron donor which is added in polymerization. The first catalyst systems contained ethyl benzoate (EB) as internal donor and a second aromatic ester as external donor,[1] but currently the catalysts most widely used in polypropylene manufacture[2] contain a diester (e.g., diisobutyl phthalate, DIBP) as internal donor and are used in combination with an alkoxysilane external donor of type $RR'Si(OMe)_2$ or $RSi(OMe)_3$. The isospecificity of the catalyst is dependent on the particular combination of internal and external donor. Recently, catalysts exhibiting high isospecificity even in the absence of an external donor have been developed and introduced.[3] This required the identification of bidentate internal donors which not only had the right oxygen−oxygen distance for effective coordination with $MgCl_2$ but which, unlike phthalate esters, were not removed from the support on contact with $AlEt_3$ and which, in contrast to alkoxysilanes, were unreactive with $TiCl_4$ during catalyst preparation. It was found that certain 2,2-disubstituted-1,3-dimethoxypropanes met all these criteria. The best performance was obtained when bulky substituents in the 2-position resulted in the diether having a most probable conformation[4] with an oxygen−oxygen distance in the range 2.8−3.2 Å. Most recently, a further family of $MgCl_2$-supported catalysts has been developed, in which the internal donor is a succinate rather than a phthalate ester.[5] As is the case with the phthalate-based catalysts, an alkoxysilane is used as external donor. The essential difference between these catalysts is that the succinate-based systems produce polypropylene having much broader molecular weight distribution (MWD).

Ziegler−Natta catalysts are multisite systems, and the molecular weight distribution of the polymer is dependent on the nature and distribution of the different active species in the catalyst. Diether-containing catalysts give relatively narrow MWD in comparison to benzoate-, phthalate-, and succinate-based systems.[5] A narrow molecular weight distribution, and relatively low molecular weight, is advantageous in fiber spinning applications. In contrast, extrusion of pipes and thick sheets requires high melt strength and therefore relatively high molecular weight and broad molecular weight distribution. A broad molecular weight distribution, along with high isotactic stereoregularity, is also beneficial for high crystallinity and therefore high rigidity.

In recent years, significant progress has been made in understanding key fundamental aspects of $MgCl_2$-supported catalysts in relation to polypropylene structure and properties. One example is polymer molecular weight control, using hydrogen as chain transfer agent

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in polymerization. The effect of hydrogen concentration on polymer molecular weight is dependent on the catalyst system. Diether-containing catalysts show high sensitivity to hydrogen, so that relatively little hydrogen is required for molecular weight control. It has been established[6] that this effect can be ascribed to chain transfer after the occasional secondary (2,1-) rather than the usual primary (1,2-) insertion. Reactivation of "dormant" (2,1-inserted) species via chain transfer with hydrogen also explains the frequently observed activating effect of hydrogen in propene polymerization, giving yields which may be around 3 times those observed in the complete absence of hydrogen.[7] These conclusions have been based on ^{13}C NMR determination of the relative proportions of *i*-Bu- and *n*-Bu-terminated chains, resulting from chain transfer with hydrogen after primary and secondary insertion, respectively.[8,9]

Comparison of the isotactic fractions of polypropylenes of similar molecular weight, prepared using the catalyst systems $MgCl_2/TiCl_4$/DIBP−$AlEt_3$−cyclohexyl(methyl)dimethoxysilane and $MgCl_2/TiCl_4$/diether−$AlEt_3$, revealed significantly higher proportions of *n*-Bu-terminated chains in the polymers prepared using the diether-containing catalyst.[10] A question still to be answered, however, was whether this arises from a greater *incidence* of secondary insertion with the diether, as opposed to the phthalate-based catalyst, or a greater *effect* of a secondary insertion in slowing down chain propagation in the diether system, making chain transfer more probable. This uncertainty has recently been resolved by Busico and Cipullo et al., who have copolymerized propene with ethene-[1-^{13}C] in order to quantify the regioselectivities of various $MgCl_2$-supported catalysts.[11,12] It is now apparent that the high hydrogen response exhibited by the $MgCl_2/TiCl_4$/diether−$AlEt_3$ system is due to the fact that in this system even the most highly isospecific species are not totally regiospecific. This is evident from very different *distributions* of 2,1-inserted propene units in polymers prepared using the diether-based catalyst and the phthalate/silane system. Polymer fractionation and analysis revealed that the latter system gives polymers with a relatively high level of 2,1-insertions in the weakly tactic fractions but much less 2,1-insertion in the isotactic fraction, whereas the diether-based catalyst gave a more uniform distribution of 2,1-insertions across polymer fractions having high and low isotacticity.[12]

In the present contribution, the fundamental implications of these results with regard to polymer molecular weight distribution are considered. Polypropylenes having different molecular weights and molecular weight distributions have been prepared using $MgCl_2$-supported catalysts with different combinations of internal and external donors to correlate catalyst composition with the rheological properties and crystallization behavior of the polymer. These properties are strongly dependent on the presence or absence of a high molecular weight polymer fraction, which in turn can be linked to the presence or absence of highly regiospecific active species in the catalyst.

Experimental Section

Regioselectivity Determination. The determination, via ^{13}C NMR microstructural analysis, of the proportions of 2,1-inserted propene units in solvent fractionated polypropylenes containing up to 6 mol % of copolymerized ethene-[1-^{13}C] has been described in detail in a preceding contribution.[12]

Table 1. Dependence of Regioirregular (2,1-) Insertion on Catalyst Type

	% 2,1-insertion		
catalyst	total polymer	isotactic fraction	soluble fraction[a]
$MgCl_2/TiCl_4$/Diether−$AlEt_3$	0.26	0.15	0.5
$MgCl_2/TiCl_4$/DIBP−$AlEt_3$−CHMDMS[b]	0.19	0.08	1.0−1.5

[a] Calculated values, derived from the values for total polymer and isotactic fraction. [b] CHMDMS: cyclohexyl(methyl)dimethoxysilane.

Polymer Preparation and Analysis. Polymers on which rheological and crystallization studies were carried out were prepared using catalysts prepared according to published procedures[1−6,13,14] and containing (a) 4.7 wt % Ti, 15.8 wt % diether; (b) 2.7 wt % Ti, 16.8 wt % DIBP; (c) 3.7 wt % Ti, 14.8 wt % EB; (d) 3.5 wt % Ti, 15.2 wt % succinate. Polymerizations were carried out in liquid propene (1.6 kg) for 1 h at 70 °C with 5−15 mg of catalyst and 120 mg of $AlEt_3$. Hydrogen concentrations in the range 5−12 vol % (measured in the gas cap) were used in order to obtain similar polymer molecular weights with the different catalyst systems used. In the polymerizations in which an external donor was used, the $AlEt_3$/external donor molar ratio was 20 for the DIBP- and succinate-containing catalysts and 2.4−3.5 for the EB-containing catalysts.

Gel permeation chromatography (GPC) was carried out at 140 °C, at Rapra Technology Ltd., Shrewsbury, U.K., using a Polymer Laboratories PL 200 (columns: PL gel guard plus 2 × mixed bed-B, 30 cm, 10 μm). The mobile phase was *o*-dichlorobenzene, and the flow rate was 1.0 mL/min.

Rheological and Crystallization Studies. Polypropylene dynamic rheology experiments were performed using a Rheometrics ARES rheometer having 25 mm diameter plates with a gap of 0.3 mm. For molecular weights lower than 80 kg/mol, a 0.1 mm gap was used. The rheological melt characterization was carried out with a frequency sweep experiment over a constant strain. The applied strain amplitude was 2%, and multiple experiments were performed at different temperatures and combined to give a master curve, with a reference temperature of 200 °C, by shifting over the frequency axis. To avoid degradation, the polymers were stabilized with 0.1 wt % Irganox 1010 and 0.05 wt % calcium stearate; these components were added as a solution in acetone, after which the polymer was dried under reduced pressure.

Polymer crystallization was monitored by single-point rheology measurements over time. The applied strain amplitude was 2%, and the frequency was 10 rad/s. The onset of polymer crystallization was determined by following the development of the dynamic moduli under isothermal conditions at 140 °C after cooling the melt from 220 °C.

Results and Discussion

Catalyst Regioselectivity. The most important results on the determination of the regioselectivities of catalyst systems of type $MgCl_2/TiCl_4$/DIBP−$AlEt_3$−cyclohexyl(methyl)dimethoxysilane and $MgCl_2/TiCl_4$/diether−$AlEt_3$, described in more detail in a previous contribution,[12] are given in Table 1. It is apparent that the overall regioselectivities of the two catalysts are not widely dissimilar. However, there are large differences in the distributions of 2,1-inserted units within each polymer, the contents of 2,1-inserted units in the *isotactic* fractions of the polymers prepared using phthalate/silane and the diether-based catalyst being 0.08% and 0.15%, respectively. The corresponding contents of 2,1-units in the soluble (weakly tactic) polymer fractions were 1.0−1.5% and 0.5%, respectively. Clearly, the diether-based catalyst gives significant levels of 2,1-inserted units in both the isotactic and weakly tactic polymer fractions, whereas with the phthalate/silane-based system the 2,1-units are concentrated mainly in

Table 2. Polymer Molecular Weight Distribution

sample	internal/external donor	XI[a] (wt %)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$	M_w/M_n	M_z/M_w
1	diether/−	98.3	75	254	610	3.4	2.4
2	DIBP/CHMDMS[b]	97.5	55	264	728	4.8	2.8
3	EB/PEEB[c]	94.5	40	281	889	7.0	3.2
4	succinate/CHMDMS	97.3	33	324	1855	9.8	5.7
5	diether/−	97.2	88	337	814	3.8	2.4
6	EB/PEEB	95.5	60	358	1040	6.0	2.9
7	succinate/DCPDMS[d]	97.6	45	341	1200	7.6	3.5

[a] Xylene-insoluble content of the polymer. [b] Cyclohexyl(methyl)dimethoxysilane. [c] Ethyl *p*-ethoxybenzoate. [d] Dicyclopentyldimethoxysilane.

the weakly tactic polymer fraction. The importance of these results lies in their relation to the very different hydrogen sensitivities of these catalysts. The high hydrogen response of catalysts containing a diether as internal donor can now, we believe, be attributed to the relatively uniform distribution of 2,1-inserted units throughout the polymer, these results providing further evidence that even the most highly isospecific species in catalysts of type $MgCl_2/TiCl_4$/diether−$AlEt_3$ are by no means completely regiospecific.[6] Conversely, the lower hydrogen response shown by phthalate/silane-based catalysts will result from the presence of active species having high stereospecificity *and* high regiospecificity, as evidenced by the relatively low content of 2,1-inserted species in the isotactic fraction, taking into account the high probability of chain transfer with hydrogen after 2,1-insertion and the fact that the hydrogen response of the catalyst will be dominated by the chain transfer behavior of the (highly isospecific) species generating the highest molecular weight fraction of the polymer.

The above considerations can be extended to a consideration of the effects of catalyst regioselectivity on PP molecular weight distribution, in the sense that catalysts containing a proportion of active species having very high regioselectivity would be expected to give not only low hydrogen response but also broad MWD. The broad MWD would result from the necessity for a high hydrogen concentration for molecular weight control at the most regioselective active sites, the presence of other sites having lower regioselectivity leading, at high hydrogen concentration, to the concomitant formation of relatively low molecular weight polymer and therefore to a broad overall distribution. In the present work, various polypropylenes differing in MWD were prepared in order to assess their rheological and crystallization behavior in relation to the above considerations on the effects of catalyst regiospecificity.

Polymer Molecular Weight Distribution. Polymers having widely differing molecular weight distributions were prepared using catalysts containing either a diether, diisobutyl phthalate, ethyl benzoate, or a dialkyl succinate[13] as internal donor. The catalysts were prepared via reaction of a spherical adduct $MgCl_2 \cdot nEtOH$ with $TiCl_4$ in the presence of the internal donor, using procedures similar to those described previously.[14] The different polymerization characteristics of these families of catalysts have been described elsewhere.[5] In the present work, polymerizating in liquid propene in the presence of different concentrations of hydrogen, polymer yields ranging from 25 to 52 kg/g catalyst were obtained. The polymers and their molecular weight distributions, determined by GPC, are listed in Table 2. Two series of polymers were prepared, having intrinsic viscosities in the range 1.5−1.7 dL/g (samples 1−4) and 2.0−2.1 dL/g (samples 5−7). Determination of the xylene-insoluble contents of the polymers using a previously described method[6] indicated isotactic (XI) fractions of around 97−98 wt % for the polymers prepared with the diether-, DIBP-, and succinate-based systems and around 95 wt % for those prepared with the EB-based catalyst.

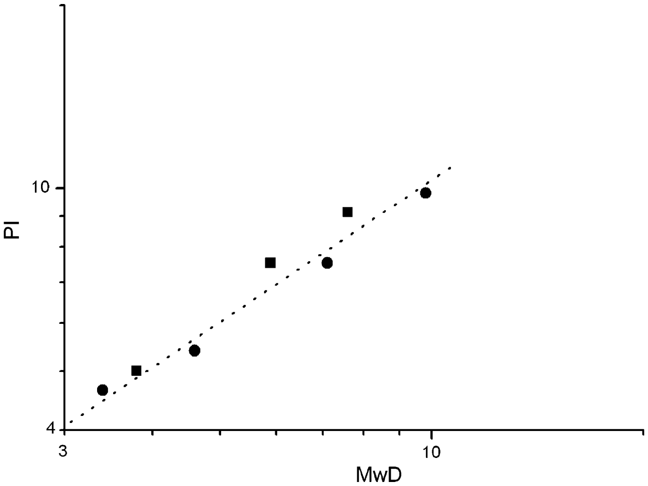

Figure 1. Correlation between polydispersity index (PI) and molecular weight distribution (M_w/M_n).

The data in Table 2 illustrate the relatively narrow molecular weight distributions of the polymers prepared using a diether as internal donor in the catalyst and at the opposite end of the scale the very broad distributions obtained with the succinate-based systems. The very different molecular weight distributions become strikingly apparent if the product of M_z/M_w and M_w/M_n is calculated, giving M_z/M_n values ranging from 8 (sample 1) to 56 (sample 4).

The polymer molecular weight distribution (polydispersity index) was also determined by dynamic rheology, measuring oscillatory shear behavior as a function of angular frequency as has been described by Zeichner and Patel.[15] In this method, the storage modulus, G', and the loss modulus, G'', are determined. At low frequencies $G'' > G'$, whereas at high frequencies $G' > G''$. The intersection of the moduli vs frequency curves gives the crossover modulus, G_c, which is a measure of the polydispersity of the polymer. The crossover frequency, ω_c, is related to molecular weight and thus to the zero-shear viscosity. The polydispersity index (PI) is defined[15] by the following relationship, with G_c in Pa:

$$\mathrm{PI} = 10^5/G_c$$

The correlation between PI and molecular weight distribution (M_w/M_n, determined by GPC) for the polymers listed in Table 2 is shown in Figure 1, revealing a linear relationship.

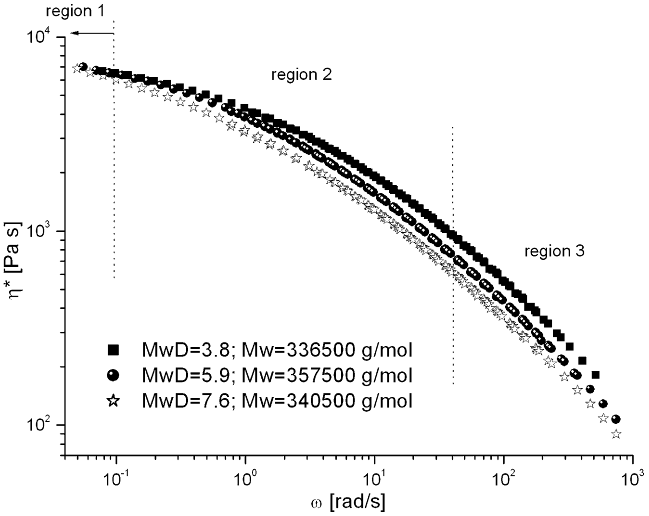

Figure 2. Dynamic viscosity−frequency plots for samples 5−7.

Polymer Rheology and Crystallization. The determination of polydispersity index represents just one of the possible applications of rheological measurements in determining the polymer molecular composition and properties. The viscoelastic response of linear polymer melts is related to reptation of the polymer chains and has been extensively described in the literature.[16,17] In polydisperse materials the shorter chains influence the relaxation of the longer chains and vice versa.[18,19]

The complex dynamic viscosity, η^*, at a given frequency, ω, can be calculated from the $G'(\omega)$ and $G''(\omega)$ data as follows:

$$\eta^* = \frac{1}{\omega}(G'^2 + G''^2)^{0.5}$$

In the present work, we have used a simple constitutive model, the Cross model,[20] to fit and describe the experimental data for the complex viscosity as a function of frequency:

$$\frac{\eta^* - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (K\omega)^{1-n}}$$

η_∞ represents the viscosity at infinite shear rate and was taken as zero. K is a time constant related to average relaxation time and is therefore linked to both molecular weight and polydispersity. n is the power law index. Dependent on the three parameters in the Cross model, three regions can be described in a plot of dynamic viscosity vs frequency, as illustrated in Figure 2 for samples 5−7 from Table 2.

Region 1: the η_0 or Newtonian region. Since the three polymers in Figure 2 had similar M_w, the curves extropolate to similar zero-shear viscosity, η_0.

Region 2: the K region, dependent on polydispersity and molecular weight.

Region 3: the higher frequency, power law n region, in which similar slopes indicate similar shear thinning for the samples studied.

The relationship between complex dynamic viscosity and frequency for samples 1−4 from Table 2 is shown in Figure 3, and the Cross parameters determined from Figures 2 and 3 by curve fitting are given in Table 3. It is apparent that the power law index (n) is nearly constant, whereas the value of K ranges from around 0.2 to 1.7 s. Taking into account the possible dependence of the time constant on the high molecular weight fraction (indicated by M_z) of the polymer, K was plotted against M_z/M_n as shown in Figure 4. It is apparent that the value of K increases with both molecular weight and molecular weight distribution, indicating a strong influence of long-chain molecules on relaxation time.

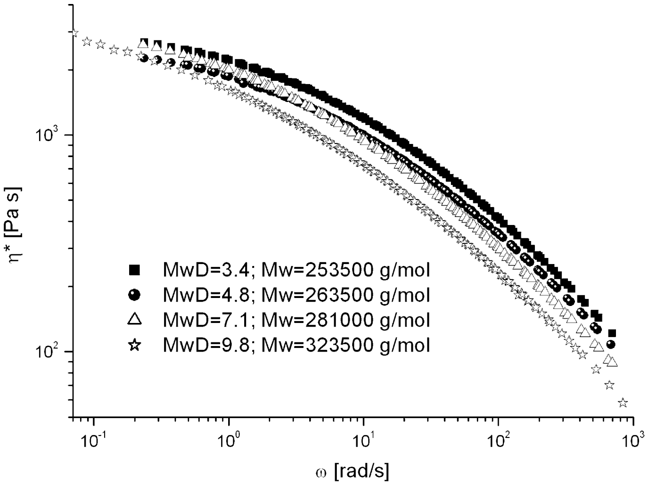

Figure 3. Dynamic viscosity−frequency plots for samples 1−4.

Table 3. Cross Parameters Determined for the Polymers Listed in Table 2

sample	η_0 [Pa s]	K [s]	n	correlation coefficient
1	2900	0.17	0.36	0.999
2	2510	0.19	0.38	0.999
3	2990	0.33	0.37	0.998
4	3000	0.68	0.40	0.995
5	6920	0.44	0.35	0.998
6	7210	0.73	0.35	0.998
7	7180	1.66	0.38	0.998

A more detailed insight into molecular relaxation in these polymers was obtained by the determination of Maxwell relaxation time spectra. The complex modulus, G^*, is described as a sum of the contributions of Maxwell models:[21]

$$G'(\omega) = \sum_k G_k \frac{\omega^2 \lambda_k^{\,2}}{1 + \omega^2 \lambda_k^{\,2}}$$

$$G''(\omega) = \sum_k G_k \frac{\omega \lambda_k}{1 + \omega^2 \lambda_k^{\,2}}$$

$$G^* = (G'^2 + G''^2)^{0.5}$$

This yields a spectrum of relaxation times (λ_k) with accompanying moduli (G_k). From these values, a characteristic relaxation time, λ_c, for each polymer was defined. λ_c is the viscosity average of the calculated relaxation times and is given by the following relationship,[22] where η_k is equal to $G_k\lambda_k$.

$$\lambda_c = \frac{\sum_k (\eta_k \lambda_k)}{\sum_k \eta_k}$$

The relaxation time spectra for samples 1−4 and 5−7

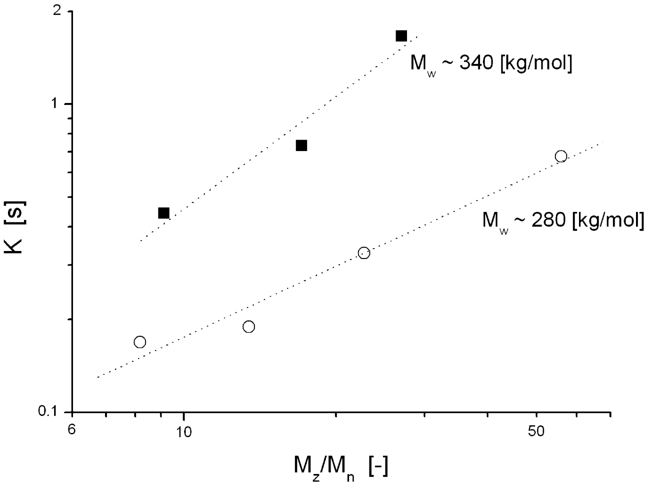

Figure 4. Relationship between the time constant (*K*) and overall polymer molecular weight distribution.

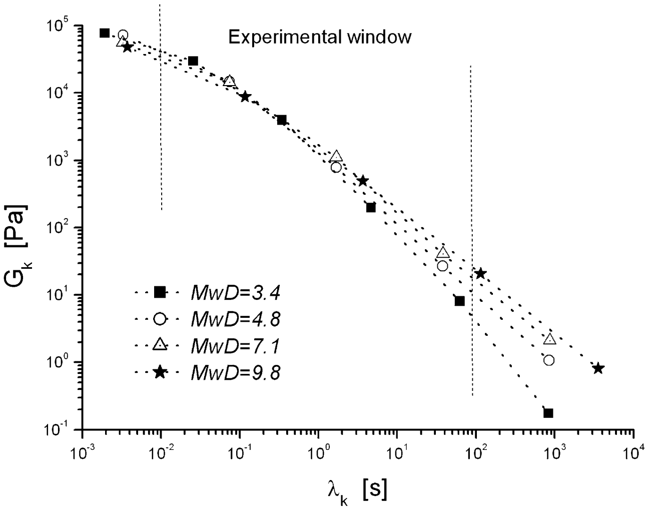

Figure 5. Maxwell relaxation time spectra for samples 1−4.

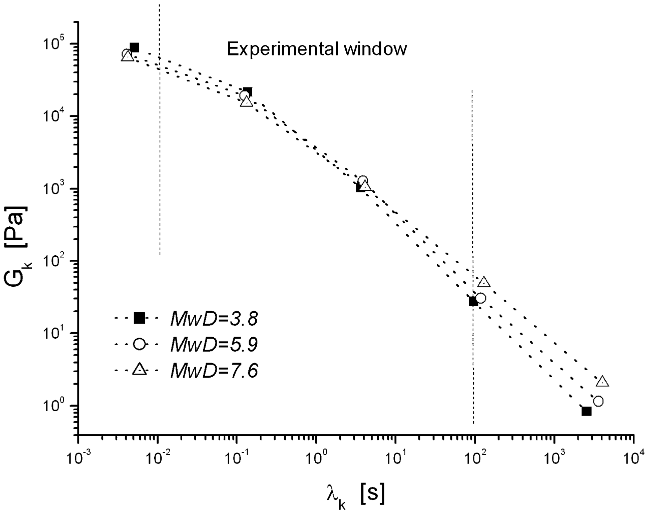

Figure 6. Maxwell relaxation time spectra for samples 5−7.

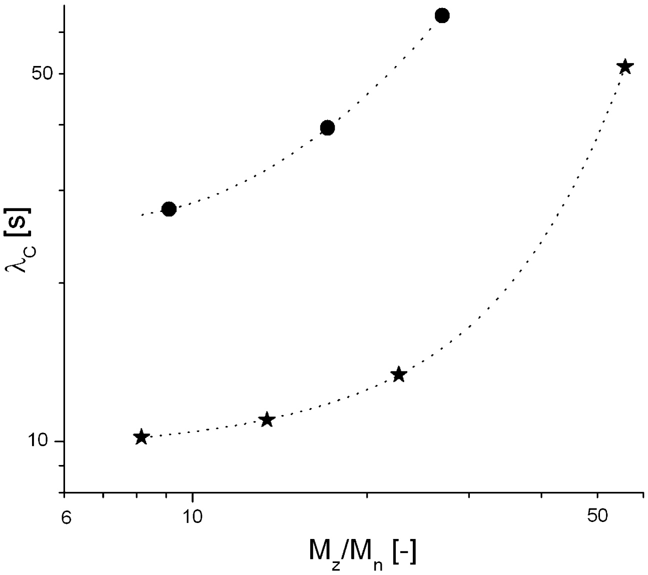

Figure 7. Effect of molecular weight distribution on characteristic relaxation time, λ_c, for samples 1−4 (★) and samples 5−7 (●).

are shown in Figures 5 and 6, respectively. The resulting λ_c values were plotted against M_z/M_n to give Figure 7, from which it is indeed apparent that the relaxation time is strongly dependent on molecular weight and molecular weight distribution, increasing strongly with increasing M_z/M_n. The λ_c values are an order of magnitude greater than the values of *K*, indicating a greater influence of the high molecular weight tail (giving long relaxation times) on λ_c. Again, M_z/M_n rather than M_w/M_n is used in order to represent the overall molecular weight distribution, including the high molecular weight tail.

Molecular weight distribution influences not only the rheological but also the crystallization behavior of polypropylene. For example, it has been shown by Cecchin[23] that the half-time of crystallization decreases when up to 10 wt % high molecular weight polypropylene (M_w 1 650 000) is blended into a sample having M_w 203 000. More recently, Alamo et al.[24] have found large increases in nucleation densities and crystallization rates with increasing M_w, particularly for high molecular weight polypropylene fractions. In the present work, we have investigated the crystallization rate of polypropylene by following the development of the dynamic modulus G', at a shear frequency of 10 s^{-1} and an applied stain amplitude of 2%, during isothermal crystallization at 140 °C after cooling the melt from 220 °C. These experiments were performed with and without first subjecting the melt at 220 °C to a steady preshear for 2 s at a shear rate of 5 s^{-1}, rheological studies by Vleeshouwers and Meijer[25] having shown that crystallization is accelerated by shearing. The development of the dynamic modulus as a function of time has also been used by Hingmann et al.[26] to follow the thickening of crystalline lamellae upon annealing of a partially molten polypropylene random copolymer. Other techniques that have been used for the investigation of shear-induced crystallization in polypropylene include small- and wide-angle X-ray scattering and optical microscopy.[27−29]

In the present studies, the onset of crystallization was apparent from a sharp increase in the storage modulus and was measured as illustrated in Figure 8. It is apparent that molecular orientation in the melt, induced by first subjecting the melt to shear, leads to a significantly shorter time to the onset of crystallization than is observed without preshearing. Furthermore, the data in Table 4 clearly indicate that, with or without preshear, the time to the onset of crystallization decreases with increasing molecular weight distribution of the polymer. It is quite possible that the faster onset of

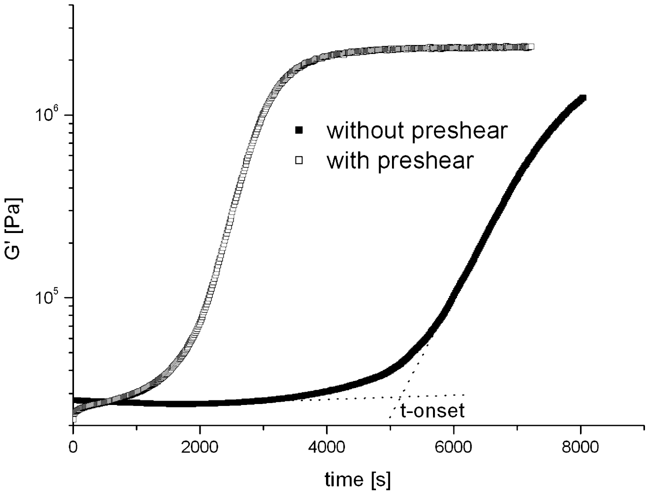

Figure 8. Onset of crystallization of sample 6 at 140 °C, indicated by an increase in the storage modulus, G'.

Table 4. Onset Times for Isothermal Crystallization at 140 °C

sample	internal/ external donor	M_z/M_n	t_{onset}, [min] without preshear	t_{onset}, [min] with preshear^a
5	diether/−	8.2	131	49
6	EB/PEEB	17.4	88	30
7	succinate/DCPDMS	26.6	61	20

^{a} Melt subjected to a steady preshear rate of 5 s^{-1} for 2 s at 220 °C.

crystallization observed with broad MWD PP (i.e., high M_z/M_n) is related to the relatively slow molecular relaxation in these polymers, high molecular weight chains initiating a high nucleation density and hence a more rapid onset of crystallization.

Conclusions

In this work, we have sought to establish fundamental characteristics of $MgCl_2$-supported Ziegler−Natta catalysts that have a major impact on polypropylene molecular structure and properties. PP molecular weight and molecular weight distribution are both highly dependent on catalyst regioselectivity. Ziegler−Natta catalysts are highly regioselective, in that the incidence of 2,1-insertion, as opposed to the dominant 1,2-insertion, is generally less than 1 in every 300 insertions for the overall polymer and less than 1 in every 1000 insertions for isospecific active species. However, one regioirregular (2,1-) insertion in every 2000 for highly isospecific active sites is, in the case of the catalyst system $MgCl_2/TiCl_4$/diether−$AlEt_3$, sufficient to give high hydrogen response and therefore easy molecular weight control as a result of a high probability of chain transfer with hydrogen at “dormant”, 2,1-inserted sites.[6] In contrast, the presence of active species with regioselectivity an order of magnitude higher, for example, would be expected to lead to much lower hydrogen response. Their detection is not possible, even via propene/ethene-[1-^{13}C] copolymerization, but on the basis of the present results we propose that the presence or absence of such highly regioselective active sites is a main factor determining not only hydrogen response but also PP molecular weight distribution.

Consequently, a relationship between Ziegler−Natta catalyst regioselectivity distribution and polypropylene molecular structure and properties can be identified. The catalyst system $MgCl_2/TiCl_4$/diether−AlR_3, in which even the most highly isospecific active species undergo measurable 2,1-insertion, therefore gives relatively narrow molecular weight distribution. The broader MWD obtained with other Ziegler−Natta catalysts, most notably the system $MgCl_2/TiCl_4$/succinate−AlR_3−alkoxysilane, is ascribed to the presence of a proportion of highly regiospecific active species, giving a high molecular weight polymer fraction. In turn, the presence of these long chain molecules has a profound effect on the polymer rheological and crystallization properties. For example, zero shear viscosity depends on molecular weight, whereas relaxation time shows strong dependence on molecular weight and molecular weight distribution and increases significantly with M_z/M_n. With this study, we hope to have illustrated the importance, for polypropylene processing and properties, of regioselectivity in propene polymerization using Ziegler−Natta catalysts.

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