Effects of the Catalyst System on the Crystallization of Polypropylene*

MARKUS GAHLEITNER,¹ CLAUDIA BACHNER,² EWA RATAJSKI,² GERALD ROHACZEK,¹ WOLFGANG NEIßL¹

¹ Borealis AG, St. Peterstr. 25, A-4021 Linz, Austria

² Johannes Kepler University Linz, Institute of Chemistry, Altenbergerstr. 69, A-4040 Linz, Austria

Received 2 July 1998; accepted 20 January 1999

ABSTRACT: In search of a better understanding of catalyst effects on final product qualities of polypropylene, an attempt was made to establish a correlation between catalyst type, polymer chain structure of homopolymers, crystallization behavior, as well as final morphology and mechanical properties. Conventional Ziegler–Natta catalyst systems as well as novel metallocene catalysts were investigated, and influences of molar mass distribution and chain regularity were investigated as separate factors. Metallocene-based isotactic polypropylene shows some special effects regarding the nucleation density and the correlation between stereoregularity and mechanics that do not fit into the general picture for Ziegler–Natta catalyst based products. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2507–2515, 1999

Key words: polypropylene; crystallization; metallocene catalyst; molecular structure

INTRODUCTION

Since 40 years ago, when polypropylene (PP) was first put on the market, it has undergone a rapid and successful development, which will make it the most used thermoplastic material before the end of this decade. The wide application range of PP results from its flexibility and the variety of possible modifications of the basic material, which already starts in the polymerization reactor.

Tailoring polymer properties in the polymerization stage requires a profound insight into the correlation chain from catalyst via the polymer structure to crystallization in processing and the final product properties.¹ Being a polymer with stereospecific chain structure (in contrast to polyethylene), it offers various structural possibilities already in the case of a homopolymer,² not to mention the wide range of copolymerization possibilities or the area of postreactor modification.

THEORETICAL BACKGROUND

The modification of PP in the polymerization step can in principle be done by regulating the molar mass (normally by feeding hydrogen as a termination agent into the process), by copolymerization with ethylene and/or other higher α -olefins, and by changing the catalyst system. Subsequently, postpolymerization modification is possible via degradation,³ compounding with fillers and reinforcements,⁴ grafting with reactive monomers, and blending with other polymers⁵ to arrive at a wide range of various material properties.

Catalyst Systems and Polymer Structure

A conventional state-of-the-art catalyst system for isotactic PP of the Ziegler–Natta type (ZN) basically

 $[\]ast$ Dedicated to Prof. Manfred Rätzsch on the occasion of his 65th birthday.

Correspondence to: M. Gahleitner.

Contract grant sponsor: Austrian Forschungsförderungsfonds für die gewerbliche Wirtschaft; contract grant number: 5/570/809.

Journal of Applied Polymer Science, Vol. 73, 2507-2515 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/122507-09

consists of a supported catalyst (Ti-chloride on $MgCl_2$) with an internal electron donor (Lewis base), an external donor (normally an organosilan), and a cocatalyst (Al-alkyl or Al-halogen-alkyl), which also acts as a scavenger to improve process stability; for a general treatment of such catalyst systems, see, e.g., the review by Albizzatti et al.⁶ This way, even with one catalyst, product variation is possible by donor selection and adjusting the ratio between monomer, catalyst, donor, and cocatalyst quantity. The tacticity of the PP chain can be varied within a wide range, thus influencing crystallinity and mechanics of the product.⁷ However, the molar mass distribution (MMD) is always rather wide $(M_w/M_n \ge 5)$ in case of ZN products and narrow MMD types are only accessible via degradation (controlled rheology process³).

The novel generation of metallocene (MC) catalysts⁸ are generally available in a wider structural variety and are additionally influenced by the supporting step as well as type and amount of cocatalyst (e.g., methyl-alumoxan (MAO)). For the polymerization of propylene, this means that besides isotactic PP, also atactic, syndiotactic, and other, more complex stereospecific structures become accessible.⁹ In contrast to ZN catalysts, MC catalysts produce polymers with a more homogenous structure (narrow MMD, constant tacticity, purely random insertion of comonomers), resulting from the different nature of catalytic sites: While ZN catalysts normally show a variety of different active sites on one type of catalyst, this is restricted to one type of site in case of MC catalysts (single-site type). On the other hand, MC catalysts produce chain defects resulting from head-head or tail-tail linkage of monomer units that do not occur in the case of ZN catalysts because of sterical restrictions. This leads to a different behavior in processing and final application of these polymers.

Crystalline Morphology and Mechanics of Polypropylene

Solid polypropylene consists of three phases^{10,11} (see also ref. 12; cf. ref. 13):

- crystalline (α monoclinic; β, hexagonal; or γ, centered orthorhombic modification),
- mesomorphic (also termed "smectic" or "paracrystalline," consisting of small α - and β -crystallites without superstructure), and
- amorphous (between and within crystalline regions, strongly influenced by those).

Generally, the mechanical properties of semicrystalline polymers like PP are significantly influenced by their crystalline structure. Apart from the overall crystallinity, the morphology, e.g., the dimension of spherulites or layered structures developed by shear-induced crystallization, also plays an important role here. These structures are in turn influenced by the molecular structure of the material on one hand and the solidification (or processing) conditions on the other hand.

In the past, effects of MMD and chain structure on the crystallization behavior and product properties have been mainly studied for the case of ZN-PP,^{2,14–19} because until recently these were the only products of technical and commercial relevance. Here, stiffness²⁰ as well as toughness²¹ effects have been observed. However, with the rise of the "metallocene revolution," polypropylenes produced with this new family of catalysts have gained substantial attention regarding their behavior in crystallization $^{22-24}$ as well as actual processing.²⁵ The wider structural variety of the polymers mentioned before makes the crystallinity and morphology of such systems a very interesting field of academic work with important implications for actual product development.²⁶⁻³⁰

Earlier studies of our group^{2,17} were focused on melt flow rate (MFR) MMD, and tacticity effects for ZN-PP. The separation of nucleation and growth effects proved essential and offered a big advantage over the "standardized" crystallization experiments like differential scanning calorimetry (DSC)-based Avrami plots. Through this, we could conclude that the first of these processes is dominated by the MMD, while the latter is mainly controlled by the stereoregularity of the chain. Additionally, some interesting features of shear-induced structure formation^{31,32} were discovered. The work presented here was carried out to gain an overview about the possible structural variations of isotactic PP (iPP) with technically relevant catalyst systems as well as the consequences of these changes in the structure. Special attention was paid to the positioning of MC-PP in relation to "conventional" products.

EXPERIMENTAL

Investigated Materials

Fourteen different propylene-homopolymers were included in the study, the basic characteristics of which have been summarized in Table I:

Material	MFR ^a g/10 min	T_m (°C)	H_m (J/g)	$\begin{array}{c} T_c \\ (^{\circ}\mathrm{C}) \end{array}$	$\operatorname{Tacticity}^{\mathrm{b}}$	${ m Skin} \ { m Thickness} \ (\mu{ m m})$	Avg. Spher. Size (µm)	Flex. Modulus (MPa)	Notched Impact ^c (kJ/m ²)
REPP 1	3.2	162	110	113	0.969	20	~ 40	1470	4
REPP 2	28	162	113	115	0.973	10	~ 20	1630	1.9
REPP 3	8.4	163	111	115	0.971	14	~ 50	1600	3.4
REPP 4	150	162	114	115	0.962	~ 1	~ 10	1890	1.3
REPP 5	300	162	114	116	0.965	0	nd	1880	1.2
CRPP 1	8	165	101	110	0.952	~ 2	~ 65	1300	3.4
CRPP 2	20	162	102	109	0.966	0	~ 30	1300	1.9
CRPP 3	8.6	164	101	110	0.959	~ 1	nd	1210	3.9
HAPP	0.5	157	55	109	0.565	nd^d	nd	280	nd
MCPP 1	28	154	100	110	0.897	2	~ 10	1360	2.3
MCPP 2	3.5	156	101	112	0.914	10	~ 25	1350	3.5
MCPP 3	21	149	89	107	0.921	4	~ 15	1385	2.0
MCPP 4	21	151	99	109	0.942	5	nd	1425	2.0
HCPP 1	8	165	115	114	0.978	2	nd	1640	2.7
HCPP 2	8	166	117	116	0.983	3	~ 60	1790	2.7
HCPP 3	8.4	166	117	115	0.981	4	nd	1750	3.3

Table IBasic Characteristics of Investigated Polymers; MFR, Crystallinity Data from DSC,Stereoregularity from IR Spectroscopy, Morphology from Polarizing Light Microscopy,Mechanical Properties Determined on Injection-Molded Specimens at +23°C

^a 230°C/2, 16 kg.

^b Chisso method.

^c International Standards Organization 179 1 eA.

^d nd: Not determined.

- 5 Reactor-iPPs (REPPs) with different average molar mass (MFR) and standard tacticity.
- 3 "Controlled rheology"-iPPs (CRPPs) produced from a standard tacticity reactor grade with MFR (230°C/2,16 kg) of 0.5 g/10 min in a twin screw extruder at 210°C with appropriate amounts of peroxide.
- One ZN-based highly amorphous PP with reduced tacticity (HAPPs).
- 4 MC-iPPs (MCPPs) with different average molar mass (MFR) and based on two different catalysts.
- 3 "High-crystallinity"-reactor-iPPs (HCPPs) with different average molar mass (MFR) and increased tacticity.

For the ZN-iPPs, fourth-generation commercial catalysts were used. The catalyst system (mainly the external donor) was identical for the REPP and CRPP grades, but different in case of the HCPP grades and the HAPP. For the MCiPPs, two different types of experimental metallocene catalysts in combination with MAO as cocatalyst and supported on silica were applied. All products were produced in a commercial or pilot scale plant at Borealis AG, Schwechat, Austria. In all cases, liquid-pool polymerization was applied.

Experimental Techniques

The MMD of all investigated products was determined using gas permeable chromatography (Waters 150 C, at 135°C in trichlorobenzene). Table I also gives the MFR values (International Standards Organization 1133, 230°C/2,16 kg), which show a rough correlation to the weight average of the MMD, M_w . Additional information about the chain structure was gained from IR spectra, where a method developed by CHISSO³³ was used to determine the tacticity (ratio between 998 and 973 cm^{-1} bands of the spectrum determined on specially compression-molded film; proportional to the isotactic decade ratio). Melting behavior and overall crystallinity were determined in DSC (TA 512 C, DIN 53765) in the second heat of a heat/cool/heat cycle between +23 and +250°C at 10 K/min. The overall crystallinity was calculated from the melting enthalpy using the formula

$$X_D = H_m/H_p$$

where H_p , the enthalpy of a totally crystalline PP, was assumed to be 209 J/g.^{10,12} The reason for choosing this value rather than the 165 J/g published before by Wunderlich¹³ was the better accordance of the resulting crystallinity level to crystallinities calculated from density and wide angle X-ray scattering (WAXS) measurements, which was experienced in our group in several earlier studies.

In most of the papers on polymer crystallization, Avrami equations are used to describe the crystallization process.³⁴ This, however, does not really reflect the reality in polymer solidification, where one can find a significant difference in temperature dependence between the formation of nuclei and the subsequent growth of crystallites. Like in our previous work, ¹⁷ the number of nuclei and the spherulitic growth rate were determined separately in special techniques at Linz University. For the nucleation density, again mostly DSC was used, but in some cases this proved not to be successful because of the high number of nuclei. For these samples, a special setup was built to allow rapid quenching from the melt to the desired crystallization temperature (a paper describing this method more precisely is being prepared). To determine the spherulitic growth rate, the same procedure as before³⁵ was applied.

As the previous literature points to a certain influence of the polymer type on the development of special crystal modifications^{27,36} four samples (REPP2, CRPP2, MCPP1, and HCPP2) were additionally characterized in WAXS on compression-molded plates of 2 mm thickness. The main purpose was to quantify overall crystallinity and the relative content of different crystal modifications. The samples were investigated in transmission on a Siemens D500 diffractometer, recording the wide angle scatter in the region of $5^{\circ} \leq 2\theta \leq$ 45°. After the usual corrections, the curves were split up into their crystalline and amorphous part, using the reference curve of an atactic polypropylene (aPP) sample as amorphous master curve.

The crystallinity (X_C) was determined from the peak areas in the region of $10^\circ \le 2\theta \le 30^\circ$; the concentrations of the β and γ modifications were expressed by the Turner–Jones index *B* and the γ concentration parameter *G*:

$$B=rac{I_{eta-300}}{I_{110}+I_{eta-300}+I_{040}+I_{130}}$$

$$G = rac{I_{\gamma-130}}{I_{130} + I_{\gamma-130}}$$

All mechanical properties—as listed in Table I—were determined on injection-molded specimens of $80 \times 10 \times 4$ mm according to standard procedures (3-point flexural test — ISO 178, Charpy notched impact test — ISO 179 1eA) at +23°C.

The actual morphology of all materials was checked directly on cross-sections microtomed out of the injection-molded samples in polarizing light microscopy as in earlier studies.¹⁷ Apart from a general judgment of the molding quality (homogeneity, absence of flow lines), this allowed a determination of the highly oriented and birefringent skin layer³² and a rough estimation of the spherulite size in the nonoriented core (see Table I). No full statistical evaluation was made for the latter quantity, as especially for the finer morphologies (high MFR values) the borders between different spherulites were increasingly difficult to distinguish.

RESULTS AND DISCUSSION

Crystallization and Crystallinity

Structural effects on the melting point appear only in case of HAPP and MCPP; smaller variations in the tacticity do not seem to influence T_m significantly (see Table I). In previous internal studies a generally good correlation between T_m and the average isotactic length in the polymer chain as determined via ¹³C-NMR could be found. A stronger variation is seen in the overall crystallinity X_D as calculated from the melting enthalpy (see Table II), where a rough classification can be made as follows:

The possibility of relating these values to final mechanical properties is limited, however, as the actual structure of the injection-molded parts is complex and also determines the performance to a great extent.

Even more differences appear if the parameters for quiescent crystallization are investigated separately (for a summary of the relevant parameters, see Table II). In case of the nucleation density, a previous study comparing reactor and CR

Material	M_w (kg/mol)	$\frac{M_w/M_n}{(\text{kg/mol})}$	$N^{ m a}$ $(1/{ m m}^3)$	$G^{\prime\mathrm{a}}_{\mathrm{(m/s)}}$	$egin{array}{c} X_D \ (\%) \end{array}$
REPP 1	426	5.5	4.8E + 13	$1.8\mathrm{E}-06$	52.6
REPP 2	222	4.5	$5.9\mathrm{E}$ + 13	$1.9\mathrm{E}-06$	54.1
REPP 3	357	5.0	$5.0\mathrm{E} + 13$	$2.0\mathrm{E}-06$	53.1
REPP 4	161	7.4	1.3E + 14	$3.3\mathrm{E}-06$	54.5
REPP 5	129	7.4	6.1E + 13	$3.7\mathrm{E}-06$	54.5
CRPP 1	353	3.2	3.2E + 12	$1.7\mathrm{E}-06$	48.3
CRPP 2	231	3.0	6.1E + 12	$1.8\mathrm{E}-06$	48.8
CRPP 3	318	3.1	$2.5\mathrm{E}$ + 12	$2.1\mathrm{E}-06$	48.3
HAPP	1168	9.7	8.5E + 12	$8.2\mathrm{E}-07$	26.3
MCPP 1	200	2.3	8.0E + 13	$1.1\mathrm{E}-06$	47.8
MCPP 2	403	3.0	3.1E + 13	$1.2\mathrm{E}-06$	48.3
MCPP 3	219	2.5	3.5E + 13	$1.1\mathrm{E}-06$	42.6
MCPP 4	224	3.3	2.8E + 13	$1.5\mathrm{E}-06$	47.4
HCPP 1	384	5.3	2.2E + 13	$2.2\mathrm{E}-06$	55.0
HCPP 2	409	5.1	3.5E + 13	$3.1\mathrm{E}-06$	56.0
HCPP 3	384	5.1	2.0E + 13	$2.9\mathrm{E}-06$	56.0

Table II Quiescent Crystallization Characteristics and Overall Crystallinity of Investigated Polymers; Molar Mass Distribution Data from GPC, Number of Nuclei (N), and Spherulithic Growth Rate G' from Special Measurements (^a at 110°C), Overall Crystallinity X_D from DSC Results

grades based on ZN catalysts² showed the width of the MMD to be the defining factor. Therefore it was of interest to see whether metallocene-based iPPs with their inherently narrow MMD fit into this picture. It turned out that this is not the case; as Figure 1 shows, the number of nuclei per unit volume is rather in the same range as for a ZNbased reactor grade or even higher. A reason for this effect may be the higher ash content (catalyst



Figure 1 Temperature dependence of nucleation density under quiescent conditions; (\bigcirc) REPP1 (ZN reactor grade, MFR 3,2), (+) MCPP2 (MC reactor grade, MFR 3,5), (\blacklozenge) CRPP1 (ZN CR grade, MFR 8).

residues) in some cases as compared to ZN grades: While for the ZN-based products the amount of ash (catalyst residues; none of the samples contained incombustible additives like SiO_2) is in the range of 150–250 ppm, for MCPPs an amount of 300–500 ppm is found. Additionally, the temperature dependency in the investigated range is quite the same. Apart from CR grades, a significantly reduced number of nuclei could only be found for the HAPP sample.

The second parameter for quiescent crystallization—namely, the spherulithic growth rate has been found to be dominated by the isotacticity of the chain for PP-homopolymers in previous studies.^{17,37} In the present work, a significantly wider range of chain tacticity was investigated, resulting in a variation of the growth speed of nearly one decade (see Fig. 2). Metallocene-based iPPs fit into the general picture in this case; their growth rates are slightly lower than ZN-based grades with standard isotacticity. In fact, a rather general correlation appears possible between the tacticity (IT) and the logarithm of the growth rate G' at a given temperature (110°C in the case of Fig. 3).

If products with similar stereoregularity (REPP and CRPP) are investigated separately, an additional molar mass effect becomes obvious (see Fig. 4). The effect, however, is much less pronounced!



Figure 2 Temperature dependence of spherulitic growth rate under quiescent conditions; (\bigcirc) HCPP1 (ZN high cryst. reactor grade, MFR 8), (\square) CRPP1 (ZN CR grade, MFR 8), (+) MCPP1 (MC reactor grade, MFR 28), (\blacklozenge) HAPP (ZN low cryst. reactor grade, MFR 0,5).

Another significant difference was found in the WAXS investigations concerning polymorphism¹¹ (see Table III). While the ZN-based reactor grade, even in the complete absence of an external β -nucleating agent shows a detectable amount of β modification, the development of the γ modification can be observed in case of the metallocenebased grade and only the α modification is found



Figure 3 Correlation between stereoregularity and spherulithic growth rate at 110°C: (\blacklozenge) ZN grades (except HAPP); (\Box) MC grades.



Figure 4 Correlation between weight average molar mass and spherulithic growth rate at 110°C for standard stereoregularity ZN-grades (REPP and CRPP).

for the CRPP and HCPP samples. In the literature, several possible reasons for the development of γ modification are given: special processing conditions like the application of extremely high pressure³⁶ or high shear rates^{38,39} on one hand and special structure of the polymer on the other hand. For the latter case, a significant γ content was found for low molar mass materials,¹¹ random copolymers with ethylene or low isotacticity products⁴⁰ and metallocene-based products.^{24,27,28} In all cases, disturbances of the chain whether caused by a higher content of chain ends (low molar mass), comonomer (random copolymers), or stereoirregularities seem to favor this modification. Interestingly enough, this is parallel to a negative effect on the spherulitic growth rate [investigations on random copolymers with ethylene (C2) show similar effects here; results of respec-

Table IIIResults of WAXS Investigation onCompression-Molded Plates

Material	MFR ^a (g/10 min)	$X_c \operatorname{Total^b}_{(\%)}$	Beta ^c	Gamma ^d
REPP 2	28	42.7	0.05	0
CRPP 2	20	41.3	0	0
MCPP 1	28	40.6	0	0.36
HCPP 2	8	43.5	0	0

^a 230°C/2, 16 kg.

^b Total crystallinity.

^c Turner–Jones index.

^d Gamma concentration index.

tive studies at Linz University have not been published yet]. Therefore we conclude that a retarded growth of the α modification favors a development of the γ modification.

Another point worth discussion is the comparatively low melting point for MCPPs, which is, again, rather similar to the behavior of random-C2-copolymers. Obviously, the chain defects resulting from head-head or tail-tail linkage of monomer units result in a stronger melting point depression than the tacticity irregularities normally present in products based on Ziegler–Natta catalysts. At the same time, the melting of MCPPs occurs in a more narrow temperature range as seen from DSC scans, resulting from the more homogeneous structure of the molecules and explaining the better relation between melting and heat deflection temperature.

Processing and Mechanics

Especially in the case of injection molding, the processability of metallocene-based iPPs was found to be only slightly different from conventional products.²²⁻²⁵ For rheological reasons, the mold-filling behavior is closer to CR grades. In our study, no negative effect of the slightly reduced growth rate could be observed, while problems were encountered in case of the extremely slow crystallization of HAPP, which led to problems in demolding (samples were not solid enough for mechanical demolding after the standard cycle time and had to be taken out by hand). Investigations of the morphology of the injection molded samples did not yield any surprising facts: The difference in skin layer thickness at comparable MFR between REPP and CRPP samples was already known from the literature³¹ and own investigations.¹⁷ The same applies for the core morphology (spherulite size), where CRPP and also HCPP exhibit a more coarse structure; in the latter case, this can be explained from the higher growth rates at comparable nucleation density. MCPP samples structurally resemble the REPP samples more with the skin layer being in thickness between REPP and CRPP as a consequence of structure determination by rheological and crystallization effects.

Regarding the mechanical properties, it appears that the stiffness is roughly correlated to stereoregularity (see Fig. 5), but only for the case of ZN-based products (in contrast to the correlation between stereoregularity and overall crystal-linity, where MCPPs just sow a somewhat higher



Figure 5 Correlation between stereoregularity and stiffness (flexural modulus): (\blacklozenge) ZN grades (except HAPP); (\Box) MC grades.

scatter). With respect to the regularity parameter, the metallocene-based iPPs have a significantly higher modulus than the rest, giving a second possible explanation for the different relation between melting point (or, in case of processing, sealing initiation temperature) and stiffness or heat deflection temperature frequently stated in the literature.⁸ As mentioned before, this is also affected by the difference in the distribution of irregularities along the chain for products based on different catalysts.

No such deviation was found in case of the toughness, where the average molar mass as primary defining factor for the impact strength appears to be generally valid (see Fig. 6). This correlation was frequently observed before for the case of PP-homopolymers.^{17,31}

CONCLUSIONS

- For PP-homopolymers based on Ziegler-Natta-type catalysts, in principle the crystallization behavior can be explained by the nucleation density (governed by the MMD) and the growth rate (governed by the chain regularity).
- At MMDs that are narrow as for CR grades of ZN-based iPP, metallocene-based products show a significantly higher nucleation density. The growth rate of these products is, as to be expected from their lower tacticity, re-



Figure 6 Correlation between molar mass (melt flow rate) and toughness (impact strength): (\blacklozenge) ZN grades (except HAPP); (\Box) MC grades.

duced and can be included into a general correlation between stereoregularity and growth rate.

- A combination of literature data with our own results leads to the conclusion that a retarded growth of the α modification favors development of the γ modification. This is observed in the case of metallocene-iPPs as well as normal ZN products with comonomers or reduced tacticity.
- The morphology observed in injectionmolded samples is in accordance with the steady-state crystallization parameters and earlier results. While the MMD only determines the skin layer formation, the core morphology is a complex function of MMD and stereostructure.
- Metallocene-based iPPs do not follow the normal correlation between tacticity and modulus for ZN products. This can explain the different relation between melting point and stiffness, which is a significant advantage of these grades.
- No general correlation can be drawn between crystallinity data from DSC or WAXS investigations and mechanical properties, as the morphology of the samples plays an important role in determining the actual behavior under load.
- For all investigated products, the average molar mass as primary defining factor for the impact strength appears to be generally valid.

Part of the work presented here was financially supported by the Austrian Forschungsförderungsfonds für die gewerbliche Wirtschaft under project no. 5/570/809. The authors are grateful to Prof. H. Janeschitz-Kriegl and Dr. G. Eder for coordinating the work carried out at J. Kepler University Linz, Prof. P. Zipper for carrying out the X-ray investigations, as well as Dr. D. Leistner of Borealis AG for preparing several of the samples in the pilot plant. Thanks also to Dr. K. Hammerschmid and Dr. C. Paulik at Borealis AG for helpful discussions.

REFERENCES

- Gahleitner, M.; Paulik, C.; Neiβl, W. Proceedings of PPS Regional Meeting; Gothenburg, Sweden, August, 1997; Vol 3, p 11.
- Gahleitner, M.; Bernreitner, K.; Neiβl, W.; Paulik;
 C.; Ratajski, E. Polym Test 1995, 14, 173–187.
- Hammerschmid, K.; Gahleitner, M. In Polypropylene—An A to Z Reference; Karger-Kocsis, J., Ed.; Kluwer Academic: Dordrecht, 1999, p 392– 398.
- Pukánszky, B. In Polypropylene; Karger-Kocsis, J., Ed.; Chapman & Hall: London, 1995; Vol. 3, pp 2–70.
- 5. Paul, D. R.; Newman, S., Eds., Polymer Blends; Academic Press: New York, 1978; Vols 1 and 2.
- Albizzati, E.; Giannini, U.; Collina, G.; Noristi, L.; Resconi, L. In Polypropylene Handbook; Moore, E. P., Ed., Hanser: Munich, 1996, pp 12–111.
- Gahleitner, M.; Ledwinka, H.; Hafner, N.; Heinemann, H.; Neiβl, W. Proceedings of SPO '96; Houston, TX, USA, September 1996; pp 251–260.
- Brekner, M. J. Proceedings of Metallocenes '96; Düsseldorf, Germany, May 1996; pp 155–1779.
- Jones, R. L.; Resconi, L.; Rheingold, A. L. Proceedings of SPO '95, Houston, TX, USA, Sept. 1995, pp. 19–39.
- Welsh, W. J. In Physical Properties of Polymers; Mark, J. E., Ed.; AIP Press: New York, 1996; pp 401-407.
- Meille, S. V.; Ferro, D. R.; Brückner, S. Macromol Symp 1995, 89, 499–51.
- Brandrup, J.; Immergut, E. H., Eds. Polymer Handbook, 3rd ed.; Wiley: New York, 1989; chaps 3-5.
- 13. Wunderlich, B. Macromol Phys 1980, 3, 126-132.
- Burfield, D. R.; Loi, P. S. T.; Doi; Y.; Meijzlik, J. J Appl Polym Sci 1990, 41, 1095–1114.
- Paukkeri, R.; Lehtinen, A. Polymer 1993, 34, 4075– 4082.
- Paukkeri, R.; Lehtinen, A. Polymer 1993, 34, 4083– 4088.
- Gahleitner, M.; Wolfschwenger, J.; Bernreitner, K.; Neiβl, W.; Bachner, C. J Appl Polym Sci 1996, 61, 649–657.

- Phillips, R. A.; Wolkowicz, M. D.; Jones, R. L. ANTEC '97, 1997, pp. 1671–1676.
- Reinshagen, J. H.; Dunlap, R. W. J Appl Polym Sci 1976, 20, 9–24.
- Jarus, D.; Scheibelhofer, A.; Hiltner, A.; Baer, E. J Appl Polym Sci 1996, 60, 209–219.
- Botsis, J.; Oerter, G.; Friedrich, K. ANTEC '96, 1996, pp 3294–3300.
- 22. Bond, E. B.; Spruiell, J. E. ANTEC '97, 1997, pp 1750–1753.
- Alamo, R. G.; Galante, M. J.; Lucas, J. C.; Mandelkern, L. Polym Prepr 1995, 36, 285–286.
- 24. Fischer, D.; Mühlhaupt, R. Macromol Chem Phys 1994,195, 1433–1441.
- 25. Cheng, C. Y.; Kuo, J. W. C. ANTEC '97, 1997, pp 1942–1949.
- Thomann, R.; Wang, C.; Kressler, J.; Jüngling, S.; Mühlhaupt, R. Polymer 1995, 36, 3795–3801.
- 27. Thomann, R.; Kressler, J.; Setz, S.; Wang, C.; Mühlhaupt, R. Polymer 1996, 37, 2627–2634.
- Thomann, R.; Kressler, J.; Rudolf, B.; Mühlhaupt, R. Polymer 1996, 37, 2635–2640.
- Maier, R.-D.; Thomann, R.; Kressler, J.; Mühlhaupt, R.; Rudolf, B. J Polym Sci B Polym Phys 1997, 35, 1135–1144.

- Zambelli, A.; Locatelli, P.; Sacchi, M. C.; Tritto, I. Macromolecules 1982, 15, 831–834.
- Fujiyama, M.; Wakino, T. J Appl Polym Sci 1991, 43, 57-81.
- Liedauer, S.; Eder, G.; Janeschitz-Kriegl, H.; Jerschow, P.; Geymayer, W.; Ingolic, E. Intern Polym Proc 1993, 8, 236–244.
- 33. Chisso Corp. EP 277.514 B1.
- Mezghani, K.; Phillips, P. J. In Physical Properties of Polymers; Mark, J. E., Ed.; AIP Press: New York, 1996; pp 417–425.
- Ratajski, E.; Janeschitz-Kriegl, H. Coll Polym Sci 1996, 274, 938–951.
- Campbell, R. A.; Phillips, P. J. Polymer 1993, 34, 4809–4816.
- Janimak, J. J.; Cheng, S. Z. D.; Giusti, P. A. Macromolecules 1991, 24, 2253–2260.
- Kalay, G.; Allan, P.; Bevis, M. J. Polymer 1994, 35, 2480–2482.
- Kalay, G.; Zhong, Z.; Allan, P.; Bevis, M. J. Polymer 1996, 37, 2077–2085.
- Marigo, A.; Marega, C.; Zannetti, R.; Paganetto, G.; Canossa, E.; Coletta, F.; Gottardi, F. Makromol Chem 1989, 190, 2805–2813.