Nonisothermal Crystallization and Melting Behavior of Syndiotactic Polypropylenes of Different Microstructure

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ABSTRACT: Syndiotactic polypropylenes and their copolymers with 1-olefins were synthesized using two metallocene/MAO catalytic systems, and the effect of the different microstructures on nonisothermal crystallization and subsequent melting was studied. Using differential scanning calorimetry (DSC) it was observed that samples with lower content of defects showed crystallization on cooling from the melt, and a double melting peak in the subsequent heating scan, the latter associated with melt, recrystallization and remelt processes that it was confirmed by its nonreversing exothermic process found by means of temperature modulated DSC (MDSC). However, polymers with high amount of defects showed cold crystallization on heating followed by a melting process, that it was observed by MDSC. Wide angle X-ray diffraction was used for characterizing the changes of crystalline forms in relationship with crystallization process. \bigcirc

Keywords: cold crystallization; melting behavior; structure-property relations; syndiotactic polypropylene; thermal properties

INTRODUCTION

Polyolefins are nowadays the most important "commodity" plastics at the industrial level, with a large and steady growth in recent years.¹ This extraordinary behavior is the result of the constant development of new production processes together with novel catalytic systems that allow the improvement of their range of applications by means of new polymeric materials having interesting physical properties. In this context, the development by Ewen et al.² of metallocene catalysts with C_s symmetry made it possible to extend the studies to syndiotactic polypropylene (sPP) with higher stereo and regio-regularity, synthesized under relatively normal conditions. In general, sPP has lower crystallinity and higher impact strength than isotactic polypropylene,³ and at least four limited-ordered crystal structures or polymorphism.^{4,5} The presence of either ordered or disordered polymorphism is highly dependent on the crystallization conditions and the stereoregularity of polypropylene.^{6–8}

With respect to the thermal behavior of sPP, it is possible to see a systematic shift of the melting temperatures to lower values when the meso unit content is increased (associated with

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lower syndiotacticity).^{9,10} These changes in the melting behavior can be explained mainly taking into account that the stereo-defects can be considered as comonomer units,^{4,9,11} so they are excluded from the crystals and therefore decrease the melting temperature of the polymer, as reported by Flory,¹² although some authors reported that could be tolerated within the crystal, at least partially.¹³ The presence of the stereo-defect is perhaps one of the reasons for the uncertainty with respect to the true equilibrium melting temperature for 100% sPP, which has been published in the range between 182 and 220 °C.^{10,11,14,15}

It has been reported that some sPP samples^{4,16,17} present double melting peaks which is more evident in samples with lower syndiotacticity,^{4,18,19} although could depends on the crystallization and melting conditions.²⁰ In general, the mechanisms and extent of the recrystallization process, that explain the last phenomenon, depends greatly on the stability of the primary and secondary crystallites formed and on the heating rate used.^{17,21} The double melting peak is reported almost exclusively in the heating scan after isothermal crystallization, but it is also found in nonisothermal conditions.²² For syndiotactic propylene/1-olefin copolymers, the presence of double melting peaks is also found when lower comonomer content and crystallization temperatures are used, regardless of the kind of comonomer,^{7,23} under isothermal conditions.

Another characteristic not well understood yet is related to the presence of cold crystallization (associated with an exothermic process in the heating scan) found in some sPP samples and their copolymers. Arranz-javier et al.²⁴ found that the second melting of sPP homopolymer shows a cold crystallization around 45 °C, but when 1-olefins (1-hexene, 1-octene, and 1octadecene) are incorporated into the sPP main chain this exothermic process disappears and the samples become amorphous under those crystallization conditions. Similar results are reported by Graef et al.²⁵ but in an opposite way, since the sPP homopolymers do not present any exothermic process on heating, but its copolymers with 1-hexene showed an important cold crystallization. Therefore, more detailed studies need to be done to explain the complete crystallization and melting behavior of syndiotactic propylene/1-olefin copolymers.

In this context, the purpose of the present work is to study the effect of the microstructure of different sPPs on their thermal behavior when they are crystallized under nonisothermal conditions, and to analyze the morphological characteristics of these samples. For the latter, a set of homopolymers synthesized with two metallocene catalysts will be used, and the addition of several 1-olefins on the sPP main chain by a copolymerization process will be discussed.

EXPERIMENTAL

Materials

The catalysts $(Me)_2C(Cp)(9-Flu)ZrCl_2$ (Cat A) and $Ph_2C(Cp)(9-Flu)ZrCl_2$ (Cat B) from Boulder Scientific, and methylaluminoxane (MAO) cocatalyst from Aldrich (10 wt %/vol % in toluene), were used as received. Toluene was distilled over sodium and distilled in an inert atmosphere. The propene was purified by passing it through three columns containing the BASF catalysts R3-11G and R3-12, and a 4 Å molecular sieve, respectively. The liquid monomers 1-hexene and 1-octadecene (from Aldrich) were dried under inert gas before use.

Homopolymerization

All polymerizations were carried out in a 1-L Büchi glass reactor, at a pressure of 2 bar and stirring at 1000 rpm. The Al/Zr mole ratio was set at 1000. All reactions and manipulations were carried out in an inert gas atmosphere using a standard Schlenk technique. The polymers were coagulated with excess methanol acidified with HCl, filtered, washed with further methanol, water and acetone, and then dried.

The sPP samples were synthesized with two different metallocene/MAO catalytic systems. Samples sPPA1 to sPPA3 were synthesized with Cat A at 50, 30, and 20 °C, respectively. Samples sPPB1 to sPPB3 were synthesized with Cat B at 50, 60, and 65 °C, respectively. The characteristics of these polymers are reported in Table 1.

Copolymerization of Propene/1-Hexene and Propene/1-Octadecene

Copolymers of propene with 1-hexene (CsP-H) and 1-octadecene (CsP-O) were synthesized with Cat B at 50 $^{\circ}$ C as described earlier, but the precipitate was filtered, washed several times with

Table 1. Main Homopolymer	Properties
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	$\overline{M}_{\mathrm{w}}$		Tacticity				
Sample	[kg/mol]	$\overline{M}_{ m w}/\overline{M}_{ m n}$	[% rrrr]	$T_{ m g}$ [°C]	$T_{ m c}$ [°C]	$T_{\rm m}$ [°C]	$X_{ m c}$
sPPA1	90	1.6	73.6	0	80	120 - 132	0.23
sPPA2	140	1.8	82.1	1	93	137 - 146	0.30
sPPA3	160	1.7	88	$^{-1}$	96	143 - 149	0.31
sPPB1	300	1.8	76.8	3	68	119 - 129	0.19
sPPB2	220	1.8	71.9	1	44	118	0.14
sPPB3	180	1.7	65.7	1	53	101 - 113	0.11

acetone, and dried. The main properties are shown in Table 2.

Characterization of Polymers

Weight average molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) on a Waters Alliance GPC2000 system equipped with a differential optical refractometer (model 150 C). A set of three columns of Styragel type HT (HT3, HT4, and HT6) was used with 1,2,4-trichlorobenzene as solvent. The analyses were calibrated with narrow molecular mass distribution polystyrene and polyethylene standards.

Tacticity and comonomer content were determined by ¹³C nuclear magnetic resonance spectra (¹³C-NMR) recorded at 125 °C on a Varian Inova 300 instrument operating at 75 MHz. Solutions of the polymer samples were prepared in *o*-dichlorobenzene and benzene- d_6 (20 vol %/vol %) using 5-mm sample tubes.

The nonisothermal melt-crystallization exotherms and subsequent melting endotherms were obtained on a Modulated TA Instruments DSC 2920 differential scanning calorimeter (DSC) in an N_2 atmosphere to minimize thermal degradation. The experiment started by heating each sample from 25 to 170 °C at a heating rate of 40 °C/min, to delete the thermal history of the samples. To ensure complete melting, each sample was melted-annealed at 170 °C for 5 min, and it was then cooled at the desired cooling rate. The subsequent melting behavior was then observed by reheating the sample to 170 °C at a rate of 10 °C/min. For the modulated differential scanning calorimetry (MDSC) scan, the modulation temperature amplitude is smaller relative to the heating rate, so there is no local cooling during the scan, which is referred to as heating-only. The specific conditions are explained later in the work.

For crystallinity fraction (X_c) determinations, a value of 196.6 J/g has been taken as the enthalpy of fusion of the perfect crystal of sPP.¹⁴

Films with a thickness of 1 mm were prepared by melting the polymer in a hot press at a temperature 20 °C higher than its melting temperature. The compression-molded film was then cooled to 40 °C in the compression press by running cold water through channels in the press plates. The films were kept at room temperature for 1 week and were then analyzed by X-ray diffraction. The as-prepared samples came directly from the reactor after precipitation, without any postreactor melting.

Table 2. Main Properties of Copolymers Synthesized with Cat B

Sample	$\overline{M}_{ m w}$ [kg/mol]	$\overline{M}_{ m w}/\overline{M}_{ m n}$	Comomer content [%]	Tacticity [% rr]	$T_{ m g} [^\circ m C]$	$T_{ m c}$ [°C]	$T_{\mathrm{m}} [^{\circ}\mathrm{C}]$	$X_{ m c}$
sPPB1	300	1.8	_	88.3	3	68	119–129	0.19
CsP-H1	270	1.6	1.3	86.9	1	45	116	0.13
CsP-H2	240	1.7	2.6	88.2	1	63	104	0.11
CsP-H3	240	1.6	3	83.4	0	no	no	no
CsP-O1	240	1.6	0.3	87.9	-2	33	116	0.14
CsP-O2	250	1.6	1.6	86.8	-6	54	100	0.11
CsP-O3	240	1.6	3.1	84.2	$^{-14}$	56	93	0.04

no = not observed.



Figure 1. Cooling scan at 10 °C/min from melting for homopolymers.

Wide-angle X-ray diffraction patterns were obtained at room temperature with a Siemens D5000 diffractometer with $CuK_{\alpha}=1.54$ Å and a step scan of 0.02° at room temperature. The diffraction scans were collected in the range of 2θ values from 2° to 40° for film and as-prepared samples.

RESULTS AND DISCUSSION

Syndiotactic Polypropylene Homopolymers

The main characteristics of the homopolymers obtained are presented in Table 1 and the DSC curves in cooling scan from the melt and the subsequent melting are shown in Figures 1 and 2, respectively. The melting point is not affected by the molecular weight of the samples,¹⁶ as seen when comparing samples sPPA1 and sPPB1. It seems that the most important variable is the number of stereo-defects present in the polymer.^{6,9} Nevertheless, the crystallization temperature not only depends on the syndiotacticity but also of the molecular weight of the polymer.

With respect to the nonisothermal crystallization shown in Figure 1, a great change is observed for the samples with higher content of stereo-defects, sPPB2, and sPPB3, since this process almost disappears, in contrast with the rest of the samples in which a narrow crystallization peak appears, especially in samples synthesized with Cat A (lower stereo-defect content). Moreover, samples that crystallized on cooling present a melting point with a double peak in the subsequent heating scan (Fig. 2). However, samples sPPB2 and sPPB3 show first an exothermic process at low temperatures and subsequent melting on heating. So, polymer microstructure not only changes both the crystallization and melting temperatures of the samples, but also their crystallization behavior.

To get more evidence about the exothermic process on heating, MDSC tests were carried out. In MDSC, the heat flux into the sample is monitored during a programmed temperature change implying superposition of a linear increase and an oscillatory part. In the resulting heat flux it is possible to find one contribution associated with the heat flux that is in-phase with the time derivative of the temperature (instantaneous heating rate), but also another part associated with a phase lag of $\pi/2$. Obviously, systems out of equilibrium will have some imaginary part associated with nonreversing processes. The MDSC for sample sPPB3 are shown in Figure 3. It is seen that the exothermic process on heating is associated almost exclusively with a nonreversing process, and supports the conclusion that the exothermic peak found on heating for these samples is due to a cold crystallization process related to macromolecular segments that were not able to crystallize during cooling.^{24,25} However, the subsequent melting process has both real and imaginary contributions²⁰ and we suppose that the out-of-phase contribution is associated with a melt, recrystallization, and remelt process, associated with the



Figure 2. Second heating at 10 °C/min for homopolymers.



Figure 3. Nonreversing, reversing, and total signals from MDSC for sPPB3 sample at a heating rate of 5 $^{\circ}$ C/min with a period of 1 min and a modulation amplitude of 0.796 $^{\circ}$ C.

small endothermic peak around 100 $^{\circ}$ C in the total heat flow in Figures 2 and 3. This phenomenon will be discussed later in this work. On the other hand, the small endothermic peak seen in the cold crystallization for the in-phase contribution may be associated with the melting process of the smallest or lowest stable crystallites formed during the cold crystallization.

To determine if it is possible to find cold crystallization in other samples, it was made DSC analysis at different rate for sample sPPA1. Within the range studied (between 5 and 20 $^{\circ}C/$ min), regardless of the scan rate used, the sample always has a normal exotherm and endotherm processes in the cooling and heating scans, respectively. The opposite occurs with sample sPPB2, where a great dependence exists between the cooling scan rate and the crystallization behavior, as seen in Figure 4. It seems reasonable that at lower cooling rates the sample has more time to relax from the melt and will be able to crystallize on cooling. So, the cold crystallization process is sensitive to the polymer's microstructure, molecular weight, and crystallization conditions.

The exothermic process on heating found in some samples, is possible to correlate it with higher amount of defects. The presence of this cold crystallization is not found in isotactic polypropylene, but had been reported in sPPs.^{24,25} It is clear that with the incorporation of defects in the polymer main chain the crystallinity and its rate decreases,^{4,7,24,26,27} specially in polyole-

fins^{16,28–30} Therefore, when the number of defects is high enough the sample is not able to crystallize from the melt because of the short time between the melt state and the glass transition temperature. However, it is not enough for the sample not to have an exothermic peak on cooling to show cold crystallization in the heating scan, in sPPs the overall crystallization rate measured in samples crystallized from the glassy state is much faster than in samples crystallized from the melt state.^{21,31} Therefore, since the samples with large numbers of defects are not able to crystallize on cooling, the cool scan process acts as a quenching, and increases the total number of activated nuclei that act as predetermined homogeneous nuclei in the subsequent heating scan, which greatly enhances the overall crystallization rate from the glassy state.^{21,32,33}

In relation to the presence of the double peak in the melting process, MDSC was carried out as shown in Figure 5 for sample SPPA3, at very low scan rates (1 °C/min). If the total heat flow of Figure 5 is compared with the melting behavior of SPPA3 at 10 °C/min (Fig. 2), is seen that by decreasing the heating rate, the height of the lower melting peak decreases relative to the higher melting peak which is indicative of a recrystallization and remelting process. The higher the heating rate used, the shorter is the time available for the diffusion of the molecular segments onto the growing recrystallizing lamellae, so the remelt process is decreased.^{17,34} The recrystallization depends on the stability of the primary and secondary crystallites,²¹ and this is confirmed by the results of Figure 2, since when



Figure 4. Second heating at 10 °C/min for sPPB2 at different cooling rates.



Figure 5. Nonreversing, reversing and total signals from MDSC for sPPA3 sample at a heating rate of 1 $^{\circ}$ C/min with a period of 1.3 min and a modulation amplitude of 0.212 $^{\circ}$ C.

the number of defects in the polymer decreases the relative weight of the higher endotherm is lower.³⁵ On the other hand, Figure 5 shows that with the first endothermic peak at 140 °C in the total heat flow there is one endothermic peak in the in-phase contribution and one exothermic peak in the out-phase contribution, the latter associated with cold-crystallization, so it is possible to find new evidence to confirm that the double melting peak is associated with recrystallization processes. After that, both contributions present a melting peak around 150 °C in the total heat flow. So, similar to what is seen in Figure 3, it seems that the remelt process causes some nonreversing melting phenomena.



Figure 6. Cooling scan at 10 $^{\circ}$ C/min from melting of copolymers.

Syndiotactic Propylene/1-Olefin Copolymers

For studying the effect of another kind of defect, a set of copolymerizations were carried out with Cat B using two comonomers, 1-hexene, and 1octadecene. The main characteristics of these copolymers are shown in Table 2. In general, the relation between the concentration of comonomer in the reactor and its final incorporation in the main polymer chain is well known,³⁶ and in this way it was possible to obtain several comonomer incorporations. The lower syndiotacticity found in copolymers had been explained by the increase in skipped insertions or site epimerization³⁷ when comonomer units are incorporated in the main chain because of the lower rate of olefin insertion.^{25,36} The DSC measurements of these copolymers are shown in Figures 6 and 7 for cooling and heating scans, respectively. Like in other systems, as the total number of defects increases, the melting temperature and crystallinity decrease or almost disappear.^{24,25,38–40}

Like in what was found for homopolymers with large numbers of defects, all the copolymers do not present significant crystallization on cooling since they have higher numbers of defects, but in heating scan they show cold crystallization and subsequent melting, as seen in Figures 6 and 7. However, the CsP-H3 sample presents neither crystallization nor melting processes in both the cooling and heating scans. This sample has the largest number of defects, so under the conditions of these tests the defects prevent any crystallization process. It is not



Figure 7. Second heating at 10 °C/min for copolymers.



Figure 8. Second heating at 10 °C/min for CsP-O2.

shown here, but this sample presents an endothermic peak when it is heated before melting (as-prepared sample), so its apparent amorphous behavior is related to the long relaxation time needed to crystallize.

To analyze the dependence between the crystallization conditions (cooling rate) and the presence of cold crystallization in copolymers, nonisothermal crystallizations at different cooling rates were carried out, from 2.5 to 10 °C/min, and the subsequent heating at 10 °C/min is shown in Figure 8 for sample CsP-O2. In the range studied, no evidence was found of crystallization on cooling, and in contrast to what was found for sample sPPB2, cold crystallization is not influenced by the kinetics of crystallization; indeed, the melting temperature is almost constant for the three cooling scans. The difference in behavior found between samples sPPB2 and CsP-O2 may be related to the partial incorporation of stereodefects in the polymer crystals, so decreasing the cooling rate increases the probability of incorporating the defect in the crystals, in contrast to the comonomer, where regardless of the kinetics it will not be able to incorporate it.

Morphological Characterization

The effect of both the number of defects and the crystallization conditions was studied, Figures 9 and 10 present the X-ray diffractograms of samples SPPB1, CsP-H1, CsP-H3, and CsP-O3, as-prepared and crystallized from the melt, respectively; the other samples did not show any difference with respect to sample SPPB1 or CsP-



Figure 9. X-ray diffraction of sPPB1 and some asprepared copolymers.

H1, except for the degree of crystallinity, so they are not shown. As-prepared samples sPPB1 and CsP-H1 show (010) reflection around $2\theta = 15.9^{\circ}$, that is associated with one orthorhombic unit cell, with the chain in the s(2/1)2 antichiral helical conformation, called Form I.³⁹ It is also seen that the (211) reflection (at $2\theta = 18.8^{\circ}$) is completely absent, so the as-prepared sample sPPB1 crystallizes completely in the Form I disordered structure. However, as-prepared sample CsP-H3 presents (110) reflection at $2\theta = 17^{\circ}$ associated with Form II, which also means an orthorhombic unit cell but with the chain in the s(2/1)2 isochiral helical conformation. It is reported that samples with large numbers of defects⁴ by comonomer incorporation⁸ or by stereo-defects⁴⁰ present some crystals in Form II, as reported here,



Figure 10. X-ray diffraction of sPPB1 and some copolymers crystallized from the melt.

especially when they are crystallized from solution. CsP-O3 has low crystallinity, but it seems that it is present to some extent as Form II. So, samples with large amounts of comonomer content are able to crystallize in Form II from solution (as-prepared).

When the samples are melted and crystallized in a press, no important changes are seen for samples with lower defect content, and no evidence is found related to the ordered Form I, since the reflection at $2\theta = 18.8^{\circ}$ is always absent, possibly due to the lower syndiotacticity of these samples.⁸ However, samples CsP-H3 and CsP-O3 change from Form II to completely disordered Form I when crystallized from the melt. The latter results are in agreement with those of Naga et.al.7 and Arranz-Javier et al.24 where it is found disordered Form I in sPP with long 1-olefins in samples crystallized from the melt under nonisothermal conditions, but with weak evidence of the presence of disordered Form II. Therefore, the dependence of the number of defects and the crystallization conditions on the crystal structures of the samples is clear.

CONCLUSIONS

By means of two metallocene catalysts it was possible to synthesize sPPs and their copolymers with 1-olefins of different molecular weight and tacticities, and the effect of the polymer microstructure on nonisothermal crystallization was studied. The number of total defects, associated with both stereo-defects and comonomer incorporation, is the main parameter related to the changes observed in the crystallization behavior of the polymers. When the number of defects is greater than some critical value, the crystallization process is not seen in the cooling scan, and cold-crystallization appears in the subsequent heating scan. The cold crystallization found in some samples was confirmed by temperature modulated DSC, since the exothermic process on heating is associated with nonreversing processes. This phenomenon is due to the fact that the overall crystallization rate measured in samples crystallized from the glassy state is much faster than in samples crystallized from the melt state. Also, MDSC showed new evidence to confirm that the double melting peak found in some samples is related with the melt, recrystallization, and remelt process, since it appears one exothermic peak in the nonreversing contribution.

On the other hand, X-ray diffraction showed that as-prepared samples with the highest defect content have Form II crystals, but when they were melted the crystals changed to disordered Form I. The rest of the samples present disordered Form I regardless of the kind of crystallization.

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REFERENCES AND NOTES

- Galli, P.; Vecellio, G. Prog Polym Sci 2001, 26, 1287–1336.
- Ewen, J. A.; Johns, R. L.; Razavi, A. J.; Ferrara, J. D. J Am Chem Soc 1988, 110, 6225–6256.
- Sinclair, K. B. Proceedings of the international conference on polyolefins VIII. Houston, Society of Plastic Engineering, 1993.
- De Rosa, C.; Auriemma, F. Prog Polym Sci 2006, 31, 145–237.
- Lotz, B.; Lovinger, A. J.; Cais, R. E. Macromolecules 1988, 21, 2375–2382.
- De Rosa, C.; Auriemma, F.; Vinti, V. Macromolecules 1997, 30, 4137–4146.
- Naga, N.; Mizunuma, K.; Sadatoshi, H.; Kakugo, M. Polymer 2000, 41, 203–209.
- De Rosa, C.; Auriemma, F.; Fanelli, E.; Talarico, G.; Capitani, D. Macromolecules 2003, 36, 1850–1864.
- Balbontin, G.; Dainelli, D.; Galimbert, M.; Paganetto, G. Maromol Chem 1992, 193, 693–703.
- De Rosa, C.; Auriemma, F.; Vinti, V.; Galimberti, M. Macromolecules 1998, 31, 6206–6210.
- Miller, R. L.; Seeley, E. G. J Polym Sci Polym Phys Ed 1982, 20, 2297–2307.
- 12. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, 1953.
- Auriemma, F.; De Rosa, C.; Corradini, P. Macromolecules 1993, 26, 5719–5725.
- Haftka, S.; Konnecke, K. J. Macromol Sci Phys B 1991, 30, 319–334.
- Hausier, G.; Schmidtke, J.; Strobl, G. Macromolecules 1998, 31, 6250–6258.
- Rodríguez-Arnold, J.; Zhang, A.; Cheng, S. Z. D.; Lovinger, A. J.; Hsieh, E. T.; Chu, P. Polymer 1994, 35, 1884–1895.
- 17. Supaphol, P. J Appl Polym Sci 2001, 82, 1083– 1097.
- Boor, J.; Youngman, E. A. J Polym Sci Polym Phys Ed 1965, 3, 577–580.
- Youngman, E. A.; Boor, J. Macromol Rev 1967, 2, 33–69.
- 20. Schmistke, J.; Strobl, G.; Thurn-Albrecht, T. Macromolecules 1997, 30, 5804–5821.

- 21. Supaphol, P.; Spruiell, J. E. Polymer 2001, 42, 699-712.
- Supaphol, P.; Thanomkiat, P.; Phillips, R. Polym Test 2004, 23, 881–895.
- Toman, R.; Kressler, J.; Mulhaupt, R. Polymer 1998, 39, 1907–1915.
- Arranz-Javier, J.; Guevara, J.; Velilla, T.; Quijada, R.; Benavente, R.; Pérez, E.; Cerrada, M. Polymer 2005, 46, 12287–12297.
- Graef, S.; Wahner, U.; Van Reenen, A.; Brull, R.; Sanderson, R.; Pasch, H. J Polym Sci Part A: Polym Chem 2002, 40, 128–140.
- Palza, H.; Lopez, J. M.; Quijada, R.; Benavente, R.; Perez, E.; Cerrada, M. Macromol Chem Phys 2005, 206, 1221–1230.
- Quijada, R.; Guevara, J. L.; Galland, G. B.; Rabagliati, F.; Lopez-Majada, J. M. Polymer 2005, 46, 1567–1574.
- Alamo, R. A.; Ghosal, A.; Chatterjee, J.; Thompson, K. L. Polymer 2005, 46, 8774–8789.
- Alamo, R. G.; Mandelkern, L. Macromolecules 1991, 24, 6480–6493.

- Supaphol, P.; Spruiell, J. E. Polymer 2000, 41, 1205–6493.
- Hoffman, J. D.; Millar, R. L. Polymer 1997, 38, 3151–3212.
- Janeschitz-Kriegl, H.; Ratajski, E.; Wippel, H. Colloid Polym Sci 1999, 277, 217–226.
- Wunderlich, B. Macromolecules Physics; Vol. 2; Academia Press: New Cork, 1976.
- Carfagna, C.; De Rosa, C.; Guerra, G.; Petraconne, V. Polymer 1984, 25, 1411–1462.
- Auriemma, F.; Lewis, H.; Spiess, H. W.; De Rosa, C. Macromol Chem 1995, 196, 4011–4024.
- Palza, H.; Velilla, T.; Quijada, R. Polym Plast Technol Eng 2006, 45, 1233–1241.
- Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. Chem Rev 2000, 100, 1253–1345.
- Naga, N.; Mizunuma, K.; Sadatoshi, H.; Kakugo, M. Macromolecules 1997, 30, 2197–2200.
- Sevegney, M.; Kannan, R.; Siedle, A.; Naik, R.; Naik, V. Vibrat Spectrosc 2006, 40, 246–256.
- 40. Auriemma, F.; Born, R.; Spiess, H. W.; De Rosa, C.; Corradini, P. Macromolecules 1995, 28, 6902–6910.