

The Deformability of Polymers: The Role of Disordered Mesomorphic Crystals and Stress-Induced Phase Transformations**

Claudio De Rosa* and Finizia Auriemma

Isotactic polypropylene (iPP) is of enormous and still increasing commercial importance because of its favored combinations of properties, such as good rigidity, high thermal resistance, low density, and ease of processability, which can be achieved at relatively low costs.^[1] The wide range of applications of iPP results from its versatility and the variety of possible modifications of the basic material, which already starts in the polymerization reactor^[1] and can be further achieved during crystallization and processing. In particular, the full understanding of the crystallization and complex polymorphic behavior made it possible to tailor the properties through control of the crystallization of the different crystalline forms (α , β , and γ forms) and of the mesophase.

As examples for these concepts, many properties are changed and enhanced by modification of the neat polymer, such as the mechanical strength by incorporation of glass fibers, optical clarification by addition of nucleation agents,^[1] or enhancement of the ductility and flexibility by crystallization in the mesophase.^[2] While highly crystalline samples of iPP crystallized in the stable α form results in a rigid material, the same sample crystallized in the mesophase by rapid quenching of the melt at low temperature results in a ductile and flexible material with greatly enhanced deformability. This effect has been related to the different morphology of the mesomorphic crystals. Mesophases are highly disordered crystals, characterized by a degree of order intermediate between the disorder of the amorphous phase and the order of crystalline phases, and are generally easily obtained by quenching the melt at low temperatures. In the cases of iPP the crystallization of solid mesophases by quenching the melt produces defective crystals of size and morphology which are very different from the spherulites obtained at low cooling rates or high crystallization temperatures. In general, with the transformation from ordered crystals to mesomorphic entities, a change of the crystallite morphology from almost perfect spherulites to bundlelike or nodular crystals is observed.^[3–5] All these variations in number, size, and perfection of the crystallites and morphological details significantly influence the mechanical behavior of the materials, that is, the rigidity, impact strength, and ductility.^[2]

The crystallization of iPP in the mesophase may offer additional options for tailoring the properties.^[2] In fact, optically transparent but highly crystalline films of iPP can be prepared by nonspherulitic crystallization, without employing optical clarifiers,^[5b] through crystallization of the nonspherulitic mesophase by rapid cooling of the melt, and then in a second step through tailoring the crystallinity and mechanical characteristics by annealing at elevated temperature, to induce the transformation from the mesophase to crystals of the α form, and maintaining the absence of higher-order organization in a spherulitic superstructure.^[4]

Here, we compare the role of the crystal morphology, in particular, the presence of lamellar crystals organized in spherulitic superstructures or of nodular non-spherulitic mesophase, and of the occurrence of stress-induced polymorphic transformations, on the deformability of crystalline polymers. Contrary to observations made in Ziegler–Natta iPP samples, we show that stereodeficient iPP samples prepared with single-center metallocene catalysts, crystallized in a lamellar γ form, show an unexpected high ductility and deformability, which is much higher than that observed in samples crystallized in the nodular nonspherulitic mesophase. We show that when phase transformations occur during deformation large values of ductility and flexibility are achieved. This effect turns out to be more important than the presence of initial nodular nonlamellar crystals of the mesophase for inducing deformability. The key is the use of single-center metallocene catalysts that make it possible to tailor the stereoregularity and to control the crystallization of the α and γ forms.^[6]

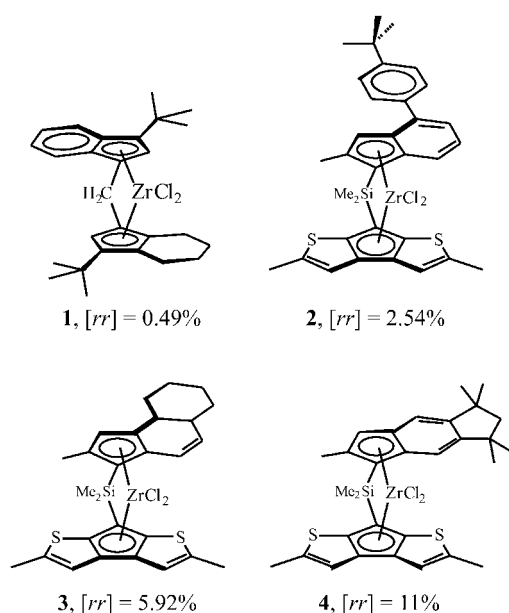
iPP samples of different stereoregularity have been prepared with the metallocene catalysts shown in Scheme 1. These catalytic systems are able to produce iPP samples characterized by chains containing largely one type of stereoirregularity (*rr* triad defects),^[6–8] the amount of which depends on the structure of the catalyst. Samples with concentration of *rr* defects ranging from 0.5 and 11% and melting temperatures in the range of 160–80 °C have been analyzed and compared with a highly stereoregular iPP sample prepared with a conventional Ziegler–Natta catalyst.

The X-ray power diffraction profiles and the stress–strain curves of a highly stereoregular and crystalline sample of iPP prepared with a Ziegler–Natta catalyst (see the Supporting Information), slowly crystallized from the melt as well as by rapid quenching from the melt at 0 °C, are reported in Figure 1. Similar data have been reported and extensively discussed by Androsch and co-workers.^[2,9] The sample slowly solidified from the melt and crystallized in the stable α form, as shown by the presence of the typical 110, 040, and 130 reflections of the α form at $2\theta = 14$, 16.8, and 18.6° of the

[*] Prof. C. De Rosa, Prof. F. Auriemma
Dipartimento di Chimica “Paolo Corradini”
Università di Napoli “Federico II”, Complesso Monte Sant’ Angelo
via Cintia, 80126 Napoli (Italy)
E-mail: claudio.derosa@unina.it

[**] Financial support from Basell Polyolefins (Italy) is gratefully acknowledged.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201105289>.



Scheme 1. Structure of the zirconocene catalysts. The concentrations of the *rr* triad stereodefects produced by each catalyst are indicated.^[7,8]

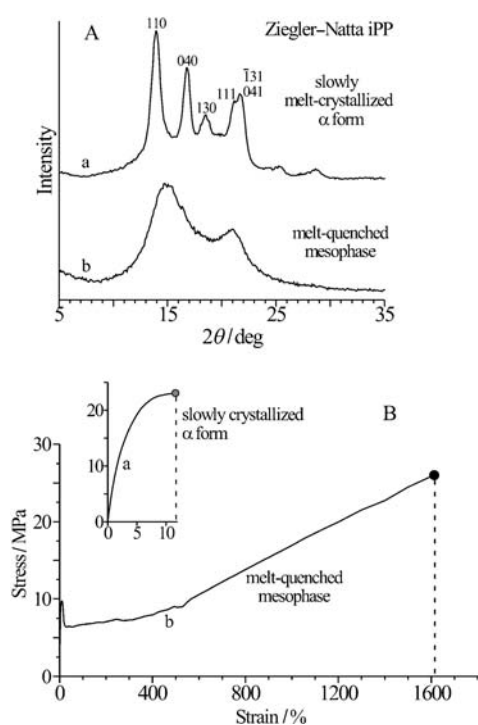


Figure 1. X-ray powder diffraction profiles (A) and stress–strain curves of samples of highly stereoregular iPP prepared with a Ziegler–Natta catalyst slowly crystallized from the melt in the α form (a) and in the mesophase by quenching the melt at 0 °C (b).

α form in the diffraction profile (a) of Figure 1 A, whereas the sample rapidly quenched at 0 °C crystallized in the mesomorphic form, as indicated by the presence of the two broad reflections at $2\theta = 15^\circ$ and 21.3° in the diffraction profile (b) of Figure 1 A.

As expected and already shown by Androsch and co-workers,^[2] the sample, crystallized in the α form with typical cross-hatched lamellae and spherulites superstructure^[2,9] and a crystallinity of about 50 %, shows mechanical tensile deformation of a brittle material, with a strain at break being of the order of only 10 % and a high modulus of 720 MPa (curve (a) of Figure 1 B).^[2] A post-yield deformation region is not detected for this particular specimen, that is, plastic crystal deformation and fibrillation is not observed.^[2] In contrast, the sample crystallized by quenching in the mesophase shows a rather ductile deformation behavior, with deformation at break higher than 1000 % and a low modulus of 36 MPa.^[2] The mass fraction of the ordered phase (or of the disordered crystals) in the mesomorphic sample is about 48 %. Despite a similar amount of the ordered phase, the tensile stress–strain behavior is distinctly different.^[2]

The deformation of crystalline polymers leads to deformation of amorphous chain segments, separation and rotation of lamellae, interlamellar shear, disintegration of spherulites, and fragmentation/dissolution of lamellae by fine and coarse slip.^[10] At larger strain, when the stress acting on the crystallites reaches a value at which the crystals are no longer stable, stress-induced mechanical melting occurs, followed by recrystallization in newly oriented crystallites, the assembly of which forms aligned fibrils.^[10d,e] These critical values of strain and stress depend on the plastic resistance and stability of the crystals and the entanglement density of the amorphous phase.^[10c] The intrinsic stability of the crystals, given by the thermodynamic stability of the crystalline form, and their organization in morphological entities define the mechanical strength and the resistance of the material to plastic deformation.

In the specific case of iPP in the α form, even at temperatures above the glass-transition temperature, a rather brittle failure is observed, as shown in Figure 1 B.^[11] The absence of plastic crystal deformation and fibrillation has been attributed to the restricted mobility of amorphous chain segments which are interlocked in regions between cross-hatched lamellar α crystals, which is a typical morphological feature of conventionally crystallized iPP.^[11,12]

The higher deformability/ductility, observed in the tensile stress–strain behavior of the mesomorphic iPP (curve (b) of Figure 1 B),^[2,13] confirms that the deformation behavior of iPP is controlled by the crystal morphology, the presence or absence of spherulitic superstructure, and by the linkage between the phases.^[2] Tensile loading of semicrystalline polymers first leads to the deformation of the amorphous phase, then this stress is transferred to the crystals by tie molecules which then contribute to the deformation by rotation and slip. The brittle and ductile response of specimens with lamellar and nodular crystals, respectively, is due to different transfers of stress between the amorphous and crystalline phases.^[2] In slowly crystallized samples containing α lamellae, the number of tie molecules is lower than in samples with nodular mesomorphic crystals, and the limited stress transfer between phases produces brittle failure prior to plastic deformation of the crystals.^[2] In contrast, in specimens, crystallized in the mesophase, nodules are embedded in the amorphous phase and are connected by a larger number of tie

molecules, which initially were formed at extremely high supercooling. Tie molecules transmit stress to nodules, causing their orientation and alignment into the draw direction.^[2] Crystal slip or disintegration of nodular crystals and fibrillation may also occur, as supported by the observation of a distinct yield point in the stress–strain curves of the mesophase.^[2]

The X-ray powder diffraction profiles of samples of stereodeficient iPP samples, prepared with the catalysts shown in Scheme 1, crystallized from the melt by slow cooling (A) and by quenching at 0 °C (B), as shown in Figure 2. The

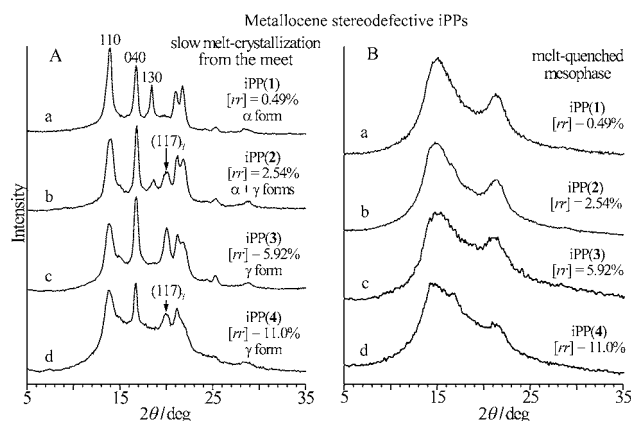


Figure 2. X-ray powder diffraction profiles of metallocene–iPP samples containing the indicated concentration of *rr* triad stereodeficiencies and prepared with the catalysts of Scheme 1, crystallized from the melt by slow cooling to room temperature at 1 °C min^{−1} (A) and by quenching at 0 °C (B). The 110, 040, and 130 reflections of the α form at $2\theta = 14$, 16.8 and 18.6°, respectively, and the (117) $_{\gamma}$ reflections of the γ form at $2\theta = 20.1^\circ$ are indicated in (A). The numbers in parentheses in the symbol iPP(n) indicate the used catalyst of Scheme 1.

most isotactic sample with *rr* contents lower than 1% crystallizes in the α form, as indicated by the presence of 110, 040, and 130 reflections of the α form at $2\theta = 14$, 16.8, and 18.6°, respectively, in the diffraction profile a Figure 2A, whereas stereoirregular samples with *rr* concentrations higher than 6–7% crystallize in the γ form, as shown by the presence of the (117) $_{\gamma}$ reflection at $2\theta = 20.1^\circ$ of the γ form in the diffraction profiles (c,d) of Figure 2A.^[6] All samples crystallize by quenching of the melt at 0 °C in the mesophase, as indicated by the presence of two broad reflections at $2\theta = 15^\circ$ and 21.3° in Figure 2B.

The stress–strain curves of the samples of iPP of Figure 2 slowly crystallized from the melt in the α and γ forms or by quenching in the mesophase are shown in Figure 3. In samples slowly crystallized in α and γ forms (curves a) the mechanical properties depends on the concentration of *rr* defects and a remarkable increase of ductility is observed with increasing content of *rr* defects (see the Supporting Information).^[6] In these samples the presence of *rr* triad defects of stereoregularity and the facile inclusion of defects in the crystals of iPP produces outstanding mechanical properties of high ductility and drawability, even when the samples are slowly crystallized in the stable α or γ forms with lamellar morphol-

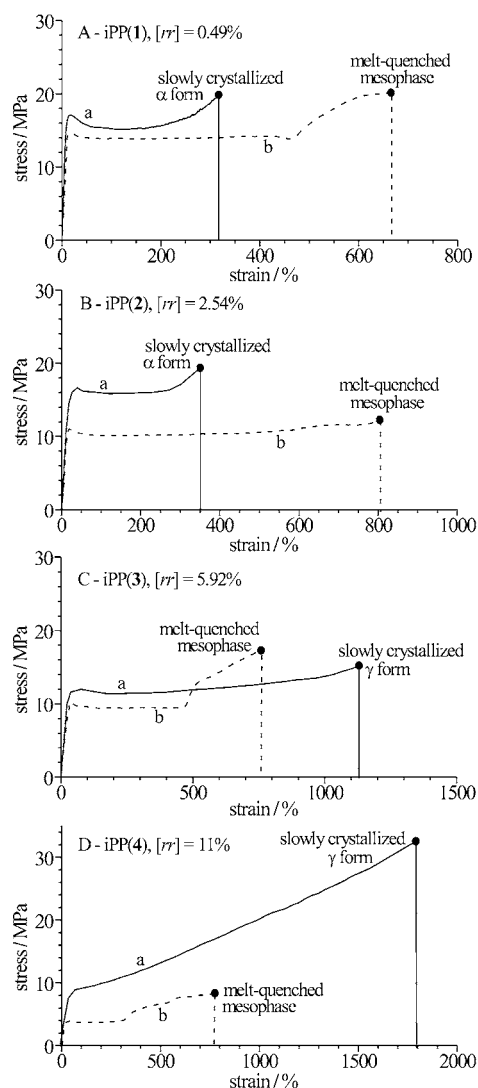


Figure 3. Comparison between the stress–strain curves of samples of metallocene–stereodeficient iPP with the indicated concentration of *rr* stereodeficiencies slowly crystallized from the melt in the α and γ forms and in the mesophase by quenching at 0 °C. The numbers in parenthesis indicate the used catalyst of Scheme 1.

ogy. By tailoring the concentration of *rr* defects, through the choice of the metallocene catalyst, samples of iPP showing a range of different mechanical properties, from stiff materials to flexible and elastomeric materials, can be prepared (Figure 3A).^[6] In particular, even highly isotactic samples, containing a low concentration of *rr* defects ($[rr] = 0.49\%$) that crystallize in the lamellar α form (profile (a) of Figure 2A) still show good ductility, with values of strain at break of 200–300%,^[6] much higher than those (less than 10%) shown in Figure 1B for Ziegler–Natta iPPs, slowly crystallized from the melt in the lamellar α form. Samples with *rr* concentrations higher than 4–5 mol% show an outstanding high flexibility and ductility with deformation at break higher than 1000%, even though the samples crystallize slowly in the γ form.^[6]

The data of Figures 1B and 3 show that the α form is harder than the γ form. This is related to the intrinsic stability of crystals of the α form, the lower concentration of included

stereodefects in the α form, and the different morphology, with cross-hatched lamellar crystals and restricted mobility of amorphous chain segments for the α form, and the needlelike, distorted, thin, elongated, and easily deformable crystals for the γ form.^[14]

The mechanical properties of the same samples crystallized by quenching in the mesomorphic form (curves (b) of Figure 3) indicate that all samples show a similar good ductility with similar values of deformation at break, regardless of the concentration of *rr* defects. Moreover, all samples in the mesomorphic form show a mechanical strength that is lower than that of the corresponding samples crystallized in the α or γ forms (Figure 3). This is in agreement with the result of Figure 1B of good drawability of the mesophase even for high degrees of ordered (crystalline) phases in the case of Ziegler–Natta iPP. It is apparent the more stereoregular samples with concentration of *rr* defects lower than 5 mol% show a better ductility when crystallized in the mesomorphic form than in the α and γ forms (Figure 3A,B), in agreement with the results of Figure 1 for the mesophase obtained with Ziegler–Natta iPP.^[2] For the more stereoirregular samples, iPP(3) and iPP(4), with concentrations of *rr* defects of 5.9 and 11 %, respectively, the samples slowly crystallized in the γ form (profiles (c,d) of Figure 2A) show deformations at break higher than those of the corresponding quenched samples crystallized in the mesomorphic form (Figure 3C,D). Therefore, stereoirregular iPP samples show an unexpected better ductility when they slowly crystallize from the melt in the γ form in lamellar morphology than when they crystallize in the nodular solid mesophase.

The behavior of the less stereoregular iPP(3) and iPP(4) samples may be explained by considering that when these samples crystallize in the γ form, polymorphic transformations occur during deformation, whereas when they crystallize in the mesophase no structural transformations occur during the stretching. The X-ray diffraction patterns of fibers of the sample iPP(3) with 5.92 % of *rr* defects, obtained by stretching at different values of deformation ε and crystallized initially in the γ form (slow crystallization from the melt) or in the mesophase (quenched sample), are shown in Figure 4. Crystals of the γ form originally present in the films slowly crystallized from the melt, and transform into the mesomorphic form during deformation, as indicated by the transformation of the three reflections of the γ form at $2\theta = 14, 17$, and 20.1° to two broad haloes at $2\theta = 15^\circ$ and 21° on the equator and first layer line, respectively, in the diffraction patterns of Figure 4A–C. Data similar to those of Figure 4A–C for samples of iPP at different concentrations of stereodefects (see Figure 2) made possible the construction of a structural–mechanical phase diagram of iPP, where the regions of stability of the different polymorphic forms of iPP are defined as a function of the stereoregularity and the degree of deformation.^[6b] In the case of the sample iPP(4) with 11 % of *rr* defects, crystals of the γ form first transform by stretching into the α form and then, at high deformation, into the mesomorphic form.^[6b]

Phase transformations occurring during deformation are gradual, and each transformation facilitates the subsequent deformation of the sample, and only at high strain the

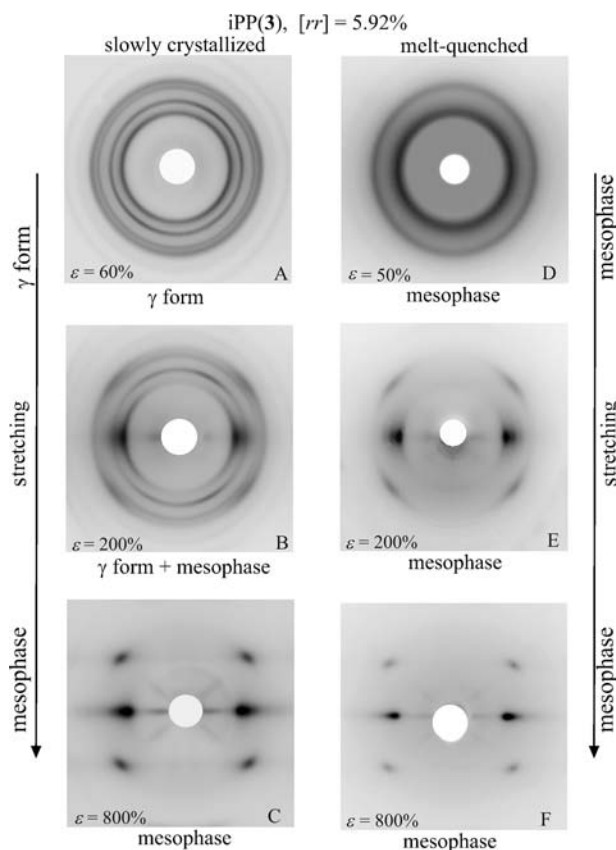


Figure 4. X-ray fiber diffraction patterns of fibers of the sample iPP(3) with a concentration of *rr* defects of 5.9 mol% initially crystallized from the melt in the γ form by slow cooling (A–C) and by quenching at 0°C in the mesophase (D–F), stretched at the indicated values of deformation ε .

crystalline forms are completely transformed to the mesomorphic form.^[6b] The occurrence of these transformations produces an effective mechanism which gradually dissipates some amount of mechanical energy and produces a neat increase of the values of the strain at break. Large values of ductility and flexibility are achieved because during the stretching the mechanical energy is converted into a latent heat of fusion that induces local melting of the crystals, followed by recrystallization at high deformation in the mesophase. This transition, indeed, occurs through mechanical destruction of the crystals by pulling chains out from the original crystals, and successive reorganization of the chains to oriented crystalline aggregates of the mesomorphic form.^[15] The formation of the mesomorphic form at low deformations facilitates the further successive deformation up to a very high deformation, resulting in a high ductility and flexibility (Figure 3C,D).

Moreover, in these samples the presence of high degrees of structural disorder and the inclusion of *rr* defects in the crystals of the γ form and the similar concentration of defects in the crystalline and amorphous phases,^[6] reduce the plastic resistance of the crystals and the stress level necessary for inducing a plastic deformation of the crystals and phase transformations. These properties lead to unusual polypropylene of outstanding high flexibility and elasticity.^[6]

In the case of samples initially crystallized in the mesomorphic form under nonthermodynamic conditions by quenching the melt, the phase behavior is necessarily not reported in the general “thermodynamic” deformation phase diagram of Ref. [6b]. In this case stretching does not produce any structural transformation, and only a high degree of orientation of the mesomorphic domains with chain axes parallel to the stretching direction is achieved (Figure 4D–F). As a consequence, samples of the mesomorphic form show lower values of deformation at break than the corresponding films crystallized in the γ form.

The data of Figures 3 and 4 highlight the fundamental role played by the stress-induced transformations on the deformability and ductility of crystalline polymers. In the case of stereodeficient iPPs, this effect is coupled to the effect of the *rr* stereodeficiencies included in the crystals of the γ form.^[6] These effects turn out to be even more important than the morphology of the initial crystals, resulting in a larger ductility of the samples with lamellar morphology than with a nodular mesophase. However, in the case of the γ -form crystals another effect that contributes to the facile deformability is related to the lateral dimension of the crystals of the γ form. Extensive investigations on the morphology of the crystals of the γ form obtained from crystallization of metallocene–iPP samples have shown that crystals of the γ form may show a needlelike morphology, that is, they are thin in two dimensions and elongated in the third dimension.^[14] The needlelike crystals are organized in bundles, and bundlelike structures form in iPP samples crystallized mainly in the γ form.^[14a] The needlelike morphology of the γ form with distorted, thin, and elongated crystals contributes to the low yield strength and Young's modulus (Figure 3C,D) and the facile deformability of the γ form.

In conclusion, the observed improved ductility of the slowly crystallized γ form in stereodeficient iPP samples compared to the mesophase shows that the deformability of semicrystalline polymers is not only related to the initial crystal morphology and classic morphological parameters (crystal dimensions, lamellar thickness) but mainly to the occurrence of phase transformations during deformation. The defective and distorted lamellar crystals or needlelike crystals of the γ form including *rr* stereodeficiencies are less resistant to the plastic deformation and, therefore, can be more easily deformed and transformed into the mesomorphic form (Figure 4C,D). Once the stiff crystals have been broken, the formation of the disordered mesomorphic form facilitates further stretching up to very high values of deformation resulting in a high ductility and flexibility (Figure 3C,D). The facile transformation during stretching of the γ form into the mesomorphic form at low degrees of deformation provides a mechanism of conversion of the mechanical energy to latent heat of fusion that induces local melting of the crystals,

followed by recrystallization at high deformation into the mesophase. These results clearly show that the single-center metallocene catalysts may offer additional options to tailor the properties of iPP through the control of the concentration of stereodeficiencies and the crystallization of the γ form and of the mesophase.

Received: July 27, 2011

Revised: November 28, 2011

Published online: December 21, 2011

Keywords: homogeneous catalysis · mechanical properties · mesophases · metallocenes · polymers

- [1] *Polypropylene Handbook* (Ed.: N. Pasquini), Hanser Publishers, Munich, **2005**.
- [2] Q. Zia, H.-J. Radusch, R. Androsch, *Polym. Bull.* **2009**, *63*, 755.
- [3] Z. G. Wang, B. S. Hsiao, S. Srinivas, G. M. Brown, A. H. Tsou, S. Z. D. Cheng, R. S. Stein, *Polymer* **2001**, *42*, 7561.
- [4] Q. Zia, R. Androsch, H.-J. Radusch, S. Piccarolo, *Polymer* **2006**, *47*, 8163; Q. Zia, H.-J. Radusch, R. Androsch, *Polymer* **2007**, *48*, 3504.
- [5] a) Q. Zia, R. Androsch, H.-J. Radusch, E. Ingolic, *Polym. Bull.* **2008**, *60*, 791; b) D. Mileva, R. Androsch, H.-J. Radusch, *Polym. Bull.* **2009**, *62*, 561.
- [6] a) C. De Rosa, F. Auriemma, A. Di Capua, L. Resconi, S. Guidotti, I. Camurati, I. E. Nifant'ev, I. P. Laishevstev, *J. Am. Chem. Soc.* **2004**, *126*, 17040; b) C. De Rosa, F. Auriemma, *J. Am. Chem. Soc.* **2006**, *128*, 11024.
- [7] L. Resconi, S. Guidotti, I. Camurati, R. Frabetti, F. Focante, I. E. Nifant'ev, I. P. Laishevstev, *Macromol. Chem. Phys.* **2005**, *206*, 1405.
- [8] L. Resconi, F. Piemontesi, I. Camurati, O. Sudmeijer, I. E. Nifant'ev, P. V. Ivchenko, L. G. Kuz'mina, *J. Am. Chem. Soc.* **1998**, *120*, 2308; L. Resconi, D. Balboni, G. Baruzzi, C. Fiori, S. Guidotti, P. Mercandelli, A. Sironi, *Organometallics* **2000**, *19*, 420.
- [9] Q. Zia, D. Mileva, R. Androsch, *Macromolecules* **2008**, *41*, 8095.
- [10] a) A. Peterlin, *J. Mater. Sci.* **1971**, *6*, 490; b) L. Lin, A. S. Argon, *J. Mater. Sci.* **1994**, *29*, 294; c) P. B. Bowden, R. J. Young, *J. Mater. Sci.* **1974**, *9*, 2034; d) A. Galeski, *Prog. Polym. Sci.* **2003**, *28*, 1643; e) Y. Men, J. Rieger, G. Strobl, *Phys. Rev. Lett.* **2003**, *91*, 95502.
- [11] a) M. Aboulfaraj, C. G'Sell, B. Ulrich, A. Dahoun, *Polymer* **1995**, *36*, 731; b) Y. Pang, X. Dong, K. Liu, C. C. Han, E. Chen, D. Wang, *Polymer* **2008**, *49*, 4259.
- [12] B. Lotz, J. C. Wittmann, *J. Polym. Sci. Polym. Phys. Ed.* **1986**, *24*, 1541.
- [13] D. M. Gezovich, P. H. Geil, *Polym. Eng. Sci.* **1968**, *8*, 210; R. Seguela, E. Staniek, B. Escaig, B. Fillon, *J. Appl. Polym. Sci.* **1999**, *71*, 1873.
- [14] a) R. Thomann, C. Wang, J. Kressler, R. Mülhaupt, *Macromolecules* **1996**, *29*, 8425; b) W. Stocker, S. N. Magonov, H. J. Cantow, J.-C. Wittmann, B. Lotz, *Macromolecules* **1993**, *26*, 5915.
- [15] S. Ran, X. Zong, D. Fang, B. S. Hsiao, B. Chu, R. A. Phillips, *Macromolecules* **2001**, *34*, 2569.