Polym. Bull. (2010) 65:623–634
DOI 10.1007/s00289-010-0274-1

ORIGINAL PAPER

Tensile properties of random copolymers of propylene with ethylene and 1-butene: effect of crystallinity and crystal habit

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Received: 11 January 2010 / Revised: 19 February 2010 / Accepted: 6 April 2010 /

Abstract The tensile modulus of elasticity and yield strength of semicrystalline random copolymers of propylene with different amount on ethylene or 1-butene co-units were analyzed as a function of the crystallinity and the crystal habit/shape. Samples were prepared by cooling the melt to ambient temperature, and subsequent annealing at elevated temperature. Variation of the cooling rate between 10^{-1} and 10^3 K s^{-1} and of the temperature of annealing allowed preparation of semicrystalline specimens with either lamellar or non-lamellar crystals of different size, and with different crystallinity between about 30 and 70%. Young's modulus and yield strength increase with increasing crystallinity and consistently are lower for samples containing nodular, that is, almost isometric, non-lamellar crystals of low aspect ratio. For samples of identical crystallinity and crystal habit, an only minor effect of presence of co-units in the crystalline and amorphous phases is observed.

Keywords Isotactic polypropylene · Random copolymers · Young's modulus · Yield strength · Crystallinity · Crystal habit

Introduction

Isotactic polypropylene (iPP) is a semicrystalline polymer in which the structure, morphology, and higher-order organization of crystals can be adjusted within wide limits by variation of the conditions of melt-crystallization [1, 2]. Crystallization at low supercooling results in formation of monoclinic lamellae which are organized within spherulites [3–5]. In contrast, solidification at high supercooling at about ambient temperature leads to formation of mesomorphic nodular domains which are

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not organized in a higher-order superstructure [6–8]. Generation of the mesophase at ambient temperature requires rapid cooling of the quiescent melt at a rate faster than about 100 K s^{-1} since only then formation of monoclinic crystals at low supercooling can effectively be suppressed [1, 2, 9, 10]. Subsequent annealing of the mesophase at elevated temperature triggers crystallization, and the mesophase transforms into monoclinic structure [11–14]. The nodular habit and the non-spherulitic organization of the crystalline phase, however, are not affected by annealing [15]. In summary, by variation of the pathway of melt-crystallization, in case of iPP, semicrystalline specimens can be generated, which contain either monoclinic lamellae, organized within spherulites, or close to isometric, monoclinic crystals in a non-spherulitic environment. In both cases, the size and amount of crystals can be adjusted by variation of the temperature and time of annealing [15–18].

The link between structure and selected optical and mechanical properties—with special emphasis on the comparison of samples containing either lamellae and spherulites, or non-organized nodular crystals—has been established recently [19, 20]. Regarding the mechanical properties it was found that the stiffness and the yield strength in both types of qualitatively different structures are mainly controlled by the crystallinity. This result is expected since at the temperature of analysis, i.e., at ambient temperature, the amorphous phase of iPP is in its rubbery state and exhibits a modulus of elasticity which is several magnitudes of order lower than the modulus of the crystalline phase. Accordingly, Young's modulus and yield strength increase within increasing crystallinity. In addition, it was observed that these properties were dependent on the shape of crystals. In samples of identical crystallinity, modulus and yield strength were in case of presence of nodular crystals lower than in case of presence of lamellae and spherulites.

In extension to a prior study of tensile properties of differently crystallized iPP [20], we analyzed in the present work the tensile behavior of random copolymers of propylene with ethylene or 1-butene. Preparation of random copolymers of propylene with low amount of 1-alkenes is an effective route to alter the crystallization behavior, and therefore the supermolecular structure and application-relevant properties [21–27]. The potential for generation of qualitatively different crystal morphologies in such copolymers has been confirmed recently [28, 29]. Similar as in the homopolymer, fast cooling and subsequent annealing at elevated temperature yields particle-like crystals while slow cooling results in formation of lamellae organized within spherulites, though the exact conditions of preparation differ due to changed crystallization kinetics [29–31]. A comparison of the tensile properties of such samples has not yet been performed, and is therefore the primary aim of the present investigation.

Experimental

Materials and sample preparation

Random copolymers of propylene with ethylene were provided by Borealis (Austria). The concentration of ethylene in the various samples is 3.4, 6.8 and

8.0 mol% (iPP-Eth.3, iPP-Eth.7, and iPP-Eth.8), and the mass-average molar mass and the polydispersity are 400 kg mol^{-1} and 3.8, respectively. Propylene-1-butene random copolymers with 6 and 10.9 mol% 1-butene (iPP-But.6 and iPP-But.11), a molar mass of 225 kg mol^{-1}, and a polydispersity of 3.1 were purchased from Sigma-Aldrich. As reference material we employed an iPP homopolymer from Montell Polyolefins, with a mass-average molar mass and polydispersity of 373 kg mol^{-1} and 6.2, respectively. This particular polymer has intensely been investigated in prior studies regarding its structure [2, 14, 32], crystallization and melting behavior [33, 34], and optical and mechanical properties [19, 20]. In a first preparation step, films with a thickness of 100 µm and an area of 24 × 24 mm^2 were prepared by compression molding. Subsequently, these films were reheated in order to obtain a quiescent liquid state, and cooled at different rate between 0.1 and 1,000 K s^{-1}, using a special device which was developed by Piccarolo, described in detail elsewhere [35]. The residence time of the polymers in the liquid state was 5 min, and the temperature of the melt was 30 K higher than the temperature of melting, measured by differential scanning calorimetry on heating at 10 K min^{-1}. The variation of the cooling rate on melt-solidification controls the crystal shape, with the low thickness of the films of 100 µm required to minimize gradients of the cooling rate, and therefore the structure. Absence of structural gradients was proven in an independent experimental study [32], however, was also predicted by model calculation of the temperature profile across the sample thickness [35]. Annealing of the films at elevated temperature, for tuning the crystallinity and crystal size, was done in vacuum at a pressure of less than 100 mbar for 60 min, using a Heraeus oven. Samples are isotropic as has been concluded from wide-angle X-ray scattering data.

Instrumentation

Atomic force microscopy

Atomic force microscopy (AFM) was employed for analysis of the shape and size of crystals in the various samples, using a Quesant USPM instrument in combination with a 5 × 5 μm^2 scanner. Phase images were collected in intermittent contact mode at ambient temperature. We used SSS-NCL tips from NanoWorld with a radius of curvature of 2 nm and a half-cone angle of less than 10° at the front end of the tip. The force constant and resonant frequency were 48 N m^{-1} and 190 kHz, respectively. Alternatively, we employed NSC 14 silicon tips from Mikromasch with a tip radius of less than 10 nm, and a force constant and resonant frequency of 5.0 N m^{-1} and 160 kHz, respectively. The crystal size was determined manually from the AFM images using the line-intersection method.

Density measurement

The density of samples was measured at ambient temperature with a density gradient column from Ray-Ran using a mixture of water and ethanol. The minimum and maximum density of the column, controlling the resolution, were 0.886 and

0.925 g cm^{-3}, respectively. Data presented are averages of at least three measurements. The density of each sample was converted into a volume fraction of ordered phase using reference values of fully amorphous, mesomorphic, and crystalline iPP of 0.8665, 0.9200, and 0.9405 g cm^{-3}, respectively [36].

Tensile testing

Tensile stress–strain curves were recorded on a miniature tensile testing machine MiniMat-200 from Rheometric Scientific. Two semi-circular notches were cut at half gauge length, imitating a shouldered test bar, and to initiate the deformation at identical position in all samples. The cross section at the notched area of the films was 0.1 × 3.5 mm^2, and the crosshead distance was 8 mm. The strain rate during the initial test period of 10 s, for determination of the modulus of elasticity, was 1 mm min^{-1}. Then, further deformation was performed at a strain rate of 10 mm min^{-1}. Modulus data were calculated manually, carefully sorting out erroneous data within the start period of the test. Data reported are averages of at least three tests.

Results and discussion

The structure of the iPP homopolymer and of random copolymers of propylene with ethylene or 1-butene at the nanometer scale, as a function of the condition of crystallization, has extensively been published before [15, 28, 32] and is therefore not fully repeated for all samples of the present study. For illustration of important differences of structure, introduced by variation of the conditions of crystallization, in Figs. 1, 2 are therefore shown AFM images of selected samples only, needed for later discussion of tensile properties. The selection of images is based on the condition that the crystallinity of all samples is close to identical, allowing to trace the mere effect of the crystal habit on the mechanical properties. Figure 1 shows the structure of the iPP homopolymer (left) and random copolymers of propylene with 3.4 (center) and 8.0 mol% ethylene (right). Figure 2, correspondingly, shows the structure of the iPP homopolymer (left) and random copolymers of propylene with 6.0 (center) and 10.9 mol% 1-butene (right). Structures shown in the top row were obtained by conventional crystallization, i.e., by slow cooling of the quiescent melt and subsequent annealing at elevated temperature. Independent on the exact chemical composition of the various samples, this crystallization route leads to formation of lamellae. The images in the bottom row were obtained on samples which were quenched to ambient temperature and subsequently annealed. This particular crystallization scheme via intermediate formation of a metastable mesophase results in generation of nodular crystals. Details of the history of crystallization of the structures shown in Figs. 1, 2 are listed in Table 1, together with information about the crystallinity, and thickness of lamellae/size of nodules.

Note again that the almost identical crystallinity of samples of different comonomer content and different history of crystallization between 40 and 50% in case of iPP-Eth copolymers shown in Fig. 1, and between about 50 and 60% in case

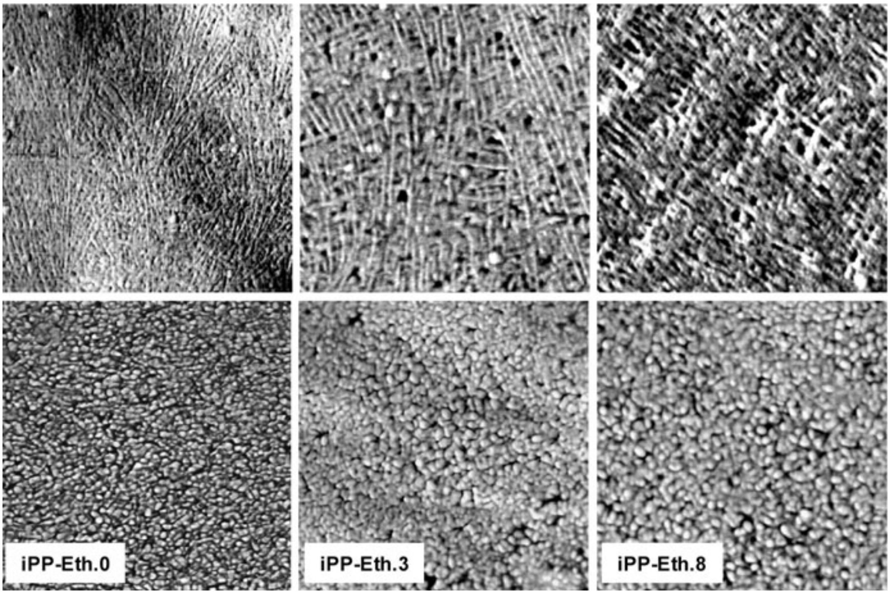

Fig. 1 AFM structure of the iPP homopolymer (*left*), and random copolymers of propylene with 3.4 (*center*), and 8.0 mol% ethylene (*right*). Structures shown in the *top* and *bottom rows* were obtained by conventional crystallization, or crystallization via intermediate formation of a mesophase, respectively. The images represent an area of 1 × 1 μm^2

of iPP-But copolymers shown in Fig. 2 was not achieved accidentally, rather was adjusted on purpose for direct comparison of the effect of crystal perfection and crystal shape on tensile properties. Quantitative analysis of the dimension of crystals shows a systematic increase of both the thickness of lamellae and the size of nodules with increasing concentration of co-units. The increase of the crystal size with increasing concentration of co-units, for samples of identical crystallinity, likely is due the final annealing step, which was performed at different supercooling. It is predicted by the theory of crystallization and melting of random copolymers [37, 38], and experimentally confirmed for random copolymers of propylene with ethylene [39] that with increasing content on co-units the equilibrium melting temperature decreases. As such, constant or even increasing temperature of annealing with increasing concentration on co-units (column 3 of Table 1) is equivalent to a decrease of the supercooling, being a key parameter for control of the size of crystals according to the classical theory of crystallization [40].

Figures 3, 4 are plots of the modulus of elasticity and the yield strength of iPP-Eth (left) and iPP-But (right) random copolymers of different content on co-units as a function of the volume fraction of ordered phase, respectively. Likely, due to the low thickness of films of only 100 μm, data scatter, however, allow at least qualitative discussion. The standard deviation of the modulus of elasticity of annealed samples—obtained by measurement of different specimens of identical history of crystallization—is about ±30 MPa for specimens containing both lamellar or nodular crystals. For quenched, non-annealed samples, containing

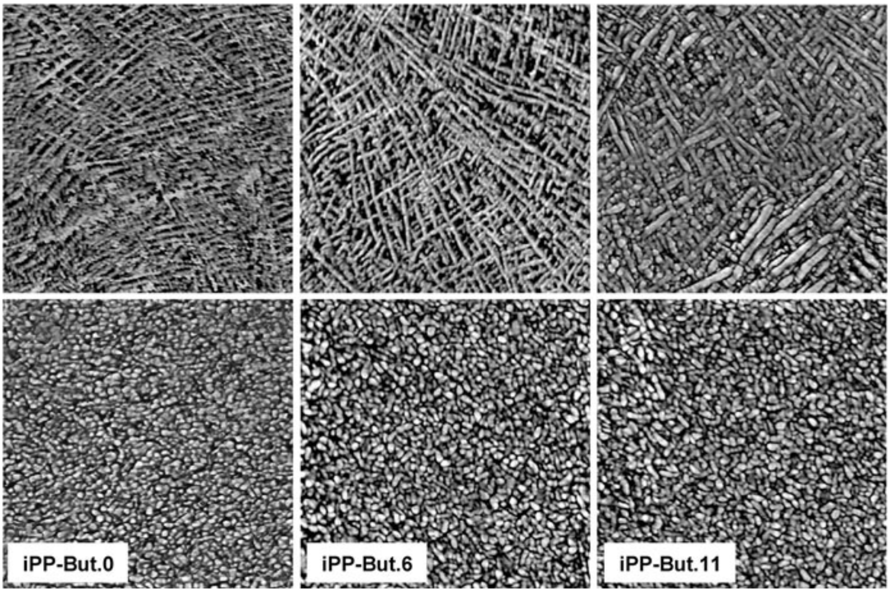

Fig. 2 AFM structure of the iPP homopolymer (*left*), and random copolymers of propylene with 6.0 (*center*), and 10.9 mol% 1-butene (*right*). Structures shown in the *top* and *bottom rows* were obtained by conventional crystallization, or crystallization via intermediate formation of a mesophase, respectively. The images represent an area of 1 × 1 μm^2

Table 1 History of crystallization, crystal habit, density-based crystallinity, and thickness of lamellae/ size of nodular crystals of the samples of iPP and random copolymers with ethylene and 1-butene shown in Figs. 1, 2

Sample	Cooling rate ($K\ s^{-1}$)	Annealing temperature (K)	Crystal habit	Crystallinity (%)	Crystal size (nm)
iPP	6	–	Lamella	46	10
iPP	750	393	Nodule	52	17
iPP-Eth.3	1	–	Lamella	44	10
iPP-Eth.3	420	383	Nodule	46	18
iPP-Eth.8	0.1	383	Lamella	40	18
iPP-Eth.8	500	383	Nodule	42	19
iPP	0.1	393	Lamella	57	12
iPP	750	393	Nodule	52	17
iPP-But.6	0.1	398	Lamella	50	17
iPP-But.6	900	398	Nodule	51	20
iPP-But.11	0.1	398	Lamella	49	23
iPP-But.11	900	398	Nodule	50	22

mesomorphic domains, it is ±55 MPa. The error bar in the left plot of Fig. 3 graphically illustrates the typical maximum error. The modulus of elasticity and the yield strength show a similar dependence on the crystallinity and the crystal habit, and are therefore not discussed separately. The yield strength (σ_y) and the modulus of elasticity (E) are linearly correlated to each other and fit the relation $\sigma_y \approx 0.025 \times E$, with the proportionality constant of 0.025 being reported in the literature as a universal average obtained by analysis of a larger number of polymers [41, 42].

Young's modulus and yield strength increase for all copolymers of different chemical composition with increasing crystallinity, which is expected for semicrystalline polymers at temperatures higher than the glass transition of the amorphous phase. This trend is independent on the exact crystal geometry, i.e., the increase of the modulus of elasticity and yield strength with increasing volume fraction of crystals is observed for systems containing both, lamellae or nodules. For easy identification, systems with lamellar crystals are represented by filled symbols while systems which contain nodular crystals are indicated with the open/cross-filled symbols. Note that we included in the plots of Figs. 3, 4 also data obtained on samples which contained mesomorphic phase, i.e., on samples which were quenched and not subsequently annealed. Beside the expected increase of the modulus and yield strength with increasing crystallinity, we are able to confirm a distinct influence of the crystal habit of the various samples, as recently proposed for the iPP homopolymer [20]. Samples which contain non-lamellar crystals with an aspect ratio of close to unity (open/cross-filled symbols) exhibit a modulus of

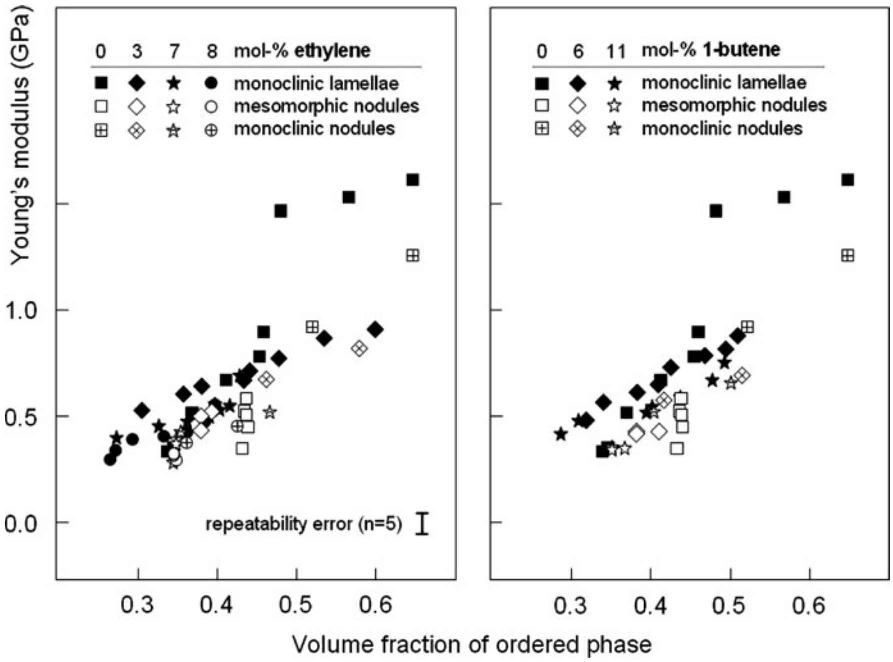

Fig. 3 Young's modulus of random copolymers of propylene with ethylene (*left*) and 1-butene (*right*) as a function of the volume fraction of ordered phase. *Filled symbols* represent samples which contain lamellae, and *open* or *cross-filled symbols* represent samples containing nodules

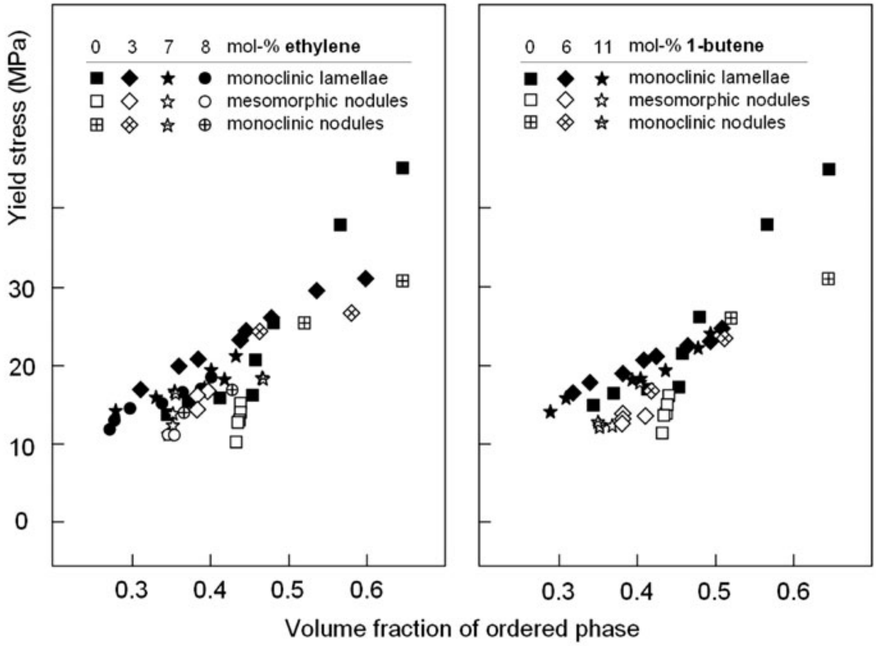

Fig. 4 Yield strength of random copolymers of propylene with ethylene (*left*) and 1-butene (*right*) as a function of the volume fraction of ordered phase. *Filled symbols* represent samples which contain lamellae, and *open* or *cross-filled symbols* represent samples which contain nodules

elasticity/yield strength which is about 10–20% lower than in case of samples which contain lamellae of high aspect ratio (filled symbols).

As far as we are aware, there exist only few experimental studies confirming an effect of the crystal shape on the modulus of elasticity of semicrystalline polymers [43–47]. Halpin and Kardos, in attempting to refine/expand the composite model for prediction of moduli of multiphase systems with different filler/reinforcement geometry, prepared and analyzed in situ grown composites of crystallized acetanilide in rubber [43]. In analogy to classical composites, it was found that increasing aspect ratio of the crystals led to an increase of the reinforcement effect to a value at least one order of magnitude higher than the lower-bound Reuss approximation [48], valid for systems with crystalline spherical particles in a liquid matrix. Shortly after, experimental evidence for an effect of the shape of polymer crystals in semicrystalline polymers has been collected on example of differently crystallized polyethylene [44, 45]. It was stated that in samples with a crystallinity of about 40–50% the stiffness is very sensitive to the reinforcement geometry. In general, there was also observed an increase of both the stiffness and strength with increasing ratio between width and thickness of lamellae. Recently, the modulus of elasticity of iPP has been compared with the modulus of high-density polyethylene (HDPE) [46]. Despite both the crystallinity and crystal stiffness are higher in case of HDPE, experimentally observed modulus data are higher in case of iPP.

Micromechanical calculations, employing a model of randomly distributed lamellar crystals of different geometry in an amorphous matrix, led to the conclusion that Young's modulus increases with increasing ratio between length and thickness of lamellae. Since the thickness of the lamellae in iPP is distinctly lower than in HDPE, the lower modulus of the latter polymer was attributed to the crystal geometry. A final example of research about the relationship between the semicrystalline structure and mechanical properties is the investigation of the dependence of Young's modulus on both the heat of fusion and temperature of crystallization in iPP homo- and copolymers. There was observed an increase of the modulus of elasticity with both increasing heat of fusion or crystallinity, respectively, and crystallization temperature. Though direct microscopic evidence was not provided, the variation of the crystallization temperature was related to a change of the thickness of lamellae, and it was suggested that it controls, among other parameters, the modulus of elasticity [47].

The direct comparison of tensile properties of semicrystalline samples of polypropylene of the present study, which contain either close to isometric or lamellar crystals at similar or even variable crystallinity, we believe, has not been done before, and is an important contribution for further understanding of the relationship between structure and mechanical behavior of semicrystalline polymers. We assume that the evaluation of the dependence of the mechanical response on the crystal morphology from point of view of crystal habit is valuable for further development of mechanistic models for prediction of mechanical properties.

Initially, it was also intended to prove an effect of the concentration of co-units on tensile properties. It was expected that the modulus of elasticity and the yield strength of random propylene copolymers is lower than in case of the homopolymer. The experiments of the present study, however, do not show a clear and unambiguous trend if data obtained on samples of identical crystallinity are plotted versus the comonomer concentration. The initial expectation was based on the experimental findings of an increase of the specific volume of the crystalline phase with increasing co-unit concentration, and a lowered glass transition temperature of the amorphous phase. For the samples of almost constant crystallinity shown in Figs. 1, 2, we observed an increase of the *hk*0 interplanar spacings with increasing co-unit content. The increase of the unit cell dimension in cross-chain direction likely is due to insertion of comonomers into the crystal lattice [21–24, 28]. Without further evidence, we speculated that the changed structure of the crystal lattice causes a decrease of the modulus of elasticity of the crystalline phase, and, correspondingly, of the total modulus of elasticity. Furthermore, there has been expected a lowering of the modulus of elasticity of the amorphous phase with increasing temperature difference between the glass transition temperature and the temperature of analysis. Obviously, the experimental data of Figs. 3, 4 do not confirm these expectations. Further, phase-sensitive information may be gained by application of more sophisticated tools like micro-hardness measurements [49], or AFM nano-indentation analyses [50]. These methods not only allow to assess the mechanical behavior in surface near regions, but are also sensitive to the fine structure of phases.

Summary

In the present work, the modulus of elasticity and the yield strength of random copolymers of propylene with ethylene or 1-butene have been determined with special emphasis put on the evaluation of the effects of crystallinity and habit of crystals. The modulus of elasticity and the yield strength increase as expected with increasing crystallinity. More important, there has been proven a distinct effect of the crystal habit/aspect ratio. Young's modulus and yield strength decrease with decreasing aspect ratio of crystals. Samples which contain nodular crystals exhibit a modulus of elasticity and yield strength, which are about 10–20% lower than in case of systems of identical crystallinity containing lamellar crystals. Variation of the defect concentration of the crystalline phase by insertion of co-units, and of the glass transition temperature of the amorphous phase, which decreases with increasing co-unit concentration, apparently, have an only minor effect on Young's modulus and yield strength.

Acknowledgment Financial support by the Deutsche Forschungsgemeinschaft (DFG) is greatly acknowledged.

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