Structure of Blown Films of Polyethylene/Polybutene-1 Blends

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The structure of blown films of blends of low-density polyethylene (PE-LD) and isotactic polybutene-1 (iPB-1) with different content of iPB-1 was investigated using wide- and small-angle X-ray scattering (WAXS and SAXS), transmission electron microscopy (TEM), and polarizing optical microscopy (POM). TEM proves formation of a matrix-particle phase structure due to immiscibility of the blend components. Within the iPB-1 particles, needle-like crystals with c-axis orientation were observed. The PE-LD matrix showed two populations of crystals. WAXS data indicate that the majority of crystals were oriented with the c-axis perpendicular to machine direction (MD), while SAXS data prove additional presence of stacks of lamellae, oriented parallel to MD. Quantitative birefringence measurements showed that the majority of molecule segments were oriented in the direction of the circumference of the film, confirming the WAXS data. The crystal orientation has direct impact on mechanical properties, which was demonstrated by measurement of the anisotropy of the modulus of elasticity. *POLYM. ENG. SCI.*, 50:249–256, 2010. © 2009 Society of Plastics Engineers

INTRODUCTION

Films of blends of low-density polyethylene (PE-LD) and isotactic polybutene-1 (iPB-1) are often used for peel film packages in the food stuff industry or in the medical

sector, and usually are produced by a blowing process [1, 2]. The structure of PE-LD/iPB-1 blown films is of importance for performance-relevant properties, including optical properties, like transparency, or the peel force, which is the force required to open a sealed peel film package. Typically, the concentration of PE-LD in blends for peel film applications is between 80% and close to 100%. Melt-mixing of PE-LD and iPB-1 in this range of concentrations leads to a heterogeneous structure that consists of a matrix of PE-LD and particles of iPB-1, caused by thermodynamic immiscibility of the two blend components [1, 2]. The thermodynamic immiscibility is a direct consequence of the chemical characteristics of the blend components [3, 4], which includes, in addition to the chemical composition parameters like molar mass, polydispersity, branching in the case of PE-LD, or concentration of stereo- and regio-defects in the case of iPB-1. The components PE-LD and iPB-1 crystallize separately, with the crystals eventually arranged in a higher-order superstructure.

The physical structure of the film is controlled by both the chemical characteristics of the blend components and the processing parameters. Processing of blown films includes, within an initial step, melt-mixing of the blend components in an extruder. It is assumed that the molecules in the PE-LD matrix and in the iPB-1 particles are oriented and, furthermore, that the iPB-1 particles are of non-isometric shape of well-controlled dimension/size due to the specific forces acting in the extruder. The melt exits the extruder and passes a die head, in which air is used to form a blown film bubble. The bubble is simultaneously drawn in transversal direction (TD), i.e., in the

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direction of the circumference, and in machine direction (MD), i.e., in the direction of the streamline. The draw ratio λ ($= l/l_0$, with l and l_0 being the length of a volume element after and before drawing, respectively) in each direction is variable, and is controlled by the amount of air blown into the bubble, and by the take-up speed or by the screw speed. Final fixing of the bubble occurs at the frost-line by cooling with refrigerated air [5–9]. In general, the sequence and ratio of drawing the film in transverse and longitudinal directions, in combination with the superimposed field of temperature, i.e., the conditions of cooling, are major factors controlling the final physical structure of the blown films. Parameters of the physical structure that are addressed in the present study include, in particular, the phase structure, and the structure, morphology, and orientation of crystals in the various phases.

The super-molecular structure, including the crystallinity, and the morphology and orientation of the crystals of blown films of polyethylene (PE) have been extensively studied [6–22]. Typically, blown films of PE are semi-crystalline with a maximum degree of crystallinity, which depends on the molecular architecture/branching-characteristics. The exact degree of crystallinity and the orientation of the crystalline phase are controlled by the processing conditions, in particular by the conditions of drawing the film in transversal and/or longitudinal directions. In an early work, Holmes et al. [11] observed a uniaxial orientation of crystals in blown films of PE-LD, with the *a*-axis of the orthorhombic unit cell oriented parallel to MD, if the ratio $\lambda_{MD}/\lambda_{TD}$ is low. This observation is in agreement with results obtained by Keller and Machin [12], who also observed a uniaxial orientation of the *a*-axis parallel to MD at low ratio of drawing in MD and TD. An increase of $\lambda_{MD}/\lambda_{TD}$, however, is connected with a change of the orientation of crystals such that the *c*-axis of the crystal lattice gets oriented parallel to MD. Reports about orientation of the *a*-axis or *c*-axis of the crystal lattice at an intermediate angle between MD and TD show that via the ratio $\lambda_{MD}/\lambda_{TD}$, the orientation can be tailored. This intermediate orientation was observed for high-density polyethylene (PE-HD) [5] in particular, and for linear low-density polyethylene (PE-LLD) [10, 12, 22].

Studies about structure formation of blown films of iPB-1 have not yet been reported in the literature. A few investigations focused on structure formation on film casting [23–25], which revealed an orientation of crystals such that the chain axis is parallel to MD. Crystallization in cast films of iPB-1 occurs on rapid cooling by formation of needle-like crystals, in which the macromolecules are oriented parallel to the long axis of the needles. Furthermore, after melt-crystallization, iPB-1 transforms spontaneously from the tetragonal crystal modification II into a hexagonal crystal modification I [26–29]. This phase transformation is connected with a reduction of the density by about 5%, and is controlled in its kinetics by the molecular architecture, and perhaps the superstructure, in which crystals may be confined.

Summarizing the scope of the present research, we intend to analyze selected parameters of the physical structure of blown films of blends of PE-LD and iPB-1 as a result of a specific condition of processing, with special emphasis on investigation of the effect of addition of iPB-1 on the structure formation. With this research, we intend to further complete our previous efforts on evaluation/characterization of structure–property relations in PE-LD/iPB-1 blown films for peel film applications, which focused on the kinetics of crystal–crystal phase transition of iPB-1 in the presence of PE-LD [29], or the mechanics of the peeling process on application [30–32].

EXPERIMENTAL

Materials

Blown films of blends of PE-LD with 0, 6, 10, 15, 20, and 100 wt% of iPB-1 were analyzed in the present study, with the blend components provided by LyondellBasell (Germany). The PE-LD was a special grade designed for film production, including blowing processes. The density of the material was 0.923 g cm^{-3} , which corresponds to a crystallinity of close to 50%. The melt-flow rate (MFR), determined at 230°C using a load of 2.16 kg, was $0.73 \text{ g (10 min)}^{-1}$. The iPB-1 was a random copolymer with a low amount of ethylene, for primary use as minority blend component in blown film extrusion. The degree of crystallinity and the MFR were similar to that of PE-LD and were about 40% and $1 \text{ g (10 min)}^{-1}$, respectively. The polymers were blended in a Collin single-screw extruder (Germany) and processed to tubular films by film blowing using lab equipment at ORBITA-FILM GmbH (Germany). Relevant processing parameters are listed in Table 1. The $\lambda_{MD}/\lambda_{TD}$ ratio was 2, which must be considered as rather low. After processing, the films were conditioned at 23°C and 50% relative humidity for a period of at least 10 days, to allow completion of the form II to form I crystal-crystal transformation of iPB-1. Specimens for subsequent structure analyses were prepared from the flattened tube/bubble, as illustrated in Fig. 1.

TABLE 1. Conditions of processing blown films of blends of PE-LD and iPB-1.

Parameters	Conditions
Extruder parameters	Maddock mix and shear elements 100 rpm screw speed Temperature profile: 140–160–180–180–180°C
Die head parameters	Temperature profile: 180–180–180–180°C Die gap: 0.8 mm
Tube formation	Time of solidification 1.8 s Blow-up ratio 1:2 Draw-down ratio 1:7.85

FIG. 1. Schematic of sample preparation and definition of machine direction (MD), transverse direction (TD), and normal direction (ND). 75 $\times$ 50 mm (600 $\times$ 600 DPI).

Instrumentation

Transmission Electron Microscopy (TEM). The phase structure, and the morphology and orientation of crystals of selected films, were analyzed by TEM using a LEO 912 microscope from ZEISS (Germany), operated at 120 kV. Ultrathin sections of about 80 nm thickness, parallel to the MD-ND and TD-ND planes of the blown film, were prepared using a Reichard Ultracut E microtome (Germany). The thin sections were deposited on a TEM copper-grid, and subsequently stained by exposure to vapors of a freshly made ruthenium tetroxide solution.

Wide-Angle X-ray Scattering (WAXS). Two-dimensional WAXS patterns were collected in transmission geometry for analysis of the crystal orientation. We used a Furnas X-ray flat film camera from Molecular Data Corporation (USA), which was equipped with a 0.5 mm pinhole collimation system. The wavelength of the Ni-filtered Cu K α radiation was 0.15418 nm, and the sample-to-detector distance was about 30 mm. The photographs were taken with the primary beam being parallel to MD, TD, and ND of the films. Selected patterns were quantitatively analyzed regarding the azimuthal intensity distribution using the FilmScan 3.0 software from Materials Data Inc. (USA).

Small-Angle X-ray Scattering (SAXS). Two-dimensional SAXS data, for analysis of the orientation of stacks of lamellae, were recorded at the A2 beamline at HASY-LAB (Germany), using an X-ray wavelength of 0.15 nm, and a Mar CCD detector for registration of the scattering. The sample-to-film distance was 2900 mm. SAXS pattern data were collected with the beam parallel to MD, TD, and ND of the films.

Polarizing Optical Microscopy (POM). POM was applied for analysis of the super-structure of the blown films at the micrometer scale, and for analysis of the average orientation of molecule segments in the MD-TD plane. A DMRX microscope from Leica (Germany) was

used for collection of images in transmission mode. The birefringence was analyzed via measurement of the optical retardation using a Leica K (30 $\times$) tilting compensator.

Dynamic-Mechanical Analysis (DMA). DMA served for measurement of the anisotropy of the modulus of elasticity in the MD-TD plane of the blown films. We used a Mark 3 analyzer from Rheometric Scientific (Germany), with the sample dynamically loaded in threshold-tension mode. The cross-section and gauge-length of the samples were 0.05 $\times$ 20 mm² and 30 mm, respectively. The films were subjected to sinusoidal oscillating strain with a programmed amplitude of 0.1% and a constant frequency of 1 Hz. Data were collected for a period of 10 min at a constant temperature of 23 $\pm$ 1 $^{\circ}$ C. The samples were prepared with their long axis, i.e., with the direction of axial loading, inclined to MD at defined angles, using an increment of 15 deg.

RESULTS AND DISCUSSION

Figure 2 shows TEM images of blown films of PE-LD/iPB-1 blends with 6 wt% (Figs. 2a and 2b) and 15 wt% iPB-1 (Figs. 2c and 2d). The left images show the structure of the MD-ND plane and the right images show the structure of the TD-ND plane. These TEM micrographs of lower magnification provide information about the global phase structure as a result of blending PE-LD and iPB-1, and indicate that the blend components are separated and form a matrix-particle structure. It can be concluded from the concentration of the components in the blends that the matrix was composed of PE-LD, in which iPB-1 particles of large aspect ratio were dispersed. The dimension of the iPB-1 particles in MD exceeded several hundred to 1000 nm, while the size was much less in TD and ND. Closer inspection of the geometry of the iPB-1 particles suggests a size of about 20 nm in ND, and perhaps 100–500 nm in TD. Accordingly, it is assumed that the iPB-1 particles were of plate-like geometry, with the smallest dimension parallel to the film surface, and the longest dimension in MD. The TEM investigation of the structure of the blends allowed us furthermore to gain information about the crystallization of both PE-LD and iPB-1. Figure 2 reveals formation of lamellae of typical thickness of 10–20 nm in the PE-LD matrix [33, 34]. Because edge-on lamellae were detected in both the TD-ND plane and MD-ND plane, unequivocal conclusions about the orientation of PE-LD crystals cannot be drawn. Figure 3 shows a further example of the structure of a blend of PE-LD with 10 wt% iPB-1. The soft zoom of the framed area of the left, original image is intended to visualize the internal structure of the iPB-1 domains. The domains seemed composed of two different phases, pointing to crystallization of iPB-1 in the form of needle-like crystals. Final conclusions regarding the crystal morphology; that is, whether these are lamellae, or indeed needles, as proposed in the literature [24, 25], cannot be

FIG. 2. TEM micrographs of PE-LD with 6 wt% iPB-1 (a and b) and 15 wt% iPB-1 (c and d). Thin sections were taken parallel to the MD-ND plane (a and c), and parallel to the TD-ND plane (b and d). 113 × 128 mm (300 × 300 DPI).

FIG. 3. TEM micrograph of the MD-ND plane of PE-LD with 10 wt% iPB-1. The right image is a soft zoom of a part of the original image, as indicated with the frame. 121 × 70 mm (300 × 300 DPI).

FIG. 4. WAXS flat film patterns of blown films of PE-LD with 15 wt% iPB-1. Samples were oriented such that the primary X-ray beam was perpendicular to the MD-TD plane (a), MD-ND plane (b), and TD-ND plane (c) of the polymer film. 141 × 132 mm (300 × 300 DPI).

drawn because it requires information about the chain orientation. Doubtless, the long dimension of the heterogeneities was parallel, or close to parallel to the long dimension of the domains, that is, parallel to MD.

Figure 4 shows tri-directional WAXS flat film photographs obtained on blown films of PE-LD with 15 wt% PB-1, which are representative for all of the investigated blends. The polymer film was oriented such that the primary X-ray beam was perpendicular to the MD-TD plane, MD-ND plane, and the TD-ND plane, which allowed a qualitative description of the orientation of crystals [35]. First of all, the WAXS pattern revealed crystallization of both blend components by observation of characteristic scattering maxima, which are indicated/indexed in Fig. 4a. Accordingly, the PE-LD was crystallized in its orthorhombic polymorph, while iPB-1 crystals were of hexagonal symmetry. Secondly, the data reveal preferred orientation of crystals. This, in particular, is true for PE-LD, as concluded from the anisotropic azimuthal scattering of the (110) and (200) lattice planes, when the blown films were analyzed with the primary beam parallel to ND (Fig. 4a) and TD (Fig. 4b). The WAXS data unambiguously suggest preferred orientation of the a-axis of the orthorhombic unit

cell in the direction of MD. The b-axis, in contrast, seems equally distributed in the TD-ND plane. This, in particular, can be concluded from the isotropic intensity distribution of the (110) and (200) reflections in the pattern obtained with the beam parallel to MD (Fig. 4c). Note that the (020) reflection was also monitored but is not shown in the photographs of Fig. 4. Based on the WAXS data, we therefore intend to describe the orientation of crystals of PE-LD in blown films of blends of PE-LD and iPB-1, which were processed at the specific condition summarized in Table 1, as a uniaxial a-texture. This result is in accord with earlier observations [6, 10, 14, 17], and shows that addition of iPB-1 does not qualitatively affect structure formation of PE-LD on film blowing from the crystal orientation angle. This is further demonstrated with the data of Fig. 5, which show the azimuthal intensity distribution of the (200) peak of PE-LD crystals in blown films of blends with variable content of iPB-1 in the MD-TD plane. The position of the maximum is not affected by the mass fraction of iPB-1 and proves for all compositions preferred orientation of the a-axis parallel to MD. Only in the blend with 20 wt% iPB-1 was there a slight broadening of the intensity distribution detected, which perhaps was caused by satellite maxima, as

FIG. 5. Azimuthal intensity distribution of the (200) interference of PE-LD crystals as a function of the concentration of iPB-1. 96×91 mm (600×600 DPI).

indicated by the arrows. These non-resolved satellite maxima may point to the presence of a minor second texture component, in which the *a*- and *c*-axes of the orthorhombic unit cell are off MD. Such a crystal orientation, intermediate between an *a*-texture and a *c*-texture, has been proven to exist in blown films of intermediate ratio of drawing in transversal and longitudinal direction, and obviously may be favored in the presence of iPB-1 [10, 12].

Further investigation of the crystal orientation in PE-LD/iPB-1 blends was performed by SAXS. Figure 6 shows tri-directional SAXS pattern of a blown film of PE-LD with 15 wt% iPB-1, taken with the primary X-ray beam parallel to ND (Fig. 6a), TD (Fig. 6b), and MD (Fig. 6c). The data clearly prove, with the meridional long-period maximum, in the pattern obtained with the beam parallel to ND and TD, the presence and orientation of stacks of lamellae parallel to MD. Within the cross-section of the film, scattering from lamellar stacks is weak and shows, at best, a maximum in TD. The result

FIG. 6. SAXS pattern of blown films of PE-LD with 15 wt% iPB-1. Samples were oriented such that the primary X-ray beam was perpendicular to the MD-TD plane (a), MD-ND plane (b), and TD-ND plane (c) of the polymer film. 132×60 mm (300×300 DPI).

of preferred orientation of stacks of lamellae parallel to MD is surprising, and not a priori expected from WAXS analyses. The orientation of molecular chains in stacks of lamellae, which contribute to the meridional SAXS scattering, is parallel to MD, which implies that the *a*-axis of the orthorhombic crystal lattice in lamellar stacks is oriented in the TD-ND plane of the blown films. The WAXS data of Fig. 4, in contrast, show only a little, although not zero, scattering intensity of the (200) peak in the TD-ND plane. Obviously, there exist two populations of crystals of PE-LD, which were oriented differently. WAXS proves that the majority of crystals, regardless of their morphology or arrangement in stacks was oriented with the *a*-axis parallel to MD. WAXS also proves there was a minor amount of crystals with the chain axis oriented parallel to MD. These crystals were of lamellar morphology and were organized within stacks according to the SAXS data. This finding confirms an earlier investigation about the structure of blown films of high-pressure PE, where similar conclusions have been drawn [9].

The conclusion of preferred orientation of crystals of PE-LD with the chain axis perpendicular to MD is additionally supported by polarizing optical microscopy. The average orientation angle of molecule segments in the MD-TD plane was determined according to a procedure that is well described in text books [36, 37] and is shown as a function of the concentration of iPB-1 in Fig. 7a.

FIG. 7. Angle of average orientation of molecule segments (a) and optical birefringence (b) in the MD-TD plane of blown films of PE-LD/iPB-1 blends as a function of the concentration of iPB-1. 111×112 mm (600×600 DPI).

FIG. 8. Modulus of elasticity of blown films of blends of PE-LD with 15 wt% iPB-1 as a function of the angle between MD and the direction of axial loading of the specimen. 95 × 83 mm (600 × 600).

Although the measurement includes contributions of segments of molecules of both PE-LD and iPB-1, and of both crystalline and amorphous phases, the experimental data clearly show that there is preferred orientation of molecule segments parallel, or close-to parallel to TD if the concentration of iPB-1 in the blend is less than 15 wt%, being in accord with the WAXS data of Fig. 4. We assume furthermore that the slight change of the angle of orientation of the chain axis toward MD with increasing concentration of iPB-1, at least partially, was due to increasing fraction of iPB-1 domains. The TEM data of Figs. 2 and 3 showed that the iPB-1 domains in the blends are elongated in MD, which indicates flow-induced alignment of iPB-1 molecules in the crystalline and amorphous phases parallel to MD during processing. Altogether, the degree of orientation, as concluded from quantitative measurement of the optical retardation of the various polymer films, was rather low. Figure 7b shows birefringence data as a function of the concentration of iPB-1 in the blends, which need to be compared with the intrinsic, that is, maximum birefringence. The maximum birefringence is the difference between the indices of refraction parallel and perpendicular to the chain direction and is about one magnitude of order larger than the experimentally observed values [38, 39]. Obviously, the different orientation of molecules segments in the PE-LD matrix and in the iPB-1 domains, and the differently oriented two crystal populations of PE-LD, lead to a cancellation of the various contributions to the total birefringence. The blown film of the blend with 20 wt% iPB-1 even showed almost complete absence of birefringence, which did not allow an accurate determination of an angle of preferred orientation. Consequently, corresponding data points were omitted in Fig. 7.

The presence of two components of texture of crystals of PE-LD in blown films of PE-LD/iPB-1 blends leads to the expectation of anisotropy of the mechanical behavior. The modulus of elasticity of a multi-phase material depends on the concentration of the various phases of different mechanical characteristic, and can be predicted regarding boundaries with the Reuss or Voigt model [40, 41]. For a multi-phase material of given composition, with the constituents being inherently anisotropic, the modulus of elasticity depends furthermore on the orientation of these constituents. In short, it is proven for PE and many other thermoplastics, that due to the anisotropy of chemical bonding, the modulus of elasticity in chain direction is about two magnitudes of order larger than in cross-chain direction [42–44]. Consequently, it is expected that the stiffness of the blown film of the present study shows anisotropy in the MD-TD plane according to the crystal orientation. Figure 8 shows a measurement of the storage modulus of elasticity on a blown film of PE-LD with 15 wt% iPB-1 as a function of the angle of inclination between MD and direction of axial loading. The modulus of elasticity is largest in TD, shows a second distinct maximum in MD, and is lowest at an intermediate angle of about 45 deg. With the assumption of negligible influence of the amorphous phase on the measurement of the modulus, the data of Fig. 8 strongly support the observation of a two component PE-LD texture in the investigated blown films.

CONCLUSIONS

In the present study, selected parameters of the physical structure of blown films of blends of PE-LD with low amount of iPB-1 were analyzed. These parameters include the phase morphology and the geometry and orientation of crystals. The blend components were phase separated with iPB-1, forming plate-like domains, being dispersed in a matrix of PE-LD. The iPB-1 platelets are aligned parallel to the film surface, with their largest dimension parallel to MD. The PE-LD matrix consists of an amorphous phase in which the majority of orthorhombic crystals of lamellar

FIG. 9. Model of the structure of the blown films of blends of PE-LD with low amount of iPB-1, accommodating the experimental results of Figs. 2–8. The objects represent crystalline lamellae, with the chain axis indicated by arrows. 86 × 56 mm (600 × 600 DPI).

geometry is oriented with the c-axis perpendicular to MD. A minor portion of PE-LD lamellae forms stacks and is aligned parallel to MD. In case of iPB-1, in contrast, hexagonal form I crystals are of needle-like geometry and probably aligned in the direction of MD. Figure 9 is a sketch of physical structure of the investigated blown films of PE-LD/iPB-1 blends, which accommodates the most important experimental observations of the present study. Though the data resemble features of former investigations of the structure of blown PE-LD films of similar history of processing, that is, $\lambda_{MD}/\lambda_{TD}$, the primary advance of this study is the proof that minor addition of iPB-1 obviously does not qualitatively affect structure formation of blown films of PE-LD. This, in combination with information about the global phase structure of the blends, is of particular importance for further understanding/evaluation of potential and limits of blown films of PE-LD/iPB-1 blends for peel film applications, and beyond.

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REFERENCES

1. P. Stober and H. Rist, *Kunststoffe*, **6**, 66 (2004).
2. C.C. Hwo, *J. Plastic Film Sheeting*, **3**, 245 (1987).
3. D.W. van Krevelen, *Properties of Polymers*, Elsevier, Amsterdam (1990).
4. M.M. Coleman, J.F. Graf, and P.C. Painter, *Specific Interactions and the Miscibility of Polymer Blends*, Technomic Publishing Company, Lancaster (1991).
5. T.A. Huang and G.A. Campbell, *Adv. Polym. Techn.*, **5**, 181 (1985).
6. E. Walenta, A. Janke, D. Hofmann, D. Fanter, and D. Geiss, *Acta Pol.*, **37**, 557 (1986).
7. D. Hofmann, D. Geiss, A. Janke, G.H. Michler, and L. Fiedler, *J. Appl. Polym. Sci.*, **39**, 1595 (1990).
8. R.J. Pazur and R.E. Prud'homme, *Macromolecules*, **29**, 119 (1996).
9. S. Marinow, G. Michler, C. Walther, and I. Naumann, *Plaste und Kautschuk*, **35**, 159 (1988).
10. H. Haberkorn, H. Hendus, and G. Kanig, *Angew. Makromol. Chem.*, **40/41**, 325 (1974).
11. D.R. Holmes, R.G. Miller, R.P. Palmer, and C.W. Bunn, *Nature*, **171**, 1104 (1953).
12. A. Keller and M.J. Machin, *J. Macromol. Sci., Part B: Phys.*, **B1**, 41 (1967).
13. D.R. Holmes and R.P. Palmer, *J. Polym. Sci., Polym. Phys.*, **31**, 345 (1958).
14. A.L. Aggarwal, G.P. Tilley, and O.J. Sweeting, *J. Appl. Polym. Sci.*, **1**, 91 (1959).
15. P.H. Lindenmeyer and S. Lustig, *J. Appl. Polym. Sci.*, **9**, 227 (1965).
16. C.R. Desper, *J. Appl. Polym. Sci.*, **13**, 169 (1969).
17. T. Tagawa, *J. Polym. Sci., Polym. Phys.*, **18**, 971 (1980).
18. M.B. Johnson, G.L. Wilkes, A.M. Sukhadia, and D.C. Rohlfing, *J. Appl. Polym. Sci.*, **77**, 2845 (2000).
19. A.C. Chang, L. Tau, A. Hiltner, and E. Baer, *Polymer*, **43**, 4923 (2002).
20. O. Guichon, R. Séguéla, L. David, and G. Vigier, *J. Polym. Sci., Polym. Phys.*, **41**, 327 (2003).
21. D.R. Breese and G. Beaucage, *Current Opinion in Solid State and Materials Science*, **8**, 439 (2004).
22. A. Ajji, X. Zhang, and S. Elkoun, *Polym. Eng. Sci.*, **46**, 1182 (2006).
23. Y. Fujiwara, *Polym. Bull.*, **13**, 253 (1985).
24. R.M. Gohil and J. Petermann, *J. Mat. Sci.*, **18**, 1719 (1983).
25. K. Wenderoth, A. Karbach, and J. Petermann, *Coll. Polym. Sci.*, **263**, 301 (1985).
26. S. Kopp, J.C. Wittmann, and B. Lotz, *J. Mat. Sci.*, **29**, 6159 (1994).
27. V. Petraccone, B. Pirozzi, A. Frasci, and P. Corradini, *Eur. Polym. J.*, **12**, 323 (1976).
28. G.C. Alfonso, F. Azzurri, and M. Castellano, *J. Therm. Anal. Cal.*, **66**, 197 (2001).
29. M. Nase, R. Androsch, B. Langer, H.J. Baumann, and W. Grellmann, *J. Appl. Polym. Sci.*, **107**, 3111 (2008).
30. M. Nase, B. Langer, and W. Grellmann, *Polym. Testing*, **27**, 1017 (2008).
31. M. Nase, A. Zankel, B. Langer, H.J. Baumann, W. Grellmann, and P. Poelt, *Polymer*, **49**, 5458 (2008).
32. M. Nase, B. Langer, H.J. Baumann, W. Grellmann, G. Geissler, and M. Kaliske, *J. Appl. Polym. Sci.*, **111**, 363 (2009).
33. G.H. Michler and R. Godehardt, *Cryst. Res. Technol.*, **35**, 863 (2000).
34. B. Wunderlich, *Macromolecular Physics, Volume 2: Crystal Nucleation, Growth, Annealing*, Academic Press, New York (1976).
35. H. Tadokoro, *Structure of Crystalline Polymers*, Krieger Publishing Company, Malabar (1990).
36. W. Grellmann and S. Seidler, *Polymer Testing*, Hanser, Munich (2007).
37. M. Kern and J. Trempler, *Observation and Measurement Microscopy in Material Science - A Guideline for Practice*, Bruenne und Bruenne, Berlin (2008).
38. W.M.D. Bryant, *J. Polym. Sci.*, **2**, 574 (1947).
39. T. Akira, T. Hashimoto, Y. Tsukahara, and H. Kawai, *Polymer*, **20**, 943 (1979).
40. A. Reuss, *Angew. Math. Mech.*, **9**, 49 (1929).
41. W. Voigt, *Lehrbuch der Kristallphysik*, Teubner-Verlag, Berlin (1928).
42. I. Sakurada, K. Kaji and S. Wadano, *Colloid Polym. Sci.*, **259**, 1208 (1981).
43. H.G. Elias, *Macromolecules, Volume 3: Physical Structures and Properties*, Wiley-VCH (2008).
44. V.B. Gupta and I.M. Ward, *J. Macromol. Sci., Phys.*, **B4**, 453 (1970).