Effect of Annealing Temperature on Phase Composition and Tensile Properties in Isotactic Poly(1-butene)

Lenka Chvátalová,[1] Lubomír Beníček,[1,2] Kristýna Berková,[1,2,3] Roman Čermák,[1,2] Martin Obadal,[4] Vincent Verney,[1,3,5] Sophie Commereuc[3,6]

[1]Department of Polymer Engineering, Faculty of Technology, Tomas Bata University in Zlin, Nam. T. G. Masaryka 275, 762 72 Zlin, Czech Republic
[2]Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, Nad Ovcirnou 3685, 760 01 Zlin, Czech Republic
[3]Clermont Université, Université Blaise Pascal, LPMM, BP 10448, F-63000 Clermont-Ferrand, France
[4]Borealis Polyolefine GmbH, St.-Peter-Strasse 25, 4021 Linz, Austria
[5]CNRS, UMR 6505, LPMM, F-63177 Aubière Cedex, France
[6]Clermont Université, ENSCCF, LPMM, BP 10448, F-63000 Clermont-Ferrand, France

ABSTRACT: The influence of annealing temperature on the kinetics of polymorphic changes and mechanical properties within the time in isotactic poly(1-butene) (PB-1) has been investigated by wide-angle X-ray scattering and tensile testing. Extruded tapes of PB-1 have been exposed to several annealing temperatures: -22, $+5$, $+22$, $+40$ and $+60°C$. The evolution of content of Phase I for various annealing temperatures upon time shows predominantly S-shaped trend. Annealing temperature considerably affects the overall rate of transformation in PB-1. On the other hand, the resulting mechanical properties are solely controlled by the polymorphic composition. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3407–3412, 2012

Key words: annealing; isotactic poly(1-butene); mechanical properties; phase transformation; wide-angle X-ray scattering

INTRODUCTION

Isotactic poly(1-butene) (PB-1) is one of the members of the polyolefin family which exhibits advantages over the other polymers. From the application point of view the outstanding resistance to creep is of crucial importance. PB-1 is polymorphic material occurring in five crystallographic modifications. The modifications I, I′ and II, II′ can be prepared by the crystallization from the melt while the modification III is formed during solution crystallization.[1–6]

Phase transformation is the most important phenomenon—upon solidification from the melt PB-1 crystallizes into phase II which is kinetically favored. The structure in this state is loosely packed and the resulting density (0.907 g/cm³) is only slightly higher than in the case of amorphous region (0.868 g/cm³).[7] The resulting material is rather ductile and mechanically weak. However, this phase is metastable and transforms slowly into a denser (0.950 g/cm³) and more stable phase I, which is thermodynamically favored.[5,8] As a result of this transformation PB-1 become to be a stiff material and satisfies application properties.[9–11]

The kinetics of this phase transformation is known to be influenced by pressure,[12] mechanical loading,[13] temperature,[14] and addition of comonomers in the structure.[15–17] Nakafuku and Miyaki[12] reported that crystallization of PB-1 melt under high pressure produces stable phase I′, which shows the same X-ray diffraction pattern as phase I but has much lower melting temperature (96 vs. 130°C) at atmospheric pressure. Above 200 MPa, phase I′ and phase II′ are crystallized from the melt. Phase II′ shows the same X-ray diffraction pattern as phase II, but lower melting temperature than phase II. Phase II′ is metastable at atmospheric pressure and transforms to phase I′ on standing at room temperature.[14] Fujiwara[18] investigated the transformation of oriented phase II specimens and found that the "untwinned" phase I′ appears by applying shear stress; the orientation of phase I changed according to the relative direction of the stress.

Nevertheless, significant delay in commercialization of PB-1 is caused by two principal reasons:

(i) The kinetics of phase transformation is slow and temperature sensitive. At room temperature, the total transformation from phase II to I is finished within a week. However, shifting of annealing temperature in both directions leads to even slower transformation rate.[5]

(ii) The answer to the question how the transformation in supermolecular structure is reflected by the changes in macroscopic properties is industrially crucial but still missing.

Present article brings evidence and explains the effect of annealing temperature on kinetics of both phase transformation and evolution of mechanical properties in PB-1 parts. In our best knowledge, the interrelations between the changes of supermolecular structure and macroscopic tensile properties of PB-1 are jointly discussed for the first time here. Extruded tapes of PB-1 have been exposed to several annealing temperatures. The evaluation of changes in supermolecular structure and mechanical properties within the time has been performed by wide-angle X-ray scattering (WAXS) and tensile testing.

EXPERIMENTAL PART

Material

Isotactic PB-1 PB 0300M produced by LyondellBasell, Louvain la Neuve, Belgium was used. According to producer information, PB 0300M is a semicrystalline homopolymer with balanced resistance to creep and environmental stress crack and performance at elevated temperature. The basic properties are following: density 0.915 g/cm^3—ISO 1183, melt flow index 4 g/10 min—ISO 1133 (190°C/2.16 kg).

Extrusion

The material was extruded using a Brabender Plasti-Corder PLE 651 single-screw extruder, the processing conditions were following: compression ratio of the screw 1 : 4; screw speed 20 rpm; barrel temperatures 135, 140, 145, 150°C; extrusion slit die with profile 2 × 20 mm^2 with temperature 150°C. The processed tapes were cut off to the pieces with length 140 mm.

Annealing

The prepared specimens were immediately after processing annealed at free stress state at various temperatures: −22, +5, +22, +40, and +60°C at atmospheric pressure. The temperatures were chosen

with respect to utilization of PB-1, which can be used for tanks, hose, tubing, molded parts, films, etc. at various temperatures. Heating and cooling chambers with precisely controlled temperature were employed for annealing. Upon given annealing time within interval 0–64 days the specimens were immediately subjected to analysis of structure and properties.

Wide-angle X-ray scattering

A URD6 diffractometer CuKα radiation monochromatized with a Ni filter (λ = 0.154 nm) was employed for evaluation of phase transformation. Measurements were performed in transmission mode, diffraction angle interval $2\theta = 7°–25°$, step of 0.05° and holding time of 5 s were used.

Tetragonal phase II of PB-1 gives the reflections at 11.9°, 16.9°, and 18.4° 2θ, corresponding to the (200), (220), and (301) planes. On the other hand, hexagonal phase I is characterized by four diffraction peaks at 9.9°, 17.3°, 20.2°, and 20.5° 2θ, originated by the (110), (300), (220), and (211) planes.[19] Phase transformation is unambiguously demonstrated by the changes of reflection intensities at 9.9° 2θ (110, phase I) and 11.9° 2θ (200, phase II). Therefore, the extent of phase transformation can be calculated.[20–23]

$$T_I = I_I/(I_I + I_{II}) \tag{1}$$

where T_I is content of phase I and I_I and I_{II} are intensities of the reflections at 9.9° and 11.9° 2θ. The intensities of the reflection peaks have been obtained by the integration of peak areas after the subtraction of amorphous halo.

Tensile testing

A Zwick 145665 multipurpose tester was used for the tensile testing of extruded tapes with a gauge length of 80 mm. The specimens were strained at room temperature up to break at a test speed of 100 mm/min. From the stress–strain traces, strength at break and elongation at break were derived. Besides, the elastic modulus was evaluated using a Zwick external extensometer (gauge length of 20 mm) at a test speed of 1 mm/min. Five specimens were tested and average values are reported.

RESULTS AND DISCUSSION

The evolution of polymorphic structure in PB-1 specimens exposed to −22, +5, +22, +40, and +60°C has been characterized by WAXS as can be seen in Figure 1. The crystallinity in all the samples was ˜85% and does not significantly vary upon annealing which is in agreement with study of Azzurri et al.[24]
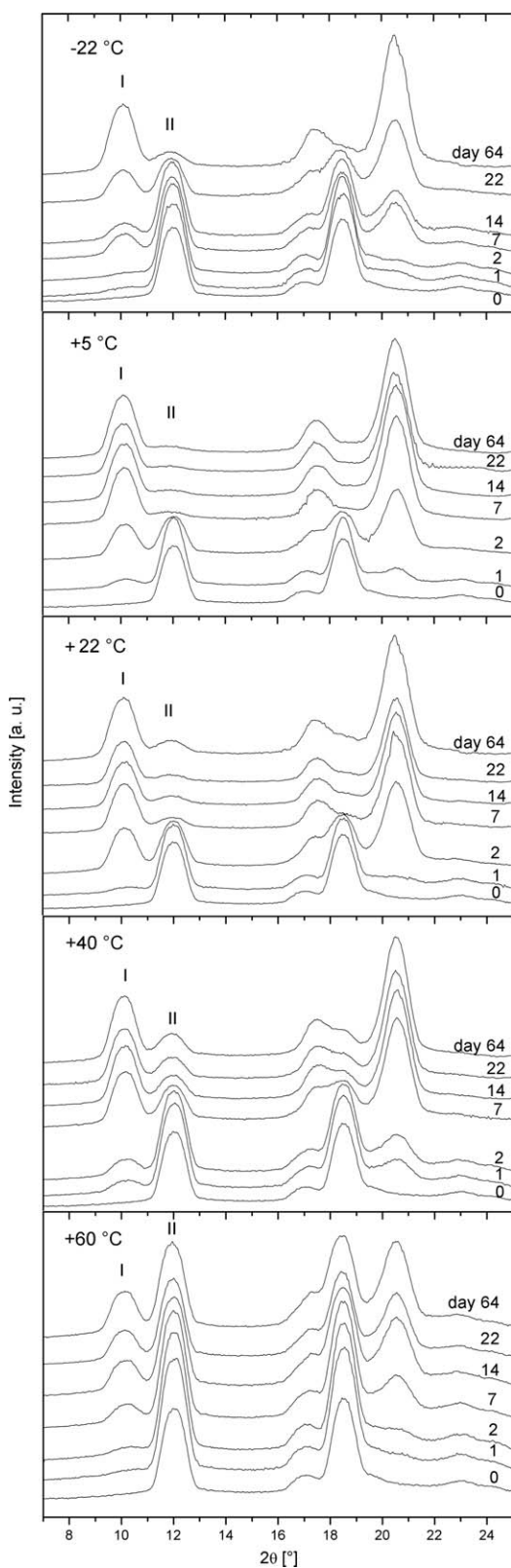
**Figure 1** WAXS patterns for various annealing temperatures upon time.

Similarly, no broad changes of orientation were observed and the samples kept the shape during annealing.

Phase transformation is followed by the changes in intensities of individual reflection peaks. The content of phase I has been evaluated in accordance with eq. (1) and the data are represented in Figure 2 (up) as a function of time. As can be seen, annealing temperature has significant effect on the transformation rate. On the basis of previous studies, the crystal–crystal transformation in PB-1 is a process consisting of two common steps, nucleation and growth.[10,25,26] Many studies[10,18,25–28] agreed that the nucleation controls the overall transformation rate, in particular. As a consequence, the dependence of content of phase I on annealing (i.e., transformation) time shows typical S-shaped curve. In Figure 2, the evolution of content of phase I follows S-shaped trend in the cases of annealing temperatures of −22, +5, +22, and +40°C. The transformation rate decreases in following order of annealing temperatures: +5, +22, +40, and −22°C. This sensitivity of transformation kinetics to temperature is in agreement with previous studies.[5,25] However, at temperature of +60°C the content of phase I is virtually linear-dependent within observed annealing time. At the same time, it should be noted that the observed transformation reached only low values, therefore one can expect following S-shaped evolution upon prolonged time.

Although, the transformation of phase II to I has been extensively studied and explained, its impact on final properties of PB-1 has not been fully described. Present study gives in direct relation the
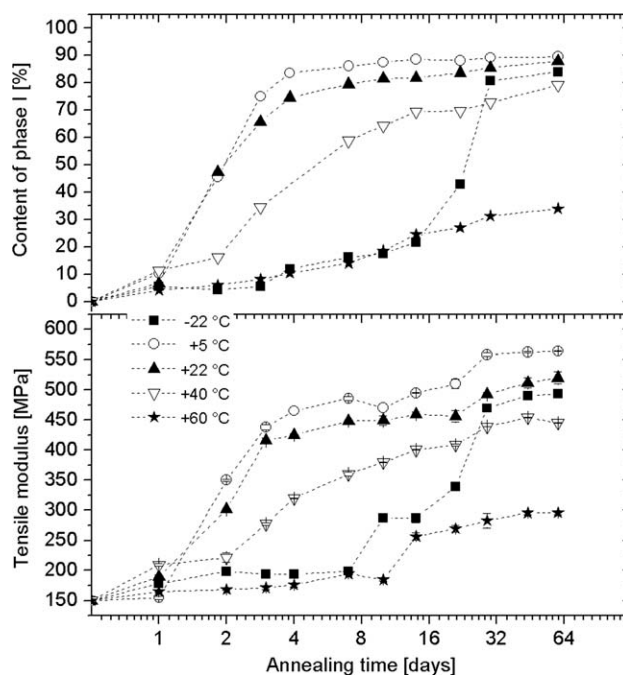
Figure 2 Evolution of the phase I content (up) and tensile modulus (down) for various annealing temperatures upon time.
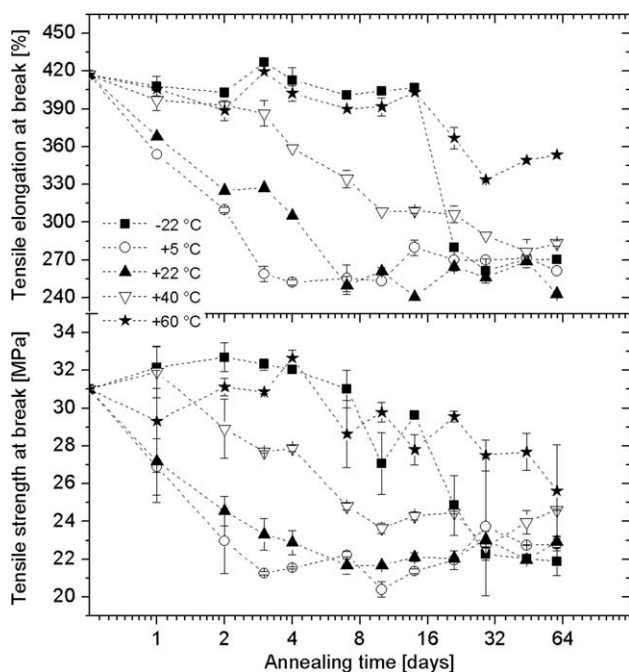
Figure 3 Evolution of tensile elongation at break (up) and strength at break (down) for various annealing temperatures upon time.

content of phase I and tensile properties. The evolution of tensile modulus at given annealing temperatures is illustrated in Figure 2 (down). Similarly to the content of phase I, tensile modulus is a growing function of annealing time. This significant improvement of stiffness reflects the changes in thermodynamic stability of the material arising from phase transformation. Figure 3 shows elongation and strength at break in tensile mode as a function of annealing time. On the contrary to the tensile modulus, the values of elongation and strength at break decrease upon annealing. Indeed, the increasing thermodynamic stability of the material upon phase transformation leads to limitation of plastic rearrangement as a response to mechanical loading. Consequently, the material with prevailing phase I cannot be dramatically oriented by cold drawing and the values of both elongation and strength at

break are lower compared to ductile material full of phase II.

From comparison of Figures 2 and 3, one can suggest that the mechanical properties of PB-1 are directly controlled by the polymorphic composition. Even by naked eye, a similar trend in evolution of content of phase I and tensile modulus can be seen. However, this simple comparison cannot be applied for the strength and elongation at break. Therefore, the normalization of values of observed characteristics was performed. For normalization of increasing functions (content of phase I and tensile modulus) following equation was given:

$$X_{\mathrm{norm}} = \frac{X - X_{\mathrm{min}}}{X_{\mathrm{max}} - X_{\mathrm{min}}} \qquad (2)$$

and for decreasing functions (tensile elongation and strength at break):

$$X_{\mathrm{norm}} = \frac{X_{\mathrm{max}} - X}{X_{\mathrm{max}} - X_{\mathrm{min}}} \qquad (3)$$

where X_{norm} is a normalized property, X is a value at given time, X_{min} is a minimal value, and X_{max} is a maximal value of property. In Table I, X_{min} and X_{max} for given characteristics are summarized. Figure 4 shows the evolution of normalized phase I content and mechanical properties of specimens annealed at various temperatures upon time. It can be clearly seen that the normalized curves of the phase I content fairly fit with those of tensile modulus, elongation and strength at break. This comparison proves that the direct interrelation between the phase composition and mechanical properties exists.

As a consequence of the demonstrated direct sensitivity of mechanical properties to phase composition of PB-1, the measured data were statistically analyzed to describe the transformation phenomenon numerically. Figure 5 displays tensile modulus, elongation and strength at break as a function of content of phase I. It is evident that the mechanical properties are linear-dependent on phase composition, as was proved by linear regression; in all the cases, the

TABLE I
Parameters of PB-1 Samples

T (°C)	WI_{max} (%)	WI_{min} (%)	E_{max} (MPa)	E_{min} (MPa)	ε_{max} (%)	ε_{min} (%)	σ_{max} (MPa)	σ_{min} (MPa)
−22	84.0	0	493	150	427	261	32.7	21.9
+5	89.5	0	564	150	417	252	31.0	20.4
+22	88.0	0	520	150	417	241	31.0	21.7
+40	79.2	0	445	150	417	283	31.9	22.6
+60	34.0	0	295	150	420	334	32.7	25.6

T, annealing temperature; WI_{max}, maximal content of phase I; WI_{min}, minimal content of phase I; E_{max}, maximal tensile modulus; E_{min}, minimal tensile modulus; ε_{min}, maximal elongation at break; ε_{min}, minimal elongation at break; σ_{max}, maximal strength at break; σ_{min}, minimal strength at break.

correlation coefficient is higher than 0.80, moreover for tensile modulus it is even higher than 0.97. Generally, lower coefficient of tensile strength and elongation at break can be expected because the values refer to the structure arising from a broad inhomogeneous rearrangement of original morphology during the tensile testing.
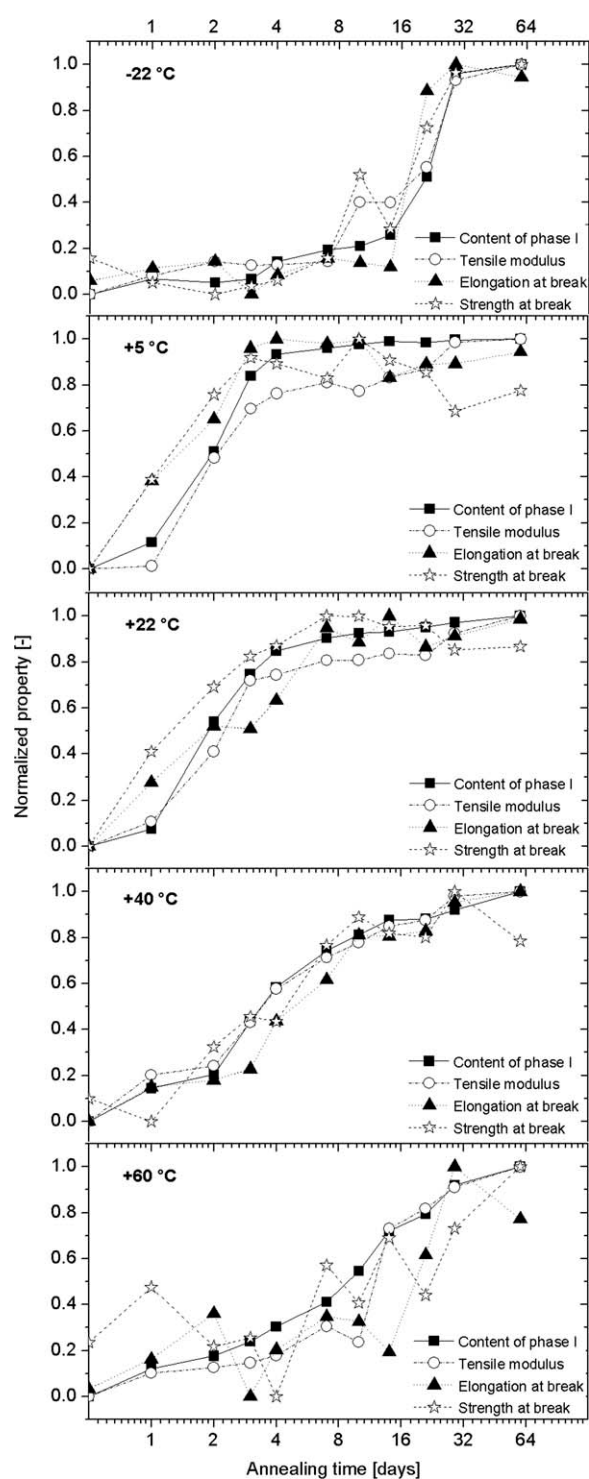
Figure 4 Evolution of normalized properties for various annealing temperatures upon time.
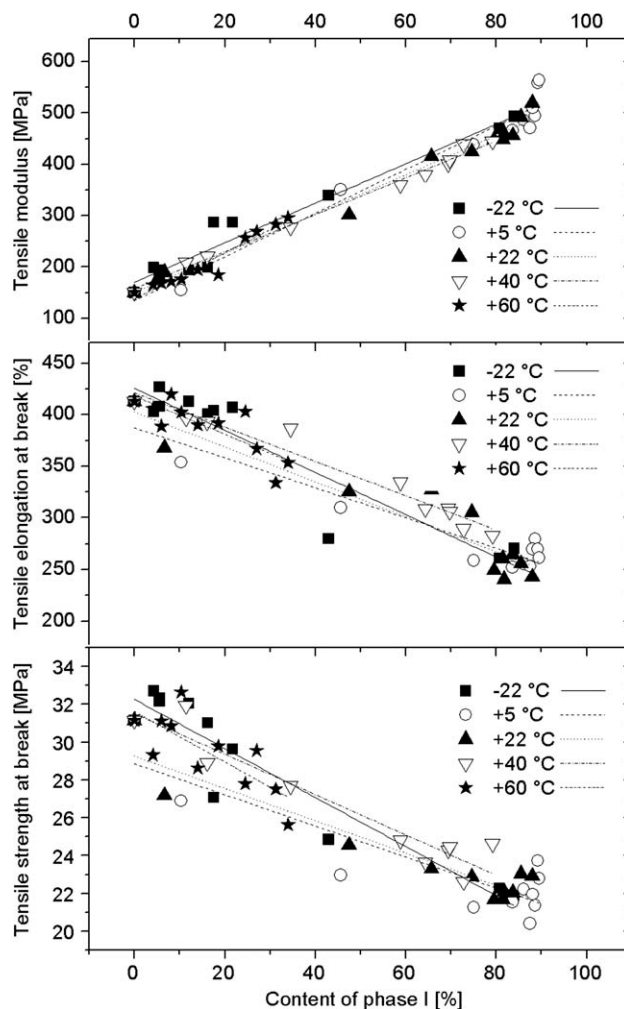
Figure 5 Dependence of tensile properties on content of phase I.

It is interesting to compare linear fits of mechanical properties as a function of phase I content for various annealing temperatures. In this context, the differences between the slopes of individual linear fits of the data at given temperatures were analyzed by the T-test. It was found that no significant variability between the slopes can be observed at a significance level of 0.05. This result leads to particularly important conclusions: (i) The kinetics of phase transformation performed at various annealing temperatures was proved to be insignificant for the tensile properties, therefore, (ii) the unique parameter which controls the mechanical properties is the phase composition of PB-1.

CONCLUSION

The experimental study has shown that the annealing temperature has significant effect on the kinetics of phase transformation in PB-1. Generally, the evolution of content of phase I upon annealing at a given temperature follows S-shaped trend reflecting

complex process of both the nucleation and growth. It was clearly demonstrated that the mechanical properties are directly controlled by the polymorphic composition; normalized curves of tensile modulus, elongation and strength at break as a function of annealing time fairly fit with that of content of phase I. From practical point of view it is important to highlight that the annealing temperature affects the overall rate of polymorphic changes in processed PB-1 but the resulting properties are controlled solely by the extent of this transformation.

References

1. Natta, G.; Corradini, P.; Bassi, I. W. Nuovo Cimento Supp 1962, 1, 52.
2. Boor, J., Jr.; Youngman, E. A. J Polym Sci 1964, B2, 903.
3. Holland, V. F.; Miller, R. L. J Appl Phys 1964, 35, 3241.
4. Brydson, J. A. Plastics materials, 7th ed.; Butterworth-Heinemann Linacre House: Oxford, 1999.
5. Kaszonyiová, M.; Rybnikář, F.; Geil, P. H. J Macromol Sci Phys 2004, 43, 1095.
6. Luciani, L.; Sepala, J.; Lofgren, B. Prog Polym Sci 1988, 13, 37.
7. Aronne, A.; Napolitano, A. R.; Pirozzi, B. Eur Polym J 1986, 9, 703.
8. Rubin, I. D. J Polym Sci 1964, B2, 747.
9. Marigo, A.; Marega, C.; Cecchin, G.; Collina, G.; Ferrara, G. Eur Polym J 2000, 36, 131.
10. Kopp, S.; Wittmann, J. C.; Lotz, B. Polymer 1994, 35, 908.
11. Oda, T.; Maeda, M.; Hibi, S.; Watanabe, S. Koubunshi Ronbunshu 1974, 31, 129.
12. Nakafuku, C.; Miyaki, T. Polymer 1983, 24, 141.
13. Goldbach, G. A. Macromol Chem 1974, 39, 175.
14. Kalay, G.; Kalay, C. R. J Polym Sci Part B: Polym Phys 2002, 40, 1828.
15. Hong, K.; Spruiell, J. E. J Appl Polym Sci 1985, 30, 3163.
16. Alfonso, G. C.; Azzurri, F.; Castellano, M. J Therm Anal Calorim 2001, 66, 197.
17. Causin, V.; Marega, M.; Marigo, A.; Ferrara, G.; Idiyatullina, G.; Mantinel, F. Polymer 2006, 47, 4773.
18. Fujiwara, Y. Polym Bull 1985, 13, 253.
19. Lauritzen, J. I., Jr.; Hoffman, J. D. J Appl Phys 1973, 44, 4340.
20. Azzurri, F.; Alfonso, G. C.; Gómez, M. A.; Martì, M. C.; Ellis, G.; Marco, C. Macromolecules 2004, 37, 3755.
21. Samon, J. M.; Schultz, J. M.; Hsiao, B. S.; Wu, J.; Khot, S. J Polym Sci Part B: Polym Phys 2000, 38, 1872.
22. Natta, G.; Corradini, P.; Bassi, I. Nuovo Cimento Suppl 1960, 15, 52.
23. Avrami, M. J Chem Phys 1940, 8, 212.
24. Azzuri, F.; Flores, A.; Alfonso, G. C.; Calleja, F. J. B. Macromolecules 2002, 35, 9069.
25. Maruyama, M.; Sakamoto, Y.; Mozaki, K.; Yamamoto, T.; Kajioka, H.; Toda, A.; Yamada, K. Polymer 2010, 51, 5532.
26. Kopp, S.; Wittmann, J. C.; Lotz, B. J Mater Sci 1994, 29, 6159.
27. Gohil, R. M.; Miles, M. J.; Petermann, J. J Macromol Sci Phys 1982, B21, 189.
28. Chau, K. W.; Yang, Y. C.; Geil, P. H. J Mater Sci 1986, 21, 3002.