

Influence of Temperature Changes on Crystallization of an Ethylene–Propylene Random Copolymer

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ABSTRACT: Unconventional procedures were used to crystallize an ethylene/propylene copolymer (E/P), with the aim of investigating the effect of temperature changes on crystallization kinetics and spherulitic morphology. The solidification process of specimens crystallizing under isothermal conditions was cyclically stopped for a while, by increasing the temperature, and afterward reestablished by cooling at the original temperature. The resulting morphology characterized by rings within spherulites was compared

to that obtained by continuous isothermal crystallization. The different temperature dependencies of the thermal expansion coefficients of liquid and solid phases account for the presence of rings within spherulites grown in a temperature field. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2008–2013, 2004

Key words: crystallization; core–shell polymers; poly(propylene) (PP); microstructure; calorimetry

INTRODUCTION

The most widely procedure used to study polymer crystallization, on cooling from the melt, is simply to keep samples in a hot-stage device at constant temperature, whereas observations of spherulite growth are performed by an optical polarizing microscope. This procedure, which is very convenient for measuring the radial growth rate as a function of temperature, hardly reproduces real cooling conditions of polymers in industrial processes, however. Indeed, isothermal crystallization may be difficult to achieve, especially in polymers that crystallize relatively rapidly.¹ Because the microstructure of polymers crystallized with isothermal procedures does not necessarily reflect that developed under considerable heat exchange,² to study the influence of real cooling conditions during crystallization is of great importance in explaining the physical properties that are strictly related to the microstructure. On the other hand, knowledge of the effect of unconventional cooling conditions on the microstructure can be very useful in choosing appropriate temperature programs during processing for the achievement of a specific level of properties.

Although the abrupt influence of temperature on crystallization and morphology of poly(propylene) (PP) has been well investigated,^{3–8} the consequence of sudden increases of temperature on crystalline growth

of PP has not yet been reported. The present article reports the investigation of morphological changes of α -spherulites of an ethylene/propylene random copolymer (E/P) as a result of short temperature increases before a sudden reestablishment of previous temperature conditions. Instead of isotactic PP homopolymer (iPP), an E/P copolymer, with a very low ethylene content, was chosen to study the influence of varying temperature fields on spherulitic morphology, given that E/P copolymers have been assessed to be highly undercoolable and crystallizable at resolvable levels, even at low temperature.³ The study was designed to discover a correlation between the optical appearance of specimens and temperature variation during crystallization. In particular, the discussion focuses on the presence of rings within spherulites.

EXPERIMENTAL

The E/P used in this study consisted of an iPP with 2.4% (weight percentage) of ethylenic units randomly distributed along the chain. This product, having a weight-average molecular weight $M_w = 216,000$, was kindly supplied by Montell Polyolefins Company (Ferrara, Italy).

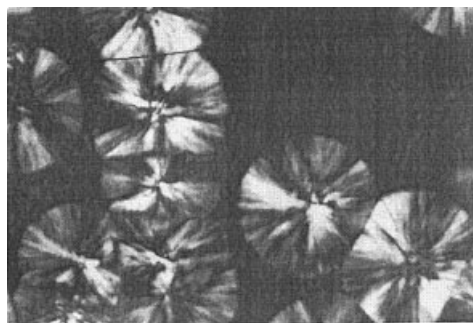
For optical observations, a small amount of E/P was pressed between a glass slide (1 mm thick) and a coverslip (0.15 mm thick) and then inserted in a Linkam LTS350 hot stage programmed by a TP92 unit. A Zeiss (Oberkochen, Germany) polarizing microscope equipped with a JVS TK-1085E video camera was used. The thickness of pressed samples was about 10 μm . In isothermal crystallization, specimens were

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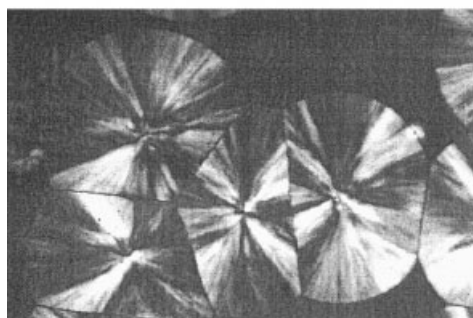
kept at 190°C for 10 min to destroy any previous trace of crystallinity and then rapidly brought (with a nominal scan rate of $-30^{\circ}\text{C}/\text{min}$) to the selected crystallization temperature, ranging between 120 and 142°C. The hot-stage device was maintained at constant temperature until primary crystallization was completed.

Crystallization was also performed in more than one step, exploiting the cessation of crystal growth caused by a sudden increase of temperature and the renewal of crystallization on cooling after each pause of growth. Specimens were rapidly cooled to a prefixed temperature T'_c in the temperature range 120–130°C after being maintained at 190°C for 10 min. Spherulites were allowed to nucleate and crystallize isothermally up to an average diameter of about 60–90 μm , sufficient to make clear observations. Then the temperature of the hot stage was rapidly set to a lower temperature, $T_c < T'_c$. By cooling at T_c , growth of E/P spherulites was observable within a shorter time, but still sufficiently long to perform repeated temperature changes before noticeable effects were observed. Indeed, after a few timed minutes (1–3) maintained at T_c , the temperature was set to a higher temperature T''_c ranging between 140 and 150°C. A few minutes later (1–5) the temperature was set again to T_c and this temperature variation $T''_c - T_c$ was repeated until primary crystallization was completed. The absolute value of the nominal scan rate was $30^{\circ}\text{C}/\text{min}$ throughout. It is worth noting that the initial step at a temperature T'_c was necessary to have uncrowded spherulites able to grow without interfering with one another during the subsequent cyclic temperature program. As a matter of fact, clear observations of spherulites during repeated temperature changes are possible only when spherulites are relatively large, well separated from one another, and grow at a relatively slow rate to appraise the effect of temperature changes.

The growth of spherulites in stepwise crystallization took place in a noncontinuous way and temporary stops were verifiable between two subsequent crystallization steps. Pictures were taken at appropriate time t and the radius r of spherulites was measured by using Image-Pro Plus software (Media Cybernetics), to estimate the linear growth rate G as the slope dr/dt of the straight line obtained by reporting r versus t . A graduated grid was used for length calibration. The maximum absolute error ΔG on experimental points (r , t) was calculated by the formula: $(|t| \cdot |\Delta r| + |r| \cdot |\Delta t|)/t^2$, assuming 1 μm as absolute error on radius Δr and 0.25 s as absolute error on time Δt . Differential scanning calorimetry (DSC) was carried out by a Mettler (Zurich, Switzerland) TA-3000, equipped with a TC10A/TC15 controller and programming unit. Weighed samples of about 10 mg sealed in 40- μL aluminium pans were first heated to 200°C, maintained at this temperature for 10 min, and then rapidly cooled (scan rate $-50^{\circ}\text{C}/\text{min}$) at a temperature T_c



(a)



(b)

Figure 1 E/P specimens isothermally crystallized at (a) 120°C and (b) 130°C. Magnification $\times 160$.

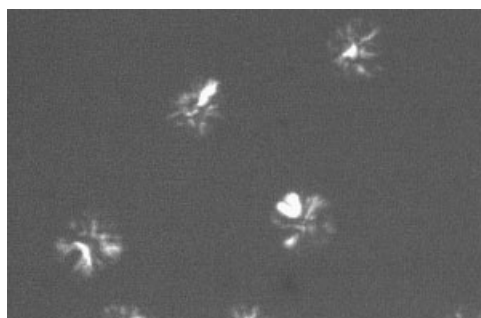
allowing partial crystallization for a few minutes. Afterward the temperature was rapidly increased (scan rate $50^{\circ}\text{C}/\text{min}$) to a high value T''_c , and kept constant for a few minutes before being decreased again to the previous temperature T_c . Conventional isothermal crystallizations were also performed by cooling from the melt and maintaining the temperature at a constant value, until heat evolution stopped.

Scanning electron microscopy (SEM) analysis on specimens crystallized in the DSC cell was performed using Philips 501 (Eindhoven, The Netherlands) equipment, after vacuum metallization of samples with Au-Pd alloy by means of a Polaron sputtering apparatus (Polaron plc, Hertfordshire, UK).

RESULTS AND DISCUSSION

Spherulites of E/P crystallized with isothermal procedures, in the range 120–142°C, appear to grow at a constant rate and do not exhibit band patterns, as shown in Figure 1.

However, when spherulites initially grown at a prefixed temperature T'_c , to a size suitable for visual observation, were submitted to repeated variation from a temperature T_c to a higher temperature T''_c , with $T_c \leq T'_c < T''_c$, a cyclic arrest of the growth was substantial at T''_c . Heating at the higher temperature T''_c during



(a)



(b)

Figure 2 (a) First isothermal stage at 130°C of a stepwise crystallization. (b) E/P spherulites whose growth at 120°C was cyclically interrupted by pauses at 150°C. Magnification $\times 160$.

crystallization at T_c caused an arrest of the growth of spherulites, whereas the growth restarted by cooling at the previous temperature T_c and concentric rings behind the growth front of spherulites were visible.

As an example, spherulites resulting from repeated temperature changes from 120 to 150°C, after an initial stage at 130°C, are shown in Figure 2. In the early isothermal stage of crystallization, shown in Figure 2(a), spherulites grew slowly at 130°C (growth rate $1.36 \pm 0.03 \mu\text{m}/\text{min}$) and no bands were seen. When spherulites reached a suitable size for observations, the temperature of the hot stage was rapidly de-

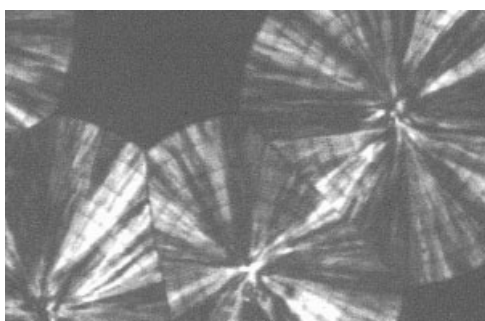


Figure 3 E/P spherulites grown under reiterated temperature variation from 140 to 120°C every 2 min. Magnification $\times 160$.

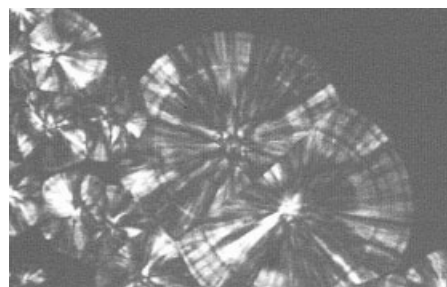


Figure 4 E/P spherulites grown under reiterated temperature changes from 140 to 120°C every minute. Magnification $\times 160$.

creased to 120°C. The rapid decrease in temperature made crystallization faster so that an enhancement of the spherulites size was readily observable and a dark concentric ring appeared within each spherulite. As the growth front of spherulites advanced, leaving behind a dark circumferential line, the temperature of the bench was raised to 150°C. The growth of spherulites progressed for 2 min before the temperature increase from 120 to 150°C caused a temporary cessation of crystallization of E/P. After 5 min, no growth was observed at all and the temperature was again decreased to 120°C and, after 2 min more, increased to 150°C. The latter temperature program was repeated many times. Thus a series of dark rings at an almost constant distance were generated, separating shells of E/P spherulites. The growth rate of spherulites during stepwise crystallization was recorded at $9.72 \pm 0.08 \mu\text{m}/\text{min}$ (i.e., equal, within experimental error, to the value obtained for mere isothermal crystallization at 120°C).

Spherulites resulting from repeated temperature changes from 120 to 140°C, after an initial stage at 130°C, are shown in Figure 3. The temperature increase from 120 to 140°C also caused a temporary stop of the crystallization of E/P because of the slow growth rate at 140°C ($0.11 \pm 0.03 \mu\text{m}/\text{min}$). After 2

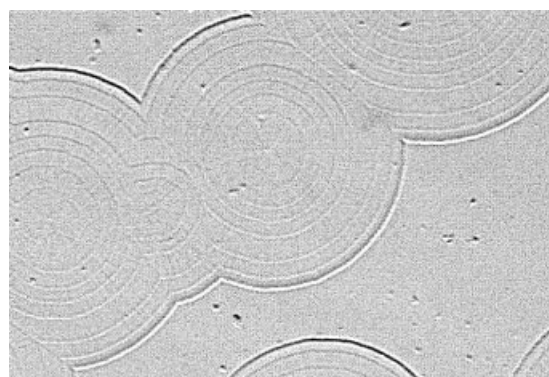


Figure 5 Micrographs of banded E/P spherulites under unpolarized light. Magnification $\times 130$.

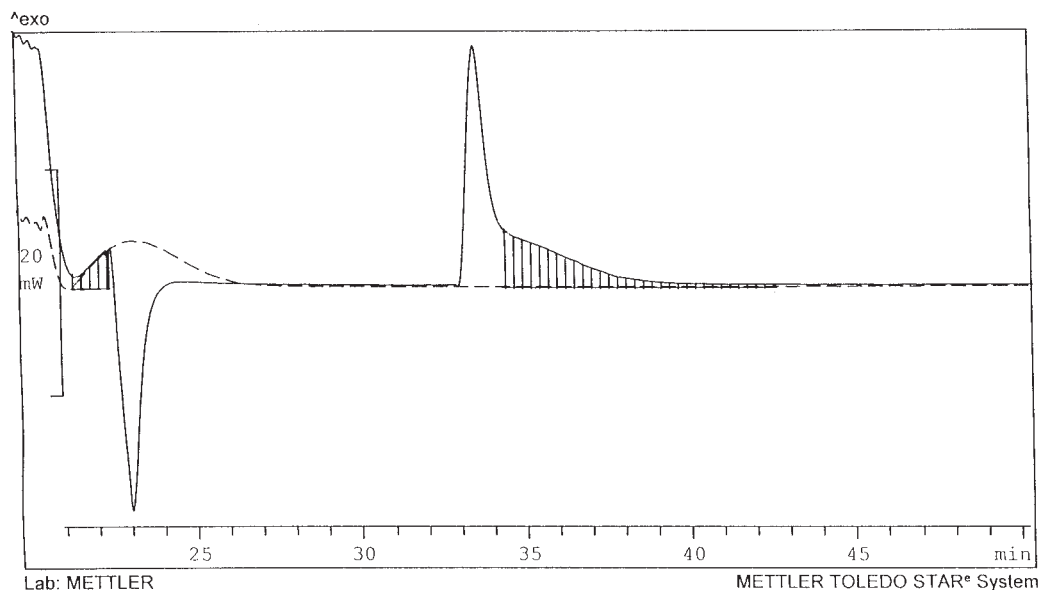


Figure 6 DSC crystallization curves. Dotted curve: isothermal crystallization peak of E/P at 112°C. Solid curve: crystallization was performed in two steps. The first step was obtained by keeping the specimen for 2 min at 112°C. The final stage of crystallization was postponed by increasing the temperature to 140°C for 10 min before reestablishing the previous crystallization temperature.

min of no observable growth, the temperature was again reduced to 120°C and, after 2 min more, raised to 140°C. The latter temperature program was repeated many times. The growth rate of spherulites during this stepwise crystallization was measured at $7.35 \pm 0.06 \mu\text{m}/\text{min}$ (i.e., slightly smaller than the value corresponding to continuous isothermal crystallization at 120°C).

By a comparison of Figure 2(b) and Figure 3, it is evident that by increasing the temperature T_c'' from 140 to 150°C, keeping constant the crystallization temperature T_c' , the thickness of shells increases as a consequence of achieving a higher crystallization rate.

Furthermore, the thickness of crystalline rims making up E/P spherulites was found to increase with increasing time elapsed at the lower crystallization

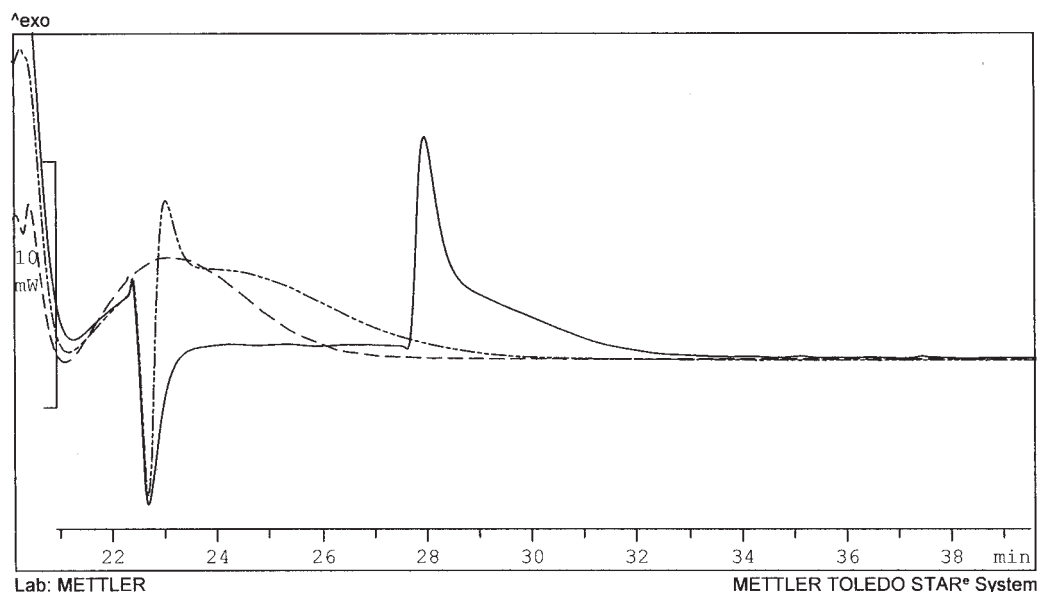


Figure 7 DSC crystallization curves. Dotted curve: isothermal crystallization peak of E/P at 112°C. Dash-dotted curve: crystallization was carried out in two steps at 112°C, separated by a short heat impulse at 122°C. Solid curve: after an initial stage of 2 min at 112°C, the final stage of crystallization at 112°C was postponed by increasing the temperature to 122°C for 5 min.

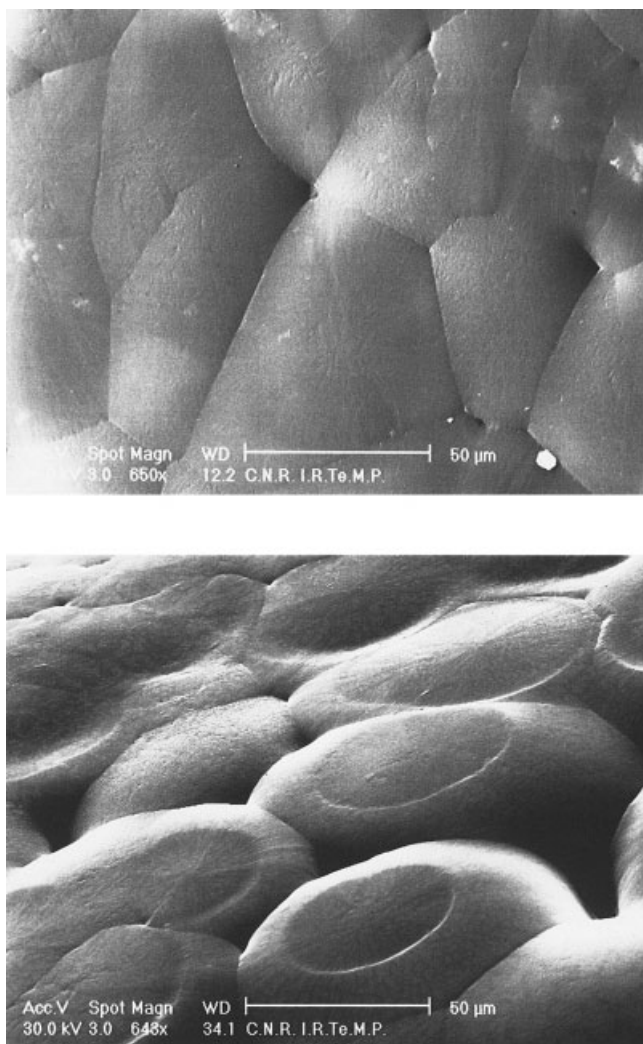


Figure 8 SEM micrographs of surfaces of E/P crystallized in a DSC cell: (a) specimen isothermally crystallized at 112°C; (b) specimen crystallized at 112°C in two steps by temporarily arresting the crystallization at 140°C for 10 min.

temperature. As an example, in Figure 4, spherulites obtained by changing the temperature from 120 to 140°C every minute, are shown. By comparison with Figure 3, it is evident that the shorter the time spent at the lower temperature, the thinner the spherulite shells.

In Figure 5 the E/P spherulites, during cyclic crystallization at 120°C, are shown under nonpolarized light. Note that the fourth shell is thicker than others because it was obtained by maintaining the specimen at 120°C for one additional minute (that is 3 instead of 2 min) before increasing the temperature to 140°C.

DSC measurements also showed that the heating of specimens during isothermal crystallization is an effective way to stop crystallization and that solidification proceeds when the previous temperature is reestablished. As an example, the DSC curve of an E/P

specimen partially crystallized at 112°C for 2 min, then kept at 140°C for 10 min before complete crystallization at 112°C, is shown in Figure 6, together with the crystallization peak of a specimen isothermally crystallized at 112°C. Note that the two sharper peaks are attributed to heat flow during temperature settling of the device, whereas heat evolution from the E/P specimens during crystallization follows the etched stretches of the broad peak, interrupted by a period of 10 min, during which no heat evolution is registered. Similar DSC curves were also obtained by heating at a temperature below 140°C, as shown in Figure 7, demonstrating that a brief temperature increase is responsible for cessation of crystallization rather than for deceleration of crystallization.

SEM analysis of E/P specimens, crystallized in two stages in the calorimetric cell, revealed the presence of a circumferential ring within the spherulites, as shown in Figure 8. These rings separate the two distinct stages of an isothermal crystallization interrupted by a heating cycle at high temperature.

Thin black rings within iPP spherulites were first noted by Way and Atkinson in specimens maintained at 157°C for 13 h and successively cooled to room temperature before the solidification was complete.^{9,10} To my knowledge, no other investigations on the origin of dark rings existing in undeformed iPP grown in a temperature field have been carried out, despite the importance of structural discontinuities in determining final properties of materials.

Although the arrest of E/P crystallization by increasing the temperature may be ascribed to heat accumulation at the spherulites' growth front,² which hinders further crystallization, the different values of the thermal expansion coefficient of liquid and solid phases should account for the appearance of rings by subsequent cooling. It is well known that the specific volume of a liquid phase varies with the temperature faster than that of the corresponding solid phase. During isothermal crystallization the contraction of specimens is attributed only to the smaller specific volume of crystals with respect to liquid, and a decrease of specific volume of crystallizing PP is observed with decreasing liquid phase. For iPP, representative specific volume ranges are 1.176–1.172 and 1.073–1.060 for liquid and solid, respectively.¹¹ In the present stepwise crystallization of E/P specimens, an expansion of the melt phase larger than that of the spherulites occurs by increasing the temperature between two subsequent crystallization steps; a higher contraction of the liquid phase surrounding spherulites also occurs by cooling. Therefore, the appearance of banding by cooling must be attributed to movement of the liquid, beginning to crystallize, around preformed spherulites.

CONCLUSIONS

This study shows an unusual banded morphology of E/P spherulites arising in the presence of varying temperature fields and observable as dark rings within spherulites under an optical microscope. SEM analysis revealed circumferential steps on the spherulites' surface of E/P specimens crystallized in a varying temperature field, leading to the conclusion that banding is the result of different percentages of volume contraction of liquid and solid phases during cooling.

The importance of banding in determining ultimate properties of the bulk material could allow modification of useful properties, such as mechanical resistance and permeability, just by exploiting temperature variations during crystallization.

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References

1. Keith, H. D.; Loomis, T. C. *J Polym Sci Part B: Polym Phys* 1984, 22, 295.
2. Raimo, M.; Cascone, E.; Martuscelli, E. *J Mater Sci* 2001, 36, 3591.
3. Varga, J. *J Mater Sci* 1992, 27, 2557.
4. Lovinger, A. J.; Chua, J. O.; Gryte, C. C. *J Polym Sci Part B: Polym Phys* 1977, 15, 641.
5. Fillon, B.; Thierry, A.; Wittmann, J. C.; Lotz, B. *J Polym Sci Part B: Polym Phys* 1993, 31, 1407.
6. Fillon, B.; Wittmann, J. C.; Lotz, B.; Thierry, A. *J Polym Sci Part B: Polym Phys* 1993, 31, 1383.
7. Varga, J.; Schulek-Toth, F.; Ille, A. *Colloid Polym Sci* 1991, 269, 655.
8. Padden, F. J.; Keith, H. D. *J Appl Phys* 1959, 30, 1479.
9. Way, J. L.; Atkinson, J. R. *J Mater Sci Lett* 1972, 7, 1345.
10. Way, J. L.; Atkinson, J. R. *J Mater Sci* 1972, 6, 102.
11. Miller, R. L. In: *Crystallographic Data for Various Polymers*; Brandrup, J.; Immergut, E. H., Eds.; Polymer Handbook; Wiley-Interscience: New York, 1996; Sect. III, pp. 1-60.