J Mater Sci (2007) 42:1245–1250
DOI 10.1007/s10853-006-1395-7

# Effect of composition on transcrystallization with reorientation of polypropylene in drawn PET/PP blend

**A. A. Apostolov · M. Evstatiev · Z. Denchev ·
K. Friedrich · S. Fakirov**

Received: 27 July 2004 / Accepted: 9 February 2006 / Published online: 21 January 2007

**Abstract** The crystallization behaviour of three blend compositions of poly(ethylene terephthalate)/polypropylene (PET/PP), namely 30/70, 50/50 and 70/30 wt.% was studied. The samples were heated up to temperature between the melting temperatures of the blend components and then cooled to 30 °C. X-ray pictures were taken at every stage and it was shown that a recrystallization with reorientation of the PP crystallites took place during the nonisothermal recrystallization. The PP crystallites in the PET/PP blend reorient with molecular axis tilted at aprox. 49° against the FA during the recrystallization. The amount of PP in the blend does not directly affect the process of trancrystallization with reorientation but has only a masking effect. Such reorientation was observed for all three blends. No reorientation occurs if the PET crystallites have been melted before the recrystallization, i.e., when oriented they induce the reorientation of the PP crystallites.

## Introduction

Recently we reported on an uncommon phenomenon—transcrystallization with reorientation in cold drawn polymer blends after melting of one of components and subsequent crystallization [1–4]. This was observed in the following blends: poly(ethylene terephthalate)/polyamide 12 (PET/PA12) [1], PET/polypropylene (PET/PP) [2, 3], PET/polyethylene (PET/PE) [2, 4], and polyamide 66/PP (PA66/PP) [3]. What is interesting, the degree of reorientation with respect to the original fibre axis (FA) direction, as revealed by wide-angle X-ray scattering (WAXS), is different in the various systems. While in the drawn PET/PA12 blend the transcrystallization of PA12 takes place with reorientation on 90° after its melting and cooling to 30 °C, in the systems PET/PP this angle is only approx. 49° (tilt of the *c*-axis against the FA after the reorientation) [3]. In PA66/PP PP no reorientation occurs after the recrystallization but the reflections are much wider (in azimuthal direction) than the point-like reflections before the recrystallization [3], i.e., the strong initial orientation worsens considerably. In addition, it was found that the epitaxial reorientational effect of PET microfibrils in the drawn blends is much stronger than that of PA66 [3]. Let us remind that melting of the low-melting component of the blend is the essential step of preparation of the new polymer–polymer composites, the nanostructured polymer composites (NPC) [2, 5–7], where the isotropic polymer matrix is reinforced by polymer nanostructures of microfibrillar type [8]. In contrast to the common glass–fibre reinforced composites when the polymer is melt-blended with fibres, the NPC are prepared by melt-blending of two components (distinguished by different melting temperatures), followed by cold drawing of the blend, aiming at a good orientation. The thermal treatment of the oriented blend is carried out at temperatures between the melting temperatures

---

A. A. Apostolov (✉) · M. Evstatiev · Z. Denchev ·
S. Fakirov
Laboratory on Structure and Properties of Polymers,
University of Sofia, 1164 Sofia, Bulgaria
e-mail: apostolov@chem.uni-sofia.bg

K. Friedrich
Institute for Composite Materials Ltd., University
of Kaiserslautern, 67663 Kaiserslautern, Germany

of the two components of the blend and results in melting of the lower melting component converting it in an isotropic state. During the subsequent cooling period, this component crystallizes, but not anymore in oriented state as proved by WAXS investigations [5, 9]. In this way, after isotropization of one of the components of the blend and preserving the microfibrillar nanostructure of the higher melting component, the NPC is produced.

Before displaying and discussing the obtained results let us remind some basic characteristics of the transcrystallization phenomenon. A special case of crystallization, first reported with short-fibre reinforced polymer composites, is the transcrystallization. It takes place when heterogeneous nucleation occurs with sufficiently high density along a fibre surface and the resulting crystal growth is restricted to the lateral direction, so that a columnar layer develops around the embedded fibre. This nucleation of the transcrystallised region on the reinforcing fibre is thought to be central to the improvement of some composite properties [10]. The transcrystallization is a function of nucleating activity of the fibre surface and crystallization kinetics of the resin matrix [10].

It has been concluded [11] that the fibre surface tends to induce nucleation of matrix under the following conditions: (i) a topographical match between the fibre and the matrix; (ii) a thermal conductivity mismatch between the fibre and the matrix; (iii) an extensional flow field developed by processing conditions, or (iv) a high surface free energy on the fibre. Depending on the mechanism involved, different cases for mutual arrangement of the polymer chains in the reinforced fibres and the surrounding matrix are reported. For instance, in cellulose/PP composites, the chains of PP are parallel to the fibre axis [12]. The same case dominates in some advanced polymer composites based on polyetherketoneketone and polyetheretherketone reinforced by carbon, Kevlar, or glass fibres [11].

In a study on aramid and carbon fibre reinforced PA66 composites, atomic force microscopy reveals radial regularity in the transcrystallinity layer, relative to the fibre, and X-ray diffraction investigations of the isolated layer suggest that the polymer chain is oriented predominantly perpendicular to the fibre axis [13].

Coming back to the system PET/PA12 it should be noted that it has also another peculiarity—further increase of the degree of crystallinity of PA12 (through additional isothermal crystallization for certain time during the cooling) results in weakening of the observed effect of reorientation possibly due to the masking from the increasing isotropic crystalline mass in the bulk [1].

Taking into account the two facts, namely the well known strong ability of PP to form transcrystalline layers in the fibre reinforced composites [14, 15] and the recently found opportunity to study the very early crystallization stages in order to determine the chain orientation by means of X-ray radiation from synchrotron source [1, 3, 4] it looks challenging to investigate the effect of blend component ratio on the crystallization behaviour of PP on a substrate representing highly oriented well documented [8] polymeric microfibrils.

## Experimental

### Blend preparation

Three blend compositions of PET/PP were prepared, namely 30/70, 50/50 and 70/30 wt.%. Melt-blended, extruded and cold drawn PET/PP bristles were obtained and subsequently annealed at 140 °C for 6 h with fixed ends in a vacuum oven. WAXS patterns were taken by means of synchrotron source at 30, at 200 °C when PP is in a completely molten state, and again at 30 °C after the subsequent cooling. More about the experimental details can be found in [3]. Isotactic polypropylene was selected for this study since its WAXS reflections were very strong, as compared, for instance, with those of PA12 and demonstrating the same ability for reorientation during crystallization [1].

### Determination of the orientation

The Miller indexes of alpha-PP were assigned to the crystallographic planes with the aid of the scattering patterns from neat $\alpha$-PP [16]. In order to characterise the orientation of the PP crystallites before and after the recrystallization, the indexes of the respective planes ($H_1K_1L_1$) and ($H_2K_2L_2$) perpendicular to the fibre axis (FA) were found as explained in [3]. Briefly, the procedure is as follows: *Before* the recrystallization the *c*-axis of the PP-crystallites is near parallel to FA, i.e. [001] direction of PP is parallel to FA. The indexes ($H_1K_1L_1$) were found using the perpendicularity condition for the monoclinic cell [17]. Than the angles $\rho_{hkl}$ between the plane ($H_1K_1L_1$) and the set of planes ($h_1k_1l_1$), ($h_2k_2l_2$), ($h_3k_3l_3$)...corresponding to the successive reflexes of $\alpha$-PP, namely (110), (040), (130) etc. were calculated on the basis of the alpha-PP unit cell parameters ($a = 6.65$ Å, $b = 20.96$ Å, $c = 6.5$ Å; $\beta = 99.33°$) [17, 18]. They were transformed into sets of angles $\alpha_{calc}$ according to Cullity [19] ($\theta$ is the Bragg's angle):

$$\cos \rho_{hkl} = \cos \theta \cos \alpha_{calc} \qquad (1)$$

that in turn were compared with $\alpha_{meas}$, the azimuthal angles of each reflex (hkl) on the respective flat X-ray pattern. The satisfactory match confirmed the right choice of ($H_1K_1L_1$) and thus the orientation of α-PP before the recrystallization.

*After* the recrystallization the PP-crystallites are oriented with a certain set of planes ($H_2K_2L_2$) near perpendicular to FA hence this set of the planes represents the orientation. The angles $\rho_{hkl}$ between the plane ($H_2K_2L_2$) and the set of planes ($h_1k_1l_1$), ($h_2k_2l_2$), ($h_3k_3l_3$)...corresponding to the successive reflexes of α-PP, namely (110), (040), (130) etc. were calculated, transformed into sets of angles $\alpha_{calc}$ and compared with $\alpha_{meas}$, as already shown above. The satisfactory match yielded the right choice of ($H_2K_2L_2$) and thus the orientation of α-PP after the recrystallization. Since α-PP cell is monoclinic all calculated numbers $H_1$, $K_1$, $L_1$, $H_2$, $K_2$, and $L_2$ turned out not to be integers and were rounded to the closest integers.

## Results and discussion

In Fig. 1 are displayed the WAXS patterns of predrawn ($\lambda = 4$) bristles of PET/PP blend in various ratios, taken by means of synchrotron radiation. The patterns are taken at different temperatures, 30 or 200 °C after the respective thermal treatment before the measurements. In Fig. 1a the scattering pattern of the initial material (30/70 wt.% blend, before the recrystallization) taken at 30 °C is shown. Typical pattern for highly oriented polymer can be seen in accordance with the expectation (both blend components, PET and PP have been subject to cold drawing ($\lambda = 4$) followed by a crystallization at temperature $T_a = 140$ °C before the X-ray analysis). What is important in this case is the fact that the two components have the same orientation direction, *c*-axis parallel to the FA direction, which is vertical and lies in the plane of the sheet (Fig. 1a). Further, one can see that the reflections arising from the two components are superimposed to a great extent. They can be separated, i.e. visualization of the reflections of only one of the components can be performed if the WAXS pattern is taken at temperature where the other component is in a molten state. Such a case is presented in Fig. 1b for the PET/PP (30/70 wt.%) blend taken at 200 °C. Only the reflections of the higher melting component (PET, melting temperature $T_m = 256$ °C against $T_m = 171$ °C of PP) can be seen. The same pattern shows that PP is in amorphous state at 200 °C. What is more, this state is completely isotropic. On the contrary, PET, being in a highly oriented state, preserves its original orientation.

The situation when the partially molten sample is cooled down from 200 to 30 °C, presented in Fig. 1c, is completely different. During cooling PP again crystallizes, but it does not crystallize isotropically. Moreover, the PP crystallites do not preserve their original orientation, i.e., *c*-axis parallel to the FA but become tilted against it. Thus, one deals with a process of transcrystallization with reorientation [3].

More detailed analysis of Fig. 1a and b, including subtraction from the starting pattern (Fig. 1a) that taken at 200 °C (Fig. 1b) as well as Fig. 1b from that on Fig. 1c, made possible to eliminate the reflections of PET and to obtain only those of PP for the starting material as well as after the non-isothermal crystallization, respectively, as it has been done in ref. [3]. Here we will briefly show the way the orientations of PP before and after the recrystallization were determined without using such subtractions. The higher amount of PP in the present case (70 vs. 50 wt.% in [3]) gave stronger PP-reflections that facilitated the determination of its orientation. As described in Experimental part, using the Miller indexes of the reflections, their number and position, by the method of trials and errors the sets of planes {–106} and {101} were found to be near perpendicular to FA before (Fig. 1a) and after (Fig. 1c) the recrystallization, respectively. The Miller indexes and corresponding twice Bragg's angles two theta of some reflections in the X-ray patterns (Fig. 1a, c) are presented in Table 1. Also given are the intensities, the angles $\alpha_{meas}$ measured from the meridian to the centre of each reflection in the corresponding X-ray patterns, and the angle $\alpha_{calc}$ calculated according to (1) and using the above values of the two sets of Miller indexes before (Fig. 1a) and after (Fig. 1c) the recrystallization.

Further on the angle between these two sets of planes was calculated according to [20] to be approx. 49° meaning that the chain axis of PP was tilted by approx. 49° against the FA after the recrystallization similarly to the previous finding [3]. It is quite clear that one deals with transcrystallization when the well-documented PET microfibrils [9, 11] play the role of nucleating agent, in analogy with various reinforcing fibres [10, 11, 21] in the common composites. The significant difference between the two cases—the classical composites and the NPC—is that in the second case the PET microfibrils do not only promote the

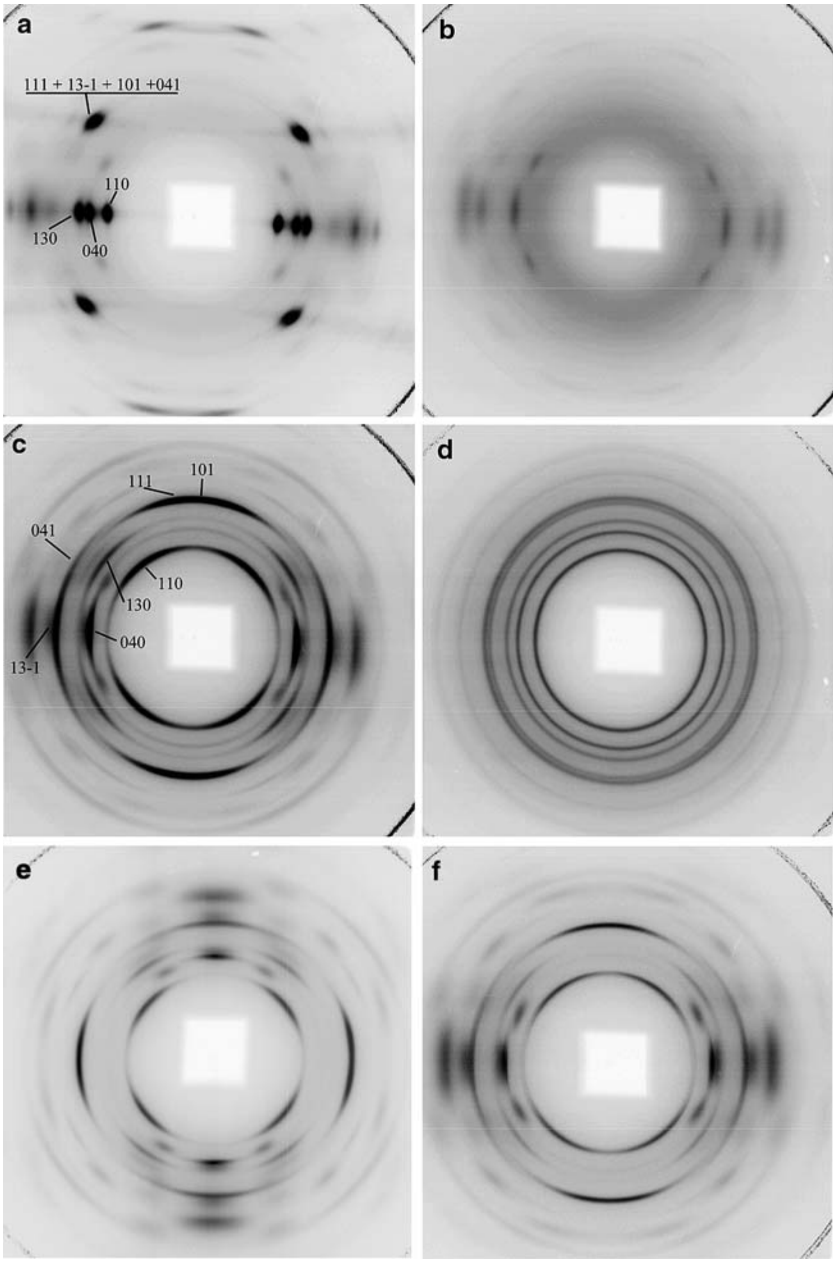

**Fig. 1** Wide-angle X-ray scattering patterns, taken using synchrotron radiation, of drawn and annealed PET/PP samples with various composition (wt.%) taken at different temperatures after respective treatment: (**a**) 30/70 blend, pattern taken at 30 °C; (**b**) 30/70 blend, pattern taken at 200 °C after keeping the blend for 1 min at 200 °C; (**c**) 30/70 blend, pattern taken at 30 °C after keeping the blend for 1 min at 200 °C; (**d**) 50/50 blend, pattern taken at 30 ° C after keeping the blend for 5 min at 280 °C; (**e**) 50/50 blend, pattern taken at 30 °C after keeping the blend for 1 min at 200 °C, and (**f**) 70/30 blend, pattern taken at 30 °C after keeping the blend for 1 min at 200 °C. FA is vertical and lies in the plane of the sheet

crystallization, but they also affect the orientation of the matrix chains during the transcrystallization in such a way that the latter are not any more parallel but tilted against the chain direction of PET, i.e. FA.

As far as the PET orientation is concerned, PET exhibits a well-known fibre texture with *c*-axis near parallel to FA [3]. This texture is better seen in Fig. 1b, but might be also recognized in Fig. 1a, c, e and f. It does not change neither after the melting of PP nor after its recrystallization. The presence of such texture, though, determines the reorientation of PP after the recrystallization. This assumption about the crucial role of the PET nanostructures for the crystallization and reorientation of the low-melting blend component can be easily checked by heating the blend up to a temperature well above the $T_m$ of PET, followed by cooling down to 30 °C in order to allow again non-isothermal crystallization.

In Fig. 1d the WAXS taken at 30 °C after keeping the PET/PP blend at 280 °C for 5 min is shown. One can see rather perfect isointensity circles arising from the two homopolymers and demonstrating that the two components crystallize in a fully isotropic state during cooling. Since in this case PET crystallizes in isotropic

**Table 1** Miller indexes and corresponding twice Bragg's angle two theta of some reflections on the X-ray pattern

| hkl | $2\theta$, deg | Before recrystallization | | | After recrystallization | | |
|---|---|---|---|---|---|---|---|
| | | Intensity | $\alpha_{calc}$, deg | $\alpha_{meas}$, deg | Intensity | $\alpha_{meas}$, deg | $\alpha_{calc}$, deg |
| 110 | 14.1 | vs | 90 | 90 | s | 38 | 43 |
| 040 | 16.9 | vs | 90 | 90 | vs | 90 | 90 |
| 130 | 18.6 | vs | 90 | 90 | w | 51–53[a] | 56 |
| 101 | 20.9 | s | 48[b] | 48 | vs | 0 | 0 |
| 111 | 21.3 | s | 49[b] | | vs | 2–8[c] | 4 |
| –131 | 21.9 | s | 50[b] | | m | 80–90[d] | 89 |
| 041 | 21.9 | s | 50[b] | | vw | 58–64[a] | 60 |

Also given are the intensity, the azimuthal angle $\alpha_{meas}$ measured from the meridian to the center of each reflection and the angle $\alpha_{calc}$ calculated according to (1) (see Experimental) both before and after the recrystallization

[a] Since this reflection is week or very week its position is only approximate

[b] These four reflections overlap before the recrystallization

[c] The two symmetrical with respect to the meridian reflections of the form {111} overlap together with (101) that is situated on the meridian

[d] The two symmetrical with respect to the equator reflections of the form {–131} overlap

state it can not induce any orientation of PP during its own crystallization.

As mentioned at the beginning, in studying the system PET/PA12 an attempt was undertaken to better express the effect of reorientation in the WAXS pattern applying isothermal crystallization during cooling from 200 °C, which failed. Possible explanation could be the known fact that the transcrystalline layers represent spherulitic columnar structures positioned perpendicular to the fibre axis. Their height is about several tenths of a micron. What is more, at larger distance from the glass fibres, i.e., outside the columnar structures, the PP matrix crystallizes completely isotropic. There is not any preferred orientation of spherulites with respect to the glass fibres axis.

In order to check the above assumption WAXS patterns were taken from PET/PP predrawn and annealed blends with various compositions (30/70, 50/50, 70/30 wt.%) at 30 °C after cooling from 200 °C. The respective patterns are shown in Fig. 1c, e, f.

One can see that all of them demonstrate the observed [3] effect of transcrystallization with reorientation (49° [3]) with respect to the initial orientation direction (FA)). What makes difference is the slight tendency of isotropisation with increase of the PP content in the blends as can be concluded by more precise inspection of the patterns (Fig. 1c, e, f). It is somewhat hard to see this tendency for the sample 50/50 (Fig. 1e) since in this sample there is better orientation of the PET component in comparison to sample 30/70 (Fig. 1c). The above-mentioned differences are hardly related to the direct effect of the composition on the transcrystallization process so far the amount of PP involved in the transcrystalline layers is negligible as compared to the respective total amount of PP in the blends. Assuming that the transcrystallization (and the reorientation of PP chains) takes place in the same way for the three blend compositions 30/70, 50/50, 70/30 wt.% (Fig. 1c, e and f, respectively) and taking into account the well known fact that the spherulitic crystallization in the bulk is completely isotropic one, another explanation of the observed differences seems more acceptable. Obviously, as assumed in the case of PET/PA12 [1], lesser-expressed tendency of reorientation during the transcrystallization is due to the masking effect of the crystallites from the bulk material. The more the PP content in the blend the stronger this masking effect should be. It is just this situation observed on the last three patterns in Fig. 1—the sample with the largest PP content in the blend (70 wt.%) shows the weakest orientation (Fig. 1c). As a matter of fact, Fig. 1c can be considered as a sum of Fig. 1f (the blend with the lowest, 30 wt.% PP) and the scattering pattern of the fully isotropically crystallized material as shown in Fig. 1d.

Quite recently, the orientation of the polypropylene matrix in PET reinforced composites was examined by scanning and transmission electron microscopy (SEM) and TEM [22]. It was directly shown that the polymer microfibrils of PET promote transcrystallization also in PP matrix. It was found that the PP lamellae were aligned perpendicular (or tilted, since in TEM we see their projection) against the microfibril surface in direct vicinity of the microfibrils and more or less parallel to them in a distance [22].

In another recent work, by the use of TEM and staining technique, the orientation of the polyethylene matrix in PET reinforced composites was examined [23]. It was found that the PE lamellae were differently organized depending on how close to the surface of the PET microfibrils they are. In the bulk material, i.e., far away from the microfibrils, the PE lamellae are dispersed quasi-homogeneously, showing no preferred orientation, whereas near the microfibrils they are placed strongly parallel to each other and perpendicular to their surface [23].

Starting from previous observations on the same system [3] and on the PET/PA12 blend [1] as well as from the present results, a conclusion can be drawn that the amount of the transcrystallising component in the blend does not directly affect the reorientation tendency of the transcrystallised material but only masks this effect.

## Conclusions

The application of synchrotron radiation for WAXS studies offers the opportunity to observe the very first stages of crystallization and to reveal the chain orientation of the crystallized fractions. A strong epitaxial effect of the nanostructures of microfibrillar type (PET) on the non-isothermal crystallization behaviour of PP during cooling from 200 to 30 °C temperature is observed in cold drawn PET/PP blend. The PP crystallites in the PET/PP blend reorient with molecular axis tilted at aprox. 49° against the FA during the recrystallisation. The amount of PP in the blend does not directly affect the process of trancrystallization with reorientation but has only a masking effect.

**Acknowledgements** The financial support of the Alexander von Humboldt Foundation, Germany, through Institute Partnership Program (Project ( 4585) is greatly acknowledged. WAXS investigations were supported by HASYLAB, Hamburg, Germany. The authors thank Dr. D. Sapoundjieva for her help during X-ray measurements.

## References

1. Sapoundjieva D, Denchev Z, Evstatiev M, Fakirov S, Stribeck N, Stamm M (1999) J Mater Sci 34:3063
2. Evstatiev M, Fakirov S, Friedrich K (2000) In: Cunha AM, Fakirov S (eds) Structure development during polymer processing. Kluwer Academic Publishers, Dordrecht, p 311
3. Apostolov AA, Samokovliyski O, Fakirov S, Stribeck N, Denchev Z, Evstatiev M, Friedrich K, Funari SS (2005) Prog Colloid Polym Sci 130:159
4. Evstatiev M, Apostolov AA, Denchev Z, Fakirov S (2004) Int J Polym Mater 53:847
5. Evstatiev M, Fakirov S (1992) Polymer 33:877
6. Fakirov S, Evstatiev M (1994) Adv Mater 6:395
7. Fakirov S, Evstatiev M, Friedrich K (2000) In: Paul DR, Bucknall CB (eds) Polymer blends, vol 2: performance. John Wiley & Sons, New York, p 455
8. Evstatiev M, Fakirov S, Nikolov N (1996) Polymer 39:1667
9. Fakirov S, Evstatiev M, Friedrich K (2002) In: Fakirov S (ed) Handbook of thermoplastic polyesters, vol 2, chapter 23. Wiley-VCH, Weinheim, p 1093
10. Peacock JA, Hill B, Niel E, Barlow CY (1986) In: Ishida H, König JL (eds) Composites interfaces. Elsevier, New York, p 143
11. Chen EJH, Hsiao BS (1992) Polym Eng Sci 32:280
12. Felix JM, Gaterholm P (1994) J Mater Sci 29:3043
13. Klein M, Marom G, Wachtel E (1996) Polymer 37:5493
14. Varga J (1995) In: Karger-Kocsis J (ed) Polypropylene structure, blends and composites, vol 1. Chapman and Hall, London, p 56
15. Riekel C, Karger-Kocsis J (1999) Polymer 40:541
16. Seth KK, Kempster CJE (1976) J Polym Sci-Pol Symp 58:297
17. Donnay JDH, Donnay G (1972) In: International tables for x-ray crystallography, vol I. The Kynoch Press, Birningam, England, p 107
18. Clark ES (1996) In: Mark JE (ed) Physical properties of polymers handbook. American Institute of Physics, Woodbury, New York, p 411
19. Cullity BD, Stock SR (2001) Elements of x-ray diffraction. Pearson Education International, USA, p 408
20. Ibid, p 621
21. Kumamaru F, Oono T, Kajivama T, Takayanagi M (1983) Polym Compos 4:141
22. Krumova M, Michler G, Evstatiev M, Friedrich K, Stribeck N, Fakirov S (2005) Progr Coll Polym Sci 130:167
23. Fakirov S, Kamo H, Evstatiev M, Friedrich K (2005) J Macromol Sci-Phys 44:149