Available online at www.sciencedirect.com

SCIENCE DIRECT

Polymer 46 (2005) 9549–9554

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Polymorphism of syndiotactic polystyrene: γ phase crystallization induced by bulky non-guest solvents

Paola Rizzo*, Alexandra R. Albunia, Gaetano Guerra

Dipartimento di Chimica, Università degli Studi di Salerno, via S.Allende, 84081 Baronissi (SA), Italy

Received 19 April 2005; received in revised form 14 July 2005; accepted 19 July 2005
Available online 21 September 2005

Abstract

The crystallization of amorphous syndiotactic polystyrene (s-PS) films when induced by bulky solvents, whose molecules are too big to be enclosed as guest of s-PS clathrate phases, generally leads to the formation of γ-phase. This kind of solvent induced crystallization in amorphous films generates a preferential (200) uniplanar orientation of the γ-crystalline phase. Moreover, the presence of highly boiling solvents in the amorphous phase of these γ-form samples can induce a γ→β phase transition, as a consequence of thermal annealing procedures at atmospheric pressure. A comparison with literature data suggests that the formation of the thermodynamically stable β-phase is generally favored with respect to the formation of the kinetically favored α-phase, by any s-PS dilution.

Keywords: Solvent induced crystallization; Syndiotactic polystyrene; Polymorphism

1. Introduction

Syndiotactic polystyrene (s-PS) is characterized by a complex polymorphic behavior, which, making some simplifications, can be described in terms of two crystalline forms, α and β, containing planar zigzag chains and two forms, γ and δ, containing s(2/1)2 helical chains (generated by TTGG conformational sequences [1,2]). Moreover, several molecular complexes between different guest molecules and s-PS s(2/1)2 helical chains (clathrate [3–7] and intercalate [8] crystalline phases) have been also obtained. The polymorphic behavior of s-PS is further complicated by the occurrence of different modifications of the trans planar α- and β-phases, ranging between limit disordered (α' and β') and limit ordered (α'' and β'') modifications [1,2,8–14]. A schematic summary of crystallization and interconversion conditions between s-PS polymorphic phases is shown in Fig. 1 and it encloses information prevailingly already available before 1992 [1,2, 15–17]. In fact, only the achievement of the nanoporous δ-phase was reported later [18,19] and disclosed in the open literature after 1997 [20–24]. For the sake of simplicity, the scheme of Fig. 1 does not enclose the mesomorphic *trans* planar [25–27] and helical [28] phases, which have been also studied in detail.

Several studies have shown that molecular interactions of s-PS with other molecules can significantly change the crystallization and phase interconversion routes, generally favoring the clathrate phases for room temperature treatments and the β-phase for high temperature treatments [12–14].

As for room temperature treatments, it is well known that hundreds of organic molecules are readily absorbed from air or water (also when present at low concentrations) as guest (*G*) of δ-form nanoporous phases, eventually leading to the formation of s-PS/G molecular complexes [20–24]. Room temperature treatments of s-PS amorphous samples (and often also of α- and γ-form samples) by some of these guest molecules (e.g. chloroform, methylenechloride 1,2-dichloroethane, tetrachloroethane, benzene, toluene, tetrahydrofuran, carbon disulfide etc. indicated as G' in Fig. 1) at high concentrations also induce the formation of molecular complexes [16,29,30]. On the other hand, other guest molecules (e.g. acetone [31,32], compressed carbon dioxide [33], limonene, carvone indicated as G'' in Fig. 1) at high concentrations induce the crystallization of amorphous samples in the γ-phase.

---

* Corresponding author. Tel.: +39 89 965362; fax: +39 89 965296.
E-mail address: prizzo@unisa.it (P. Rizzo).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.07.063

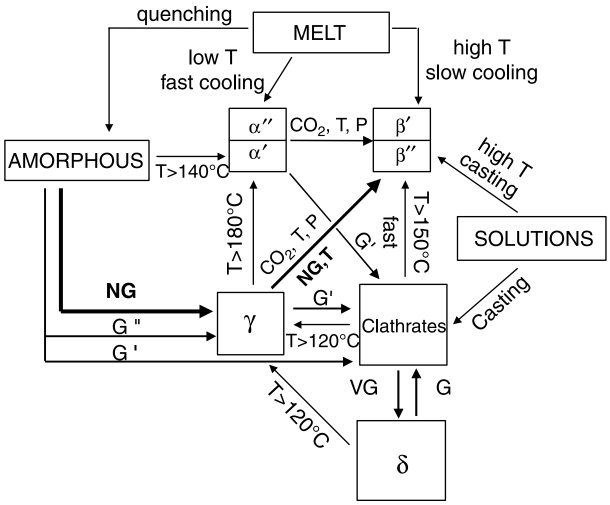

Fig. 1. Schematic representation of the main crystallization and interconversion conditions for the polymorphic crystalline phases of syndiotactic polystyrene. G, VG and NG stand for molecules, which are guest (G), or volatile guest (VG), or non-guest (NG) of the nanoporous δ-phase. G' and G'' stand for subclasses of guest molecules defined in the introduction. T and P indicate increases of temperature and pressure, respectively. Thick lines indicate interconversion routes shown in this paper.

As for high temperature treatments, most of the observed changes of the interconversion routes between s-PS phases, due to molecular interactions with other molecules, tend to favor the thermodynamically stable β-phase [2,34–36] with respect to the kinetically favored α-phase. For instance, while all annealing procedures on samples presenting the nanoporous δ-phase always lead to the γ-phase and subsequently to the α-phase, the high temperature annealing (above 150 °C) of clathrate samples, when the annealing temperature is suddenly reached [1] can produce a direct transformation into the β-form [13–14]. In addition, as for cold-crystallization of glassy samples, direct crystallization in the β-phase (rather than in the usual α-phase) has been achieved for miscible blends of s-PS with poly(2,6-dimethyl-1,4-diphenyleneoxide) (PPO) [37,38] as well as a consequence of treatments with compressed CO_2 [39]. It has been also shown that s-PS annealing with compressed CO_2 (57 atm) can produce α → β [39] as well as γ → β phase transitions [39,40]. This latter transition has also been observed for thermal treatments in the presence of suitable solvents like cyclohexanol [41] or 1,1,2,2-tetrachloroethane [42].

In this paper, we show that room temperature treatments of s-PS amorphous samples with bulky solvents, whose molecules are too big to be enclosed as guest of s-PS clathrate phases [23,43] indicated as non-guest (NG) in Fig. 1, induce direct crystallization in the γ-phase. This NG solvent induced crystallization in amorphous films generally leads to the formation of γ-phase presenting a preferential (200) uniplanar orientation. Moreover, we show that when a significant amount of bulky solvents remains absorbed in the amorphous phase of these semicrystalline samples, a γ → β phase transition can be easily achieved, by thermal annealing procedures at atmospheric pressure.

2. Experimental section

Syndiotactic polystyrene was supplied by Dow Chemical under the trademark Questra 101. ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic polystyrene triads was over 98%. The weight-average molar mass obtained by gel permeation chromatography (GPC) in trichlorobenzene at 135 °C was found to be $M_w = 3.2 \times 10^5$ with the polydispersity index, $M_w/M_n = 3.9$.

Amorphous s-PS films 100–150 μm thickness, obtained by extrusion, were crystallized by immersion in pure liquids for 3 days at room temperature. The solvent content was determined by thermogravimetric analysis (TGA).

Unoriented γ form sample of Fig. 2(A) was obtained by following procedures analogous to those described in detail in Ref. [1].

The molecular volume of the guest molecules has been simply evaluated from their molecular mass (M) and density (ρ): $V_{guest} = M/\rho N$, where N is the Avogadro's number (6.02×10^{23} molecules/mol).

Wide-angle X-ray diffraction patterns with nickel filtered Cu Kα radiation were obtained, in reflection, with an

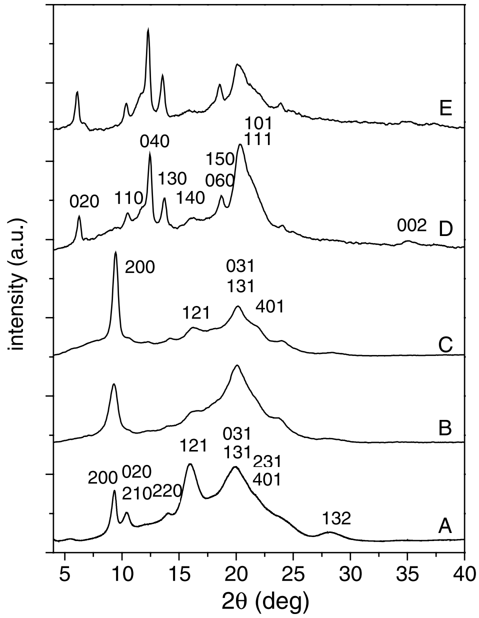

Fig. 2. X-ray diffraction patterns (Cu Kα) of semicristalline sPS samples: powder (γ-form, A); amorphous s-PS film after crystallization by immersion in CD (γ-form, B) and subsequent annealing at 160 °C, (uniplanar oriented γ-form, C) and at 220 °C (β-form, D); γ-form including nearly 15 wt% of CTD after heating up to 230 °C at a heating rate of 10 K/min (planar oriented β-form, E). The main Miller indexes of the most intense reflections of the γ-phase (A), (C) and of the β-phase (D) are also indicated.

automatic Philips powder diffractometer as well as, in transmission, by using a cylindrical camera (radius = 57.3 mm). In the latter case the patterns were recorded on a BAS–MS Imaging Plate (FUJIFILM) and processed with a digital imaging reader (FUJIBAS 1800).

In particular, in order to recognize the kind of crystalline orientation present in the samples, photographic X-ray diffraction patterns were taken by placing the film sample parallel to the axis of the cylindrical camera and by sending the X-ray beam parallel or perpendicular to the film surface, as shown on the left of Fig. 3(A) and (B), respectively.

The degree of uniplanar orientation of the crystallites with respect to the film plane has been formalized on a quantitative numerical basis using Hermans' orientation functions [32,44–47], in analogy to that one defined for the axial orientation in Ref. [44]:

$$f_{\mathrm{hkl}} = \frac{(3\,\overline{\cos^2 x_{\mathrm{hkl}}} - 1)}{2} \tag{1}$$

by assuming $\overline{\cos^2 x_{\mathrm{hkl}}}$ as the squared average cosine value of the angle, x_{hkl}, between the normal to the film surface and the normal to the (hkl) crystallographic plane.

Since, in our cases, a θ_{hkl} incidence of X-ray beam is used, the quantity $\overline{\cos^2 x_{\mathrm{hkl}}}$ can be easily experimentally evaluated:

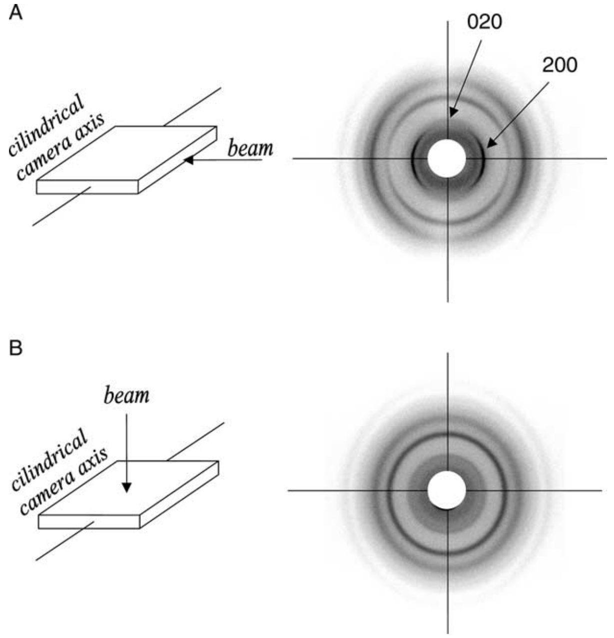

Fig. 3. X-ray diffraction patterns taken with beam parallel (A) and perpendicular (B) to the film plane, of the s-PS γ-form film of Fig. 2(C) (obtained by immersion in CD of an amorphous film followed by annealing at 160 °C). The patterns clearly indicate the occurrence of the γ-phase (200) uniplanar orientation.

$$\overline{\cos^2 x_{\mathrm{hkl}}} = \overline{\cos^2 \chi_{\mathrm{hkl}}} = \frac{\int_0^{\pi/2} I(\chi_{\mathrm{hkl}}) \cos^2 \chi_{\mathrm{hkl}} \sin \chi_{\mathrm{hkl}} \, \mathrm{d}\,\chi_{\mathrm{hkl}}}{\int_0^{\pi/2} I(\chi_{\mathrm{hkl}}) \sin \chi_{\mathrm{hkl}} \, \mathrm{d}\,\chi_{\mathrm{hkl}}} \tag{2}$$

where $I(\chi_{\mathrm{hkl}})$ is the intensity distribution of a (hkl) diffraction on the Debye ring and χ_{hkl} is the azimuthal angle measured from the equator.

The diffracted intensities $I(\chi_{\mathrm{hkl}})$ of Eq. (2) were obtained by using an AFC7S Rigaku automatic diffractometer (with a monochromatic Cu Kα radiation), and were collected sending the X-ray beam parallel to the film surface and maintaining an equatorial geometry. Because the collection was performed at constant 2θ values and in the equatorial geometry, the Lorenz and polarization corrections were unnecessary.

In these assumptions, f_{hkl} is equal to 1 and -0.5 if (hkl) planes of all crystallites are perfectly parallel and perpendicular to the plane of the film, respectively.

TGA measurements were carried out with a Mettler TG50 Thermobalance in a flowing nitrogen atmosphere, at a heating rate of 10 °C/min, in the temperature range 25–300 °C.

Differential scanning calorimetry (DSC) measurements were carried out with a DSC 2920 TA Instruments in a flowing nitrogen atmosphere, at a heating rate of 10 °C/min.

3. Results and discussion

3.1. NG solvent induced crystallization

The X-ray diffraction pattern obtained by an automatic powder diffractometer of an amorphous s-PS film after crystallization by immersion in liquid 1-chloro-decane (CD), whose molecular volume (338 Å^3) is much bigger than the cavity of the nanoporous δ-phase (120–160 Å^3) [23], is shown in Fig. 2(B). For the sake of comparison, the X-ray diffraction pattern of an unoriented γ-form (powder) of s-PS is shown in Fig. 2(A). It is clearly apparent that, as a consequence of immersion in CD, the amorphous s-PS film has been crystallized in the γ-form. As usual, the quality of the γ-phase crystallites can be improved by annealing in the range 160–170 °C. In particular, the X-ray diffraction of the sample of Fig. 2(B) after annealing at 160 °C for 2 h, is shown in Fig. 2(C). It is worth noting that the quality of the pattern of Fig. 2(C) has been improved with respect to the pattern of Fig. 2(B) not only due to the increased size and perfection of the crystallites (as clearly shown by the reduced half-height width of the 200 reflection at $2\theta_{\mathrm{Cu\ K\alpha}} = 9.25°$) but also due to the removal of CD molecules absorbed in the amorphous phase and contributing to the amorphous halo.

For a better comparison between the patterns of Fig. 2, the Miller indexes of the most intense γ-phase reflections [45] have been explicitly indicated close to the patterns A and C. Substantial differences between the relative intensities of the reflections, (compare Fig. 2(A) and (C)), clearly indicate the occurrence of crystalline phase orientation. In particular, the largely increased intensity of the (200) reflection (at $2\theta_{\mathrm{Cu\ K}\alpha}=9.25°$) [45,46], suggests a preferential parallel orientation of this crystalline plane with respect to the film plane.

A better understanding of the crystalline phase orientation of the film of Fig. 2(C), can be achieved by the X-ray diffraction patterns taken with beam parallel and perpendicular to the film plane and collected on a photographic cylindrical camera, which are shown in Fig. 3(A) and (B), respectively. The pattern B presents only Debye rings while the pattern A presents intense (200) reflection arcs centered on the equatorial line and weak nearly meridional (020) reflection arcs. These X-ray diffraction data clearly indicate the occurrence of the (200) uniplanar orientation and a quantitative evaluation indicates that the degree of uniplanar orientation is not far from $f_{200}=0.6$.

Similar γ-form semicrystalline films, presenting different degrees of (200) uniplanar orientation are achieved by crystallization of amorphous films induced by other bulky molecules like, for instance, 1-bromo-octane (287 $\mathrm{Å}^3$), ethyl nonanoate (357 $\mathrm{Å}^3$), 1-dodecene (369 $\mathrm{Å}^3$), 3,5-di-*tert*-butyltoluene (395 $\mathrm{Å}^3$), or 1-chloro-tetradecane (450 $\mathrm{Å}^3$).

A (200) uniplanar orientation of the γ-phase was already obtained by annealing of δ-phase films presenting a $(\bar{2}10)$ crystalline phase orientation [47].

3.2. NG solvent induced γ → β transition

Thermal annealing procedures at atmospheric pressure on γ-form samples, when a significant amount of highly boiling solvents remains absorbed in the amorphous phase, can lead to a direct γ → β phase transition. In particular, for γ-form films with an absorbed amount of CTD or CD or BO higher than 5 wt%, the γ → β transition can be easily achieved by sudden heating in the temperature range 210–250 °C. Just as an example, the X-ray diffraction pattern of the γ-form film of Fig. 2(B) (including at room temperature 23% of CD) after heating at 220 °C (Fig. 2(D)) clearly shows the formation of a nearly unoriented β-phase [13,14].

When the absorbed solvent is the highly boiling CTD ($T_b=292$ °C), also heating rates as low as 10 °C/min are sufficient to generate the β-phase. Just as an example, a film whose crystallization in the γ-form has been induced by CTD and including at room temperature nearly 15 wt% of CTD (presenting a X-ray diffraction pattern similar to that one of Fig. 2(B)), after heating up to 230 °C at a heating rate of 10 K/min, presents the X-ray diffraction pattern shown in Fig. 2(E). This pattern clearly presents the typical reflections of the β-phase, although the intensity of the first layer line peak, nearly located at 20°, is strongly reduced with respect to the intensities of the equatorial reflections. This indicates the presence for the β-phase of a partial planar orientation, with the chain axes, which tend to be parallel to the film plane [46,48].

Hence, the γ → β transition, as already observed for the clathrate → β transitions [46,48], can imply a partial maintenance of the crystalline phase orientation, being uniplanar for the starting helical phases and planar for the final *trans*-planar phase.

Differential scanning calorimetry (DSC) scans, at a heating rate of 10 °C/min, of γ-form films with different concentrations of absorbed CTD are compared in Fig. 4. It is clearly apparent that the position of the exothermic peak corresponding to the formation of the *trans*-planar crystalline phases is markedly shifted toward lower temperatures, as a consequence of plasticization due to the presence of the solvent in the amorphous phase. In fact, thermogravimetric measurements on these samples show that most CTD molecules are removed from the s-PS film only in the temperature range 160–220 °C. The influence of the concentration of the plasticizing CTD molecules on the transition temperature between helical and *trans*-planar crystalline phases ($T_{\mathrm{h}\rightarrow\mathrm{t}}$, maximum of the exothermic peak) is more clearly shown by the plot of Fig. 5. In that plot, the experimental point is labeled with the symbol of the crystalline phases, which are correspondingly obtained, when the DSC scans are stopped at 230 °C.

These data could suggest that the direct γ → β transition could be favored with respect to the usual γ → α transition by the reduction of the transition temperature, which for some reason could make more efficient the nucleation of the β, being generally more difficult than the nucleation of the α-phase [1,2].

However, it is worth recalling that the also addition to s-PS of poly-2,6-dimethyl-1,4-phenylene oxide (PPO), a rigid polymer ($Tg\approx 220$ °C) being miscible at molecular level in the amorphous phase, tends to favor the formation of the β-phase of s-PS with respect to the α-phase. This phenomenon occurs not only for the cold crystallization from the amorphous phase (associated with increases of

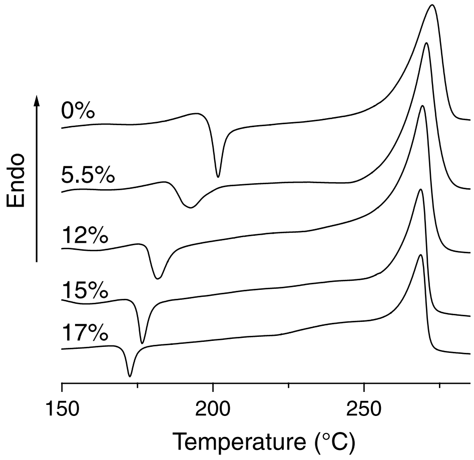

Fig. 4. DSC scans, at heating rate of 10 °C/min, of γ-form s-PS films with different CTD content (weight percent).

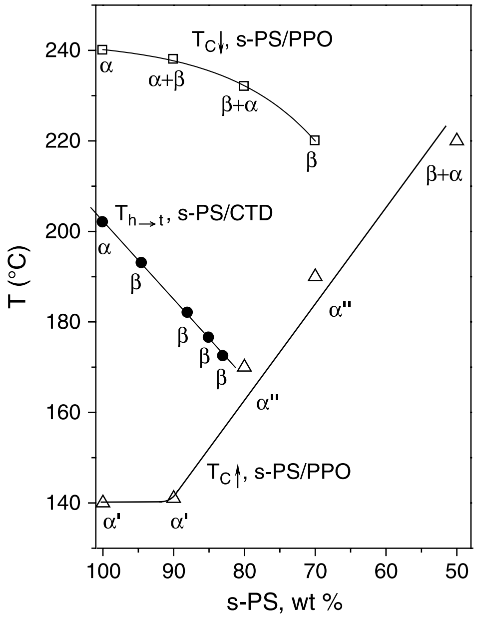

Fig. 5. Temperatures of the maximum of exothermic DSC peaks, corresponding to the formation of trans-planar crystalline phases, versus the s-PS content for: (●, $T_{h\rightarrow t}$) heating of γ-form films in the presence of CTD; (△, $T_{c\uparrow}$) heating of amorphous films in the presence of PPO [37]; 88(□, $T_{c\downarrow}$) cooling from the melt in the presence of PPO [49]. The experimental points are labeled with the symbols of the crystalline phases, which are obtained.

the cold crystallization temperature, $T_{c\uparrow}$, due to large glass transition temperature increases) [37] but also for the melt crystallization (associated with a decrease of the crystallization temperature from the melt, $T_{c\downarrow}$) [49], as reported in Fig. 5.

The data of Fig. 5 suggest that independently on the nature of the diluent molecular species (being more mobile as for the low molecular mass compounds, or less mobile as for the highly rigid miscible polymer) the s-PS dilution tend to favor the thermodynamically stable β-phase with respect to the kinetically favored α-phase.

This conclusion also helps to rationalize the well-known observation that by solution crystallization, the β-phase is always obtained at high temperatures while the α-phase has been never obtained [1,2,12–14].

4. Conclusions

The sorptions into s-PS amorphous samples of bulky solvents, whose molecules are too big to be enclosed as guest of s-PS clathrate phases, generally induce crystallization in the γ-phase. This NG solvent induced crystallization in amorphous films generally leads to a (200) uniplanar orientation of the γ-crystalline phase, with degree of orientation as high as $f_{200}=0.6$.

The presence of these highly boiling solvents in the amorphous phase of γ-form samples can induce a γ→β phase transition, as a consequence of thermal annealing procedures at atmospheric pressure. In particular, for γ-form films with an absorbed amount of the considered bulky solvents higher than 5 wt%, the γ→β transition can be easily achieved by rapid heating in the temperature range 210–250 °C. Moreover, when the absorbed solvent has a very high boiling point ($T_b \geq 300$ °C), also heating rates as low as 5 °C/min are sufficient to generate the β-phase.

These γ→β transitions, as already observed for the clathrate→β transitions [46,48], can imply a partial maintenance of the crystalline phase orientation. In fact, γ-form films presenting the (200) uniplanar orientation can lead to β-form films with planar orientation of the chain axes.

The decrease of the transition temperature between the helical γ-phase and the *trans*-planar crystalline phases ($T_{h\rightarrow t}$) associated with the increase of the absorbed amount of CTD (evaluated by DSC measurements) clearly indicate the occurrence of a large plasticizing effect of the highly boiling solvent. However, a comparison of these data with literature data relative to s-PS/PPO miscible blends, indicates that, independently on the nature of the diluent molecular species (being more mobile as for the low molecular mass compounds, or less mobile as for the highly rigid miscible polymer), the formation of the thermodynamically stable β-phase is favored with respect to the formation of the kinetically favored α-phase, by any kind s-PS dilution at molecular level.

Acknowledgements

Financial support of the ‘Ministero dell’Istruzione, dell’Università e della Ricerca’ (PRIN 2004 and FIRB2001) of ‘Regione Campania’ (Legge 5 and Centro di Competenza per le Attività Produttive) is gratefully acknowledged. We thank Dr Anna Spatola and Dr Elisa Cipolletti of the University of Salerno for experimental support.

References

[1] Guerra G, Vitagliano VM, De Rosa C, Petraccone V, Corradini P. Macromolecules 1990;23:1539.
[2] Corradini P, Guerra G. Adv Polym Sci 1992;100:183.
[3] Chatani Y, Inagaki T, Shimane Y, Ijitsu T, Yukimori T, Shikuma H. Polymer 1993;34:1620.
[4] Chatani Y, Shimane Y, Inagaki T, Shikuma H. Polymer 1993;34: 4841.
[5] De Rosa C, Rizzo P, Ruiz de Ballesteros O, Petraccone V, Guerra G. Polymer 1999;40:2103.
[6] Tarallo O, Petraccone V. Macromol Chem Phys 2004;205:1351.
[7] Venditto V, Milano G, De Girolamo Del Mauro A, Guerra G, Mochizuki J, Itagaki H. Macromolecules 2005;38:3696.
[8] Petraccone V, Tarallo O, Venditto V, Guerra V. Macromolecules, 2005;38:6965.
[9] De Rosa C, Guerra G, Petraccone V, Corradini P. Polym J 1991;23: 1435.

[10] Corradini P, De Rosa C, Guerra G, Napolitano R, Petraccone V, Pirozzi B. Eur Polym J 1994;30:1173.

[11] De Rosa C. Macromolecules 1996;29:8460.

[12] Cartier L, Okihara T, Lotz B. Macromolecules 1998;31:3303.

[13] De Rosa C, Rapacciuolo M, Guerra G, Petraccone V, Corradini P. Polymer 1992;33:1423.

[14] Chatani Y, Shimane Y, Ijitsu T, Yukinari T. Polymer 1993;34:1625.

[15] Chatani Y, Fujji Y, Shimane Y, Ijitsu T. Poly Prep Jpn (Eng Ed) 1988; 37:E428.

[16] Immirzi A, De Candia F, Iannelli P, Vittoria V, Zambelli A. Makromol Chem Rapid Commun 1988;9:761.

[17] Sun Z, Morgan RJ, Lewis DN. Polymer 1992;33:660.

[18] Guerra G, Manfredi C, Rapacciuolo M, Corradini P, Mensitieri G, Del Nobile MA. Italian Patent RM94A30; 1994.

[19] Guerra G, Reverchon E, Venditto V. Italian Patent SA98A8; 1998.

[20] Manfredi C, Del Nobile MA, Mensitieri G, Guerra G, Rapacciuolo M. J Polym Sci, Polym Phys Ed 1997;35:133.

[21] De Rosa C, Guerra G, Petraccone V, Pirozzi B. Macromolecules 1997;30:4147.

[22] Reverchon E, Guerra G, Venditto V. J Appl Polym Sci 1999;74:2077.

[23] Milano G, Venditto V, Guerra G, Cavallo L, Ciambelli P, Sannino D. Chem Mater 2001;13:1506.

[24] Daniel C, Alfano D, Venditto V, Cardea S, Reverchon E, et al. Adv Mater 2005;17:1515.

[25] de Candia F, Filho AR, Vittoria V. Makromol Chem Rapid Commun 1991;12:295.

[26] Petraccone V, Auriemma F, Dal Progetto F, De Rosa C, Guerra G, et al. Makromol Chem 1991;194:1335.

[27] Auriemma F, Petraccone V, Dal Progetto F, De Rosa C, Guerra G, Manfredi C, et al. Macromolecules 1993;26:3772.

[28] Manfredi C, De Rosa C, Guerra G, Rapacciuolo M, Auriemma F, Corradini P, et al. Macromol Chem Phys 1993;196:2795.

[29] Vittoria V, Russo R, de Candia F. Macromol Sci Phys 1995;B28:419.

[30] Rapacciuolo M, De Rosa C, Guerra G, Mensitieri G, Apicella A, Del Nobile MA. J Mater Sci Lett 1991;10:1084.

[31] de Candia F, Romano G, Russo R, Vittoria V. Colloid Polym Sci 1993;271:454.

[32] Rizzo P, Costabile A, Guerra G. Macromolecules 2004;37:3071.

[33] Ma W, Yu J, He J. Macromolecules 2004;37:6912.

[34] Bu W, Li Y, He J, Zeng J. Macromolecules 1999;32:7224.

[35] Ho RM, Lin CP, Tsai HY, Woo EM. Macromolecules 2000;33:6517.

[36] De Rosa C, Ruiz de Ballesteros O, Di Gennaro M, Auriemma F. Polymer 2003;44:1861.

[37] Guerra G, De Rosa C, Vitagliano VM, Petraccone V, Corradini P, Karasz FE. Polym Commun 1991;32:30.

[38] Guerra G, De Rosa C, Petraccone V. Polym Network Blends 1992;2: 145.

[39] Handa YP, Zhang Z, Wong B. Macromolecules 1997;30:8499.

[40] Ma W, Yu J, He J. Macrom Rapid Commun 2005;26:112.

[41] De Rudder J, Berghmans H, Arnauts J. Polymer 1999;40:5919.

[42] Sen SY, Woo EM, Wu MC, Ho R-M. Polymer 2003;44:5293.

[43] Daniel C, Alfano D, Guerra G, Musto P. Macromolecules 2003;36: 5742.

[44] (a) Samuels RJ. Structured polymer properties. New York: Wiley; 1971 p. 28 [chapter 2].
  (b) Kakudo M, Kasai N. X-Ray diffraction by polymers. Amsterdam: Elsevier; 1972. p. 252 [chapter 10].
  (c) Alexander LE. In: Krieger Robert E, editor. X-ray diffraction methods in polymer science. New York: Huntington; 1979. p. 210 [chapter 4].

[45] As for the γ-phase, an orthorhombic unit cell with $a=19.15$ Å, $b=17.0$ Å, $c=7.7$ Å has been derived by electron diffraction measurements on single crystals (Ruiz de Ballesteros, O., unpublished data) and confirmed by X-ray diffraction patterns of films with (200) [46], (020) [47] and (002) [48] uniplanar orientations

[46] Rizzo P, Della Guardia S, Guerra G. Macromolecules 2004;37: 8043.

[47] Rizzo P, Spatola A, De Girolamo Del Mauro A, Guerra G. Macromolecules, in press.

[48] Rizzo P, Lamberti M, Albunia AR, Ruiz de Ballesteros O, Guerra G. Macromolecules 2002;35:5854.

[49] Guerra G, De Rosa C, Vitagliano Vm, Petraccone V, Corradini P. J Polym Sci, Part B: Polym Phys 1991;29:265.