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Influence of the quenching temperature on the crystallization of the *trans*-planar mesomorphic form of syndiotactic polypropylene

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Abstract

The crystallization from the melt of the *trans*-planar mesomorphic form of syndiotactic polypropylene is investigated at different quenching temperatures. The formation of the *trans*-planar mesomorphic form at − 5, 0 and 6 °C is followed as a function of the residence time at these temperatures by X-ray diffraction and FTIR spectroscopy. The quenching temperature influences the rate of formation of the mesomorphic form as well as the maximum amount of the obtained mesomorphic form. By increasing the quenching temperature, in the examined range between − 5 and + 6 °C, an increase in the rate of formation of the mesomorphic form is observed. The maximum amounts of mesomorphic form obtained at 6 and − 5 °C are lower than the amount achieved at 0 °C, which corresponds to nearly 100% of the total crystalline phase.

Keywords: Syndiotactic polypropylene; Mesomorphic form; Quenching temperature

1. Introduction

The polymorphism of syndiotactic polypropylene (sPP) has been widely studied [1–13]. Four different crystalline forms have been described in the literature. Forms I [2–7] and II [8,9,14] are characterized by chains in $(T_2G_2)_n$ helical conformation, whereas forms III [10] and IV [11,12] present chains in *trans*-planar and $(T_6G_2T_2G_2)_n$ conformation, respectively.

Besides the four crystalline forms, a disordered modification of sPP, characterized by chains in *trans*-planar conformation, has been recently obtained by quenching the melt at 0 °C and keeping the sample at 0 °C for long time [15,16]. In a recent paper [17] we have shown that this modification should be properly defined as the mesomorphic form of sPP, characterized by disorder in the packing of the *trans*-planar chains.

The crystallization from the melt of sPP at 0 °C depends on the residence time of the sample at 0 °C [15–20]. X-ray diffraction and FTIR spectroscopy measurements have shown that sPP samples kept at 0 °C for short time rapidly crystallize in the more stable helical form I at room temperature, whereas longer residence at 0 °C increases the stability of the *trans*-planar mesomorphic form, which remains stable at room temperature and inhibits the normal crystallization of the sample into the helical form I at room temperature [15–20]. It was found by high resolution solid state ^{13}C NMR that the average value of the fraction of C–C bonds in the *trans*-planar conformation, measured at 0 °C, is about 0.80 after 10 min of residence of the sample at 0 °C and increases with increase in the residence time [16,18]. These results have been interpreted considering that portions of chains in *trans*-planar and twofold helical conformations are in equilibrium in the amorphous state at 0 °C. The slight mobility of the chains, still present at 0 °C, allows the *trans*-planar portions of chains to organize in small disordered crystalline bundles, originating the mesomorphic form [16]. When the residence time at 0 °C is long enough, these crystalline mesomorphic bundles become stable and prevent the crystallization of the helical form I at room temperature [16,19].

The crystallization of the mesomorphic form of sPP also depends on the stereoregularity of the polymer samples [19]. The stereoregularity influences the rate of formation of the mesomorphic form at 0 °C, and the maximum amount of the mesomorphic form present in the sample at room temperature. Higher the syndiotacticity, easier the formation

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of the *trans*-planar mesomorphic form [19]. For highly stereoregular sPP samples, short residence time at 0 °C are enough to form and stabilize the mesomorphic form, whereas for stereoirregular samples the amount of mesomorphic form observed in the sample at room temperature is always very low even for very long residence time at 0 °C, and the crystallization into the stable helical form at room temperature is not inhibited [19]. This behavior has been explained considering that the configurational defects (i.e. mm triads or isolated m diads) are probably more easily tolerated in the twofold helical conformation than in the *trans*-planar conformation of sPP. As a consequence, in low stereoregular samples long portions of sPP chains are able to crystallize only if they assume the helical conformation [19].

The crystallization of the mesomorphic form of sPP has been mainly studied at 0 °C [15–20]. In a recent paper Nakaoki et al. [21] have studied the crystallization process of sPP at different temperatures, between −5 and 15 °C, after quenching the melt at 0 °C. They have found that just after the quenching at 0 °C the sample is in a non-crystalline state. Below 0 °C only the *trans*-planar mesomorphic form is crystallized from the non-crystalline state, whereas when the sample is kept at temperatures above 5 °C after quenching at 0 °C also the crystalline helical form I is obtained [21].

In this paper the influence of the quenching temperature from the melt on the formation of the *trans*-planar mesomorphic form of sPP and on its stability with respect to the crystalline helical form I, is investigated through X-ray diffraction and FTIR spectroscopy.

2. Experimental

The sPP sample was synthesized at 0 °C with the single center syndiospecific catalyst isopropylidene(cyclopentadienyl)(9-fluorenyl)$ZrCl_2$ activated with methylaluminoxane [22]. The polymer sample presents high stereoregularity, with a fully syndiotactic pentad *rrrr* content of 95.8%, molecular weight of 2.66×10^5 and melting temperature of 153 °C. The structural and thermal characterization of the sample has been extensively described in Refs. [1,6–9].

Films of sPP, 0.2–0.3 mm thick, were prepared by melting the polymer powders in a hot press at 170 °C and rapidly quenching at different temperatures (−5, 0, and 6 °C) in a ethyl alcohol bath. The films were kept at the quenching temperature for different times and, then, analyzed at room temperature by X-ray diffraction and infrared spectroscopy.

X-ray powder diffraction profiles were obtained with an automatic Philips diffractometer using a Ni-filtered Cu Kα radiation.

The Fourier transform infrared (FTIR) spectra were recorded in the wave number range of 700–1200 cm^{-1} using a JASCO FT/IR-430 spectrophotometer with a resolution of 0.5 cm^{-1} (32 scans).

3. Results and discussion

The X-ray diffraction profiles recorded at room temperature of the sPP films quenched from the melt at −5, 0 and 6 °C, and kept at these temperatures for different times are shown in Figs. 1–3, respectively. Samples immediately taken out from the bath are in all cases in the crystalline helical form I, as indicated by the presence in the patterns a of Figs. 1–3 of the 200, 020 and 121 reflections at $2\theta =$ 12.3, 16 and 20.9°, respectively ($d = 7.2$, 5.54 and 4.25 Å, respectively) [2]. At any crystallization temperature T_c the amount of the helical form I crystallized at room temperature upon removing the samples from the low-temperature bath, decreases with increase in the residence time of the films in the bath, whereas the amount of the *trans*-planar mesomorphic form increases. This is indicated in the pattern of Figs. 1–3 by the decrease in the intensities of the reflections of the helical form I, in particular the 200 reflection at $2\theta = 12.3°$, and the increase in the intensity of the peak at $2\theta = 17°$, typical of the *trans*-planar mesomorphic form [15,17], by increasing the residence time (Figs. 1–3(b)–(f)). The X-ray diffraction patterns of the samples kept at low temperatures for long time (Figs. 1(f), 2(f), and 3f) present only the diffraction peaks at $2\theta = 17$

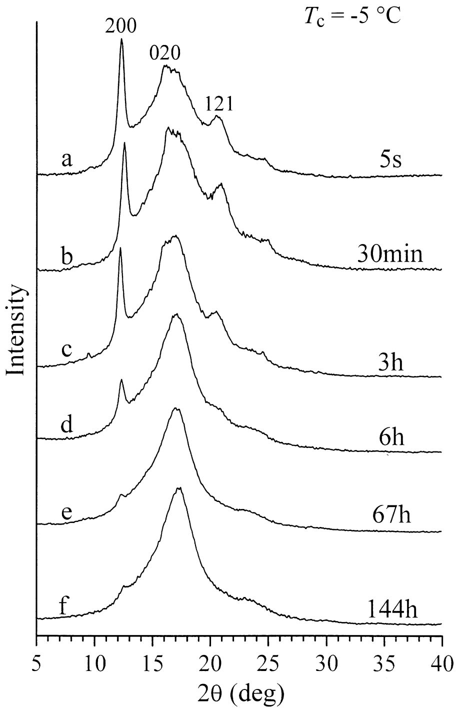

Fig. 1. X-ray powder diffraction patterns of sPP samples quenched from the melt at −5 °C and kept at −5 °C for 5 s (a), 30 min (b), 3 h (c), 6 h (d), 67 h (e), and 144 h (f).

and 24° typical of the *trans*-planar mesomorphic form of sPP [15,17,19].

It is also apparent from Figs. 1–3 that in the analyzed temperature range between −5 and +6 °C, higher the temperature at which the sample is maintained in the bath, shorter the residence time necessary to stabilize the *trans*-planar mesomorphic form. For instance, 1 h of residence at 6 °C is sufficient for the mesomorphic form to be stable and to prevent almost totally the crystallization of the helical form at room temperature (Fig. 3(c)). At lower temperatures longer residence times are necessary to obtain the same result; samples in almost pure mesomorphic form are obtained after 3 h at 0 °C, and 67 h at −5 °C (Figs. 2(d) and 1(e), respectively).

The FTIR spectra recorded at room temperature of the sPP samples kept at −5, 0, and 6 °C for different times are shown in Figs. 4–6, respectively. These data confirm the formation of chains in *trans*-planar conformation by increasing the residence time at low temperatures. The bands at 812, 868, 977, and 1005 cm^{-1}, typical of the helical form of sPP [23], are present in the spectra of the samples kept at low temperatures for short time (Figs. 4(a) and (b)–6(a) and (b)) and are strongly reduced for longer residence time (Figs. 4(d)–6(d)). At variance, the intensities of bands corresponding to long portions of chain in *trans*-planar conformation [24] at 831, 963 and 1140 cm^{-1}, increase with increase in the residence time (Figs. 4–6). It is also apparent from Figs. 4–6 that, in the temperature range

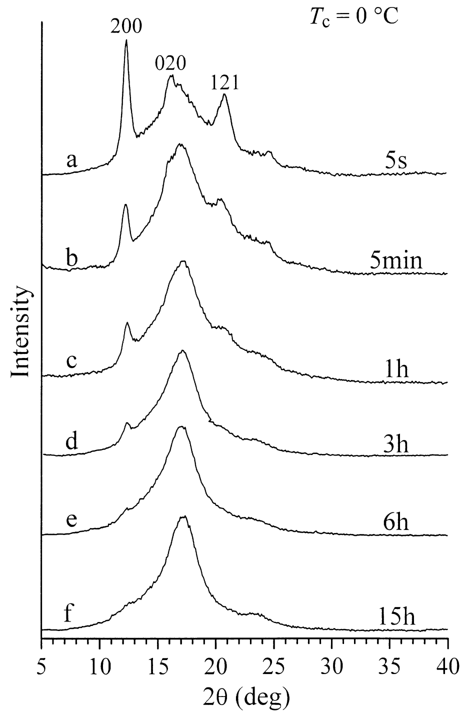

Fig. 2. X-ray powder diffraction patterns of sPP samples quenched from the melt at 0 °C and kept at 0 °C for 5 s (a), 5 min (b), 1 h (c), 3 h (d), 6 h (e), and 15 h (f).

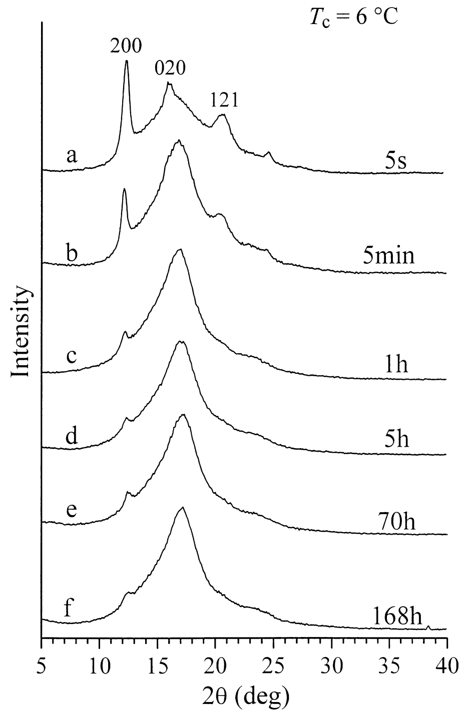

Fig. 3. X-ray powder diffraction patterns of sPP samples quenched from the melt at 6 °C and kept at 6 °C for 5 s (a), 5 min (b), 1 h (c), 5 h (d), 70 h (e), and 168 h (f).

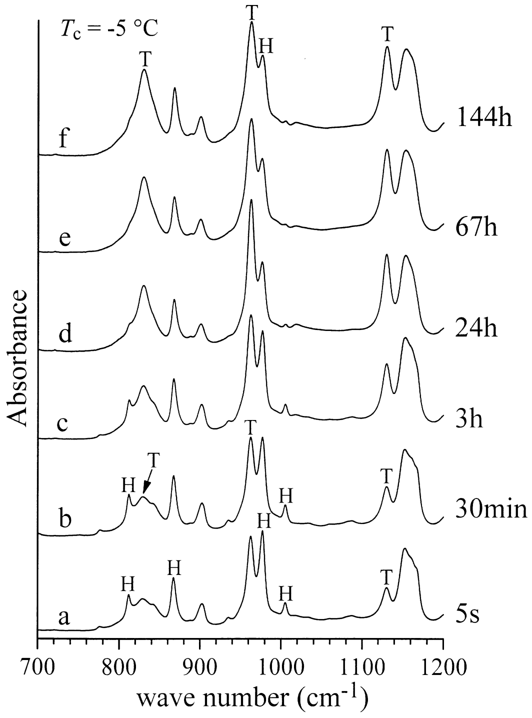

Fig. 4. FTIR spectra of sPP samples quenched from the melt at −5 °C and kept at −5 °C for 5 s (a), 30 min (b), 3 h (c), 24 h (d), 67 h (e), and 144 h (f). The FTIR bands relative to the long strands of chains in the twofold helical (H) and in the *trans*-planar (T) conformations are indicated.

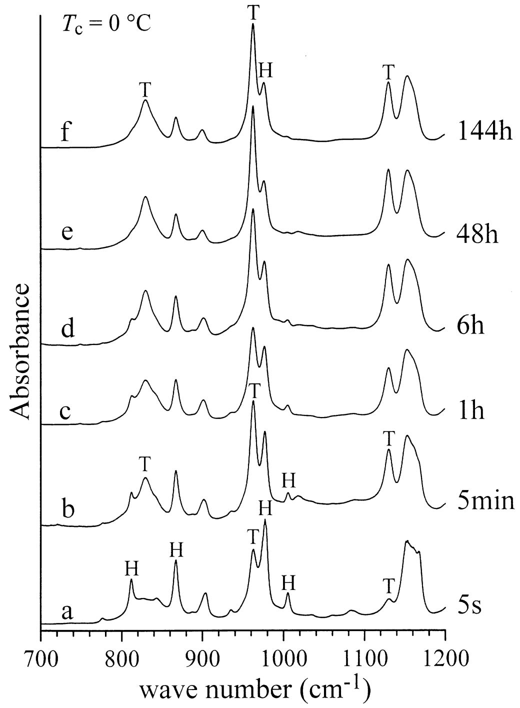

Fig. 5. FTIR spectra of sPP samples quenched from the melt at 0 °C and kept at 0 °C for 5 s (a), 5 min (b), 1 h (c), 6 h (d), 48 h (e), and 144 h (f). The FTIR bands relative to the long strands of chains in the twofold helical (H) and in the *trans*-planar (T) conformations are indicated.

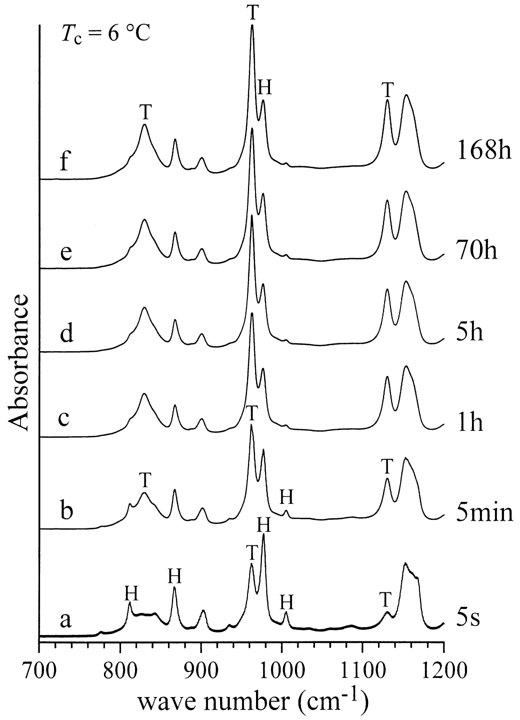

Fig. 6. FTIR spectra of sPP samples quenched from the melt at 6 °C and kept at 6 °C for 5 s (a), 5 min (b), 1 h (c), 5 h (d), 70 h (e), and 168 h (f). The FTIR bands relative to the long strands of chains in the twofold helical (H) and in the *trans*-planar (T) conformations are indicated.

between −5 and +6 °C, higher the temperature at which the samples are kept in the bath, faster the formation of long and stable portions of chains in *trans*-planar conformation, originating the mesomorphic form. For a same value of the residence time, the ratio between the intensities of the IR bands of the *trans*-planar conformation (for instance that at 963 cm^{-1}) and of the bands of the helical conformation (for instance that at 977 cm^{-1}) is indeed, higher for the sample kept at 6 °C than for the samples kept at 0 and −5 °C (for instance compare the IR spectra at 1 h of Figs. 5(c) and 6(c) and at 3 h of Fig. 4(c)).

The amount of the *trans*-planar mesomorphic form in the samples kept at −5, 0, and 6 °C for different times can be obtained from the X-ray diffraction patterns of Figs. 1–3. The presence of the reflection at $2\theta \approx 16°$ in the pattern of Figs. 1(a)–3(a), shows that the crystalline helical form which crystallize at room temperature, upon removing the samples from the bath, is basically the form I of sPP. As demonstrated in Ref. 7, the absence of the reflection at $2\theta = 18.8°$ indicate that disordered modification of form I, characterized by disorder in the alternation of right and left-handed helical chains, are obtained. Therefore the X-ray diffraction patterns of Figs. 1–3 arise from the contributions of the mesomorphic phase, the amorphous phase and the crystalline helical form I, which can be easily separated by deconvolution, knowing the diffraction profiles of the three single phases. The factions of the three phases can be easily evaluated by the ratios between the area subtending the diffraction profile of a single phase and the total area of the diffraction profile [19]. The fractions of the amorphous phase, mesomorphic form and crystalline form I are shown in Fig. 7(A)–(C), as a function of the residence time at −5, 0, and 6 °C, respectively.

It is apparent from Fig. 7 that the total fraction of the crystalline phase, evaluated as the sum of the fractions of mesomorphic and helical forms, is nearly constant and equal to about 30% for all the samples, and quite independent of the temperature at which the samples are maintained and of the residence time. All the samples always develop the maximum crystallinity achievable at room temperature, regardless of the quenching temperature and the residence time. For short residence times at −5, 0, and 6 °C, the samples fully crystallize at room temperature in the helical form I in a fractional amount of nearly 30%. For longer residence times at the three temperatures, the samples partially crystallize in the mesomorphic form and, at room temperature, crystallize in the helical form I, the sum of the mesomorphic and helical form forms being always 30%. The relative amounts of mesomorphic form and helical form I depend on the crystallization temperature and the residence time at that temperature. For very long residence times at 0 °C the crystallization of the helical form I is almost completely inhibited and a fractional amount of mesomorphic form of 28% is obtained. At −5 and +6 °C the pure mesomorphic form is not obtained even for a very

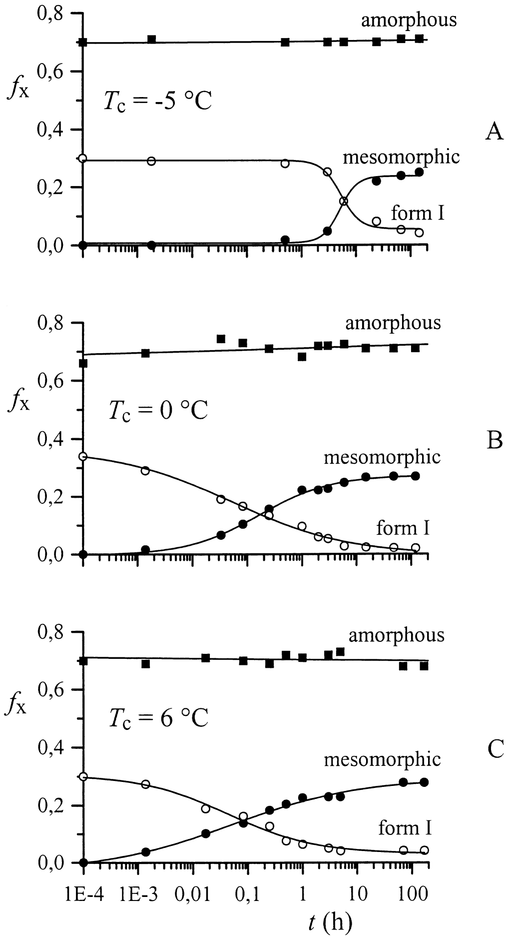

Fig. 7. Fractions of the *trans*-planar mesomorphic form (●), helical form I (○) and amorphous phase (■) in the samples quenched at −5 °C (A), 0 °C (B), and 6 °C (C) as a function of the residence time at these temperatures.

long time and crystallinities of 26% from the mesomorphic form and 4% from the helical form I are obtained.

The fraction of the mesomorphic form, with respect to the total fraction of crystalline phase, in various samples of Figs. 1–3 is shown in Fig. 8 as a function of the residence time at −5, 0, and 6 °C. It is apparent from Figs. 7 and 8 that by increasing the quenching temperature, in the range between −5 and +6 °C, the rate of formation of the *trans*-planar mesomorphic form increases. Indeed, at −5 °C the amount of mesomorphic form remains negligible up to 30 min of residence time, whereas at 0 °C appreciable amounts of the mesomorphic form are observed after few minutes, and, finally, in only 1 h of residence at 6 °C the amount of mesomorphic form is nearly equal to the maximum amount achievable at this temperature (Fig. 8).

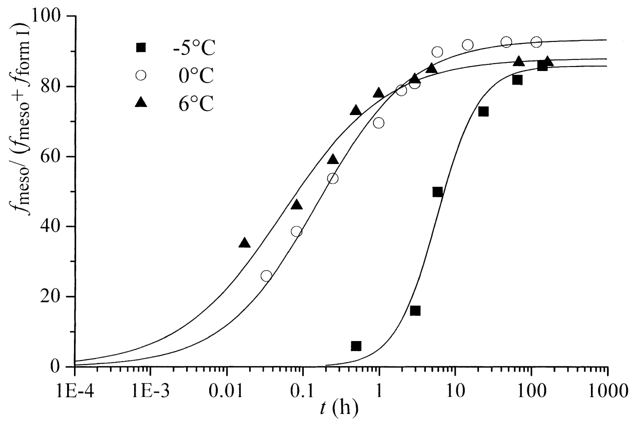

Fig. 8. Fraction of the *trans*-planar mesomorphic form, with respect to the total crystalline phase, as a function of the residence time at −5 °C (■), 0 °C (○) and 6 °C (▲).

As discussed above, even though the formation of the mesomorphic form is faster at 6 °C, the maximum amount of mesomorphic form obtained at 6 °C, as well as at −5 °C, is lower than that obtained at 0 °C. The maximum amount of mesomorphic form developed at 0 °C corresponds, indeed, to 93% of the total crystalline phase (28% crystallinity), whereas it corresponds to 86% of the total crystalline phase (26% crystallinity) at −5 and 6 °C.

These data are consistent with the hypothesis proposed to explain the crystallization of the mesomorphic form by quenching the melt at 0 °C [16,17], based on the equilibrium between portions of sPP chains in the *trans*-planar and twofold helical conformations in the amorphous state at 0 °C. If the sample is kept at the quenching temperature for enough time, the slight mobility of the chains, still present at low temperature, allows the *trans*-planar portions of chains to organize in small crystalline bundles, characterized by lateral disorder in the packing, forming the mesomorphic form [16]. When the residence time at the quenching temperatute is long enough, the crystalline *trans*-planar mesomorphic bundles are well-formed and stable and prevent the crystallization at room temperature of the stable crystalline helical form I, when the sample is removed from the bath at the quenching temperature.

If the quenching temperature is lower than 0 °C and close to the glass transition temperature (for instance −5 °C), the mobility of the sPP chains is rather limited, and longer residence times are necessary in order that the portions of chains in *trans*-planar conformation organize in small crystalline aggregates, forming the mesomorphic form. At temperatures slightly higher than 0 °C (for instance at 6 °C) the chain mobility increases and, correspondingly, a shorter residence time is necessary to form stable mesomorphic bundles. On the other hand, it is apparent from Fig. 8 that the amount of mesomorphic form observed at room temperature, is maximum for sPP samples crystallized at 0 °C. Above 0 °C the formation of mesomorphic bundles is faster, but, probably, the bundles are not large enough to be stable at room temperature. Therefore, even for long residence times at 6 °C the crystallization in the helical form I at room temperature is not completely inhibited. Of course, at higher quenching temperature the mesomorphic modification does not form and only disordered modifications of the helical form I are obtained [7]. The quenching temperature of 0 °C seems to be the best compromise between the rate of formation and the stability of the small bundles of mesomorphic form. At 0 °C the mesomorphic bundles can grow in reasonable time, so that they become stable preventing the crystallization of the sample in the helical form I at room temperature.

4. Conclusions

The crystallization from the melt of the *trans*-planar mesomorphic form of sPP has been studied at the different quenching temperatures of −5, 0, and 6 °C. This analysis has shown that at any temperature mixtures of crystals of the *trans*-planar mesomorphic form and helical form I of sPP are obtained, and a total degree of crystallinity of nearly 30% is always achieved. The relative amounts of the two forms depend on the quenching temperature and the residence time of the sample at this temperature. A novel result of this study is that the quenching temperature influences the rate of formation of the mesomorphic form as well as the maximum amount of the obtained mesomorphic form. By increasing the quenching temperature, in the examined range between −5 and +6 °C, an increase in the rate of formation of the mesomorphic form is observed. However, the maximum amount of mesomorphic form, nearly 100% of the total crystalline phase, is achieved only at 0 °C. In fact, even though the formation of the mesomorphic form is faster at 6 °C, the maximum amount of mesomorphic form obtained at 6 °C, as well as at −5 °C, is lower than that obtained at 0 °C, and nearly corresponds to 86% of the total crystalline phase (26% crystallinity).

These results can be explained considering that below 0 °C, approaching the glass transition temperature of sPP, portions of chain in *trans*-planar conformation, at equilibrium in the amorphous state with the portions of chain in helical conformation, organize slowly in crystalline aggregates, forming the mesomorphic bundles, because of the low mobility of the system. At higher crystallization temperatures (slightly above 0 °C), the higher chain mobility allows the faster formation of the crystalline mesomorphic bundles. However, the mesomorphic aggregates, rapidly formed above 0 °C, or slowly formed below 0 °C, are not large enough to be stable at room temperature, so that the crystallization of the helical form I at room temperature is not completely inhibited. The mesomorphic bundles formed at 0 °C are instead stable enough to prevent the crystallization of form I at room temperature. This could explain the experimental observation that the maximum amounts of mesomorphic form obtained at 6 and −5 °C are lower than the amount achieved at 0 °C.

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References

[1] De Rosa C, Corradini P. Macromolecules 1993;26:5711.
[2] Lotz B, Lovinger AJ, Cais RE. Macromolecules 1988;21:2375.
[3] Lovinger AJ, Lotz B, Davis PD. Polymer 1990;31:2253.
[4] Lovinger AJ, Davis DD, Lotz B. Macromolecules 1991;24:552.
[5] Lovinger AJ, Lotz B, Davis DD, Padden FJ. Macromolecules 1993;26:3494.
[6] De Rosa C, Auriemma F, Corradini P. Macromolecules 1996;29:7452.
[7] De Rosa C, Auriemma F, Vinti V. Macromolecules 1997;30:4137.
[8] De Rosa C, Auriemma F, Vinti V. Macromolecules 1998;31:7430.
[9] De Rosa C, Auriemma F, Vinti V, Galimberti M. Macromolecules 1998;31:6206.
[10] Chatani Y, Maruyama H, Noguchi K, Asanuma T, Shiomura T. J Polym Sci, Part C 1990;28:393.
[11] Chatani Y, Maruyama H, Asanuma T, Shiomura T. J Polym Sci, Polym Phys 1991;29:1649.
[12] Auriemma F, De Rosa C, Ruiz de Ballesteros O, Vinti V, Corradini P. J Polym Sci, Polym Phys Ed 1998;36:395.
[13] Auriemma F, Born R, Spiess HW, De Rosa C, Corradini P. Macromolecules 1995;28:6902.
[14] Corradini P, Natta G, Ganis P, Temussi PA. J Polym Sci, Part C 1967;16:2477.
[15] Nakaoki T, Ohira Y, Hayashi H, Horii F. Macromolecules 1998;31:2705.
[16] Ohira Y, Horii F, Nakaoki T. Macromolecules 2000;33:1801.
[17] Vittoria V, Guadagno L, Comotti A, Simonutti R, Auriemma F, De Rosa C. Macromolecules 2000;33:6200.
[18] Ohira Y, Horii F, Nakaoki T. Macromolecules 2001;34:1655.
[19] De Rosa C, Auriemma F, Ruiz de Ballesteros O. Polymer 2001;42:9729.
[20] Ohira Y, Horii F, Nakaoki T. Macromolecules 2000;33:5566.
[21] Nakaoki T, Yamanaka T, Ohira Y, Horii F. Macromolecules 2000;33:2718.
[22] Ewen JA, Jones RJ, Razavi A, Ferrara JD. J Am Chem Soc 1988;110:6255.
[23] Natta G, Pasquon I, Corradini P, Peraldo M, Pegoraro M, Zambelli A. Rend Accad Naz Lincei 1960;28:539.
[24] Natta G, Peraldo M, Allegra G. Makromol Chem 1964;75:215.