Effects of *p*-Methylstyrene Comonomeric Units on the Polymorphic Behavior of Syndiotactic Polystyrene

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ABSTRACT: The change of the polymorphic behavior of syndiotactic polystyrene after introduction of different amounts (3–20 mol %) of *p*-methylstyrene comonomeric units is presented. Variations of the polymorphic behavior have been observed for solvent extraction procedures, for annealing processes,and for solution and melt crystallizations. The behavior of samples subjected to extraction and annealing procedures indicates that the introduction of *p*-methylstyrene comonomeric units tends to destabilize the clathrate δ-form. For the solution as well as for the melt crystallization, the increase of *p*-methylstyrene content favors obtaining the α-form over the β-form and, in particular, for the 20 mol % *p*-methylstyrene copolymer, the β-form is never obtained. Both kinetic and thermodynamic factors seem to be involved. Structural variations for the α-form with the introduction of *p*-methylstyrene units are also investigated.

Introduction

The synthesis of fully syndiotactic polystyrene (s-PS) has been reported in recent years.[1–3] Several structural studies, essentially by X-ray diffraction (XRD),[4–19] electron diffraction,[20] Fourier-transform infrared spectroscopy (FTIR),[21–29] and solid-state nuclear magnetic resonance,[30,31] have shown a very complex polymorphic behavior for this polymer. Using the nomenclature proposed in ref 9, this 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. The general pattern is further complicated by the fact that both the α (hexagonal) and β (orthorhombic) forms can exist in different modifications characterized by differing degrees of structural order, which are intermediate to those of two limiting disordered modifications (α′ and β′), and two limiting ordered modifications (α″ and β″). In these descriptions, structural disorder refers to the positioning of the polymer backbone, while the order in the positioning of the substituent phenyl rings remains unaltered.[4,9,12,15]

The polymorphic behavior of s-PS can be altered by blending with poly(2,6-dimethyl-1,4-diphenylene oxide) both for the melt crystallization[10] and for the crystallization from the amorphous phase.[11]

It is well known that also the presence of comonomeric units can alter the polymorphic behavior of a polymer, favoring, in particular conditions, obtaining a given crystalline form with respect to the other ones.

As usual, this can be due to both thermodynamic and kinetic reasons. In fact, the presence of comonomeric units increases, in general, the energy content of all the crystalline forms (also in the case of exclusion of the comonomeric units from the crystallites by reduction of the crystal sizes) but, since the extent of increase may be different, it may destabilize some chain conformation or some kind of packing more than other ones. On the other hand, the influence of the comonomeric units on the polymorphic behavior of a polymer can be due to a change in the crystallization rates of the various forms.

A review relative to changes in the polymorphic behavior of different polymers in the presence of comonomeric units is presented in ref 32.

The s-PS is generally polymerized in the presence of homogeneous catalytic systems consisting of soluble titanium or zirconium compounds and methylaluminoxane (MAO).[1–3] As previously reported, these catalytic systems promote polymerization of several substituted styrenes to syndiotactic polymers. Binary copolymerization of styrene and substituted styrenes with the same catalytic systems was also performed.[33,34]

Although binary copolymerization of styrene with *p*-methylstyrene (*p*-MS) to cosyndiotactic copolymers has been studied by Zambelli[33] and Soga,[34] the polymorphic behavior of the copolymers has not yet been investigated.

In the present paper, the change of the polymorphic behavior of s-PS after introduction of different amounts (3–20 mol %) of *p*-MS comonomeric units is presented. In particular, the polymorphic behavior is studied after solvent extraction, annealing, melt crystallization, and solution crystallization procedures.

Experimental Section

All the copolymerizations were performed for 0.5 h at 50 °C in a stirred 100 mL flask under an argon atmosphere, by using toluene (10 mL), $CpTiCl_3$ (5×10^{-6} mol), and methylaluminoxane (5×10^{-3} mol).

The styrene (S), *p*-MS, and $CpTiCl_3$ were purchased from Aldrich Chemie, and the methylaluminoxane was purchased from Shering S.p.A. The monomers were dried over calcium hydride for 48 h under a nitrogen atmosphere and distilled under a reduced pressure before use. All copolymerizations were stopped by pouring the reaction mixture into acidified methanol. The copolymers were washed several times with fresh methanol and dried at 60 °C.

The crystalline samples were extracted with boiling methyl ethyl ketone (MEK) by conventional methods.

The ^{13}C NMR spectra were measured with a Bruker spectrometer at 80 °C in a solution of tetrachlorodideuterioethane. The compositions of the S/*p*-MS copolymers have been evaluated from the ratio of the areas of the signals of the corresponding quaternary carbons of the monomeric units.

Three different S/*p*-MS copolymers are considered: (1) sample 1, 3 mol % of *p*-MS; (2) sample 2, 7 mol % of *p*-MS; (3) sample 3, 20 mol % of *p*-MS.

The intrinsic viscosities, determined in tetrahydronaphthalene at 135 °C with an Ubbelohde viscosimeter, are 0.50 $dL \cdot g^{-1}$ for s-PS, 0.50 $dL \cdot g^{-1}$ for sample 1, 0.45 $dL \cdot g^{-1}$ for sample 2, and 0.45 $dL \cdot g^{-1}$ for sample 3.

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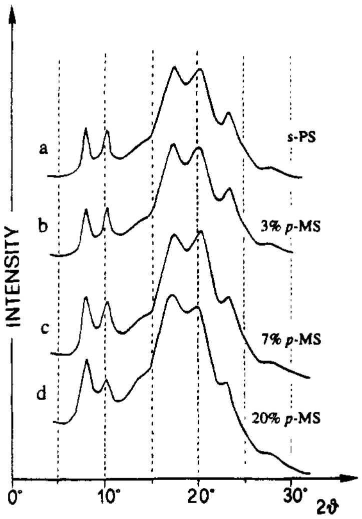

Figure 1. X-ray diffraction patterns (Cu Kα) of as-polymerized samples in the δ-form: (a) s-PS; (b) S/p-MS, 3 mol % of p-MS; (c) S/p-MS, 7 mol % of p-MS; (d) S/p-MS, 20 mol % of p-MS.

The melt crystallization processes were generally conducted in a molding press. The copolymer powders were introduced in the press, already heated at the maximum temperature (T_{max}), and held at that temperature under pressure (≈2 kg/cm^2) for a given time (t_{max}). The samples were cooled to room temperature in the press at a cooling rate close to 10 °C/min. The samples obtained were about 0.5 mm thick. To achieve better controlled conditions for T_{max} and for the cooling rates, some melt crystallization processes were also conducted in a differential scanning calorimeter (DSC).

Wide-angle X-ray diffraction patterns were obtained with nickel-filtered Cu Kα radiation with a Philips automatic powder diffractometer.

From the diffraction patterns, quantitative evaluations of the content of the two crystalline forms (α and β), possibly present in the melt-crystallized samples, were performed by the procedure described in ref 9.

The differential scanning calorimetry (DSC) measurements were carried out with a Mettler TA 3000 (DSC 20) in a flowing-nitrogen atmosphere at a heating or cooling rate (if not otherwise specified) of 10 °C/min. The peak temperatures of the melting endotherms and of the crystallization exotherms have been indicated as melting temperature (T_m) and crystallization temperature (T_c), respectively.

The thermogravimetric analyses were carried out with a Mettler TG50 thermobalance in a flowing-nitrogen atmosphere at a heating rate of 10 °C/min.

The casting procedures have been generally conducted using 10% by weight solutions.

Results and Discussion

As-Polymerized and Extracted Samples. The X-ray diffraction patterns of the as-polymerized s-PS homopolymer and copolymers 1, 2, and 3 are shown in Figure 1a–d, respectively. It is apparent that all these samples, containing 5–8% (by weight) of solvent (toluene), present X-ray diffraction patterns typical of the δ-form (typical are, in fact, the reflections at $2\vartheta \approx 8$, 10, 17, 20, and 23°).

We only recall here that the term "δ-form" has been used to indicate different clathrate structures (which include molecules of solvent) of s-PS, for which the relative intensities and the precise locations of the crystalline reflections in the XRD patterns change with the kind and the amount of the included solvent.[5,9,35]

The X-ray diffraction patterns of the homopolymer and copolymers 1 and 2 after extraction with boiling MEK for 5 h (the polymer fraction insoluble for all these samples, which is the higher stereoregular fraction, is ≈90% by weight) are reported in Figures 2a–c. The location and the relative intensities of the two peaks in the low-2ϑ (Cu Kα) region ($2\vartheta \approx 8.5, 10.6°$; $I_{8.5°}/I_{10.6°} \approx 9$) are typical of a substantially emptied δ-form.[35,36]

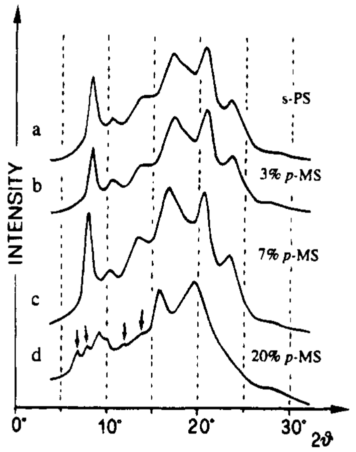

Figure 2. X-ray diffraction patterns (Cu Kα) of extracted samples: (a) s-PS (emptied δ-form); (b) S/p-MS, 3 mol % of p-MS (emptied δ-form); (c) S/p-MS, 7 mol % of p-MS (emptied δ-form); (d) S/p-MS, 20 mol % of p-MS (γ-form + α-form). The arrows indicate diffraction peaks typical of the α-form.

Completely different however, is the X-ray diffraction pattern of the copolymer with 20 mol % of p-MS after extraction with MEK (the fraction insoluble in MEK is 80% by weight), reported in Figure 2d. This pattern is typical of the γ-form (two intense peaks at $2\vartheta \approx 15.8$ and 19.5° and two peaks of lower intensity at 9.2 and 10°), although other peaks of lower intensity in the range of $2\vartheta = 6–14°$ are present ($2\vartheta \approx 6.8$, 7.9, 11.6, and 13.6°, indicated by arrows in Figure 2, whose origin will be clarified in the next subsection).

Hence for the p-MS-rich copolymer, the polymer extraction, rather than removal of the solvent from the δ-form (as usual), produces a transition from the δ-form to the γ-form, which, however, generally occurs only by thermal treatments above T_g.[5,9,35] [It is worth noting that suitable solvent treatments can induce the transition from the δ-form to the γ-form also for the homopolymer. This is, for instance, observed for treatment of δ-form samples at room temperature with long-chain halogenated hydrocarbons like 1-chlorooctane or 1-bromoheptane. The same solvents are able to crystallize s-PS directly into the γ-form by casting or by diffusion in amorphous samples. This indicates that solvent molecules, which are not suitable for the cavities of the δ-form (clathrate), tend to favor formation of the γ-form. It is also worth noting that solvents like acetone or n-hexane, which induce crystallization of amorphous s-PS samples in the γ-form,[37] do not induce, for treatment of δ-form samples, transition from the δ-form to the γ-form.]

Annealed Samples. The structural changes in the extracted samples of Figure 2 after consecutive annealings of 20 min from 90 to 170 °C (with steps of 10 °C) have also been studied.

For substantially emptied clathrates of the s-PS homopolymer (like the clathrate of Figure 2a), the transition from the δ-form to the γ-form involves destruction of the δ-form and formation at 110 °C of a mesomorphic form, which contains in the crystallizable fraction a noticeable amount of helical chains (with a TTGG conformation).[35] This "helical" mesomorphic form, for annealing at temperatures higher than T_g,

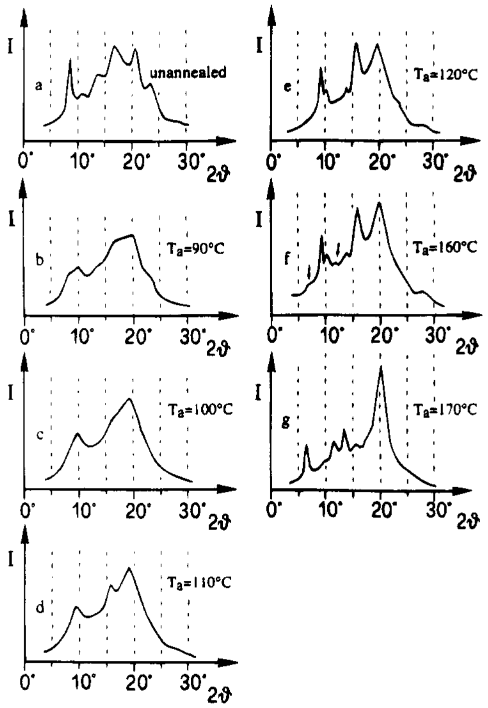

Figure 3. X-ray diffraction patterns (Cu Kα) of the copolymer containing 7 mol % of *p*-MS (as-polymerized sample after extraction with boiling MEK) after annealings at different temperatures: (a) unannealed (emptied δ-form); (b) 90 °C; (c) 100 °C (helical mesomorphic form); (d) 110 °C; (e) 120 °C (γ-form); (f) 160 °C (γ-form + α-form) (the arrows indicate diffraction peaks typical of the α-form); (g) 170 °C (α′-form).

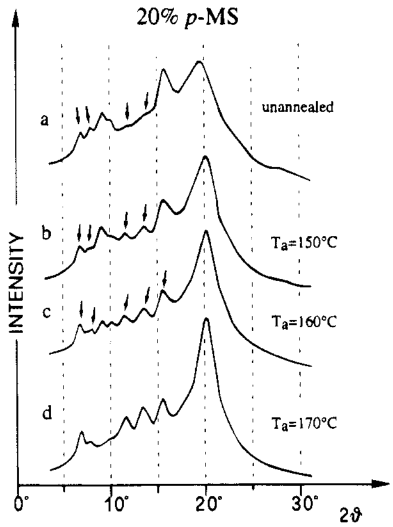

Figure 4. X-ray diffraction patterns (Cu Kα) of the copolymer containing 20 mol % of *p*-MS (as-polymerized sample after extraction) after annealings at different temperatures: (a) unannealed (γ-form + α-form); (b) 150 °C (γ-form + α-form); (c) 160 °C (γ-form + α-form); (d) 170 °C (α-form). The arrows indicate peaks typical of the α-form.

recrystallizes into the "helical" crystalline γ-form, which by suitable annealing procedures at higher temperatures (180–220 °C) is transformed into the *trans*-planar α′-modification.[35]

The XRD patterns for the extracted samples which contain 7 mol and 20 mol % of *p*-MS after some of the successive annealing steps are reported in Figures 3 and 4, respectively.

The XRD patterns of the 7 mol % *p*-MS copolymer of Figure 3 are analogous to those of the homopolymer (see Figure 2 in ref 35). In fact, a gradual disappearance of the peaks typical of the δ-form up to T_a = 100 °C and the achievement of a "helical" mesomorphic form are observed (Figure 3c).[35] By annealing at higher temperatures, the typical peaks of the γ-form (first the intense peaks at $2\vartheta \approx 16°$) gradually appear and a well-developed pattern of the γ-form is obtained for T_a = 120 °C (Figure 3e). For T_a = 160 °C typical peaks (indicated by arrows in Figure 3f) of the α-form have already appeared. For T_a = 170 °C the typical pattern of the α′-form is obtained (Figure 3g).

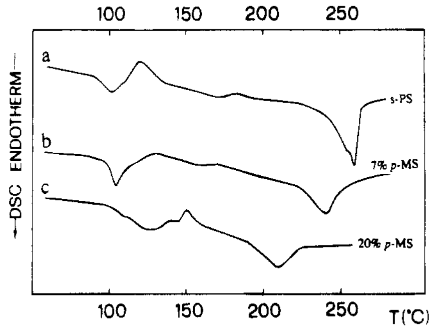

Figure 5. DSC scans of extracted samples: (a) s-PS (emptied δ-form); (b) S/*p*-MS, 7 mol % of *p*-MS (emptied δ-form); (c) S/*p*-MS, 20 mol % of *p*-MS (γ-form + α-form).

Hence, the polymorphic behavior in annealing experiments of this copolymer is very similar to that of the homopolymer, the only difference being a shift of the transition temperatures toward lower values.

The XRD pattern of the copolymer with 20 mol % of *p*-MS after extraction with boiling MEK (which, as previously discussed, is mainly in the γ-form) (Figure 4a) remains essentially unaltered for successive annealings up to 140 °C. By annealing at higher temperatures (150, 160 °C), the typical peaks (at $2\vartheta \approx$ 6.8, 7.8, 11.6, 13.4, 15.4, and 20.2°) of the α-modification (some of which are already present as minor peaks in the unannealed sample) gradually increase in intensity and a well-developed pattern of the α-form is obtained for T_a = 170 °C (Figure 4d).

Some information relative to the polymorphic behavior of these samples can also be obtained by an analysis of the DSC scans. The DSC scans of the extracted homopolymer and copolymers 2 and 3 are shown in Figure 5.

A reduction of the melting temperature (corresponding in all cases to the melting of α-form crystals, as indicated by the X-ray studies of Figures 3 and 4) with increasing amount of *p*-MS is observed (265, 240, and 210 °C from curves a, b, and c, respectively). Correspondingly, a reduction of the melting enthalpy (26, 22, and 18 J/g, respectively) is observed.

The DSC scans of the extracted homopolymer and 7 mol % copolymer (curves a and b of Figure 5) are typical of emptied δ-form samples and present a complex behavior in the range 90–140 °C.[35] This behavior has been interpreted in terms of an exothermic peak, corresponding to a recrystallization of the emptied δ-form or of the "helical" mesomorphic form[35] into the γ-form, with a maxima at nearly 125 °C (for s-PS sample, curve a) and 130 °C (for the copolymer, curve b), immediately following the variation of the specific heat typical of the glass-transition (as usual, with a midpoint at nearly 100 °C). Small exothermic peaks, corresponding to the γ → α transition, are located at 183 °C (curve a) and 168 °C (curve b).

The DSC scan of the extracted 20 mol % *p*-MS copolymer (which is essentially in the γ-form) is ill-

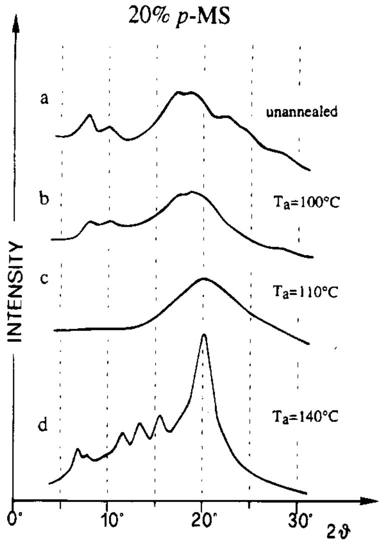

Figure 6. X-ray diffraction patterns (Cu Kα) of a 20 mol % of *p*-MS copolymer initially in a δ-form including nearly 10 wt % of *o*-DCB after annealings at different temperatures: (a) unannealed (δ-form); (b) 100 °C (amorphous + δ-form); (c) 110 °C (amorphous); (d) 140 °C (α-form).

defined. However, besides the melting endothermic peak (at $T \approx 210$ °C), an exothermic peak corresponding to the $\gamma \rightarrow \alpha$ transition (as suggested by the X-ray studies of Figure 4), with a maximum at nearly 155 °C, is clearly present.

For the 20 mol % *p*-MS copolymer, the XRD patterns after consecutive annealings of a δ-form sample including about 10% by weight of the less volatile *o*-DCB solvent (obtained by casting procedures from *o*-DCB solutions at 80 °C) are reported in Figure 6. In this case, the γ-form is never formed, while a transition to the α-form is already observed for temperatures as low as 140 °C. The transition from the δ-form to the α-form involves a gradual destruction of the δ-form up to T_a = 120 °C. In fact, for T_a = 120 °C only a broad halo, typical of the amorphous phase, is observed. The transition from the δ-form toward the α-form rather than, as usual, γ-form is of course related to the formation, for intermediate temperatures, of an amorphous rather than a "helical" mesomorphic sample.[35]

This is largely different from the behavior of the clathrate of s-PS with *o*-DCB, which is transformed into the γ-form at 120–130 °C. Moreover, in that case no substantial disappearance of the peaks of the δ-form before the appearance of the peaks of the γ-form is observed.[35]

The melting of the δ-form by annealing at 110 °C (Figure 6) and the transition toward the γ-form by solvent extraction (Figure 2d) for the 20 mol % *p*-MS copolymer indicate that the introduction of *p*-MS comonomeric units substantially destabilizes the δ-form of s-PS.

Solution-Crystallized Samples. Solution crystallizations of s-PS samples by casting from *o*-DCB solutions produce clathrate structures (δ-form) at low temperatures (T < 130 °C) and ordered β″-modifications at higher temperatures. In particular, modifications very close to the β″ limiting one are obtained in the casting temperature range 130–140 °C.[15]

X-ray diffraction patterns of the 7 and 20 mol % *p*-MS samples, obtained by casting procedures from *o*-DCB solutions at different temperatures, are reported in Figures 7 and 8, respectively.

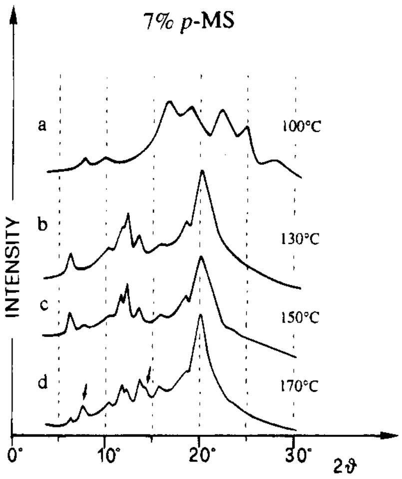

Figure 7. X-ray diffraction patterns (Cu Kα) of samples of the copolymer containing 7 mol % of *p*-MS crystallized by casting from solutions in *o*-DCB at different temperatures: (a) 100 °C (δ-form); (b) 130 °C (β″-form); (c) 150 °C (β″-form); (d) 170 °C (α-form + β″-form). The arrows indicate diffraction peaks typical of the α-form.

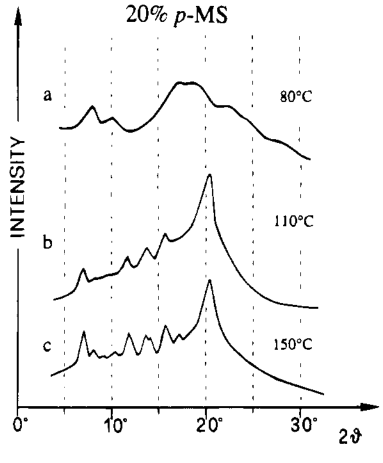

Figure 8. X-ray diffraction patterns (Cu Kα) of samples of the copolymer containing 20 mol % of *p*-MS crystallized by casting from solutions in *o*-DCB at different temperatures: (a) 80 °C (δ-form); (b) 110 °C (α-form); (c) 150 °C (α-form).

The patterns of the 7 mol % sample show that for casting temperatures lower than 100 °C a clathrate structure (δ-form) is obtained: the diffraction patterns present, in fact, the typical reflections at $2\vartheta \approx$ 7.8, 10.0, 16.9, 19.1, 22.6, 25.0, and 28.3° (Figure 7a). By casting at 130 and 150 °C, samples which present only the diffraction peaks (at $2\vartheta \approx$ 6.1, 10.3, 11.7, 12.2, 13.5, 15.8, 18.6, and 20.2°) typical of the β″-modification are obtained (Figure 7b,c). For higher casting temperatures, e.g., 170 °C, mixed β″ + α crystals are obtained. This appears from the pattern of Figure 7d, for which, for instance, the peaks at $2\vartheta \approx$ 7.7 and 13.7° of the α-form (indicated by arrows) are also clearly present.

The patterns of the 20 mol % sample show that for casting temperatures lower than 100 °C a clathrate structure (δ-form) is obtained (Figure 8a); for higher casting temperatures (110 and 150 °C), samples which present only the diffraction peaks typical of the α-form are obtained (Figure 8b,c).

Hence, for the case of solution crystallization, the presence of *p*-MS comonomeric units drastically changes the polymorphic behavior of s-PS. In particular, by increasing the *p*-MS content, the crystallization into the

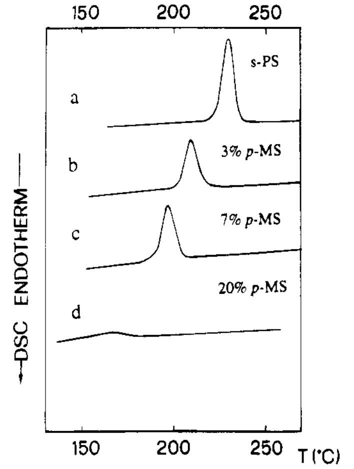

Figure 9. DSC cooling scans at 10 °C/min after 5 min at 330 °C of samples originally in the γ-form: (a) s-PS; (b) copolymer with 3 mol % of *p*-MS; (c) copolymer with 7 mol % of *p*-MS; (d) copolymer with 20 mol % of *p*-MS.

α-form (hexagonal) tends to be favored with respect to crystallization into the β-form (orthorhombic).

Melt-Crystallized Samples. Both crystalline forms containing planar zigzag conformations (pure or mixed) can be obtained by melt crystallization of s-PS.[4,5,9] Some of the factors which influence the polymorphic behavior in the melt-crystallized samples have been described: the cooling rate from the melt, the crystalline form of the starting material, the maximum temperature to which the melt is heated, the time of residence of the melt at that temperature, and, in some cases, also the heating rate to reach the melting. In particular, for the case of rapid cooling from the melt, the hexagonal α-form is obtained,[4,5,9] while for low cooling rates or for isothermal crystallizations, the crystalline form which is obtained (α, β, or mixed) depends on the crystalline structure of the starting material:[9] if the starting material is in the β-form, always β-form crystals are obtained; if the starting material is in the α- or γ-form, the produced material is in the α- or β-form depending on the maximum temperature reached in the melt and on the residence time at that temperature.[9] These results can be interpreted by considering the α-form as kinetically favored, particularly in the presence of a "memory" of the hexagonal crystals in the melt. When this memory in the melt is absent, or deleted at sufficiently high temperature, the orthorhombic β-form is obtained. It is interesting to note that the relative stabilities of the two forms are probably very similar. The similarity is indicated by the fact that the melting temperature for both forms is close 270 °C and that neither form is transformed into the other up to the melting.[9]

In this subsection the polymorphic behavior for the melt-crystallized samples of s-PS after introduction of *p*-MS comonomeric units is investigated.

DSC scans for a cooling rate of 10 °C/min after 5 min at 330 °C (the "memory" of the hexagonal crystals in the melt is deleted at this temperature) of the homopolymer and copolymers 1, 2, and 3, originally in the γ-form, are shown in Figure 9. The X-ray diffraction patterns of the samples melt crystallized in these cooling DSC scans are shown in Figure 10.

It is apparent that the presence of *p*-MS comonomeric units generates large differences in T_c. In fact, values of T_c of 233 (homopolymer), 211 (3 mol % of *p*-MS copolymer), 200 (7 mol % of *p*-MS copolymer), and 170 °C (20 mol % of *p*-MS copolymer) are observed.

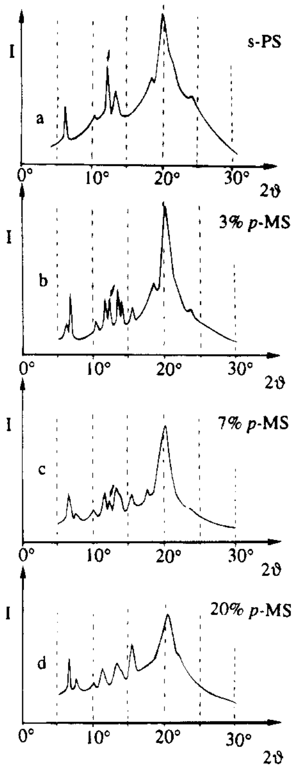

Figure 10. X-ray diffraction patterns (Cu Kα) of samples melt crystallized in the DSC cooling scans of Figure 9: (a) s-PS (β′-form); (b) copolymer with 3 mol % of *p*-MS (β-form + α-form); (c) copolymer with 7 mol % of *p*-MS (α-form + β-form); (d) copolymer with 20 mol % of *p*-MS (α-form). The arrows indicate a diffraction peak typical of the β-form.

A comparison of the X-ray diffraction patterns (Figure 10) of the copolymers (curves b–d) and the homopolymer (curve a) shows that for the chosen crystallization conditions the content of the β-form in the crystalline phase decreases gradually with increasing *p*-MS content (as shown, for instance, by reduction of the intensity of the peak at $2\vartheta \approx 12.2°$, typical of the β-form, indicated by an arrow) and, correspondingly, the content of the α-form increases. In particular, the percent of the α-form evaluated for the samples of Figure 10a–d is 0, 60, 80, and 100%, respectively.

The percent content of the α-form (% α) in the crystalline phase of samples crystallized at cooling rates (c.r.) in the range 1–60 °C/min ($T_{\max} = 330$ °C, $t_{\max} = 5$ min) is plotted versus the c.r. in Figure 11a. It is worth noting that, for the considered conditions, the 7% *p*-MS copolymer cannot be obtained in the pure β-form, while the 20% *p*-MS copolymer is always obtained in the pure α-form.

The % α data of Figure 11a are reported in Figure 11b versus the crystallization temperatures (T_c) taken from DSC scans analogous to those of Figure 9. It appears that all the data for the homopolymer and copolymers can be roughly interpolated by a single S-shaped curve. This suggests that when no memory of hexagonal (α-form) crystals is present in the melt (and, hence, the phenomenon of self-seeding is absent), the content of the α-form in the crystalline phase is essentially dependent on the crystallization temperatures on cooling from the melt. Hence, we conclude that the effect of comonomeric units in the polymorphic behavior of s-PS in the melt crystallization is mainly due to the reduction of the crystallization temperature.

Relative Stability and Melting of the α- and β-Crystalline Forms. Although the easier melt crys-

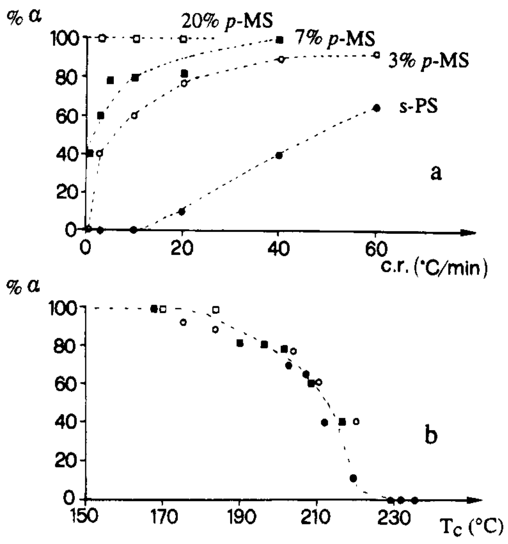

Figure 11. Content (%) of the α-form in the crystalline phase for melt-crystallized samples of s-PS (●), copolymer with 3 mol % of p-MS (○), copolymer with 7 mol % of p-MS (■), and copolymer with 20 mol % of p-MS (□) (after 5 min at 330 °C) in two different representations: (a) versus cooling rates (c.r.); (b) versus the crystallization temperature peaks (T_c) of the corresponding DSC scans.

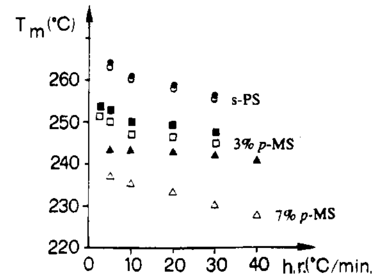

Figure 12. Melting temperatures (T_m) as a function of heating rates (h.r.) for melt-crystallized α-form and solution-crystallized β-form samples: (●) α-form and (○) β-form of the s-PS homopolymer; (■) α-form and (□) β-form of the copolymer with 3 mol % of p-MS; (▲) α-form and (△) β-form of the copolymer with 7 mol % of p-MS.

tallization into the α-form for the copolymer samples can be substantially rationalized only in terms of higher supercoolings, comparison of the melting temperatures, presented in the following, indicates that the presence of comonomeric units tends also to destabilize the β-form.

The melting temperatures of melt-crystallized α-form samples and solution-crystallized (casting at 130 °C from o-DCB solutions) β-form samples of the homopolymer and of the 3 and 7 mol % p-MS copolymers measured at different heating rates are reported in Figure 12.

The decrease of the melting temperatures with the heating rate indicates the occurrence, at low heating rate, of recrystallization phenomena. It is apparent that the melting temperatures of the α-form and β-form samples of the s-PS homopolymer, independent of the heating rate, are very similar. In contrast, for the copolymers the melting temperatures of the β-form samples are always lower than the corresponding melting temperatures of the α-form samples. In particular, the difference between the melting temperatures of the α- and the β-form samples increases with the content of p-MS comonomeric units. Let us recall that for the 20 mol % copolymer the β-form was never obtained in our experiments. This clearly indicates that the presence of p-MS comonomeric units destabilizes the β-form more than the α-form.

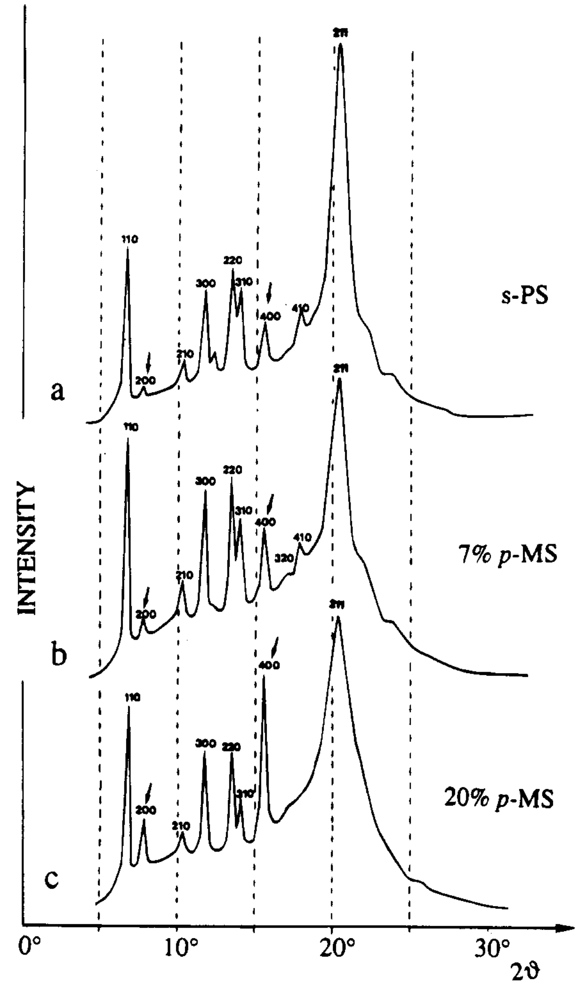

Figure 13. X-ray diffraction patterns (Cu Kα) of α-form compression-molded samples: (a) s-PS (α″-form); (b) copolymer with 7 mol % of p-MS; (c) copolymer with 20 mol % of p-MS. The arrows indicate reflections with $-h + k + l \neq 3n$, for which an increase of the relative intensities with the comonomer composition is observed.

Structural Variations in the α-Form. In recent papers,[12,38] through quantitative comparisons between X-ray diffraction intensities and calculated structure factors, detailed models for the chain packing in the hexagonal unit cell (having axes a = 26.26 Å and c = 5.04 Å, as reported by Greis[20]) for the limiting α′- and α″-modifications have been proposed. On the basis of systematic (α′) and quasi-systematic (α″) extinctions of the hkl reflections with $-h + k + l \neq 3n$, it has been shown that the sextets of phenyl rings (corresponding to triplets of *trans* planar chains) must satisfy a rhombohedral mode of packing (see Figures 2 and 3 in ref 12). The disorder, which is present in the α′-modification, would correspond to the statistical occurrence of two different, nearly isosteric, orientations of triplets of *trans*-planar chains, which leaves unaltered the positions of the barycenters of the phenyl rings at well-defined positions in the three-dimensional lattice. In contrast, for the ordered α″-modification the presence of the hkl reflections with $-h + k + l \neq 3n$ (and their weakness) suggests that the packing of the phenyl rings could maintain a substantial rhombohedral symmetry, while an ordering process of the positions of the polymer backbones could be involved.

Table 1. Bragg Distances Observed in the Powder Spectra for α-Form Melt-Crystallized Samples of the s-PS Homopolymer (α″-Form) and Copolymers with *p*-MS

	d_{obs} (Å)		
hkl	s-PS	7 mol % *p*-MS	20 mol % *p*-MS
110	13.12	13.12	13.28
200	11.33	11.34	11.45
210	8.56	8.57	8.65
300	7.57	7.57	7.62
220	6.54	6.55	6.60
310	6.30	6.30	6.34
400	5.67	5.66	5.71
320	5.18	5.17	5.21
410	4.93	4.94	
211	4.38	4.38	4.39
510	4.00	4.10	4.14
600	3.75	3.74	3.78

As shown in the previous sections, the X-ray diffraction patterns of the α-form samples for the copolymers (e.g., Figure 7d, 8c, or 10d) present, independent of the crystallization procedures, a high number of peaks which make them more similar to the patterns of the ordered α″-modification rather than the disordered-α′ modification of s-PS.

The X-ray diffraction patterns of α-form compression-molded (perfectly unoriented) samples of the homopolymer (α″-form) and the copolymers with 7 and 20 mol % of *p*-MS (obtained for T_{max} = 290, 260, and 240 °C, respectively) are shown in Figure 13. The Bragg distances observed in the powder patterns, compared in Table 1, increase with the comonomer content.

A gradual reduction of the degree of crystallinity (55, 50, and 40%, respectively) and an increase of the intensities of some reflections with $-h + k + l \neq 3n$ (indicated by arrows in Figure 13) with the *p*-MS content are also observed.

The small increase of the Bragg distances observed for the copolymer with 20 mol % of *p*-MS rules out full inclusion of the comonomer units in the crystallites of the α-form. Indeed, assuming a constant crystalline density, only 6 mol % of *p*-MS could be incorporated in the lattice at most.

Although the increase of the Bragg distances could be also due to a reduction of the size of the crystallites,[39] the change of the relative intensities of the reflections with the comonomer content suggests a partial inclusion of the comonomer units in the crystallites of the α-form.

The similarity between the patterns of the α″-modification of s-PS and those of the α-form of the copolymers seems to indicate that the more ordered α″-modification is favored by the introduction of *p*-MS comonomeric units. This result is unexpected, since the introduction of constitutional defects should tend to favor more disordered modifications.

Conclusions

The polymorphic behavior of s-PS is substantially altered by the introduction of *p*-MS comonomeric units. In fact, variations of the polymorphic behavior have been observed for solvent extraction procedures, for annealing processes, and for solution and melt crystallizations.

For instance, extraction with methyl ethyl ketone of samples in the clathrate δ-form produces for high *p*-MS contents (20 mol %) the γ-form rather than the usual emptied δ-form. Again for the 20 mol % *p*-MS sample, an annealing process at 110 °C on a clathrate δ-form sample containing *o*-DCB produces a substantially amorphous sample, which for annealing at 140 °C crystallizes into the α-form, while the corresponding δ-form sample of s-PS containing *o*-DCB is transformed into a γ-form sample by annealing at 130 °C.

These data on extraction and annealing experiments indicate that the introduction of *p*-MS comonomeric units substantially destabilizes the emptied and clathrate δ-form of s-PS.

For the solution as well as for the melt crystallization, the increase of *p*-MS favors obtaining the α-form over the β-form, and, in particular, for the 20 mol % *p*-MS copolymer, the β-form is never obtained.

The evaluation of the percent content of the α- and β-forms in the crystalline phases and of the crystallization temperatures for the homopolymer and the copolymer samples melt crystallized at different cooling rates has allowed us to conclude that the effect of the comonomeric units in favoring the α-form (with respect to the β-form) in melt crystallizations is mainly due to the reduction of the crystallization temperature.

However, the melting temperatures of pure α- and β-form samples of the homopolymer and copolymers measured at different heating rates indicate that the introduction of the comonomeric units destabilizes the β-form more than the α-form.

A comparison of the diffraction patterns of the homopolymer and copolymer samples in the α-form shows an increase of the spacings and a change of the relative intensities of the reflections, indicating a partial inclusion of the comonomeric units in the crystalline phase. Independent of the crystallization procedure, the α-form samples of the copolymers present X-ray diffraction patterns with high intensities of reflections with $-h + k + l \neq 3n$ that are more similar to those of the more ordered α″-modification of s-PS.

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