

Polymorphic Behavior of Copolymers of Syndiotactic Polystyrene with *m*-Methylstyrene

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ABSTRACT: The influence of the presence of different amounts *m*-methylstyrene (*m*-MS), in the composition range 4–21 mol %, on the polymorphic behavior of syndiotactic polystyrene (s-PS) is presented. A comparison with the effect of the presence of *p*-methylstyrene is also presented. The behavior of copolymers subjected to solvent extraction or annealing procedures indicates that the presence of *m*-MS stabilizes the γ form of s-PS, which remains stable in a large temperature range, up to 210–220 °C. The helical mesoporous δ form of s-PS has not been observed in copolymers with *m*-MS. The presence of low contents of *m*-MS induces crystallization of the β form from polymer solution (by casting at high temperatures), whereas high concentrations of *m*-MS tend to stabilize the γ form. The copolymer samples crystallize from the melt in α and β forms depending on the concentration of *m*-MS, which stabilizes the β form for composition around 11 mol %, and induces crystallization in the α form for lower (4 mol %) and higher (21 mol %) concentration. Moreover, even when the memory of the α form is maintained in the melt, the presence of *m*-MS in a concentration around 11 mol % induces the crystallization of the β form, whereas, even though no memory of the α form is present in the melt, samples with 4 and 21 mol % of *m*-MS crystallize in the α form. The α form obtained in these copolymers, by melt-crystallization or annealing of the γ form, does not correspond to neither the disordered α' , nor the ordered α'' modifications observed in s-PS. The presence of *m*-MS comonomeric units induces structural variation in the crystal packing of the trans-planar chains, and a new crystalline form is obtained.

Introduction

Syndiotactic polystyrene (s-PS) presents a complex polymorphic behavior.^{1–17} Four different crystalline forms,^{1–7} two mesomorphic forms,^{8,11,12} and various clathrate forms^{14–16} have been described. Following the nomenclature proposed in ref 1, the crystalline α and β forms are characterized by chains in trans planar conformation,^{1–5} whereas the crystalline γ and δ forms contain chains in a $s(2/1)2$ helical conformation.^{1,6}

The most stable α and β forms are obtained by crystallization from the melt,^{1,17,18} and present high melting temperatures (nearly 270 °C). γ and δ forms, as well as all the clathrate forms, are obtained by crystallization from solutions or by solvent-induced crystallization of amorphous s-PS samples.^{1,13–16} They are thermally unstable, and the δ form and clathrate structures transform into the γ form by annealing at nearly 130 °C and into the α form by annealing at higher temperatures (180 °C).^{1,6,8}

The polymorphism of s-PS is complicated by the fact that both α and β forms can exist in different modifications having different degrees of structural order.^{1–5} The crystal structures of α and β forms are, indeed, described in term of limit-ordered α'' and β'' models, and limit-disordered α' and β' models.^{2–5} In particular, melt crystallization procedures generally produce crystalline modifications of the α and β forms close to the limit-ordered α'' and limit-disordered β' models, respectively.^{1,18} Crystalline modifications close to the limit-disordered α' model are obtained by annealing amor-

phous s-PS samples or specimens in the crystalline γ form,^{1,2,5} whereas crystalline modifications close to the limit-ordered β'' model are obtained by crystallization from solutions, when the solvent is rapidly removed at high temperatures (>150 °C).⁴

The crystallization from the melt of α and β forms strongly depends on the experimental conditions. In the pioneer work,¹ it has been reported that for moderate cooling rates from the melt the obtained crystalline form is essentially related to the thermal history of the melt and the presence of a memory of the α form in the melt. Moreover, it has been shown that α form crystals are obtained by fast cooling from the melt^{1,4} and by cold crystallization from the quenched amorphous glass.^{1,19}

The polymorphic behavior of s-PS is altered in blends^{19,20} and in the presence of comonomeric units.²¹ In particular, the effect of the presence of *p*-methylstyrene comonomeric units on the polymorphic behavior of s-PS has been studied.²¹ Variations of the polymorphic behavior have been observed in almost all the crystallization procedures.²¹ The presence of *p*-methylstyrene comonomeric units tends to destabilize the clathrate structures and the δ form, and favors obtaining the α -form over the β -form in melt and solution crystallizations.²¹

In this paper a structural characterization of copolymers of s-PS with *m*-methylstyrene comonomeric units is reported. The effect of the presence of *m*-methylstyrene on the polymorphic behavior of s-PS is investigated and compared to the effect of *p*-methylstyrene.

Experimental Section

Syndiotactic styrene/*m*-methylstyrene copolymers (sPS/*m*MS) have been prepared in our laboratories using a homogeneous catalytic system composed of pentamethylcyclop-

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tadienyltitanium trichloride (Cp^*TiCl_3) and methylaluminoxane (MAO) in toluene.^{22,23}

Styrene (S) and *m*-methylstyrene (*m*-MS) (Aldrich) were purified by distillation under reduced pressure over CaH_2 . MAO was prepared by reaction of $\text{Al}(\text{CH}_3)_3$ with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in toluene.²⁴ Cp^*TiCl_3 was prepared according to a published procedure.²⁵ Toluene was refluxed 48 h over metallic sodium and distilled under a nitrogen atmosphere.

The copolymerization runs were carried out in a 100 mL glass flask provided with a magnetic stirrer and thermostated at 40 °C in an oil bath. The reactor was charged under nitrogen sequentially with toluene (30 mL), the two comonomers styrene and *m*-methylstyrene (total volume of 30 mL), Cp^*TiCl_3 (7×10^{-6} mol), and MAO (5×10^{-3} mol). The polymerization was stopped after 12 h by injecting acidified methanol. The copolymer samples were recovered by filtration, washed with fresh methanol, and dried in vacuo at 60 °C.

The crystalline samples were extracted with boiling 2-butanone by conventional methods. The polymer fraction insoluble in 2-butanone was 95%. The syndiotacticity of the polymer was evaluated by ^{13}C NMR; the fraction of the fully syndiotactic pentads [*rrrr*] was higher than 95%. Three different sPS/mMS copolymer samples have been prepared; sample sPS/4mMS with 4 mol % of *m*-MS, sample sPS/11mMS with 11 mol % of *m*-MS, and sample sPS/21mMS with 21 mol % of *m*-MS. The compositions of the copolymer samples have been evaluated from the ^{13}C NMR solution spectra by the ratio of the areas of the signals of the corresponding quaternary carbons of the monomeric units. The intrinsic viscosities, determined in tetrahydronaphthalene at 135 °C with an Ubbelohde viscosimeter, are ≈ 1 dL/g for all the samples.

^{13}C NMR spectra were obtained with an AM 250 Bruker spectrometer operating at 62.89 MHz in the Fourier transform mode and at temperature of 413 K. The sample was prepared by dissolving 30 mg of polymer in 0.5 mL of tetrachloro-1,2-dideuterioethane. Hexamethyldisiloxane (HMDS) was used as the internal chemical shift reference.

Crystallizations from solution were conducted by casting procedures at different temperature from 10 wt % solutions in various solvents.

Crystallizations from the melt were generally conducted in a molding press. The copolymer powders were melted in the press, heated to the maximum temperature T_{max} , and held at this temperature under pressure (~ 2 kg/cm²) 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.

Crystallizations from the melt were also performed by cooling the melt from T_{max} to room temperature at different cooling rate in a differential scanning calorimeter (DSC).

X-ray powder diffraction patterns were obtained with nickel-filtered $\text{Cu K}\alpha$ radiation, at room temperature with an automatic Philips diffractometer, and at higher temperatures, using an attached Anton Paar TTK camera. Quantitative evaluations of the content of the two crystalline α and β forms, possibly present in the melt-crystallized samples, were performed from the X-ray diffraction profiles by using the procedure described in ref 1.

Differential scanning calorimetry (DSC) measurements were carried out with a Perkin-Elmer DSC-7 in a flowing nitrogen atmosphere at specified heating or cooling rates. 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.

Results and Discussion

As-Prepared and Extracted Samples. The X-ray diffraction profiles of the as-prepared copolymer samples are shown in Figure 1 and compared with the diffraction profile of s-PS homopolymer in a clathrate form.^{1,8}

It is apparent that all copolymer samples present X-ray diffraction patterns (curves b–d) similar to that of s-PS (curve a), and typical of the clathrate forms of s-PS, as indicated by the presence of reflections at $2\theta = 8, 10, 17, 20,$ and 23° .^{1,8,13–16} In this case, since the polymerizations have been performed using toluene as solvent, the clathrate structures include toluene in the cavities as guest molecules. Thermogravimetric analysis, indeed, indicates that the copolymer samples include 8–10 wt % of toluene. As for copolymers of s-PS with *p*-MS,²¹ also copolymers with *m*-MS form clathrate structures including guest molecules. It is worth noting that, in clathrate structures of s-PS, the relative intensities and the precise locations of the crystalline reflections in the X-ray diffraction patterns change with the kind and the amount of the included guest molecules.^{1,6,8} In the patterns of Figure 1, the ratio between the intensities of the two peaks at $2\theta = 8^\circ$ (010 reflection) and at $2\theta = 10.3^\circ$ ($\bar{2}10$ reflection), $I_{010}/I_{\bar{2}10}$, is nearly 1, as expected for clathrate structures containing almost all the crystalline cavities occupied by the guest toluene molecules.^{6,8}

The X-ray diffraction profiles of homopolymer s-PS and copolymer sPS/mMS samples after extraction with boiling 2-butanone for 6 h (insoluble fractions corresponds to 95% of the whole samples) are reported in Figure 2. It is well-known that extraction procedures with 2-butanone or acetone of clathrate forms of s-PS, produce removal of the guest molecules and the formation of the pure helical δ form,^{6,8} containing empty cavities (Figure 2a). It is worth noting that in first papers the pure helical δ form, containing empty cavities, was originally called “ δ_e form”,⁶ whereas the term “ δ form” has been used to indicate different clathrate structures.¹ In successive papers on this matter the emptied δ_e form has been renamed mesoporous δ form. The removal of guest molecules from the clathrate structures is generally indicated by the strong reduction of the intensity of the $\bar{2}10$ reflection at $2\theta = 10.3^\circ$, while only a slight change of the 2θ positions of the 010 and $\bar{2}10$ reflections occurs.⁶ The intensity of the $\bar{2}10$ reflection decreases with decreasing the amount of guest molecules included in the crystals, and the ratio $I_{010}/I_{\bar{2}10}$ increases from nearly 1 in the case of clathrate forms (as in Figure 1a), to a value of 9–10 for the mesoporous δ form⁶ (profile a in Figure 2). It is apparent from Figure 2 that, in the case of the sPS/4mMS (Figure 2b) and sPS/11mMS (Figure 2c) copolymers, values of the ratio $I_{010}/I_{\bar{2}10} \approx 3$ are obtained, indicating that the solvent molecules are not completely removed and an appreciable amount is still included in the crystals. This indicates that for these copolymer samples the mesoporous δ form is not obtained.

In the case of the sPS/mMS copolymer with 21 mol % of *m*-MS (sample sPS/21mMS), the extraction process induces the formation of the γ form of s-PS, as indicated by the presence in the X-ray diffraction profile of Figure 2d of the intense peaks at $2\theta = 15.8$ and 19.5° , and two peaks of lower intensity at 9.2 and 10.3° , typical of the γ form.¹ Similar results have been obtained by performing the extraction process with acetone.

Therefore, for sPS/mMS copolymers with high *m*-MS contents, the polymer extraction does not produce removal of the solvent from the cavities of the clathrate structures, as generally occurs for s-PS,^{6,8} but induces a transition from the clathrate form into the γ -form, which generally occurs for s-PS only by thermal treat-

ments above the glass transition.¹ For copolymers with low *m*-MS contents only a partial removal of the guest molecules is achieved, and the mesoporous δ form of s-PS is not obtained.

We recall that copolymers of s-PS with *p*-MS show a slightly different behavior upon extraction with 2-butanone.²¹ In fact, for samples with low concentrations of *p*-MS the behavior is the same as for s-PS homopolymer, i.e., the extraction procedures produce complete removal of the guest molecules.²¹ For higher *p*-MS content (20 mol %) the extraction induces transformation of the clathrate form into a mixture of α and γ forms.²¹

It is worth noting that suitable solvent treatments can induce the transition from the clathrate forms into the γ form also for the s-PS homopolymer. This is, for instance, observed for treatments of clathrate samples at room temperature with long-chain halogenated hydrocarbons, like 1-chlorooctane or 1-bromoheptane.²¹ The same solvents induce crystallization of 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, do not form clathrate structures but favor the formation of the γ form.

Thermal Treatments. The structural changes occurring in the extracted samples of Figure 2 with increasing the temperature have been studied performing X-ray diffraction analysis at different temperatures from 90 to 260 °C. We recall that in the case of the δ form of s-PS homopolymer (like the sample of Figure 2a), annealing at increasing temperatures induces transition from the δ form into the γ -form.^{6,8} This transition (see Figure 2 of ref 8) involves destruction of the δ form and formation at 110 °C of a mesomorphic form containing chains basically in helical TTGG conformation.⁸ This "helical" mesomorphic form recrystallizes, by annealing at 130 °C, into the "helical" crystalline γ -form,⁸ which, in turn, transforms by annealing at higher temperatures (180–220 °C) into the trans-planar α' form.¹ Annealing of clathrate forms of s-PS, including guest molecules, induces, instead, direct transformation of the clathrate structures into the γ form (see Figure 3 of ref 8), and no intermediate mesomorphic form is obtained.⁸ Also in the case of copolymers of s-PS with *p*-MS with low contents of *p*-MS, it has been found that the δ form is stable up to 80 °C, and annealing procedures induce transition into the mesomorphic form at 90–100 °C,²¹ which, in turn, recrystallize in the γ form at 110–120 °C (Figure 3 of ref 21). Moreover, the γ form transforms into the α form at 170–180 °C.²¹ For higher contents of *p*-MS (20 mol %) the extracted samples, already in mixtures of γ and α forms, transform completely into the α form by annealing at nearly 170 °C (Figure 4 of ref 21). Annealing of clathrate structures of copolymers with *p*-MS induces instead a transition into the trans-planar α form without formation of the γ form (Figure 6 of ref 21). This is due to the formation at intermediate temperatures of an amorphous phase, rather than the helical mesomorphic form.²¹ The polymorphic behavior of copolymers of s-PS with *p*-MS in annealing experiments is, therefore, very similar to that of the homopolymer, the only difference being a shift of the transition temperatures toward lower values.²¹

The X-ray diffraction profiles for the extracted samples of copolymers sPS/4mMS, sPS/11mMS and sPS/21mMS,

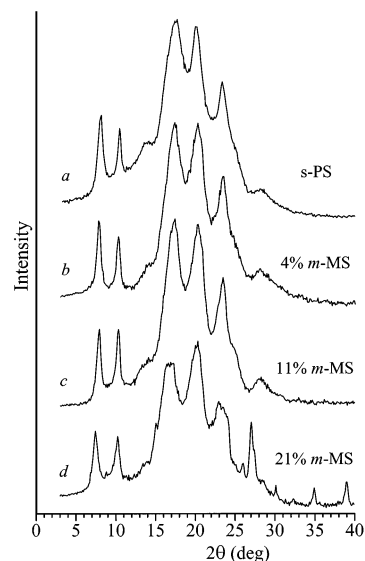


Figure 1. X-ray powder diffraction profiles of as-prepared samples of s-PS homopolymer and sPS/mMS copolymers in clathrate forms including toluene: (a) s-PS; (b) sample sPS/4mMS, 4 mol % of *m*-MS; (c) sample sPS/11mMS, 11 mol % of *m*-MS; (d) sample sPS/21mMS, 21 mol % of *m*-MS.

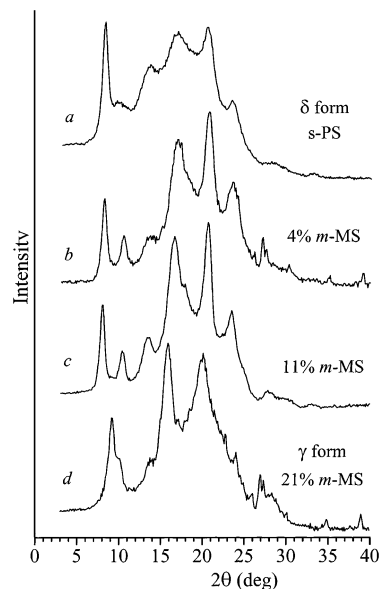


Figure 2. X-ray powder diffraction profiles of s-PS homopolymer and sPS/mMS copolymer samples extracted in boiling 2-butanone: (a) s-PS (δ form); (b) sample sPS/4mMS, 4 mol % of *m*-MS (clathrate form); (c) sample sPS/11mMS, 11 mol % of *m*-MS (clathrate form); (d) sample sPS/21mMS, 21 mol % of *m*-MS (γ form).

recorded at various temperatures are reported in Figure 3, parts A, B, and C, respectively.

Copolymers with lower *m*-MS contents (samples sPS/4mMS and sPS/11mMS) show a similar behavior. Both samples are initially in a clathrate structure containing low amount of toluene molecules (profiles *a* in Figure 3, parts A and B), which remains stable up to 100–110 °C (profiles *b*, *c* in Figure 3, parts A and B). At higher temperatures, in the range 110–120 °C the γ form develops, as indicated by the appearance of the diffraction peaks at $2\theta = 9.2$ and 16° , typical of the γ form,^{1,8} while the intensity of the reflections typical of the clathrate structure at $2\theta = 8, 13, 17$ and 23° decrease (profiles *c*, *d* in Figure 3A,B). The pure γ form is obtained at nearly 160 °C (profiles *e* in Figure 3A,B),

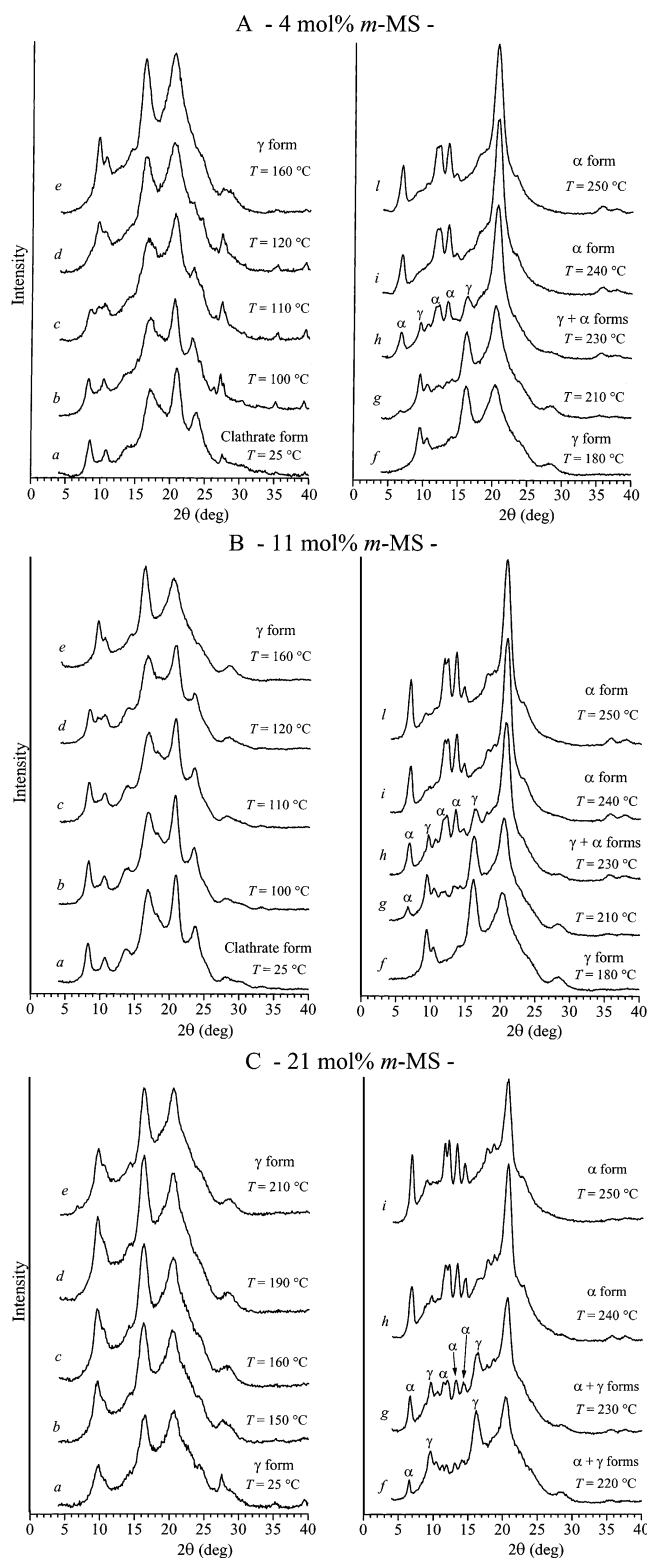


Figure 3. X-ray powder diffraction profiles recorded at the indicated temperatures of sPS/mMS copolymer samples extracted in boiling 2-butanone: (A) sample sPS/4mMS, 4 mol % of *m*-MS; (B) sample sPS/11mMS, 11 mol % of *m*-MS; (C) sample sPS/21mMS, 21 mol % of *m*-MS. Reflections typical of α and γ forms are indicated.

and remains stable up to nearly 210 °C (profiles *f*, *g* in Figure 3A,B). At this temperature the transition of the γ form into the α form starts, as indicated by appearance of the reflections at $2\theta = 6.8, 11.7, 13.5, 17.9$ and 20.4° typical of the α form,^{1,2,5} in the X-ray diffraction profiles

g, *h* of Figure 3A,B. The transition of the γ form into the trans-planar α form is complete at 250 °C (profiles *l* of Figure 3A,B). The extracted sample sPS/21mMS with higher *m*-MS content (21 mol %) is initially at room temperature in the γ form (profile *a* of Figure 3C), which remains stable up to 210 °C. Also in this case, the γ form transforms into the α form at temperatures higher than 210 °C, (profiles *f*–*i* of Figure 3C), and a complete transformation occurs at 250 °C (profile *i* of Figure 3C).

These data indicate that the polymorphic behavior of sPS/mMS copolymers in annealing treatments is different from that of the s-PS homopolymer⁸ and from that of copolymers with *p*-MS.²¹ In fact, the transition of clathrate structures of copolymers sPS/mMS into γ form occurs without forming intermediate mesomorphic or amorphous phases, as occurs for s-PS⁸ and copolymers with *p*-MS.²¹ Since the mesomorphic form is obtained, in s-PS and in copolymers with *p*-MS, only by annealing of the δ form, the absence of the helical mesomorphic form in the copolymers with *m*-MS is related to the fact that for these copolymers the pure helical δ form containing empty cavities is not obtained by extraction procedures (Figure 2). Another difference between copolymers of s-PS with *p*-MS and *m*-MS consists of the different stability of clathrate and γ forms. While the presence of *p*-MS destabilizes the clathrate structures, as well as the γ form,²¹ producing a shift of the transition temperatures to values lower than those of the homopolymer, the presence of *m*-MS comonomeric units prevents the formation of the δ form and increases the thermal stability of the γ form, which is stable up to 210 °C, regardless of the comonomer content, and transforms into the α form at high temperatures, in the range 220–250 °C (Figure 3).

Remarkable differences between s-PS copolymers with *p*-MS and *m*-MS comonomeric units are also observed upon annealing clathrate, δ and γ forms at high temperatures to obtain the α form. In the case of copolymers with *p*-MS, the γ form, produced by annealing the δ form at 110 °C, or already present in the extracted samples, transforms at 170 °C into disordered modifications of the α form, close to the disordered α' model structure (Figures 3 and 4 of ref 21). This behavior is similar to that of s-PS homopolymers,¹ apart from the shift of the transition temperature toward lower values. In the case of the copolymers with *m*-MS, the X-ray diffraction profiles of samples annealed at 250 °C are very similar, regardless of the different concentration of *m*-MS (profiles *l* of Figure 3A,B and *i* of Figure 3C), and clearly show that the γ form transforms at 250 °C in an ordered modification of the α form. As we will discuss in a next session, this modification of the α form obtained in sPS/mMS copolymers, does not correspond to neither the disordered α' modification nor the ordered α'' modification observed for s-PS^{1,2,5} and copolymers with *p*-MS,²¹ in annealed and melt-crystallized samples, and can be considered as a new modification of the α form of s-PS.

The DSC scans of the extracted samples of the sPS/mMS copolymers of Figure 2 are reported in Figure 4. The DSC curves show multiple and broad endotherms, indicative of the superposition of endothermic and exothermic effects due to melting and recrystallization phenomena. The origin of the DSC peaks can be understood on the basis of the X-ray diffraction data of Figure 3. The DSC scans of the copolymer samples with 4 and 11 mol % of *m*-MS (Figure 4, parts a and b,

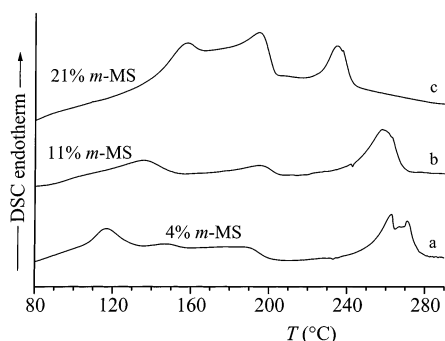


Figure 4. DSC heating scans, recorded at heating rate of 10 °C/min, of sPS/mMS copolymer samples extracted in boiling 2-butanone: (a) sample sPS/4mMS, 4 mol % of *m*-MS; (b) sample sPS/11mMS, 11 mol % of *m*-MS; (c) sample sPS/21mMS, 21 mol % of *m*-MS.

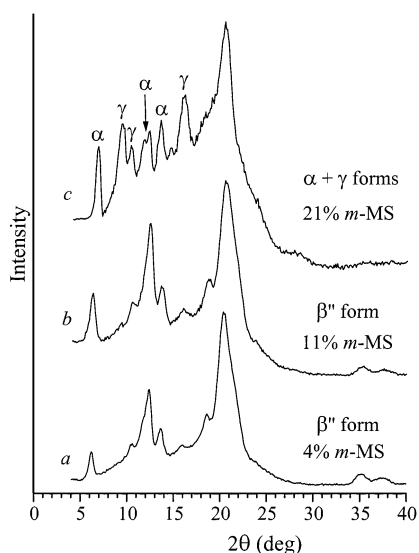


Figure 5. X-ray powder diffraction profiles of sPS/mMS copolymer samples obtained by casting from *o*-DCB solutions at 180 °C: (a) sample sPS/4mMS, 4 mol % of *m*-MS (β'' form); (b) sample sPS/11mMS, 11 mol % of *m*-MS (β'' form); (c) sample sPS/21mMS, 21 mol % of *m*-MS ($\gamma + \alpha$ form).

respectively) are typical of clathrate structures (profiles *a* of Figure 3A,B), which gradually transform into γ form at 120–160 °C, which, in turn, transforms into the α form at higher temperatures. It is apparent from the DSC curves of Figure 4, parts a and b, that, for low *m*-MS content (4 mol %), the transition into γ form occurs at 110–120 °C (Figure 4a), in agreement with the X-ray diffraction profile of Figure 3A (profiles *c*, *d*), whereas for higher *m*-MS content (11 mol %) the transition into γ form occurs at higher temperatures, in the range 120–150 °C (Figure 4b), in agreement with the X-ray diffraction data of Figure 3B (profiles *d*, *e*). The γ form transforms into the α form at 190–200 °C, for the sample with 4 mol % *m*-MS (Figure 4a), and at 200–210 °C, for the sample with 11 mol % of *m*-MS (Figure 4b). These data confirm the increased stability of the γ form with increasing the *m*-MS content.

The extracted sample of the copolymer with 21 mol % of *m*-MS is in the γ form (profiles *d* of Figure 2 and *a* of Figure 3C), which transforms into the α form in a large temperature range between 150 and 210 °C (Figure 4c). The presence of multiple peaks in this temperature range probably indicates that the transition of the γ form into the α form occurs through melting and recrystallization. The X-ray diffraction patterns of

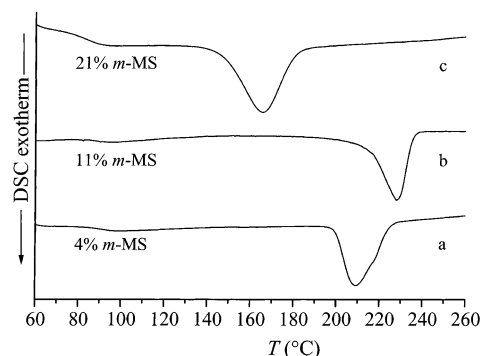


Figure 6. DSC cooling scans, recorded at cooling rate of 10 °C/min, after 5 min at 330 °C of sPS/mMS copolymer samples extracted in boiling 2-butanone: (a) sample sPS/4mMS, 4 mol % of *m*-MS; (b) sample sPS/11mMS, 11 mol % of *m*-MS; (c) sample sPS/21mMS, 21 mol % of *m*-MS.

Figure 3C are not exactly consistent with the DSC curve of Figure 4c because reflections of the α form are observed only at higher temperatures, at 220 °C (profile *f* of Figure 3C). This is probably due to the fact that during recording X-ray diffraction profiles at different temperatures, the sample is progressively annealed for 30 min at the various temperatures. This increases the stability of the γ form and produces a shift of the transition into the α form at a temperature higher than that observed in the DSC scan of Figure 4c. The final melting temperature of the copolymer samples, corresponding to the melting of the new modification of the α form, decreases with increasing *m*-MS content. Values of melting temperature of 265, 260, and 235 °C are observed for the samples with 4, 11, and 21 mol % of *m*-MS, respectively. The melting temperature of 235 °C of the sample with 21 mol % of *m*-MS is also inconsistent with the X-ray diffraction patterns of Figure 3C, which show the presence of crystalline reflections still at 250 °C. Also this effect is probably due to the annealing of the sample during recording X-ray diffraction profiles, which produces the increase of the melting temperature of the α form at temperatures higher than 250 °C.

Crystallization from Solution. Crystallizations from solution of s-PS homopolymer samples, by casting from *o*-dichlorobenzene (*o*-DCB) solutions, produce clathrate structures at low temperatures ($T < 130$ °C), and the ordered β'' form at higher temperatures.^{1,4} In particular, modifications very close to the limit-ordered β'' form are obtained in the range of casting temperatures 130–140 °C.⁴

In the case of copolymers of s-PS with *p*-MS, it has been shown that the presence of *p*-MS comonomeric units drastically changes the polymorphic behavior of s-PS.²¹ Casting at low temperatures (< 100 °C) induces the formation of clathrate structures for any composition,²¹ whereas at higher temperatures (130–170 °C) mixtures of crystals of α and β'' forms are obtained for low comonomer contents (7 mol % of *p*-MS),²¹ and only crystals of the α form are obtained for higher *p*-MS concentration (20 mol %).²¹ Therefore, by increasing the *p*-MS content, the crystallization into the α form is favored over that of the β form.²¹

In the case of sPS/mMS copolymer samples, casting at low temperatures (< 100 °C) produces the formation of clathrate structures. The X-ray diffraction profiles of copolymers s-PS/mMS samples obtained by casting from *o*-dichlorobenzene (*o*-DCB) solutions at higher temperature (180 °C) are reported in Figure 5.

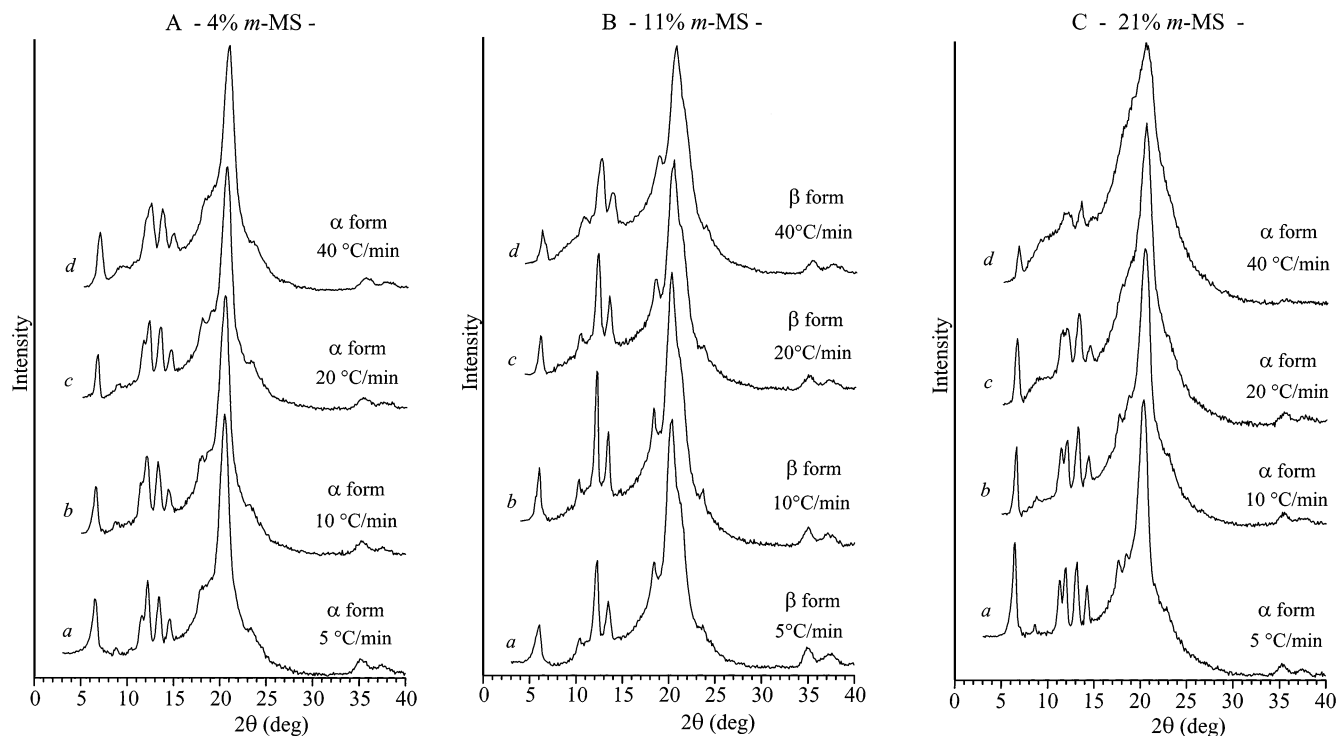


Figure 7. X-ray powder diffraction profiles of sPS/mMS copolymer samples, originally in the clathrate or γ forms (samples extracted in 2-butanone), crystallized from the melt by cooling the melt, kept for 5 min at 330 °C, to room temperature at the indicated cooling rates: (A) sample sPS/4mMS, 4 mol % of *m*-MS; (B) sample sPS/11mMS, 11 mol % of *m*-MS; (C) sample sPS/21mMS, 21 mol % of *m*-MS.

Copolymers with low *m*-MS content (4 and 11 mol %) crystallize in the ordered β'' modification of s-PS, as indicated by the presence, in the X-ray diffraction profiles *a* and *b* of Figure 5, of reflections at $2\theta = 6.2, 10.4, 11.8, 12.3, 13.6, 15.9, 18.6, 20.3$ and 21.1 , typical of the β'' form.⁴ The copolymer sample with higher *m*-MS content (21 mol %) crystallize instead in a mixture of crystals of γ and α forms, as indicated by the presence of the typical reflections of the γ form at $2\theta = 9.2, 10.3$ and 16° , and the reflections of the α form at $2\theta = 6.8, 11.7, 12.3, 13.5, 14.6,$ and 20.4° in the profile *c* of Figure 5 (the α form corresponds to the new α modification described in the previous section). These data indicate that while the presence of *p*-MS, even for low concentration, destabilizes the β form and stabilizes the α form of s-PS,²¹ the presence of low content of *m*-MS, instead, stabilizes the β form. The presence of a high concentration of *m*-MS stabilizes the γ form in a temperature range larger than that of the s-PS homopolymer, and also induces the crystallization of the α form.

Crystallization from the Melt. As discussed in the Introduction, s-PS homopolymer crystallizes from the melt in α or β forms depending on the condition of crystallization.^{1,17,18} It has been reported that the α form is obtained by fast cooling from the melt,^{1,4} whereas for moderate cooling rate or for isothermal crystallizations,^{1,18} the obtained crystalline form depends on the crystalline structure of the starting material and, basically, on the memory of the α form present in the melt.^{1,18} It has been recently demonstrated that the memory effect is the most important effect, and the crystallization of α and β forms does not depend on the crystallization temperature, at least in the range of accessible crystallization temperatures, between 240 and 270 °C.¹⁸ A pure β form is obtained only if no memory of the crystals of α form remains in the melt,

e.g., when the melt is heated at high temperature and kept at that temperature for long time. Crystals of α form are instead obtained in the presence of the memory of α form in the melt, that is when the melt is heated at temperatures relatively low (e.g., 10 °C above the melting temperature).¹ These results have been interpreted considering the α form as kinetically favored, particularly in the presence of its memory in the melt. When this memory is erased at sufficiently high temperature, the stable β -form is obtained.^{1,18}

In this section the polymorphic behavior for the melt-crystallized samples of s-PS after introduction of *m*-MS comonomeric units is investigated. Crystallizations from the melt have been performed under different conditions, changing the cooling rate from the melt to room temperature and the maximum temperature at which the melt is heated (T_{\max}).

Extracted samples of Figure 2, initially in the clathrate or γ forms have been melted at $T_{\max} = 330$ °C, kept at this temperature for $t_{\max} = 5$ min, and then cooled to room temperature at cooling rates of 5, 10, 20, and 40 °C/min. The high values of the melt temperature T_{\max} , 70–100 °C above the melting temperatures of the crystals of α form in the copolymer samples (Figure 4), guarantees that the memory of the α form, eventually present in the melt, is completely erased.^{1,18} These experimental conditions favor, in the case of s-PS, the crystallization of the β form at low cooling rates, and the α form at high cooling rates.^{1,4}

The DSC curves of copolymer samples recorded during the cooling from 330 °C to room temperature, are reported in Figure 6 in the case of the cooling rate of 10 °C/min. The X-ray diffraction patterns of the copolymer samples with 4, 11, and 21 mol % of *m*-MS crystallized at the cooling rates of 5, 10, 20, and 40 °C/min are reported in Figure 7, parts A, B, and C, respectively. It is apparent from the DSC curves of Figure 6 that, as

expected, the crystallization temperature of the copolymer sample with 21 mol % of *m*-MS (166 °C) is lower than those of the samples with 4 and 11 mol % (209 and 222 °C, respectively). Surprisingly, the sample with 11 mol % of *m*-MS crystallizes at a temperature (222 °C) higher than the crystallization temperature of the sample with 4 mol % of *m*-MS (209 °C). This behavior is observed at any cooling rate.

The X-ray diffraction profiles of Figure 7 indicate that the copolymer sample with 11 mol % of *m*-MS always crystallize in the β' form regardless of the cooling rate, even for fast cooling rates (Figure 7B), as indicated by the presence of the reflections at $2\theta = 6.2, 10.4, 12.3, 13.6, 18.6, 20.3$ and 21.1° , typical of the β' form,⁴ in the diffraction profiles of Figure 7B.

Copolymers with 4 and 21 mol % of *m*-MS instead crystallize in the new modification of the α form at any cooling rate, as indicated by the diffraction peaks at $2\theta = 6.8, 9.0, 10.3, 11.7, 12.3, 13.5, 14.6, 17.9, 18.8,$ and 20.4° in the patterns of Figure 7, parts A and C. The experimental data of Figure 6, which have shown that the crystallization temperature of the copolymer with 11 mol % of *m*-MS (Figure 6b) is higher than those of the other two samples, are in agreement with the X-ray result, which indicates that these samples crystallize in different polymorphic forms (Figure 7). Content of *m*-MS of 11 mol % always induces crystallization of the β form (probably the most stable form), whereas different concentrations induce crystallization in the new modification of the α form.

It is worth noting that the copolymers of s-PS with *p*-MS, crystallized in similar conditions, present a different behavior.²¹ The presence of *p*-MS, indeed, destabilizes the β form and favors the crystallization of the α form; pure α form is obtained at high cooling rates for any composition of the copolymers, up to 20 mol % of *p*-MS. Samples with the highest concentration of *p*-MS always crystallize in the α form regardless of the cooling rate.²¹

Literature data of the fraction of α form crystals, with respect to the β form, for s-PS homopolymer and copolymers of s-PS with *p*-MS crystallized from the melt by cooling to room temperature at different cooling rates,²¹ are reported in Figure 8 as a function of the cooling rate (Figure 8A) and the crystallization temperature (Figure 8B).²¹ It appears that all the data for the homopolymer and copolymers with *p*-MS can be roughly interpolated by a single S-shaped curve. This behavior has been explained suggesting that when no memory of the 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.²¹ The effect of *p*-MS comonomeric units on the polymorphic behavior of s-PS, inducing the crystallization of the α form from the melt, is mainly due to the reduction of the crystallization temperature.²¹

On the same plot of Figure 8 also the data relative to copolymers of s-PS with *m*-MS, calculated from the experiments of Figures 6 and 7, are reported. In the case of copolymers with *m*-MS the crystallization of α and β forms seems to be independent of the cooling rate and crystallization temperature but only depends on the concentration of the *m*-MS comonomeric unit, which stabilizes the β form for composition around 11 mol % and induces crystallization in the α form for lower (4 mol %) and higher (21 mol %) concentrations of *m*-MS.

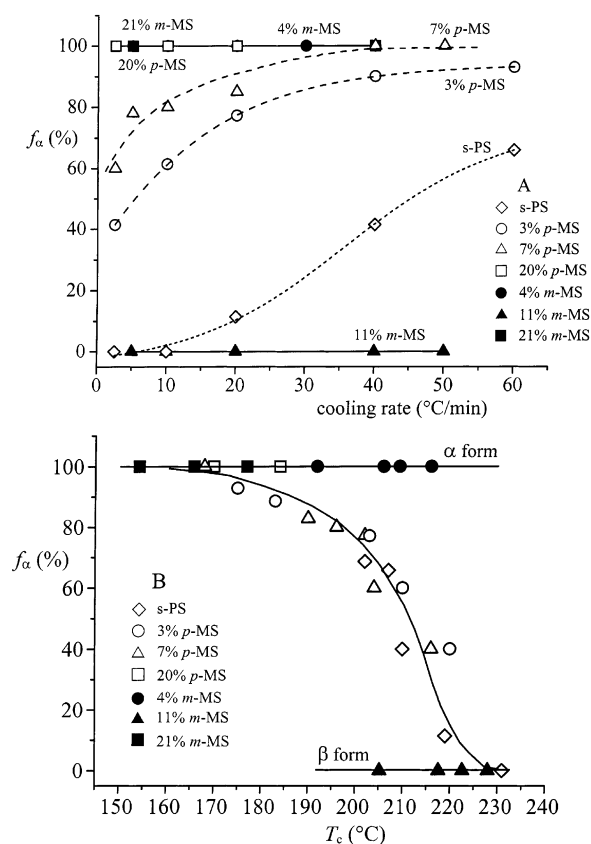


Figure 8. Fraction of the α form (f_α) in the crystalline phase of samples of s-PS homopolymer and copolymers of s-PS with *p*-MS and *m*-MS crystallized from the melt by cooling the melt, kept for 5 min at 330 °C, to room temperature at different cooling rates, as a function of the cooling rate (A) and the crystallization DSC temperature T_c (B) evaluated from the corresponding DSC cooling scans (as in Figure 6). Key: (\diamond) s-PS homopolymer; (\circ) copolymer with 3 mol % of *p*-MS; (\triangle) copolymer with 7 mol % of *p*-MS; (\square) copolymer with 20 mol % of *p*-MS; (\bullet) sample sPS/4mMS, 4 mol % of *m*-MS; (\blacktriangle) sample sPS/11mMS, 11 mol % of *m*-MS; (\blacksquare) sample sPS/21mMS, 21 mol % of *m*-MS. The data corresponding to the s-PS homopolymer and copolymers with *p*-MS are taken from the ref 21.

Crystallization experiments in conditions in which for s-PS homopolymer a memory of the α form is maintained in the melt have also been performed. Extracted samples initially in the clathrate forms or in the γ form (Figure 2) have been melted at different values of T_{\max} , kept at these temperatures for a time t_{\max} , and cooled to room temperature at 10 °C/min. The X-ray diffraction patterns of sPS/mMS copolymer samples crystallized with this procedure for $T_{\max} = 270, 280,$ and 330°C and $t_{\max} = 30\text{ s}, 3\text{ min},$ and $5\text{ min},$ respectively, are reported in Figure 9, parts A, B and C, respectively.

As shown in Figure 4, the lowest value of T_{\max} (270 °C) is only few degrees higher than the melting temperatures of the α form crystallized in the copolymer samples (265, 260, and 235 °C for 4, 11, and 21 mol % of *m*-MS, respectively). It is apparent that, for any values of T_{\max} , samples with 4 and 21 mol % of *m*-MS crystallize in the new modification of the α form, as indicated by the presence of the diffraction peaks at $2\theta = 6.8, 9.0, 10.3, 11.7, 12.3, 13.5, 14.6, 17.9, 18.8,$ and 20.4° in the profiles *a* and *c* of Figure 9, parts A, B, and C, whereas the sample with 11 mol % of *m*-MS crystallizes mainly in the β' form, as indicated by the presence of reflections at $2\theta = 6.2, 10.4, 12.3, 13.6, 18.6, 20.3,$ and 21.1° , typical of the β' form,⁴ in the diffraction

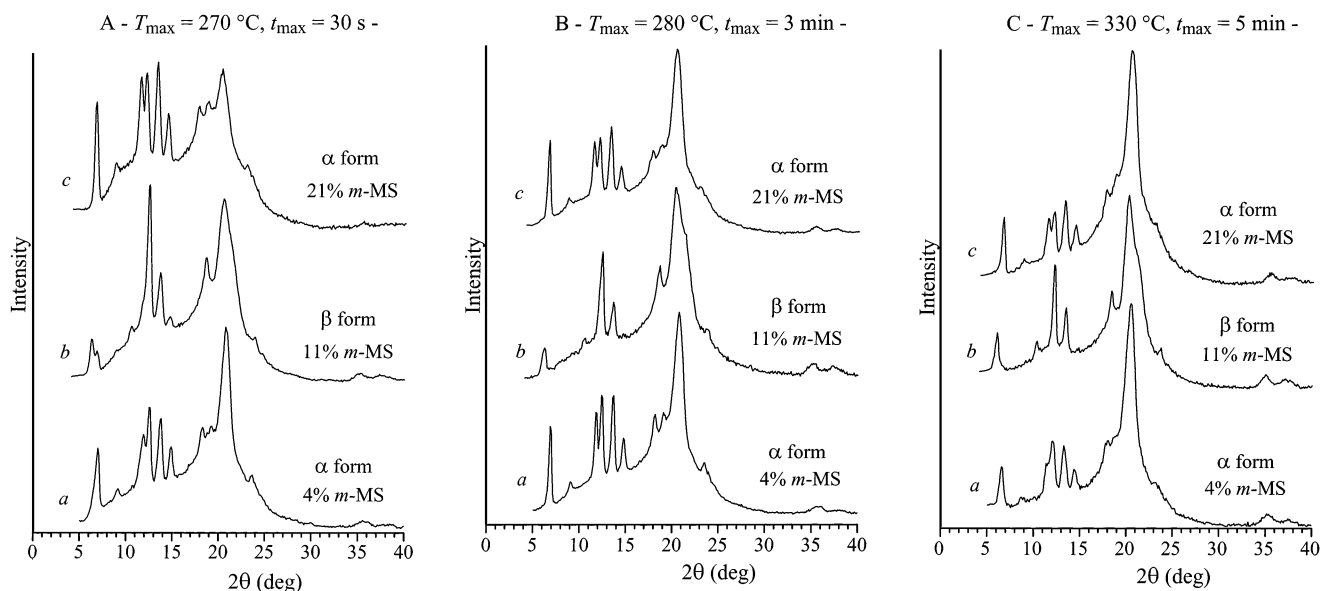


Figure 9. X-ray powder diffraction profiles of sPS/mMS copolymer samples with 4 (a), 11 (b), and 21 mol % of *m*-MS (c), originally in the clathrate or γ forms (samples extracted in 2-butanone), crystallized from the melt by cooling to room temperature at cooling rate of 10 °C/min. The melt has been heated to different maximum temperatures T_{\max} and kept at T_{\max} for a time t_{\max} . Key: (A) $T_{\max} = 270$ °C, $t_{\max} = 30$ s; (B) $T_{\max} = 280$ °C, $t_{\max} = 3$ min; (C) $T_{\max} = 330$ °C, $t_{\max} = 5$ min.

profiles *b* of Figure 9, parts A, B, and C. For the lower value of T_{\max} (270 °C), a small amount of the α form crystallizes for the sample with 11 mol % of *m*-MS, as indicated by the presence of small peaks at $2\theta = 6.8, 11.7, 14.6^\circ$ in the profile *b* of Figure 9A. For $T_{\max} = 280$ and 330 °C, this sample crystallizes instead in the pure β form (profiles *b* in Figure 9, parts B and C). These data show that at low T_{\max} , even though the memory of the α form is maintained in the melt, the presence of *m*-MS in a concentration around 11 mol % induces the crystallization of the β form. As already shown in Figure 7, at high T_{\max} , even though no memory of the α form is present in the melt, the samples with 4 and 21 mol % of *m*-MS crystallize in the new modification of the α form. For these compositions the *m*-MS units destabilize the β form, which, indeed, has never been obtained for the sample with 21 mol % of *m*-MS.

Cold Crystallization. Amorphous samples of the copolymers sPS/mMS have been obtained by quenching the melt in liquid N_2 . Only for the sample with 11 mol % of *m*-MS, not completely amorphous samples, containing very small amounts of crystals of the β form, are obtained. The X-ray powder diffraction profiles of the amorphous samples of the copolymer annealed at 180 °C are reported in Figure 10. It is apparent that all copolymer samples crystallize from the amorphous phase mainly in the disordered modification of α form, as indicated by the presence of the reflections at $2\theta = 6.8, 11.8, 13.6, 17.9, \text{ and } 20.5^\circ$, typical of the α' form,^{1,2} in the profiles of Figure 10. This behavior has been observed also for the s-PS homopolymer.¹ The copolymer with 11 mol % of *m*-MS presents a small amount of β form, as indicated by the reflection at $2\theta = 12.3^\circ$, typical of the β form,⁴ in the profile of Figure 10b. This small amount of β form crystallize during the quenching from the melt, whereas crystals of the α' form crystallize by annealing treatment. In the case of the sample with 21 mol % of *m*-MS, some reflections of the new modification of the α form at $2\theta = 12.3, 14.6, \text{ and } 18.8^\circ$ are also present (profile *c* of Figure 10).

Melting of α and β Forms. DSC heating scans performed at different heating rates of samples in α and

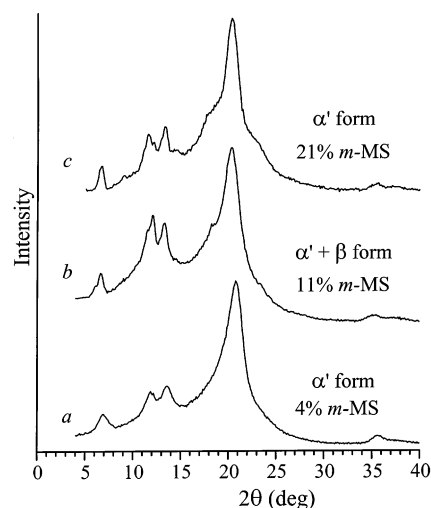


Figure 10. X-ray powder diffraction profiles of sPS/mMS copolymer samples crystallized by annealing at 180 °C quenched amorphous samples: (a) sample sPS/4mMS, 4 mol % of *m*-MS (α' form); (b) sample sPS/11mMS, 11 mol % of *m*-MS (α' form + small amount of β form); (c) sample sPS/21mMS, 21 mol % of *m*-MS (α' form).

β forms of the copolymer sPS/11mMS with 11 mol % of *m*-MS, are reported in Figure 11, parts A and B, respectively. The sample in the new modification of the α form (Figure 11A) has been obtained by annealing at 250 °C the sample extracted in 2-butanone (sample corresponding to the X-ray diffraction profile *l* of Figure 3B). The sample in the β form has been obtained by crystallization from the melt heated at $T_{\max} = 280$ °C, by cooling to room temperature (sample corresponding to the X-ray diffraction profile *b* of Figure 9B).

It is apparent that the melting endotherms of the β form (Figure 11B) are broader than those of the α form (Figure 11A) at any heating rate and show multiple peaks. The area of the peak at higher temperature decreases with increasing heating rate and disappears at 20 °C/min (Figure 11B), indicating the occurrence of recrystallization during heating.

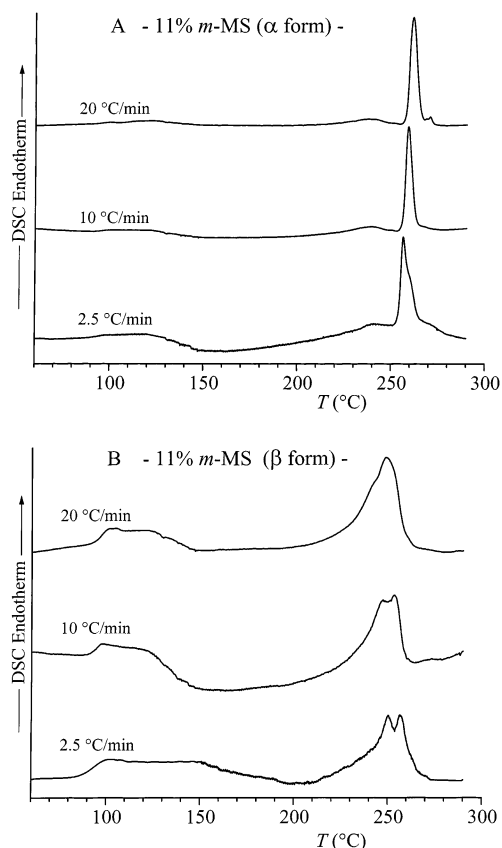


Figure 11. DSC heating scans performed at the indicated different heating rates of samples of the copolymer sPS/mMS with 11 mol % of *m*-MS in the α form (A) and in the β form (B). The sample in the α form (A) has been obtained by annealing at 250 °C the sample extracted in 2-butanone (sample corresponding to the X-ray diffraction profile *l* of Figure 3B). The sample in the β form (B) has been obtained by crystallization from the melt, from $T_{\max} = 280$ °C, by cooling to room temperature (sample corresponding to the X-ray diffraction profile *b* of Figure 9B).

The melting temperatures of samples in the α and β forms of the copolymers with 4 and 11 mol % of *m*-MS, measured at various heating rates from the DSC scans of the kind of Figure 11, are reported in Figure 12, compared to the melting temperatures of α and β forms of s-PS homopolymer.¹⁸

The β form sample of the copolymer with 4 mol % of *m*-MS has been obtained by casting at 180 °C from *o*-DCB solution (sample corresponding to the X-ray diffraction profile of Figure 5a), whereas the α form sample corresponds to the sample crystallized from the melt at cooling rate of 40 °C/min (sample corresponding to the X-ray diffraction profile *d* of Figure 7A). The data for s-PS homopolymer are taken from ref 18 and correspond to the melting temperatures of samples in the pure α and β forms obtained by isothermal crystallizations from the melt at 260 °C, from values of the melt temperature $T_{\max} = 280$ and 340 °C, respectively. As shown in the ref 18, in these samples, melt-crystallized at high temperature, the occurrence of recrystallization phenomena during the DSC heating scans is negligible. For both α and β forms of s-PS only a slight increase of the melting temperature with increasing the temperature, due to superheating, is indeed observed (Figure 12).

It is apparent from Figure 12 that the melting temperature of the sample of the copolymer with 11 mol

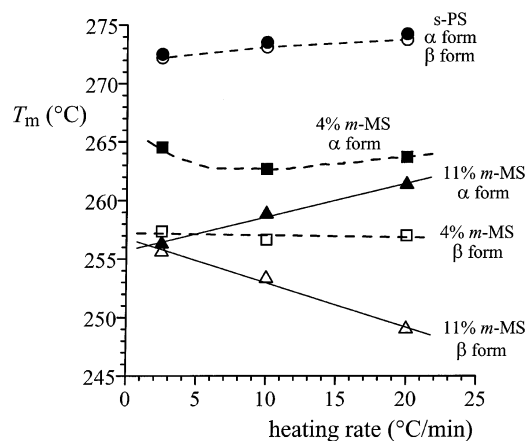


Figure 12. Melting temperatures T_m , evaluated from DSC scans, as a function of the heating rate for samples of s-PS homopolymer and copolymers sPS/mMS in the α and β forms: (●) α form and (○) β form of s-PS; (■) α form and (□) β form of sPS/4mMS copolymer samples with 4 mol % of *m*-MS; (▲) α form and (△) β form of sPS/11mMS copolymer samples with 11 mol % of *m*-MS.

% of *m*-MS in β form decreases with increasing the heating rate, indicating the occurrence of recrystallization phenomena during heating (Figure 11B), whereas that of the sample in the α form increases with increasing the heating rate, indicating the occurrence of superheating (Figure 11A). The data of Figure 12 clearly show that, while the melting temperatures of the α and β form samples of the s-PS homopolymer are very similar regardless of the heating rate, the melting temperatures of the α form samples of the copolymer with 4 mol % of *m*-MS are always higher than those of the β form samples. Moreover, it is worth noting that in the case of the copolymer with 21 mol % of *m*-MS the β form was never obtained in our experiments. This indicates that for copolymers with 4 and 21 mol % of *m*-MS the presence of *m*-MS induces higher stability of the α form. In the case of the copolymer with 11 mol % of *m*-MS, the melting temperatures measured at low heating rates of α and β forms are very similar. This confirms the experimental results that for this concentration of *m*-MS α and β forms have similar stabilities. The α form is obtained by annealing of the γ forms (Figure 3B), whereas the β form crystallizes from the melt in any conditions (Figures 7B and 9).

Structural Variations in the α Form. As shown in previous sections, annealing at high temperatures (240–260 °C) of sPS/mMS copolymers in clathrate or γ forms (Figure 3, curves *i* and *l*), or crystallizations from the melt of copolymers with 4 and 21 mol % of *m*-MS (Figures 7A,C and 9), induce the crystallization of a new modification of the α form of s-PS. The X-ray diffraction profile of this modification, obtained for the three sPS/mMS copolymer samples, is compared in Figure 13 with the X-ray diffraction profiles of samples of s-PS homopolymer in the disordered α' , ordered α'' , disordered β' , and ordered β'' forms.

The pattern of Figure 13a corresponds to the copolymer sample with 4 mol % of *m*-MS obtained by crystallization from the melt, by cooling the melt kept at $T_{\max} = 280$ °C for $t_{\max} = 3$ min to room temperature at 10 °C/min (profile *a* in Figure 9B). Similar patterns have been obtained for the samples with 11 and 21 mol % of *m*-MS annealed at 250 °C or by melt crystallization of the sample with 21 mol % of *m*-MS (Figures 7A,C and 9).

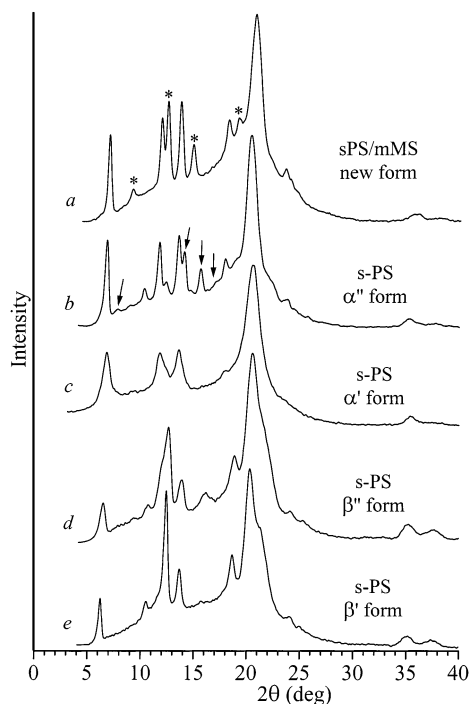


Figure 13. X-ray powder diffraction profiles of sPS/4mMS copolymer sample with 4 mol % of *m*-MS obtained by crystallization from the melt, by cooling the melt kept at $T_{\max} = 280$ °C for $t_{\max} = 3$ min to room temperature at 10 °C/min (a) and of samples of s-PS homopolymer in the α'' form (b), α' form (c), β'' form (d), and β' form (e). In profile a of the copolymer sample, the reflections at $2\theta = 9.0, 12.3, 14.6,$ and 18.8° , which are not present in the diffraction profile of the α'' form of s-PS (profile b), are indicated with asterisks. In profile b of the α'' form of s-PS, the reflections at $2\theta = 7.8, 14.0, 15.6,$ and 17.1° , which are not observed in diffraction profile a of the copolymer sample, are indicated with arrows.

The Bragg angles 2θ of the reflections observed in the X-ray diffraction profiles of α' , α'' , β' , β'' forms of s-PS,^{2–5} compared to those observed in the diffraction profile of the sPS/mMS copolymer samples crystallized in the α form (profile a of Figure 13), are reported in Table 1.

The X-ray diffraction profile of Figure 13a presents all the reflections typical of the disordered α' modification (Figure 13c) of s-PS at $2\theta = 6.8, 11.7, 13.5, 17.9,$ and 20.4° .^{1,2} Additional reflections at $2\theta = 9.0, 10.3, 12.3, 14.6,$ and 18.8° are however present in the diffraction profiles of Figure 13a. The comparison of Figure 13 and Table 1 indicates that these reflections are not accounted for by neither the ordered α'' modification (Figure 13b)^{2,3,5} nor the β form (Figure 13d,e) of s-PS.^{3,4} The weak reflection at 14.6° (Figure 13a) could be interpreted as the 310 reflection of the α'' form^{2,5} (Table 1). However, as shown in Figure 13b and Table 1, this reflection occurs at 14.0° and presents a strong intensity in the diffraction profile of the α'' form of s-PS homopolymer.^{2,5} Moreover, reflections typical of the ordered α'' modification at $2\theta = 7.8, 14.0, 15.6,$ and 17.1° (Figure 13b),^{2,5} are absent in the diffraction profile of the copolymer sample of Figure 13a. This indicates that the crystalline modification obtained in the sPS/mMS copolymers, giving the diffraction profile of Figure 13a, does not correspond to the ordered α'' modification of s-PS.

The presence of the additional reflections at 12.3 and 18.8° in the diffraction profile of Figure 13a could be interpreted with the presence of crystals of the β form, in mixture with crystals of the α' form. These diffraction

peaks could, indeed, correspond to the 040 and 060 reflections of the β form (Figure 13d,e)⁴ (Table 1), but the absence of other typical reflections of both β' and β'' forms, at $2\theta = 6.2, 15.9, 21.1^\circ$ (Figure 13d,e, Table 1) allows ruling out this hypothesis. Therefore, the X-ray diffraction profile of Figure 13a cannot be interpreted by a mixture of crystals of α and β forms, and it indicates that the crystalline form obtained by annealing at high temperatures the γ form in copolymers of s-PS with *m*-MS (Figure 3 curves *i, l*) or by crystallization from the melt of samples with 4 and 21 mol % of *m*-MS (Figures 7 and 9) does not correspond to the α or β forms observed for the s-PS homopolymer. Since most of the reflections, in particular the reflections at $2\theta = 6.8, 10.3, 11.7, 13.5,$ and 20.4° , correspond to crystals of the α form (Table 1), we can assume that for copolymers of s-PS with *m*-MS a new crystalline modification, close to the α form of s-PS, has been obtained. The presence of *m*-MS comonomeric units, for concentration up to 21 mol %, not only influences the polymorphic behavior of s-PS but also induces changes of the crystal packing of the trans-planar chains in the hexagonal unit cell of the α form.^{2,5,10} The *m*-MS would be included, at least in part, in the crystals of the α form, producing changes in the arrangement of the three independent triplets of trans-planar chains in the unit cell (probably different rotation of the triplets around the 3-fold axes). This would explain the change in the intensity of the reflections observed in the diffraction profiles of the copolymers with respect to that of the α form of s-PS. Moreover, changes in the symmetry and dimension of the unit cell cannot be excluded. This new modification could be considered either close to the α form of s-PS, or a completely different crystalline form, if relevant deviations from the hexagonal symmetry of the unit cell are assumed. At moment there are no evidences which allow excluding the latter hypothesis. Work is in progress to clarify this point.

It is worth noting that a variation of the intensity of some reflections of the α'' form has also been observed in samples of copolymers of s-PS with *p*-MS crystallized from the melt.²¹

Conclusions

The polymorphic behavior of s-PS is substantially altered by the introduction of *m*-MS comonomeric units. Variations of the polymorphic behavior have been observed for solvent extraction procedures, for annealing processes, and for solution, melt and cold crystallizations. The change of the polymorphic behavior is different from that observed in copolymers of s-PS with *p*-MS, indicating a different effects of the comonomeric units on the crystallization of the four polymorphic forms of s-PS.

As for s-PS homopolymer and copolymers with *p*-MS, as-prepared samples, crystallized from the polymerization solvent, are in clathrate structures, including solvent molecules in the crystalline phase.

Extraction procedures with boiling 2-butanone of samples of copolymers with low content of *m*-MS in the clathrate form do not induce complete removal of the guest molecules. For high *m*-MS concentration a pure γ form is instead obtained by extraction. In this condition of crystallization, the presence of *m*-MS comonomeric units stabilizes the γ form and the helical mesoporous δ form has never been observed.

The polymorphic transitions of s-PS upon annealing processes are also altered by the presence of *m*-MS. In

Table 1. Bragg Angles 2θ and Intensities I of the Reflections Observed in the X-ray Powder Diffraction Profile of the New Crystalline Form (Probably a New Modification of the α Form) of the Copolymer Sample sPS/4mMS with 4 mol % of *m*-MS of Figure 13a, Compared with the Bragg Angles and Intensities of the Reflections Observed in the X-ray Diffraction Profiles of Samples of s-PS Homopolymer in the α' , α'' , β' , and β'' Forms (Figure 13b–e)^{2–5}

sPS/mMS copolymers		s-PS homopolymer									
new crystalline form		α' form		α'' form		β' form		β'' form			
2θ (deg)	I^a	hkl^b	2θ (deg)	I^a	2θ (deg)	I^a	hkl^c	2θ (deg)	I^a	2θ (deg)	I^a
6.80	s	110	6.76	ms	6.74	s	020	6.15	ms	6.16	ms
		200			7.77	w					
8.98	w										
10.34	vw	210			10.33	w	110	10.46	w	10.43	w
11.73	ms	300	11.78	m	11.67	ms	120			11.83	m
12.34	ms						040	12.33	vs	12.34	vs
13.53	ms	220	13.56	m	13.50	ms	130	13.58	m	13.64	m
14.65	mw	310			14.03	ms					
		400			15.63	m	140			15.94	mw
		320			17.12	vw					
17.89	mw	410	17.95	w	17.96	mw					
18.85	mw						060	18.56	m	18.56	m
20.40	vs	211	20.46	vs	20.32	vs	111	20.23	vs	20.27	vs
							041	21.25	ms	21.15	ms
		510			22.17	vw					
23.21	w	600	23.60	w	23.79	w	170	23.92	w	23.92	w
							080	24.87	vw	25.01	vw
35.65	mw	002	35.19	mw	35.34	mw	002	35.05	m	35.19	mw

^a Key: vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, and vw = very weak. ^b hkl indices of the reflections of α' and α'' forms,^{2–5} corresponding to the hexagonal unit cell with axes $a = b = 26.26$ Å and $c = 5.1$ Å. ^c hkl indices of the reflections of β' and β'' forms,⁴ corresponding to the orthorhombic unit cell with axes $a = 8.81$ Å, $b = 28.82$ Å, and $c = 5.1$ Å.

fact, the transition of clathrate structures of copolymers sPS/mMS into γ form occurs without forming intermediate mesomorphic or amorphous phases, as occurs for s-PS⁸ and copolymers with *p*-MS.²¹ Since in s-PS the mesomorphic form is obtained only by annealing the δ form, the absence of the helical mesomorphic form in the copolymers with *m*-MS is related to the fact that for these copolymers the δ form is not obtained by extraction procedures. The presence of *m*-MS comonomeric units prevents the formation of the δ form and increases the thermal stability of the γ form, which is stable up to 210 °C, regardless of the comonomer content, and transforms into the α form at high temperatures, in the range 220–250 °C.

Crystallization from solution of sPS/mMS copolymers, by casting at low temperatures (<100 °C), produces the formation of clathrate structures. At higher casting temperature (180 °C), copolymers with low *m*-MS content (4 and 11 mol %) crystallize in the ordered β'' modification of s-PS, whereas the sample with higher *m*-MS content (21 mol %) crystallize in a mixture of crystals of γ and α forms. These data indicate that the presence of low contents of *m*-MS stabilizes the β form, whereas the presence of high concentrations of *m*-MS stabilizes the γ form in a large temperature range and also induces crystallization of the α form.

The copolymer sample with 11 mol % of *m*-MS always crystallize from the melt in the β form regardless of the cooling rate and the maximum temperature of the melt. Copolymers with 4 and 21 mol % of *m*-MS crystallize instead in the α form under any condition. The crystallization of α and β forms seems to be independent of the cooling rate and crystallization temperature, but only depends on the concentration of the *m*-MS comonomeric unit. Moreover, even when the memory of the α form is maintained in the melt, the presence of *m*-MS in a concentration around 11 mol %, induces the crystallization of the β form, whereas, even though no memory of the α form is present in the melt, samples with 4 and 21 mol % of *m*-MS crystallize in the α form.

All copolymer samples crystallize by annealing the quenched amorphous samples (cold crystallizations) in the disordered α' form of s-PS.

The comparison of the polymorphic behaviors of copolymers of s-PS with *p*-MS and *m*-MS has clearly shown that both comonomeric units have an important effect inducing the crystallization of α or β forms. The effect of *m*-MS, inducing the crystallization of the β form, is strong for a concentration around 11 mol % of *m*-MS, whereas the effect of *p*-MS, inducing the crystallization of the α form, is strong for concentration of 20 mol % of *p*-MS.

It is worth noting that in the case of the copolymers with *m*-MS crystallized in the α form from the melt or in annealed samples, a new modification of the α form has been obtained. This form does not correspond neither to the disordered α' , nor the ordered α'' modifications observed for s-PS^{1,2,5} and copolymers with *p*-MS,²¹ in annealed and melt-crystallized samples. The X-ray diffraction profile of this new modification of α form presents remarkable changes in the intensities of various reflections. The presence of *m*-MS comonomeric units not only influences the polymorphic behavior of s-PS, but also induces changes of the crystal packing of the trans-planar chains in the hexagonal unit cell of the α form. The *m*-MS would be included, at least in part, in the crystals of the α form, producing changes in the arrangement of the three independent triplets of trans-planar chains in the unit cell (probably different rotation of the triplets around the 3-fold axes).

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References and Notes

- Guerra, G.; Vitagliano, V. M.; De Rosa, C.; Petraccone, V.; Corradini, P. *Macromolecules* **1990**, *23*, 1539.

- (2) De Rosa, C.; Guerra, G.; Petraccone, V.; Corradini, P. *Polym. J.* **1991**, *23*, 1435.
- (3) De Rosa, C.; Guerra, G.; Corradini, P. *Rend. Fis. Acc. Lincei* **1991**, *2*, 227.
- (4) De Rosa, C.; Rapacciuolo, M.; Guerra, G.; Petraccone, V.; Corradini, P. *Polymer* **1992**, *33*, 1423.
- (5) De Rosa, C. *Macromolecules* **1996**, *29*, 8460.
- (6) De Rosa, C.; Guerra, G.; Petraccone, V.; Pirozzi, B. *Macromolecules* **1997**, *30*, 4147.
- (7) Chatani, Y.; Shimane, Y.; Inoue, Y.; Inagaki, T.; Ishioka, T.; Ijitsu, T.; Yukinari, T. *Polymer* **1992**, *33*, 488.
- (8) Manfredi, C.; De Rosa, C.; Guerra, G.; Rapacciuolo, M.; Auriemma, F.; Corradini, P. *Makromol. Chem. Phys.* **1995**, *196*, 2795.
- (9) Chatani, Y.; Shimane, Y.; Ijitsu, T.; Yukinari, T. *Polymer* **1993**, *34*, 1625.
- (10) Cartier, L.; Okihara, T.; Lotz, B. *Macromolecules* **1998**, *31*, 3303.
- (11) Petraccone, V.; Auriemma, F.; Dal Poggetto, F.; De Rosa, C.; Guerra, G.; Corradini, P. *Makromol. Chem.* **1993**, *194*, 1335.
- (12) Auriemma, F.; Petraccone, V.; Dal Poggetto, F.; De Rosa, C.; Guerra, G.; Manfredi, C.; Corradini, P. *Macromolecules* **1993**, *26*, 3772.
- (13) Immirzi, A.; De Candia, F.; Iannelli, P.; Vittoria, V.; Zambelli, A. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 761.
- (14) Chatani, Y.; Shimane, Y.; Inagaki, T.; Ijitsu, T.; Yukinari, T.; Shikuma, H. *Polymer* **1993**, *34*, 1620.
- (15) Chatani, Y.; Inagaki, T.; Shimane, Y.; Shikuma, H. *Polymer* **1993**, *34*, 4841.
- (16) De Rosa, C.; Rizzo, P.; Ruiz de Ballesteros, O.; Petraccone, V.; Guerra, G. *Polymer* **1999**, *40*, 2103.
- (17) Woo, E. M.; Sun, Y. S.; Yang, C. P. *Prog. Polym. Sci.* **2001**, *26*, 945.
- (18) De Rosa, C.; Ruiz de Ballesteros, O.; Di Gennaro, M.; Auriemma, F. *Polymer* **2003**, *44*, 1861.
- (19) Guerra, G.; De Rosa, C.; Vitagliano, V. M.; Petraccone, V.; Corradini, P.; Karasz, F. E. *Polym. Commun.* **1991**, *32*, 30.
- (20) Guerra, G.; De Rosa, C.; Vitagliano, V. M.; Petraccone, V.; Corradini, P. *J. Polym. Sci., Polym. Phys. Ed.* **1991**, *29*, 265.
- (21) Manfredi, C.; Guerra, G.; De Rosa, C.; Busico, V.; Corradini, P. *Macromolecules* **1995**, *28*, 6508.
- (22) Grassi, A.; Longo, P.; Proto, A.; Zambelli, A. *Macromolecules* **1989**, *22*, 104.
- (23) Soga, K.; Nakatani, H.; Monoi, T. *Macromolecules* **1990**, *23*, 953.
- (24) Tornquists, E. G. M.; Welborne, H. C., Jr. Eur. Pat. Appl. 208561, 1987 (to Exxon Chemical Patents Inc.); *Chem. Abstr.* **1988**, *106*, 120391.
- (25) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

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