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Effects of Comonomer Structure on the Polymorphic Behavior of Syndiotactic Polystyrene-Based Random Copolymers

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The polymorphic behavior of syndiotactic polystyrene (sPS) is very complex.[1−12] Four major crystalline forms, α, *β*, *γ*, and *δ*, are proposed. The α- and *β*-forms consist of molecular chains with a planar zigzag conformation (T_4). The α-form has been shown to exist in a hexagonal[2,3] or perhaps rhombohedral[4] structure, whereas the *β*-form exists in an orthorhombic structure.[5] The *γ*- and *δ*-forms consist of molecular chains with a helical conformation (T_2G_2).[6,7] The *γ*-form, which may have a monoclinic structure, is a completely dried crystalline form, whereas the *δ*-form, which exists in a monoclinic structure, is always formed in the presence of a solvent and includes some solvent molecules.

It has been known that the presence of a comonomer can influence the polymorphic behavior of a crystalline polymer.[13] In the case of syndiotactic poly(styrene-*co*-*p*-methylstyrene)[14] and syndiotactic poly(styrene-*co*-*p*-*n*-butylstyrene),[15] it is observed that the relative amount of α-form to *β*-form increases with increasing comonomer content in the copolymers, indicating that the comonomer favors the α-form rather than the *β*-form. In an attempt to investigate the effect of the comonomer structure, such as flexibility and bulkiness of the comonomer unit, on the polymorphic behavior of sPS-based random copolymers, in this study, isoprene and 2-vinylnaphthalene are chosen as a representative flexible and rigid (bulky) comonomer, respectively. Syndiotactic poly(styrene-*co*-isoprene), sP(S-*co*-I), and syndiotactic poly(styrene-*co*-2-vinylnaphthalene), sP(S-*co*-2VN), are synthesized using metallocene catalysts[16,17] and their polymorphic behaviors are investigated using wide-angle X-ray diffraction (WAXD).

According to the method in the literature, styrene was copolymerized with isoprene[16] or with 2-vinylnaphthalene[17] using $CpTiCl_3$ (Cp = cyclopentadienyl)/methylaluminoxane (MAO) catalyst or $IndTiCl_3$ (Ind = indenyl)/MAO catalyst, respectively. The sPS homopolymer was obtained by polymerizing styrene using the $CpTiCl_3$/MAO catalyst. All the polymerizations were performed in a stirred glass flask at 40 °C under vacuum with an [Al]/[Ti] molar ratio of 2000. As-polymerized powders were purified by extraction with boiling acetone for 10 h in a Soxhlet extractor, and then dried in vacuo at 40 °C. The composition of sP(S-*co*-I) was determined by a ^1H NMR spectrometer (JEOL Lambda-300) at 120 °C using $C_2D_2Cl_4$ and hexamethyldisiloxane as a solvent and an internal reference, respectively. In the case of sP(S-*co*-2VN),^1H NMR spectra were obtained on a Varian 200 MHz spectrometer at 25 °C using $CDCl_3$ and TMS. Characteristics of all samples are summarized in Table 1.

Table 1. Characteristics of Samples

sample	comonomer content in copolymer[a] (mol %)	polymer fraction insoluble in acetone[b] (wt %)	T_m[c] (°C)
sPS	0.0	95	262
sP(S-*co*-I)-3	3.1	83	256
sP(S-*co*-I)-6	5.7	72	245
sP(S-*co*-2VN)-4	4.2	91	247
sP(S-*co*-2VN)-7	6.9	91	233

[a] Evaluated from ^1H NMR spectra. [b] Determined from extraction in boiling acetone for 10 h. [c] Determined from DSC scans at 20 °C/min.

WAXD patterns were obtained on a diffractometer (MAC MXP18A-HF) using nickel-filtered Cu Kα radiation at a scanning rate of 2°/min. Melt-crystallized samples were prepared by compression-molding powders into thin films in a hot press at 290 °C for 5 min, and then by cooling the films to room temperature in air. To obtain WAXD patterns of annealed samples, powder samples were directly put in an oven previously controlled at a given annealing temperature (T_a) and then annealed for 1 h under vacuum.

When the sPS homopolymer is melt-crystallized, pure α- and *β*-form crystals, or mixed crystals of (α + *β*)-form can be obtained, depending upon the crystallization conditions.[1,11,14] When the sPS is nonisothermally melt-crystallized, the formation of α-form crystals is more favored than that of *β*-form crystals at high cooling rates, whereas the formation of the *β*-form is more favored at low cooling rates.[1,14] Under the isothermal melt crystallization, the relative content of *β*-form to α-form is increased with increasing crystallization temperature.[11] Therefore, the α-form is considered as a kinetically favored form, while the *β*-form is a thermodynamically favored one.[1,14] Figure 1 shows WAXD patterns of melt-crystallized samples. It is observed that sPS, sP(S-*co*-2VN)-4, and sP(S-*co*-2VN)-7 form mixed crystals of the ($\alpha + \beta'$)-form, whereas both sP(S-*co*-I)-3 and sP(S-*co*-I)-6 exhibit only the β'-form with typical reflections at $2\theta \approx 6.0°$, 10.2°, 12.2°, 13.5°, 18.5°, 20.1°, 23.8°, and 34.9°. For both sP(S-*co*-2VN)-4 and sP(S-*co*-2VN)-7, the relative peak intensity at $2\theta \approx 11.6°$ (α-form) to $2\theta \approx 12.2°$ (*β*-form) is much stronger than that of sPS. According to the method of Guerra et al.,[1] the percentage contents of the α-form (P_α) are quantitatively evaluated. The values obtained for sPS, sP(S-*co*-I)-3, sP(S-*co*-I)-6, sP(S-*co*-2VN)-4, and sP(S-*co*-2VN)-7 are 56.4, 0.0, 0.0, 83.2, and 93.4%, respectively. It is also revealed that the amount of α-form increases with the increasing in the content of 2VN comonomer in sP(S-*co*-2VN). When compared with sPS, it is found that sP(S-*co*-I)-3 and sP(S-*co*-I)-6 favor the thermodynamically favored *β*-form crystals, whereas sP(S-*co*-2VN)-4 and sP(S-*co*-2VN)-7 favor the kinetically favored α-form crystals. When the dependence of P_α of the copolymers on the melt temperature (280, 290, and 310 °C) is examined, it reveals that the P_α values of the copolymers are decreased with increasing melt temperature,[18] which is consistent with the results of sPS.[1]

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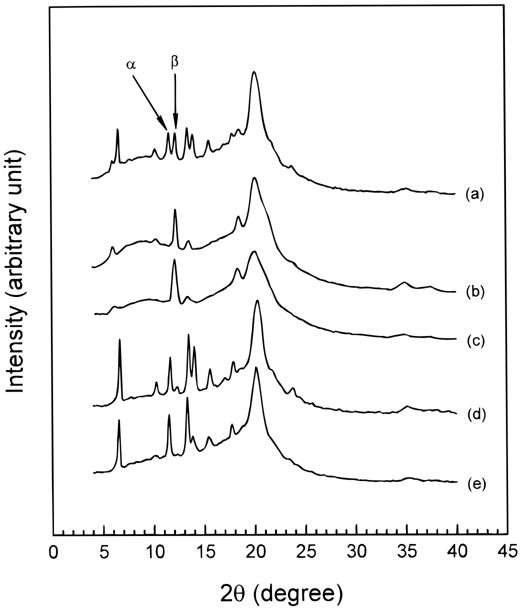

Figure 1. WAXD patterns of melt-crystallized samples: (a) sPS (($\alpha + \beta'$)-form; $P_\alpha = 56.4\%$); (b) sP(S-*co*-I)-3 (β'-form; $P_\alpha = 0.0\%$); (c) sP(S-*co*-I)-6 (β'-form; $P_\alpha = 0.0\%$); (d) sP(S-*co*-2VN)-4 (($\alpha + \beta'$)-form; $P_\alpha = 83.2\%$); (e) sP(S-*co*-2VN)-7 (($\alpha + \beta'$)-form; $P_\alpha = 93.4\%$).

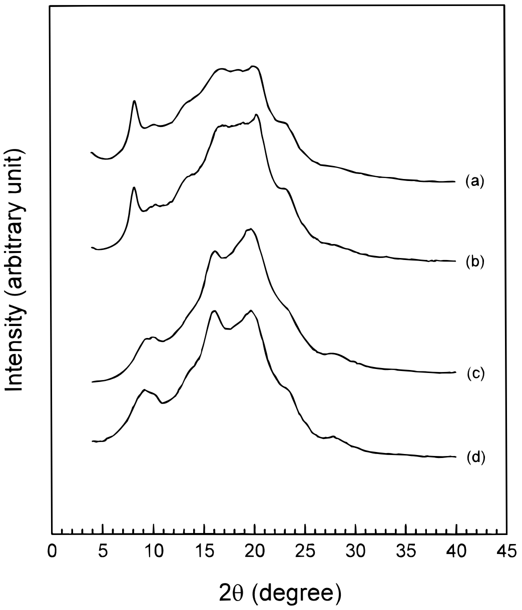

Figure 2. WAXD patterns of unannealed powder samples: (a) sP(S-*co*-I)-3 (δ_e-form); (b) sP(S-*co*-I)-6 (δ_e-form); (c) sP(S-*co*-2VN)-4 (γ-form); (d) sP(S-*co*-2VN)-7 (γ-form).

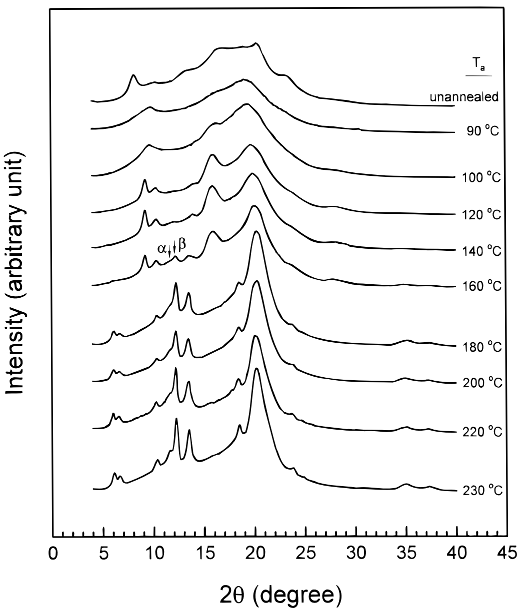

Figure 3. WAXD patterns of sP(S-*co*-I)-6 powders annealed for 1 h at various temperatures.

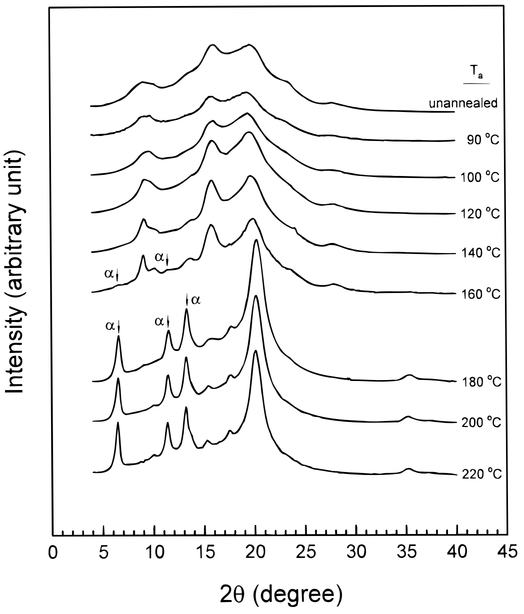

Figure 4. WAXD patterns of sP(S-*co*-2VN)-7 powders annealed for 1 h at various temperatures.

Figure 2 shows WAXD patterns of unannealed powder samples after extraction with boiling acetone for 10 h. The WAXD patterns of sP(S-*co*-I)-3 and sP(S-*co*-I)-6 exhibit reflection peaks located at $2\theta \approx$ 8.2°, 10.2°, 13.5°, 17.2°, 20.0°, and 23.3°, and the peak intensity at $2\theta \approx$ 8.2° is much stronger than that at $2\theta \approx$ 10.2°, which are typical features of a substantially "emptied" clathrate, δ_e-form, of sPS homopolymer.[12] In contrast to sP(S-*co*-I)-3 and sP(S-*co*-I)-6, both sP(S-*co*-2VN)-4 and sP(S-*co*-2VN)-7 exhibit peaks of γ-form crystals, indicated by reflections located at $2\theta \approx$ 9.4°, 10.0°, 16.1°, 19.7°, and 28.5°. When compared with the well-developed γ-form, however, it is revealed that the shape of peaks is broader, implying that the γ-form crystals in sP(S-*co*-2VN)-4 and sP(S-*co*-2VN)-7 are not fully developed ones.

Figure 3 shows WAXD patterns of sP(S-*co*-I)-6 annealed at various temperatures (T_a). When the sP(S-*co*-I)-6 is annealed, the WAXD pattern of the δ_e-form gradually disappears with increasing T_a and the typical patterns of the γ-form appear at 120 °C with reflections at $2\theta \approx$ 9.2°, 10.3°, 13.9°, 15.9°, 19.9°, and 28.1°. When the annealing temperature is further increased, the peaks of mixed crystals of the ($\alpha + \beta$)-form gradually appear at about 160 °C, implying that the γ-form crystals transform into mixed crystals (($\alpha + \beta$)-form) having a planar zigzag conformation. Finally, when sP(S-*co*-I)-6 is annealed above 180 °C, the sample has mainly β-form crystals with a small amount of α-form.

Figure 4 shows WAXD patterns of sP(S-*co*-2VN)-7 annealed at various temperatures. It is observed that the sP(S-*co*-2VN)-7 samples annealed at lower temperatures show broader γ-form reflection peaks, indicating that these crystals are not perfect γ-form crystals. When the sample is annealed at higher temperatures, e.g., 140 °C, the imperfect crystals are gradually reorganized into more perfect γ-form crystals, as indicated by an improvement of resolution of peaks at $2\theta \approx 10.2°$ and 13.8°. When the annealing temperature is increased further to 160 °C, the WAXD pattern exhibits the presence of α-form crystals as indicated by reflections located at $2\theta \approx 6.6°$, 11.6°, and 13.4°, implying a transition from γ- to α-form crystals. Finally, when the sample is annealed at a temperature higher than 180 °C, the sample has mostly α-form crystals as indicated by typical reflections located at $2\theta \approx 6.6°$, 10.1°, 11.6°, 13.4°, 15.4°, 17.7°, 20.2°, 23.5°, and 35.2°.

Changes in the crystal structure of sPS upon annealing generally depend on the crystalline form of the starting materials.[1] Samples initially in δ- or δ_e-forms are transformed into mixed $(\alpha + \beta)$-forms by annealing at temperatures higher than 200 °C, while samples initially in the γ-form transform into the α-form by annealing. Therefore, the results of Figures 3 and 4 can also be explained by considering different crystalline forms of the starting materials; that is, the sP(S-*co*-I)-6 sample, initially in the δ_e-form, transforms into mixed $(\alpha + \beta)$-forms, while the sP(S-*co*-2VN)-7 sample, initially in the γ-form, transforms into the α-form by annealing at high temperatures.

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