

Crystallization of Newly Synthesized Syndiotactic Graft Copolymers

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Crystallization behavior of newly synthesized syndiotactic graft copolymers of polystyrene having side chains of atactic polystyrene (APS) or of polyisoprene were studied. The APS side chains were found to have rather strong effect to prevent crystallization of the main chain of syndiotactic polystyrene.

Recently, we could successfully synthesize graft copolymers with stereoregular main chains, namely syndiotactic polystyrene (SPS) having side chains of atactic polystyrene (APS)¹ or side chains of polyisoprene (PIP).^{2,3} Though depression of crystallinity is well known by the introduction of chain branching in the case of polyethylene,⁴ more complicated behavior is expected for these graft copolymers in terms of polymorphism and miscibility between the main chain and side chains. The constituent of the main chain, SPS, is known to present complicated polymorphic behavior.⁵ APS (homopolymer) is reported to be miscible to SPS,⁶ while PIP is immiscible to SPS. It is interesting to compare the effects of these two kinds of side chains on the crystallization of the SPS main chain.

There are some reports about the influence of heterogeneity on polymorphic behavior of SPS.⁷⁻⁹ For example, Manfredi et al.⁸ studied random copolymers of SPS with *p*-methylstyrene (*p*-MS) comonomeric units. The copolymer samples were crystallized from the melt and their polymorphism was discussed. The influence of blending SPS with miscible amorphous polymers on the polymorphic behavior was reported by Guerra et al.⁹ While the APS did not affect the polymorphism of SPS, blending with poly(2,6-dimethyl-1,4-diphenylene oxide) (PPO) changed the polymorphic behavior. How about the case of the graft copolymers of SPS? The study on the polymorphic behavior of syndiotactic graft copolymers is now in progress. In this letter, we report an unexpected finding that graft copolymerization with side chains of APS strongly prevents crystallization of the main chain of SPS from the melt, along with some preliminary results about the polymorphic behavior.

By utilizing the CpTiCl₃ catalyst in combination with methylaluminoxane, which gives SPS homopolymer, we prepared graft copolymers of SPS having PIP side chains (SPS-*graft*-PIP) by copolymerization of styrene with the PIP macromonomer bearing a terminal styryl group.^{2,3} After the copolymerization in toluene solvent, the solution containing the copolymer was poured into a large amount of methanol with dilute hydrochloric acid. The precipitated copolymer was filtered and washed with methanol and dried, and then further washed with methyl ethyl ketone to remove unpolymerized macromonomer and stereoirregular components. By using of the similar process, we also prepared graft copolymers of SPS having APS side chains (SPS-*graft*-APS).¹ The characteristic of each sample is listed in Table 1.

Table 1. Characteristic of the samples

Code	MM ^a / wt%	M _n × 10 ⁻⁴	M _w /M _n	f ^b
SPS	0	3.90	1.73	0
SPS- <i>graft</i> -PIP-9.2	9.2	2.88	1.57	1.4
SPS- <i>graft</i> -PIP-19.4	19.4	1.79	1.68	1.8
SPS- <i>graft</i> -APS-11.8	11.8	3.10	1.67	3.3
SPS- <i>graft</i> -APS-17.3	17.3	3.64	1.77	5.7

^aContent of macromonomers. ^bNumber of macromonomers per molecules.

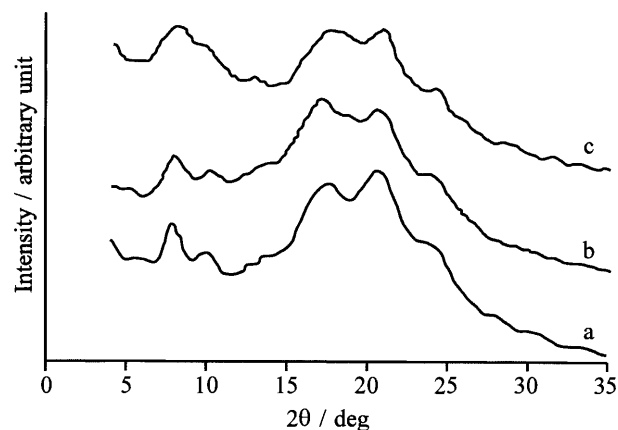


Figure 1. X-Ray diffractograms of as-prepared samples: a, SPS; b, SPS-*graft*-PIP-19.4; c, SPS-*graft*-APS-17.3. The CuK α radiation monochromatized with a graphite monochromator was used for the X-ray beam source.

Figure 1 shows the X-ray diffractograms of as-prepared samples. The major reflections were indexed using the unit cell of the clathrate δ -form^{5,10,11} of the SPS homopolymer. On heating the as-prepared samples up to the melting region, each sample showed complicated behavior in the DSC scan (Figure 2). By examining the X-ray diffractograms of the samples annealed at 130 °C, the exothermic peaks between 100 and 140 °C was attributed to transformation of the δ -form to the γ -form for all the samples; by annealing at the higher temperature, SPS (annealed at 220 °C) transformed to the α' -form, while SPS-*graft*-PIP-11.4 (annealed at 210 °C) and SPS-*graft*-APS-17.3 (annealed at 170 °C) transformed to the β' -form.

The molten samples were then slowly cooled to room temperature, and their X-ray diffractograms were taken. While distinct crystalline reflections attributed to the β' -form^{5,12-14} were observed for both the SPS and the SPS-*graft*-PIP-19.4, only diffuse scattering was observed for SPS-*graft*-APS-17.3.

Then the samples were subjected to the DSC measurements again; the results are shown in Figure 3. A distinct endothermic peak of crystal melting is observed for SPS

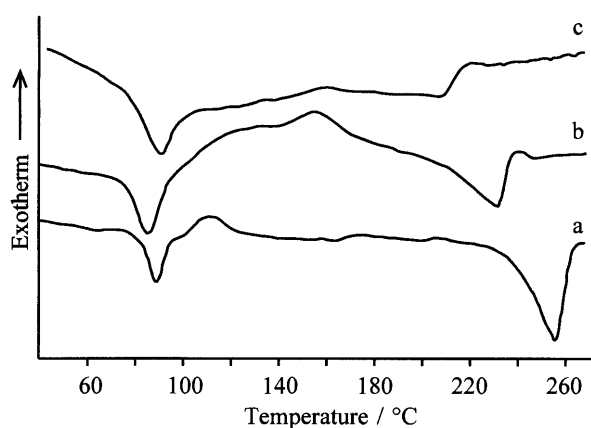


Figure 2. DSC scans for the as-prepared samples at a rate of 10 °C/min: a, SPS; b, SPS-*graft*-PIP-9.2; c, SPS-*graft*-APS-17.3.

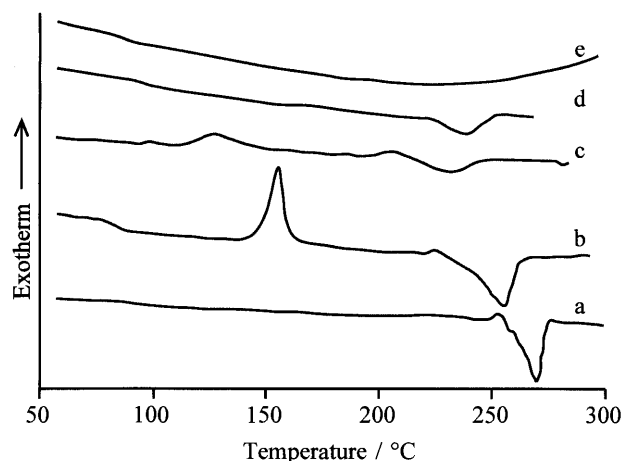


Figure 3. DSC scans for the melt-crystallized samples at a rate of 10 °C/min: a, SPS; b, SPS-*graft*-PIP-9.2; c, SPS-*graft*-PIP-19.4; d, SPS-*graft*-APS-11.8; e, SPS-*graft*-APS-17.3.

homopolymer. As for SPS-*graft*-PIP samples, exothermic peaks which may be attributed to recrystallization into more perfect crystallites appeared between 110 and 160 °C. Endothermic peaks of crystal melting are also clearly observed though the melting temperatures are depressed and the peaks are broadened with increasing PIP content. In the case of SPS-*graft*-APS-11.8, the exothermic peak of recrystallization is not observed. The melting temperature is depressed and the melting peak is broadened; the degree of the broadening of the melting peak for SPS-*graft*-APS-11.8 is comparable to that for SPS-*graft*-PIP-19.4. As for SPS-*graft*-APS-17.3, the crystalline melting peak disappeared, though the weight fraction of heterogeneity is not so different from SPS-*graft*-PIP-19.4. A slow crystallization rate was suspected as a reason for the disappearance of the melting peak. However, even when SPS-*graft*-APS-17.3 was cooled much more slowly from the melt in another run, the melting peak did not appear. Accordingly, the crystallinity of SPS (from the melt) may have lost by introducing ca. 17 wt% of APS side chains, though as-prepared SPS-*graft*-APS-17.3 has been crystallized in the δ -form. This depression of crystallinity is a rather strong effect which is not expected from the preceding studies.⁷⁻⁹

As for the blends of SPS with APS, crystallinity is reported for the samples up to 75 wt% of APS content.¹⁵ We also confirmed a distinct crystal melting peak in the DSC scan for the blend sample containing 78 wt% of APS, which was melt-crystallized. Blending a crystalline polymer with a noncrystalline polymer seems to have only a weak influence on the crystallization of the former. Even in the case of miscible combination, the effects may be, at most, a dilution which may reduce the growth rate of the crystallites.⁶

On the other hand, it is naturally presumed that crystallinity of a crystalline polymer is suppressed by copolymerization. Crystallites will be disordered by the heterogeneity which is connected to the main chain, and accordingly, the depression of crystallinity and the melting temperature may result. In this experiment, the "miscible" side chains (APS) of the graft copolymer had the stronger influence on crystallization of the main chain than the "immiscible" ones (PIP), probably because the segments of the latter may separate from the segments of the main chain.

However, in the case of SPS-*graft*-APS-17.3, the influence of the side chain appears to be still strong when it was compared with the random copolymer of SPS with 20 wt% of *p*-MS.⁸ The former could not crystallize from the melt, while crystallinity of the latter has been reported;⁸ the two have comparable amount of heterogeneity. In this case, one would rather expect higher crystallinity for SPS-*graft*-APS, because the graft copolymer should have a longer average length of successive SPS constituents than the random copolymer, when the same amount (molar ratio) of heterogeneity is introduced: heterogeneity is localized in the graft copolymer. The discrepancy between this expectation and the experimental result may come from the topological feature of the graft copolymer and from the miscibility between the SPS main chain and the APS side chains.

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