Polymorphism and Phase Transitions upon Annealing in Solvent-Cast vs Quenched Syndiotactic Polystyrene and Its Blends with Atactic Polystyrene

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ABSTRACT: The crystal polymorphism and phase transition mechanisms upon specific annealing schemes imposed on either neat syndiotactic polystyrene (sPS) or its miscible blends with atactic polystyrene (aPS) were examined using Fourier transform infrared (FT-IR) and wide-angle X-ray diffraction (WAXD). The neat sPS or blends were made in such ways that they started as either initially an amorphous/quenched material or solvent-treated to contain initially some trace crystalline γ-form. Cold crystallization imposed on the initially quenched/amorphous sPS led to the random-coil chains being crystallized into initially a mesomorphic form and subsequently into a more perfect crystalline α′-form. IR spectroscopy characterization confirmed a series of structural changes with respect to the annealing temperature imposed on initially quenched/amorphous sPS and revealed a transition from a mesomorphic form to a crystalline α′-form via a nucleation and growth process. Conversely, cold crystallization imposed on the initially quenched miscible blends (sPS/aPS) did not involve a mesomorphic form but developed directly into a crystalline α- and/or β-form upon further annealing to higher temperatures. However, the transition behavior was similar between the solvent-cast neat sPS and solvent-cast sPS/aPS blend upon annealing to higher temperatures. The solvent (1,1,2,2-tetrachloroethane)-induced γ-form in the sPS/aPS blend or neat sPS samples, upon heating to temperatures above 200 °C, both exhibited crystal reorganization of the melted crystalline γ-form originally present, which led to formation of the crystalline α′-form. The mechanisms and causes for the different routes of phase transitions in neat sPS or its miscible blends were discussed and analyzed.

Introduction

Studies on syndiotactic polystyrene (sPS) have been extensive since the discovery of successful synthesis of highly stereoregular sPS in 1986.[1−3] Typically, the crystalline α (α′, α″)- and β'-forms can be obtained by melt and/or cold crystallization of sPS.[4−8] Of these two, the crystalline α-form is kinetically favorable while the crystalline β-form is thermodynamically favorable.[4−11] For melt crystallization, a combination of α″- and β'-forms is produced at lower temperatures, and differences in thermal treatments lead to variation of relative proportions of these two crystalline forms.[4] By significant contrast, the crystalline β'-form becomes the only discernible species if sPS is melt-crystallized at temperatures equal to or higher than 260 °C.[4]

Furthermore, it is known that the preference of crystal packing in sPS may be altered as sPS is mixed with other polymers to form miscible blend systems. For example, when sPS is melt-blended with either atactic polystyrene (aPS) or poly(1,4-dimethyl-*p*-phenylene oxide) (PPO), only a crystalline β-form and no α-form is present in the miscible sPS blends with either of these two amorphous polymers (aPS or PPO).[4,7,8] In addition, cold crystallization (from quenched amorphous sPS) at temperatures lower than 200 °C has been found to produce only the crystalline α′-form, while the α″-form is obtained at temperatures higher than 200 °C.[6−8] Recently, De Rosa et al. have found that a mesomorphic form having chains with zigzag planar backbone conformation is present in sPS when cold-crystallized at lower temperatures (<150 °C).[12,13] The meso form can eventually transform into a more perfect crystalline α′-form with a higher degree of crystallinity by further annealing the cold-crystallized sPS at certain higher temperatures.[13,14] Additionally, solvent-induced crystals in sPS undergo a different route of transformations. For examples, it has been reported that sPS first develops a polymer−solvent complex of crystalline δ-form with a TTGG helical conformation as sPS is exposed to vapor of organic solvents.[15−21] Solvent-induced crystals of mesoforms in sPS, when heated to high temperatures, can go through some transformations, eventually to a more perfect α′-form. A common solvent-induced crystal in sPS is originally in the crystalline δ-form, which is a meso form containing some solvent molecules. The solvent-trapped crystalline δ-form can be transformed into a γ-form by heating to ca. 130 °C. Eventually at higher temperatures, the crystalline α′-form can be obtained by a transformation from the melting of the solvent-free crystalline γ-form via a melting and recrystallized process at temperatures above 200 °C. Alternatively, acetone extraction of the solvent-induced crystals in sPS undergo yet different routes of crystal transformations. De Rosa et al. have reported that a $\delta_{\mathrm{emptied}}$-form of a clathrate structure is obtained by removal of the trapped solvent (by extracting the fresh solution-cast sPS with boiling acetone).[19,22] The $\delta_{\mathrm{emptied}}$-form sPS can then be subjected to annealing of about 110 °C to produce a mesomorphic form having helical

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conformations, which is different from the mesomorphic form consisting of all-trans conformations (obtained in low-temperature cold crystallization under no solvents). Further annealing at 130 °C of the helical mesomorphic form can lead to a transformation to a crystalline γ-form.[19,22]

The polymorphism and crystalline forms in sPS can be determined by X-ray diffraction, while the Fourier transform infrared spectroscopy is a useful tool to identify and characterize the chain conformation changes associated with the different polymorphic crystal forms as well as the different vibrational frequencies between the amorphous and crystalline phases. For instance, a very characteristic peak at 1222 cm^{-1} has been assigned to the presence of an all-trans planar zigzag conformation packed in a crystalline form, and this peak is virtually absent in sPS possessing only the helical-conformation crystal and/or amorphous form.[3,23-25] The absorbance bands at 858 and 910 cm^{-1} are clarified as the vibrational frequency of the crystalline β'-form while the 852 and 902 cm^{-1} bands are attributed to the absorptive frequency of the crystalline α''-form. As for the noncrystalline or helical phases, only the bands at 841 and 906 cm^{-1} are evident.[10,14] The 852 and 856 cm^{-1} bands, whose intensity changes with the degrees of crystallinity, are present simultaneously in the spectrum for the cold-crystallized sPS comprised of only the α'-form.[14] By labeling the characteristic absorption bands, the crystallinity as well as absorptive ratios of the α''- and β'-forms can be quantitatively determined for the sPS samples subjected to cold and melt crystallization by using the Fourier transform infrared spectra in the frequency range from 820 to 865 cm^{-1}.[10] In addition, Tashiro et al.[20,21] have proposed that the peak half-width and position changes as a function of swollen time can be used to detect the molecular motion alteration as glassy/amorphous sPS samples are exposed to various solvent vapors. It has been also found that the half-width increases and the vibrational absorbance shifts toward the lower-frequency side as the amorphous sPS chains are activated by solvent molecules.[20,21] The solvent molecules trapped in sPS have acted as plasticizers and eased the polymer chains in going from the amorphous phase to the crystalline δ-form.[20,21]

As listed above, there have been many studies on the structure and polymorphism in sPS. However, there are still many unsolved issues. For example, according to the models proposed by De Rosa et al. and co-workers,[12,13] the local organization in triplets of trans-planar chains, typical of the different modifications of the crystalline α-form, can be also present in the disorder chain agglomerates of the mesomorphic form.[12] Later, they proposed the mesomorphic form to be composed of small imperfect crystals of the hexagonally crystalline form.[13] This so-called "planar mesomorphic form" in sPS (using the nomenclature proposed in ref 19) may be different from the "mesophase" which is often considered as a partial order without crystalline order. Thus, the nature of the mesomorphic form and its relationship with crystalline form in sPS have not been completely understood. Here and below, the original terminology labeled the intermediate phase (between amorphous phase and crystalline α'-form) as a mesomorphic form, although it has been shown that mesomorphic form can possess some partial crystalline order, as clarified by WAXD.[13] Thus, the mesomorphic form as addressed in this work may include short-chain segments of an all-trans conformation as well as small imperfect crystals with an all-trans conformation, if any.

In continuing our previous work,[5-7] the objective of this study was to examine how individual initial starting form (amorphous phase and/or γ-form) in sPS and sPS/aPS blends may be related to structural transitions in thermal-treated sPS and its mixtures with aPS. A mesomorphic form was identified, and the mechanism of its transformation gradually into a perfect α'-form via a nucleation and growth was examined and proven using various techniques. Relationships between the structural changes and the temperature of cold crystallization were examined in direct comparison with miscible sPS blend samples. In addition, we briefly discussed factors affecting the crystallization of α- or/and β-type crystals in the solution-cast sPS blends with various aPS contents subjected to similar slow heating process. Infrared absorbance peaks are quite sensitive to intermolecular interactions between polymers and solvents, polymer−polymer, or the ordered states of polymer chains, etc. Thus, the crystal phases and chain conformations in the polymer−solvent complexes or polymer crystals can be effectively analyzed using FT-IR spectroscopy. To this purpose, the decomposed well-defined IR bands were employed to investigate the mesomorphic form as well as the α'-type crystal. Effects of miscibility in the blend states on the development of crystal types and crystal transition of planar mesomorphic form and/or initial γ-form to a more perfect α'-form in miscible sPS/aPS blends vs neat sPS were proposed and examined.

Experimental Section

Materials and Procedures. Semicrystalline syndiotactic polystyrene (sPS) was obtained as a courtesy sample material from Idemitsu Petrochemicals Co., Ltd. (Japan), with a high M_w = 241 000 g/mol and PI (M_w/M_n) = 2.3. The supplier-furnished data of percent syndiotacticity of the sPS indicate very high tacticity (greater than 95%). Atactic polystyrene (aPS) was chosen (Chi-Mei, Inc., Taiwan; M_w = 237 000 g/mol (GPC), PI = 3.1, and T_g (onset) = 87.5 °C).

For each of the thermal treatments, the two types of the initial starting form of sPS and its blends with various fractions of atactic polystyrene (aPS) were prepared: quenched amorphous glass materials and solution-cast polymer−solvent complexes of crystalline γ-form. Hot-melt mixing was used for preparing blend samples of sPS with aPS. The as-blended sPS/aPS (90/10, 75/25, and 50/50) mixtures were molded between two KBr films and quenched into liquid nitrogen to obtain amorphous samples with virtually no crystallinity. Transparent, crystal-free, amorphous sPS or blend material was obtained upon fast quenching from melt. Then, the quenched amorphous sample films (neat sPS or blends) were heated by scanning or step-heating between the T_g and T_m for annealing to induce "cold crystallization". Subsequently, phase transitions or polymorphism changes in the annealed neat sPS or miscible blends were characterized. Here, "cold crystallization" means that crystallization takes place from amorphous neat sPS or blends that have been quickly brought from a melt state to a glassy/amorphous state by quenching into liquid nitrogen.

Another set of samples was obtained by solvent-casting. The crystalline γ-form in neat syndiotactic polystyrene or its blends was produced in procedures as follows. First, the materials were dissolved in 1,1,2,2-tetrachloroethane ($Cl_2CHCHCl_2$) in glass tubes at about 130 °C (below the boiling point of $Cl_2CHCHCl_2$, 146.2 °C at atmospheric pressure). The polymer concentration of 2% (w/w) was determined from the amounts of the polymer and solvent weighed into the sample tubes. The polymer solution was then cast into films of ca. 100 μm at 60 °C and desiccated at 60 °C for 12 h in a vacuum. Prior to various thermal treatments, all cast neat sPS or sPS/aPS blends of three compositions were prepared: 90/10 75/25, and 50/50, with each starting form as the polymer−solvent complexes of the γ-form. Similar heating schemes were imposed on the as-cast sPS/aPS blends for the solvent-cast neat sPS subjected to the same thermal histories. The crystal forms and the $\gamma \rightarrow \alpha'$-form transitions were similarly examined for the neat sPS as well as the blends in order to compare the results. The cast sPS and its blend films were then subjected to various thermal annealing schemes, as more clearly specified in the following discussion sections.

Apparatus. Wide-angle X-ray instrument (WAXD) was Shimadzu XRD-6000 with copper Kα radiation (30 kV and 40 mA) and a wavelength of 1.542 Å. The scanning 2θ angles ranged from 3° to 30° with a scanning speed of 2°/min. Further thermal treatments of the quenched glassy sPS samples were performed in situ directly in the XRD high-temperature oven (VOS-200SD) with a PID controller with an accuracy of ±1.5 °C from 60 °C to various holding temperatures.

Fourier transform infrared spectroscopy (FT-IR, Magna-560, Nicolet) was used for investigating conformations and crystal types in sPS. Spectra were obtained at 2 cm^{-1} resolution and average was obtained from at least 64 scans in the standard wavenumber range of 400−4000 cm^{-1}. Thin films for FT-IR studies were obtained by casting sPS solutions onto potassium bromide (KBr) disks, and then solvent was removed in a vacuum at 60 °C. Thermal annealing of specific schemes was then imposed on the KBr-cast sPS film and its blends as well as quenched glassy film samples. In this study, owing to concerns and problems in temperature precision, less heat transfer delay, and IR baseline stability, the in-situ IR heating cell was not used. Instead, the samples (neat sPS or blends) were heated on a microscope hot stage (which has much better thermal contact and precise temperature control) and rapidly quenched to “freeze” and “preserve” the phase or morphologies that developed in the sPS or sPS/aPS blend samples. These thermal schemes were done and completed on samples prior to placing them in the IR beams for spectroscopic characterization at ambient temperatures. Much better temperature precision and baseline stability could be assured in the IR data.

FTIR Analysis Procedures. Peaks were identified, and proper deconvolution/decomposition was performed. From the IR spectra in the frequency region of 820−940 cm^{-1}, the spectral profile was separated into several components by the software Origin 6.1. Peak-fit routines could be used to fit the IR spectra to separate the amorphous phase, the mesomorphic form, and the crystalline form absorption bands. The absorption bands in two different regions were deconvoluted by either Gaussian or Lorenzian peak function (see the inset shown on the top of Figure 1). In the frequency region of 820−870 cm^{-1}, the Gaussian peak function is as follows:

$$f(x) = f_0 + \frac{H}{\sqrt{\pi/2}} \mathrm{e}^{-2[(x - x_c)/w]^2} \tag{1}$$

In the frequency region of 870−940 cm^{-1}, the Lorenzian peak function is as follows:

$$f(x) = f_0 + \frac{2}{\pi} \frac{H}{4\left(\frac{x - x_c}{w}\right)^2 + 1} \tag{2}$$

In eqs 1 and 2, x_c is the peak position, w is the full width of half-maximum, and H represents the height of the peaks. To ensure the uniqueness of the result, the baseline, the band shape, and the number of components were obtained by the same data-treating procedure. The programs were allowed to evaluate, by nonlinear curve fitting of experimental data, the height, the full width at half-maximum, and the position of individual components. The position of individual components and band shape are described as follows: amorphous phase: 841 cm^{-1} (Gaussian); 906 cm^{-1} (Lorentzian); crystalline γ-form: 932 cm^{-1} (Lorentzian), 944 cm^{-1} (Lorentzian); mesomorphic form: 856 cm^{-1} (Gaussian), 903 cm^{-1} (Lorentzian); crystalline α'-form: 852 cm^{-1} (Gaussian), 902 cm^{-1} (Lorentzian); crystalline β'-from: 858 cm^{-1} (Gaussian), 910 cm^{-1} (Lorentzian).

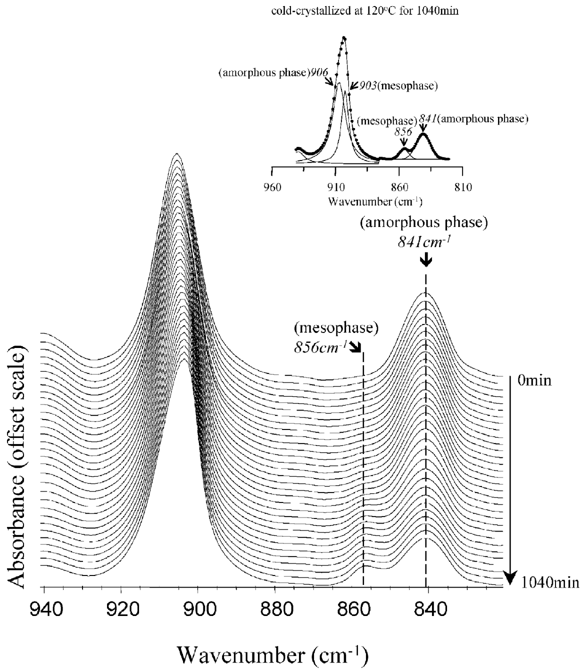

Figure 1. IR spectra in the frequency range of 820−940 cm^{-1} for the neat sPS isothermally cold-crystallized at 120 °C for various times (0−1040 min). The inset in the upper right represents the decomposed IR profile of the bottom curve.

Results and Discussion

IR Characterization of Mesomorphic Form. A mesomorphic form is known to develop by isothermally annealing at 120 °C on a quenched amorphous sPS sample.[12,13,19] To identify the possible characteristic IR bands giving structural information on the mesomorphic form, the 120 °C isothermally cold-crystallized neat sPS was first analyzed via Fourier transform infrared spectroscopy. The IR spectrum between 820 and 940 cm^{-1} changes markedly when sPS undergoes phase changes. The IR spectral profiles in the frequency region of 820−940 cm^{-1} are shown in Figure 1, which show the spectral changes in quenched/amorphous sPS subjected to cold crystallization done isothermally at 120 °C for various periods of time. The 856 cm^{-1} band starts to emerge, with the 841 cm^{-1} peak showing a gradual depressed absorbance, after 30 min of cold-crystallization at 120 °C, and then the 856 cm^{-1} band becomes more evident with longer times of crystallization imposed on sPS. At the same time, a band shifting from 906 cm^{-1} toward 903 cm^{-1} is seen, implying that the cold crystallization on sPS starts to induce the original random-coiled chains to pack into an ordered state after 30 min at 120 °C. The intensity of the peak at 856 cm^{-1} remains constant for sPS postannealed at 120 °C for 250 min or more, confirming that the crystallization is completed after 250 min. Decomposition of the absorbance band, shown on top of Figure 1, was done using the software Origin 6.1 for revealing the details. The inset in the upper right of Figure 1 exhibits two Gaussian bands, being at 841 and 856 cm^{-1}, and two Lorentzian bands, being at 903 and 906 cm^{-1}. We can clearly see the appearance of new absorption bands at 856 and 903 cm^{-1} for the cold-crystallized sPS, showing that the packing of the chains is in the mesomorphic form.[13,14] According to Musto et al., the 856 cm^{-1} band

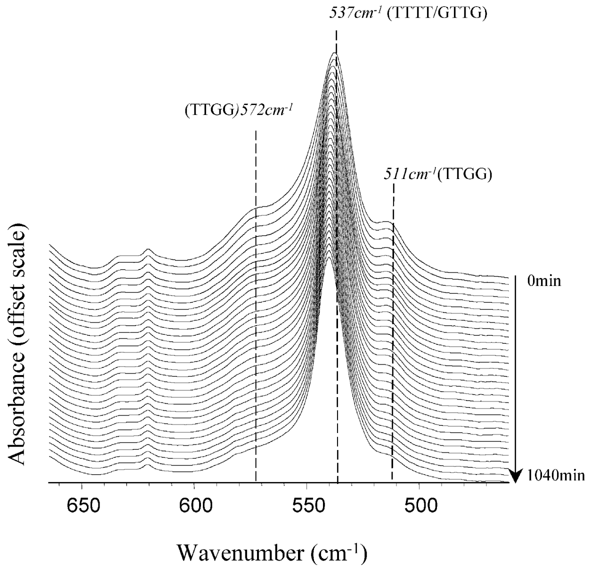

Figure 2. IR spectra in the frequency range of 450−665 cm^{-1} for the neat sPS isothermally cold-crystallized at 120 °C for various times (0−1040 min).

is caused by the packing of the chains in the crystalline state.[14] This evidence has demonstrated that isothermal cold crystallization at 120 °C imposed on the quenched amorphous sPS yielded a mesomorphic form possessing a certain extent of crystalline order.

As discussed above, the mesomorphic form was not present in sPS subjected to isothermal annealing at 120 °C until 30 min. The IR spectral changes in the frequency range from 450 to 660 cm^{-1} are shown in Figure 2. In the early stage of cold crystallization at 120 °C, the 537 cm^{-1} band gradually moves to 539 cm^{-1} during the first 30 min of annealing and retains unaltered later. The frequency shift can be ascribed to the chain conformational change from GTTG to TTTT.[26] Meanwhile, the peaks at 511 (TTGG), 548 (GTTG), and 572 cm^{-1} (TTGG) show a decrease in intensity with increase of annealing time, while the peak at 539 cm^{-1} shows an enhanced intensity. Kaji et al.[26] have suggested that the absorption band at 539 cm^{-1} increases in intensity, owing to chain segments consisting of an all-trans conformation growing not only through the induction period but also after crystallization. At annealing times shorter than 30 min, short chain segments consisting of an all-trans sequence start to develop. At time of 30 min, the segments with all-trans conformation grow continuously and gather together to pack in crystalline lattice as indicated by a band at 856 cm^{-1}.

On the other hand, after crystallization, the band at 539 cm^{-1} is getting shaper and the half-width of the band is decreasing. In fact, the reduction of the full width at half-maximum of the band may be considered to be in the reduction of molecular chains motion.[20] After 30 min of cold crystallization at 120 °C, the mesomorphic form of small size starts to develop and grows. Thus, the reduced half-width of the band at 539 cm^{-1} can be considered to be attributed to reduction of molecular motion of the noncrystallized polymer chains which are restrained more or less in between the developed mesomorphic form of small size.

Crystals in Quenched Amorphous sPS Subjected to Slow Heating. Figure 3 shows FT-IR spectra in the frequency range of 820−940 cm^{-1} for the amorphous sPS samples (quenched by liquid nitrogen) subjected to post-slow heating (1 °C/min) to various temperatures. The IR evidence shows that the amorphous peaks at 906 and 841 cm^{-1} decrease in intensities, while the 856 cm^{-1} peak shows an opposite trend as well as the band at 902 cm^{-1}, when annealing at temperatures above 126.4 °C. Further annealing at a higher temperature of 190.6 °C, the 856 cm^{-1} peak decreases in intensity while the 852 cm^{-1} peak starts to emerge, where its intensity becomes greater with increase of the annealing temperatures (>190.6 °C). The results reveal that the amorphous chains of sPS start to develop into the crystals with an initially mesomorphic form upon annealing at 126.4 °C. At higher annealing temperatures, for examples at temperature of 190.6 °C or higher, the crystalline α′-form of a higher degree of perfection started to form, which is evidenced by the depressed intensity of the band 856 cm^{-1} and the enhanced band at 852 cm^{-1}.

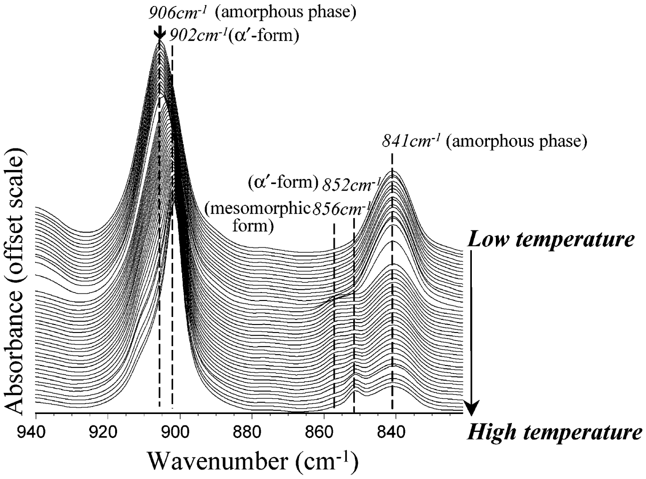

Figure 3. FTIR spectra in the frequency range 820−940 cm^{-1} for the neat sPS sample subjected to 5 °C stepwise heating in the temperature range 60−260 °C.

To make a quantitative analysis of IR bands of the interested range, IR spectra were decomposed using the software. The spectra in Figure 3 were subjected to such procedures for further analysis. The decomposed spectra in the frequency range from 815 to 940 cm^{-1} for the glassy amorphous sPS samples thermally treated at various temperatures are shown in Figure 4 (diagram A). The IR spectral profiles in the frequency region from 815 to 875 cm^{-1} were magnified for clearly seeing IR spectral alteration as a function of annealing temperature in this region, as shown in diagram B. Obvious differences are observed in the spectra for the sPS subjected to annealing at various temperatures. The band at 841 cm^{-1} for the quenched amorphous sPS is especially interesting (trace a). Upon appearance of the reduced intensity of the 841 cm^{-1} band after annealing at 126.4, 146.2, and 175.8 °C, a band at 856 cm^{-1} starts to emerge. This evidence suggests that the mesomorphic form as crystal nucleus is preferred way of packing in sPS cold-crystallized at lower temperatures below 150 °C (traces b and c). This band shows a gradually enhanced intensity with increasing temperature (trace d). This fact suggests that the mesomorphic form grows initially during slow heating. At 225.2 or 245.0 °C, the reduced intensity of the band at 856 cm^{-1} is seen (traces e and f), with an enhanced intensity of the band at 852 cm^{-1} being present. This fact demonstrates that the appearance of another new peak of 852 cm^{-1} represents the growing presence of the crystalline α′-form. In

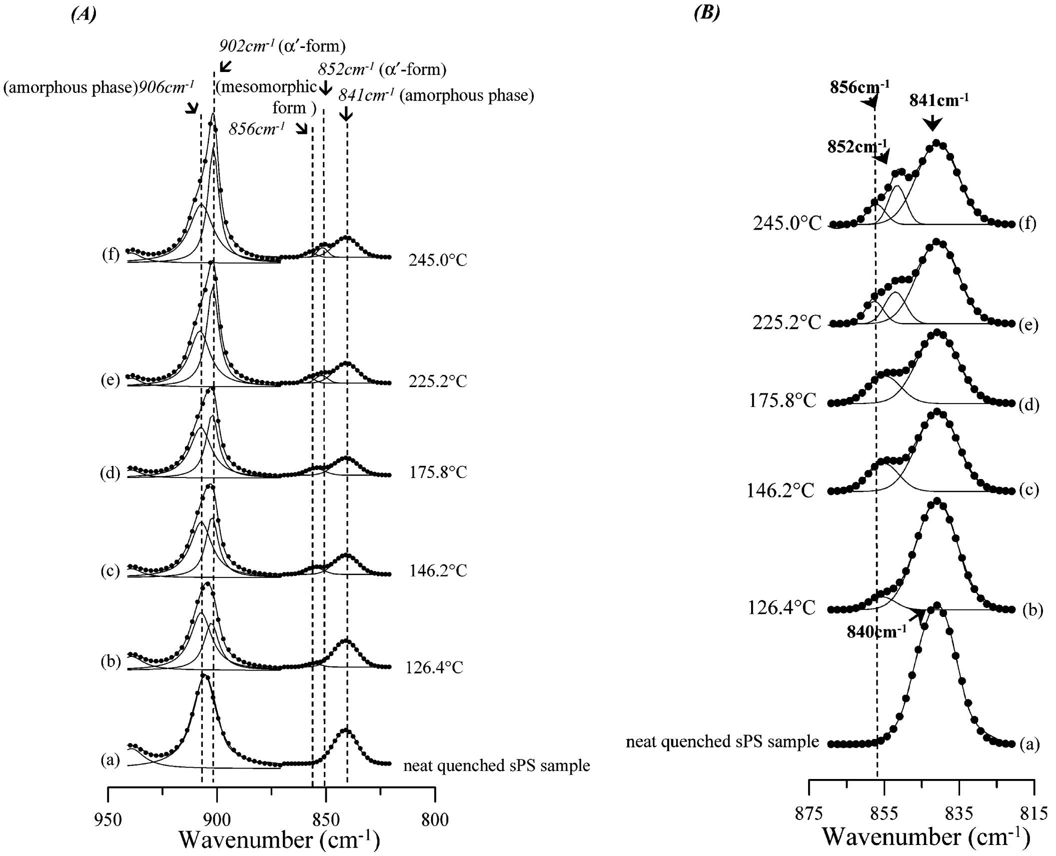

Figure 4. FTIR spectra: (A) 815−940 cm^{-1} and (B) 815−875 cm^{-1} (close-up view). In each of the two diagrams: (a) neat quenched sPS sample and the quenched sPS samples further postannealed at (b) 126.4, (c) 146.2, (d) 175.8, (e) 225.2, and (f) 245.0 °C.

addition, a decrease of the band at 856 cm^{-1} seems to coincide with an increase of the band at 852 cm^{-1}, while the reduced band at 841 cm^{-1} remains unaltered at 225.2 and 245.0 °C (traces e and f). Like the band at 841 cm^{-1}, the reduced band at 906 cm^{-1} remains unaltered at 225.2 and 245.0 °C, while the band at 902 cm^{-1} shows the enhanced intensities with rising temperature (traces e and f). On the other hand, the 852 cm^{-1} band becomes more evident, with the reduced band intensity of the 856 cm^{-1} peak. This may be considered that the crystalline α′-form yields by a reorganization of the mesomorphic form when annealing above 200 °C. This IR spectra region provides other definite proof for the possibility of the reorganization of the mesomorphic form into a crystalline α′-form.

Furthermore, the coexistence of the mesomorphic form and the α′-form supports that the transformation likely undergoes by a nucleation and growth process where the α′-form grows at the expense of the mesomorphic form. Note that the crystalline α″-form can be favored and becomes an alternative route as a quenched/amorphous sPS was rapidly brought to isothermal annealing at higher temperatures above 200 °C.[5] By contrast, upon slow heating imposed on the quenched amorphous glass, particularly, up to higher temperatures above 200 °C with a slow heating rate of 1 °C/min, the crystalline α′-form packing is more favored rather than the α″-form packing. This fact suggests that annealing imposed above 200 °C on sPS that contained an initially mesomorphic form leads to formation of the α′-form.[12]

XRD Characterization of Mesomorphic Form and Crystalline α′-Form. Figure 5 reveals the XRD patterns of the amorphous/glassy neat sPS (quenched by liquid nitrogen) postannealed at various temperatures in the range of 60−245 °C. An amorphous halo centered at $2\theta = 19.4°$ remains broad for the samples annealed at temperatures below 140 °C, and no peaks

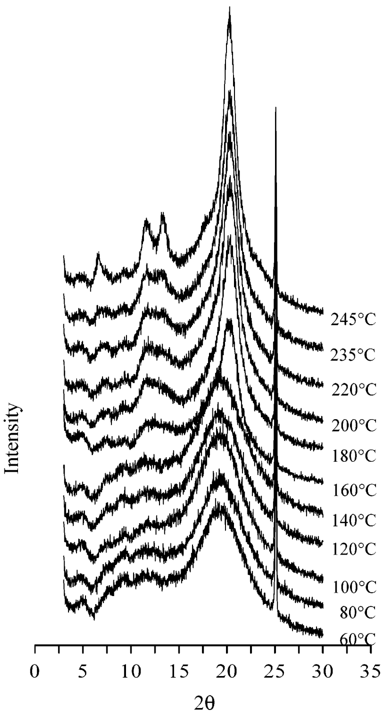

Figure 5. XRD patterns of neat sPS subjected to stepwise heating in the temperature range 60−245 °C. The peak at 25.6° shows the aluminum oxide (Al_2O_3) [0 1 2] reflection, which is used as the internal standard.

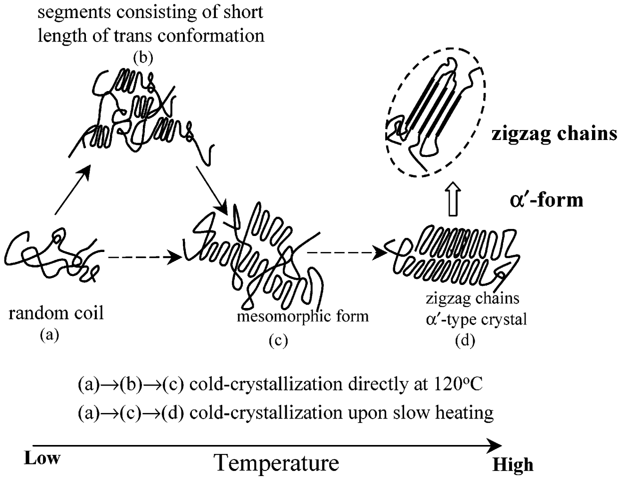

Figure 6. Schematic illustrations showing the temperature-dependent phase changes: (a) random coil, (b) chain segments with an all-trans conformation, (c) mesomorphic form, and (d) α′-form, for neat sPS subjected to 120 °C isothermal cold crystallization or heating-induced cold crystallization. The solid and dotted arrowheads represent the isothermal and heating-induced cold crystallization, respectively.

could be attributed to crystalline phases. For samples annealed at above 140 °C, we can clearly see the appearance of an enhanced sharp peak at $2\theta = 20.2°$ as well as a new diffraction peak at 11.7° for the annealed sPS, revealing that the predominant crystal structure present is of the mesomorphic form.[12,13,19] Additionally, the observed broad diffracted peak at 11.7° can be considered as an indication of the existence of either poorly formed crystallites or very small crystalline domains.[27,28] Ultimately, for the neat sPS samples subjected to annealing at even higher temperatures of 220, 235, and 245 °C, characteristic peaks of the typical α′-crystal form (De Rosa et al.,[29] $2\theta = 6.7°$, 11.7°, 13.1°, 18.3°, and 20.2°) are clearly seen. Thus, for the amorphous/glassy sPS, the amorphous chain segments first crystallize into an imperfect mesomorphic form and then propagated into a more perfectly packed crystal (i.e., α′-form).

Hypothesis of Growth of α′-Form as Well as Mesomorphic Form from Random Coil. In summary, from X-ray diffraction and FT-IR evidence shown above, hypothesis of a transition to the mesomorphic form from a random coil is proposed. A schematic plot is illustrated in Figure 6, showing the transform of an originally random-coiled chains going to a mesomorphic form for quenched/amorphous sPS subjected to 120 °C isothermal cold crystallization. This is illustrated by the solid-arrow routes represented by schemes a−c. At the beginning of the transform, because the annealing temperatures are above the glass transition temperature (T_g) of 95 °C, the amorphous sPS chains (scheme a) develop first the short chain segments consisting of an all-trans conformation (scheme b).[26] After 30 min, the polymer chains of an all-trans conformation start to pack into the mesomorphic form (scheme c). As for the possible transformation from the mesomorphic form to a crystalline α′-form, another route of transform is also shown in the same figure by the dashed-line arrows (schemes a, c, and d). This route is proposed here to interpret the transition from a mesomorphic form → α′-crystal during slow heating. The original random-coil chains (scheme a) first develop into a mesomorphic form having partial chains with a zigzag planar conformation (scheme c). Further annealing at higher temperatures finally led to reorganization from the mesomorphic form to a more perfect crystalline α′-form (scheme d) through a nucleation and growth process. The α′-crystal is illustrated by the scheme showing a closer packing of the all-trans chains or segments.

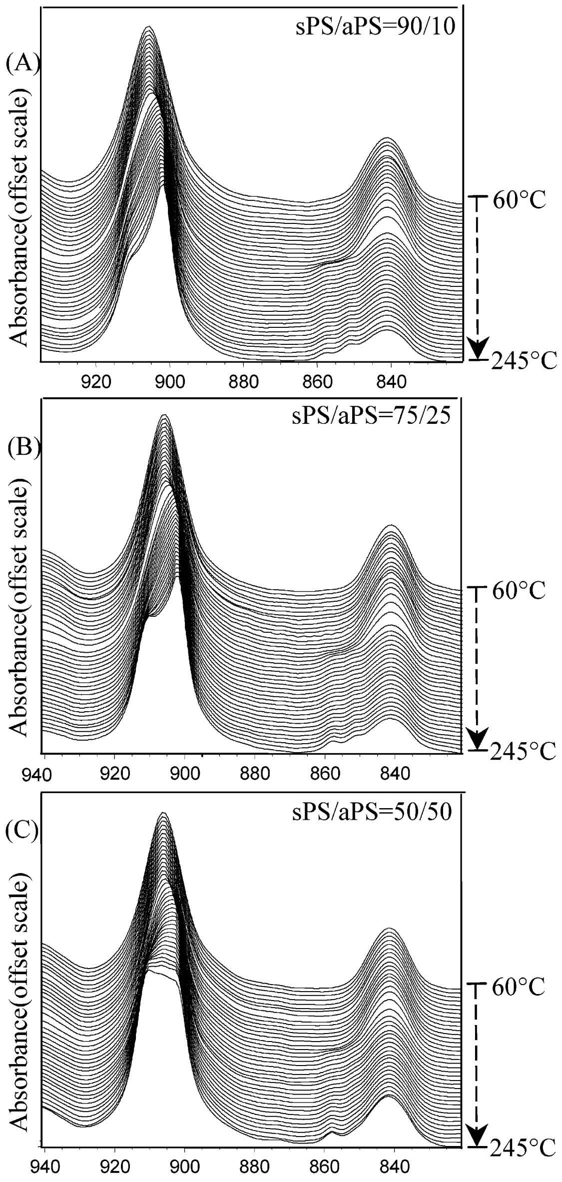

Figure 7. IR spectra for the quenched amorphous sPS/aPS blends of compositions of (A) 90/10, (B) 75/25, and (C) 50/50 subjected to 5 °C stepwise heating in the temperature range 60−245 °C.

IR Characterization of Crystals and Transitions in the Quenched sPS/aPS Blend System. To compare with the neat sPS, similar thermal treatments were imposed on the known miscible sPS/aPS blend system,[30] with each of samples starting as quenched amorphous/glassy material. The IR evidence is shown in Figure 7 for sPS/aPS blends of three compositions: (A) 90/10, (B) 75/25, and (C) 50/50. Again, prior to IR characterization, all blends were subjected to 5 °C step increase in the temperature range 60−245 °C. For the sPS/aPS (90/10) blend, with heating at 140 °C, peak shifting (from 906 to 903 cm^{-1}) occurs as sPS chains undergo a change from random-coil to an all-trans conformation packed in the crystalline form. Meanwhile,

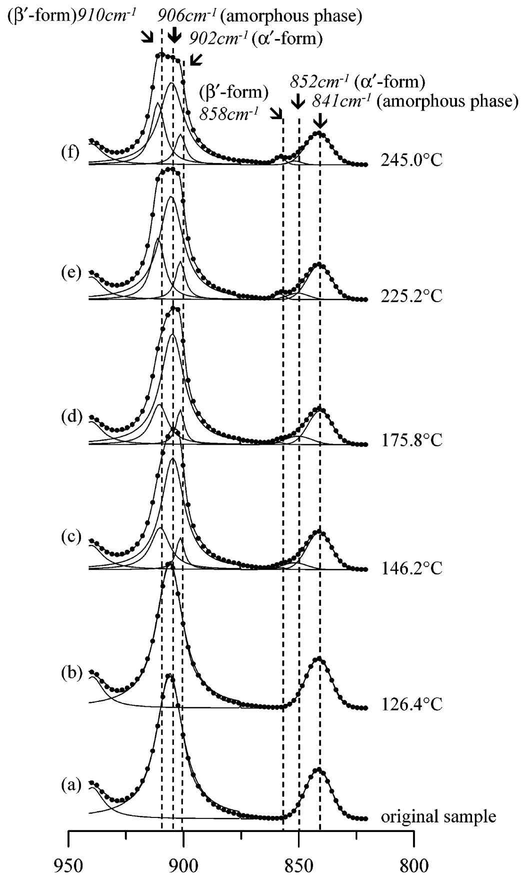

Figure 8. IR spectra for the quenched sPS/aPS blend (50/50) further postannealed at various temperatures.

the intensity of the peak at 841 cm^{-1} was obviously depressed, with two new bands at 856−858 and 852 cm^{-1}, becoming evident (diagram A). Upon further annealing at temperatures above 140 °C, these two bands (852 and 858 cm^{-1}) became more evident. Eventually, the peak at 910 cm^{-1} is not present until annealing at higher temperatures above 200 °C. With increasing aPS contents in the mixed blends, the 910 cm^{-1} band becomes more evident. On the other hand, the intensity of peak at 852 cm^{-1} decreases with an increase of the amorphous aPS contents in the aPS/sPS blends (diagram C), suggesting that mixing aPS to sPS affords a lower content of α-form. Apparently, cold crystallization at most accessible temperatures produced solidified sPS/aPS blends containing both α- and β-type crystals of various fractions, whose IR spectra varied apparently with the contents of atactic polystyrene (aPS) as well as cold crystallization temperatures. It is worth noting that the IR result in diagram C reveals that the specific peak of the α-form at 902 cm^{-1}, originally originating from the chain packed in the crystalline α′-form, is decreasing at the expense of growing peak intensities of band at 910 cm^{-1} (β'-form) when the annealing temperature is higher (200−245 °C). This evidence may be critical in probing whether a transition from the α′-form (or the mesomorphic form) into β'-form can be more realistic in the blends than neat sPS. This will be discussed in the following paragraphs.

For proving the phenomenon observed in the blends, the decomposed method is imposed on the spectra of the sPS/aPS (50:50) blend. The evidence shown in Figure 8 displays that the peaks at 852 and 902 cm^{-1} attributed to the α′-form, and the peaks at 858 and 910 cm^{-1} due to the β'-form are present (trace c), indicating that the random coil transformed directly into a mixture of the α′-form and β'-form without the intermediate mesomorphic state (in sequences of random coil to the fractions of α- and β-forms). Upon further annealing at 175.8 °C, the 910 and 858 cm^{-1} peaks corresponding to the β'-form are more pronounced (trace d). At 225.2 and 245 °C, an intensity of these two bands (858 and 910 cm^{-1}) is gradually increasing with the rising annealing temperature (traces e and f). This suggests that the quenched glassy sPS chains, in the 50/50 blend, crystallize. The peaks at 858 and 852 cm^{-1} show an interesting trend, where depressed peak intensity at 852 cm^{-1} and enhanced peak intensity at 858 cm^{-1} are apparent (trace f). The trend suggests that the α′-form could likely transform into the β'-form upon annealing of 245 °C on the quenched amorphous sPS/aPS (50/50) blend.[9]

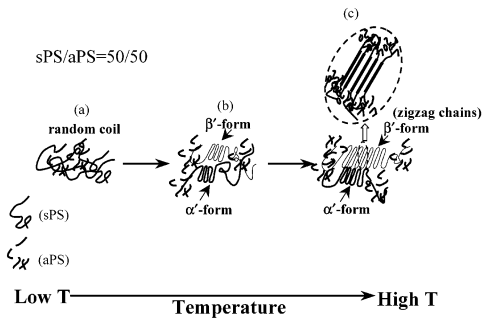

Figure 9. Schematic illustration showing the temperature-dependent changes in sPS/aPS blend (50/50) subjected to heating-induced cold crystallization from low to high temperatures: (a) amorphous random coils, (b) initial α′- and β'-type crystals, and (c) more perfected α′- and β'-type crystals.

A scheme shown in Figure 9 is proposed here to interpret the polymorphic behavior for the cold crystallization in the blends. The random-coil conformation is illustrated by the dotted line for atactic polystyrene and by the solid line for syndiotactic polystyrene. The crystalline domain packed in the β-form is illustrated as polymer chains segments consisting of an all-trans sequence by a thin solid-line, and a similar profile for the α structure is illustrated by a thick solid line. As cold crystallization occurs at lower temperatures, the random-coil sPS polymer chains transform rapidly and directly into a combination of α- and β-type nuclei of an all-trans conformation, and no mesophases are involved. Subsequent cold crystallization at higher temperatures only leads to the continuous growth of mixed α- and β-forms. The aPS polymer chains are in a miscible state with the noncrystalline domain of the sPS chains. By comparison, a mesomorphic form is favored in the neat sPS subjected to cold crystallization at low temperatures, while α- and β-forms of various fractions are the more favored crystal species in the sPS/aPS blends cold-crystallized at the same annealing temperatures.

As discussed above, polymorphism and phase transitions can take place in originally quenched/amorphous sPS or its miscible blends. The α′-form can develop in neat sPS by going through a meso form as it is subjected to heat-scan-induced cold crystallization from the quenched/amorphous state, but the sPS/aPS blends, on the other hand, develop into an α-crystal without going through the meso form when subjected to similar thermal schemes as those for the neat sPS. By comparison, solvent-cast sPS or blends, however, may undergo different routes of transitions and eventually

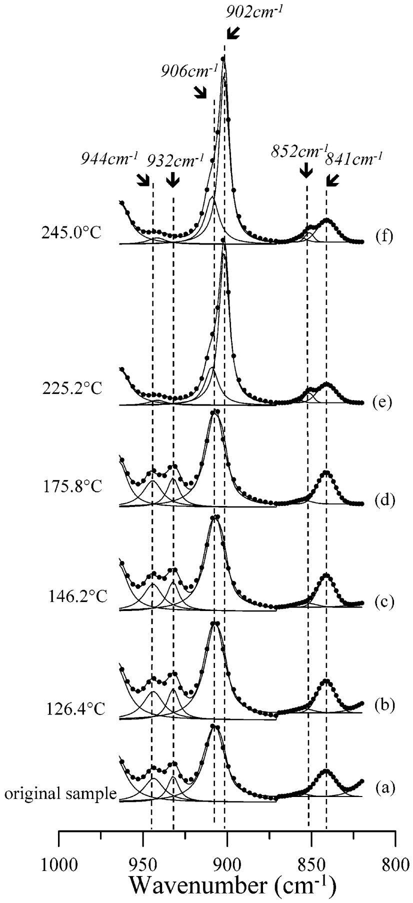

Figure 10. IR spectra for (a) solvent-cast neat sPS and the cast sPS sample further postannealed at temperatures: (b) 126.4, (c) 146.2, (d) 175.8, (e) 225.2, and (f) 245 °C.

different polymorphisms. For examples, concurrent studies[31] have revealed that the 1,1,2,2-tetrachloroethane solvent can solvent-induce crystallization in sPS, which yields an ordered γ-form of a helical conformation possessing lower degrees of perfection; subsequently, upon heating/annealing, the γ-form gradually grows into more perfect packing and finally undergoes a $\gamma \rightarrow \alpha'$ transition at a temperature of 200 °C or higher. For comparison purposes, solvent-cast neat sPS or its miscible sPS/aPS blends were analyzed in terms of the transitions and polymorphism behavior in order to compare with the cold-crystallized systems. The relevant results and discussion follow.

IR Characterization of Phase Transition in the Solvent-Cast sPS or Its Blends. To more clearly identify the changes in peak intensities related to the crystal transformation, the IR spectral profile was separated into several components, and the integral intensity of each component was evaluated. Figure 10 shows the IR spectral changes (traces a−f) of the neat sPS samples, being cast from 1,1,2,2-tetrachloroethane, that were further postannealed at different temperatures. Obviously, the bands at 841 and 906 cm^{-1} were present in the γ-type sPS sample with the helical conformation (traces a−c). In addition, the bands at 932 and 944 cm^{-1} are interesting as they appear only in the polymer−solvent complexes of γ-form shown in traces a−d. No significant spectral changes were observed prior to a $\gamma \rightarrow \alpha'$ phase transition. Further annealing the as-cast sPS films above 200 °C, the bands at 932 and 944 cm^{-1} diminish, and at the same time the band at 902 cm^{-1} starts to emerge obviously (traces e and f). On the other hand, one sharp peak (at 852 cm^{-1}), which corresponds to the specific absorbance of the α-form in high degree of perfection, is present when annealing at temperatures at 225.2 and 245 °C. Like the band at 902 cm^{-1}, it remains sharp with the intensity independent of the annealing temperature after the phase transition. This demonstrates that the unstable γ-form is transformed immediately to the α'-form with a high degree of perfection (traces e and f).

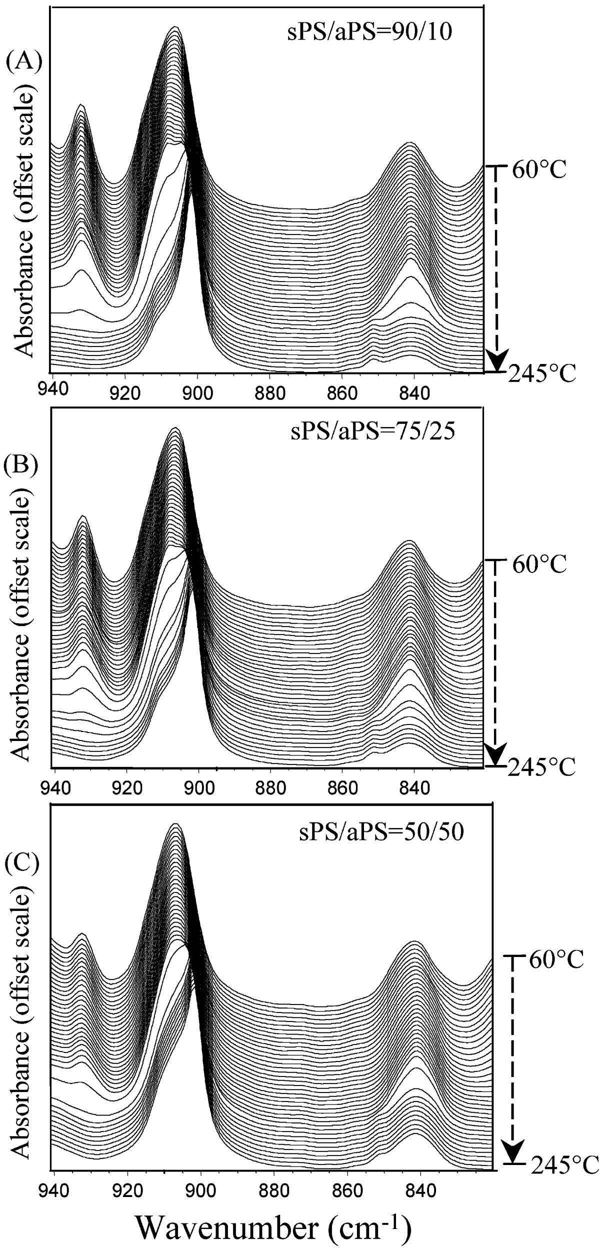

Figure 11. IR spectra for the solvent-cast sPS/aPS blends of compositions: (A) 90/10, (B) 75/25, and (C) 50/50 subjected to 5 °C stepwise heating in the temperature range 60−245 °C.

By comparison, similar solvent and postthermal treatments were imposed on the samples of sPS/aPS (90/10, 75/25, and 50/50) blends. The IR evidence reveals that the $\gamma \rightarrow \alpha'$ transition is not affected by the aPS contents. The interpretation is as follows on the basis of the IR evidence. The IR results for the three blend compositions (A, B, and C) subjected to postannealing at various temperatures are shown in Figure 11. Again, prior to IR characterization, all solvent-cast blends were subjected to 5 °C step increase in the temperature range 60−245 °C. The IR spectral changes show similar features and trends. In diagram A, IR spectral results reveal that two bands at 932 and 944 cm^{-1}(shown in the decomposed spectra), which are associated with the helical conformation packed in the monoclinic γ-form, are present in the initially as-cast sPS/aPS blend (90/10). Upon annealing at temperatures higher than 200 °C, the bands at 932 and 944 cm^{-1} were absent from the IR spectrum. This fact suggests that the γ-form was absent. Instead, the bands at 852 and 902 cm^{-1} are seen, indicating that the α′-form may dominate the crystalline domain of as-cast sPS/aPS blend (90/10). Upon disappearance of the bands at 932 and 944 cm^{-1} as well as a depressed intensity of the band at 906 cm^{-1}, the band at 902 cm^{-1} becomes more evident and sharper. With increasing the aPS contents in the blends, the two bands at 932 and 944 cm^{-1} are found in the as-cast sPS/aPS blends (75/25 and 50/50) as well, as shown in diagrams B and C. This demonstrates that the γ-form was obtained in the freshly cast blends. Upon slow heating above 200 °C, the characteristic bands (852 and 902 cm^{-1}) of the α′-form are seen. The IR spectra reveal that a slow heating imposed on solution-cast sPS/aPS blends as well as neat sPS leads to a transition from the γ- to α′-form. In addition, a $\gamma \rightarrow \alpha'$ transition takes place via a rapid recrystallization of the melted γ-form (i.e., a melting/recrystallization process) in the solvent-cast sPS/aPS blends.

The rapid recrystallization is considered to be a kinetically preferred phase transition mechanism. In general, the α′-type form is the kinetically favorable crystal, while the β'-type form is the thermodynamically favorable crystal.[7,8] Thus, the α′-form is proposed to originate favorably from a rapid recrystallization of the melting of the γ-type form. Furthermore, chain intermixing in polymer−polymer miscibility leads to a thermodynamic state of sPS favoring predominant formation of β-form and depressed fraction of α-form.[4−8,32,33] However, in this study solvent-cast process leads to crystallization-induced macrophase separation in the solvent-cast sPS/aPS samples. That is, the amorphous aPS chains were likely excluded from the sPS−solvent complex of the γ-form. The amorphous aPS chains were only miscible with the noncrystallized sPS chains. As the solvent-cast sPS/aPS blends were brought to an annealing at temperatures above 200 °C, the γ-form melted, and the subsequent crystal transition was quickly followed by a rapid recrystallization of the melted γ-form species.

It is believed that chain intermixing in polymer−polymer miscibility leads to a thermodynamic state of sPS favoring predominant formation of the more stable β-form but depressed factions of the α-form (or other mesomorphic forms) in the course of crystallization from either a liquid state (i.e., melt crystallization) or a rubbery state (cold crystallization). In the course of thermal schemes imposed on the solvent-cast samples, the γ-form melts (forming rubbery sPS chains) and subsequently recrystallizes to form the α′-form for both solvent-cast neat sPS and sPS/aPS blend system. This is attributed to the fact that the solvent-cast process leads to aPS chains being excluded from the sPS−solvent complex of γ-form. Upon heating to induce further phase transitions in the solvent-cast blends, the aPS chains were not fully mixed with the amorphous sPS chains from the melted γ-form. That is, chain intermixing in scale of polymer−polymer miscibility could not be achieved within the short time frame of recrystallization of the melted γ-form species. This results in that the α-form is the dominating mechanism of molecular packing following recrystallization of the sPS chains from the melted γ-form species in the sPS/aPS blends. This leads to that the transition behavior and final polymorphism of the sPS/aPS blend are similar or almost the same as that of the neat sPS in the transform of γ-form to α-form. That is, aPS in the blends does not have any miscibility effect in promoting alternative routes of crystal transitions as long as the samples are solvent-cast to contain some mesophases.

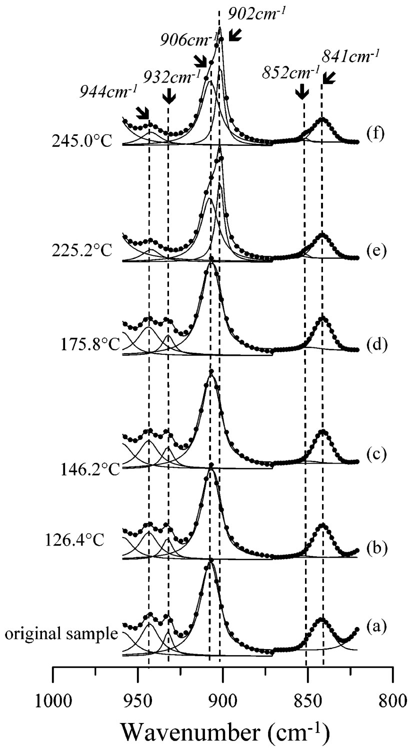

Figure 12. IR spectra for (a) solvent-cast sPS/aPS blend (50/50) and the cast sPS/aPS blend samples further postannealed at various temperatures: (b) 126.4, (c) 146.2, (d) 175.8, (e) 225.2, and (f) 245 °C.

To more clearly identify the changes in peak absorbance in relation with the crystal transformation, similar evaluation of IR relative absorbance was performed again. For the solvent-cast blend system, using sPS/aPS (50/50) as an example, curve fitting in the range 820−960 cm^{-1} revealed several separate bands as shown in the solid curves of Figure 12. The IR evidence was examined and identified carefully. The bands at 932 and 944 cm^{-1} associated with the vibration of the helical chains packed in the monoclinic γ-form are observed in traces a−d. Upon further annealing of the solvent-cast sPS/aPS blend of 50/50 at temperatures above 200 °C, the bands at 932 and 944 cm^{-1} diminish while the band at 902 cm^{-1} emerges (traces e and f). It suggests a transition from a γ-form with helical chains to a different crystal with a zigzag structure (crystalline α-form). In addition, in traces e and f, the band at 906 cm^{-1} originates from the vibration motion of the aPS as well as that of the noncrystalline amorphous domain of the sPS chains.

Figure 13 is a scheme illustrating an initial γ-form in (A) the solvent-cast neat sPS and (B) solvent-cast sPS/aPS blends. Thermal treatments imposed on the solu-

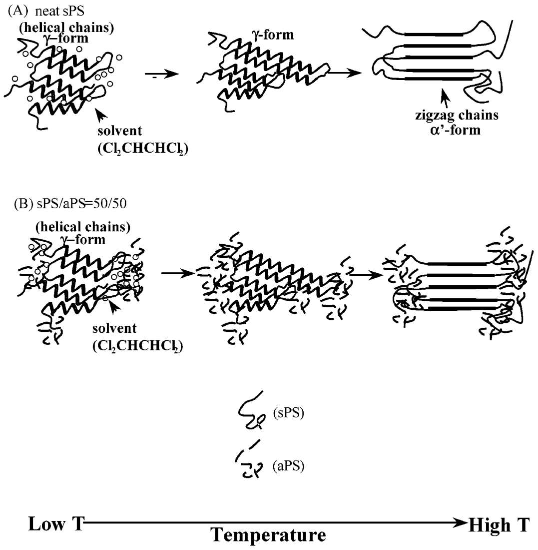

Figure 13. Schematic illustrations showing the temperature-dependent phase/conformations evolutions for the solvent-cast samples of (A) neat sPS and (B) sPS/aPS blend (50/50).

tion-cast sPS samples lead to not only the removal of solvent but also a structural change (γ → α′). By comparison, the solvent-induced crystallization leads to a crystallization-induced phase separation in the sPS blends with aPS. The aPS chains are only imitmately mixed (miscible) with the amorphous portion of sPS chains in the as-cast sPS/aPS blends. The γ-form is comprised of the chains with helical conformation dominating in the crystalline domains. Upon heating, the γ-form gradually grows into much perfect packing and finally goes through a γ → α′ transformation at temperatures above 200 °C. Generally, the α′-form is the favored species in neat sPS under two conditions: (1) cold crystallization upon slow heating from quenched amorphous glass or (2) slow heating imposed on sPS–solvent complexes of γ-form. The features and trends are the same as those found in the solvent-cast sPS samples.[31] It demonstrates that the phase transition is similar for the solvent-cast samples of the sPS/aPS blend system and neat sPS. Moreover, it can be considered that the amorphous aPS chains entangled with the noncrystalline phase of sPS have a negligible effect on the structural change of the crystalline phase of the γ-phase (with helical chains) during thermal treatments.

Conclusion

Crystal polymorphism and phase transitions in neat syndiotactic polystyrene (sPS) or its miscible blends with atactic polystyrene (aPS) showed interesting behavior. Neat sPS or its miscible sPS/aPS blends were originally either quenched to an amorphous state or treated with organic solvents, to be followed with several thermal schemes at higher temperatures, and the alteration of polymorphism and phase transitions were examined and analyzed. Neat sPS and miscible sPS/aPS blends exhibited different routes of crystal transitions upon cold crystallization from the originally quenched states. The infrared spectral evidence on the quenched amorphous neat sPS samples confirmed that the cold crystallization (by slow heating of the quenched materials) proceeds upon heating via following two stages: (1) a mesomorphic form (in the form of nuclei) initially develops at temperatures above ca. 130 °C, and (2) upon further heating at higher temperatures above 190 °C, an α′-form of a higher degree of perfection develops at the expense of the mesomorphic form via a nucleus-and-growth process. That is, the chains in mesomorphic phase reorganize and transform into the α′-form neither via melting/recrystallization nor through additional crystallization from the originally noncrystallized species. However, for the cold-crystallized sPS/aPS blends, mixed α- and β-type nucleuses of various fractions developed in the early stage without going through a mesomorphic form generation. Further annealing on the blends only leads to continuing growth of the originally developed α- and β-type nuclei. The difference in the transition routes in the neat sPS vs blend is attributed to the fact that the aPS chains are mixed and miscible with the quenched amorphous sPS chains on a molecular level. Thus, upon cold crystallization of the sPS/aPS blends during heating from the quenched state, the sPS polymer chain motion is eased in going from the random coil directly to a more stable α′- or β′-nuclei without going through a mesomorphic form.

In contrast with the cold-crystallized systems, the solvent-cast neat sPS and sPS/aPS blends (initially containing some γ-form crystal), upon slow heating, went through different route of transition. They (i.e., solvent-cast neat sPS and sPS/aPS blends) both similarly exhibited a γ → α′ transition via rapid recrystallization of the melted γ-form species. The transitions and resulted polymorphism in the final phases were the same for the solvent-cast neat sPS and sPS/aPS blends regardless of the aPS contents. Interpretation is proposed. For the solvent-cast blends, the aPS chains were mostly excluded from the initial γ-form, which is an sPS/solvent complex. The amorphous aPS chains were restricted and only mixed with the noncrystallized sPS chains. As the solvent-cast sPS/aPS blends were brought to annealing above 200 °C, the γ-form melted, and subsequent crystal transition was immediately followed by a rapid recrystallization of the melting of the γ-form into an α′-form. In the solvent-cast blends, the aPS chains were not fully mixed on the molecular level with the amorphous sPS domain; thus, the aPS chains did not have a significant miscibility effect in promoting the sPS polymer chains in going different routes of transition from those for the neat sPS.

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