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FTIR Spectroscopic Evidence of Lowered Chain Interpenetration in Thin Polymer Films

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Introduction. Physical properties of polymers confined into thin films can differ substantially from those in the bulk. In particular, freely standing polystyrene (PS) films (i.e., no solid substrate, but two polymer−air interfaces) exhibit a dramatic decrease of glass transition temperature by up to 80 °C if the film thickness approaches the chain size.[1,2] The modification of properties in thin-film geometries implies that chain conformations should also be perturbed in these situations. Brown and Russell[3] suggested that chains in thin films have a lowered degree of intermolecular overlap (interpenetration): spatial limitations imposed by the surfaces cause the chain to fold back into the volume it occupies and, because of the constraints of bulklike density and an essentially Gaussian conformation parallel to the surface, squeeze out neighboring chains. This effect was recently observed in Monte Carlo simulations of polymer chains confined in a slitlike pore.[4] Experimentally, however, the overlap of chemically identical chains cannot be directly measured. An indirect way is to measure the chain dimensions parallel to the surface. Unperturbed in-plane dimensions, in combination with the bulklike mass density, would imply that these chains have lowered intermolecular overlap.[5] However, the respective measurements performed by neutron scattering on thin PS films produced contradictory results between different research groups.[5−7] Thus, the existence of lowered chain interpenetration in thin polymer films has remained controversial.

On the other hand, greatly reduced chain interpenetration can be attained when a dilute polymer solution is rapidly frozen and the solvent removed subsequently by sublimation.[8,9] In a recent FTIR study of PS samples prepared in this way, Sasaki et al.[10,11] found that isolated or weakly overlapped PS chains produce several IR bands absent from the spectra of normal bulk PS. Here, we report the FTIR results for freely standing PS films, which reveal that the films thinner than ~200 nm also display these specific bands. This is strong experimental evidence of lowered chain interpenetration in these thin films.

Experimental Section. Thin films of PS (atactic, M_w = 200 000 and M_w/M_n = 1.06, Chemco Scientific Co., Japan) were prepared by spin-casting 1.25−3 wt % solutions of the polymer in toluene (99.8%, anhydrous, Aldrich) onto glass slides (Mitsunami Glass Ind., Japan) at 1500−3000 rpm. The glass slides were cleaned in piranha solution for 20 min, thoroughly rinsed with large amounts of water (Milli-Q quality) and 2-propanol (spectral grade, Nacalai Tesque, Japan), and dried under a stream of nitrogen. After spin-casting, the PS films on the substrates were annealed in a vacuum at 120 °C for 6 h and then cooled to room temperature at a rate of 1 °C/min. The annealed and as-cast films were floated onto water (Milli-Q quality). The floating film was transferred onto a sample holder containing a 6 mm diameter hole, resulting in a freely standing film which was then dried in air at room temperature for approximately 2 days to remove residual water.

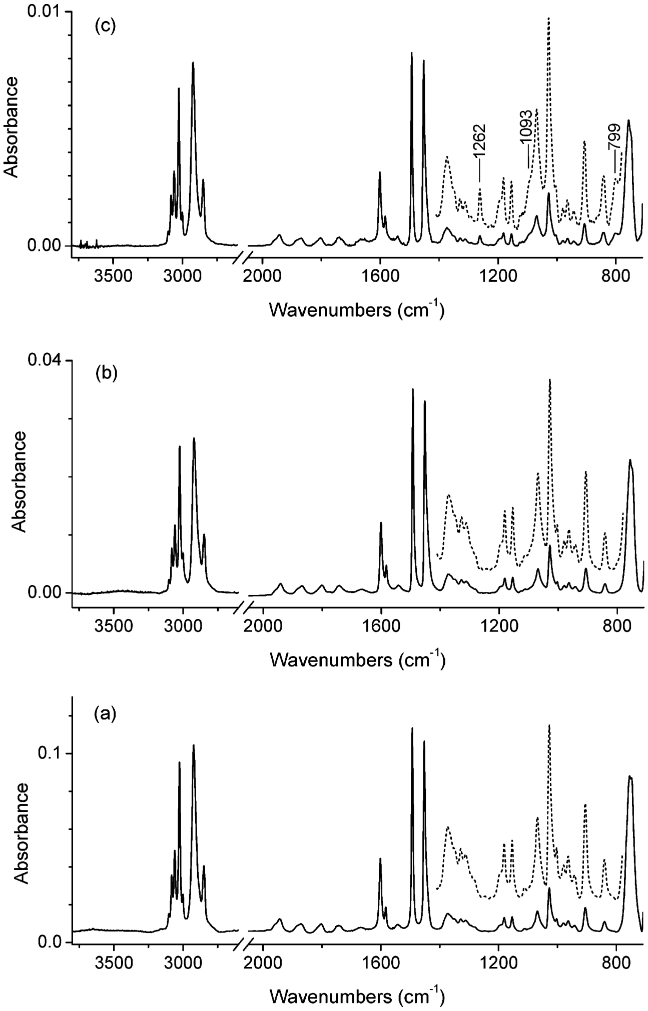

Figure 1. FTIR spectra of (a) static-cast and (b, c) spin-cast free-standing PS films with thicknesses 1530 (a), 391 (b), and 107 nm (c). The films were annealed in a vacuum at 120 °C for 6 h. The dashed lines show in more detail the region 750−1400 cm^{-1}.

The thickness of thin PS films (h) was calculated from the intensity of IR band at 3026 cm^{-1} (A_{906}) using the relation $h = 1.87 \times 10^4 A_{3026}$ (nm) obtained from FTIR measurements on a series of thick (1.5−10 μm) PS films prepared by static casting whose thicknesses were measured using a stylus profiler with a sensitivity of ±0.05 μm. The 3026 cm^{-1} band of atactic PS (the ν_{20b} stretching mode of aromatic C−H)[12] is conformationally insensitive,[13] and therefore its intensity depends only on the film thickness. The FTIR spectra were measured on a Perkin-Elmer Spectrum One FTIR spectrometer. The spectra were collected with 50−200 scans at a resolution of 2 cm^{-1} using a TGS detector.

Results and Discussion. Figure 1 shows the FTIR spectra, in the 700−3800 cm^{-1} region, of spin-cast PS

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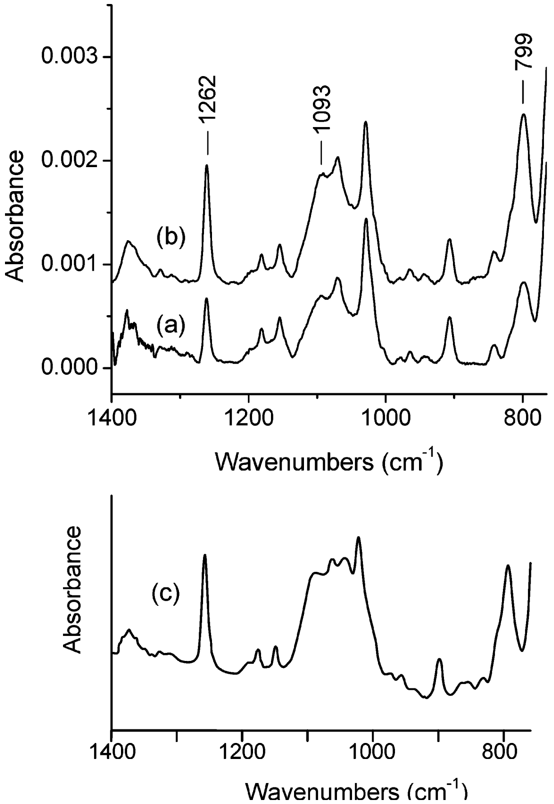

Figure 2. FTIR spectra, in the 750–1400 cm^{-1} region, of (a) as-cast and (b) annealed free-standing PS films with thickness 51 and 53 nm, respectively, prepared by spin-casting a 1.25 wt % solution, and (c) the spectrum of single-chain PS particles isolated from a 0.006 wt % solution by freeze-drying (adapted from ref 11).

films with thicknesses 107 and 391 nm as well as the spectrum of static-cast film with thickness 1530 nm. The spectrum of 391 nm spin-cast film is undistinguishable from that of static-cast film, and the both totally reproduce the FTIR spectra reported in the literature (e.g., in ref 13) for bulk films of atactic PS. In contrast to the 391 nm film, the 107 nm film exhibits additional bands located at 1262, 1093, and 799 cm^{-1}.

Parts a and b of Figure 2 show the FTIR spectra, in the 750–1400 cm^{-1} region, of as-cast and annealed PS films with thicknesses 51 and 53 nm, respectively. The three additional bands found in the 107 nm film discussed above have greatly increased intensities in these thinner films. Besides, while the two films have a practically equal thickness, the intensity increase is stronger for the annealed film. In Figure 3, the intensity of 1262 cm^{-1} band normalized to the intensity of the internal reference band at 3026 cm^{-1} is plotted vs the film thickness. As is seen, the band is detectable only in the films thinner than ~200 nm, and its relative intensity increases with decreasing film thickness. The intensity vs thickness behavior of the other two bands was qualitatively similar to that of the 1262 cm^{-1} band.

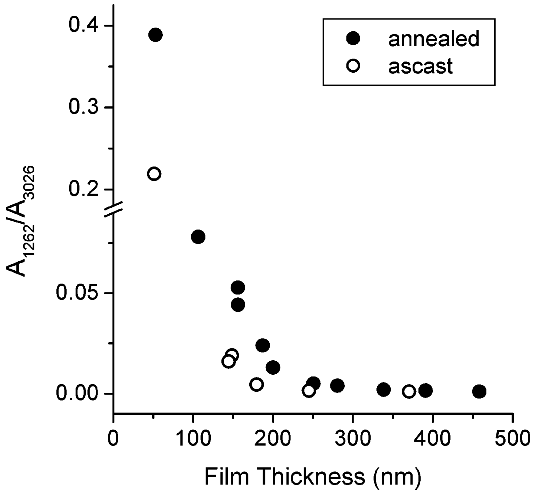

Figure 3. Intensity of the 1262 cm^{-1} band normalized to that of internal reference band at 3026 cm^{-1} in the FTIR spectra of as-cast and annealed PS films as a function of film thickness.

The appearance of bands at 1262, 1093, and 799 cm^{-1} cannot be due to contamination of the thin-film samples because our experimental procedures exclude any possibility of contamination. Besides, if the bands in question were caused by contamination, they would not show any systematic changes in the intensity with film thickness. An enhanced oxidative degradation of PS in thin spin-cast films must also be excluded because it would result, in the first instance, in the carbonyl and hydroxyl bands at 1650–1750 and 3300–3500 cm^{-1}, respectively, which are absent from the spectra of the PS films studied here (Figure 1c). On the other hand, the bands that we found in the spectra of thin PS films were observed by Sasaki et al.[10,11] for PS freeze-dried from dilute solutions and naturally ascribed to greatly reduced interpenetration of polymer chains. The FTIR spectrum of PS freeze-dried from a 0.006 wt % solution from the work of above authors[11] is shown in Figure 2c. The spectrum of this “single-chain” sample is similar to the spectrum of 53 nm thick film (Figure 2b) not only in the position of the three bands under consideration but also in their shape and relative intensities. The only way to explain this striking spectroscopic resemblance is to conclude that, like the freeze-dried sample, the thin film has a greatly reduced degree of intermolecular overlap.

The reduced intermolecular overlap in thin spin-cast polymer films may, in principle, be caused by two independent reasons. One is the effect of confinement[3] outlined in the Introduction. The other is high-speed solvent evaporation in the spin-casting method, which can freeze the chains in disentangled states characteristic of dilute polymer solutions used in the film formation process.[14] If the latter mechanism were the only reason, the degree of chain overlap would increase upon annealing the as-cast films at temperatures above the glass transition temperature. However, the systematically higher relative absorbance at 1262 cm^{-1} for the annealed films, as compared to the as-cast films of similar thickness, seen in the data shown in Figure 3 indicates that annealing enhances the separation of polymer chains. Though this result does not exclude the possibility of *artificial* chain separation by the spin-casting method, it clearly reveals the presence of a *natural*, thermodynamic driving force associated with the effect of confinement.

In summary, we have for the first time conducted FTIR spectroscopic experiments on freely standing polymer films with thicknesses ranging from 500 nm down to 50 nm. We found that the thin films ($h < 200$ nm) of atactic PS display the IR bands characteristic of isolated or weakly overlapped chains, and these bands increase in intensity with decreasing film thickness and upon annealing the films above the glass transition temperature. These results provide the first strong evidence that in thin polymer films the chains are less overlapped than in the bulk, and there is certainly the natural, thermodynamic cause of this phenomenon, associated with the effect of confinement.

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