[†] Contribution No. 4973.

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Received December 8, 1988;
Revised Manuscript Received April 4, 1989

A Spectroscopic Study of Syndiotactic Polystyrene

Fully syndiotactic polystyrene has been recently reported in the literature.[1-8] Only quite recently has the synthetic process been developed;[1,2,7] however, only limited structural information is available. The attractive and interesting physical characteristics of this polymer can be summarized as follows: (1) a melting temperature of 270 °C, (2) a fully trans planar zigzag backbone, and (3) the presence of a solid–solid phase transition.[1,3-6] Because of its inherent backbone stiffness and strong intermolecular interactions, the macroscopic properties such as modulus and strength are expected to exceed those of most polymers, even those of some liquid-crystalline polymers.

A variety of crystal forms have been suggested, including a helical conformation upon crystallization from dilute solution and an all-trans conformation with annealing. The helical phase has been proposed to have a TTGG or T_3GT_3G' conformation.[3,9] We are interested in the nature of these crystalline forms and the amorphous state, and the transition between them. Vibrational spectroscopy is our primary characterization technique. Its sensitivity to local conformation and chain packing changes allows us to observe microstructural changes with annealing, orientation, or solvent treatments. In this paper we examine structural differences between samples of different tacticities observed from their infrared spectra. Evidence will be presented for the presence of two different conformational forms and the transition between them caused by thermal treatment or orientation.

Experimental Section. Polystyrene samples with syndiotacticity greater than 98% were obtained from Idemitsu Kosan Co. Ltd., Japan. Isotactic (90%) and atactic polystyrene samples were obtained from Scientific Polymer Products Inc. and Polysciences Inc., respectively. Thin films were obtained by casting from a 1 wt % solution in chloroform and drying up to 14 days under vacuum at room temperature. Melt-quenched films were prepared by heating the films cast on a AgCl window to 270 °C under a nitrogen atmosphere in order to prevent oxidation and then quenching into liquid nitrogen. Oriented samples were obtained by solid-state coextrusion at 100 °C in a polyethylene billet. Infrared spectra were obtained with a Bruker IFS 113v FTIR spectrometer. Generally 250 scans were collected at a resolution of 2 cm^{-1}. For annealing experiments, samples were heated in a cell constructed in our laboratory. Low-temperature spectra were obtained in a liquid nitrogen cooled cell.

Results and Discussion. The infrared spectra of atactic, isotactic, and syndiotactic polystyrene (sPS) are shown in Figure 1. Large differences in both the infrared and Raman data, related to the different chain conformations of these isomers, are observed, especially in the regions of 540, 750, 900, 1070, and 1200–1400 cm^{-1}. We also found that the vibrational spectra can be perturbed significantly by thermal annealing. The spectra obtained for the sPS generally contain bands that are sharp (approximately 6 cm^{-1} in half-width) as compared to the relatively broad features observed for both isotactic or atactic isomers. From the intensity decrease in the helical bands and the corresponding sharpening of the spectroscopic features observed upon annealing, we intend to show that annealed sPS is of high crystallinity and has a planar zigzag backbone conformation. One of the primary objectives is to seek explicit evidence of vibrations that can be assigned to the all-trans planar zigzag backbone.

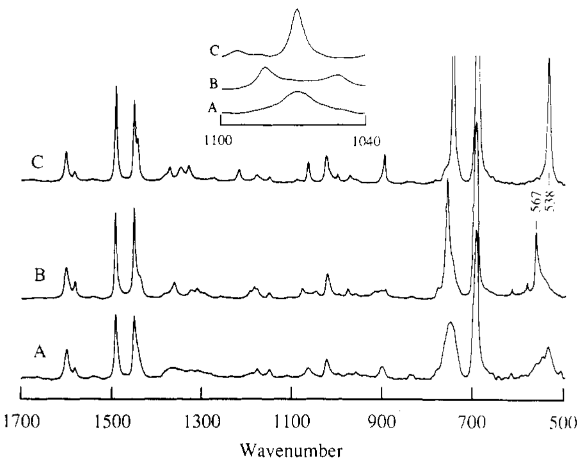

Figure 1. Infrared spectra of (A) atactic, (B) isotactic, and (C) syndiotactic polystyrene.

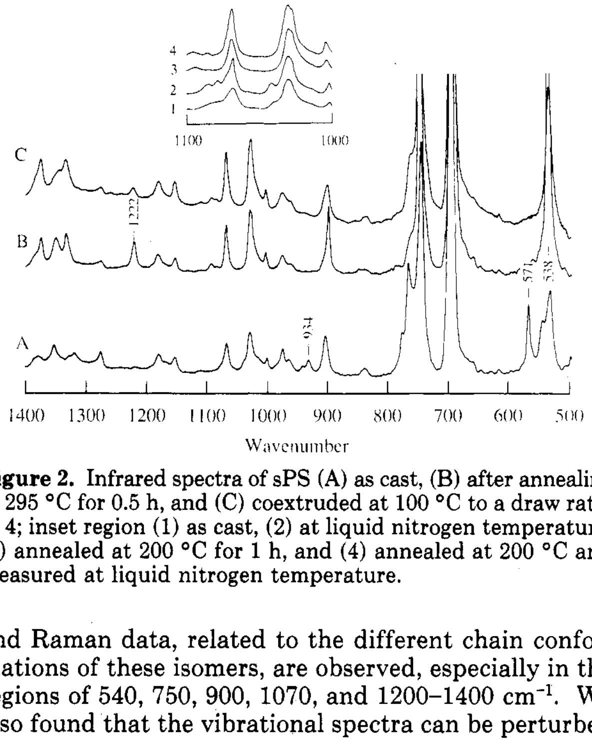

Figure 2. Infrared spectra of sPS (A) as cast, (B) after annealing at 295 °C for 0.5 h, and (C) coextruded at 100 °C to a draw ratio of 4; inset region (1) as cast, (2) at liquid nitrogen temperature, (3) annealed at 200 °C for 1 h, and (4) annealed at 200 °C and measured at liquid nitrogen temperature.

In the 1100–1400-cm^{-1} region, a number of conformation-sensitive skeletal vibrations exist. It is also quite likely that these bands are sensitive to chain packing. The infrared spectrum of the cast film contains spectroscopic features that disappear when the sample temperature is raised. Some of the weak features (1079, 1086, and 1042 cm^{-1}) that are hard to observe at room temperature are seen quite clearly at liquid nitrogen temperature, and this is shown in the inset region in Figure 2. The intensity and position of these weak features are especially sensitive to thermal annealing. One of the more interesting features observed for sPS is the 1030-cm^{-1} band. This band, as-

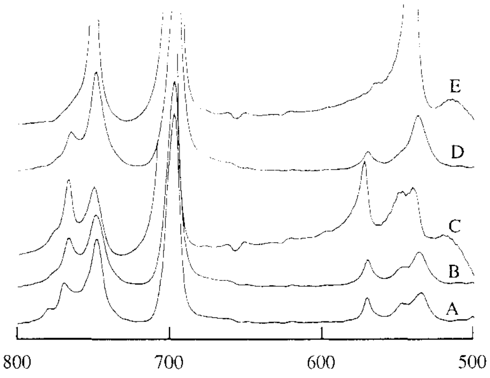

Figure 3. Infrared spectra of sPS at various temperatures: (A) 25 °C; (B) 111 °C; (C) 185 °C; (D) 212 °C; (E) 238 °C.

signable to the combination of CH in-plane bending, CC ring stretching, and CCC ring bending vibrations,[10] seems to be sensitive to chain packing and clearly splits into two components at 1030 and 1028 cm^{-1} at low temperature. A 1069-cm^{-1} band is present as a broad feature in the cast film. However, after annealing, the band sharpens but remains as a singlet even at low temperature. Two bands of medium intensity have also been observed in this region for isotactic polystyrene (1052 and 1083 cm^{-1}). These bands, seen in the inset region in Figure 1, have been assigned previously to ring–backbone and ring CC stretching and to ring stretching and CH in-plane bending, respectively. In that case, they are thought to be associated with the sequence length of preferred conformations in the amorphous phase.[10] From our evidence we conclude that both of these medium-intensity bands at 1030 and 1069 cm^{-1} in sPS are crystalline in nature. Atactic PS has been shown to possess a significant amount of syndiotactic trans isomers.[11] Therefore we expect the spectrum of sPS to be more similar than that of iPS to that of atactic polystyrene, and this is generally observed.

As mentioned previously, a variety of crystal forms have been suggested for sPS, including a helical structure upon crystallization from dilute solution,[3] although the conformation of this structure is uncertain. Spectra of solution-cast, annealed, and coextruded films are shown in Figure 2. A number of well-defined bands are unique to sPS. Some appear in the solution-cast film, but not in the annealed or drawn samples. In the cast film a doublet at 943 and 934 cm^{-1}, unique to sPS, is observed. The intensity of this pair changes even more dramatically than the bands in the 1000-cm^{-1} region, disappearing almost completely for annealed samples. We have assigned these two bands to the helical conformation found for the cast sample, which is removed by annealing. In the 500-cm^{-1} region, bands are observed at 571, 548, and 535 cm^{-1}. After annealing at 200 °C, only a single band at 539 cm^{-1} remains. In iPS a single band at 567 cm^{-1} is observed and is assigned to the ν_{16b} skeletal out-of-plane mode of the aromatic ring.[10,12] The sPS spectra in this region are consistent with studies of polystyrene model compounds in which a 540-cm^{-1} band is observed when at least four backbone carbons atoms are in a trans conformation, whereas a band at 554 cm^{-1} is assigned to a second conformation containing gauche isomers.[12] Thus the 539-cm^{-1} band of sPS is consistent with a syndiotactic all-trans structure, while the cast film exhibits a 548-cm^{-1} band, indicating the presence of gauche conformers. Atactic PS exhibits a broad band at 541 cm^{-1}, suggesting a broad conformation distribution. As shown in Figure 2, extrusion of a cast film at 100 °C produces spectral changes similar to those observed on annealing. We expect that the drawing process would also transform the helical form present in the cast film to the more extended all-planar zigzag form, and this is observed. Bandwidths are broader for this oriented sample than for the annealed film, indicating that thermal treatment produced greater structural regularity than extruding the sample to a draw ratio of 4.

As seen in Figure 2, the 1222-cm^{-1} band is entirely absent in the cast film but appears as a sharp band in the annealed sample spectrum. It is expected that for a solution-cast film there must be a distribution of both trans and gauche conformations. The absence of the 1222-cm^{-1} band for the cast sample suggests that this band is associated with long trans sequences, which are not present in large number in a solution-cast film but only in the annealed or drawn material. Upon annealing, all vibrational bands appear much sharper, indicating an increase in structural regularity.

The transformation or the removal of structural defects is highly dependent on the temperature of annealing. We have obtained infrared spectra as a function of temperature, and these are shown in Figure 3. Only a small amount of structural transformation occurs below 200 °C. Heating up to 185 °C produces intensity increases of the 548-, 571-, and 769-cm^{-1} bands associated with the helical conformation. This is indicative of the increase in crystallinity of the helical phase upon annealing.

Heating to 212 °C produces intensity decreases in the bands assignable to the helical conformation and increases in the 1222- and 539-cm^{-1} bands assigned to the all-trans conformation. The details of this structural transformation are not clear at this time. Undoubtedly, the transition is a cooperative process and thus the rate and amount of transformation are strongly dependent on the specificity and magnitude of intermolecular interactions.

In conclusion, we have found that infrared spectra of syndiotactic polystyrene obtained under different crystallization and thermal conditions are characteristic of the overall structural regularity and the specific chain conformations present. Spectra of samples cast from dilute solution are consistent with previous studies, suggesting a helical conformation. Heat treatment causes a transition to an all-trans phase. Long trans sequences can only be obtained by annealing or drawing.

Acknowledgment. The financial support of a grant from the National Science Foundation, Polymers Program, Grant DMR# 8407539, is deeply appreciated.

Registry No. sPS, 28325-75-9.

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Received February 16, 1989;
Revised Manuscript Received April 10, 1989

On the Propagating Radical of Macromonomers

Recently, the number of studies on the synthesis and application of macromonomers has been rapidly increasing since macromonomers are very useful in the preparation of various kinds of functional graft copolymers having well-defined structure.[1-3] However, polymerization as well as copolymerization behavior of macromonomers is not yet well understood.[4-6] In comparison with small monomers, the polymerization system of macromonomers has the following characteristic features: (i) the viscosity of polymerization media is high from the beginning of polymerization, (ii) the concentration of the polymerizable end group is low, (iii) the propagating step is repeat of polymer–polymer reaction, and (iv) the segment density or multibranched structure is high around the propagating radical site. These features suggest that the polymerization of macromonomers might be unusually sensitive to the diffusion-controlled step of the polymerization reaction. Therefore, it is very interesting and worthwhile to investigate the polymerization behavior of macromonomers to understand how the diffusion-controlled step influences the chemically-controlled nature of polymerization reaction in general.

In the previous paper,[5] we reported that the specific features of the polymerization system of macromomomers mentioned above strongly influences the radical polymerization behavior. It was shown that there is a unique dependence of the degrees of polymerization (Dp) and the apparent kinetic order of the polymerization upon the feed macromonomer concentration [M] and the initiator concentration [I] and this requires further investigations.

In this study, we intended to investigate the polymerization behavior of macromonomers by means of ESR spectra in order to obtain direct information about the propagating macromonomer radicals. ESR measurements on the propagating radicals in solution polymerization of the small monomers are difficult to obtain because the concentration of the radicals is too low. Thus, the use of ESR spectra is limited to polymerization systems in highly viscous solution or in bulk.[7,8] However, in macromonomer systems, the propagating radicals are expected to be stable and accordingly detectable by ESR, because of the specific feature of the macromonomer polymerization system mentioned above.

The macromonomer used is the same as that in the previous paper,[5] that is, a styrene macromonomer having a methacryloyl end group that was prepared by deactivation of polystyryl living anion with ethylene oxide, followed by the reaction with methacryloyl chloride. The number-average molecular weight (M_n) is 1.24×10^4 and polydispersity index (M_w/M_n) is 1.06. The macromonomer, AIBN, and benzene were carefully placed in the ESR sample tube, degassed, and sealed under high vacuum. ESR measurements were carried out during the polymerization reaction with a JEOL ME-3X X-band spectrometer with 100-kHz modulation.[9,10] The signal of diphenylpicrylhydrazyl (DPPH) was used as a *g* value standard. The magnetic field sweep was calibrated with the splitting constant of Mn^{2+}. The concentrations of macromonomer [M] and initiator [I] are shown in Table I. In the case of run d in Table I, a mixture of MMA monomer and inert PSt standard (number-average molecular weight 1.0×10^4, $M_w/M_n = 1.06$) was used instead of the macromonomer. In this case, the vinyl end group of macromonomer becomes separated from its tail or remaining part (polymerization of MMA in the presence of PSt).

Table I
Polymerization Systems of Methacryloyl-Ended St Macromonomer and MMA/PSt Mixture for ESR Measurement[a]

run	monomer	[M], 10^{-2} mol/L	[I], 10^{-2} mol/L
a	St macromonomer	1.1	16.4
b	St macromonomer	4.0	1.6
c	St macromonomer	4.0	16.4
d	MMA + PSt	4.0	16.4

[a] ESR measurements were carried out during the polymerization.

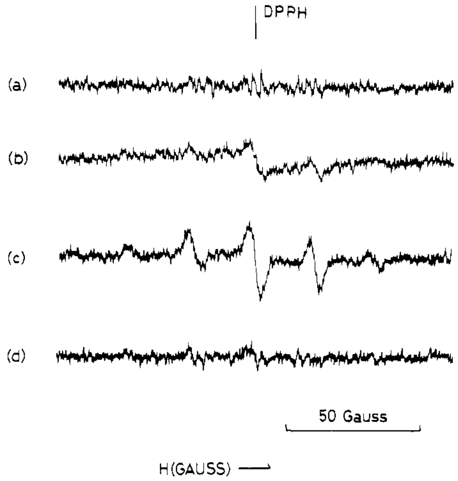

Figure 1. ESR spectra measured during polymerization of the macromonomer. Polymerization temperature was 60 °C in all cases: (a) [M] = 1.1×10^{-2} mol/L, [I] = 1.6×10^{-1} mol/L; (b) [M] = 4.0×10^{-2} mol/L, [I] = 1.6×10^{-2} mol/L; (c) [M] = 4.0×10^{-2} mol/L, [I] = 1.6×10^{-1} mol/L; (d) [M] = 4.0×10^{-2} mol/L, [I] = 1.6×10^{-1} mol/L. Sweep time is 4 min, response time is 0.1 s. The vertical line in the figure is DPPH, $g = 2.0036$.

Typical examples of ESR spectra are shown in Figure 1. It is seen that there is a broad five-line spectrum in run (b) and that the signal becomes more clear in run (c), as another weak four-line spectrum seems to superimpose to give the nine-line spectrum. This spectrum becomes sharper at −196 °C, as shown in Figure 2(ii) and it is almost identical with that of the spectrum of the MMA propagating radical in the literature,[7,8,12,13] which is characterized by nine lines consisting of five strong lines having a hyperfine splitting constant of 23.4 G (intensity distribution is 1:4:6:4:1) and of four weak lines, appearing between the five lines. On the other hand, there is no clear signal from the radical in spectra (a) and (d) other than the small signals ascribed to cyanoisopropyl radicals arising from AIBN.[7,11] In Figure 1(a), [M] decreases to 1.1×10^{-2} mol/L but [I] is the same as that in (c). This macromonomer concentration is not high enough to produce the poly(macromonomer) of large Dp as shown in Figure 3 in a previous paper. The signal cannot be observed in Figure 1(d) either, where the polymerizable end group is separated from the remaining part of the macromonomer. These

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