Molecular Conformation in Glasses and Gels of Syndiotactic and Isotactic Polystyrenes

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ABSTRACT: Local and long-range conformational structures of syndiotactic (SPS), isotactic (IPS), and atactic polystyrene (APS) molecules in the glassy state were investigated by means of infrared and low-frequency Raman spectroscopy. The content of trans skeletal C–C bonds, estimated from the infrared absorption intensities, was found to be richer in SPS glass than in IPS glass. The infrared spectrum of an APS sample was reproducible by the superposition of the spectra of IPS and SPS glasses in the ratio of its diad tacticity measured by ^{13}C NMR. The stiffness of disordered chain segments estimated from the "disordered longitudinal acoustic mode" (D-LAM) frequency, as well as the specific volume of glassy samples, was found to increase in the order of IPS < APS < SPS. It was shown that by allowing SPS solutions to stand at room temperature a clear gel was formed, as in the case of decalin solution of IPS. Infrared spectra of SPS gels formed from different solvents were essentially identical with one another and were very close to that of the crystalline β modification containing predominantly TTGG conformations, suggesting the presence of gel-forming coagulates containing highly ordered TTGG conformations. Differences in the behavior and structure between the SPS and IPS gels are considered in relation to the molecular mechanism of the gelation process.

Introduction

Quite recently Ishihara et al.[1] succeeded in preparing highly syndiotactic samples of polystyrene using a specific catalytic system. With these samples, together with previously obtained isotactic and atactic samples, we are now able to perform a full-scale investigation of the effects of stereoregular configuration on molecular structure in crystalline and noncrystalline states as well as on various physical properties of the bulk materials.

Concerning molecular structure in crystalline phases, it is well established that isotactic polystyrene (abbreviated as IPS) crystallizes into a (3/1) helical structure consisting of a regular repetition of trans (T) and gauche (G) conformations of the skeletal C–C bonds.[2,3] By recent studies[1,4-8] it has been shown that syndiotactic polystyrene (SPS) is crystallizable in two different molecular conformations described as TT (referred to as the α form with a fiber period of 0.5 nm) and TTGG (β form with a fiber period of 0.75 nm) as in syndiotactic polypropylene (SPP).[9-11] The TT form has been shown to be thermally more stable than the TTGG form.[7]

Both IPS and SPS samples form a glassy state when they are rapidly quenched from the melt in ice water. Atactic polystyrene (APS) is in a glassy state below the glass transition temperature $T_g = 82$ °C. Although molecular structure in IPS and APS glasses has been studied by infrared and Raman spectroscopy,[12-14] there still remain uncertainties. Therefore, investigation of SPS glass in comparison with IPS and APS glasses seems of importance for understanding the role of stereochemical configuration in the molecular conformation and physical properties of polystyrene glasses.

Another fascinating problem of stereoregular polystyrenes is their gel-forming character. It was demonstrated first by Keller and co-workers[15,16] that decalin solutions of IPS formed a clear gel at sufficiently high supercoolings. From X-ray diffraction[15-17] and infrared spectroscopic investigations,[18] it was concluded that gel-forming crystals were in a conformational state different from the familiar (3/1) helical structure. Although a planar or near-planar conformation was proposed for the new conformation, the details are still unclear. In addition to the structure of the gel itself, the elucidation of the molecular mechanism of the gelation process in relation to the process of crystallization from solution is one of the important current problems of polymer science. For this purpose it is of importance to investigate the gel-forming character and structure of the resultant gels of SPS and to compare them with the case of IPS.

In the present work, we deal with molecular structures of SPS in a glassy state as well as in gels investigated by infrared and Raman spectroscopy. The results obtained are compared with those obtained for IPS and APS.

Experimental Section

(1) Samples. The SPS samples used were supplied from Idemitsu Petrochemical Co., Ltd. Their weight average molecular weights were found to be 7×10^4 and 114×10^4. The syndiotacticity was evaluated as being greater than 96% racemic pentad configuration by ^{13}C NMR. The melting points were in the range of 260–270 °C. The IPS samples were obtained by polymerization with a Ziegler type catalyst [$TiCl_3$–$(C_2H_5)_3Al$] in *n*-heptane at 70 °C. The polymers obtained were purified in the usual way, and the portion insoluble in boiling methyl ethyl ketone (MEK) and soluble in boiling toluene was used as the IPS sample. It was highly crystalline with the melting point of 230 °C, and the diad isotacticity was evaluated as being greater than 95% by ^{1}H NMR. The APS sample was supplied from Sekisui Chemical Co., Ltd. (Styron 666-7). The viscosity average molecular weight was measured (benzene solution at 30 °C) to be 1.56×10^5, and the diad syndiotacticity was evaluated to be 68% by ^{13}C NMR.

SPS and IPS powder samples were dissolved first in a suitable solvent (chloroform for SPS and hot toluene for IPS), and film specimens were cast from the solution. The cast films were wrapped in aluminum foil, held between two polished metal plates, heated in a Wood's alloy bath kept a little above the

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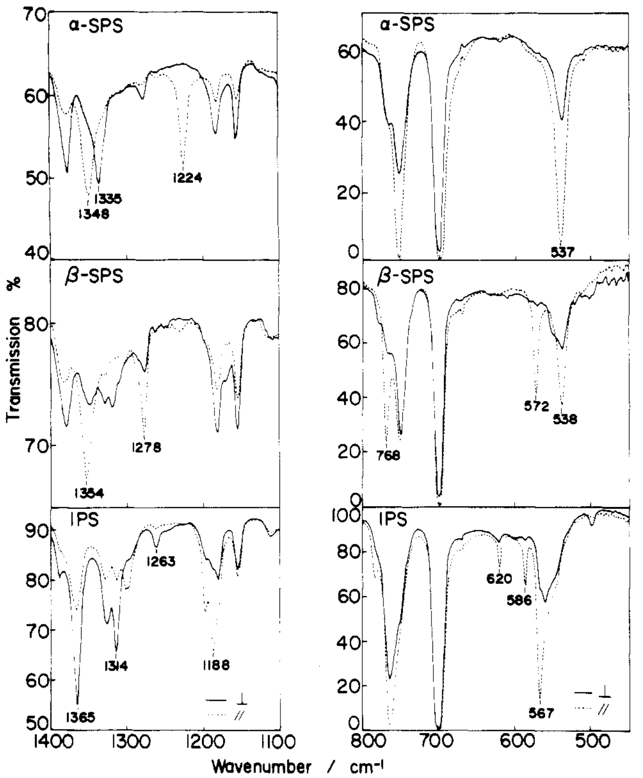

Figure 1. Polarized infrared spectra of uniaxially oriented films of α-SPS (having TT skeletal conformation), β-SPS (TTGG), and IPS (TG). The solid and broken curves represent the spectra taken with perpendicular and parallel polarizations, respectively.

melting point of the polymer films, and then quenched in ice water, yielding noncrystalline glassy films. Film samples of amorphous APS were cast from benzene solution.

SPS gels were prepared as follows: SPS was dissolved in chloroform, carbon tetrachloride, or benzene at elevated temperature, and the solution was cooled to room temperature. After a certain time, an initially clear gel was formed. It became turbid with time as in the case of IPS gels.

(2) Spectral Measurements. Infrared spectra were taken using a Jasco 5MP and 8000 type FT-IR spectrometer equipped with a DTGS detector. The number of accumulation cycles was in the range of 50–100. Raman spectra were taken using a Jasco R-500 double monochromator with 514.5-nm excitation light from an Ar^+ laser.

(3) Density Measurements. Densities of the glassy SPS, IPS, and APS samples were measured at 25 °C by a flotation method using water–glycerol mixtures.

Stereochemical Configuration and Molecular Structure of Polystyrene in the Glassy State

(1) Preferred Conformation in the Glassy State. The local conformation of a polymer molecule is reflected sensitively in the infrared and Raman spectra. In the case of polystyrene, we are able to see how the spectrum changes dramatically with a change in conformation by comparing the spectra among three crystalline phases comprising different molecular conformation; α phase of SPS (TT), β phase of SPS (TTGG), and IPS (TG) (Figure 1). There are absorption bands characteristic of each conformation: TT, 1349, 1224, and 537 cm^{-1}; TTGG, 1354, 1277, 572, and 502 cm^{-1}; TG, 1327, 1197, 1185, 920, 896, 620, 580, 566, and 500 cm^{-1}. It should be noted here that the intensities of these conformational-sensitive bands are influenced not only by the type of conformation but also by its sequential length and that the sensitivity to the regular sequential length of a particular conformation differs from band to band depending on the vibrational mode to which the band is due, in other words depending on the strength and the interacting distance of the intrachain coupling among the monomeric units. As a measure of the sensitivity, we have introduced the concept of a "critical sequence length", which is defined as the shortest length of the sequence of a particular conformation (represented by the number m of the monomeric units contained in the sequence) necessary for the appearance of the band.[12,19] For the IPS bands the values m were estimated by an isotope dilution technique: 1194, $m = 6$; 1085, 5; 1052, 10; 920, 10; 896, 16. Although we have no quantitative data about the critical lengths of the SPS bands, the 1224-cm^{-1} band of α-SPS and the 1277-cm^{-1} band of β-SPS might be as sensitive as the 1194-cm^{-1} band of IPS, since these three bands are assigned to a similar vibrational mode.[4]

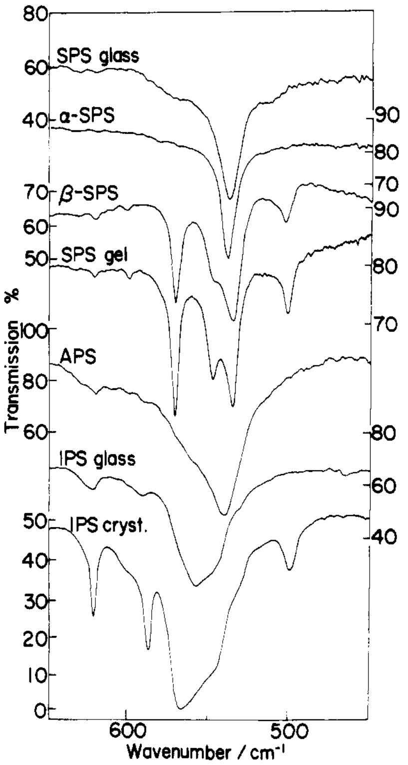

Figure 2. Infrared spectra in the 650–450-cm^{-1} region of SPS, APS, and IPS in various states.

The bands in the region of 650–450 cm^{-1} are due to the phenyl ring modes. They reflect the local conformation rather than its sequential array. The infrared spectra in this region of SPS, IPS, and APS in various states are compared in Figure 2. In crystalline α-SPS there is only one sharp band at 537 cm^{-1}. In glassy SPS, there appear broad peaks at the both sides of the 537-cm^{-1} band. They correspond to the bands at 572 and 502 cm^{-1} of crystalline β-SPS. At the same time, the 537-cm^{-1} band becomes a little broader, suggesting a superposition of the absorptions corresponding to the 548 and 536 cm^{-1} of β-SPS. In glassy IPS, all the bands, except for that at 500 cm^{-1}, characteristic of the TG conformation appear, though some of them are weakened and broadened. From these experimental facts we conclude that in glassy SPS there exist some fraction of gauche C–C bonds. Judging from the relative intensities of the gauche bands, the trans content may be greater in glassy SPS than in glassy IPS. However, from the disappearance of the 1224-cm^{-1} band, there must be no detectable amount of long TT sequences in glassy SPS.

The infrared spectrum of an APS sample is reproduced by adding the spectra of glassy SPS and IPS in a

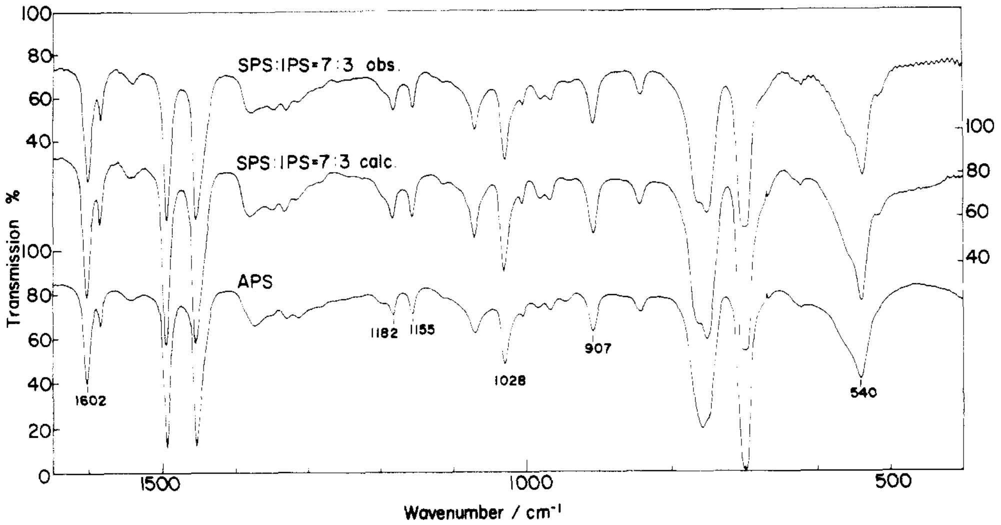

Figure 3. Infrared spectrum of a 7/3 glassy blend of SPS and IPS (upper), that simulated from the spectra of pure SPS and IPS glasses (middle), and the spectrum of an APS sample with 68 mol % racemo diad tacticity (bottom).

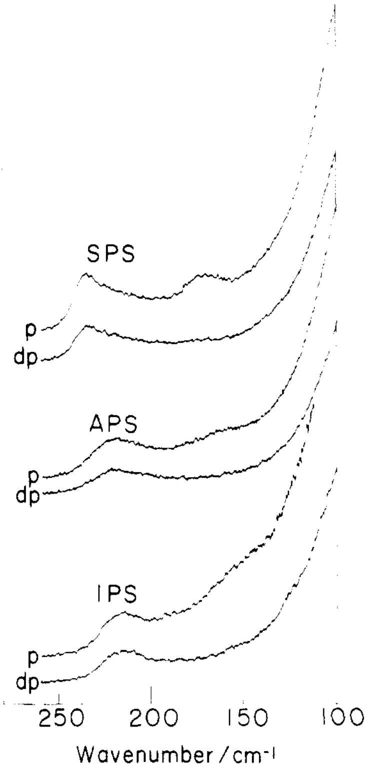

Figure 4. Low-frequency Raman spectra of SPS, APS, and IPS glasses.

ratio of 7/3, as shown in Figure 3. Here, the spectrum of a 7/3 blend of SPS and IPS (upper), simulated from the spectra of pure SPS and IPS (middle) and that of APS (bottom), are compared with one another. Since the diad tacticity of the APS sample was measured as $P_r = 0.68$ (or $P_m = 0.32$) by ^{13}C NMR, a simple additivity in intensity with respect to diad tacticity is found to be valid. This indicates that the preferred local conformations in the glassy state are controlled by the stereochemical configuration.

(2) Long-Range Conformational Structure and Stiffness of Polymer Molecules in the Glassy State. The molecular form as a whole in the glassy state might be influenced by the preferred local conformation as well as the stiffness of the polymer molecule. It is known that such long-range conformational order as well as the stiffness of the disordered polymer molecules is reflected in the frequency of a particular low-frequency Raman-active mode, the so-called "disordered longitudinal acoustic mode", abbreviated as D-LAM. The D-LAM band has been identified first in the low-frequency isotropic Raman spectra of a series of liquid *n*-alkanes[20] and thereafter in those of polyethylene[21] and poly(tetrafluoroethylene).[22] This band was also found in various polymers in the liquid and glassy states.[23] In the present work, we measured the D-LAM bands of SPS, IPS, and APS in the glassy state. Figure 4 reproduces the polarized (p) and depolarized (dp) Stokes Raman profiles of the three samples measured on melt-quenched film specimens. As proposed by Snyder et al.,[24] we obtained the isotropic spectrum free from the background $I_{\mathrm{iso}}(\nu)$ by subtracting the dp component from the p component. The scattering power $S(\nu)$ was obtained according to the equation

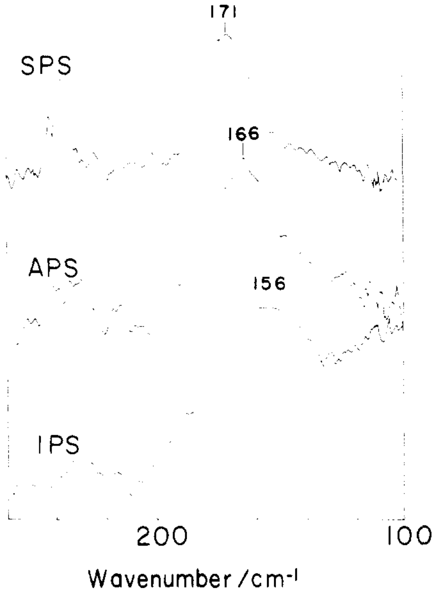

Figure 5. Scattering powers of the D-LAM of SPS, APS, and IPS glasses.

$$S(\nu) = BI_{\mathrm{iso}}(\nu) \tag{1}$$

$$B = 1 - \exp(-hc\nu/k_{\mathrm{B}}T) \tag{2}$$

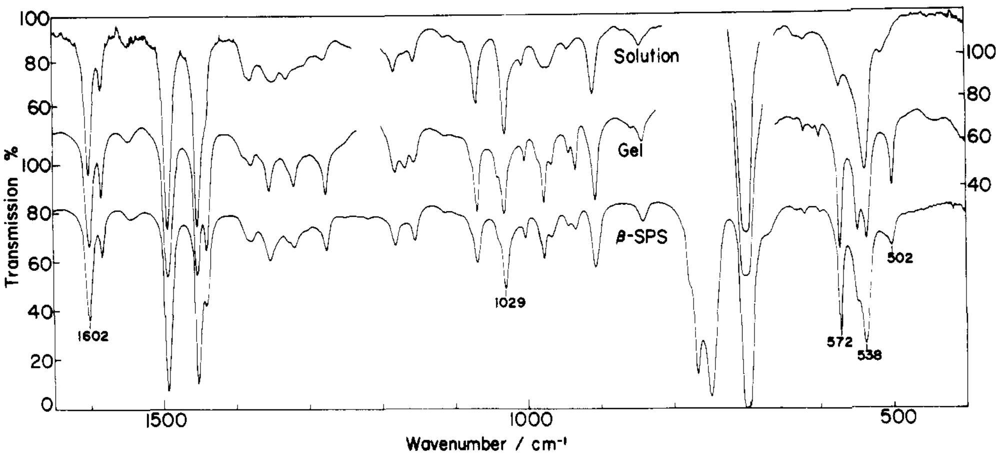

Figure 6. Infrared spectra of a chloroform solution (upper), a clear gel formed from the solution (middle), and crystalline β form (bottom) of SPS, measured at room temperature.

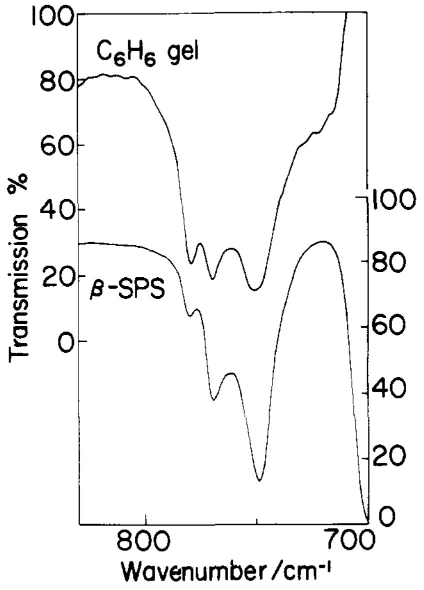

Figure 7. Infrared spectra of a clear gel formed from benzene solution (after subtraction of the solvent absorption) and crystalline β form of SPS. The intensities of the bands at 778 and 769 cm^{-1} characteristic of the TTGG conformation reduced to the internal standard band at 750 cm^{-1} are stronger in gel than in β form.

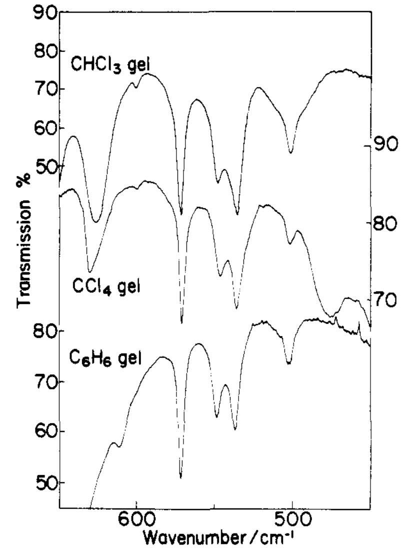

Figure 8. Infrared spectra of SPS gels formed from various solvents.

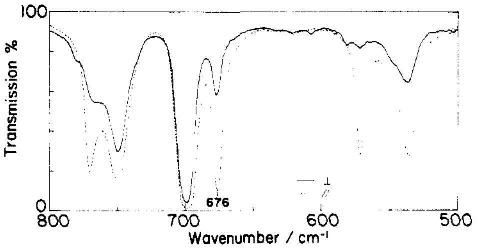

Figure 9. Polarized infrared spectra of uniaxially oriented film of β-SPS moistened with benzene. The 676-cm^{-1} band due to benzene shows a definite parallel polarization.

where ν denotes the Stokes Raman shift (in cm^{-1}), T the absolute temperature, c the velocity of light in vacuo, h the Planck constant, and k_B the Boltzmann constant. Figure 5 shows $S(\nu)$ thus transferred from Figure 4.

The peak frequency of the D-LAM band increases in the order IPS < APS < SPS. The shift of the D-LAM frequency means that either the long-range conformational order decreases or the stiffness increases in this order.[21] The long-range conformational order in the three samples should be almost the same, since the presence of long TT (in SPS) or TG (in IPS) sequences was not detected, and they differ from each other in the local conformation caused by different stereochemical configuration, as mentioned in the preceding subsection. Therefore, the difference in D-LAM frequency is probably to be ascribed to the difference in stiffness. The stiffness of a chain segment is expected to increase with an increase in the content of the TT conformation.

The difference in the local conformation is reflected also in the density of the glass. The densities of glassy SPS, APS, and IPS samples at 25 °C were measured as 1.0448, 1.0471, and 1.0575 g cm^{-3}, respectively. This result seems quite reasonable because the unperturbed radius of gyration expands, so that the density decreases as the content of straight (TT) segments increases.

Molecular Structure in the Gel

(1) Spectral Features of SPS Gel. As shown in Figure 2, the infrared spectrum of a chloroform gel of SPS in the 650–450-cm^{-1} region is quite similar to that of crystalline β-SPS. Infrared spectra of a starting chloroform solution, a clear gel formed from it, and a crystalline β-SPS film cast from the solution in the whole fingerprint region are reproduced in Figure 6. The spectra of gel and crystalline β form are very close to each other. The only difference is the appearance of the 1168-cm^{-1} band in the gel. This band remains in β-SPS cast from benzene solution even after complete removal of the sol-

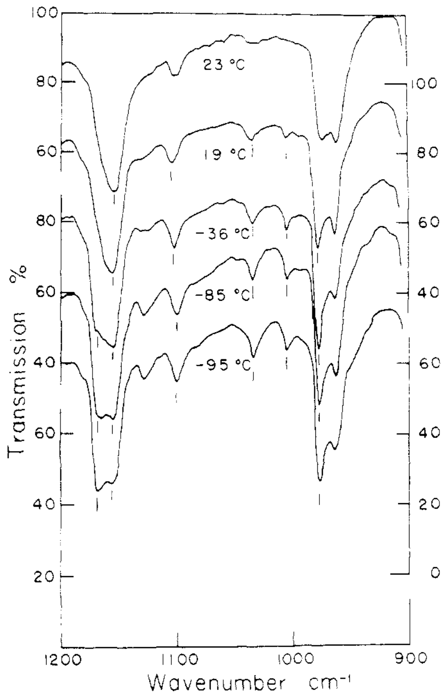

Figure 10. Temperature dependence of a gel of syndiotactic polypropylene (SPP) formed from carbon disulfide solution. The bands indicated by the vertical lines are due to regular sequences of TTGG conformation.

vent. It is rather surprising that all of the bands in gel due to the TTGG conformation, even those corresponding to long sequences, are as intense (or even more intense) as in the crystalline β phase. This trend is very remarkable for the bands around 750 cm^{-1} (Figure 7) obtained by the subtraction of the solvent absorption. The intensities of the 778- and 769-cm^{-1} bands characteristic of the TTGG conformation reduced to that of the internal standard band at 750 cm^{-1} (due to a localized C–H out-of-plane bending of the phenyl ring) are much stronger in the gel than in β-SPS. The spectral features of the SPS gel do not depend on the solvent, as shown in Figure 8, although relative intensities vary a little with condition of gelation (concentration, molecular weight, supercooling, etc.).

It is known that gelation from a solution takes place through a separation into two phases, polymer rich and polymer poor. In the former, polymer molecules coagulate in crystallike particles that act as cross-linking points. In the case of SPS, it is evident that the molecules in the coagulates assume regular TTGG conformation. Judging from the strong intensities of the characteristic TTGG bands superimposed on a very weak background due to disordered chains, most of the chain segments might be accommodated in the gel-forming coagulates which are joined to each other by small amounts of disordered chain segments. The stability of such a specific regular structure may be attributed to strong polymer–solvent interactions. Presence of a specific solvated structure is suggested by the polarized infrared spectra of an oriented β-SPS film moistened with benzene (Figure 9). The 676-cm^{-1} band due to adsorbed benzene molecule exhibits a definite parallel polarization like the bands due to the oriented polymer molecules, indicating a specific interaction between the adsorbate and the substrate.

(2) Comparison with IPS Gel. According to Keller and co-workers,[15-17] the X-ray pattern of a stretched specimen of a clear gel formed from a decalin solution of IPS gives a sharp meridional reflection at a spacing of 0.51 nm. The fiber period is significantly different from the well-established trigonal (3/1 helix) crystal phase of IPS. On standing at room temperature, the clear gel becomes turbid with time over a period of days. The turbidity originates from the formation of suspended particles crystallized in the ordinary 3/1 helix, as has been confirmed by X-ray diffraction. Thus, in the IPS gel there are two types of crystallike structures: one (form A) is formed in the first stage of gelation and supposed to be of the fringed micellar type, and the other (form B) is the lamellar-formed particles of the ordinary IPS crystal. DSC thermograms showed that form A melted around 60 °C and form B around 120 °C.[15]

As for the molecular structure in form A, a near-planar conformation was suggested based on the observed fiber period of 0.51 nm and the result of conformational energy calculation.[17] The infrared spectrum of the clear gel of IPS (after subtraction of the solvent absorption) is interpreted as a superposition of amorphous IPS and form A, the latter giving rise to many sharp bands at the positions shifted from those of crystalline IPS. By a computer-assisted subtraction technique it was revealed that approximately 35% of the monomeric units are accommodated in the ordered domain of form A.[18] This ordered domain is considered to be of a fringed-micelle type that provides the connectedness necessary for gelation.

Also in the case of SPS, the clear gels become turbid on standing at room temperature for a long time. A DSC thermogram measured on a gel formed from a 10 wt % *o*-dichlorobenzene solution exhibits two endothermic peaks (on heating) at about 70 and 120 °C. This suggests the presence of two types of structures in the SPS gel, although no spectral differences have been detected between the clear and turbid gels.

There are significant differences between IPS and SPS gels. First, the amount of the chain segments having a specific ordered conformation is extremely high in the case of SPS compared to IPS. Second, the conformations in crystallike coagulates of clear gels are different. It seems rather puzzling that IPS assumes a near-planar structure rather than its most stable TG form and that SPS assumes a TTGG structure rather than its most stable TT form.

It is known that the crystalline β form is obtained only by crystallization from solution and is converted to the α form by heating above 180 °C.[4,7] Therefore, the TTGG conformation is stabilized by solvent molecules in both the gelation and crystallization processes.

(3) Comparison with the Gel of Syndiotactic Polypropylene (SPP). As in the case of SPS, two crystal modifications with the TTGG and TT skeletal conformations are known for SPP. A highly syndiotactic sample of SPP yields a clear gel from carbon disulfide solution. Figure 10 shows the infrared spectra of the SPP gel at various temperatures. Substantial increases in intensity with decreasing temperature are observed for the bands at 1154, 1085, 1035, 1006, and 977 cm^{-1}, assignable to the TTGG conformation.[25,26] Thus, in the SPP gel the TTGG structure is stabilized, as in the SPS gel.

More comprehensive studies on SPS gels are in progress in order to elucidate the molecular mechanism of gelation and crystallization.

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Registry No. SPS, 28325-75-9; IPS, 25086-18-4; APS, 9003-53-6.

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Dynamic Features of Side Chains in Tyrosine and Serine Residues of Some Polypeptides and Fibroins in the Solid As Studied by High-Resolution Solid-State ^{13}C NMR Spectroscopy

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ABSTRACT: We have recorded high-resolution ^{13}C NMR spectra of silk fibroins in the solid state from *Bombyx mori* and *Philosamia cynthia ricini* and appropriate model peptides and polypeptides to gain insight into the dynamic features of side-chain groups of Tyr and Ser residues. First, ^{13}C NMR peaks of Tyr residues were identified, except for the peak of C$_\beta$, by comparing ^{13}C NMR peaks of the *B. mori* fibroin with those of the crystalline fraction whose Tyr residue is reduced to less than 2%. It turned out that the phenolic ring of Tyr residues undergoes a flip-flop motion with a rate constant of $>10^2$ s^{-1}, as inferred from the coalesced single peaks of Tyr C$_\epsilon$. The aromatic side chains of $(\text{Tyr})_n$ and $(\text{Phe})_n$, however, undergo rotational diffusion with a correlation time on the order of 10^{-8} s, as manifested from selective reduction of the ^{13}C spin-lattice relaxation time of the laboratory frame ($T_1{}^{\text{C}}$). The shortened $T_1{}^{\text{C}}$ values (<1 s) of Ala C$_\beta$ in $(\text{Ala})_n$ and fibroins were ascribed to the presence of C$_3$ rotation. The $T_1{}^{\text{C}}$ of Ser C$_\beta$ in $(\text{Ser})_n$ and fibroins appears to arise from two different relaxation processes, a shorter (0.6–1 s) and a longer (10–40 s) component. The former and latter were obviously ascribed to the presence of free hydroxymethyl groups and those hydrogen bonded to either carbonyl or other hydroxyl groups, respectively.

Introduction

It has been demonstrated[1-4] that the ^{13}C NMR signals of Ala, Gly, and Ser residues in silk fibroins are well resolved in the solid state, and the characteristic displacements of individual residues can be used as a convenient means for distinction of polymorphic structures in *Bombyx mori* and *Philosamia cynthia ricini* fibroins. This view is based on the fact that relative displacements of ^{13}C chemical shifts from individual amino acid residues in peptides, polypeptides, and proteins are in many instances independent of amino acid sequence and significantly vary (up to 8 ppm) with the local conformation of the amino acid residue under consideration.[5-16] The major advantage in using this solid-state NMR approach for conformational characterization is that NMR spectroscopy is a nondestructive means and can be equally applied to systems of noncrystalline as well as crystalline samples.

To make this NMR methodology more effective, it is essential to resolve and assign as many ^{13}C NMR signals as possible. No assignment of peaks, however, has been

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