# Analysis of Raman-Active Low-Frequency Bands Observed for Syndiotactic Polystyrene

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ABSTRACT: Low-frequency Raman spectra for syndiotactic polystyrene (sPS) and their solvent complexes are reported. A broad, intense, polarized band centered at approximately 50 cm$^{-1}$ is observed for polystyrene independent of tacticity, degree of crystallinity, or molecular weight, and is assigned to the phenyl ring torsion about the backbone. The intensity and polarization characteristics of this vibration have been analyzed. The 50-cm$^{-1}$ band has different intensities and bandwidths in different crystalline phases of syndiotactic polystyrene. Another intense, relatively sharp component observed at 52 cm$^{-1}$ is present only in the helical crystalline polymer–solvent complex. The 52-cm$^{-1}$ component disappears upon removal of solvent and is sensitive to interaction of the sPS phenyl ring with solvent. The observation of a sharp component for a specific crystalline state suggests that examination of this band may be useful as a molecular probe of the environment, and possibly free volume, of the phenyl ring in polystyrenes.

## Introduction

The synthesis of nearly 100% syndiotactic polystyrene (sPS) has recently been reported.[1-4] Even at relatively high temperatures, sPS exhibits attractive stable mechanical properties related to its highly stereoregular structure. The solid-state structures of sPS include several well-defined crystalline phases which display at least two principal types of chain conformations.[5-12] The all-trans planar zigzag chain conformation is the more thermodynamically favored state as compared to the ttgg helical conformation.[13] Transformation from the helical phase of sPS to the all-trans phase can be accomplished by thermal annealing, while the helical phase can be generated in sPS by exposing the polymer to or recrystallizing the polymer from suitable solvents.[5-9,11] Thus, if solvent is present during the crystallization process, as in the preparation of films by solvent casting or by isothermally growing crystals from dilute solution, the chain conformation obtained is always helical in nature. An exception occurs when cyclohexanol is used as the solvent, whereby the chain conformation for the gels and crystals produced is the extended all-trans conformation.[14] Variations in chain conformation and packing of these structures have been extensively studied by both vibrational spectroscopy and diffraction methods.[6,7,11] From these studies, sPS crystallized in the presence of solvents have revealed the existence of at least two helical phases. It has been proposed that in many such instances polymer–solvent complexes are obtained,[6,9,15] but little experimental evidence has been advanced to establish the nature of these crystalline complexes. These sPS crystals do not exhibit the same degree of crystallinity as found for other highly regular polymers.[17,19]

It has been found difficult to characterize the helical crystalline phase due to slight differences in the crystalline structure of polymer complexes depending on the solvent used, and variations in unit cell dimensions have been attributed to the size and shape of the guest solvent molecules.[6,7,15] Vibrational spectroscopy yields information about structure at the segmental level and has been found useful for characterization of regular chain conformation and structural defects. A number of bands, such as those at 1222, 749, and 538 cm$^{-1}$, can be assigned to the all-trans state, while bands at 943, 934, 767, 571, and 501 cm$^{-1}$ can be assigned to the helical phase. These bands have been used to follow changes in chain conformation distribution as a function of temperature and crystallization conditions.

Particular attention has recently been given to the low-frequency region where spectroscopic data are especially useful for examination of the crystalline state. Virtually all bands observed in this region are due to delocalized vibrations that can be extremely sensitive to changes in chain conformation or packing. However, few of these bands can be assigned unambiguously. For all three tacticities of glassy polystyrene, the band at ~170 cm$^{-1}$ has been postulated to arise in disordered longitudinal acoustic mode (D-LAM) vibrations.[16] The ~170-cm$^{-1}$ band was used to determine chain stiffness for each isomer in the amorphous state, and it has also been assigned as an in-plane bend of the ring.[17] A band at ~20 cm$^{-1}$ in atactic polystyrene has been proposed as due to LAM-like motion for sequences of conformational order present in the material.[18] Although these band assignments are consistent with expected frequencies, definitive proof of these assignments is presently unavailable.

An extremely intense band found near 50 cm$^{-1}$ in the Raman spectrum of polystyrene has been associated with chain dynamics. In this study, the 50-cm$^{-1}$ vibration in polystyrene is examined and its usefulness assessed for determining the detailed intermolecular environment in various syndiotactic polystyrene crystals, including polymer–solvent complexes.

## Experimental Section

Syndiotactic polystyrene with greater than 98% syndiotactic content and a number-average molecular weight of 600 000 was provided by the Dow Chemical Co. Highly crystalline samples were grown from a dilute ethylbenzene solution. A solution of sPS in ethylbenzene that was 0.05% by weight was prepared by heating the components above the approximately 120 °C dissolution temperature of the polymer. The solution was quickly transferred to a preequilibrated flask in a large constant-temperature bath held at a crystallization temperature of 50 °C. The crystals that formed were collected by filtration at 50 °C on Teflon filters. Oriented crystal mats sufficiently thin for spectroscopic and diffraction experiments were obtained in this way. For annealing studies, crystal mats were cut into segments and each segment annealed at a different temperature, ensuring that the initial state was identical for each series. Annealing was performed in a differential scanning calorimeter (DSC) in order to provide accurate control of thermal history. Samples from the same mat were used for infrared, Raman, and X-ray measurements. For polarization studies it is more convenient to

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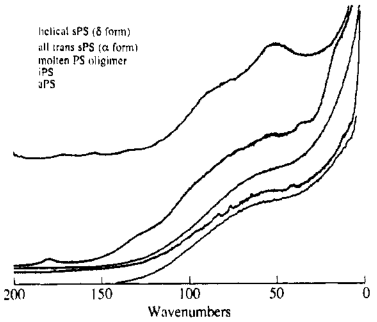


**Figure 1.** Low-frequency Raman spectra of various polystyrenes.

eliminate multiscattering by studying the molten state. A low molecular weight polystyrene standard with a number-average molecular weight of 504 (VPO) and a weight-average molecular weight of 517 (LS) was obtained from Scientific Polymer Products, Inc.,[32] and used as supplied.

Amorphous sPS was obtained by quenching hot (~300 °C) samples into liquid nitrogen. Highly oriented thin films of sPS were drawn from a 0.1% solution in ethylbenzene at 210 °C following the method described previously.[20] The films obtained were ~1000 Å in thickness and were overlaid to obtain samples of sufficient thickness for spectroscopic and X-ray diffraction measurements.

Raman spectra were obtained with a Jobin-Yvon U1000 spectrometer. The 5145-Å line of the Spectra Physics 165-08 argon ion laser was used as the excitation source. Laser power was maintained at 100 mW at the sample. A polarization scrambler was placed before a mirror that reflected the Raman scattered light onto the entrance slit of the monochromator, in order to suppress intensity differences in parallel and perpendicular polarizations due to anisotropic diffraction properties of the monochromator gratings and reflections from beam handling mirrors. Infrared spectra were obtained with an IBM IR38 FTIR spectrometer. Generally, 200 scans were collected at 2-cm$^{-1}$ resolution. DSC traces were measured with a Du Pont 2910 calorimeter at heating rates of 15 and 20 °C/min. Thermogravimetric analysis (TGA) data were obtained from a Du Pont Model TGA 2950 thermogravimetric analyzer at a scan rate of 5 °C/min. Wide-angle X-ray diffraction patterns were observed on flat photographic plates with a Statton X-ray camera using nickel-filtered Cu K$\alpha$ radiation.

## Results and Discussion

Low-frequency Raman data are shown in Figure 1 for various stereoregular polystyrenes and for the low molecular weight polystyrene oligomer. A most striking feature of these spectra is the presence of the intense, broad band centered at approximately 50 cm$^{-1}$ in all of the polystyrene samples. The high intensity and large width of the band is demonstrated by comparison to the skeletal deformation band shown at 170 and 178 cm$^{-1}$ for helical and all-trans syndiotactic polystyrene, respectively. The large bandwidth, ~80 cm$^{-1}$, is indicative of a large distribution of vibrational states and therefore a large distribution of environments in which the mode occurs. The intensity and width of this band is observed to be independent of tacticity and degree of crystallinity, as shown by the presence of the band in the molten polystyrene oligomer spectrum (Figure 1). Differences in the shape of this band are, however, observed for various modifications, $\delta$ or $\alpha$ unit cells, of sPS crystals grown from ethylbenzene. In some samples, the band appears to sharpen. The possibility also exists that these sharper components are different bands superimposed on the broad component.

A broad band observed at 60 cm$^{-1}$ has been reported for atactic polystyrene.[18] This vibration was assigned to the torsional motion of the phenyl group. Substitution on the ring in the meta or the ortho position shifted the band frequency by as much as 15 cm$^{-1}$, whereas substitution at the para position led to little or no shift in band position. It has also been reported that the band intensity decreases with increasing mass of the phenyl ring substituent.[18] These observations are consistent with assignment of this vibration to the ring torsion and are also in agreement with normal-coordinate analyses of the vibrations of syndiotactic and isotactic polystyrenes.[17,21]

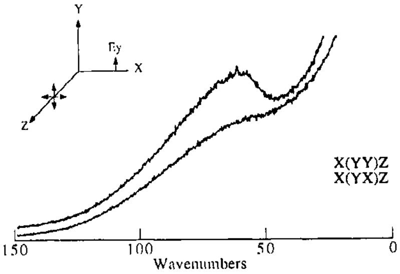


**Figure 2.** Polarized Raman spectra of molten oligomeric polystyrene and the definition of coordinates for the measurement of the depolarization ratio.

In order to use these vibrations as a characterization tool to explore the packing order of sPS chains as well as explore its utility for examination of various polymer–solvent complexes, the polarization characteristics of the band were examined for the liquid oligomer. For freely reorienting molecules the depolarization ratio, $\rho$, is experimentally defined in a conventional 90° Raman scattering experiment as the ratio of the intensity of the Raman scattered light polarized perpendicular to the scattering plane to that polarized parallel.[22] This quantity is defined in terms of changes in the isotropic ($\alpha'^2$) and anisotropic ($\gamma'^2$) components of the polarizability tensor, defined in terms of changes in the individual components $\alpha'_{ij}$ of the polarizability tensor. When the polarizability tensor is symmetric, as in gases or liquids, the depolarization ratio is given by[22,23]

$$\rho = \frac{3\gamma'^2}{45\bar{\alpha}'^2 + 4\gamma'^2} \tag{1}$$

where

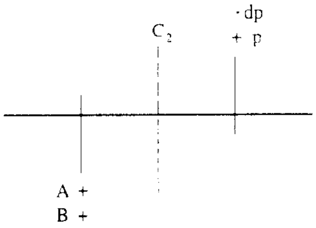
$$\bar{\alpha}' = \frac{1}{3}(\alpha'_{xx} + \alpha'_{yy} + \alpha'_{zz}) \tag{2}$$

and

$$\gamma^2 = \frac{1}{2}[(\alpha'_{xx} - \alpha'_{yy})^2 + (\alpha'_{xx} - \alpha'_{zz})^2 + (\alpha'_{yy} - \alpha'_{zz})^2] + 3(\alpha'^2_{xy} + \alpha'^2_{yz} + \alpha'^2_{xz}) \tag{3}$$

For a depolarized band, $\rho = 0.75$. A polarized band has a value of $\rho < 0.75$ and is defined as completely polarized when $\rho = 0$. Examination of Figure 2 shows that the broad, intense, 50-cm$^{-1}$ band is not completely polarized, with $\rho \approx 0.22$. We propose to show that the measured depolarization ratio is in fact consistent with the proposed assignment.

A completely disordered isotropic structure cannot have depolarized bands in the Raman spectrum. That is, in the complete absence of molecular symmetry, or for molecules with cubic symmetry, nontotally symmetric vibrations cannot occur. Therefore, no depolarized Raman bands can be observed. However, the fact that this band has a depolarization ratio less than 0.75 is not inconsistent with the existence of some local symmetry lower than cubic.[23,24] The depolarization ratio is predominantly determined by the local electronic structure and may be difficult to predict exactly. Figure 1 shows that the broad band centered at about 50 cm$^{-1}$ is independent of tacticity and degree of crystallinity. The



| $C_2$ | E | $C_2$ | |
|---|---|---|---|
| A | + | + | $\alpha_{xx}$ $\alpha_{yy}$ $\alpha_{zz}$ $\alpha_{xy}$ |
| B | + | - | $\alpha_{yz}$ $\alpha_{zx}$ |

**Figure 3.** Schematic drawing of the local symmetry of syndiotactic polystyrene in an all-trans conformation with symmetry $C_2$.

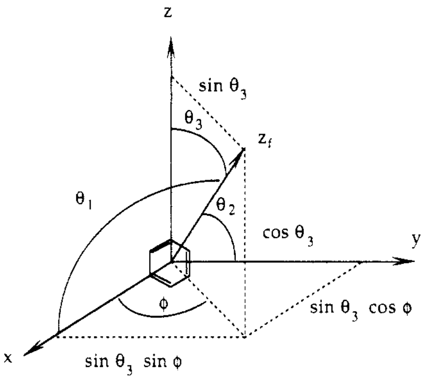


**Figure 4.** Definition of coordinates for the calculation of the intensity of the phenyl ring torsion about the backbone of a polystyrene chain.

possibility of strong coupling along the chain for this vibration is eliminated; therefore, only a nearest-neighbor approximation need be considered. Suppose this were the case. Consider one syndiotactic sequence in an all-trans conformation of the oligomer. The point group is $C_2$, and the elements of symmetry are the identity and a $C_2$ rotational axis perpendicular to the chain, shown schematically in Figure 3. The + and − signs indicate the relative directions of torsional ring motion with respect to the chain backbone as the nuclei pass through their equilibrium positions in the vibration. For the two benzene rings shown, there are two torsional ring vibrations. In one of these, both rings move in phase (+ +), and in the other the motion is exactly out of phase (+ −). One of these torsional vibrations is totally symmetric and gives rise to a polarized Raman band, but the other is nontotally symmetric, Raman active, and expected to give rise to a depolarized Raman band.

If a more rigorous analysis is required, consider a segment of the low molecular weight polystyrene (five styrene units) in an all-trans conformation. The point group is $C_s$, provided the central benzene ring either lies in the plane of symmetry or is exactly perpendicular to it and provided the remaining four benzene rings fall into two symmetrically equivalent sets. Then the central benzene ring torsion must violate the symmetry plane while each of the two sets of symmetrically equivalent torsions may be selected so as to either violate or preserve the plane. The structure of the ring torsions of this conformation of this molecule is then $2A' + 3A''$, and the $3A''$ torsional vibrations are all nontotally symmetric, Raman active, and expected to give rise to depolarized Raman bands. There are a very large number of conformations of the polystyrene oligomer. The mathematical maximum is approximately $3^8 = 6561$. Many of these are symmetrically equivalent and must be removed from the maximum, and many of the remaining mathematically possible conformers are so sterically hindered that their populations in a real sample must be trivially small. There remains a substantial number of truly different thermodynamically accessible conformers which must be present in a room-temperature sample of low molecular weight polystyrene, many of which will possess true molecular symmetry and thus give rise to depolarized ring torsional Raman bands located at a variety of frequencies near the ring torsional modes in the all-trans molecule.

The observed feature in the spectrum of the oligomer is broad, ~150 cm$^{-1}$, suggesting that it is a statistical composite of many contributors representative of a wide variety of local molecular environments and conformational sequences. Roughly half of these contributors are expected to be apparently depolarized for the symmetric conformers by either of the above arguments, and if this is the case, the composite depolarization ratio of the band should be greater than would be the case if all the benzene ring torsional vibrations were polarized. It is not possible to state by how much since the relative intensities of the polarized and depolarized components of the parallel and perpendicular scattering for the benzene ring torsional vibrations are unknown. However, depolarized Raman bands are often less intense than polarized Raman bands in spectra of small molecules, and this may in part explain why the depolarization ratio is as small as 0.22. The fact that cubic symmetry cannot exist for the molecule means that the band cannot be completely polarized, and some part of the depolarization ratio of 0.22 derives from this fact. All of these considerations show that the polarized band observed in Figure 2 is consistent with an assignment of the band to benzene ring torsional vibration.

The high intensity of the band observed at ~50 cm$^{-1}$ is also consistent with the torsion of a ring about a fixed attachment point. Figure 4 shows a diagram of such a vibration. Let $z_f$ be the space-fixed direction of oscillation of the electric vector of the incident light, $x$, $y$, and $z$ be molecule-fixed Cartesian axes defined according to the Mulliken convention,[25] and $\theta_1$, $\theta_2$, and $\theta_3$ be directional cosine angles between $z_f$ and the molecule-fixed axes. Directional cosines obey the relation

$$\cos^2\theta_1 + \cos^2\theta_2 + \cos^2\theta_3 = 1 \tag{4}$$

In terms of the molecule-fixed polarizabilities, the fluctuating diagonal component of the polarizability expressed in terms of the space-fixed coordinate $z_f$ is

$$\alpha_{z_f z_f} = \alpha_{xx}\cos^2\theta_1 + \alpha_{yy}\cos^2\theta_2 + \alpha_{zz}\cos^2\theta_3 \tag{5}$$

where $\alpha_{ii}$ are the diagonal components of the polarizability tensor of the ring. It is assumed that the benzene ring maintains its essential electronic structure, even in the maximally distorted position, as it undergoes torsional motion. Therefore, the changes in $\alpha_{xx}$ and $\alpha_{yy}$ with unit change in torsion angle $\phi$ are regarded as negligibly small quantities. From Figure 4

$$\cos\theta_1 = \sin\theta_3\cos\phi$$

$$\cos\theta_2 = \sin\theta_3\sin\phi \tag{6}$$

allowing $\cos\theta_1$ and $\cos\theta_2$ to be eliminated from eq 5. Upon substitution

$$\begin{aligned}\alpha_{z_f z_f} &= \alpha_{xx}\sin^2\theta_3\cos^2\phi + \alpha_{yy}\sin^2\theta_3\sin^2\phi + \alpha_{zz}\cos^2\theta_3 \\ &= (\alpha_{xx}\cos^2\phi + \alpha_{yy}\sin^2\phi)\sin^2\theta_3 + \alpha_{zz}\cos^2\theta_3 \qquad (7)\end{aligned}$$

Let $\theta_3$ be a constant, representing the orientation of the benzene ring to the incident electric vector. Allow $\phi$ to vary as the ring executes torsional motion about the *z* axis, with torsions about *x* and *y* suppressed, thus simulating a phenyl ring attached to a polymer backbone undergoing torsional motion about the attachment point. Expanding about $\phi = 0$

$$\langle v'|\alpha_{z_f z_f}|v\rangle = \langle v'|\alpha^0_{z_f z_f}|v\rangle + \left\langle v'\left|\left(\frac{\partial \alpha_{z_f z_f}}{\partial \phi}\right)_0 \phi\right|v\right\rangle + \frac{1}{2}\left\langle v'\left|\left(\frac{\partial^2 \alpha_{z_f z_f}}{\partial \phi^2}\right)_0 \phi^2\right|v\right\rangle + \ldots \quad (8)$$

Then

$$\frac{\partial \alpha_{z_f z_f}}{\partial \phi} = 2 \sin \phi \cos \phi \sin^2 \theta_3(\alpha_{yy} - \alpha_{xx}); \quad \therefore \left(\frac{\partial \alpha_{z_f z_f}}{\partial \phi}\right)_0 = 0$$

$$\frac{\partial^2 \alpha_{z_f z_f}}{\partial \phi^2} = 2(\cos^2 \phi - \sin^2 \phi) \sin^2 \theta_3(\alpha_{yy} - \alpha_{xx});$$

$$\therefore \left(\frac{\partial^2 \alpha_{z_f z_f}}{\partial \phi^2}\right)_0 = 2 \sin^2 \theta_3(\alpha_{yy} - \alpha_{xx}) \quad (9)$$

and the matrix element of the oscillating polarizability is

$$\langle v \pm 2|\alpha_{z_f z_f}|v\rangle = \sin^2 \theta_3(\alpha_{yy} - \alpha_{xx})\langle v \pm 2|\phi^2|v\rangle \quad (10)$$

Other terms either vanish or do not lead to a change in the vibrational state. Therefore, the first overtone is responsible for the observed intensity, while the fundamental is forbidden. The intensity of the Raman scattering is thus proportional to the product

$$\sin^4 \theta_3(\alpha_{yy} - \alpha_{xx})^2 \quad (11)$$

For a phenyl group, ab initio calculations performed with the GAUSSIAN 86 package of programs[26] for the related compound *p*-difluorobenzene at the 3-21G level of theory give principal components *xx*, *yy*, and *zz* in atomic units of the molecular polarizability of 14.634 316 6, 63.778 485 2, and 62.370 959 2.[27] The Mulliken convention[25] is used in GAUSSIAN 86, and these results suggest a large difference between the two components of the polarizability tensor involved in the intensity expression derived above. This large difference is as would be expected for a planar phenyl group. One component, $\alpha_{yy}$, is defined as through the plane of the ring while the other is perpendicular to the face of the ring. Thus, the origin of the large observed intensity of the band is the large difference in $\alpha_{xx}$ and $\alpha_{yy}$, even though the transition which is Raman active is the first overtone, which is generally weak for most vibrations.

A quite strong $2 \leftarrow 0$ phenyl torsion transition, in fact, has been reported in the 112–128-cm$^{-1}$ region of the Raman spectrum of styrene, and a torsional barrier of 623 cm$^{-1}$ (1.78 kcal/mol) has been estimated from these data.[28] This mode has not been seen in the infrared spectrum.[29] This reported Raman-active overtone band has approximately the same relative intensity as observed for polystyrene. The torsional barrier height in styrene directly determines its torsional frequency and has been predicted by use of the ab initio method.[30] It is generally accepted that ab initio methods applied to high levels of the theory tend to overestimate the height of potential barriers when multiple double-bonded structures are calculated to be artificially short.

Styrene is not a good model for the phenyl ring torsions in polystyrene, since the torsional barrier is enhanced by conjugation of the vinyl group with the ring. It has long been known that the barrier to rotation of the methyl group in toluene is very low at ~5 cm$^{-1}$ (14 cal/mol).[31]

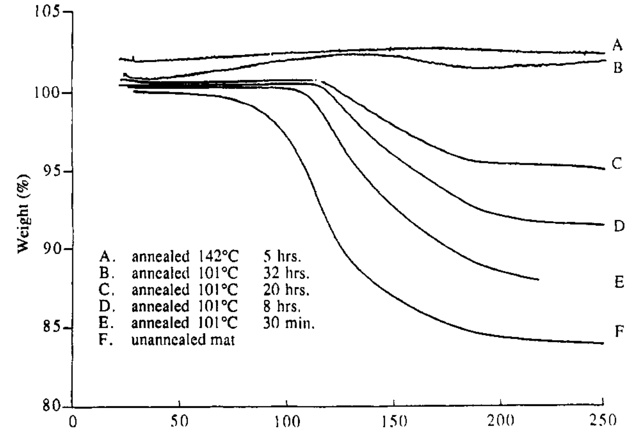


**Figure 5.** TGA scans of annealed syndiotactic polystyrene crystals.

Ethylbenzene was felt to be a much better model than styrene for describing phenyl torsion, and the barrier should lie between that for toluene and that for styrene. Therefore, an ab initio method has been carried out to obtain the barrier height and the torsional frequency of the phenyl ring. Geometry optimizations conducted at the 3-21G level of the theory with the GAUSSIAN 86 set of programs gave restricted Hartree–Fock energies of −307.059 976 3 and −307.057 085 679 hartrees, respectively, for the orthogonal and planar structures of ethylbenzene, assuming a planar benzene ring. The planar structure has all heavy atoms coplanar, while the orthogonal ground-state structure has the plane of the benzene ring perpendicular to the plane formed by the two carbon atoms in the ethyl group and the carbon atom in the phenyl group to which the ethyl group is attached. The energy difference is 0.002 890 621 hartrees, which corresponds to 1.81 kcal/mol or about 634 cm$^{-1}$ consistent with earlier calculations.[32] These optimized geometries were used to estimate the *F* numbers, the internal rotation constant, for the phenyl ring, taking the torsion angle to be 0° for the orthogonal conformer and 90° for the planar. The *F* number for the 45° structure was estimated roughly and fit to a three-term Fourier expansion of the form[33]

$$B(\phi) = B_0 + B_2 \cos 2\phi + B_4 \cos 4\phi \quad (12)$$

where $\phi$ is the torsion angle. The result was $B_0 = 0.924\,399$, $B_2 = -0.070\,979\,5$, and $B_4 = -0.012\,600\,75$. These were then used to explore the phenyl torsional transitions expected for a torsional barrier of 634 cm$^{-1}$ (the 3-21G result) and for a barrier half that. For a 634-cm$^{-1}$ barrier, Raman transitions would be expected near 90.4, 89.0, 87.5, and 85.8 cm$^{-1}$. For a 317-cm$^{-1}$ barrier Raman bands would appear near 63.3, 61.8, 60.1, and 58.3 cm$^{-1}$ for the $2 \leftarrow 0$, $3 \leftarrow 1$, $4 \leftarrow 2$, and $5 \leftarrow 3$ transitions, respectively. Although gas-phase Raman data for ethylbenzene do not appear to have been reported, these calculations suggest that our assignment of the broad Raman feature around 60 cm$^{-1}$ to phenyl torsion is consistent with the value expected for this torsional vibration in at least one small compound that must display such a torsion in its Raman spectrum.

Examination of the X-ray, TGA, and infrared data conclusively shows that when first grown the crystals are complexed structures of syndiotactic polystyrene and ethylbenzene. Figure 5 presents TGA scans for crystal mats annealed at the onset temperature of decomplexation (101 °C) as a function of time. The thermograms of the unannealed mat and a mat annealed at 142 °C for 5 h are shown for reference. The weight loss as a function of annealing time presents strong evidence that decomplexation occurs.

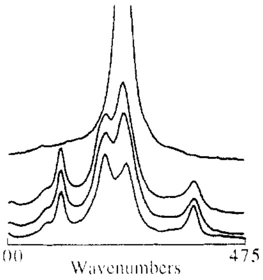


**Figure 6.** Infrared spectra of syndiotactic polystyrene crystals, from bottom to top: unannealed; annealed at 106 °C; annealed at 142 °C; and annealed at 202 °C. The annealing time was 5 h in each case.

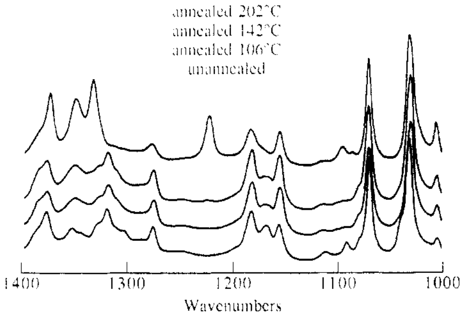


**Figure 7.** Infrared spectra of annealed syndiotactic polystyrene crystals. The annealing time was 5 h in each case.

Figure 6 shows the absence of the intense 486-cm$^{-1}$ band of liquid ethylbenzene in the infrared spectrum, and this demonstrates that the large observed weight loss cannot be due to loss of residual free solvent. On the basis of earlier studies,[15,34] observed changes in the wide-angle X-ray diffraction patterns upon heating through the first phase transition temperature, along with the thermal and infrared data, provide definitive proof that the initial structure is a crystalline complex of the solvent and syndiotactic polystyrene molecules. After annealing above the first phase transition temperature, the solvent is driven off, altering the crystalline structure and overall morphology of the sPS.

The chain conformation of the sPS crystals remains helical upon decomplexation, as demonstrated by infrared spectroscopy. Figures 6 and 7 show the spectra of the crystal mats as a function of annealing time. Bands at 501, 548, 571, 934, and 943 cm$^{-1}$ are indicative of gauche linkages in the main chain, which are present in the helical crystalline phases of syndiotactic polystyrene. The disappearance of these bands, along with the emergence of the band at 1222 cm$^{-1}$ due to extended trans sequences, is indicative of the transformation from a helical to an all-trans crystal structure.[5,8,9,35] The mats annealed at 106 and 142 °C for 5 h and the unannealed sample are all in a helical chain conformation. The mat annealed at 202 °C for 5 h, which is above the helix to all-trans phase transition temperature, is in an all-trans conformation.

The low-frequency Raman spectra of solution-grown syndiotactic polystyrene crystals are shown in Figure 8. Slight differences are observed as a function of annealing. The sharp band at 52 cm$^{-1}$ is especially interesting as it appears only in the unannealed complexed, or $\delta$, crystalline form.[11,34] Upon disappearance of the sharp band at 52 cm$^{-1}$ after annealing at 106 °C for 5 h, the broad band remains. Therefore the sharper band is directly due to the complexed structure. The large intensity of the band could not be accounted for if the band were due to the relatively small amount of ethylbenzene present in the complex. The observation of a band that is sensitive to the presence of the complexed structure may contribute to understanding the mechanism of helical crystal phase formation for syndiotactic polystyrene. Selectively choosing solvents of different size, chemical functionality, and solvent quality and repeating the sample preparation and spectroscopic methods employed here should provide a much better understanding of this interesting crystallization process.

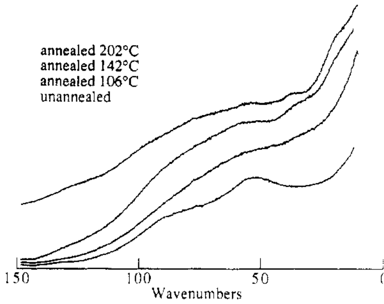


**Figure 8.** Low-frequency Raman spectra of annealed syndiotactic polystyrene crystals. The annealing time was 5 h in each case.

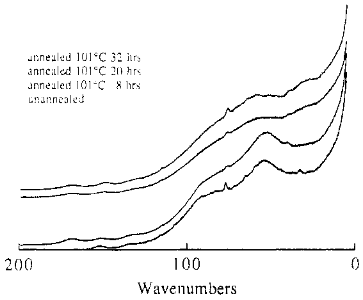


**Figure 9.** Low-frequency Raman spectra of syndiotactic polystyrene crystals annealed at 101 °C for 0, 8, 20, and 32 h.

A similar observation was made earlier for isotactic polystyrene.[36] A sharp band at 70 cm$^{-1}$ for a crystalline sample was observed superimposed on a broader component. The broad component remained for samples of low crystallinity. It has been postulated that the sharp component in the crystalline isotactic isomer may be due to a narrower distribution of states of the same mode. The quite similar behavior of bands observed in both isotactic and syndiotactic isomers suggests that this vibration is sensitive to the local environment of the ring and can be used to examine hindrance to the ring torsional motion in polystyrenes and therefore the free volume associated with the polymer chain for different environments.

The correlation between different bands in the low-frequency region can also be examined in greater detail by annealing the samples close to the first phase transition temperature. Figure 9 shows Raman spectra for sPS crystals annealed at 101 °C at different times. The unannealed mat is included for reference. It can be seen that the appearance of the 35-cm$^{-1}$ band coincides with the decrease in the 52-cm$^{-1}$ band as a function of time for the series annealed at 101 °C. Therefore, the bands may be of the same origin, with the sharper conformationally insensitive 35-cm$^{-1}$ band assigned to ring torsion as well. The difference in these two bands may simply lie in the degree of coupling to other highly localized modes. Earlier normal vibrational analysis has shown bands at 35 and 36 cm$^{-1}$ to be completely due to ring torsion, whereas a band at 49 cm$^{-1}$ is calculated to be coupled strongly to the CC torsion of the backbone and the out-of-plane bending vibration.[17] This calculation indicates that, for syndiotactic polystyrene, more than one band may exist due to the ring torsion, along with the possibility of coupling to other localized intramolecular modes. Comparison with TGA data (Figure 5) indicates that changes in these two bands occur as a function of the decomplexation process.

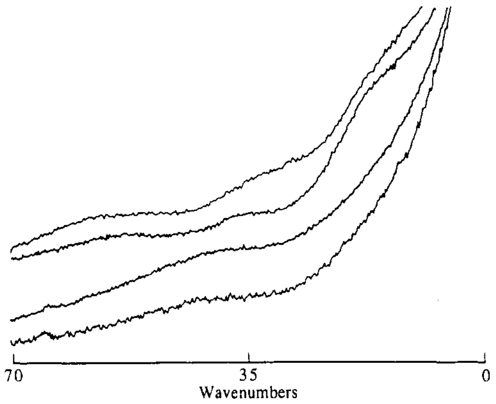


**Figure 10.** Low-frequency Raman spectra of syndiotactic polystyrene, from bottom to top: amorphous sPS quenched from the melt; highly oriented film ($\alpha$ form); crystal mat annealed at 202 °C ($\alpha$ form); crystal mat annealed at 142 °C ($\gamma$ form).

One additional band was observed in some annealed samples. From Figure 9 it can be seen that the band at 18 $\mathrm{cm}^{-1}$ is not directly related to those at 35 and 52 $\mathrm{cm}^{-1}$ as it does not appear for samples annealed at 101 °C for 20 and 32 h. A band is clearly observed at low temperature in atactic polystyrene at $\sim$20 $\mathrm{cm}^{-1}$. Spells et al.[18] observed this band to be completely insensitive to substitution on the phenyl ring and proposed it to be due to LAM-like vibrational motion for small sequences of conformational order. The low-frequency Raman spectra of different crystalline forms of syndiotactic polystyrene are shown in Figure 10. The 18-$\mathrm{cm}^{-1}$ band, present in both the $\gamma$- and $\alpha$-phase solution-grown crystals, is conformationally insensitive and is absent in the extremely highly oriented film prepared. From X-ray and electron diffraction, it is known that the crystalline domains in the film are packed in the $\alpha$ modification of *all-trans*-sPS.[37] Therefore, the absence of the band for the film cannot be attributed to a change in packing from the annealed solution-grown crystals. From bright-field electron microscopy, the lamellar thicknesses of the annealed crystal mat and highly oriented film are 100 and 150 Å, respectively.[34,37] With use of the elastic rod model, the relationship between the LAM frequency and the lamellar thickness $L$ can be given by

$$\nu = \frac{1}{2cL}(E/\rho)^{1/2} \tag{13}$$

where $\rho$ is the density of the material, $c$, the velocity of light in a vacuum, and $E$, the modulus. Using the density of $\alpha$-phase sPS from Greis[37] and the observed frequency, the modulus can be calculated to be 116 GPa, a value close to the value calculated earlier in this laboratory (115 GPa). The absence of an observed band in the oriented film may be due to a decrease in the frequency as the lamellar thickness increases, bringing the band too close to the Rayleigh line to be resolved. Although this behavior can be attributed to LAM-type motion, and the observed frequency is reasonably close to estimations from calculations of modulus in the literature, there is no definitive assignment of this band.

## Conclusions

Highly crystalline syndiotactic polystyrenes were prepared by isothermal growth from dilute solution, minimizing the amorphous contribution to the structure and facilitating studies of structural transitions in the crystalline state as well as crystallization behavior in the presence of solvent. The solution-grown crystals are observed to consist of a complexed structure of ethylbenzene and syndiotactic polystyrene. A very strong, multicomponent low-frequency vibration has been observed in the 50-$\mathrm{cm}^{-1}$ region and is assigned to torsion of the phenyl ring against the backbone. Although the vibration is intramolecular in origin, the bandwidth is highly sensitive to the solvent-complexed crystalline state and therefore the intermolecular ring environment. This observation suggests that such a vibrational band may be useful for examining the polymer–solvent specific interaction spectroscopically and therefore the mechanism of formation of the helical crystalline phase in syndiotactic polystyrene. The similarity of the behavior of this band in syndiotactic, atactic, and isotactic isomers suggests that this region of the Raman spectrum may be useful in the determination of the free volume associated with polymer chains in a variety of environments.

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