Vibrational Relaxation in Atactic Polystyrene: An Infrared Spectroscopic Study

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ABSTRACT: The shapes and widths of infrared bands and Raman lines are an important source of information on interactions and molecular dynamics and have been used to study vibrational and rotational relaxation processes in the picosecond time range. Most of this work has focused on small molecules, however, and the analysis of bandwidths and band shapes has been a largely neglected topic in polymer vibrational spectroscopy. The characterization of polymers introduces both advantages and new problems. One simplification is a consequence of the large mass and moments of inertia of these molecules. Relaxation times associated with the reorientation of chain segments and many side groups are long compared to vibrational relaxations, and their contribution to band and line contours can be neglected. Unfortunately, this simplification is accompanied by new problems: the multiplicity of overlapping bands observed in many systems and the complications introduced by conformational sensitivity. Some of these experimental problems are addressed in this paper, where an analysis of the ring stretching modes in the 1600 cm^{-1} region of the infrared spectrum of atactic polystyrene is presented. It is shown that the shape of one of the fundamental modes in this region of the spectrum changes significantly as the polymer is heated through the glass transition temperature. This is interpreted in terms of a coupling of this mode to lattice vibrations through a combination vibration. It is thought that the α-relaxation process in glassy solids succeeds much faster than picosecond scale motions, and vibrational relaxation, as suggested by these results, would appear to be a sensitive indicator of the type of cooperative motions thought to be involved.

Introduction

A wealth of information on molecular dynamics lies buried in the shapes of infrared bands and Raman lines.[1−4] Data obtained in the frequency domain has a counterpart in the time domain in the form of a time correlation function, which is sensitive to molecular dynamics and relaxation processes in the picosecond time range. Band-shape studies can provide information on rotational relaxation (usually in small molecules), the duration of “sticky” collisions (e.g., those involving hydrogen bonds), the dynamics of strong interactions, the coupling of local vibrations with lattice motions, and so on.

Unfortunately, information on molecular relaxation times is not easily extracted from conventional infrared absorbance bands or Raman lines. Not only are there considerable experimental problems, well documented in the literature, but even when excellent data have been obtained (most often on small, symmetric molecules), the range of relaxation phenomena that contribute to the band or line shapes has complicated an interpretation of the results.[1−4]

In spite of these difficulties, the field has advanced considerably in the past few years, and considerable insight into the dynamics of small molecules and their relaxation behavior in the liquid, glassy, and confined states has been gained.[1−14] However, as Rothschild[2] pointed out more than 20 years ago, the study of the shapes of the infrared bands and Raman lines of polymers remains a largely neglected area, with just a few studies that have used infrared spectroscopy to study phase changes.[18−21] This older work generally focused on frequency shifts and overall intensity changes, as opposed to band shapes and widths. More recently, however, Tashiro and Yoshioka[22] argued that the sensitivity of the half-width of infrared bands to molecular motion could be used to probe the crystallization process in syndiotactic polystyrene. As part of this study, these authors also monitored the peak position and half-width of the 907 cm^{-1} band of atactic polystyrene (*a*-PS) as a function of temperature. A plot of the peak position vs temperature displayed an inflection point near the T_g, similar to observations made in a number of older studies of polymer transitions.[18−21] Plots of the half-width of this band displayed more intriguing features, however. The plot was relatively flat at temperatures well below the T_g, decreased to a minimum at temperatures near the T_g, and then increased abruptly at higher temperatures.

In polymer spectroscopy, it is usual to regard the shapes and widths of infrared bands and Raman lines as being directly related to the distribution of local environments experienced by an oscillator. Each oscillator may relax by some mechanism (e.g., vibrational dephasing or energy relaxation), but the band due to a particular normal mode largely reflects the superposition of different frequencies that are a result of interactions in slightly different local environments. In fact, this is also a central assumption made in many studies of low molecular weight liquids and glassy solids.[1−14] As we will discuss in more detail in a subsequent paper, the widely used Kubo−Rothschild model assumes that each oscillator relaxes in an exponential fashion (hence has a Lorentzian band shape), but there is a Gaussian distribution of such bands (i.e., local environments). If the time scale of the fluctuations in the system is large, then a Gaussian band shape is observed, and the bandwidth (or second moment of the band) simply reflects the distribution of states. On the other hand, if the modulation process is fast (e.g., if there is a rapid change in local environments), then local differences in environment are “averaged out” by a rapid loss of memory, and a Lorentzian band shape is recovered. If the relaxation

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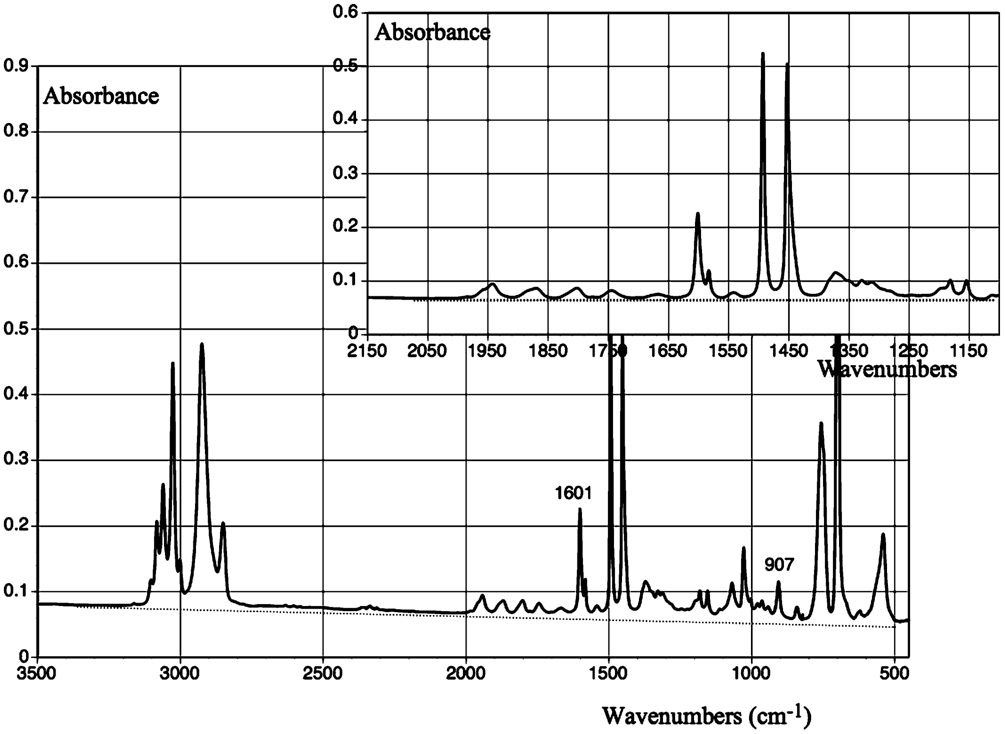

Figure 1. Infrared spectrum of atactic polystyrene showing the position of a linear but sloping baseline.

process is dominated by a single mechanism (or there is a relaxation process that is much faster than the others), then the half-width of the band can be related to the relaxation time. (The width at half-height is inversely related to the relaxation time.) Tashiro and Yoshioka essentially assumed that they were in the fast modulation limit and interpreted their results in terms of an apparent “slowing down” of the dynamics at the T_g. We found this intriguing and attempted to repeat the experiment and determine whether the shapes of other bands of *a*-PS are sensitive to relaxation processes near the T_g. We will report the results of our experimental work here, focusing on methodology, as this is crucial if reproducible results are to be obtained. Calculations of time correlation functions will be presented in a separate publication.

Experimental Section

The *a*-PS (M_w = 190 000) used in this study was obtained from Scientific Polymer Products, Inc. Thin films were prepared by casting 4% (w/v) THF solutions onto KBr windows. The solvent was removed slowly under ambient conditions for a minimum of 24 h. The sample was then dried in a desiccator for an additional day. After that, the sample was placed in a vacuum oven at 120 °C to remove residual solvent.

Infrared spectra were obtained on a Digilab FTS-45 Fourier transform infrared (FTIR) spectrometer using a minimum of 256 coadded interferograms at a resolution of 1 cm^{-1}. All films were sufficiently thin to be within the absorbance range where the Beer–Lambert law is obeyed.

Results and Discussion

The infrared spectrum of atactic polystyrene between 3500 and 450 cm^{-1} is shown in Figure 1. This spectrum has not been “smoothed” or baseline adjusted. One problem is immediately apparent: the band near 907 cm^{-1} is relatively weak, and there is considerable overlap with close-lying modes. The measured width at half-height strongly depends upon the position of the baseline. Tashiro and Yoshioka[22] did not describe their procedures in detail, so we do not know whether the approach we will now describe duplicates theirs.

We believe that the most accurate way to measure the half-width (and other band parameters) of bands in the spectra of polymers, which usually overlap to some degree with one or more neighbors, is through curve fitting. Our methodology is based on the approach we have used to analyze the infrared spectra of polymer blends, described in detail in a recent review.[23] The procedure involves an initial examination of a broad region of the spectrum to identify where a baseline can be placed. It is very difficult to obtain cast films of even thickness, so that even excellent spectra often display some degree of slope in the baseline, as can be seen in Figure 1. As a result of several factors (source and detector characteristics, etc.), there is more noise at the edges of the mid-infrared region (near 4000 and 450 cm^{-1}), and the precise position of the baseline is less well-defined. (To observe this in the spectrum shown in Figure 1, it is necessary to examine the spectrum in a narrower absorbance range, between 0.05 and 0.1 absorbance units.) Compounding this problem, scattering and reflections can lead to a curvature in the baseline that becomes more pronounced at lower wavenumbers, a factor that will depend on how well a sample is prepared. A careful examination of Figure 1 shows that a linear baseline drawn from a point near 3500 cm^{-1} through a point near 2100 cm^{-1} (where there do not appear to be any absorption bands) deviates slightly from absorption minima in the spectra near 500 and 800 cm^{-1}, where we would expect the baseline to be positioned. Although most modern instruments have automatic baseline correction routines, we consider these to be an abomination, as they often adjust all the minima in the spectra to an assumed zero absorbance value. This leads to significant distortions in band shape, particularly when applied to spectra with strongly curving baselines. We think it is necessary to reject spectra that display anything but a minimal degree of deviation from a linear baseline and cast new films.

A careful examination of the baseline in the narrow absorbance range mentioned above (0.05–0.1 absorbance units) led us to conclude that, first, polystyrene is perhaps not an ideal choice of polymer to pursue studies of vibrational relaxation

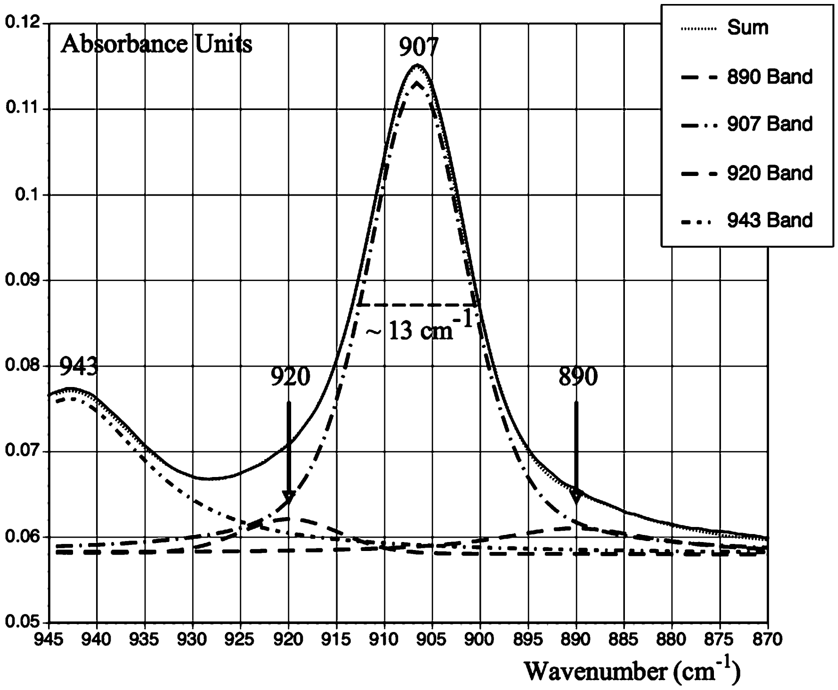

Figure 2. Curve-resolved infrared spectrum of atactic polystyrene in the 907 cm^{-1} region of the spectrum.

because of the multiplicity of overlapping bands and, second, the baseline is very slightly curved, particularly in the lower wavenumber region. However, in narrower regions, particularly in the range of about 2200−1100 cm^{-1} (where the background transmission is at a maximum), the baseline appears to be linear, to a very good approximation, as illustrated in the inset displayed in Figure 1. We will consider this region of the spectrum in more detail below, but first we will describe our attempts to measure the width of the 907 cm^{-1} band.

Initially, we used scale-expanded spectra to fix the position of the baseline, using minima near 500 and 800 cm^{-1}. This procedure is no doubt imperfect for the determination of absolute band shapes but allows us to curve-fit spectra obtained as a function of temperature in a reproducible manner. The 907 cm^{-1} band was then curve-resolved using a program developed in our laboratories. Experimental bandwidths are often a convolution of Gaussian and Lorentzian (Cauchy) shapes (resulting in a Voigt profile), but these are often approximated using a sum function. We use the following expression:

$$I(\nu) = fA_0 \exp[-\ln 2(\nu - \nu_0)/\Delta\nu_{1/2}]^2 + (1 - f)A_0/\{1 + [(\nu - \nu_0)/\Delta\nu_{1/2}]^2\} \quad (1)$$

The Gaussian and Lorentzian shapes that combine to make up the overall band profile are assumed to have equal half-widths at half-height, $\Delta\nu_{1/2}$, and are present in the proportions of f to $(1 - f)$. A_0 is the peak height, ν_0 is the wavenumber coordinate of the peak maximum, and ν are the frequencies of the points that describe the bands. Liu et al.[24] have recently shown that this particular sum function is actually an excellent approximation to a true Voigt profile.

Initial estimates of these parameters for a defined number of bands are then least-squares fit to the observed spectrum in a limited wavenumber range, 945−870 cm^{-1}, shown in Figure 2. We initially employed just two bands, near 907 and 943 cm^{-1}. Because Lorentzian bands have “tails” that extend a considerable distance from the peak position, it is necessary to include neighboring bands that are close to the absorption of interest. (In this particular, case we have truncated the latter peak in the fitting process, so as to exclude the influence of higher wavenumber modes on its band shape.) Initial results from this procedure were unsatisfactory, in that there were clear differences between the profile obtained from adding the two component bands and the original spectra, and it was necessary to also include bands near 920 and 890 cm^{-1} to obtain a good fit. We will not go into the details of how we came to this conclusion for this particular band, as we will describe the methodology in more detail below, where it is applied to a region of the spectrum where the baseline is better defined. This is clearly not a satisfactory procedure, in many ways, of course. In our work, we try to justify the inclusion of such weak bands in a fitting procedure on more fundamental grounds, using either the second derivative of the spectrum or a prior knowledge of the presence of, say, a weak overtone or combination mode. However, our purpose here was to simply obtain a measure of the width at half-height of the band near 907 cm^{-1} as a function of temperature. In this case fitting to two bands or four gave similar results in terms of overall trends.

The curve-fitting program we use in our work determines the peak position and intensity at maximum absorption, the (full) bandwidth at half-height ($2\Delta\nu_{1/2}$), and the band shape (in terms of fraction Gaussian) and from these parameters also calculates the overall integrated intensity of the band (in its entirety, not just the portion of truncated bands that appear in the plots). Plots of the frequency at maximum absorption vs temperature displayed results very similar to those observed by Tashiro and Yoshioka.[22] Plots of the bandwidth at half-height, obtained by fitting to both two bands and four bands, as shown in Figure 3, were very different, however. First, the values we determined were about half of those reported by these authors (∼13 cm^{-1} vs ∼26 cm^{-1}). The spectrum shown in Figure 2 strongly suggests to us that the (full) width at half-height should be about 13 cm^{-1}, however. Second, we do not observe the same type of fluctuations near the T_g, but there are some interesting changes. Starting at a temperature of about 80 °C, the bandwidth increases and appears to level off at temperatures near 100 °C, the thermally measured T_g of this polymer. We do not observe any apparent discontinuity in this parameter at the T_g.

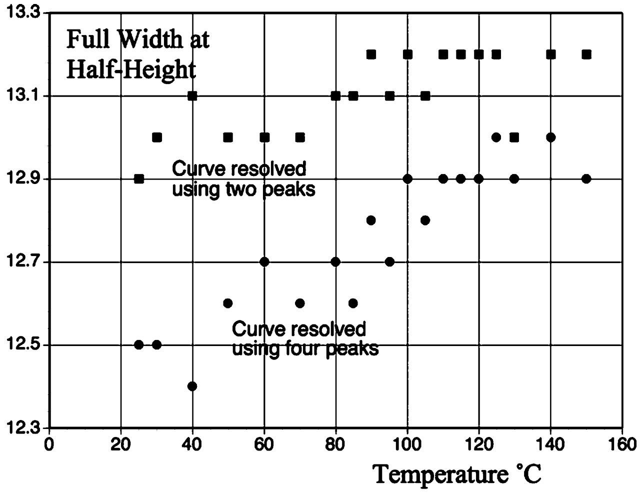

Figure 3. Plot of the (full) width of half-height of the 907 cm^{-1} band as a function of temperature. Measurements were made on a spectrum curve-resolved into two bands (top) and one curve-resolved into four bands (bottom).

There also appear to be changes in the shape of the band that follow a corresponding pattern. We will not consider these results in any depth, however, because they are subject to significant uncertainty as a result of the difficulty in accurately fixing a baseline in this region of the spectrum. This, in turn, affects the contribution of the weaker modes near 920 and 890 cm^{-1} to the spectrum and hence the band shape of the 907 cm^{-1} mode. However, they do suggest one possible reason for the difference in results. If the width at half-height is measured from a computer or instrument baseline corrected spectrum, such that the half-widths were measured at a lower point in the profile (hence the larger value of the measured half-width), then the overlapping weak modes, if they are real, would be included in this measurement and any band shape changes (in all three bands) would affect the results. If the weak bands that we have included are not real, then the shape of this band is changing in a very interesting manner with temperature. The possibility of a band shape change at the T_g is intriguing, suggesting these modes are sensitive to local environment and relaxation phenomena. Normal mode calculations of toluene[25] and isotactic polystyrene[26,27] indicate that the 907 cm^{-1} band in *a*-PS is a localized (conformationally insensitive) out-of-plane bending mode of the hydrogen atoms on the phenyl ring. We therefore thought it would be interesting to see whether some of the in-plane modes were also sensitive to the changes in dynamics that occur near the T_g. Furthermore, we believe it is possible to fix the baseline with more certainty in the higher wavenumber region of the spectrum.

Before getting to this, there are two additional points we wish to make. Our experiments were conducted a little differently to those of Tashiro and Yoshioka.[22] We raised the temperature in small increments, pausing to take the spectrum at each temperature. This is because we wanted to obtain the spectra at a resolution of 1 cm^{-1} (to include more data points for each band and thus improve the accuracy of our curve resolving), and we also wanted to obtain a large number of scans or coadded interferograms (usually >250) to obtain high signal-to-noise ratio spectra. Tashiro and Yoshioka used a constant heating rate of 2 °C/min and took spectra continuously. Accordingly, we repeated the experiment in the same way, obtaining essentially the same results as those reported above. The only difference was that the data displayed more scatter, as the spectra (obtained using just 16 “scans” at 2 cm^{-1} resolution) were not as good. The second point is that we observed a small degree of baseline drift over time. An interlaboratory study that compared FTIR measurements of aqueous solutions noted that this appeared to be a fairly common occurrence, particularly when ratioing spectra taken over time against a common reference (background) spectrum.[28] Nevertheless, baseline correction was apparently sufficient to compensate for this problem.[28]

As mentioned above, one possible reason for the difference in the results presented here and those in the literature is that there is a change in band shape as a function of temperature, which can influence half-width measurements, depending on how the latter are made. This would be very interesting, suggesting not only that there is a change in the dynamics of the system as the sample is heated through the T_g but also that the mechanism of vibrational relaxation is changing as collective motions within the sample become significant. Accordingly, we examined the 1600 cm^{-1} region of the spectrum, shown for spectra obtained at 50, 100, and 140 °C in Figure 4. There are two fundamental normal modes of vibration in this wavenumber range, near 1601 and 1583 cm^{-1}, at room temperature. (They shift to lower wavenumbers as the temperature is raised.) These are both in-plane ring-breathing modes.[25−27] The phenyl ring attached to the polystyrene backbone has C_{2v} local symmetry, with the 1601 cm^{-1} band belonging to symmetry species B_1, while the 1583 cm^{-1} band belongs to symmetry species A_1. This will be important in terms of the interpretation of our results. There are also two obvious weak overtone or combination modes, near 1667 and 1541 cm^{-1}. Less obvious, at first site, is the presence of the weak band near 1592 cm^{-1}, an overtone or combination mode that at least at high temperatures may be in Fermi resonance with one of the fundamentals. To engage in Fermi resonance interactions, modes must belong to the same symmetry species, which means that the 1592 cm^{-1} band must be either an overtone (which would be a totally symmetric A_1 mode) or a combination that results in either A_1 or B_1 symmetry. We will return to this point below.

The spectra in Figure 4 show clear changes in both the frequencies and intensities of the fundamental modes as the temperature is increased. To put these spectra on the same scale and facilitate subsequent curve resolving, we adjusted the baselines of all spectra so that a minimum in the absorbance near 2050 cm^{-1} was set to zero. We also assumed that the baselines were almost (but not quite) flat in this region of the spectra, passing through a second minimum near 1150 cm^{-1} (see inset in Figure 1). No corrections for slope or possible curvature in this region of the spectrum were made. Close examination showed that this baseline indeed sloped slightly, such that the position of the baseline between 1690 and 1510 cm^{-1} was actually at −0.002 absorbance units, after adjustment. We will report curve-fitting results using a baseline fixed at this position, but we also repeated the procedure with the baseline fixed at 0 and −0.001, obtaining the same results, within error.

An aside is in order here. An examination of the spectra shown in Figure 4 might suggest that a good baseline could be drawn connecting points near 1635 and 1560 cm^{-1}. For ordinary quantitative analysis, where all that is necessary is to define a reproducible baseline and establish a calibration plot, this would be a good choice. Here, however, we are attempting to determine band shapes as accurately as possible, given the limitations of dealing with a sample such as polystyrene with numerous overlapping modes. Band shapes can be dramatically affected by a choice of baseline. The intensity of a Lorentzian (Cauchy) peak is about 1% of the peak height at a distance of 10 times the width at half-height from the frequency of maximum

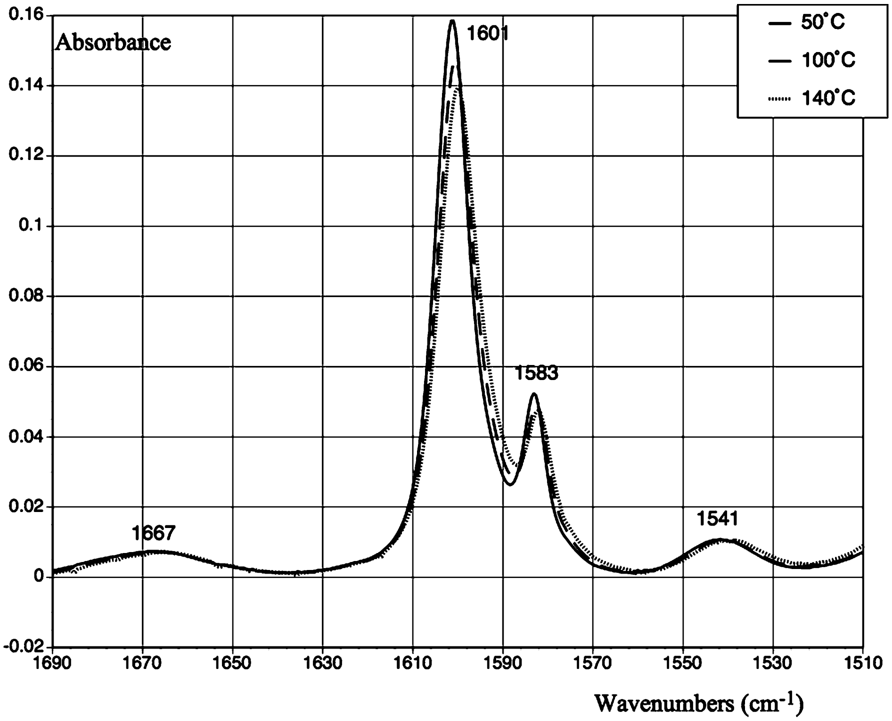

Figure 4. The 1600 cm^{-1} region of the infrared spectrum of atactic polystyrene at 50, 100, and 140 °C.

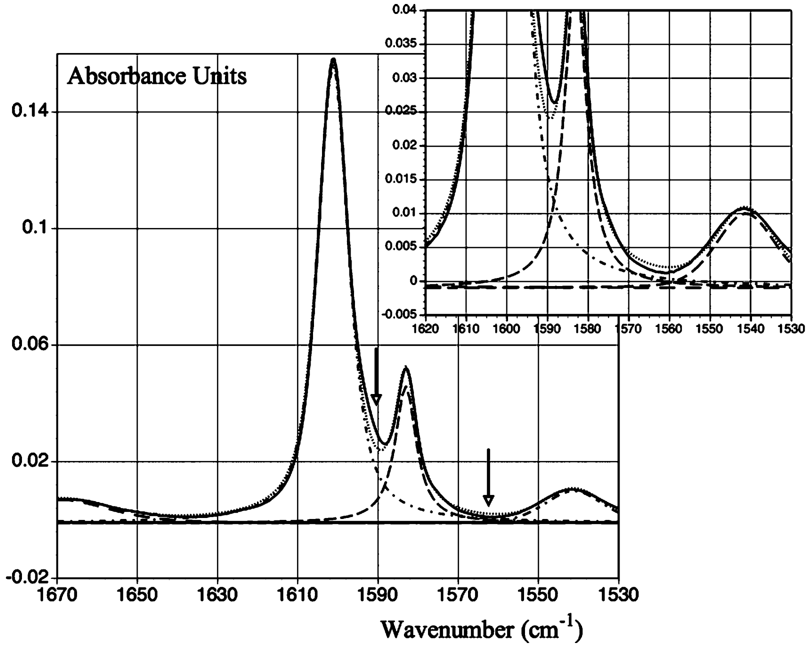

Figure 5. Initial results of curve resolving the 1600 cm^{-1} region of the infrared spectrum of atactic polystyrene held at 50 °C.

absorption. For the 1601 cm^{-1} band in the spectra reported here, this would be an absorption value of about 0.001 units 50 cm^{-1} from the peak position. Because of band overlap, we would therefore expect that the profile in this region of the spectrum would sit slightly above the true baseline. Defining a baseline locally (i.e., between 1635 and 1560 cm^{-1}) would force these bands to be somewhat more Gaussian, as the tails of the bands would be cut off. (This is why we chose a region free of bands to set the zero point when normalizing our spectra and why we changed the baseline by 0.001 units to check its effect on our curve fitting.) Fortunately, careful examination of the results of curve fitting can often reveal when this occurs, as the profile generated in the curve fitting process cannot match both the main portions of the band and its wings, so that small deviations in both become apparent.

This brings us to our curve fitting results. The 1600 cm^{-1} region of the spectrum obtained at 50 °C is shown in Figure 5. We initially attempted to fit the profile to the four obvious bands near 1601, 1583, 1667, and 1541 cm^{-1}. Arrows and the scale-expanded spectra (shown as an inset) demonstrate significant deviations between the original spectrum and the profile obtained by summing the curve-resolved bands. These deviations are not just at the positions indicated by the arrows, but at other positions in the spectrum. Essentially, by attempting to fit all frequencies as closely as possible, the curve-fitted profile is inevitably pulled away from the true spectrum at certain

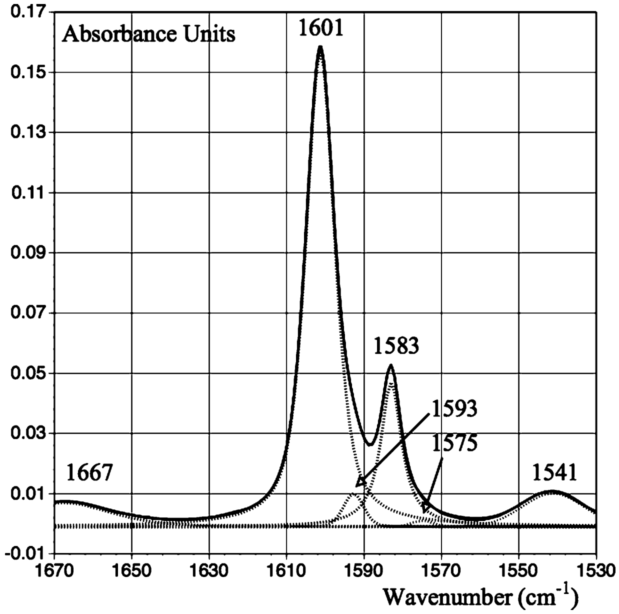

Figure 6. Results of curve resolving the 1600 cm^{-1} region of the infrared spectrum of atactic polystyrene held at 50 °C after including additional overtone/combination modes.

positions. We found it necessary to include two additional bands, near 1593 and 1577 cm^{-1}, in order to obtain a good fit, as shown in Figure 6. Of course, one can always obtain a better fit (in terms of least-squares deviations) by adding more bands (one reason we prefer to use knowledge and experience in making such judgments, as opposed to some arbitrary goodness-of-fit criteria), but the inclusion of such bands must make spectroscopic sense. First, we should be able to assign them to likely overtone or combination modes; second, if they can be assigned to such modes, we need to see clear evidence of their presence.

Given this limitation and assuming that the most likely candidates are also ring modes, there are several possibilities: a combination of the very strong A_1 Raman line near 1000 cm^{-1} with the 621 cm^{-1} B_1 band, resulting in a B_1 symmetry species combination; a combination of the two B_2 modes near 906 and 698 cm^{-1} (which would have A_1 symmetry); or a combination of the two A_1 modes near 558 and 1027 cm^{-1}. Because observed overtones and combination modes are usually observed at a lower frequency than the sum of the fundamentals, these last two assignments are the most likely origin of the 1592 and 1577 cm^{-1} modes, respectively. (If the former is in Fermi resonance with the fundamental observed near 1583 cm^{-1}, the 1583 cm^{-1} mode has presumably been pushed to a lower frequency by this interaction.)

The 1577 cm^{-1} mode is suspiciously weak, and in initial work curve fitting the spectra obtained at low temperature we were reluctant to include it. However, this band becomes discernible to the naked eye in the spectra obtained at higher temperatures. The (truncated) spectrum shown in Figure 7 was obtained at 120 °C, and the presence of an underlying weak band (indicated by the arrow) is now apparent. (It is interesting to note that in a critical review of the scope and limitations of curve fitting, published 25 years ago, Maddams[29] observed that the value of visual inspection in the detection and location of peaks in a profile should not be underestimated, as the eye and brain use a search routine which, in essence, is based on derivative functions!) Note that the intensities of the two weak modes near 1592 and 1577 cm^{-1} appear to have increased and their widths broadened. This is certainly true of the band near 1592 cm^{-1} (more on this shortly), but the 1577 cm^{-1} band does not change a lot as the temperature is raised. It is the decrease in the intensity of the fundamental near 1582 cm^{-1} and its shift to lower wavenumber that are more responsible for the enhanced prominence of this latter peak.

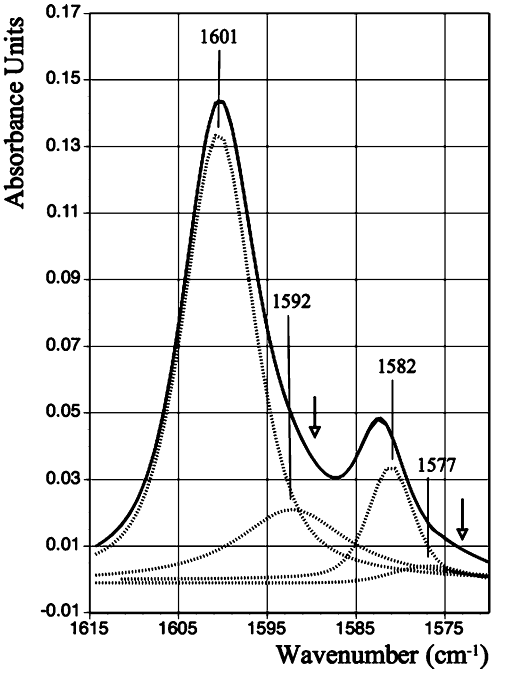

Figure 7. Results of curve resolving the 1600 cm^{-1} region of the infrared spectrum of atactic polystyrene held at 120 °C after including additional overtone/combination modes.

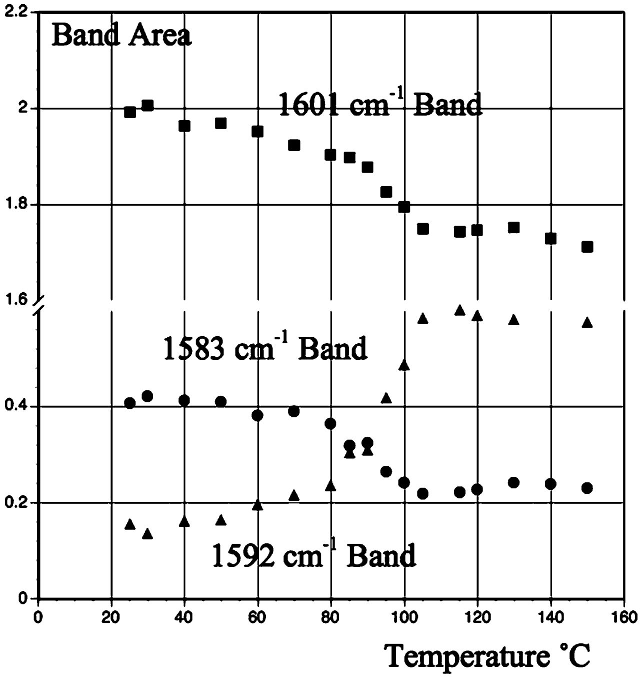

Figure 8. Plot of the band areas of the 1601 and 1583 cm^{-1} fundamental bands and the 1592 cm^{-1} combination mode as a function of temperature.

The areas of the bands near 1601, 1583, and 1592 cm^{-1} plotted as a function of temperature are shown in Figure 8. It can be seen that the fundamental modes (1601 and 1583 cm^{-1}) decrease in intensity as the temperature increases. In contrast, the area of the 1592 cm^{-1} band increases significantly. The change in the area of this band appears to be gradual at first and then increases at a faster rate in the temperature range of about 80−100 °C, before settling back at higher temperatures.

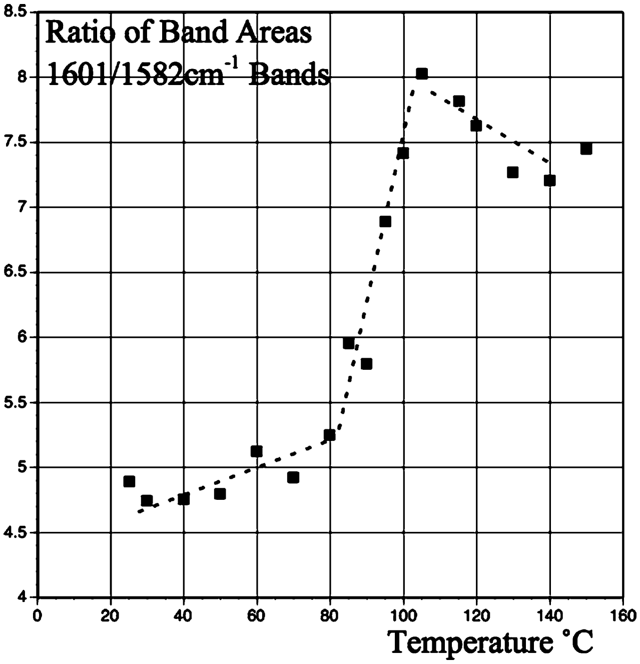

Figure 9. Plot of the ratio of the band areas of the 1601 and 1583 cm^{-1} bands as a function of temperature. The lines have been placed only as a guide to the eye.

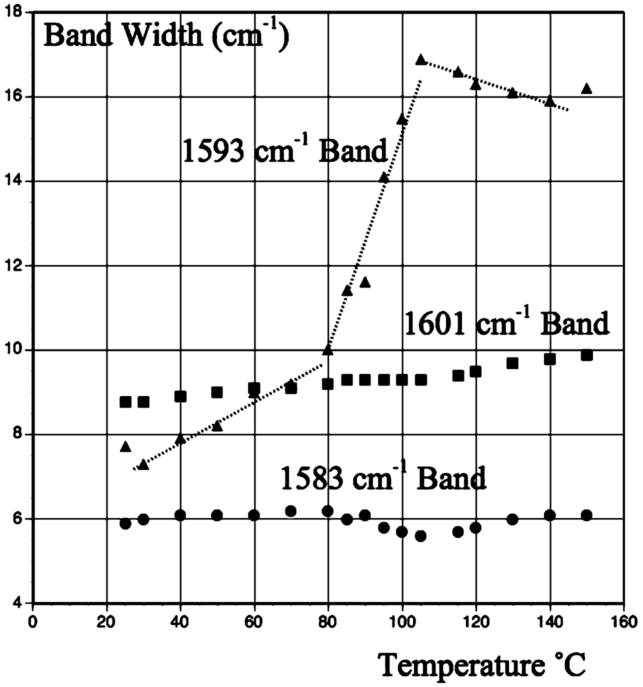

Figure 10. Plot of the (full) width of half-height of the 1601, 1583, and 1593 cm^{-1} bands as a function of temperature. The lines have been placed only as a guide to the eye.

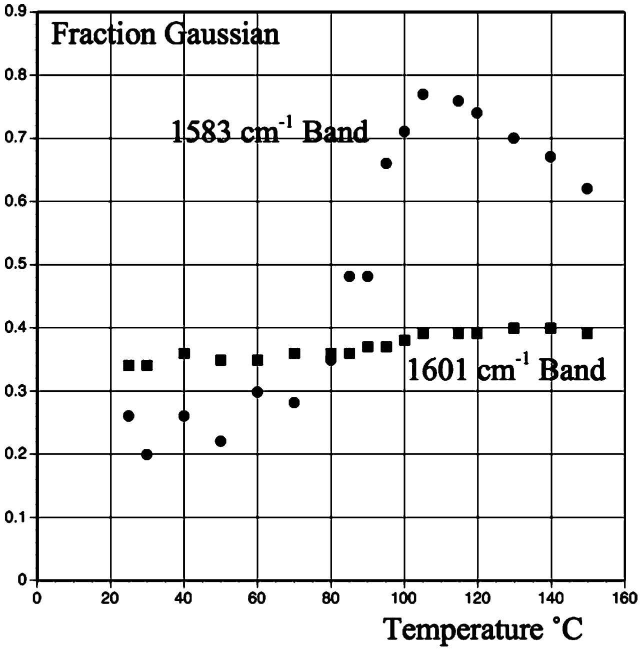

Figure 11. Plot of the shapes (fraction Gaussian) of the 1601 and 1583 cm^{-1} bands as a function of temperature.

If examined on a larger scale, the area of the 1601 cm^{-1} band appears to decrease in an essentially linear fashion with increasing temperature, while the 1583 cm^{-1} band appears to mirror the 1592 cm^{-1} combination mode, with the largest change occurring in the 80−100 °C temperature range. The greater rate of change in this temperature range is more clearly seen if the ratios of the band areas of the 1601 and 1583 cm^{-1} bands are examined, as shown in Figure 9. These results suggest that as the temperature is increased and the frequencies of the modes move to lower wavenumbers, there is an interaction between the 1583 and 1592 cm^{-1} modes, presumably as a result of Fermi resonance.

A plot of the width at half-height of the 1601, 1583, and 1592 cm^{-1} modes as a function of temperature is shown in Figure 10, while the band shape of the two fundamental modes are plotted in Figure 11. (The band near 1592 cm^{-1} stays essentially Lorentzian.) The half-width of the 1601 cm^{-1} band appears to increase gradually between temperatures of 25 and about 100 °C (near the thermally measured T_g) and then, perhaps, at a somewhat greater rate above this temperature. (We would need to have a better handle on errors to be sure of this.) The shape of this band becomes slightly more Gaussian as the temperature is raised. In contrast, the half-width of the band near 1582 cm^{-1} appears to remain essentially constant, but its band shape changes significantly with increasing temperature, becoming much more Gaussian. The change in band shape occurs most rapidly in the temperature range of about 80−110 °C. The bandwidth of the 1592 cm^{-1} absorption increases significantly with temperature, with the largest change also occurring in the 80 to 100 or 105 °C temperature range. These changes were reproducible and were also observed in melt-pressed (thicker) films.

At first sight, the changes in the band shape of the 1583 cm^{-1} mode appears to be counterintuitive. One would anticipate that frozen in the glassy state the dynamics of the system would approach what is called the slow modulation limit,[1−4] resulting in a Gaussian band profile that simply reflects the distribution of oscillator environments. Then, as the temperature is raised, motional narrowing and hence a more Lorentzian profile might be observed, as segmental motion within the polymer chain becomes more pronounced. However, the observations reported here are not unusual. In a study of the vibrational dynamics associated with glass formation in As_2O_3, Kirillov and Yannopoulos[11] determined that the profiles of certain Raman lines were more Gaussian in the liquid state than in the glass, with the line profile changing at temperatures below the T_g, as observed here. Rothschild and Cavagnat[6] note that this type of behavior is characteristic of modes where vibrational energy relaxation becomes important at the expense of vibrational dephasing, as the two have an opposite dependence on temperature. In this regard, we suggest that the band near 1592 cm^{-1}, which we have assigned to a combination mode, is crucial.

Energy transfer from fundamental to overtone or combination modes that are close in frequency is known to occur. Furthermore, if, for example, an overtone is separated from a fundamental by a few wavenumbers, a lattice or bath mode can "make up" the energy difference between the fundamental and the combination, ensuring a conservation of energy and providing a mode of relaxation. This would explain why the shape of the band near 1583 cm^{-1} is more sensitive to temperature than the band near 1602 cm^{-1}, even though both are within 10 cm^{-1} of the combination mode near 1592 cm^{-1}. The 1583 cm^{-1} band has A_1 symmetry and can therefore engage in Fermi resonance interactions with the combination mode (which must also have A_1 symmetry), while the 1602 cm^{-1} mode has B_1 symmetry and cannot engage in a similar interaction.

It is possible that the coupling of the two modes through lattice or bath vibrations becomes more pronounced as the latter become thermally excited. Certainly, the overtone near 1592 cm^{-1} becomes more intense at higher temperatures, with the largest changes occurring some 20 °C below the thermally measured T_g. It is thought that the α-relaxation process in glassy solids succeeds much faster picosecond scale motions and vibrational relaxation, as suggested by these results, would appear to be a sensitive indicator of the type of cooperative motions thought to be involved. In this regard, it would clearly be very useful to be able to extract time correlation functions from this type of data, together with the temperature dependence of the relaxation times. We will report the results of these calculations in a separate publication.

Conclusions

The shapes and widths at half-height of certain absorption bands in the infrared spectra of *a*-PS appear to be sensitive to temperature and the onset of the glass transition temperature. Great care must be taken in establishing baselines and accounting for weak overlapping modes in performing the analysis, however.

It is often assumed in polymer vibrational spectroscopy that the shapes and widths of infrared bands and Raman lines largely reflect the distribution of local environments. Indeed, as we will show in a subsequent paper, the second moment of the band is largely determined by the local distribution of states. However, there are additional subtle effects. If the only effect was the distribution of oscillator environments, one would expect that the 1601 and 1583 cm^{-1} bands observed in the spectrum of a-PS would be largely Gaussian and behave in a very similar manner, in that both are localized in-plane ring modes. Their band shapes are more complex, and they behave differently. The 1583 cm^{-1} ring mode appears to be far more sensetive to temperature, showing changes at about 20 °C below the thermally measured T_g. This is interpreted in terms of a coupling to low-frequency modes as a result of a Fermi resonance interaction with a close-lying combination mode.

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