Concerning the Determination of Conformational States in Polymers by Infrared Spectroscopy: A Study of Poly(methyl methacrylate)

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ABSTRACT: Changes in the infrared spectra of poly(methyl methacrylate) as a function of temperature have been examined. The results presented here, together with a consideration of normal coordinate calculations reported in the literature, suggest that previous assignments of bands in the 1300−1050 cm^{-1} region of the spectrum to specific conformations of the ester pendant group are incorrect. Certain bands in this and other regions of the spectrum are nevertheless very sensitive to temperature. It is proposed that this sensitivity is a function of both conformational effects and vibrational relaxation effects. The latter are usually neglected in vibrational spectroscopic studies of polymers, and it is proposed that more attention be paid to changes in band shapes when considering changes in the spectra of polymers as a function of temperature.

Introduction

Infrared spectroscopy has been an important tool in studies of polymer conformation. In some systems it has been possible to assign modes to specific local arrangements of groups (e.g., trans and gauche). In other polymers band assignments are not as certain, although there is often a clear sensitivity to temperature, as revealed by changes in the relative intensities of bands known to be associated with backbone or flexible side-chain modes. In this paper, we will argue that there are additional factors related to vibrational relaxation that are often ignored in the polymer literature. Although these complicate matters considerably, they also offer the potential for insight into very fast relaxation phenomena on the picosecond time scale.

We will consider in some detail the spectra of syndiotactic and atactic poly(methyl methacrylate) (*s*-PMMA and *a*-PMMA), as these are classic examples of polymers where there is apparently a clear degree of sensitivity to local conformation but a large degree of uncertainty concerning band assignments. Modes appearing between 1300 and 1050 cm^{-1} appear to be particularly sensitive to tacticity and conformation and have been widely studied.[1–12] Unfortunately, the intensity changes that have been observed in this region of the spectrum have been interpreted in different ways. In early work, for example, Havriliak and Roman[2] sought to understand why simple molecules like methyl acetate have just one (intense) band in this region of the spectrum, assigned to the C−O ester stretching mode, while PMMA has a number of bands. They concluded that these modes were most likely due to "discrete side-chain arrangements with respect to one another or to the polymer backbone". In subsequent work, Dybal et al.,[6] referring to a publication in a Czech journal, noted that IR spectra of the crystalline form of a model ester, which only has a single conformer present, also display a multiplicity of bands in this range. They concluded that several bands correspond to ester group vibrations of a single conformational form. This suggests that these modes are delocalized. Later, O'Reilly and Mosher[4] argued that spectroscopic changes could be related to the energy difference between combined backbone and side-chain conformational states. Their methodology relied upon the use of difference spectra and was cast into considerable doubt by Dybal et al.,[6] who interpreted changes in this region of the spectrum largely in terms of conformations of the side-chain ester group. Following a hiatus of some 15 years, Grohens et al.[8] revisited the temperature dependence of the infrared spectra of PMMA polymers and measured the peak heights of bands they labeled ν_1, found between 1260 and 1275 cm^{-1} (depending on the tacticity of the sample), and ν_2, which appears near 1240 cm^{-1}. They interpreted their results in terms of the ratio of backbone conformational energy to the overall energy of the chain segment (i.e., backbone plus side chain). More recently, Tretinnikov and Ohta[11] applied a curve-fitting methodology to the analysis of spectroscopic changes as a function of temperature. They proposed that the ν_1 and ν_2 modes, identified above, could be unambiguously assigned to C−C−O vibrations of the pendant ester group, associating each band of the pair with a specific rotational-isomeric state. In one state the C=O bond is cis to the C−CH$_3$ group, while in the other state it is trans. A pair of bands labeled ν_3 and ν_4 (observed near 1194 cm^{-1} and in the range 1175−1164 cm^{-1}, respectively) were also assigned to specific conformations, in this case to C−O–C vibrations, with each band being assigned to a particular rotational-isomeric state of the methoxy group.

Early work in this area was limited by a lack of detailed knowledge of the nature of the normal modes of PMMA. Assignments were based largely on group frequencies and studies of low-molecular-weight model compounds. This approach is useful when vibrational modes are localized and can be assigned to specific chemical groups, but bands in this region of the spectrum of polymers are usually highly coupled or mixed and delocalized down the chain. Such coupling and mixing of modes can be revealed by normal-mode calculations. Dybal and Krimm[13,14] performed a vibrational analysis of isotactic PMMA, while the normal modes of syndiotactic PMMA have been calculated by Dybal[15] and more recently by Jain et al.[16] These calculations show that the normal modes between 1300 and 1000 cm^{-1} are indeed highly mixed and delocalized, as one would intuitively expect. Accordingly, in this paper we will examine this region of the spectrum in some detail and attempt to put band assignments on more solid ground. More generally, we will argue that intensity and band-shape changes observed as a function of temperature are probably related not only to conformational energy differences but also to vibrational

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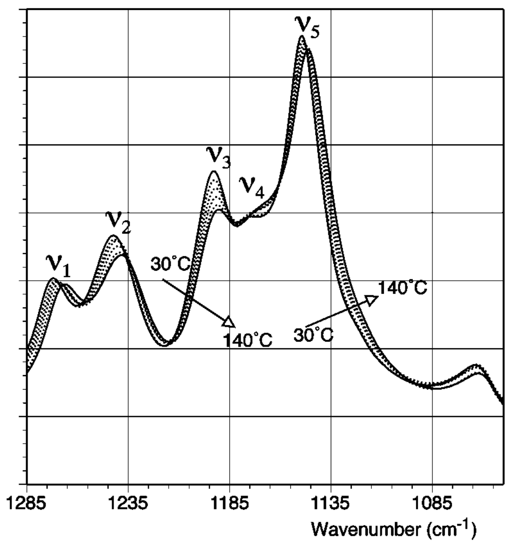


Figure 1. Plot of the infrared spectra of *s*-PMMA between 1285 and 1050 cm^{-1} obtained at various temperatures between 30 and 140 °C.

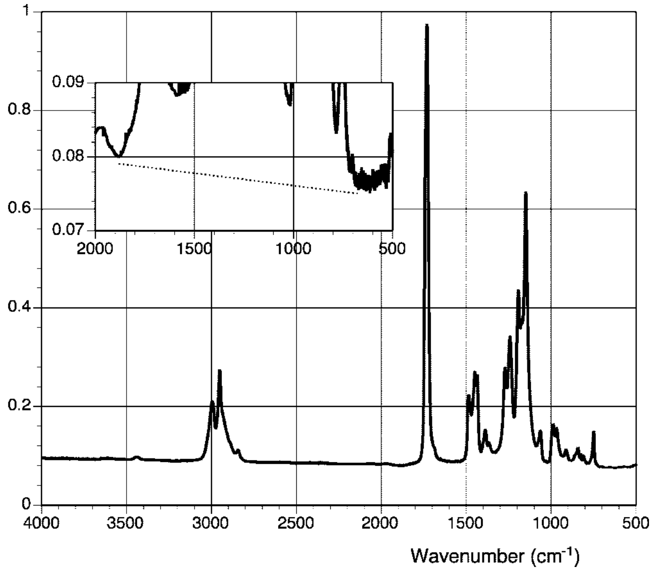


Figure 2. Plot of the infrared spectra of *s*-PMMA obtained at 30 °C. The inset shows the scale expanded region used to define the baseline.

relaxation effects. As mentioned above, until recently these have been largely neglected in studies of the infrared and Raman spectra of polymers.

Experimental Section

Atactic and syndiotactic PMMA samples were purchased from Scientific Polymer Products. Deuterated methyl methacrylate monomers were obtained from Polymer Source, Inc., and atactic polymers were synthesized at room temperature via bulk polymerization using azobis(isobutyronitrile) (AIBN) as the initiator.

Solutions were prepared by dissolving appropriate amounts of the polymer in THF to yield 4% (w/v) solutions. Thin films were obtained by casting these 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 a temperature of 130 °C to remove residual solvent. Infrared spectra were obtained on a Digilab FTS-60 Fourier transform infrared (FTIR) spectrometer using a minimum of 64 coadded scans at a resolution of 2 cm^{-1}. All films were sufficiently thin to be within the absorbance range where the Beer–Lambert law is obeyed.

Results and Discussion

It is useful to start by considering the spectrum of *s*-PMMA as a function of temperature. Figure 1 shows selected spectra obtained at temperatures between 30 and 140 °C in the region between 1285 and 1050 cm^{-1}. We have labeled the bands that are of most interest in this study υ_1 through υ_5, following previous authors.[8,11] It can be seen that the peak height of the band near 1271 cm^{-1} (υ_1) appears to change only slightly with increasing temperature (although its frequency shifts to lower wavenumbers), while the bands near 1241 cm^{-1} (υ_2), 1193 cm^{-1} (υ_3), and 1148 cm^{-1} (υ_5) all decrease noticeably in intensity. Although peak heights decrease, overall intensity as measured by band area can increase. Two important factors in measuring intensity changes as a function of temperature are changes in the shapes and half-widths of the bands. However, unless a band of interest is in an isolated region of the spectrum, such changes are difficult to observe directly because of overlap with other modes. One has to rely on curve-resolving, which unless done carefully can lead to erroneous conclusions. We will therefore describe the steps we went through in some detail, so others can reproduce our results or use our methodology, if they have a mind to.

Curve-Resolving the Spectra. The first and one of the most crucial steps in curve-resolving is setting the baseline. The procedure we employ involves an initial examination of a broad region of the spectrum to identify where a baseline can be placed, as shown in Figure 2 for the spectrum of *s*-PMMA. Several factors affect the baseline, one of the most crucial being the preparation of films of even thickness. Scattering and reflections in uneven films can lead to a curvature and a sloping baseline. Although most modern instruments have automatic baseline correction routines, we consider these to be dangerous, as they often adjust all or chosen minima in the spectra to an assumed zero absorbance value. This often 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.

The spectrum shown in Figure 2 appears to have an essentially linear but slightly sloping baseline, which could be defined at positions near 3300, 2400, 1900, and 600 cm^{-1}. For reproducibility, we chose to define a baseline using minima near 1900 and 600 cm^{-1}, as illustrated on an inset in Figure 2. Note that we did not place the baseline directly on the minimum in the spectrum, but at a position 0.001 absorbance units below this. 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 absorption. The tails of such bands are superimposed on the true baseline in regions of the spectrum with large numbers of overlapping bands. To check whether this procedure gave satisfactory and reproducible results, the baseline is then changed in steps of ±0.001 units and the curve-resolving is repeated.

Having fixed the position of the baseline, the region of the spectrum between 1285 and 1080 cm^{-1} 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 can be 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 (first and second terms on the right-hand side of eq 1) that combine to make up the overall

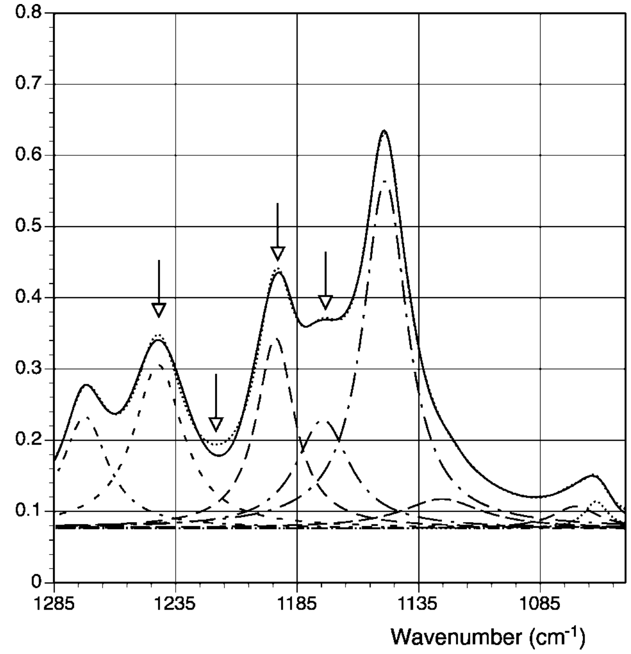


Figure 3. Plot of the infrared spectra of *s*-PMMA between 1285 and 1050 cm^{-1} obtained at 94 °C together with the results of curve fitting to Lorentzian bands. The dotted line is the result of adding the contributions, and the arrows highlight regions where there are deviations from the observed spectrum (solid line).

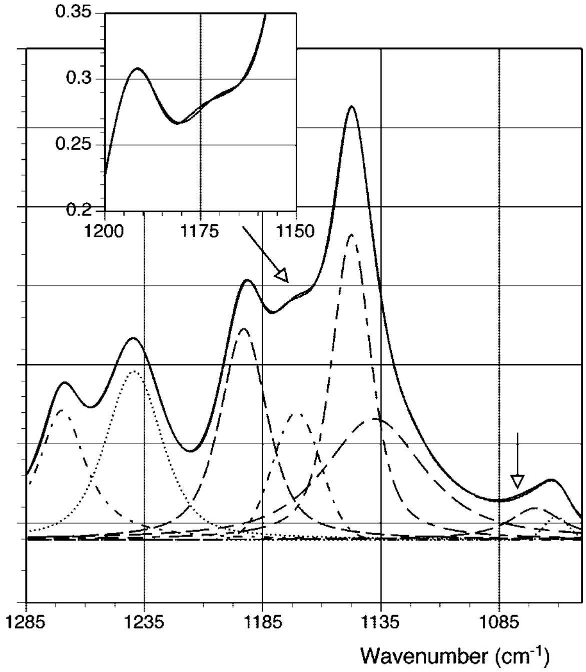


Figure 4. Plot of the infrared spectra of *s*-PMMA between 1285 and 1050 cm^{-1} obtained at 94 °C together with the results of curve fitting to a band shape that is a sum of Gaussian and Lorentzian contributions. The arrows and the inset highlight regions where there are deviations from the observed spectrum.

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 υ are the frequencies of the points that describe the bands. Liu et al.[17] have shown that this particular sum function is actually an excellent approximation to a true Voigt profile.

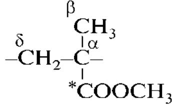
We chose to truncate the curve resolving at 1285 cm^{-1} on the high wavenumber side of this region. This is to prevent any contribution from the tails of the modes between 1350 and 1500 cm^{-1} from interfering with the results. Initially, we attempted to fit the spectral profile to pure Lorentzian bands (by setting $f = 0$ in eq 1) following previous work reported in the literature.[11] Eight bands were chosen, the modes υ_1 through υ_5 identified in previous work, together with weaker bands near 1128, 1070, and 1066 cm^{-1} whose presence is clearly evident to the naked eye. The results are shown in Figure 3 (for the spectrum obtained at 94 °C), which demonstrates that this assumption does not give a good fit, as deviations between the original spectrum and that obtained by adding the contributions of the resolved bands are clearly evident.

This is not surprising for polymers that are glassy in nature, such as *s*-PMMA and *a*-PMMA. If one assumes a damped harmonic oscillator approximates each normal mode, one would anticipate a Lorentzian band shape. However, there is a distribution of local environments and conformations in these materials, and as a result, there is no longer a single transition energy, but a band. The absorption due to a particular normal mode then reflects a superposition of the frequencies of the individual oscillators, often resulting in a Gaussian profile. The situation is complicated by relaxation processes, however, as we will discuss in more detail below. If relaxation processes are fast, all the molecules (or chain segments in this case) can appear to be the same or very similar to the radiation field, so that a narrower, Lorentzian profile could still be observed. Often, infrared bands are a convolution of Gaussian and Lorentzian shapes, and a fit to a Voigt function or a very close approximation (eq 1) is most appropriate.

We then attempted to fit the bands to eq 1, allowing the fraction Gaussian factor, f, to vary for each band. A much better fit was obtained, as can be seen in Figure 4, but there were still some deviations from the curve-fitted profile, as indicated by the inset and arrow on this figure. Changing the position of the baseline did not improve matters.

We came to the conclusion that instead of a single broad band, υ_4, near 1174 cm^{-1}, there are actually two bands, which we could label υ_{4a} and υ_{4b}. Of course, one can always get a better fit in curve resolving by adding bands. The presence of such bands has to be justified on other grounds. In this case, υ_4 is essentially a shoulder between much stronger bands, and techniques such as taking the second derivative are no help. However, there are two reasons to believe that there are two bands here. First, the normal coordinate calculations of Dybal[15] and Jain et al.[16] indicate that an additional band is present in this region of the spectrum. The calculated frequencies and the potential energy distribution of modes found between 1300 and 1050 cm^{-1} determined by these authors are summarized in Tables 1 and 2. Second, a close examination of the spectra shown in Figure 1 indicates that there are significant changes in the mode or modes labeled υ_4 with increasing temperature. We therefore attempted to reveal these changes using spectral subtraction. Because the frequencies of the bands in this region of the spectra shift as a function of temperature, it was necessary to choose spectra that were obtained at temperatures that were not too far apart; otherwise, significant distortions in the difference spectra would result. Figure 5 shows two difference spectra obtained by subtracting the spectrum obtained at 120 °C from that obtained at 140 °C using slightly different degrees of subtraction. The criterion for subtraction was the reduction of the contributions of the υ_3 and υ_5 modes near 1191 and 1147 cm^{-1} to the point that the mode or modes near 1170 cm^{-1} are revealed. The difference spectra indicate that there are indeed two modes here, near 1180 and 1163 cm^{-1}. Including these two modes (υ_{4a} and υ_{4b}) in subsequent curve-resolving then resulted in an excellent fit to the spectra, as shown in Figure 6. (The calculated profile superimposes almost exactly on the experimental profile.)

Table 1. Results of a Normal Coordinate Analysis by Dybal[15]


$$-\overset{\delta}{C}H_2-\overset{\overset{\beta}{C}H_3\,|\,\alpha}{C}-\underset{|\,{}^{*}COOCH_3}{}$$

	calculated normal modes (in-phase)	calculated normal modes (π out-of-phase)
1273	*1271*: $C^{\alpha}{-}C^{*}s$ (38%); $C^{*}{-}Os$ (15%)	*1282*: $C^{\alpha}{-}C^{\delta}s$ (34%); $C^{\alpha}{-}C^{\beta}s$ (14%)
1242	*1282*: $C^{\alpha}{-}C^{\delta}s$ (42%); $C^{\alpha}{-}C^{\beta}s$ (21%)	
1193	*1191*: $C^{\alpha}{-}C^{\delta}Hb$ (98%)	*1183*: $C^{*}{-}Os$ (29%); $C^{\alpha}{-}C^{\delta}Hb$ (23%); $O{-}Cs$ (17%)
1177	*1181*: $C^{*}{-}Os$ (34%); $C^{\alpha}{-}C^{\delta}Hb$(12%); $O{-}Cs$ (21%)	
1169	*1156*: $C^{\alpha}{-}C^{\delta}Hb$ (43%); $C^{\alpha}{-}C^{\delta}s$ (24%); $C^{\alpha}{-}C^{\beta}Hb$ (15%)	*1167*: $C^{\alpha}{-}C^{\delta}Hb$ (32%); $C^{\alpha}{-}C^{\delta}s$ (25%); $C^{\alpha}{-}C^{\beta}Hb$ (15%)
1149	*1156*: $O{-}Cs$ (44%); $C^{*}{-}Os$ (29%)	
1127	*1118*: $O{-}C{-}Hb$ (30%); $O{-}Cs$ (20%); $C{-}O{-}C^{*}b$ (12%)	*1122*: $O{-}Cs$ (28%); $C^{\alpha}{-}C^{\delta}Hb$ (23%); $O{-}C{-}Hb$ (30%)
1071		*1087*: $O{-}C{-}Hb$ (46%); $C^{\alpha}{-}C^{\delta}Hb$ (12%)
1062	*1068*: $O{-}C{-}Hb$ (34%); $C^{\alpha}{-}C^{\delta}Hb$ (16%); $O{-}Cs$ (12%); $C^{\alpha}{-}C^{*}s$ (10%)	

Table 2. Results of a Normal Coordinate Analysis by Jain et al.[16]

observed IR bands (cm^{-1})	calculated frequencies (cm^{-1})	calculated normal modes
1273	1282 (A_1)	$C^{\alpha}{-}C^{\beta}s$ (14%); $C^{*}{-}Os$ (17%); $C{=}Ob$(14%); $C^{\alpha}{-}C^{\delta}Hb$(23%); $C^{\alpha}{-}C^{*}s$ (11%)
1242	1228 (B_2)	$C^{\alpha}{-}C^{\delta}s$ (40%); $C^{\alpha}{-}C^{\beta}Hb$ (13%); $C^{\alpha}{-}C^{\delta\ \alpha}b$ (10%)
1193	1194 (A_2), 1192 (B_2)	$C^{\alpha}{-}C^{\delta}Hb$ (98%) $O{-}C{-}Hb$ (32%); $O{-}Cs$ (19%)
1177	1182 (A_1)	$O{-}C{-}Hb$ (50%); $O{-}Cs$ (14%); $C{=}Ob$ (14%)
1169	1178 (B_1)	$C^{\alpha}{-}C^{\beta}Hb$ (32%); $C^{\alpha}{-}C^{\delta}Hb$(21%); $C^{\alpha}{-}C^{\delta}s$ (17%)
1149	1156 (B_2)	$C^{\alpha}{-}C^{\delta}s$ (29%); $C^{*}{-}Os$ (18%); $O{-}Cs$ (18%); $C^{\alpha}{-}C^{\beta}Hb$ (14%)
1127	1128 (A_2, B_1)	$O{-}C{-}Hb$ (82%); $O{-}C{-}Hb$ (16%)
1071	1047 (A_1)	$O{-}Cs$ (65%); $O{-}C{-}Hb$ (16%)
1062	1036 (B_2)	$O{-}Cs$ (76%); $O{-}C{-}Hb$ (10%)

On the basis of an assignment of the υ_1 and υ_2 modes to trans and cis arrangements of the C=O bond is relative to the $C{-}^{\alpha}CH_3$ group, Tretinnikov and Ohta[11] constructed a van't Hoff plot of the logarithm of the ratios of the areas of these bands against 1/*T*. A similar plot of our data is shown in Figure 7. Because of the difference in curve-resolving methodology, our results are different, in that we see a decrease rather than an increase in the ratio of band areas as temperature is increased, with a clear break in the curve at a temperature close to the T_g (~120 °C). If the band areas are considered separately, as shown in Figure 8, it can be seen that the intensity of the υ_1 mode, near 1273 cm^{-1} at room temperature, changes only slightly with temperature, while the υ_2 mode appears to increase significantly. Also shown on this plot are data obtained from a study of *a*-PMMA, showing a similar trend. Each plot shows a change in slope near the T_g of each polymer, about 100 °C for *a*-PMMA and 120 °C for *s*-PMMA. If these bands were due to different conformations of the side-chain ester group, one of them would be expected to increase in intensity in proportion to a decrease in intensity of the other (with a constant of proportionality that would depend on any difference in absorption coefficients). The band area of υ_1 mode changes very little with temperature, however. We will address band assignments in more detail later.

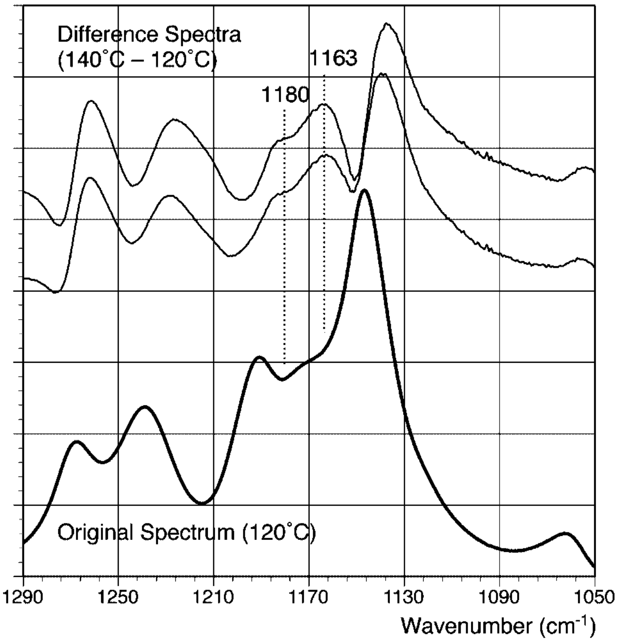


Figure 5. Plot of the infrared spectra of *s*-PMMA between 1290 and 1050 cm^{-1} obtained at 120 °C together with the results of subtracting this spectrum from that obtained at 140 °C.

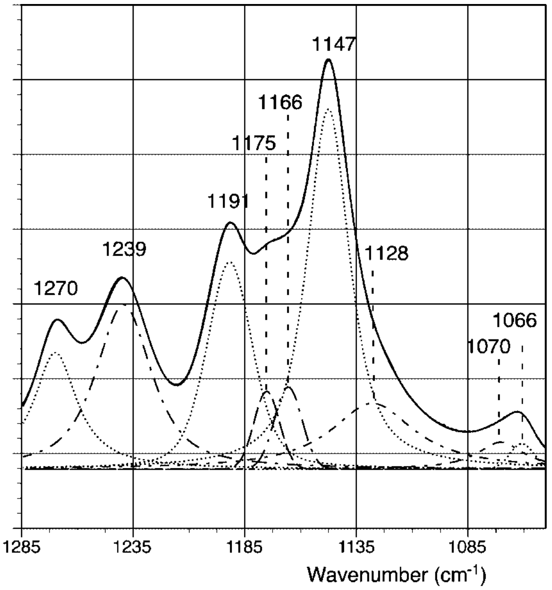


Figure 6. Plot of the infrared spectra of *s*-PMMA between 1285 and 1050 cm^{-1} obtained at 94 °C together with the results of curve fitting to Lorentzian bands. The sum of the curve fitted bands superimpose upon the original spectrum.

The peak height of the υ_2 mode decreases with increasing temperature (see Figure 1). The calculated increase in band area is a consequence of a change in bandwidth and shape. Figure 9 shows a plot of the full width at half-height of modes υ_1 and υ_2, while the calculated fraction Gaussian of each curve is shown in Figure 10. The υ_1 mode is essentially Lorentzian ($f = 0$ in eq 1), while the υ_2 band changes from about 50% Gaussian to essentially Lorentzian at high temperatures. Also shown in this plot are the band shapes determined for the υ_3 and υ_5 modes, near 1193 and 1149 cm^{-1} at room temperature, respectively. Both become more Gaussian as the temperature increases.

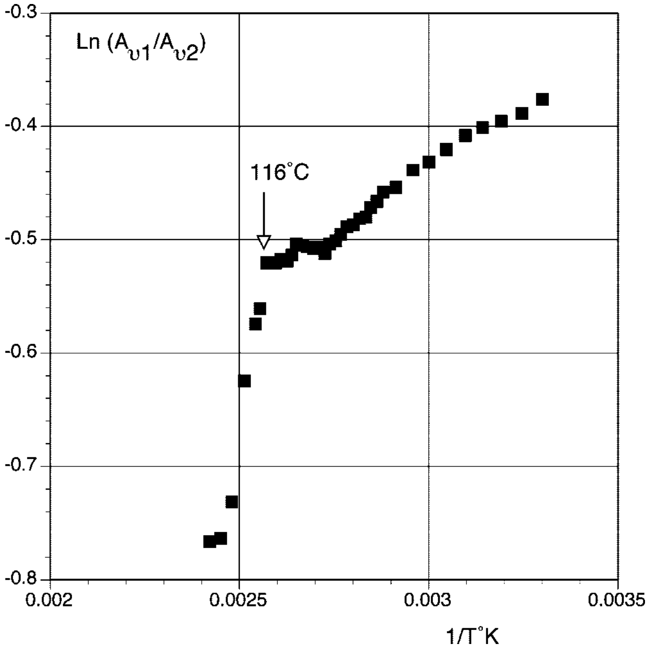


Figure 7. Plot of logarithm of the ratio of the intensities of the υ_1 and υ_2 modes of *s*-PMMA plotted against the inverse of the temperature.

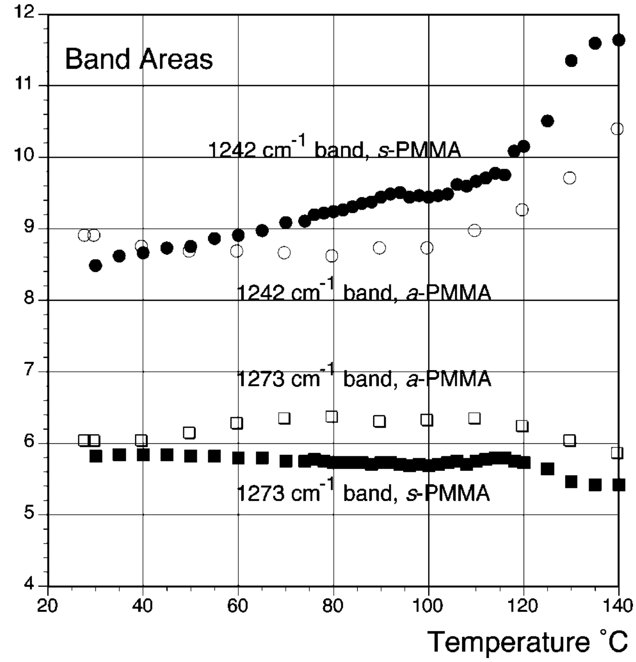


Figure 8. Plot of band areas of the υ_1 and υ_2 modes of *s*-PMMA and *a*-PMMA plotted as a function of temperature.

Because the modes we labeled υ_{4a} and υ_{4b} are relatively weak and defined by only a few data points between the much stronger υ_3 and υ_5 modes, we have less confidence in the parameters that define them and so will not try to draw any conclusions from their values. Corresponding changes in band shape were observed in *a*-PMMA, as shown in Figure 11. There is a change in the slope of each curve occurring near the respective T_g of each polymer.

Deuterated PMMA Samples and Band Assignments. We now turn to band assignments. In the spectra of simple, low-molecular-weight esters such as methyl acetate, there is an intense band that can be assigned to the C—O stretching mode.[18] The normal mode calculations of Dybal[15] and Jain et al.[16] indicate that there is not a single mode that can be assigned to a C—O stretch, but instead all the bands in this region of the spectrum are highly mixed and coupled, with contributions from various C—C stretching and C—C—H bending vibrations. The highly mixed nature of these modes is confirmed by an examination of the spectra of various deuterated *a*-PMMA samples, shown in Figure 12. First, if just the methyl group attached to the ester is deuterated, modes υ_1 and υ_2 are only slightly affected (small frequency shifts), but modes υ_3–υ_5 between 1200 and 1100 cm^{-1} are affected significantly,

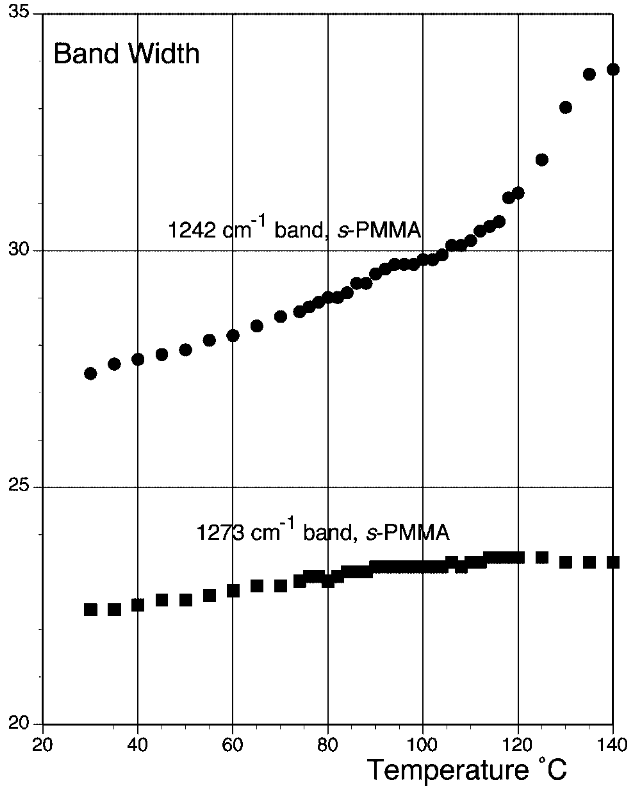


Figure 9. Plot of the bandwidths of the υ_1 and υ_2 modes (near 1273 and 1242 cm^{-1} at room temperature) of *s*-PMMA plotted as a function of temperature.

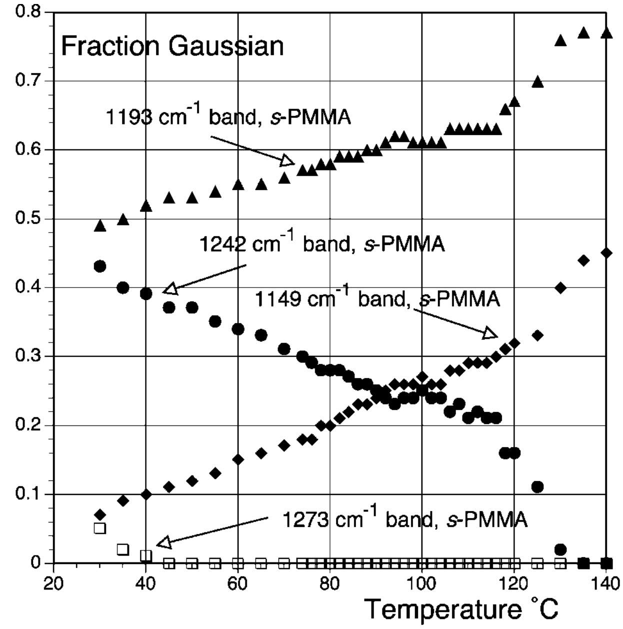


Figure 10. Plot of the fraction Gaussian component of the principal modes of *s*-PMMA between 1285 and 1050 cm^{-1} plotted as a function of temperature.

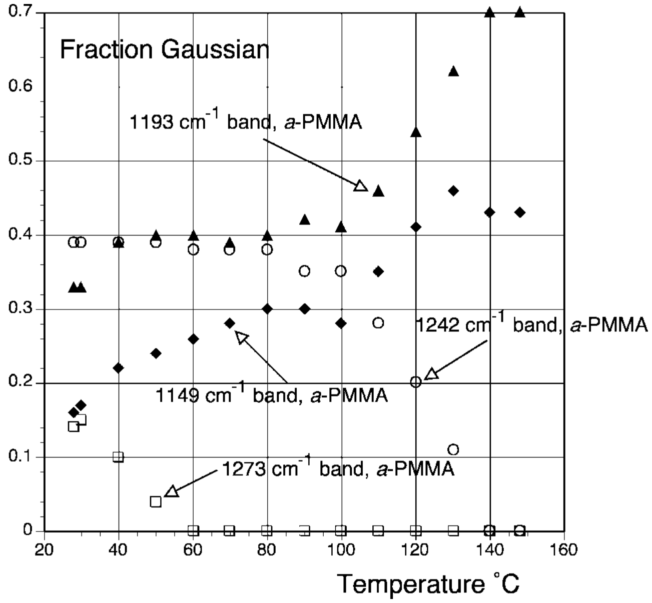


Figure 11. Plot of the fraction Gaussian component of the principal modes of *a*-PMMA between 1285 and 1050 cm^{-1} plotted as a function of temperature.

demonstrating that there is a large contribution from vibrations of this methyl group to these bands. Furthermore, if the main chain CH_2 group and C$-$$CH_3$ groups are replaced with their deuterated counterparts (top two spectra in Figure 12), then the spectra change significantly, with a relatively intense band near 1270 cm^{-1} now dominating this part of the spectrum. Clearly, the modes in this region of the spectrum of nondeuterated *a*-PMMA are highly mixed and/or coupled to various C$-$C, CH_2, and CH_3 vibrations. The spectrum of *s*-PMMA is very similar to *a*-PMMA, and it is likely that the form of the normal modes in the two polymers is similar, particularly as they demonstrate corresponding changes in band shape and intensity as a function of temperature.

On the basis of these observations and normal-mode analysis, it would seem likely that all of the bands in this region of the spectrum can be assigned to individual, highly mixed normal modes of vibration, as opposed to assigning pairs of bands to different conformations of the ester group. This conclusion is also supported by the spectra of the fully deuterated PMMA, where a single band between 1300 and 1220 cm^{-1} is now observed. Methyl acetate and its deuterated derivatives have strong bands in range 1240$-$1280 cm^{-1} assigned to (predominantly) the C$-$O stretch,[14,18] and it would seem likely that in the fully deuterated polymer the band near 1264 cm^{-1} has a large contribution from this vibration. There is but a single band, however, with no evidence that there is a contribution from different conformations. This is not to say that this region of the spectrum is insensitive to conformation. Certainly, the fact that the modes are highly coupled to various C$-$C stretching and C$-$C$-$H bending vibrations would suggest otherwise. It would seem that this sensitivity is revealed in more subtle ways, however, and changes may also be linked to modes of vibrational relaxation.

Band Shapes and Vibrational Relaxation Processes. There are various effects that lead to changes in infrared band intensities with increasing temperature. These include changes in the Boltzmann factors and density of the sample (hence refractive index), but these factors usually result in only small perturbations that can be neglected.[19] In the spectra of polymers, changes in conformation can also lead to significant intensity changes, but as noted above, it does not appear that bands observed in the region of the spectrum considered in this study can be related to specific conformational states, although the observed intensity changes could well be a result of a change in the distribution of conformations. However, there are other factors that should be taken into account.

It is well-known that Raman and infrared bandwidths and shapes are sensitive to vibrational relaxation processes and picosecond dynamics (see refs 20–36 and citations therein). Although there is a rich literature concerned with studies of small molecules, the band shape of polymers has been a largely neglected area.[37–39] In the vibrational spectra of amorphous

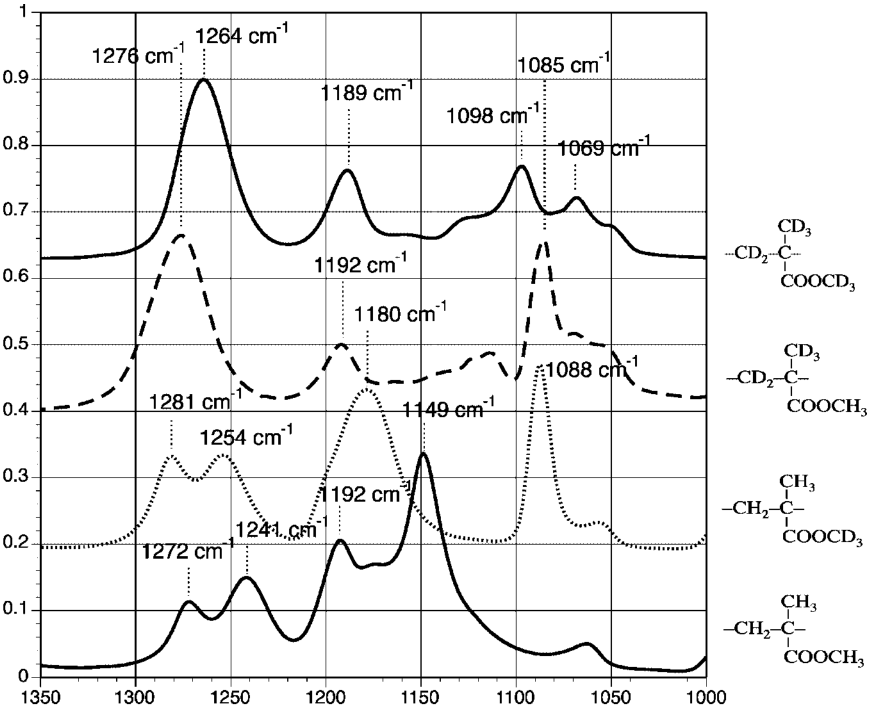


Figure 12. Plot of the infrared spectra of *a*-PMMA and various deuterated samples between 1350 and 1000 cm^{-1}.

polymers, even modes that are insensitive to conformation are broad relative to low-molecular-weight liquids and display changes in intensity and shape as a function of temperature. This is usually considered a consequence of what is called inhomogeneous broadening. In the disordered state, there is a distribution of local environments, and as a result, there is no longer a single transition energy, but a band. Each individual oscillator may relax by some mechanism (e.g., vibrational dephasing or energy relaxation), but the band due to a particular normal mode would then reflect a superposition of the frequencies of the individual oscillators. The term "inhomogeneous broadening" has been used in a number of contexts, however, and it is meaning is related to the speed of relaxation. In what is termed pure phase relaxation, even if the normal modes on each molecule in a system are excited simultaneously, because they have slightly different frequencies (as a result of interactions and small differences in local environments), they get out of phase with one another as time progresses, resulting in destructive interference. The shape and breadth of a band then depend on how fast this happens. If dephasing is fast, the effects of local differences in environment are averaged out by the rapid "loss of memory". If it is assumed that a single, fast process governs relaxation, then the resulting band shape will be Lorentzian, and the relaxation time will be inversely proportional to the bandwidth. In low-molecular-weight liquids, for example, local interactions fluctuate rapidly as a result of the translational and rotational motion of the molecules. All the molecules then appear to be the same or very similar to the radiation field, so that a motional narrowing of the inhomogeneously broadened band is observed. On the other hand, if "modulation" is slow, the observed band shape will be Gaussian and simply reflect the static and dynamic effects of a distribution of local environments. Often, intermediate band shapes are observed because the relaxation time of the dominant process is somewhere between these extremes or because the spectrum reflects more than one relaxation mechanism (e.g., dephasing and vibrational energy relaxation, resonance energy transfer between chain dipoles), with slow processes superimposed upon fast ones.

Conformational Sensitivity. If one examines the potential energy distributions reproduced in Tables 1 and 2, it would appear that the interpretation of Grohens et al.[8] that intensity changes observed in modes υ_1 and υ_2 are related to the ratio of backbone conformational energy to the overall energy of the chain segment (i.e., backbone plus side chain) appears to be reasonable. The change in band shape of the υ_2 band near 1242 cm^{-1} is intriguing, however, and cannot be interpreted simply in terms of conformational changes. If the modes in this region of the spectrum are highly mixed, as the evidence presented here suggests, all should be sensitive (in varying degrees) to backbone or side-chain conformations, local environment, or some combination of these. A broader distribution of conformations and environments would be expected as the temperature is raised, resulting in a more Gaussian band shape. In addition, there is now considerable evidence that glassy systems are dynamically heterogeneous,[40–44] and additional inhomogeneous broadening could occur as a result of slow transitions between domains of different mobility as the temperature of the sample is raised. Modes υ_3 and υ_5 (near 1193 and 1149 cm^{-1} at room temperature) indeed become more Gaussian as the temperature is raised, and it is possible that both conformational and relaxation related factors are contributing to these changes. The 1242 cm^{-1} mode becomes Lorentzian at high temperatures, however, while the υ_1 band near 1272 cm^{-1} is essentially Lorentzian at all temperatures. This would suggest that vibrational relaxation, through either dephasing or vibrational energy transfer, occurs rapidly at all temperatures for the latter mode. The υ_2 (1242 cm^{-1}) mode only approaches this "fast modulation" regime at higher temperatures, however. For Lorentzian bands, the bandwidth is inversely proportional to the relaxation rate. The significant increase in the width of this band (υ_2) with increasing temperature and its increasing Lorentzian band shape suggests that a fast relaxation process plays a more prominent role in the change in intensity of this band as a function of temperature, either because this mode is able to transfer vibrational energy more rapidly to lower frequency vibrations or because there is a degree of motional narrowing (or some combination of these mechanisms).

Conclusions

Band assignments in the 1300−1000 cm^{-1} region of the infrared spectra of *s*-PMMA and *a*-PMMA have been examined. The results obtained from deuterated and partially deuterated samples, together with a consideration of normal coordinate calculations reported in the literature, suggest that previous assignments of bands in the 1300−1050 cm^{-1} region of the spectrum to specific conformations of the ester pendant group are incorrect. In addition, vibrational relaxation processes could significantly affect changes in the band shapes and widths of bands in the spectrum of atactic PMMA. This interpretation, if correct, has consequences for other studies where spectroscopic changes as a function of temperature are interpreted in terms of energy differences between conformational states. Intensity changes and band broadening effects due to vibrational relaxation must also be taken into account in such studies.

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