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Hydrogen Bonding in Polymers: Effect of Temperature on the OH Stretching Bands of Poly(vinylphenol)

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ABSTRACT: A detailed analysis of the bands appearing in the OH stretching region of the infrared spectrum of poly(vinylphenol) and their changes with temperature is presented. Bands usually assigned to "free" (non-hydrogen-bonded) groups contain overlapping contributions from both monomeric and end-group species, both hydrogen-bonded to π orbitals. Assignments of bands due to hydrogen-bonded groups are made on the basis of whether the proton and oxygen in a particular OH group are both involved in hydrogen bonds (as "donors" and "acceptors", respectively) or whether one or the other is "free" (not hydrogen-bonded). The assignment of other modes is more uncertain, and various possibilities are discussed. Changes in absorption coefficient with temperature appear to affect bands due to hydrogen-bonded groups in the interior of chains and monomeric species by essentially the same amount. The large change in absorption coefficient of the hydrogen-bonded band relative to a band assigned to free groups postulated in a previous study is more likely due to a change in the distribution of hydrogen-bonded and "free" species that were not resolved in previous work.

Introduction

Hydrogen bonds play a crucial role in the properties of many materials, and there is a rich literature stretching back many years concerning the application of vibrational spectroscopy to the study of these interactions.[1−3] Work in this laboratory has been largely concerned with the effect of hydrogen bonding on the miscibility of polymer mixtures, and as part of this effort we studied the effect of temperature on the NH stretching region of the spectra of nylons,[4−6] polyurethanes,[7] and polyureas.[8] This work was primarily focused on changes in bands that were assigned to "free" (non-hydrogen-bonded) and bonded groups in order to obtain parameters that could be used to understand the balance of interactions that determine miscibility. It was observed that in order to explain the large changes in intensity of the band or bands due to hydrogen-bonded groups relative to the band due to nonbonded groups that occur as temperature is increased, one would have to invoke very large changes in absorption coefficients.[5] However, the band profiles of hydrogen-bonded NH and OH stretching modes are broad and complex, and band assignments have often been in dispute, imposing some limits on use of vibrational spectroscopy in structural studies. In recent work, we have studied the OH stretching region of the infrared spectrum of ethylphenol as a model for phenolic polymers.[9] By systematically studying and curve-resolving spectra obtained as a function of composition, the most prominent bands contributing to the overall profile were identified. In effect, two different types of free and bonded bands were assigned. This has ramifications concerning the use of this region of the spectrum to study interactions in polymer materials, and here we will present the results of a study of the infrared spectrum of poly(vinylphenol), PVPh, as a function of temperature.

Experimental Section

Methyl ethyl ketone, MEK (2-butanone, 99.5+%), was purchased from Aldrich Chemical Co. and used without further purification. Poly(4-vinylphenol) was purchased from Polysciences, Inc. PVPh was dissolved in MEK at 2% (w/v) and cast onto potassium bromide (KBr) windows for FTIR analysis. The windows were left in a vacuum oven overnight at 100 °C to remove residual solvent and water. (Solvents such as THF are not completely removed unless PVPh is heated to about 140 °C.) The individual films were then pressed between two KBr windows while still hot, to achieve an even distribution of polymer over the entire area.

Films that best obeyed the Beer−Lambert law (maximum absorption ~0.7 in the wavenumber range of interest) were used in this study. Spectra were obtained as a function of temperature using a temperature-controlled, custom-made, horizontal cell (to prevent flow at high temperatures) and a Bio-Rad model FTS-45 Fourier transform infrared (FTIR) spectrometer. Spectra were acquired at a resolution of 1 cm^{-1}, with a minimum of 256 interferograms, or scans, being signal averaged at every 10 °C from 25 to 190 °C.

Curve Resolving

Curve-resolving spectra that consist of a number of broad, overlapping bands, such as those observed in the OH and NH stretching region of the infrared spectrum, can easily give spurious results, so we will describe our methodology in some detail. First, one has to be concerned with the band shape used in the fit. Experimental infrared absorption bands 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 in a program developed in our laboratory:

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

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

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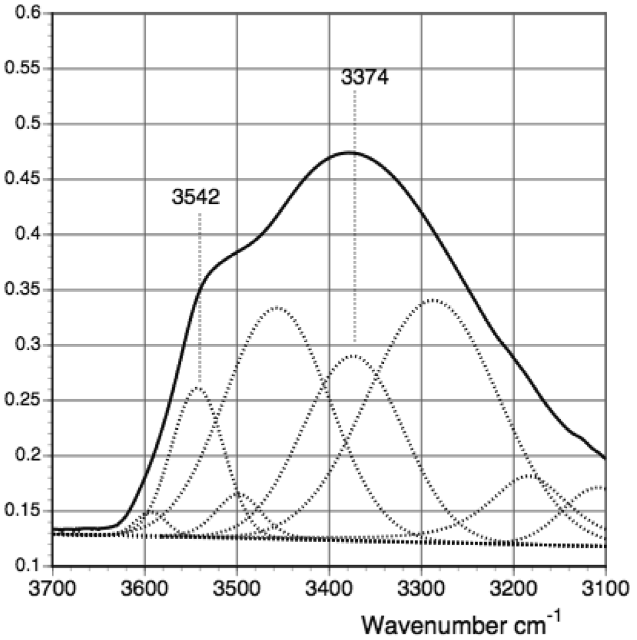

Figure 1. Infrared spectrum of poly(vinylphenol) obtained at 60 °C curve-resolved in a manner that leads to results that make no spectroscopic or chemical sense.

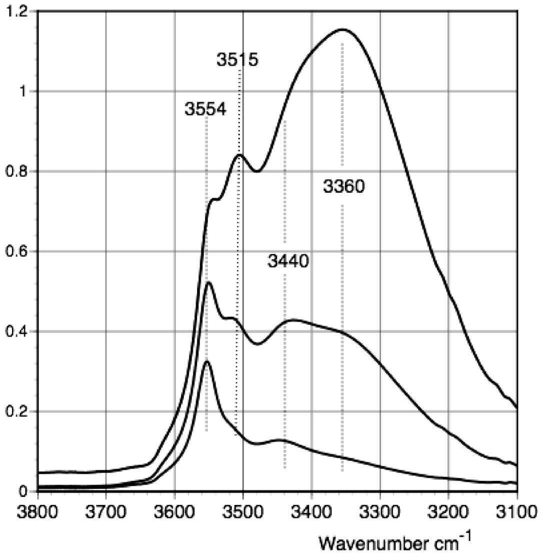

Figure 2. Infrared spectra of ethylphenol in toluene at three different concentrations. Top spectrum, 50 wt % solution; middle spectrum, 25 wt % solution; bottom spectrum, 10 wt % solution.

describe the bands. Liu et al.[10] have shown that this particular sum function is an excellent approximation to a true Voigt profile.

When curve-fitting complex band profiles, one can often obtain results that are good in terms of a least-squares fit but make no spectroscopic sense in terms of things like relative intensities and band widths. A number of steps have to be taken to mitigate problems. First, it is important that a baseline be accurately set (and one should not use the automatic baseline correction programs available on modern instruments, as these can seriously distort the spectra). Second, a prior knowledge of the number of bands present together with good estimates of their positions, intensities, etc., need to be used as a starting point to ensure (as far as possible) a convergence to a fit that is spectroscopically and chemically meaningful. In this study, baselines appeared to slope slightly, and a linear baseline was set at minimum absorption positions near 3700 and 2200 cm^{-1}. The most difficult problem involved identifying the number of bands in this region of the spectrum. Second derivative techniques are of little use when bands are very broad and overlap considerably. As Maddams[11] pointed out a number of years ago, however, the human eye is quite adept at identifying inflections and changes in shape that are due to the presence of overlapping bands. Good, but not perfect, alas. Figure 1 shows the results obtained by curve-resolving the spectrum of PVPh obtained at 60 °C using bands identified initially by the eye. The sum of the curve-resolved bands fit the experimental profile extremely well, but one would anticipate that the strongest band in the spectrum should correspond to a mode near the position of maximum absorption (3374 cm^{-1} in this figure), as this is well-known to be characteristic of hydrogen-bonded groups. Instead, the program converged to a solution where two modes on each side of this band appeared to be the most intense. This is a major problem with fitting broad profiles to a number of bands, and if convergence to an acceptable solution is to be achieved, one usually has to initiate the fit using peak positions, band widths, and intensities that are not too far from the "correct" solution. Of course, one cannot always know what that is, but in this case we were able to use the results of a systematic study of ethylphenol, EtPh. We recently reported a detailed analysis of the spectrum of solutions of this material in both cyclohexane and toluene as a function of concentration.[9] Because phenolic OH groups can form weak hydrogen bonds to the π-bonds of an aromatic ring,[12,13] it is the latter solutions that interest us here. For the purposes of this discussion, we have reproduced spectra of three solutions (10, 25, and 50 wt %) in Figure 2. Because of the systematic variation in the relative intensities of various modes with concentration, we were able to identify the major bands contributing to the overall profile and their characteristics (frequency, width at half-height, etc.). At low concentrations in toluene, the strongest band in the spectrum can be observed near 3554 cm^{-1}. The strongest OH bands in the spectra of dilute solutions of a non-hydrogen-bonding solvent can be assigned to free or nonbonded groups. However, this band is shifted more than 50 cm^{-1} from the "monomer" band observed in cyclohexane solutions and can be assigned to monomer OH-π hydrogen-bonded groups.[9] We will discuss the assignment of bands in more detail below, but as the concentration of EtPh in toluene is increased, the band near 3554 cm^{-1} decreases in intensity relative to other modes, while bands near 3515 and 3440 cm^{-1} initially become more prominent. At high concentrations a band near 3360 cm^{-1} dominates the band profile. (The actual peak position is revealed to be at 3349 cm^{-1} after curve resolving—overlap with other modes results in the maximum absorption appearing at a higher wavenumber in the overall band profile.) Other modes can be clearly identified by the eye in various spectra, and we concluded that there are eight bands present in this region of the spectrum. The result obtained by curve-resolving the spectrum of a 50% EtPh/toluene solution using these bands is shown in Figures 3. The peak positions, width at half-height, etc., were then used as starting points to curve resolve the spectrum of PVPh.

Results and Discussion

Infrared spectra of PVPh as a function of temperature in the range 25−190 °C were obtained. As examples, spectra obtained at 25, 60, and 150 °C are shown in Figure 4. It can be seen that as the temperature is increased, the peak position of maximum absorption, near 3360 cm^{-1} at room temperature, usually assigned to hydrogen-bonded groups in general, shifts to higher frequency. The intensity of this mode also decreases with increasing temperature. In contrast, the band or bands contributing to the shoulder near 3515 cm^{-1}, usually assigned to "free" OH

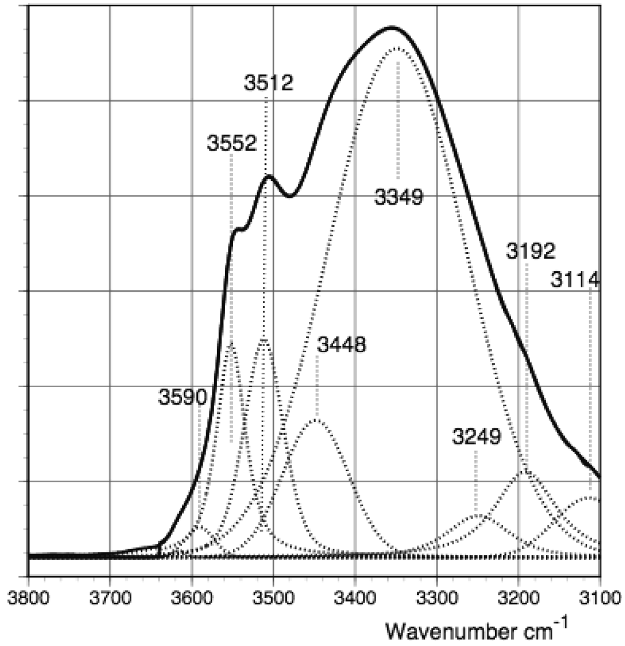

Figure 3. Infrared spectrum of a 50 wt % solution of ethylphenol in toluene curve-resolved into its component bands.

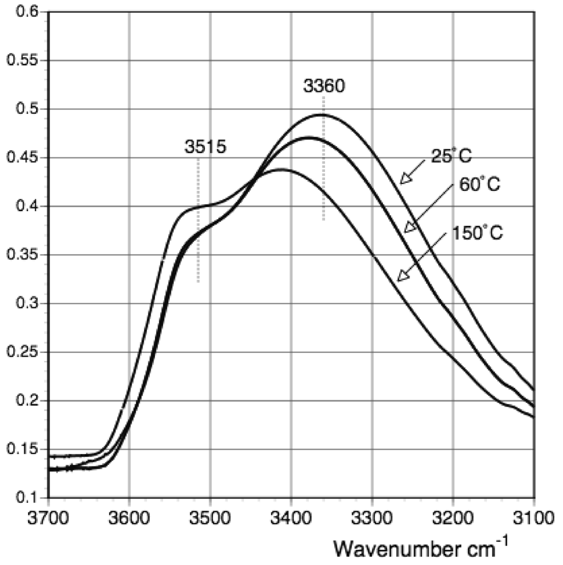

Figure 4. Infrared spectra of poly(vinylphenol) obtained at 25, 60, and 150 °C.

stretching modes, does not appear to change much at low temperatures but is somewhat more intense at the higher temperatures in the range studied here. It is this type of observation that in previous studies led to the conclusion that there is a extremely large change in the absorption coefficient of hydrogen-bonded bands with increasing temperature and frequency shift, a result of the decreasing strength of the hydrogen bonds in these systems.[4,5]

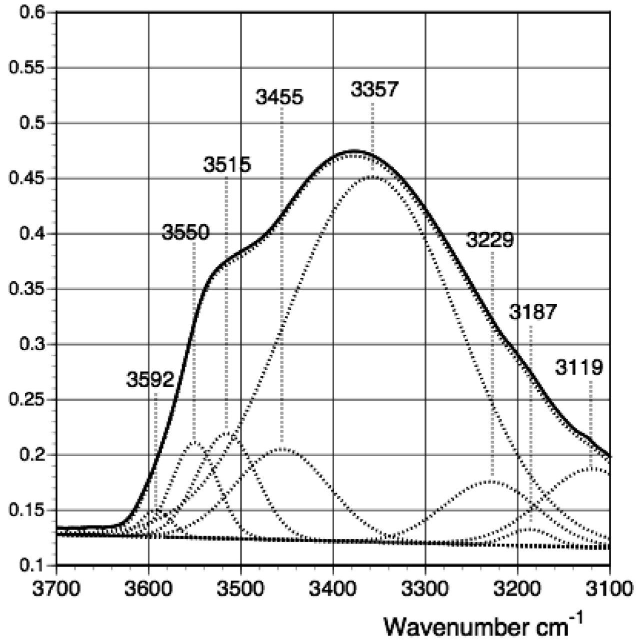

Figure 5. Infrared spectrum of poly(vinylphenol) obtained at 60 °C curve-resolved into its component bands.

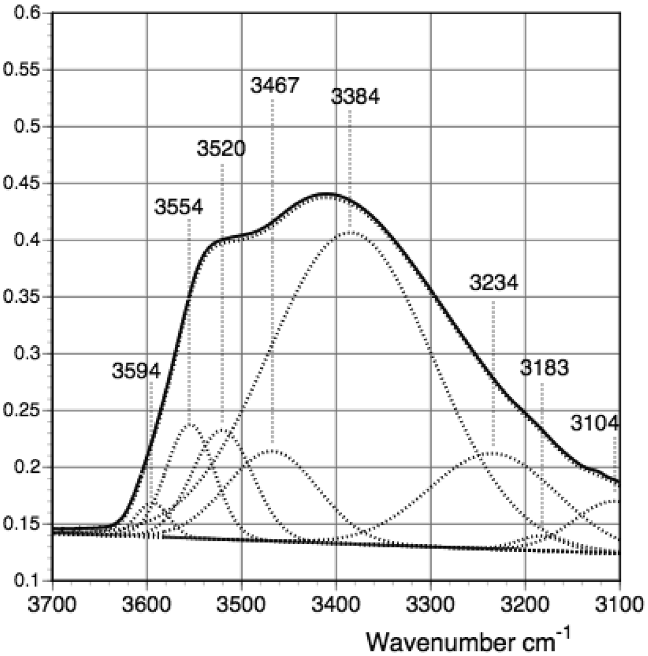

Figure 6. Infrared spectrum of poly(vinylphenol) obtained at 150 °C curve-resolved into its component bands.

The results of curve-resolving the spectra obtained at 60 and 150 °C are shown as examples in Figures 5 and 6. All the bands were determined to be Gaussian. The spectrum of the sample was offset slightly from the profile obtained by summing the individual curve-resolved bands to show that an excellent fit has been obtained. Unfortunately, the results are subject to a much larger error than one would like because changes in the width and intensity of one of the weaker modes can be compensated by equivalent changes in one or more of its neighbors. Nevertheless, there are clear trends with temperature that make spectroscopic sense when compared to studies of model compounds as a function of composition. (PVPh cannot be studied as a function of composition in non-hydrogen-bonding solvents because of its lack of solubility in such solvents.)

The bands that can be readily assigned to hydrogen-bonded or "free" groups are those resolved near 3548, 3514, 3456, and 3351 cm^{-1} at 25 °C. All move to higher wavenumbers as the temperature is increased. This is typical of bands assigned to groups involved in hydrogen-bonding interactions, as this interaction weakens with increasing temperature. In what follows we will usually refer to the peak positions at 25 °C to identify a band.

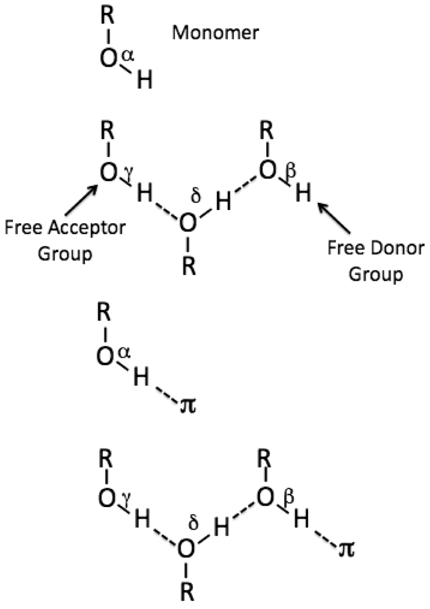

Figure 7. Schematic representation of the types of hydrogen-bonded groups found in poly(vinylphenol).

In past studies, it has been usual to assign bands to free (non-hydrogen-bonded) groups, dimers, and multimers.[12,14] In some materials cyclic species have also been identified.[15] Hall and Wood[16] suggested a different approach to band assignments, based on observable characteristics, an approach also taken more recently by Ohta and Tominaga.[17] They identified four functionally different groups, which they labeled α, β, γ, and δ, illustrated schematically at the top of Figure 7. The α group corresponds to the monomer, where neither the oxygen atom nor the proton of an OH group is involved in hydrogen bonding; the β group corresponds to an end group where the proton is not acting as a donor, but the oxygen atom acts as an acceptor; the γ group to an end group where the proton is acting as a donor, while the oxygen atom is not acting as an acceptor; the δ group is where both the oxygen atom and proton act as acceptor and donor, respectively. We found that this basis for assignments made sense in terms of the changes in intensity of the OH stretching modes of EtPh with concentration reported previously.[9] In cyclohexane solutions, the monomer (α) and free end group band (β) of EtPh could not be distinguished, and both contributed to a band observed near 3620 cm^{-1}. In toluene solutions, however, both bands are shifted to lower wavenumber as a result of hydrogen bonding to aromatic π orbitals and can now be separately observed near 3552 and 3512 cm^{-1} (see Figure 3). Accordingly, the bands curve resolved near 3550 and 3515 cm^{-1} in the spectrum of PVPh can be assigned to these groups, which are illustrated schematically at the bottom of Figure 7 and which we designate α−π and β−π, respectively. In a similar fashion, the bands near 3456 and 3351 cm^{-1} (at 25 °C) can be assigned to γ groups (where the proton is acting as a donor, while the oxygen atom is not acting as an acceptor) and δ groups (where both the oxygen atom and proton act as acceptor and donor, respectively). The latter is the strongest in the spectrum of PVPh at low temperatures and corresponds to bands that were previously assigned to hydrogen-bonded groups in general or to multimers.

Before examining changes in the intensities of these modes with temperature, we will say a few words about the other bands in this region of the spectrum, the very weak modes resolved near 3592 and 3187 cm^{-1} and two more intense modes resolved near 3228 and 3121 cm^{-1} (at room temperature). The presence of clearly discernible shoulders in the spectra of both EtPh and PVPh indicates the presence of at least two bands in the 3250−3100 cm^{-1} range, and we found that we could not fit the overall band profile accurately without including a third band. However, both the 3187 and 3121 cm^{-1} modes move to lower wavenumbers with increasing temperature, in contrast to the bands assigned to hydrogen-bonded groups, which move to higher wavenumbers. This suggests that these bands are not associated with OH stretching fundamentals but are probably overtone/combination modes of some description. The band near 3228 cm^{-1} at room temperature shifts to higher wavenumber (3234 cm^{-1} at 150 °C), however, suggesting that it is associated with hydrogen-bonded OH groups. One possibility is a cyclic structure with very strong hydrogen bonds. These have been identified in the spectra of phenolic resins and calixarenes. The former can be observed in the range 3200−3250 cm^{-1}, while the stronger hydrogen bonds found in certain calixarenes are found between 3130 and 3170 cm^{-1}.[13,18,19] However, these materials consist of phenols linked together by methylene bridges in a specific manner, and there appears to be a link between the conformation of these molecules, which brings the OH groups into close proximity, and the ability to form strongly hydrogen-bonded cyclic structures. It is not clear that there are equivalent conformational constraints on PVPh segments, and we suggest an alternative assignment.

Table 1. PVPh Band Assignments (Room Temperature)

band (wavenumber)	assignment
3592	unknown (combination mode?)
3550	OH-π hydrogen-bonded monomer groups (α−π)
3515	OH-π hydrogen-bonded end groups (β−π)
3455	γ hydrogen-bonded OH groups (see Figure 4)
3357	δ hydrogen-bonded OH groups in linear chains (see Figure 4)
3229	unknown—possibly a result of transition dipole
3187	coupling, combination modes, or strongly
3119	hydrogen-bonded cyclic structures

In liquids with polar functional groups, local structure, as influenced by strong interactions between permanent dipole moments, coincides with strong vibrational coupling that is a consequence of transition dipole interactions. The former influences the latter as a result of the tendency of the molecules to align to some degree, even in the liquid state. In ordered systems consisting of a finite number of such coupled oscillators, one observes a series of bands of systematically decreasing intensity that map the dispersion curve of the theoretically infinite oscillator chain. In disordered systems, one would expect to see a superposition of the effect of finite chain length and imperfect alignment, resulting in an asymmetric broadening of the observed vibrational mode that in some cases appears as a resolvable shoulder. The highly polar nature of hydrogen bonds and their preference for a (more or less) linear alignment would suggest that this might be what we are observing here.[20,21] A summary of these band assignments (room temperature frequencies) is given in Table 1.

Returning now to the bands that can be clearly assigned to hydrogen-bonded species, the peak heights of the bands assigned to α−π and β−π groups are plotted as a function of temperature in Figure 8. It can be seen that the 3548 cm^{-1} mode assigned to α−π (monomer-π) groups increases significantly in intensity as the temperature is increased, with the rate apparently changing near the T_g of the sample, 140 °C. This mode is curve resolved with greater accuracy than its immediate neighbors because it lies on the outer edge of the overall band profile and is defined by more data points. Accordingly, the peak height of the β−π groups, resolved near 3514 cm^{-1}, shows more scatter but appears to increase to a much smaller extent than the band due to α−π groups. (Plots of band areas show the same trend.) Plots of

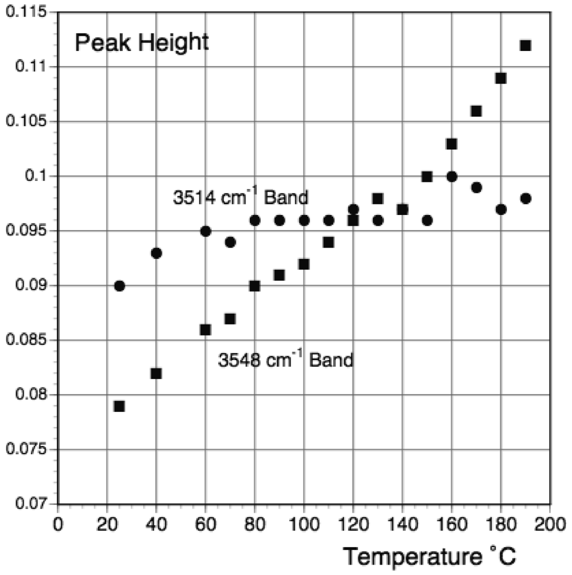

Figure 8. Peak heights of the monomer and end-group OH bands (α−π and β−π) plotted as a function of temperature.

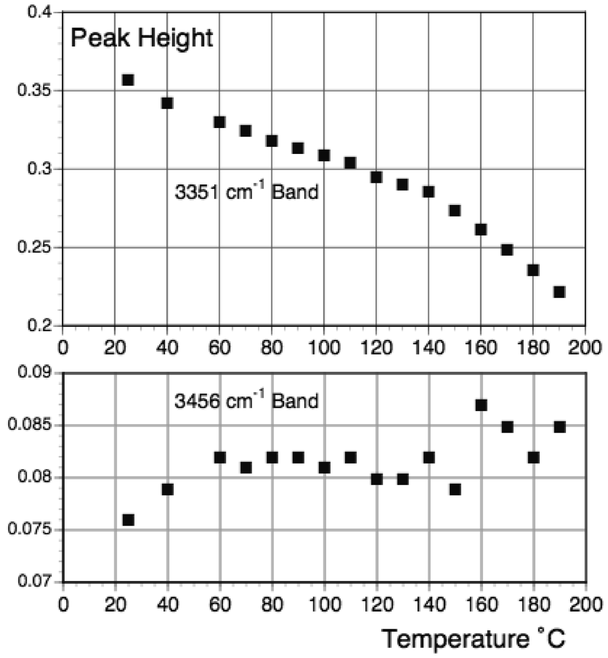

Figure 9. Plot of the peak heights of the hydrogen-bonded bands observed (at room temperature) near 3351 cm^{-1} (δ group) and 3456 cm^{-1} (γ group) at 25 °C.

the peak heights of the hydrogen-bonded modes corresponding to γ and δ groups shown in Figure 9 display a similar trend, in the sense that one mode shows greater changes than the other. The peak height of the band due to δ groups, the most intense OH band at 25 °C resolved near 3351 cm^{-1}, decreases significantly in intensity as the temperature is increased, with an inflection point in the curve near 140 °C. On the other hand, the band due to γ hydrogen-bonded groups appears to increase slightly with increasing temperature, although as with the band due to β−π groups (OH end groups hydrogen-bonded to π orbitals), there is significant scatter in the data because these bands are curve-resolved with less accuracy.

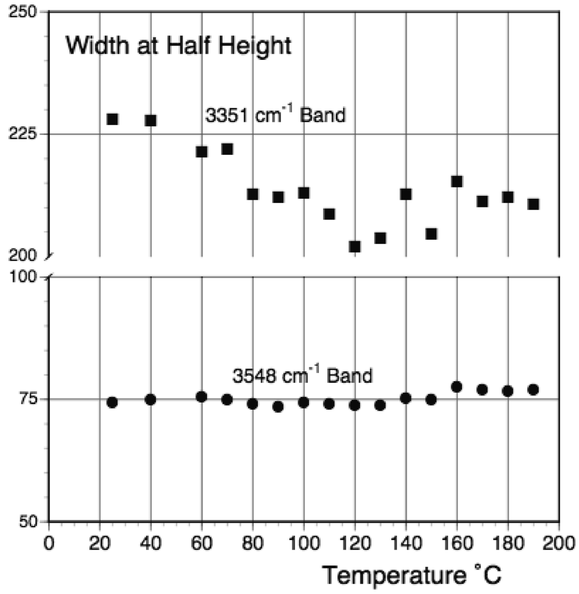

Figure 10. Plot of the width at half-height of the hydrogen-bonded bands observed (at room temperature) near 3351 cm^{-1} (δ) and 3548 cm^{-1} (γ) as a function of temperature.

These results are consistent with a change in the distribution of hydrogen-bonded chain lengths with increasing temperature. As the average length of these chains gets shorter, there are more end groups present, both oxygen acceptors and proton donors (and there must be equal numbers of each of these species), relative to groups residing in the interior of hydrogen-bonded chains. This is reflected in the large decrease in the intensity of the band due to δ groups relative to the intensities of bands assigned to γ and β−π groups. In previous work, this large decrease in intensity was largely attributed to a change in the absorption coefficient as the strength of the hydrogen bond decreased and the band center shifted to higher wavenumber, but as we will show below such changes are actually very small. Before getting to that point we will point out two more related observations that we think are interesting.

A number of years ago we observed that the statistics of hydrogen bond formation in the form of linear chains is the same as linear polycondensation reactions between bifunctional monomers.[22] There are two consequences of this. First, monomers are the most prevalent species by number, but not by weight. However, at low degrees of conversion in polymerizations, equivalent to higher temperatures and shorter hydrogen-bonded chains in this study, their (weight) concentration relative to other species increases significantly. This is why the band due to α−π groups increases dramatically with increasing temperature while the band due to β−π groups increases only slightly. Second, the polydispersity of the chain lengths also decreases with decreasing conversion or, in this case, increasing temperature. Accordingly, we would anticipate that the band due to hydrogen-bonded δ groups should reflect a narrower distribution of environments. Band shapes and widths are also affected by various relaxation phenomena,[23] but we found that all the bands in this region of the spectrum are Gaussian, reflecting what is called the slow modulation limit, so that the width of the band at half-height reflects the distribution of local environments. We found that the width of the 3351 cm^{-1} δ band did indeed decrease with increasing temperature, as shown in Figure 10, while the (full) width at half height of the 3548 cm^{-1} band (γ groups) remained essentially constant (within error), as also shown in Figure 9, consistent with this interpretation.

Finally, we will consider relative changes in absorption coefficients. As we have show above, the band assigned to monomer groups, α−π, increases in intensity with temperature, while the band due to δ groups decreases. The bands due

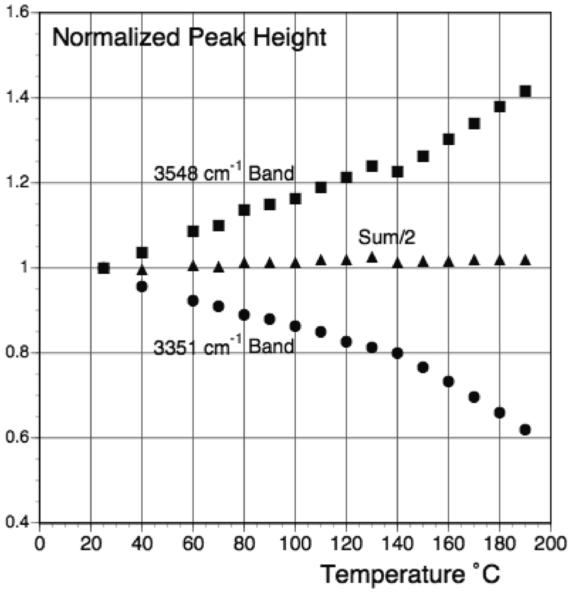

Figure 11. Plot of the peak heights of the hydrogen-bonded δ group (near 3351 cm^{-1} at 25 °C) and the monomer α−π group (near 3548 cm^{-1} at 25 °C) as a function of temperature. Both sets of data are normalized to the values determined at 25 °C. Also shown is the sum of the values determined at each temperature divided by 2.

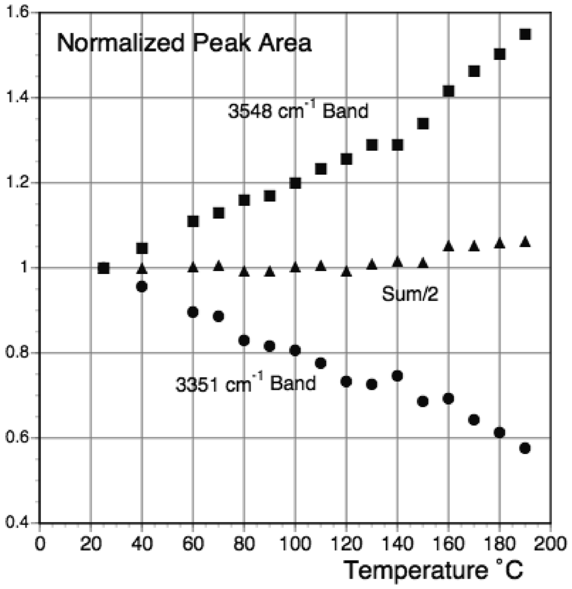

Figure 12. Plot of the peak area of the hydrogen-bonded δ group (near 3351 cm^{-1} at 25 °C) and the monomer α−π group (near 3548 cm^{-1} at 25 °C) as a function of temperature. Both sets of data are normalized to the values determined at 25 °C. Also shown is the sum of the values determined at each temperature divided by 2.

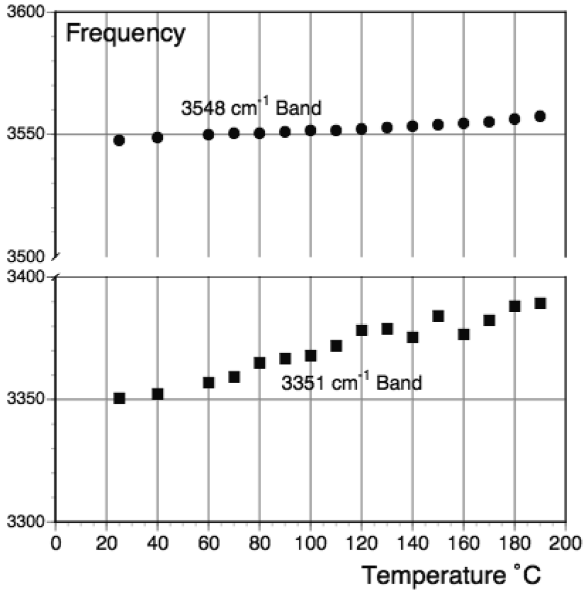

Figure 13. Plot of the frequencies of the hydrogen-bonded δ group (near 3351 cm^{-1} at 25 °C) and the monomer α−π group (near 3548 cm^{-1} at 25 °C) as a function of temperature.

to γ and β−π groups change only a small amount, so we will focus on the former. We normalized the both the peak heights and band areas of the 3351 cm^{-1} (δ) and 3548 cm^{-1} (α−π) modes (frequencies observed at 25 °C) to the values determined at room temperature and plotted the results in Figures 11 and 12. The frequencies of both increase with temperature, as shown in Figure 13, and the peak height values were determined at these peak positions. The plots of normalized peak heights and band areas should reflect the change in relative concentrations of the hydrogen-bonded δ groups and monomer α−π groups with temperature, if there is no change in absorption coefficients or if the changes were in proportion. Accordingly, if one band increases in intensity about 40% (to a normalized value of 1.4), the other should decrease by about 40% (to a normalized value of about 0.6) because of the relatively small changes in the intensities of the β−π and γ groups. The sum of normalized peak heights and areas when divided by two should then be unity. The sum is very close to a value of 1 for both areas and peak heights, as also shown in Figures 11 and 12. Accordingly, changes in absorption coefficient with temperature appear to affect both bands by essentially the same amount. The large change in absorption coefficient of the hydrogen-bonded band relative to a band assigned to free groups postulated in a previous study is most probably due to a change in the distribution of hydrogen-bonded species that were not resolved in this previous work.

Conclusions

The OH stretching region of the infrared spectrum of phenolic compounds is complicated. In this study of poly(vinylphenol), we attempted to identify the major bands present and make assignments using careful curve-resolving methods. Spectra were obtained as a function of temperature. Assignments were based on identifying four major types of OH groups labeled α, β, γ, and δ.[16,17] The α group corresponds to the monomer; the β group to an end group where the proton is not acting as a donor, but the oxygen atom acts as an acceptor; the γ group to an end group where the proton is acting as a donor, while the oxygen atom is not acting as an acceptor; the δ group is where both the oxygen atom and proton act as acceptor and donor, respectively. Both the α and β groups were hydrogen-bonded to π orbitals. The strongest band in the spectrum obtained at the lowest temperature is due to OH groups present in linear chains of hydrogen-bonded OH groups (as recognized in numerous other studies). There was little change in the absorption coefficient of this mode relative to α−π groups with increasing temperature. The apparent change detected in previous work is more probably associated with a change in the distribution of bonded and "free" species present.

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