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Hydrogen bonds in poly(methyl methacrylate)–poly(4-vinyl phenol) blends

2. Quantification near the glass transition temperature

Dean Li and Josée Brisson*
Centre de recherche en sciences et ingénierie des macromolécules,
Département de chimie, Faculté des sciences et de génie, Université Laval, Qué.,
Canada G1K 7P4
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Changes in the proportion of hydrogen bonds of poly(4-vinyl phenol) (PVPh) and poly(methyl methacrylate) (PMMA) blends have been investigated by *FT*i.r. spectroscopy both above and below the glass transition temperature T_g. Changes in three spectral regions, namely the carbonyl, hydroxyl and aromatic ring vibration regions, are attributed to variations in hydrogen bonding with increasing temperature. Both hydrogen bonded O–H and C=O stretching vibrations shift to higher frequencies, indicating a weakening of interassociated hydrogen bonds at higher temperatures. A clear transition is observed in the absorbance behaviour of these vibrations at T_g. The reduction in total area of O–H and C=O vibration regions is attributed not only to the breaking of hydrogen bonds at T_g, but also to the decrease of absorption coefficients of hydrogen bonded O–H and C=O stretching vibrations. Quantification of the decrease in concentration ratio of hydrogen bonds between carbonyl groups vs. total carbonyl groups showed a decrease of 0.5% in the number of hydrogen bonds was occurring at $T_g + 30$, when T_g is taken as the midpoint of the transition as determined by DSC, for the 30 wt% PVPh composition. For higher compositions, this percentage increased, reaching 3.5% for the 80 wt% PVPh composition, which is related to the increase in T_g of the blend. © 1997 Elsevier Science Ltd.

(Keywords: polymer blends; hydrogen bonds; temperature effect)

INTRODUCTION

The poly(4-vinyl phenol)–poly(methyl methacrylate) (PVPh–PMMA) blend has been selected as a model system to investigate the effect of hydrogen bonds on orientation behaviour of both PVPh and PMMA chains in a miscible blend. In order to do so, it is necessary to have a better idea of the evolution of hydrogen bonding in the blends with composition. In the first paper of this series, quantitative and semi-quantitative evaluation of the number of OH and C=O groups participating in inter- and intra-association through hydrogen bonds was reported for the PVPh–PMMA blend.

Orientation is strongly dependent on the temperature at which the deformation is performed. It is customary to define this temperature with respect to its deviation from the glass transition temperature T_g of the system studied. It is expected that hydrogen bonds will decrease with increasing temperature, especially above T_g, and such quantifications are not unique in the literature. However, to our knowledge, no orientation study of a systems for which such a quantification had been done have ever been published, in spite of the importance such an information can bear on the interpretation of the orientation behaviour. This is particularly important near the T_g of the system, which is generally chosen as a reference, since it is slightly above around this temperature that most deformation processes are conducted.

It is well known that the absorbance of the stretching vibrations pertaining to hydrogen bond formation are significantly affected when increasing the temperature[1–4]. It is difficult to measure precisely the absorbance variation of O–H vibrations with temperature due to the overlap of the 'free' O–H band with the broad hydrogen-bonded vibration. Studies on the effect of temperature on the N–H stretching vibrations involving polyurethanes[5,6] and polyamides[7–9] show that, when thermal expansion of the polymer film is neglected, the reduction in total area of N–H vibration region is related to two main factors. The first, which is also the only factor that was identified in earlier studies, is the transformation of part of the hydrogen bonded groups to free groups, which have a lower absorption coefficient[10–12]. The second factor is the variation of the absorption coefficient with temperature[7,9]. Furthermore, the absorption coefficient is proportional to the strength of the hydrogen bonds, which also causes frequency shifts.

When PVPh is blended with other polymer components which contain carbonyl groups, such as polyacrylates, the carbonyl vibration region can provide an alternate 'window' to determine variations of inter-hydrogen bonds with temperature through the changes of C=O vibrations. Because of the greater frequency difference between the two vibrations, and because they are narrower that the O–H valence vibrations, the C=O valence vibrations lend themselves more easily to spectral decomposition. Separation of the 'free' and hydrogen bonded C=O vibrations allow us to determine not only the vibration shift, but also the individual absorbance accurately.

In the first article of this series, the carbonyl vibration absorbance coefficients were measured for the PVPh–PMMA blend at room temperature[13]. Using this information,

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* To whom correspondence should be addressed

the present paper will focus on the effect of temperature on the hydrogen bonds of the PVPh–PMMA near T_g, in order to determine to what extent the hydrogen bond changes observed at room temperature are still valid at temperatures near T_g. The conclusions, along with those of the first paper, will be used in a forthcoming paper dealing with orientation of this blend.

EXPERIMENTAL

Poly(4-vinyl phenol) (PVPh) and poly(methyl methacrylate) (PMMA) employed in this study have been described previously[13]. Their molecular weights and the glass transition temperatures (defined as the midpoint of the glass transition) of the blends are summarised in *Table 1*. Abbreviations for blends are as follows: PM37 stands for 30 wt% PVPh and 70 wt% PMMA in the blend, and so forth.

Samples for infrared analysis were prepared by casting a 1% (w/v) solution of methyl ethyl ketone (MEK) as described in Ref. [13]. Spectra were recorded by holding the KBr window on which the polymer film was cast in an oven enclosed by two clear KBr windows, using a Mattson SIRIUS 100 Fourier transform infrared spectrometer. The oven temperature controller had an accuracy of ± 0.1°C. Each spectrum recorded at a given temperature was taken 5 min after the desired temperature was reached in order to allow temperature equilibration, using 100 scans at a resolution of 2 cm^{-1} with a MCT detector. GRAMS (Galactic Industries Corp.) was used to analyse spectra using a least-squares fitting method.

Table 1 Properties of pure polymers and blends used in this study

Sample	PVPh/PMMA (wt%)	Molecular weight (g mol^{-1})	T_g^a (°C)
PMMA	0/100	100 000	94
PM37	30/70	–	114
PM54	54.5/45.5	–	129
PM73	70/30	–	136
PM82	80/20	–	142
PVPh	100/0	30 000	156

[a] T_g reported as midpoint of heat capacity jump as determined by d.s.c.

RESULTS AND DISCUSSION

As can be in *Figure 1*, which shows infrared spectra of a typical PVPh–PMMA blend (PM73) recorded at ambient and elevated temperatures with a solid and a dashed line, respectively, important changes in the absorbance and position of various vibrations occur with temperature. Also included at the bottom of this figure is the result of the subtraction of the two spectra using a 1:1 ratio. The most important changes are seen in three spectral regions, the O–H stretching vibration region (3100–3700 cm^{-1}), the C=O stretching vibration region (1650–1800 cm^{-1}) and the region spanning 1000–1650 cm^{-1}, which is mostly composed of aromatic ring vibrations. To ascertain that the spectral changes are not caused by thermal and thermo-oxidative degradation at higher temperature, track spectra were recorded by cooling of the sample after reaching 200°C. When using a very slow cooling rate (about 0.5°C min^{-1}), spectra recorded after cooling to ambient temperature were almost completely superimposable to those before heating. No obvious spectral changes could be related to sample degradation.

The carbonyl stretching vibration region (1650–1800 cm^{-1})

A typical υ(C=O) vibration region recorded as a function of temperature is shown in *Figure 2a*. Two contributions are easily separated: vibrations assigned to 'free' and to hydrogen-bonded C=O groups appear at 1733 cm^{-1} and 1706 cm^{-1}, respectively. The hydrogen bonded groups are taking part in inter-hydrogen bonds, or 'inter-association', association between carbonyls of PMMA and hydroxyls of PVPh. Intra-association also exists between PVPh chains, but does not affect the carbonyl vibrations. It can be seen that, when the temperature increases, the absorbance of the hydrogen bonded C=O vibration, centred at 1706 cm^{-1}, shows an apparent decrease. To quantitatively investigate the effect of temperature on the individual C=O vibrations, a curve fitting procedure was used to separate these 'free' and hydrogen bonded C=O vibration bands. A gaussian

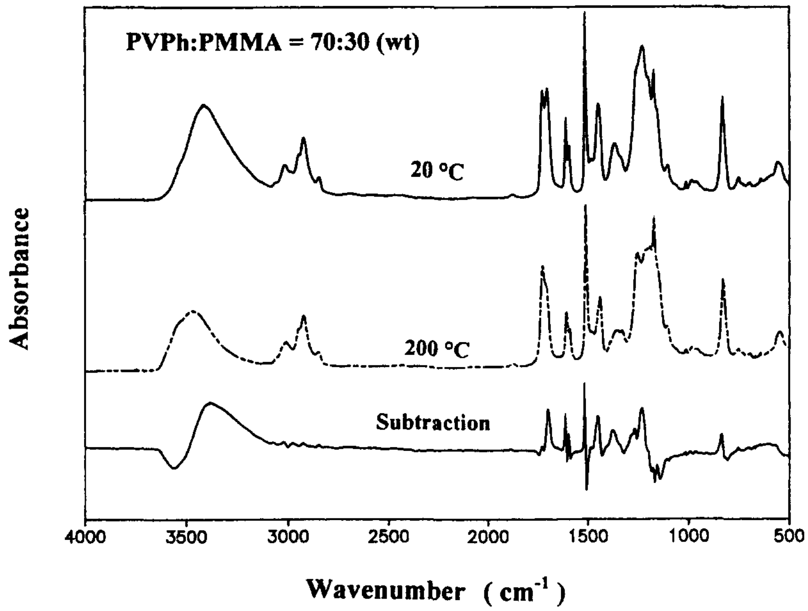

Figure 1 *FT*i.r. spectra of the PM73 blend recorded at 20°C (solid line) and 200°C (dashed line) (top), and the result of their subtraction (bottom)

peak shape was selected, and the position of the peaks was determined using the second derivative of the spectral region. The position of the free C=O vibration was kept constant during the calculations. Because the peaks are relatively well separated in the initial spectra, and because both the peak position and width are known to vary with temperature, which results in a poor fit when these factors were not varied, it was decided to let the position of the hydrogen bonded vibration and the peak width vary. Typical curve fits are shown in *Figure 2b* and *c* for spectra taken at 20 and 200°C, respectively. Results of the curve-fit are also reported in more detail in *Table 2*. The same curve-fitting procedure has been used for blends containing 30, 54.5, 70 and 80 wt% PVPh.

The frequency of the 'free' C=O vibration remains unaltered with composition and temperature changes, and is the same, within experimental error, as in pure PMMA (1733 cm^{-1}). In contrast, the frequency of the hydrogen bonded C=O vibration changes, not only slightly with composition, but also more markedly with temperature. The hydrogen bonded C=O vibration shifts to a higher frequency when the temperature increases. This could be expected, since it reflects the weakening of the hydrogen bonds, which result in an increase in the strength of the C=O bonds involved in hydrogen bonding.

Variations of C=O absorbance with temperature, which are plotted in *Figure 3* for the four compositions studied, clearly exhibit a break for both 'free' and hydrogen bonded C=O groups at approximately 120°C for all compositions. Before this break, the free C=O absorbance was constant within experimental error, whereas only a small decrease in absorbance was observed for the hydrogen-bonded C=O vibration. After the break, however, a sharp decrease in absorbance of the hydrogen bonded C=O vibration is observed at all compositions, as well as a significant increase in the absorbance of the free C=O vibration. The transition therefore coincides with the onset of hydrogen bond breaking. A least squares calculation was performed on each of the two linear sections of each curve, and the resulting slope m and y-axis intercept e are reported in *Table 3*. The transition temperature was calculated as the intersect of these two linear curves for free and hydrogen bonded groups. However, since the absorbance was more intense for the hydrogen bonded vibration, the accuracy of the linear regression was higher, and therefore only this value was used in *Figure 4* as the *FT*i.r. transition temperature.

It can clearly be seen that, although this may not have been evident in *Figure 3*, the transition temperature varies almost linearly with composition. Furthermore, it is

Table 2 Curve fitting results for the carbonyl region of PVPh/PMMA blends

Temperature	'Free' C=O vibration			Hydrogen bonded C=O vibration		
(°C)	υ (cm^{-1})	$W_{1/2}$ (cm^{-1})	A (cm^{-1})	υ (cm^{-1})	$W_{1/2}$ (cm^{-1})	A (cm^{-1})
PVPh:PMMA = 30:70						
20	1733	21	20.4	1709	27	10.9
50	1733	21	20.3	1709	28	10.9
80	1733	20	20.2	1709	28	10.8
110	1733	20	20.4	1710	28	10.9
140	1733	20	20.9	1710	27	10.3
170	1733	20	21.1	1710	27	9.7
PVPh:PMMA = 54.5:45.5						
20	1733	19	14.5	1708	28	17.0
50	1733	18	14.4	1708	29	16.9
80	1733	18	14.5	1708	29	16.9
110	1733	18	14.5	1709	29	16.8
140	1733	18	14.6	1710	29	16.2
170	1733	18	14.8	1711	29	15.2
200	1733	18	15.7	1711	30	14.2
PVPh:PMMA = 70:30						
20	1733	19	18.8	1707	28	32.3
50	1733	19	18.8	1707	28	32.0
80	1733	18	18.9	1707	29	31.6
110	1733	18	19.0	1708	29	31.2
140	1733	18	19.6	1709	29	30.2
170	1733	18	19.9	1710	29	27.4
200	1733	17	20.4	1711	30	24.9
PVPh:PMMA = 80:20						
20	1732	20	14.2	1705	28	31.2
50	1732	19	14.3	1705	29	30.8
80	1732	19	14.4	1706	29	30.2
110	1732	18	14.5	1706	29	29.8
140	1732	18	15.1	1707	30	29.0
170	1732	18	15.8	1708	30	26.8
200	1732	18	16.9	1710	30	24.2

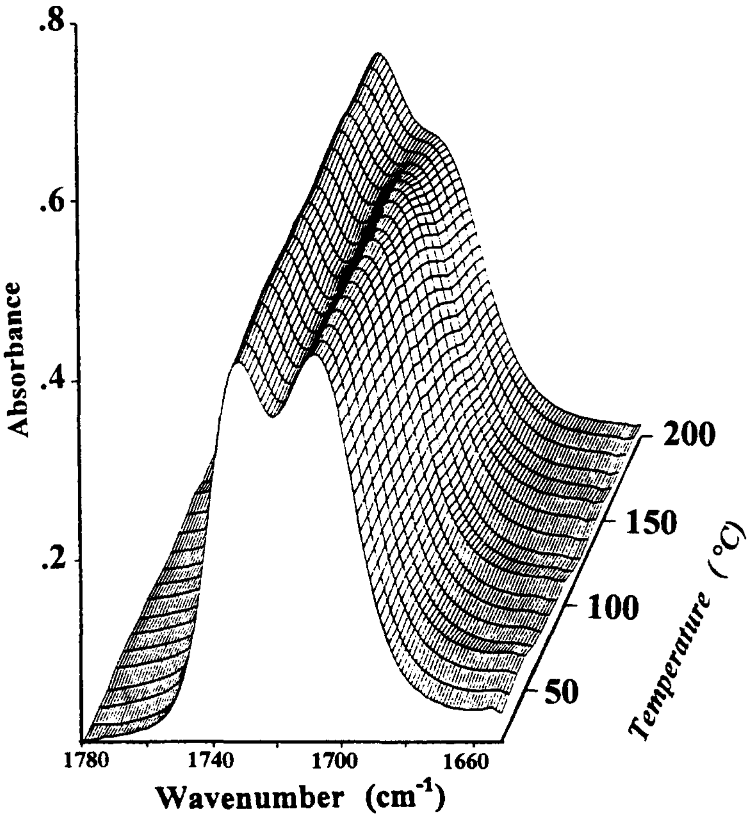

Figure 2 Spectra recorded with increasing temperature for the PM73 blend (a), and examples of curve-fitting for 20°C (b) and 200°C (c)

comparable or slightly lower than T_g as determined by the onset of the differential scanning calorimetry (d.s.c.) observed transition or the midpoint of the transition (triangles). This is related to the fact that d.s.c.-determined transition temperatures are always higher than the expected value because of the heating speed during measurement (10 °C min^{-1} in this case). The variation of the *FT*i.r. transition temperature with composition also runs almost parallel to that of the d.s.c. midpoint-determined T_g, but is shifted by 7 to 12°C. Such behaviour could be expected, since T_g values measured as the midpoint of the d.s.c. heat capacity jump represent the temperature at which the average polymer chain of the sample experiences the long-range movements which appear at T_g, whereas *FT*i.r. indicates the onset of hydrogen bond breaking associated with these movements.

Once it is established that the transition corresponds to T_g, it is clear (and was indeed expected) that, after this transition, the decrease in C=O vibration absorbance is mainly related to changes in the proportion of hydrogen bonds, since the onset of longer-range movements at T_g will allow disruption of hydrogen bonds. On the other hand, this may not be the sole factor affecting the absorbance, since it has been reported for some systems that the absorption coefficient changes with temperature[1–4]. This is not always the case, however, as can be seen from Ref. [14]. Therefore, it is necessary to estimate the variations in absorption coefficient with temperature.

It is interesting, at this point in the discussion, to first look at the temperature behaviour of the 'free' C=O vibration. *Figure 5* shows the carbonyl vibration spectra of pure PMMA at 20 and 200°C in an absolute scale. In this case, no hydrogen bond donor is present, and the vibration is solely due to 'free' C=O groups. It can be seen that the intensity at maximum absorbance decreases slightly at higher temperatures, while the peak tail at high frequencies increases in intensity. These variations in intensity distribution can be attributed to geometry changes with temperature. These changes are small, and the total decrease in area of the peak can be estimated via integration as being 0.3 ± 0.2%, while the centre of the vibration remains constant at 1733 cm^{-1}. Within experimental error, the influence of temperature on the 'free' C=O vibration is therefore negligible in the pure polymer. This observation seems to hold true for the blends, since for the free C=O vibration, no significant change in absorbance was observed in *Figure 3*. The absorbance coefficient determined in the first paper of this series (750 ± 40 cm^{-1} m^2 mol^{-1}) will therefore be used for this vibration at temperatures higher than T_g.

Under T_g, as can be seen from *Figure 3*, the free C=O absorbance remains virtually constant. This indicates that, within experimental error, no hydrogen bonds are broken before T_g. In reality, there may be a small number of hydrogen bonds broken before T_g, related to the temperature as described by the van't Hoff relationship, or related to the dynamic nature of hydrogen, but these clearly appear to be negligible in the present case.

Before T_g, the slight decrease in absorbance of the hydrogen bonded C=O vibration is therefore mainly attributed to the decrease in absorption coefficient, which is related to a change in the strength of hydrogen bonds with temperature. A small portion of this decrease may also be related to a decrease in hydrogen bonds. Although this was unmeasurable for free groups, it may not be so for the hydrogen-bonded vibration, since its absorption coefficient is larger (910 ± 50 cm^{-1} m^2 mol^{-1} at room temperature, as determined in the first paper of this series). The same fraction will therefore lead to a greater decrease in

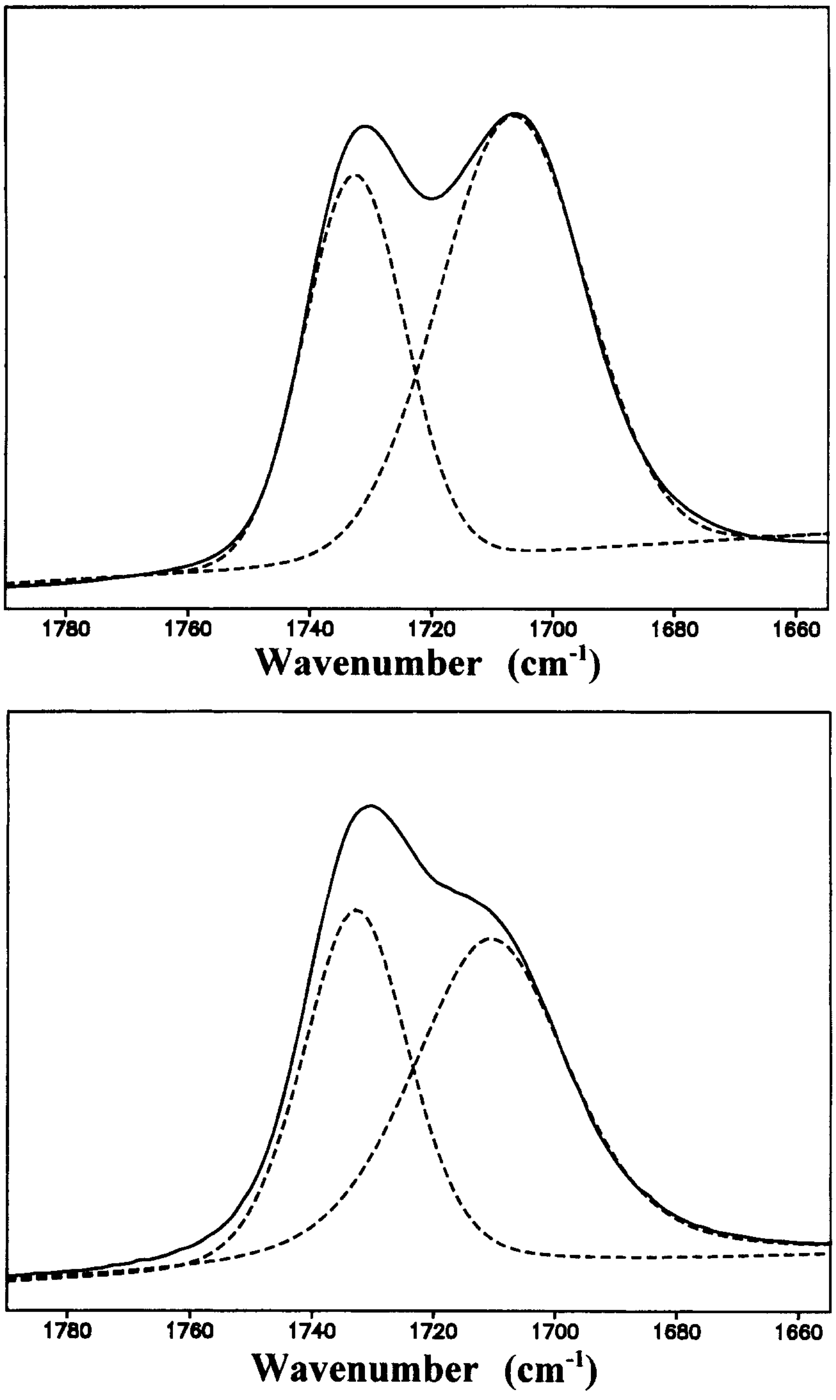

Figure 2 Continued

absorbance. Nevertheless, very few additional free C=O groups are believed to appear before T_g.

After T_g, in the glassy state, dynamic movements of the whole chain become possible. The hydrogen bond distribution therefore reflects the dynamic nature of the whole system, and not only the local dynamics of proton transfer between virtually immobile atoms, as the hydrogen bond in the glassy state can be described. The resulting increase in absorbance of the 'free' C=O vibration with temperature corresponds to the expected increase in the number of 'free' C=O groups. This was expected, and is coupled with a more abrupt decrease in the intensity of the hydrogen-bonded C=O vibration. The difference in slope is simply a reflection of the different absorption coefficients of these two vibrations.

These curves can be used to estimate the relative decrease in hydrogen bonded groups. As indicated in the first paper of this series, the Beer–Lambert law states that

$$A = abc \qquad (1)$$

where A is the absorbance, a the absorption coefficient, b the sample thickness and c the concentration of vibrating groups. For the carboxyl groups, this concentration is separated in two contributions, namely the hydrogen bonded groups, with concentration c_{HB}, and the free carbonyl groups, with concentration c_F. Since

$$c = c_{HB} + c_F \qquad (2)$$

one can write, combining equations (1) and (2)

$$c_{HB} = A_{HB}/(a_{HB}b) \qquad (3)$$

and

$$c_F = A_F/(a_F b) \qquad (4)$$

If neglecting thermal expansion of the films, the thickness b remains constant in all cases, and combination of equations (3) and (4) yields:

$$c_{HB}/c = A_{HB} a_F/(A_{HB} a_F + A_F a_{HB}). \qquad (5)$$

The absorbance was measured for $T = 20$ to $T = 200°C$. As mentioned previously, two linear relationships were established for the free carbonyl vibrations, and two for the hydrogen bonded vibrations, one for $T < T_g$ and one for $T > T_g$. Deviations at $T_g \pm 5$ are present, due to the random nature of the amorphous phase of a polymer, which causes all transitions to occur over a relatively large temperature domain. However, the remaining data obey the following relationship;

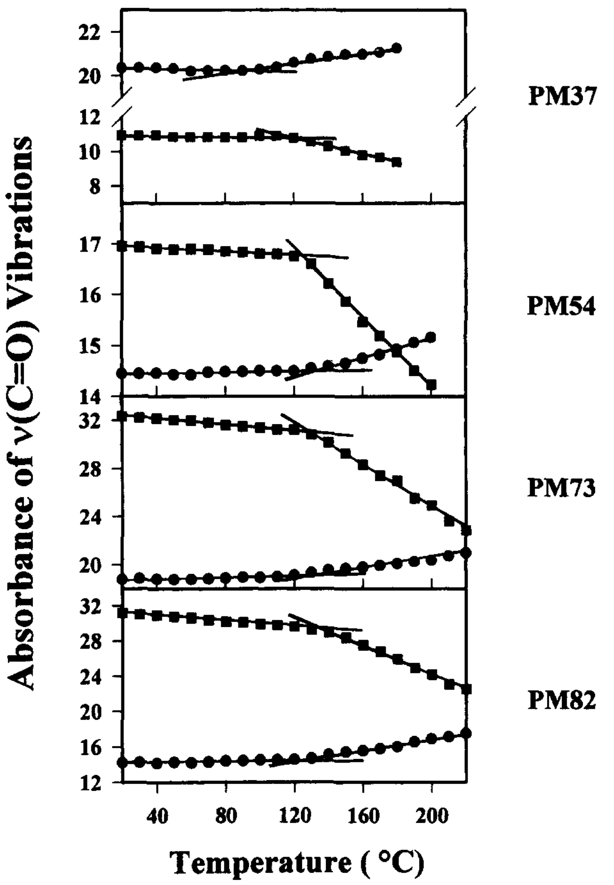

Figure 3 Variations in absorbance of 'free' and hydrogen bonded C=O vibrations with temperature for PM37, PM54, PM73 and PM82 blends: squares, hydrogen-bonded carbonyl vibration; circle, free carbonyl vibration

$$A(T) = mT + e \qquad (6)$$

where m is the slope of the straight line and e the intercept to the y axis. Subscripts HB and F are used, respectively, for the hydrogen bonded carbonyl and the free carbonyl vibrations. Superscripts b and a indicate, respectively, the relationship at T below T_g and at T above T_g. Values of m and e for the four curves at various concentrations appear in *Table 3*.

Using these equations, the value of c_{HC}/c can be calculated for any temperature. The difference between c_{HC}/c above T_g (at the temperature at which deformation is induced) and c_{HC}/c at room temperature, designated by $\Delta c_{HC}/c$, has been calculated using this approach as a function of composition and appears in *Figure 6a*. It must be stressed that T_g is taken here as the midpoint of the transition, as determined by d.s.c. and not as the transition temperature determined by *FT*i.r. The difference between the two is roughly 10°C. This definition of T_g is used here for two reasons. First, it is convenient, since most studies dealing with orientation in the literature report deformations as $T_g + x$, with T_g being the midpoint of the transition. A

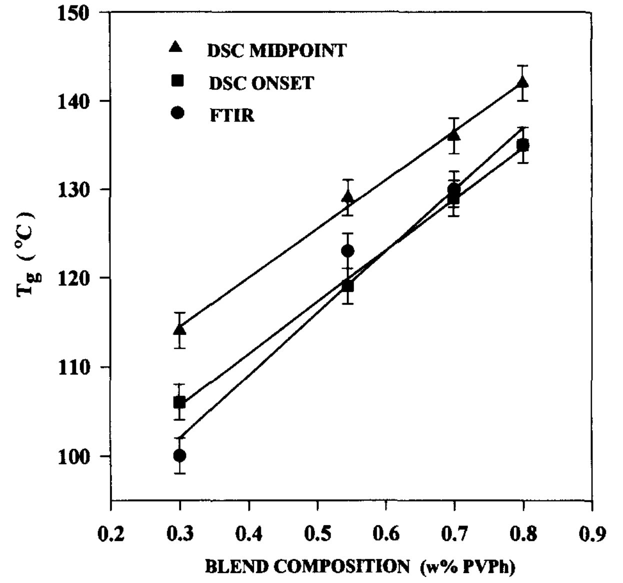

Figure 4 Variations of transition temperatures as determined by *FT*i.r. and d.s.c. as a function of composition

Table 3 Results from linear regression of the absorbance–temperature relationship for the carbonyl vibration region

	PM37	PM54	PM73	PM82
m_F^u ($\times 10^2$ cm^{-1} °C^{-1})	− 0.24	0.07	0.27	0.39
e_F^u (cm^{-1})	20.4	14.4	18.7	14.1
m_F^a ($\times 10^2$ cm^{-1} °C^{-1})	1.11	0.96	2.19	3.06
e_F^a (cm^{-1})	19.3	13.2	16.3	10.9
$T_F^{transition}$ (°C)	88	124	125	134
m_{HB}^u ($\times 10^2$ cm^{-1} °C^{-1})	− 0.19	− 0.18	− 1.30	− 1.61
e_{HB}^u (cm^{-1})	11.0	17.0	32.7	31.5
m_{HB}^a ($\times 10^2$ cm^{-1} °C^{-1})	− 2.22	− 3.00	− 8.70	− 7.92
e_{HB}^a (cm^{-1})	13.4	20.9	42.3	40.0
$T_{HB}^{transition}$ (°C)	100	123	130	135

Note: $T_F^{transition}$ indicates the transition temperature as determined by the intercept of the two linear functions determined for the free carbonyl stretching vibration, whereas $T_{HB}^{transition}$ is determined using data of the hydrogen bonded vibration

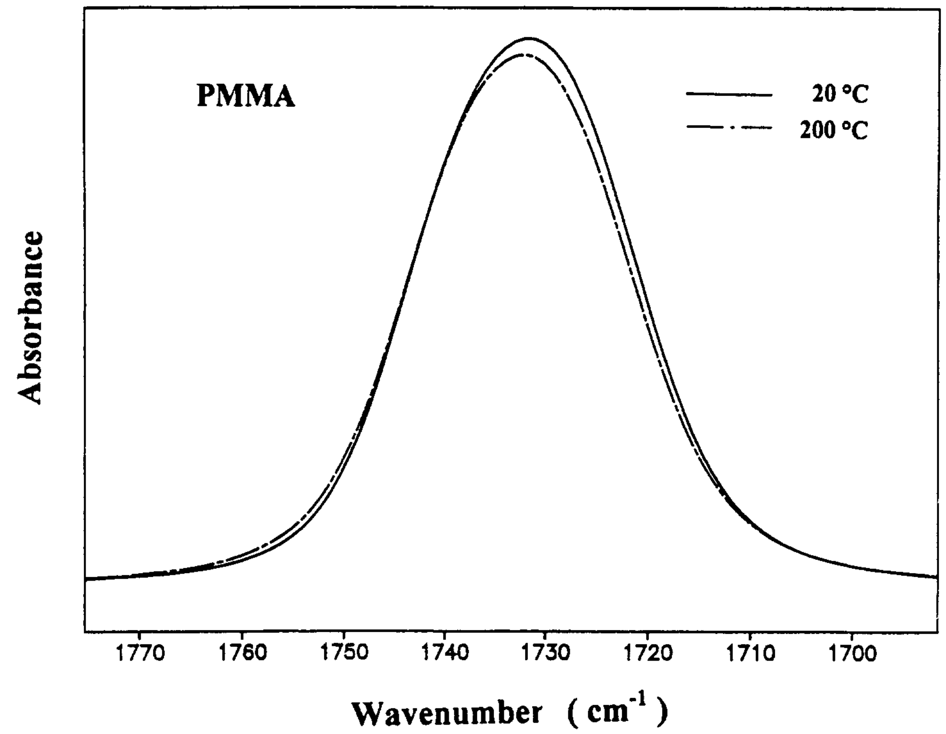

Figure 5 Spectra of the carbonyl vibration region recorded at 20 and 200°C for pure PMMA

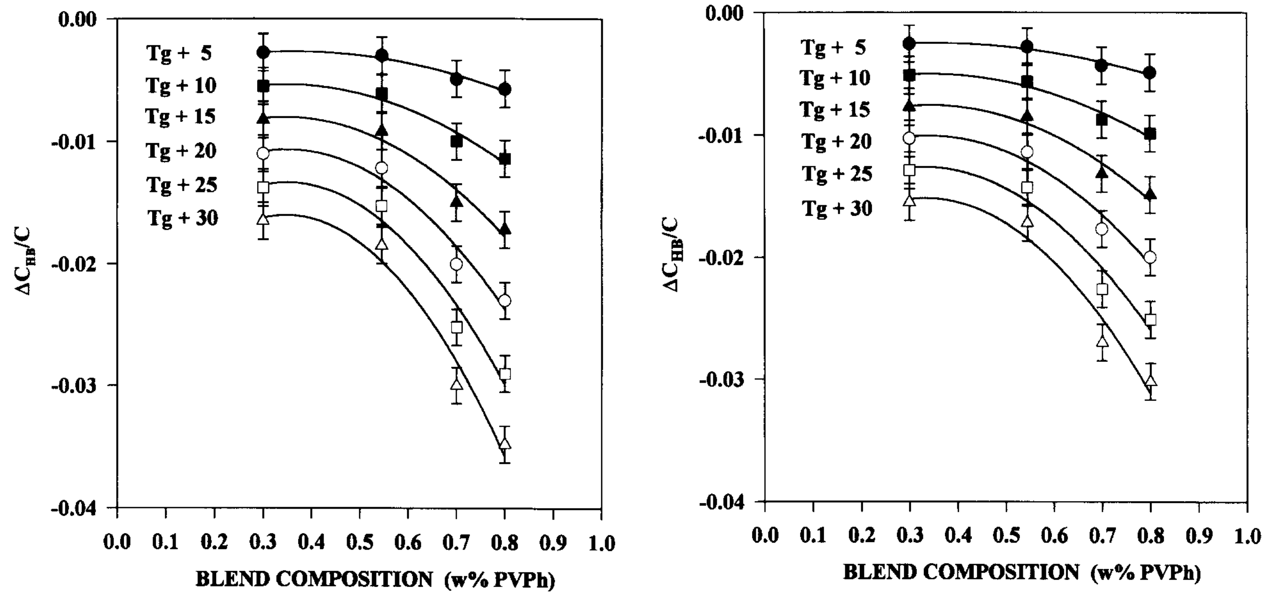

Figure 6 Variations of change in the ratio of hydrogen bonded vs. total C=O concentrations, $\Delta c_{\mathrm{HB}}/c$, at various deviations from T_g (d.s.c. midpoint): (a) using the absorption coefficients determined at room temperature; (b) after correction for changes in the absorption coefficient of the hydrogen bonded C=O vibration

second reason is that, since the glass transition spans several degrees, the midpoint should offer a better image of the average state of the system.

As can be seen from *Figure 6a*, the ratio of hydrogen bonded species decreases with increasing temperature and with increasing PVPh composition. The maximum calculated value is slightly lower than 4%. However, it is necessary to estimate deviations due to absorbance coefficient variations before anything can be concluded quantitatively.

As mentioned previously, a fair estimation of the decrease in absorption coefficient can be made using experimental data before T_g if the approximation is made that, from room temperature to T_g, the decrease in A_{HB} is only due to a decrease in a_{HB} and not to the increase in the number of free groups. In this case, c_{HB} remains constant, and the value obtained at room temperature can be used for the calculation. One can then write

$$A^{\mathrm{b}}_{\mathrm{HB}}(T) = a_{\mathrm{HB}}(T)c_{\mathrm{HB},25}b \qquad (7)$$

where $c_{\mathrm{HB},25}$ is the concentration of hydrogen bonded groups at room temperature. This yields, when combined with equation (6)

$$a_{\mathrm{HB}}(T) = (m^{\mathrm{b}}_{\mathrm{HB}}T + e^{\mathrm{b}}_{\mathrm{HB}})/(bc_{\mathrm{HB},25}) \qquad (8)$$

Since, for the free carbonyl groups, the slope is very close to zero, no correction is necessary for a_{F}, although a similar approach could be used for this coefficient using the data reported in *Table 3*.

The ratio of c_{HB}/c corrected for the decrease in absorbance from the combination of equations (5) and (8) can be calculated at any temperature. The difference between this ratio at room temperature and at various temperatures above T_g is reported in *Figure 6b* with respect to blend composition. Compared with *Figure 6a*, which showed data calculated without correction for changes in a_{HB}, it can be seen that the general trend is very similar, although before correction the absolute values for $\Delta c_{HB}/c$ were larger, which indicates an overestimation. In both cases, the increase in absolute value of $\Delta c_{HB}/c$ is related to the increase in T_g of the blends with PVPh composition, since higher temperatures will favour the existence of higher energy conformations. These are more liable not to allow hydrogen bond formation, the hydrogen bond contribution to energy being negative. Higher temperatures will also increase the total time during which dynamic hydrogen bonds are effectively broken, which also contributes to the apparent decrease in $\Delta c_{HB}/c$.

More interesting is the evolution of this curve at a function of deviation from T_g. It must first be stressed that results at temperatures close to the onset of the transition are inaccurately estimated, since no provision is made to take into account non-linearity observed by *FT*i.r. near the transition temperature. Therefore, at $T_g + 5$, where the calculation indicates that virtually no change in hydrogen bonds are observed within experimental error when comparing various compositions, the change may be underestimated. As the deviation from T_g increases, this effect becomes negligible, and deviations plotted should represent better the reality. At higher PVPh compositions, the blends begin to experience important differences in $\Delta c_{BC}/c$ compared with low PVPh compositions. For $T_g + 30$, which is the maximum temperature for which deformation of the blends was performed, the $\Delta c_{BC}/c$ reaches a value of -3.5×10^{-2} (or -3.5%) for a 80 wt% blend, whereas it was only -0.005 (or -0.5%) for the 30 wt% blend.

Values of c_{HB}/c at room temperature and at $T_g + 30$ are reported as a function of composition in *Figure 7*. As can be seen, changes in composition far exceed those versus temperature. Therefore, although changes of up to 3.5% have been observed for the inter-hydrogen bonds, these changes are minor compared with fluctuations which are liable to occur with blend inhomogeneities.

The use of room temperature data for the interpretation of orientation of PMMA–PVPh blends therefore appears fully justified from the present data. However, this may not be the case for all systems, since it has been clearly shown that, at higher temperatures, larger percentages of hydrogen bonds are broken. For systems where deformations are induced at higher temperatures (when T_g is higher or for semi-crystalline blends), this approximation may not hold true. Systems where hydrogen bonds are significantly weaker or stronger may also behave differently.

Hydroxyl stretching vibration region (3100–3700 cm^{-1})

Semi-quantitative analysis in our previous paper [13] shows that in the O–H stretching vibration region, three O–H vibrations are present, namely the 'free', intra- and inter-associated O–H stretching vibrations. The fraction of each in the blends depends strongly on blend composition. In pure PVPh, intra-association is predominant, while in blends containing low PVPh content, most hydroxyls are associated with PMMA carbonyl groups, forming inter-associated hydrogen bonds.

Unfortunately, the three vibrations present in the O–H stretching region are so overlapped that, at room temperature, only semi-quantitative work was possible. The problem becomes further complicated with increasing temperature, since the position and width of the intra- and inter-associated O–H stretching vibrations change. Furthermore, as was the case for the carbonyl group, the absorbance coefficient varies with the strength of the hydrogen bond, and will therefore vary with temperature. Accordingly, no spectral decomposition of this region was attempted. However, the total absorbance of the O–H stretching vibration was integrated and is reported in *Figure 8* as a function of temperature for the PM37 blend. As can be seen, as in the case of the carbonyl stretching vibration, a break is clearly observed at 120°C, which corresponds to the transition temperature determined using the carbonyl vibration for this composition.

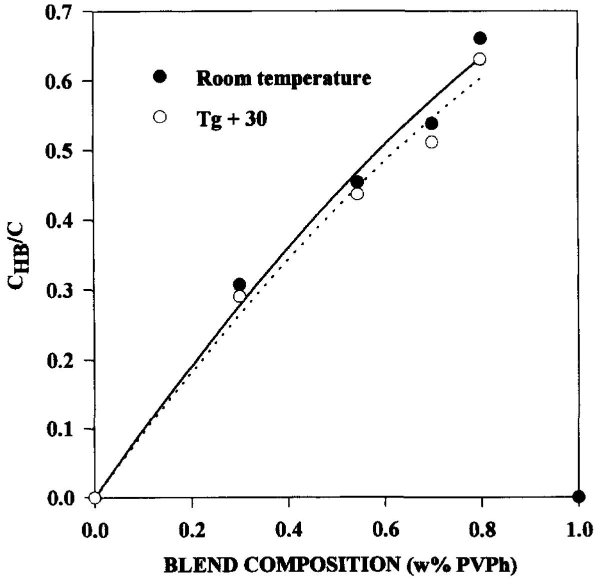

Figure 7 Comparison between the ratio of hydrogen bonded vs. total C=O vibration at room temperature and at 30°C above the T_g (d.s.c. midpoint)

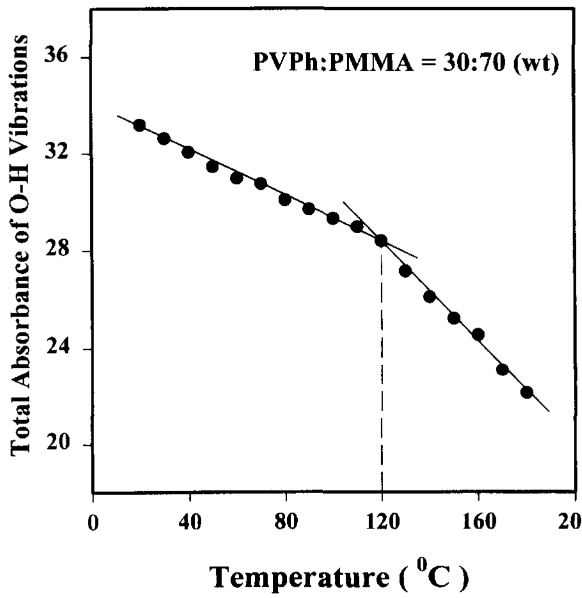

Figure 8 Changes in total absorbance of the O–H vibration region for the PM37 blend with temperature

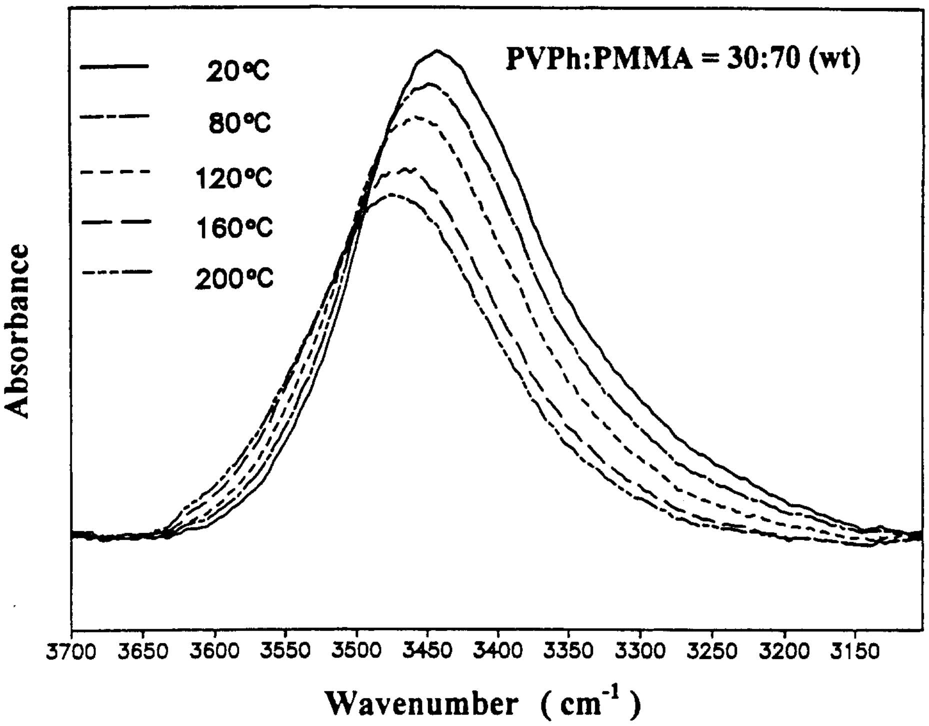

Figure 9 Hydroxyl stretching vibration region for the PM37 blend recorded at various temperatures

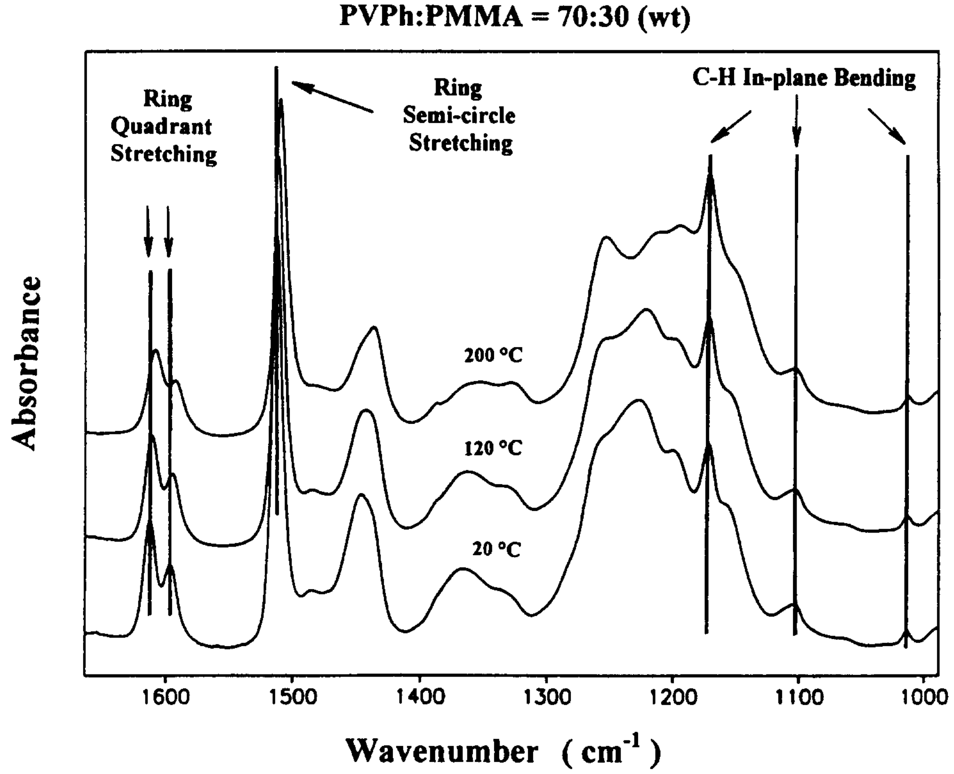

Figure 10 Scale-expanded spectra of the aromatic ring vibration region of the PM73 blend, recorded at 20, 120 and 200°C

Qualitative information can also be obtained from the analysis for these spectra. To avoid complex effects of intra-hydrogen bonds, a lower PVPh content blend, PM37, was studied more thoroughly. This blend contains, at room temperature, approximately 70% hydroxyl groups which are inter-associated. Spectra of the O–H vibration region of the PM37 blend recorded as a function of increasing temperature are shown in *Figure 9*. It must be emphasised that spectra are reported without changing their relative absorbance scale. Upon elevating the temperature, two effects are seen: the frequency of the maximum absorbance shifts to higher wavenumber, and the absorbance decreases markedly. Since inter-hydrogen bonds are predominant at this composition, changes in the O–H stretching vibration region are mostly due to the influence of temperature on the inter-associated hydrogen bonds. The weaker the hydrogen bond, the stronger the O–H valence bond, and therefore the shorter the length of the O–H bond. This leads to higher values in the O–H bond vibration constant, and as a result, the inter-hydrogen bonded O–H vibration shifts towards

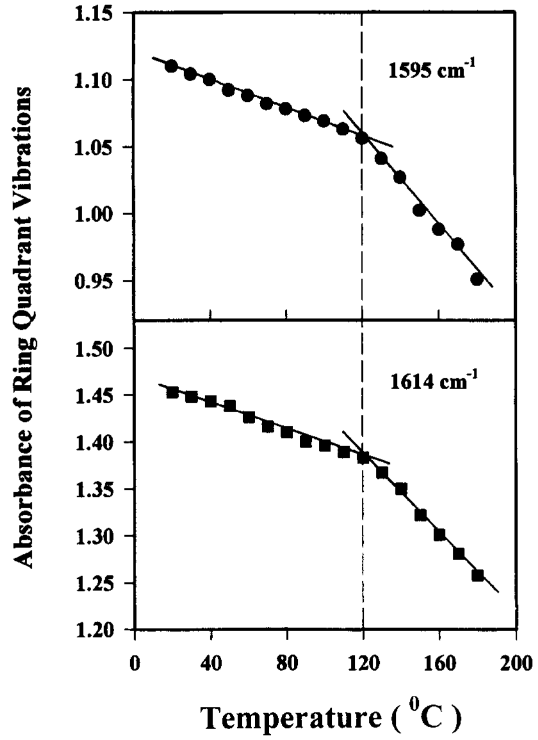

Figure 11 Changes in absorbance of ring quadrant stretching vibrations centred at 1595 and 1614 cm^{-1} as a function of temperature for the PM37 blend

higher frequencies. The 35 cm^{-1} shift to higher frequency from 20 to 200°C is in agreement with the weakening of the inter-associated hydrogen bonds. The same phenomenon has been observed in small molecules containing hydrogen bonds[15] and is also expected for intra-associated hydrogen bonds.

Aromatic ring vibration region (1000–1650 cm^{-1})

In the subtraction of spectra at 20°C and 200°C, shown in *Figure 1*, the third region which was most affected by temperature was that between 1000 and 1650 cm^{-1}, mostly related to aromatic ring vibrations. A scale-expanded spectra of this region, shown in *Figure 10*, will be used to analyse the trends of temperature effect.

It is interesting to note that vibrations at 1014, 1104 and 1173 cm^{-1}, pertaining to C–H in-plane bending of aromatic rings, remain almost constant with increasing temperature. On the other hand, vibration bands centred at 1510, 1595 and 1614 cm^{-1}, assigned to ring semicircle and quadrant stretching vibrations, systematically shift to slightly lower wavenumber. Various effects can be invoked to explain these features, including packing effects or, as proposed by Wang *et al.*[6] for an amorphous linear polyurethane, to the O–H...π interactions.

Absorbance of the ring quadrant stretching vibrations centred at 1595 and 1614 cm^{-1} is plotted vs. temperature in *Figure 11*. These two vibrations were chosen because of the absence of other vibrations in this spectral region for PMMA. It can be observed that the vibration absorbance gradually decreases with increasing temperature. A clear transition point occurs at 120°C, as was the case for O–H and C=O vibrations. This clearly indicates the relationship between aromatic ring vibration disruption and the glass transition temperature.

CONCLUSIONS

The influence of increasing temperature on the hydrogen bonds, particularly on the inter-associated hydrogen bonds, has been investigated by *FT*i.r. spectroscopy.

As expected, a clear transition in the absorbance behaviour of the υ(C=O), υ(O–H) and ring semi-circle and quadrant stretching vibrations was related to the onset of glass transition. For the carbonyl vibration, it was possible to quantify the decrease in hydrogen bond species at temperatures above T_g. At $T_g + 30$, T_g being the midpoint of the transition as determined using d.s.c., approximately 3.5% hydrogen bonds are broken comparing with room temperature, for blends containing 20 wt% and 80 wt%, respectively, of PVPh. Although these changes are significant, they are small compared with variations of hydrogen bonds with composition. Therefore, for the PVPh–PMMA blends, the use of the hydrogen bond fraction determined at room temperature for comparison with orientation behaviour appears to be justified, the error introduced being small compared with variations of the fraction of hydrogen bonds with composition.

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