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

## 1. Quantitative analysis using *FT*i.r. spectroscopy

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*FT*i.r. was used to investigate quantitatively hydrogen bonds in poly(methyl methacrylate) (PMMA) and poly(4-vinyl phenol) (PVPh) blends. An absorption coefficient of free (or non-hydrogen bonded) carbonyl vibration of $750 \pm 40 \, \text{cm}^{-1} \, \text{m}^2 \, \text{mol}^{-1}$ was determined from pure PMMA using the Beer–Lambert law, along with precise measurements of film thickness and density. By making the approximation that this value is the same for pure PMMA and for PMMA in blends, the absorption coefficient of the hydrogen bonded carbonyl vibration was calculated as $910 \pm 50 \, \text{cm}^{-1} \text{m}^2 \, \text{mol}^{-1}$. Using these values, it was deduced that less than 45% of carbonyl groups are involved simultaneously in hydrogen bonding for a blend where the PVPh to PMMA mole ratio was 1 to 1. In pure PVPh, O–H groups exist as $n$-mers, with a predominance of shorter mers such as trimers or tetramers. Upon addition of PMMA to PVPh, the fraction of intra-associated O–H bonds remains, within experimental error, constant whereas inter hydrogen bonds between PVPh and PMMA chains increase, resulting in a decrease in free O–H groups. Above 45.5 wt% PMMA, almost all 'free' O–H groups have disappeared, and intra- and inter-associated hydrogen bonds are distributed among the available OH groups. Finally, at high PMMA content (90 wt% PMMA, or 10 wt% PVPh), the probability of two PVPh chains to be close enough to allow intra-hydrogen bond formation is small, and only inter-hydrogen bonds between PVPh and PMMA are observed. © 1997 Elsevier Science Ltd.

## INTRODUCTION

When submitted to an external force, polymer chains rearrange. The preferential orientation generated by this process depends on many factors such as chain friction, entanglements, stiffness and formation of favourable interactions (van der Waals, hydrogen bonds and electrostatic interactions being the most common). In order to study the relative importance of hydrogen bonds in orientation, a blend system for which it was possible to quantify, as much as possible, the evolution of hydrogen bonded species was sought.

One of the systems which had been studied in the literature in terms of miscibility by *FT*i.r. spectroscopy, the poly(vinyl phenol)–poly(methyl methacrylate) blend, was selected[1-3]. Studies by Coleman, Graf and Painter clearly showed that the carbonyl vibration region was amenable to quantitative or semi-quantitative measurements[1]. Poly(4-vinyl phenol) (PVPh) is similar to polystyrene, but possesses a hydroxyl function attached to the aromatic ring. This group can act as a proton donor and as a proton acceptor, and form intra-associated hydrogen bonds between two PVPh repeat units in pure polymers and in blends. Poly(methyl methacrylate) (PMMA), on the other hand, only possesses carbonyl groups which are liable to act as proton acceptors, and can only participate in inter-associated hydrogen bonds with PVPh. *FT*i.r. has been

shown to be a suitable technique for the observation of changes of hydrogen bonds in the blends, especially in the hydroxyl ($3100–3700 \, \text{cm}^{-1}$) and carbonyl ($1660–1760 \, \text{cm}^{-1}$) vibration regions[2,3]. Although the PVPh–PMMA system has been studied by the group of Painter and Coleman, only data pertaining to miscibility are found in the literature. It was therefore decided to re-investigate this system with the aim of gaining a better understanding of the hydrogen bonding network present and its possible influence on chain friction during the orientation process. The conclusions of this work will serve in the analysis of the orientation of PVPh–PMMA blends in a forthcoming article.

Quantitative evaluation of this system, and of similar systems, have been discussed in the literature. Coleman and Painter's group have developed a model to predict the phase diagram of polymer blends containing hydrogen bonds, in which the equilibrium constants of hydrogen bond association were calculated from the absorptivity ratio of 'free' and hydrogen bonded vibrations[1]. One of the basic assumption made was that the absorption coefficients remain constant with temperature. It was found that the absorptivity ratio of carbonyl vibrations varies from 1.2 to 1.75, depending on the systems. Wang et al.[4] modified this model to be able to calculate the absorptivity ratio in the temperature range of the measurements.

In the PMMA/PVPh system, preliminary studies confirmed that the absorption coefficient of the free carbonyl vibration remains unaltered by temperature changes.

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**Table 1** Properties of polymer blends used in study

| Blends | Molecular weight (g mol$^{-1}$) | Weight fraction of PMMA in blend | O–H:C=O (mole) | $T_g$(°C) | $d$ (g cm$^{-3}$) | $b$( × 10$^6$ m) |
|---|---|---|---|---|---|---|
| PMMA | 100 000 | 1 | 0:1 | 94 | 1.178 | 4.0 ± 0.2 |
| PM54 | — | 0.455 | 1:1 | 129 | 1.180 | 13.0 ± 0.3 |
| PM73 | — | 0.3 | 2:1 | 136 | 1.184 | 9.7 ± 0.3 |
| PM82 | — | 0.2 | 3.3:1 | 142 | 1.187 | 23.0 ± 0.5 |
| PVPh | 30 000 | 0 | 1:0 | 156 | 1.194 | 12.7 ± 0.4 |

However, temperature appears to affect the absorption coefficient of the hydrogen bonded carbonyl vibration. This is particularly significant when studying the orientation of these blends. The determination is usually carried out near the $T_g$, which varies with blend compositions. Therefore, a method to investigate the quantitative change of hydrogen bonds in the blends was needed. In this study, the absorption coefficient of the free carbonyl vibration is obtained through the use of the absolute thickness measurement of PMMA films. An average absorption coefficient of hydrogen bonded carbonyl vibration is calculated from three different compositions of the blend. Finally, the hydrogen bond association scheme is discussed, based on quantitative and semi-quantitative calculations of group concentrations.

## EXPERIMENTAL

The polymers used in this study, poly(4-vinyl phenol), abbreviated PVPh ($M_w$ = 30 000 g) and poly(methyl methacrylate), abbreviated PMMA ($M_w$ = 100 000 g) were purchased from Polysciences Co. Thermal analysis revealed that the glass transition temperatures of PMMA and PVPh are 94°C and 156°C, respectively, as obtained from the mid-point of the heat capacity jump obtained on a Perkin–Elmer DSC-4 instrument, with a heating rate of 20°C min$^{-1}$ and calibration with indium. Blends of various compositions were prepared using a Rheocord System 40 Mixer at 180°C for 30 min. No evidence of a crystalline melting point can be observed on differential scanning calorimetry (d.s.c.) measurements, and only one glass transition temperature appears, as expected, for all blends. Evidence for a slight phase separation related to tacticity of the chains has, however, previously been obtained[3].

Samples for i.r. analysis were prepared by casting a 1% (w/v) solution of methyl ethyl ketone (MEK) on to a potassium bromide (KBr) window. This window was placed on a horizontal holder in a desiccator to reduce the evaporation rate and to avoid film cracking. After evaporation of most of the solvent at room temperature, the sample was placed in a vacuum oven at 60°C for at least 2 weeks to remove residual solvent and water. Under these conditions, Landry and Teegarden have shown that the blends were monophasic[5]. Only one $T_g$ is observed in d.s.c., as the same position as that of melt blended samples.

Film thickness measurements were performed using a Dektak IIA instrument, with a precision of 1 nm, by moving a probe over the polymer-coated KBr window surface. An average was taken from three positions on the film. In order to meet the needs for quantitative analysis, the films were cast on a mirror-like KBr window to produce uniform films and allow precise measurements. Thickness values of the films were obtained by adjusting the window surface as zero.

Spectra were recorded using a Mattson SIRIUS 100 Fourier transform i.r. spectrometer. For each spectrum, 100 scans were taken at a resolution of 2 cm$^{-1}$ using a MCT

detector. GRAMS (Galactic Industries Corp.) was used to decompose spectra with the least-squares fitting method.

Densities of polymers and their blends were determined using an hydrometer in a 20°C water bath[6]. Selected properties for both polymers and blends are listed in *Table 1*, in which, for example, the PM73 abbreviation stands for a 70 wt% PVPh and 30 wt% PMMA blend. As mentioned in *Table 1*, the PM54 blend contained 54.5 wt% PVPh. This specific concentration was prepared in order to have a 1:1 mole ratio of PVPh to PMMA.

## RESULTS AND DISCUSSION

### Principle of measurements

Beer–Lambert law[7] controls the quantitatively observed absorbance in *FT*i.r.. It is related to the concentration of the relevant vibration groups by

$$A = a \cdot b \cdot c \qquad (1)$$

where $A$ is the absorbance of a given vibration, $a$ represents the absorption coefficient, $b$ the thickness of the film, and $c$ the concentration of the vibration group. In the case of polymers, the latter can be calculated from the density, $d$, and the molecular weight of the repeat unit, $M$, by

$$c = \frac{d}{M} \qquad (2)$$

Therefore, for the quantitative measurement of carbonyl groups, the absorption coefficient of C=O vibration could be directly calculated from the absorbance of pure PMMA:

$$a_{F_{CO}}^0 = \frac{A_{F_{CO}}^0 \cdot M_1}{b^0 \cdot d^0} \qquad (3)$$

where the subscript $F$ denotes free vibration, $CO$ indicates that the carbonyl vibration is considered, and superscript 0 denotes the pure PMMA state.

In the blends, some of the carbonyl groups of PMMA associate with hydroxyl groups of PVPh to form inter-associated hydrogen bonds. As a result, part of the free carbonyl groups become hydrogen bonded carbonyl groups. Nevertheless, the total concentration of carbonyl groups does not vary, and is equal to the sum of free and hydrogen bonded carbonyl groups, described as follows:

$$c_{T_{CO}} = c_{F_{CO}} + c_{HB_{CO}} = \frac{A_{F_{CO}}}{a_{F_{CO}} \cdot b} + \frac{A_{HB_{CO}}}{a_{HB_{CO}} \cdot b} \qquad (4)$$

with

$$c_{T_{CO}} = \frac{d \cdot w_1}{M_1} \qquad (5)$$

where $w_1$ is the weight fraction of PMMA in blends, $M_1$ is the molecular weight of PMMA repeat unit, and subscripts $T$ and $HB$ present total and hydrogen bonded groups, respectively.

It was assumed that the absorption coefficients of free $C=O$ vibrations in the blends, $a_{F_{CO}}$, is the same as in pure PMMA, $a^0_{F_{CO}}$. The absorption coefficient of the hydrogen bonded carbonyl vibration can then be calculated as:

$$a_{HB_{CO}} = \frac{\dfrac{A_{HB_{CO}}}{A_{F_{CO}}} \cdot M_1}{\dfrac{d \cdot b \cdot w_1}{A_{F_{CO}}} - \dfrac{d^0 \cdot b^0}{A^0_{F_{CO}}}} \qquad (6)$$

The hydroxyl groups of PVPh do not form only intra-associated hydrogen bonds with carbonyl group of PMMA, but also intra-associated hydrogen bonds with other hydroxyl groups. For the hydroxyl vibrations, similarly, the concentrations of hydroxyl groups in the blends could be expressed as

$$C_{T_{OH}} = C_{F_{OH}} + C_{I_{OH}} + C_{A_{OH}} \qquad (7)$$

where subscript $I$ and $A$ represent inter- and intra-associated groups, respectively. The total O–H concentration can be obtained by

$$C_{T_{OH}} = \frac{d \cdot w_2}{M_2} \qquad (8)$$

where $w_2$ is the weight fraction of PVPh in the blends, and $M_2$ is the molecular weight of the PVPh repeat unit.
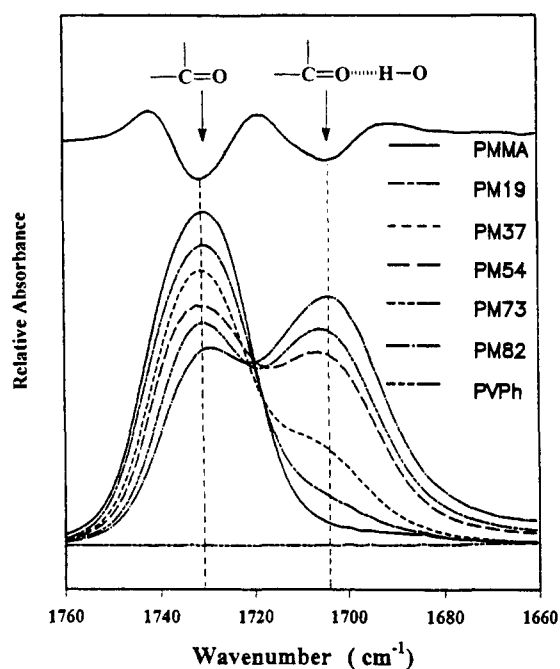
In principle, the concentration of inter-associated



**Figure 1** *FT*i.r. spectra of the carbonyl vibration region. Lines from bottom to top are pure PVPh, PM82, PM73, PM54, PM37, PM19, pure PMMA and the second differential of the PM73 spectrum

hydroxyl groups in the blend should be equal to that of the hydrogen bonded carbonyl groups and, therefore, $C_{I_{OH}} = C_{HB_{CO}}$. The absorption coefficient of inter-associated O–H vibrations can be derived if it is assumed that the absorption coefficients of inter- and intra-associated O–H vibrations are the same. This approximation is necessary since the intra- and inter-associated vibrations are completely overlapped in most of the samples. Strictly speaking, this is not the case, since it has been shown that the absorption coefficient is a function of the frequency shift[8]. However, since the intra and inter-associated vibrations are completely overlapped, this assumption seems justified. It will be one of the major sources of error of the calculation, which is, therefore, only semi-quantitative. Finally, the concentration of 'free' O–H groups can be calculated by subtracting the concentrations of inter-and intra-associated O–H groups from the total O–H concentration.

*Quantitative measurement of carbonyl concentration in the blends*

*FT*i.r. spectroscopy is particularly suitable for quantitatively investigating carbonyl concentrations in blends. For the PVPh/PMMA system studied here, one of the components (PMMA) contains a carbonyl group, yielding a $\nu(C=O)$ stretching mode at $1733 \text{ cm}^{-1}$, while the other (PVPh) shows no absorptivity in carbonyl vibration region ranging from 1660 to $1760 \text{ cm}^{-1}$. Any *FT*i.r. spectrum change related to this region is, therefore, directly attributed to changes in the carbonyl group environment, such as the formation of hydrogen bonds with O–H groups. As an illustration of typical trends observed for the various blends, the carbonyl vibration region of PVPh/PMMA blends are shown in *Figure 1*, in relative scaling, as a function of composition.

For pure PMMA, the carbonyl vibration band centred at $1733 \text{ cm}^{-1}$ shows a typical Gaussian-type distribution. When blending with PVPh, part of the carbonyl groups of PMMA will associate with hydroxyl groups of PVPh. This causes the appearance of a second band, the hydrogen bonded carbonyl vibration, observed at a lower wavenumber, as can be seen in *Figure 1*. It can be clearly seen that, with the increase of PVPh composition in the blends, the relative absorbance of the hydrogen bonded carbonyl vibration increases, while the free carbonyl band decreases, indicative of the transformation of free carbonyl to hydrogen bonded carbonyl groups. It can be qualitatively estimated that, with the increase of the global PVPh composition in the blends, the concentration of hydrogen bonded carbonyl groups increases, while the free $C=O$ concentration decreases. In order to calculate quantitatively the concentrations of carbonyl groups in the blends, four key terms have to be known: the absorption coefficients and the absolute absorbances for both free and hydrogen bonded carbonyl vibrations.

**Table 2** Curve fitting results for PVPh/PMMA blends at room temperature

| Blends | Free $\nu(C=O)$ | | | Hydrogen bonded $\nu(C=O)$ | | |
|---|---|---|---|---|---|---|
| | $\upsilon$ (cm$^{-1}$) | $W_{1/2}$ (cm$^{-1}$) | $A_{F_{CO}}$ (cm$^{-1}$) | $\upsilon$ (cm$^{-1}$) | $W_{1/2}$ (cm$^{-1}$) | $A_{HB_{CO}}$ |
| PMMA | 1733[a] | 20[a] | 35.3 | — | — | — |
| PM54 | 1733[a] | 20[a] | 28.7 | 1707 | 28 | 31.3 |
| PM73 | 1733[a] | 20[a] | 12.3 | 1707 | 28 | 18.3 |
| PM82 | 1733[a] | 20[a] | 13.4 | 1705 | 29 | 26.0 |

[a]Value fixed during curve fitting

**Table 3** Absorption coefficients and concentrations of both free and hydrogen bonded carbonyl vibrations

| Blends | $C_{T_{CO}}$ ($\times 10^{-3}$ mol m$^{-3}$) | $C_{F_{CO}}$ ($\times 10^{-3}$ mol m$^{-3}$) | $C_{HB_{CO}}$ ($\times 10^{-3}$ mol m$^{-3}$) | $C_{HB_{CO}}/C_{T_{CO}}$ | $a_{F_{CO}}$ (cm$^{-1}$ m$^2$ mol$^{-1}$) | $a_{HB_{CO}}$ (cm$^{-1}$ m$^2$ mol$^{-1}$) |
|---|---|---|---|---|---|---|
| PMMA | 11.78 | 11.78 | 0 | 0 | 750 ± 40 | — |
| PM54 | 5.40 | 2.95 | 2.45 | 0.45 | 750 ± 40 | 994 ± 32 |
| PM73 | 3.66 | 1.69 | 1.97 | 0.54 | 750 ± 40 | 1015 ± 46 |
| PM82 | 2.30 | 0.78 | 1.52 | 0.66 | 750 ± 40 | 709 ± 44 |
| Average | — | — | — | — | 750 ± 40 | 910 ± 50 |
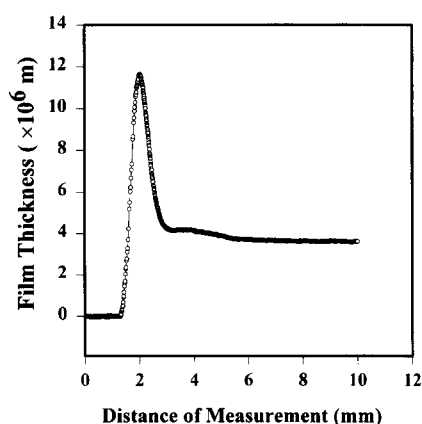


**Figure 2** Thickness measurement of PMMA film. Zero is the surface of the KBr window
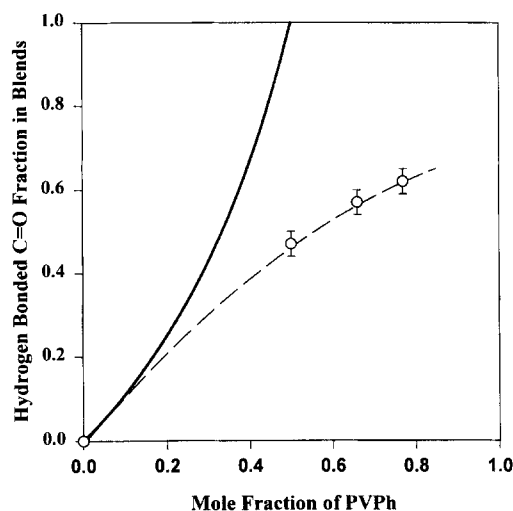


**Figure 3** Percentage of hydrogen bonded carbonyl groups in the blends. Solid line presents a theoretical prediction ( = $C_{OH}/C_{C=O}$ if $M_2 < 0.5$, = 1 if $M_2 > 0.5$). Dashed line denotes experimental results (= $C_{HB\ C=O}/C_{TOTAL\ C=O}$)

A curve-fitting procedure was used to resolve the absorbance of both carbonyl vibrations. However, because of a serious peak overlap at low PVPh compositions, the calculation was performed only at higher PVPh compositions (up to 54.5 wt%). The second differential of these spectra shows clearly two bands pertaining to carbonyl groups, which are centred at 1733 and 1707 cm$^{-1}$, corresponding to free and hydrogen bonded C=O vibrations, respectively. In the case of the 1733 vibration, its position is exactly the same as that of pure PMMA, as expected. This supports the assumption that the absorption coefficients are the same for free carbonyl vibrations in both pure PMMA and the blends. However, for the

hydrogen-bonded vibration, variations of 1–2 cm$^{-1}$ were observed, and are attributed to the changes in hydrogen bond geometry distribution and strength as a function of composition in the blends. During curve fitting, accordingly, the position and width of the free C=O vibration were kept fixed at the position observed for the pure polymer, whereas those of the hydrogen bonded vibration were allowed to vary. In all cases, a Gaussian bandshape was used. The results of the curve-fitting (vibration positions $v$, absorption intensities $A$ and peak widths at half height $W_{1/2}$) are listed in *Table 2*.

The absorption coefficient of the free carbonyl vibration can be directly calculated from the pure PMMA spectrum according to equation (3). A key parameter in these calculations is the film thickness. Although a horizontal plane was used to prepare the film on mirror-like KBr windows, a perfectly uniform film was difficult to obtain by solution casting, a rim appearing at the outer edge of the film, due to the interactions which control the contact angle between the solution and the KBr surface. A typical measurement of film thickness is illustrated in *Figure 2*. As can be seen, the thickness of the film rim is twice that of the centre part of the film. When measuring the *FT*i.r. spectra, a mask was used to select only the centre of the film, for which the measurements show that the thickness is almost constant. The value for the film thickness reported in *Table 1* relates to the value of the centre of the film. Using this value, the absorption coefficient of the free carbonyl vibration is calculated as 750 ± 40 cm$^{-1}$ m$^2$ mol$^{-1}$.

For the blends, the total concentration of C=O groups can be calculated from the measurement of the blend densities, according to equation (5). Taking the curve-fitting results listed in *Table 2*, the concentration of free and hydrogen bonded C=O groups, individually, can be obtained. For each composition, the absorption coefficient of the hydrogen bonded C=O stretching mode is calculated in *Table 3*. An average value of 910 ± 50 cm$^{-1}$ m$^2$ mol$^{-1}$ can be obtained for the hydrogen bonded C=O group for these three compositions. The ratio $a_{HB}/a_F$ is, therefore, 1.2, a value comparable with previously published data for similar systems, which varied from 1.2 to 1.75[9–11].

The proportion of hydrogen bonds determined is listed in *Table 3*, whereas the percentage of hydrogen bonded carbonyl groups calculated from the results of C=O concentrations listed in *Table 3* is shown in *Figure 3* as a function of PVPh mole fraction. It is observed that, with the increase in PVPh content, the fraction of hydrogen bonded carbonyl groups markedly increases.

If one thinks strictly in terms of number of interacting groups, since there is one hydrogen donor per repeat unit in PVPh, and one hydrogen acceptor per repeat unit in PMMA, one can calculate the maximum number or inter-hydrogen bond that can be experienced by the C=O groups as being equal to the proportion of PVPh repeat units in the blend, if PVPh is the minor constituent, and likewise as

equal to the proportion of PMMA repeat units in the blend when PMMA is the minor constituent. As the mole ratio of O–H to C=O is 1 to 1 in the PM54 blend, one could expect a maximum of 100% hydrogen bonded carbonyl groups. The fraction of hydrogen bonded C=O groups in the blends can be expressed as:

$$\frac{C_{HB_{CO}}^{m}}{C_{T_{CO}}} = \frac{w_2/M_2}{w_1/M_1} \quad \text{for } w_2 \le 0.545 \qquad (9)$$

where $m$ stands for the maximum 'theoretical' concentration of inter hydrogen bonds at a given PMMA concentration. For $w$ higher than 0.545, or when the mole fraction of PVPh exceeds that of PMMA, all C=O groups have the possibility to form hydrogen bonds with O–H groups. Therefore

$$\frac{C_{HB_{CO}}^{m}}{C_{T_{CO}}} = 1 \quad \text{for } w_2 > 0.545 \qquad (10)$$

The calculated values for this 'theoretical' prediction of maximum hydrogen bonded C=O fraction are plotted in *Figure 3*, as represented by a solid line. The experimental values, represented by a dashed line, fall systematically below this prediction and barely reaches a maximum of 0.7 for a mole fraction of 0.8 PVPH (for the PM82 blend), clearly showing the shortcomings of this type of approach.

This is clearly related to the fact that the number of interactions between polymers will not be ruled by the sole stoichiometry, but by the balance of thermodynamical energy terms in the blend, namely enthalpy, combinatorial and non-combinatorial entropy, which in turn are related to the energy of the various interactions and to backbone and steric hindrance. According to Flory's RIS theory[12], it is very unlikely that all C=O groups will hydrogen bond with O–H groups, because of the rigidity of backbones of both polymer chains. Furthermore, the self-association ability of hydroxyl groups may also compete with the formation of inter-hydrogen bonds. The self-association model proposed by the group of Painter and Coleman takes these factors into account through the use of an equilibrium constant. However, since the aim of this work is not to evaluate such effects, a fit with equilibrium constants has not been attempted here.

*Qualitative evaluation of changes in the hydroxyl stretching region*

As mentioned in the Introduction, the hydroxyl region is not as easily amenable to quantitative evaluation because of vibration overlap and possible changes in absorption coefficients of the intra- and inter-associated O–H component. A semi-quantitative evaluation can nevertheless shed light on the fundamental changes in hydrogen bonding with composition. Spectra of the hydroxyl stretching vibration region are shown in *Figure 4*.

Two vibration bands related to 'free' and intra-associated O–H group populations appear in pure PVPh, as reported in the literature[13]. The second differential clearly shows that these groups are centred at 3532 and 3380 cm$^{-1}$, respectively. It must be noted that the 'free' O–H groups, as reflected by the O–H stretching vibration, indicate O–H groups where the hydrogen atom is not involved in hydrogen bonding. The oxygen atom, however, is liable to be involved in a hydrogen bond with a neighbouring O–H group. It is not possible to determine experimentally from these spectra the proportion of oxygen atoms of the hydroxyl groups that are involved in hydrogen bonding. However, if one neglects bifurcated hydrogen bonds, where
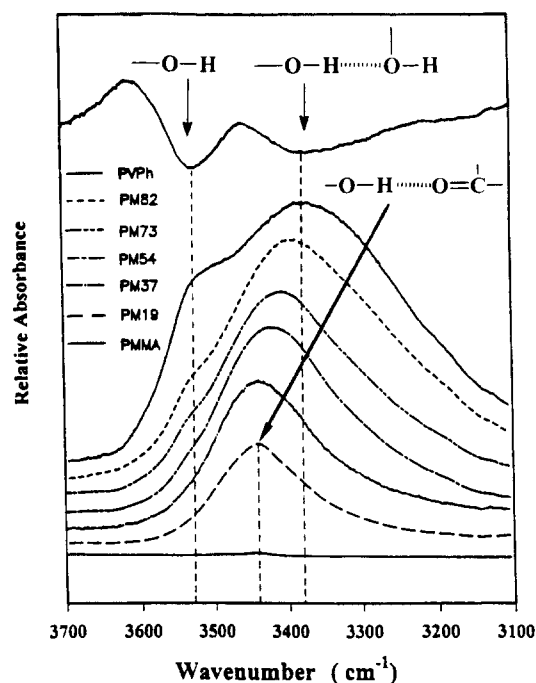


**Figure 4** FTi.r. spectra of hydroxyl vibration region. Lines from bottom to top are pure PMMA, PM19, PM37, PM54, PM73, PM82, pure PVPh and the second differential of the PVPh spectrum

an oxygen atom forms hydrogen bonds with two different hydrogen atoms, there must be as many hydrogen atoms involved in hydrogen bonding as there are oxygen atoms acting as acceptors, whether they belong to hydroxyl or, in the case of the blends, to carbonyl groups. Therefore, the information afforded by FTi.r. spectroscopy will allow a complete description of the system.

In blends with PMMA, the shoulder of the 'free' band becomes undetectable, while the main peak shifts to a higher wavenumber. This peak shift is interpreted as being due to the appearance of a third contribution at slightly lower wavenumber, that of inter-association between PVPh and PMMA through hydrogen bonding. Peak changes qualitatively indicate that 'free' and intra-associated O–H groups are decreasing to the benefit of the formation of inter-associated hydrogen bonds at higher PMMA compositions. For the 10 wt% PVPh composition (or 8.5 mol% PVPh), however, a single Gaussian-shaped band is observed, centred at an intermediate position of 3443 cm$^{-1}$. This vibration is assigned to inter-associated O–H groups.

When more carbonyl groups of PMMA are blended in, the number of 'free' O–H groups decreases due to the formation of inter-associated hydrogen bonds with C=O groups. Intra- and inter-associated O–H group vibrations are approximately centred at 3350 and 3440 cm$^{-1}$, respectively. From the point of view of energy potentials, the higher the wavenumber, the stronger the bond[14,15]. Therefore, the bond of the intra-associated O–H groups should be weaker than that of the inter-associated O–H groups. This indicates that intra-associated hydrogen bonds are stronger than inter-associated hydrogen bonds. It could be difficult to understand why, when C=O groups are blended in, a large part of the intra-association, which corresponds to stronger hydrogen bonds, is replaced by inter-association. However, from a statistical point of view, it is easily understood, since at a 10 wt% PVPh composition, the total concentration of C=O group, $C_{T_{CO}}$, is about 11 times that of O–H group, $C_{T_{OH}}$. As a result, the O–H groups

**Table 4** Curve-fitting results in hydroxyl vibration region

| Blends | 'Free' ν(O–H) | | | | Intra-bonded ν(O–H) | | | | Inter-bonded ν(O–H) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\nu^*$ (cm⁻¹) | $W_{1/2}^*$ (cm⁻¹) | $A_{FOH}$ (cm⁻¹) | $C_{FOH}$ ($\times 10^{-3}$ mol m⁻³) | $\nu^*$ (cm⁻¹) | $W_{1/2}^*$ (cm⁻¹) | $A_{AOH}$ (cm⁻¹) | $C_{AOH}$ ($\times 10^{-3}$ mol m⁻³) | $\nu^*$ (cm⁻¹) | $W_{1/2}^*$ (cm⁻¹) | $A_{IOH}$ (cm⁻¹) | $C_{IOH}$ ($\times 10^{-3}$ mol m⁻³) | $C_{TOH}$ ($\times 10^{-3}$ mol m⁻³) | $C_{FOH}/C_{TOH}$ | $C_{IOH}/C_{TOH}$ | $C_{AOH}/C_{TOH}$ |
| PM54 | 3532 | 70 | 0.8 | 0.2 | 3350 | 240 | 88 | 3.0 | 3442 | 140 | 74 | 2.45 | 5.41 | 0.04 | 0.45 | 0.6 |
| PM73 | 3532 | 70 | 3 | 1.5 | 3350 | 240 | 85 | 3.9 | 3442 | 140 | 44 | 1.97 | 6.92 | 0.2 | 0.28 | 0.6 |
| PM82 | 3532 | 70 | 17 | 2.5 | 3350 | 240 | 245 | 4.8 | 3442 | 140 | 74 | 1.52 | 7.89 | 0.3 | 0.19 | 0.6 |
| PVPh | 3532 | 70 | 17.9 | 4.1 | 3350 | 292 | 186 | 6.5 | — | — | — | — | 10.0 | 0.4 | 0 | 0.6 |

*Values fixed during curve fitting.

of PVPh are randomly distributed among a large number of C=O groups. Almost all O–H groups will form inter-hydrogen bonds with C=O groups of PMMA, and only 5% of the O–H groups will remain 'free' or intra-associated. When the PVPh composition is increased, the probability that O–H groups bind to other O–H groups instead of only to C=O groups increases, and the energy potential will play a more important role in the resulting ratio of intra- and inter-associated hydrogen bonds.

As expected, in the PM54 blend there exist three distinct contributions to O–H stretching modes: 'free', intra- and inter-associated O–H vibrations. In order to estimate the fraction of these three vibrations, curve fitting was used to separate the absorbance of each. As mentioned previously, results should be taken as semi-quantitative in this case, since the vibrations are strongly overlapped, rendering the spectral separation procedure less trustworthy, because of the proximity of $CH_2$ asymmetric and symmetry stretching vibrations, and, last but not least, because of the approximation that has been made that the inter- and intra-vibrations have the same absorption coefficient. During fitting, the centre of the vibrations and their width were fixed at the same position as in pure PVPh, except for the width of the 3350 cm⁻¹ vibration, since it was found necessary to vary this parameter in order to have a reasonable fit. This indicates that the geometries adopted by intra-bonded groups are slightly different in the blends as compared with the pure polymer, owing to the disruption caused by the presence of PMMA chains.

As proposed previously, the concentration of inter-associated hydroxyl groups must be equal to that of the hydrogen bonded carbonyl groups. The absorption coefficient of inter-associated O–H vibration, $a_{I_{OH}}$, can then be calculated as approximately 2240 cm⁻¹ m² mol⁻¹. Because the intra-associated O–H vibration shows a vibration behaviour and distribution similar to that of the inter-associated O–H vibration, it can be proposed that, for this system, as a first approximation, these two vibrations have the same absorption coefficient. Using this approximation, the concentration of intra-associated O–H, $C_{A_{OH}}$, can be estimated from the absorption coefficient value of the inter-associated O–H vibration. The total concentration of hydroxyl groups can be obtained from equation (8). Finally, the concentration of 'free' O–H groups can be calculated by subtracting the value of intra- and inter-associated O–H groups from the total initial O–H concentration. These results are listed in *Table 4*.

Before discussing these results further, it is necessary to verify their reliability. Unlike the carbonyl vibration region, in the hydroxyl vibration region, the intra-associated O–H band is seriously overlapped with the inter-associated O–H band. Consequently, absorbance values of these vibrations as obtained from curve-fitting can seem arbitrary. An internal verification can be made by calculating the absorption coefficient of inter-associated O–H vibration directly from the 10 wt% of PVPh blend. For this composition, it was estimated that the spectrum of hydroxyl region involves 95% inter-associated O–H groups. This yields a value of $a_{I_{OH}} = 2610$ cm⁻¹ m² mol⁻¹, in good semi-quantitative agreement with the value found from curve-fitting results, which was 2240 cm⁻¹ m² mol⁻¹.

*Description of the chain association scheme*

The quantitative and semi-quantitative evaluation of the proportions of free and hydrogen bonds, combined with qualitative observations of spectral changes, can be used to

(a) (b) (c)
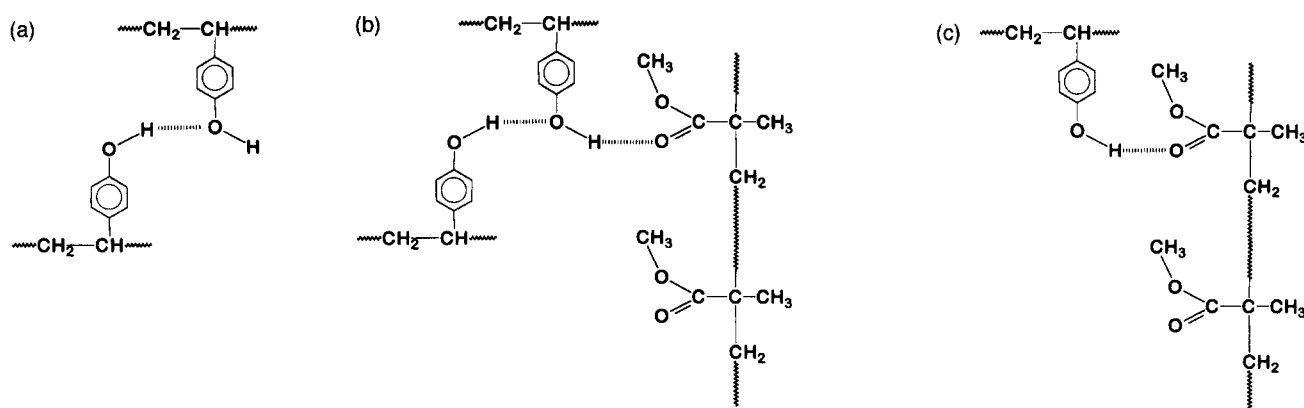
**Figure 5** Scheme of hydrogen bond association in PVPh/PMMA blends: (a) pure PVPh, exhibiting intra-associated dimer; (b) High PVPh composition (>54.5 wt%), showing intra- and inter-associated hydrogen bonds; (c) low PVPh composition ( $\approx$ 10 wt%), exhibiting inter-associated dimers

understand better the chain association scheme present in the blends. Since the pure polymers as well as the blends are amorphous, this association is not regular, as in a crystalline phase. A wide array of chain associations are expected, and variations will occur both in the local conformations of the interacting chains and in the geometry of the hydrogen bonds. PVPh–PVPh (or intrachain) as well as PVPh–PMMA (or interchain) associations will both be submitted to these factors. Nevertheless, energetic (both entropic and enthalpic) and steric considerations favour some types of association. O–H groups show a strong tendency to form hydrogen bonds, which is related to the stabilizing energy the hydrogen bond affords to the system. However, the quantity of hydrogen bonds will be determined by the total energetics of the system, and formation of hydrogen bonds can be hindered by steric repulsion. Therefore, the distribution of hydrogen bonds will yield insight on the overall organization of the blend.

Temperature will also have an effect on this association scheme, as higher temperatures will increase the probability of existence of higher-energy conformers and associations. Indeed, the temperature history has been shown to affect the number of hydrogen bonds formed in the blends[3]. A 2% variation in the number of hydrogen bonds formed was observed for a 30% PVPh–PMMA blend when cooling the blend slowly as compared with quenching with liquid nitrogen. Furthermore, this change was also associated with a change in the proportion of a higher $T_g$ component and a lower $T_g$ component, which have been assigned to different local organizations or conformations in the blends[3]. Nevertheless, in view of its small effect as compared with that of composition, temperature history will be neglected in the following discussion.

For pure PVPh, only 'free' and intra-associated O–H vibrations are present. The fraction of intra-associated hydroxyl hydrogen atoms, as determined by the ratio $C_{A_{OH}}/C_{T_{OH}}$, is 0.7. This does not mean, however, that approximately 70% of the O–H groups participate in hydrogen bonding, since the oxygen atom of O–H is liable to be bonded without affecting the spectra. In order to understand better the effect of different types of associations on the spectra, it is necessary to consider the theoretical fraction of hydroxyl groups which would remain free in various $n$-mers. For a dimer, one would have a H···O–H entity, and a half or 50% hydroxyl hydrogens would remain free. For a trimer, H···O–H···O–H, 2/3 hydroxyl groups or 67% would be free, for tetramers, 1/4 or 75%, and so forth. The fact that the observed value of

70% lies between that of a trimer and a tetramer is in agreement with the existence of various types of chain associations, but also indicates that the majority of chains will probably be in the form of short mers, although some free O–H groups and some longer $n$-mers will undoubtedly also be present.

When blending with PMMA, it is surprising to observe that the percentage of intra-associated hydroxyl groups, as given by $C_{A_{OH}}/C_{T_{OH}}$, does not vary much, remaining around 60% in these three blends. Compared with the 70% value of pure PVPh, the slight difference is well within the estimated error, but could also be due to the increasing probability that a PMMA chain will act as a 'chain stopper' in the formation of longer $n$-mers. Viewed in a slightly different way, the probability that PMMA will be part of an $n$-mer increases, decreasing the number of free hydroxyl hydrogens of the $n$-mer. The size of the $n$-mers may, therefore, not be affected.

The only quantitative value in this analysis is that of the fraction of inter-associated groups, $C_{I_{OH}}/C_{T_{OH}}$, which varies from 0% in pure PVPh to 45% in PM54. This dramatic increase is accompanied by a decrease in 'free' hydroxyl hydrogens, as denoted by the $C_{F_{OH}}/C_{T_{OH}}$ value. Eventually, the 'free' O–H groups almost disappear for the PM54 blend. If PMMA merely acted as a diluant in the system, one would expect a decrease in intra-association, but not in the number of free groups. In the present case, within experimental error, no decrease in intra-association is observed, although there could be one since the precision of the measurements is not very good. However the decrease in free groups is clear, and cannot be rationalized in terms of dilution. Energetics of the system must be taken into account. Hydrogen bonds between PVPh and PMMA are stronger and, therefore, more stable, than hydrogen bonds between PVPh chains. This means that a further loss of entropy will be 'tolerated' energetically by the system without inducing phase separation. The energy is such that even the hydroxyl groups that were previously 'free' (or that formed the end of $n$-mers), are now able to form hydrogen bonds with PMMA. The fraction of intra-associated O–H bond remains constant, while the 'free' O–H groups (or more aptly the free hydroxyl hydrogens) are consumed. As mentionned previously, at 10 wt% PVPh (or 90 wt% PMMA), the O–H vibration region is clearly dominated by the inter-associated O–H vibration. At this concentration, the PMMA network is clearly dominant, and PVPh chains organize along with it. The probability that PVPh chains are close enough to allow hydrogen

bond formation is small, and interchain hydrogen bonds dominate.

A schematic illustration of the major hydrogen bonded species present is depicted in *Figure 5*. For pure PVPh, only intra-hydrogen bonds exist, which have been depicted in the figure as dimeric, although a variety of *n*-mer length is bound to be present. Roughly speaking, very few O–H groups are really single, most being part of *n*-mers. It cannot, however, be determined whether the intra-associated hydrogen bonds link O–H groups belonging to two different polymer chains or to the same chain.

As depicted in *Figure 5b*, when PMMA is blended in, the C=O group of PMMA will be able to form inter-associated hydrogen bonds with the end proton of the *n*-mers, or the 'free' O–H bonds. At low PMMA composition (PM82 and PM73), three types of O–H vibrations are present simultaneously: 'free', intra- and inter-associated O–H vibrations. Eventually, the 'free' O–H group intensity almost disappears at 1:1 O–H to C=O mole ratio (PM54 blend). The fraction of intra-associated O–H bond then stays constant. Not all PMMA C=O groups are used to form inter-associated hydrogen bonds, because of energetic considerations (both enthalpic and entropic). This could be taken into account quantitatively by the association model proposed by Painter and Coleman[1].

With the increase of PMMA composition in the blend, the organization shifts to one dominated by the PMMA chains. At 10 wt% PVPh, one C=O group will be surrounded by an average of 11 O–H groups. As a result, inter-associated hydrogen bonds form predominately, as shown in *Figure 5c*.

## CONCLUSIONS

(1) The absorption coefficient of free carbonyl groups can be calculated from the *FT*i.r. absorbance when the film thickness and density are measured accurately. From the assumption that the absorption coefficients of free carbonyl groups are the same in both pure PMMA and the blends, the absorption coefficient of hydrogen bonded C=O vibration has been calculated for three compositions, and the average value used for further calculations.

(2) From the calculations of C=O concentrations, it can be shown that less than 50% C=O groups of PMMA form hydrogen bonds with PVPh at 1:1 O–H to C=O mole ratio. With the increase in O–H to C=O mole ratio to 2 and 3.3, the percentage of hydrogen bonded C=O groups slightly increases to 54% and 66%, respectively.

(3) In pure PVPh, O–H groups participate in the formation of intra-associated hydrogen bonds and very few single O–H groups are believed to remain. The 'free' O–H bond is mainly related to hydroxyl hydrogens at the end of *n*-mers. Semi-quantitative analysis is compatible

with the hypothesis that a large proportion of intra-associated hydrogen bonds exist as short *n*-mers, such as trimers. These are likely to be favoured because of steric hindrance factors and because of polymer tacticity. Longer mers would also be more compatible with ordered structures of the type found in crystal structures. When blending in a small fraction of PMMA, the overall organization of PVPh is probably only slightly disrupted. The C=O group will tend to form inter-associated hydrogen bonds with the 'free' O–H groups at the end of the *n*-mers. At a 1:1 O–H to C=O mole ratio, all 'free' O–H groups become hydrogen bonded to C=O partners. When a higher proportion of PMMA is used, the network becomes dominated by PMMA chains, and PVPh chains become isolated in this network. This decreases the probability that intra association takes place. At 10 wt % PVPh, almost all O–H groups take part in inter-association through hydrogen bonding.

## ACKNOWLEDGEMENTS

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