Infra-red dichroic study of orientation in poly(vinyl phenol)

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Fourier transform infra-red (*FT*i.r.) spectroscopy was used to investigate the orientation of uniaxially stretched films of poly(vinyl phenol) (PVPh). The α angles of the various vibrations were determined with respect to the $CH_2 \cdots CH_2$ axis. No evidence was found for any influence of the hydrogen bonds on the orientation of PVPh when compared to polystyrene (PS). On the other hand, it was noted that, upon formation of hydrogen bonds, the α angle of the hydroxyl groups changes from 26 to 65°.

(Keywords: poly(vinyl phenol); orientation; *FT*i.r. spectroscopy)

INTRODUCTION

It is well known that orientation affects the behaviour of polymers, and in particular their mechanical, optical and electronic properties. Uniaxial orientation is indeed commonly used to enhance the tensile properties of fibres. The most striking examples of this are probably Kevlar (Du Pont) and Spectra (Allied-Signal) fibres, where the chains are almost perfectly oriented uniaxially. This results in outstanding tensile properties along the orientation direction. Molecular orientation is largely controlled by the processing conditions and by the molecular properties. Therefore, a better understanding of the orientation process at the molecular level is needed to achieve a better control of the mechanical properties through orientation.

Orientation can be described as a process in which chains align along the direction of the extensional forces. This phenomenon is particularly marked above the glass transition temperature, where local movements allow rearrangements to take place more easily. Although various techniques can be used to quantify the orientation, *FT*i.r. spectroscopy is particularly powerful since it allows the study of the orientation of isolated vibration vectors which are related to different chemical groups[1,2].

Specific interactions, for example, chain entanglement, charge transfer and hydrogen bonding, have been proposed as influencing the chain orientation behaviour[3–5]: the stronger the interactions, the greater the final orientation will be. However, very few studies have focused on such specific interactions. Zhao *et al.*[3] found that the presence of ionic domains in styrene-based ionomers leads to a higher chain orientation. These act as effective cross-links. On the other hand, randomly distributed hydrogen bonds in poly(styrene-*co*-(methacrylic acid)) did not lead to any increase of chain orientation, when compared to polystyrene[3].

Poly(vinyl phenol) (PVPh) is an amorphous polymer which shows a strong tendency to undergo either self-association through hydrogen bonds or to form intermolecular hydrogen bonds with guest polymers containing proton acceptors. For this reason, PVPh has been used as a model to investigate the influence of hydrogen bonds on the miscibility of various blends[6–9]. The presence of hydrogen bonds has been shown to increase the miscibility. Such blend systems could yield an interesting insight into the effect of hydrogen bonds on orientation. However, the orientation behaviour of pure PVPh must first be established.

In this work, the orientation of pure PVPh was studied. Infra-red dichroism was used to determine the transition moment angles of various vibrations, and the orientation behaviour was compared to that of PS in order to determine the effect of hydrogen bonds on the orientation of the pure polymer. This information will be useful for subsequent studies on the orientation of various PVPh blends.

EXPERIMENTAL

Sample preparation

The poly(vinyl phenol) ($M_w = 30\,000$) used in this work was supplied by Polysciences. The glass transition temperature (T_g) was measured as 156°C by using a Perkin–Elmer DSC-4 instrument, with a heating rate of 20°C min^{-1}, after calibration with indium. Films, with a thickness of 50–100 μm, which were slightly tinted and brittle, were prepared by melt compression at 180°C. Prior to their use, they were treated in an oven at a temperature above the T_g to allow for the relaxation of internal stresses.

Quantitative *FT*i.r. measurements can only be made on peaks for which the absorption intensities are below 1. For this reason, very thin (40 μm) samples were necessary, but these, however, were difficult to manipulate owing to their brittleness. Instead, thicker films (i.e. 100 μm) were subjected to a two-stage stretching procedure. First, the films were drawn at a high temperature (180°C) and at a low drawing rate ($\delta = 0.01\ \mathrm{m\,s^{-2}}$) until the desired

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thickness was achieved. These were then kept at this high temperature for ~20 min to allow the molecular chains to relax. At this stage, no residual dichroism could be measured either by *FT*i.r. spectroscopy or by birefringence. In a second step, the oven temperature was reduced to the desired stretching temperature (±1°C) and the films were stretched again and then rapidly quenched in order to retain the induced orientation. Sample stretching was performed using a linear deformation at a constant strain rate of either 0.05 or 0.1 mm s^{-1} s^{-1}, at a constant temperature, which was varied from 165 to 175°C, in all cases. The samples were quenched to room temperature immediately after stretching to minimize the chain relaxation. The final draw ratios varied from 1 to 5.

Infra-red dichroism

Polarized spectra were recorded by using a Mattson SIRIUS 100 Fourier transform infra-red spectrometer. For each spectrum 100 scans were taken at a resolution of 2 cm^{-1} by using a MCT detector. Oriented films were rotated through 90° in order to obtain the two polarization measurements. The infra-red dichroism was calculated as $R = A_{\parallel}/A_{\perp}$, in which $A_{\parallel}$ and $A_{\perp}$ are the integrated intensities of the peaks in the parallel and perpendicular directions, respectively. Only the peaks for which the absorption was lower than 1.0 were used in these calculations.

The dichroic ratio measurement allows us to calculate the second-order moment of the orientation function, which is based on the relationship[11]:

$$\langle P_2(\cos\theta)\rangle = \frac{1}{2}(3\langle\cos^2\theta\rangle - 1) = \left(\frac{R_0+2}{R_0-1}\right)\left(\frac{R-1}{R+2}\right) \quad (1)$$

where $R_0 = 2\cot^2\alpha$, with α being the angle between the chain axis and the dipole transition moment vector of the vibration being considered, and θ the angle between the chain axis and the stretching direction.

Spectral separation of free and hydrogen bonded OH vibrations

Spectracalc software (Galactic Industries Corp., Salem) was used to separate the vibration bands due to the free and hydrogen bonded OH vibrations in the 2700–3750 cm^{-1} range, using a least-squares fitting method and a log normal peak shape[10].

Molecular modelling

Energy calculations and conformational analysis were carried out using Quanta/CHARMm software (version 3.30), running on a Silicon Graphics IRIS 4D workstation. Relaxed conformational maps were calculated by minimizing the energy of each conformation, using a steepest-descend minimization method, until convergence was reached.

RESULTS AND DISCUSSION

Determination of the α angle

To the best of our knowledge, the orientation behaviour of PVPh has not been previously reported. To determine the orientation based on equation (1), the α angle, between the dipole transition moment of a vibration and the chain axis, needs to be known. The three vibrations, found at 2850, 1445 and 1014 cm^{-1}, as shown in *Figure 1*, were used to determine these angles. They are assigned to the CH_2 symmetrical stretching, the CH_2 scissoring and the CH in-plane bending of the aromatic ring, respectively.

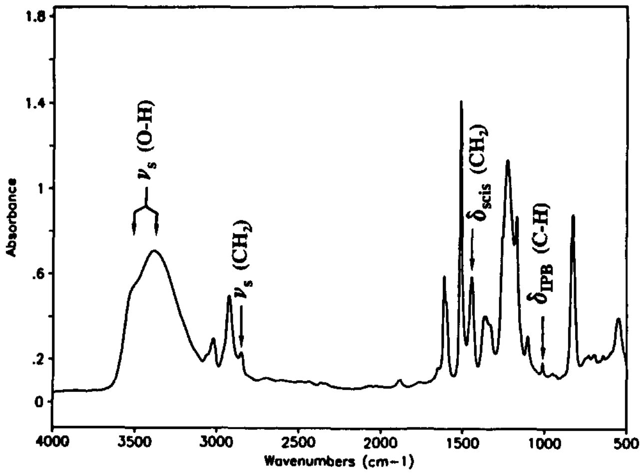

Figure 1 Typical i.r. spectrum of PVPh showing the bands used in this study

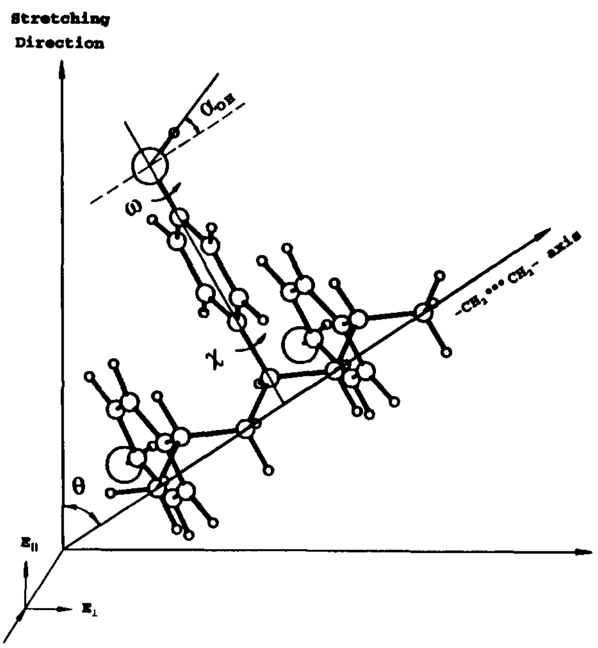

Figure 2 Schematic representation of the angles used in this study

As a first approximation, the chain axis was chosen as the axis passing through two successive CH_2 groups, as shown in *Figure 2*. Following this assumption, the vectors of the CH_2 symmetrical stretching and scissoring vibrations are thus perpendicular to the chain axis. Both of the α angles should therefore be equal to 90°. These two vectors are, however, not in the same direction, but are perpendicular to each other and to the chain axis. Therefore, conformational changes will alter the relative position of both of the vibration vectors, as CH_2 vibrations are sensitive to conformational changes. For polystyrene, an α angle of 70° has been proposed for the CH_2 symmetrical stretching vibration[11], based on data obtained for polyethylene[12]. This corresponds to a helical conformation of the backbone.

The frequency of the in-plane bending vibration of PVPh shifts from 1028 cm^{-1} in PS to 1014 cm^{-1} in PVPh because of the *para*-position of the hydroxyl group. The conformation of the aromatic cyclic group with respect

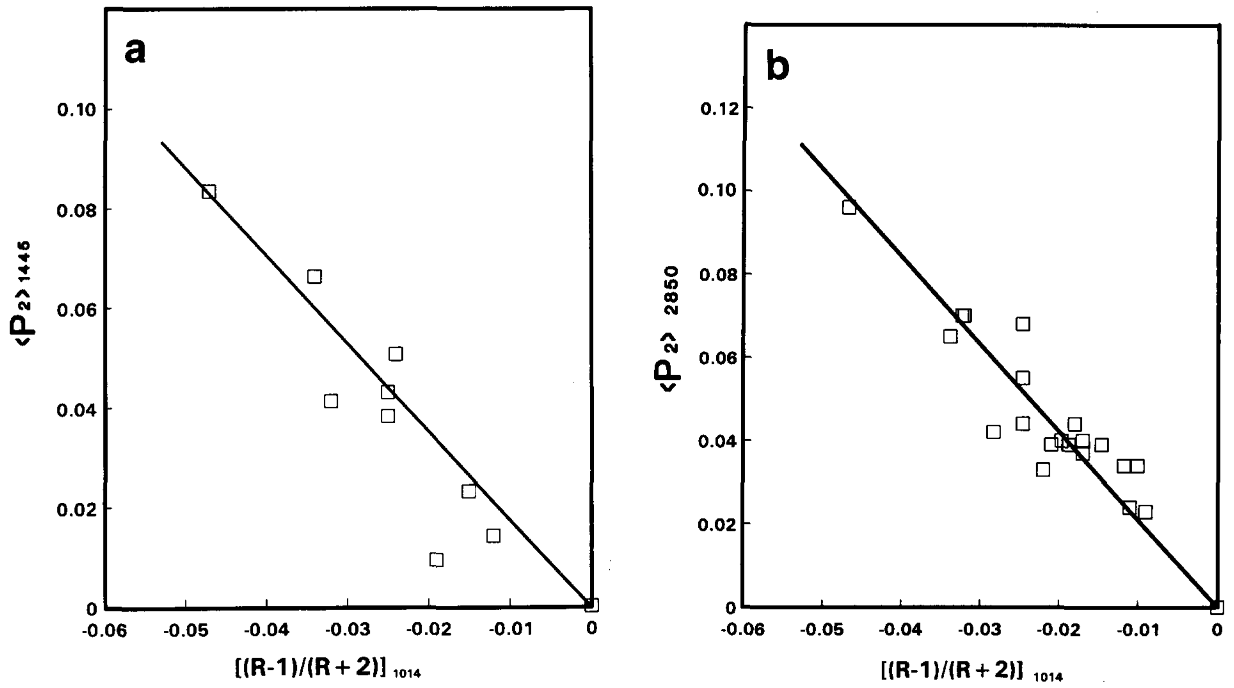

Figure 3 Dichroic ratio of CH in-plane bending vibration *versus* the orientation function, calculated from (a) the CH_2 scissoring vibration and (b) the CH_2 symmetrical stretching vibration

to the chain is not necessarily the same as in PS. Taking as a reference an α angle of 90° for the CH_2 scissoring vibration, the orientation function $\langle P_2(\cos\theta)\rangle_{1445}$ can be calculated from the dichroic ratio, $R=A_{\parallel}/A_{\perp}$, at $1445\,cm^{-1}$. A plot of $\langle P_2(\cos\theta)\rangle$, obtained in this way with respect to $[(R-1)/(R+2)]$ of the $1014\,cm^{-1}$, in-plane bending vibration, is shown in *Figure 3a*. From the slope of this curve, which is calculated as -2.01, the α angle of the CH in-plane bending vibration vector is determined as 90°. This implies that this vibration vector is perpendicular to the chain axis, as was the case in PS, and is not affected by the *para*-substitution of the OH group.

The CH_2 symmetrical stretching vibration has also been used to ascertain the value of the α angle of the CH in-plane bending vibration (as shown in *Figure 3b*). The result confirms not only that the vector of the CH in-plane bending vibration is perpendicular to the chain axis, but also that the assumption of an α angle of 90° for both the CH_2 scissoring and symmetrical stretching vibrations is valid. In the rest of this paper, we will use $\alpha=90°$ to calculate the chain orientation function for these three vibrations.

Chain orientation behaviour

The vibration of the CH in-plane bending at $1014\,cm^{-1}$, which is well isolated, was used to calculate the orientation function. Its low absorption intensity is suitable for a quantitative calculation in the case of thick films[13]. From the plots of orientation function vs. draw ratio, as shown in *Figure 4*, it can be seen that, as expected, the macromolecular chains reach higher orientations with an increase in draw ratio and a decrease in stretching temperature. The orientation of PVPh was found to be comparable (within experimental error) to that reported for polystyrene[3,11,14] (see *Table 1*). Sources of discrepancy include the low molecular weight of the PVPh used in this work, as well as tacticity differences in the polymers, and the speed of sample quenching.

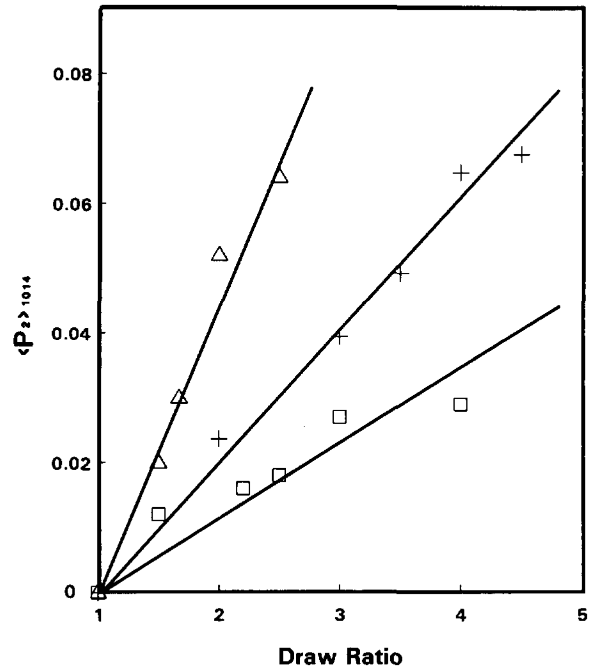

Figure 4 Orientation function of PVPh *versus* draw ratio, measured under different draw conditions: (□) $\delta=0.1\,mm\,s^{-1}\,s^{-1}$, 175°C; (+) $\delta=0.1\,mm\,s^{-1}\,s^{-1}$, 170°C; (Δ) $\delta=0.05\,mm\,s^{-1}\,s^{-1}$, 165°C

Table 1 Comparison between the orientation function of PVPh and those of various PS samples

Polymer	M_w (g)	T_g (°C)	T_D^a (°C)	$<P_2(\cos\theta)>$	Ref.
PS	250000	98	108	0.05	3
PS	–	–	100	0.25	10
PS	110000	–	110	0.10	14
PS	149000	105	110	0.2	15
PS	254000	107	118.5	0.08	16
PVPh	30000	156	165	0.07	

^{a} Drawing temperature

The main difference between PVPh and PS lies in the self-association of PVPh through hydrogen bonds. This self-association does not seem to influence the orientation behaviour of PVPh. Indeed, the relative areas of the free and hydrogen bonded OH peaks before and after orientation were measured at room temperature on non-polarized spectra of the samples showing the highest orientation. This revealed that orientation has not modified the relative proportion of these groups in samples at ambient temperature.

A possible reason for this behaviour could be the effect of the stretching temperature on the hydrogen bonding: although hydrogen bond variations have not been observed on stretched samples at room temperature, variations are likely to have occurred during sample preparation, which is performed at temperatures above T_g. It is well known that chain orientation is a temperature-dependent process. Increasing the temperature not only increases the chain relaxation, which results in a lower chain orientation, but also affects the interactions. In nylon-6, above the glass transition temperature, part of the hydrogen bonds are broken and the number of free amide groups increases[10]. A similar phenomenon was reported for PVPh: the relative absorbance of the free hydroxyl band increases while that of the hydrogen bonded hydroxyl band decreases with increasing temperature[17]. At the same time, the OH vibration of the hydrogen bonded group shifts to higher frequencies, indicating a decrease in strength of these interactions. This change is particularly dramatic at the glass transition temperature of PVPh.

Differences in intensity have traditionally been attributed to changes in the proportions of free vs. hydrogen bonded OH groups[18]. More recent work[19] on polyamides has shown that quantitative evaluation is difficult, since the absorption coefficient of the hydrogen bonded group changes dramatically with temperature. Nevertheless, for PVPh, the sharp increase in the absorbance of the free OH group, coupled with a decrease in that of the hydrogen bonded OH group, reported when raising the temperature to $\sim T_g$, can be interpreted qualitatively as being due to a marked decrease in the number of hydrogen bonded groups. Therefore, during stretching, the influence of the hydrogen bonds on the chain orientation would become weaker because of the decrease of the hydrogen bonded OH fraction and of the strength of the remaining hydrogen bonds. When the samples are quenched to room temperature, the hydrogen bonds are formed again, and the spectra of the oriented samples do not show any variation in hydrogen bond population, as mentioned earlier. This may explain the similarities observed between PVPh and PS, and the lack of any effects on the chain orientation due to hydrogen bonding.

Orientation of the hydroxyl groups

Hydrogen bonds present in PVPh result in a broad OH stretching vibration centred at 3370 cm^{-1}, whereas the free OH vibration appears as a shoulder at 3534 cm^{-1}, as shown in *Figure 1*. If the absorbance of the whole OH stretching region in used to calculate the dichroic ratio, no linear relationship can be obtained between the latter and P_2, as can be seen in *Figure 5a*. These two bands were separated as described in the Experimental section, and the dichroic ratios of the free and hydrogen bonded hydroxyl groups are reported separately in *Figures 5b* and *5c*. As can be seen from these figures, the dichroic ratio for both types of hydroxyl group behave linearly with respect to P_2, but at the same time behave very differently to each other.

Two reasons can be invoked to explain this difference: chain sections containing each type of OH group could be orienting differently, or the two OH vibrations could have different α angles. Although the occurrence of sequences of different orientation values is possible, and has indeed been suggested for poly(ethylene terephthalate)[20], various reasons have led to the choice of the second explanation. No evidence of differing behaviour was found for other vibrations. Indeed, for all of the vibrations used, the P_2 values that were obtained through the chosen definition of the chain axis were equal within experimental error. Furthermore, the fact that hydrogen bonds have been found not to influence the orientation, and also that their relative number was found not to vary, seems incompatible with the first explanation. From the experimental data obtained, and supposing a constant P_2 value, α angles of 26 and 65°, for the free and hydrogen bonded vibrations, respectively, have been calculated. The physical significance of these differences is worthy of attention.

Molecular modelling has been used in the interpretation of this phenomenon. As a first approximation, energy calculations were performed on a single repeat unit. As can be seen in *Figure 2*, the α angle of the hydroxyl groups depends on two factors, namely χ, the torsion angle fixing the position of the aromatic ring about the chain axis, and ω, the torsion angle of the hydroxyl group. Any change in either of these will result in a variation of the α angle related to the hydroxyl group.

To better understand the system, a conformational analysis on a model compound, consisting of three repeat units in a syndiotactic configuration, was performed and is reported in *Figure 6*. In this relaxed isoenergy contour map, the energy of each calculated χ–ω conformation has been minimized while keeping the χ and ω torsion angles fixed. As can be observed, the rotation of the hydroxyl group around the ω torsion angle is energetically 'easy', inducing changes of only 0.5 kcal mol^{-1}, whereas the energy needed to rotate the aromatic ring around the χ torsion angle is much higher, i.e. $\sim$8 kcal mol^{-1}. This reveals that rotation of the aromatic ring is more difficult than that of the hydroxyl groups. Furthermore, in the case of a real macromolecular chain, rotation of the aromatic rings would also be affected by adjacent aromatic rings. Therefore, the rotation of the aromatic ring linked to the backbone is expected to vary by only a small amount.

The torsion angle of the aromatic ring shows two energy minima, both at 60°, corresponding to a position where the plane of the aromatic ring is perpendicular to the chain axis. The energy climbs continuously until a maximum is reached at 145°, which is 8.6 kcal mol^{-1} higher than the minimum, and this difference would be even greater for a real polymer chain because of possible interactions between the successive aromatic groups. Variations of $\pm 10°$, however, induce an energy change of only 0.3 kcal mol^{-1} near the observed minima. This is in agreement with the work of Tonelli and co-workers[21,22] who proposed that, in PS, this rotation was restricted to rotations of $\sim$20 to 30° around the equilibrium position of 60°. It must be noted that the α angle for the in-plane bending vibration is insensitive to this rotation angle, and can therefore not be used to determine the χ torsion angle. Such information might have been obtained

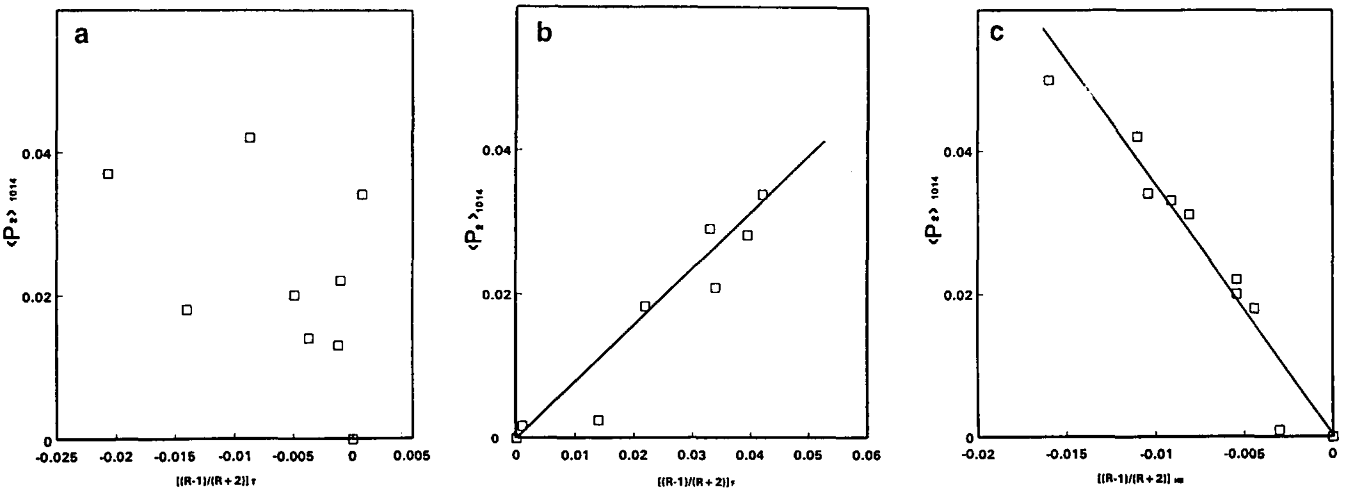

Figure 5 Determination of the transition moment angle of the hydroxyl stretching vibration: (a) total OH vibration; (b) free OH group vibration; (c) hydrogen bonded OH group vibration

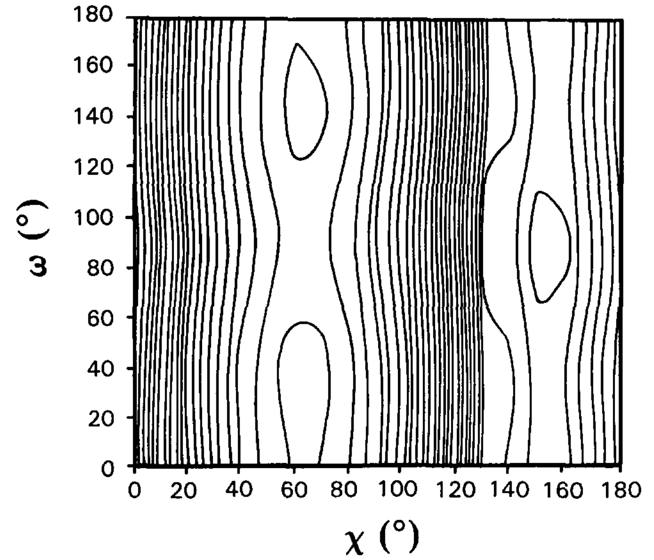

Figure 6 Relaxed isoenergy contour map for the rotation of the aromatic ring (χ) and the hydroxyl group (ω) in a model compound (contours drawn at intervals of $0.33 \mathrm{kcal\,mol^{-1}}$)

Table 2 Calculated values of the α angle obtained for different conformations of the aromatic ring and the hydroxyl groups

	ω(°)				
χ(°)	70	80	90	100	110
50	35.2	28.3	23.4	22.1	24.8
60	28.8	24.0	22.5	25.2	30.8
70	24.5	23.3	26.0	31.6	39.3

through the out-of-plane bending vibration, which was unfortunately overlapped with other vibrations in PVPh.

To reproduce the α angle, as mentioned previously, both the χ and ω torsion angles must be determined. The ω torsion angle is much more flexible and to determine its value, the α angles resulting from combinations of χ of 60 ± 10° and ω, which was allowed to vary freely, were calculated and are reported in *Table 2*. The best fit was

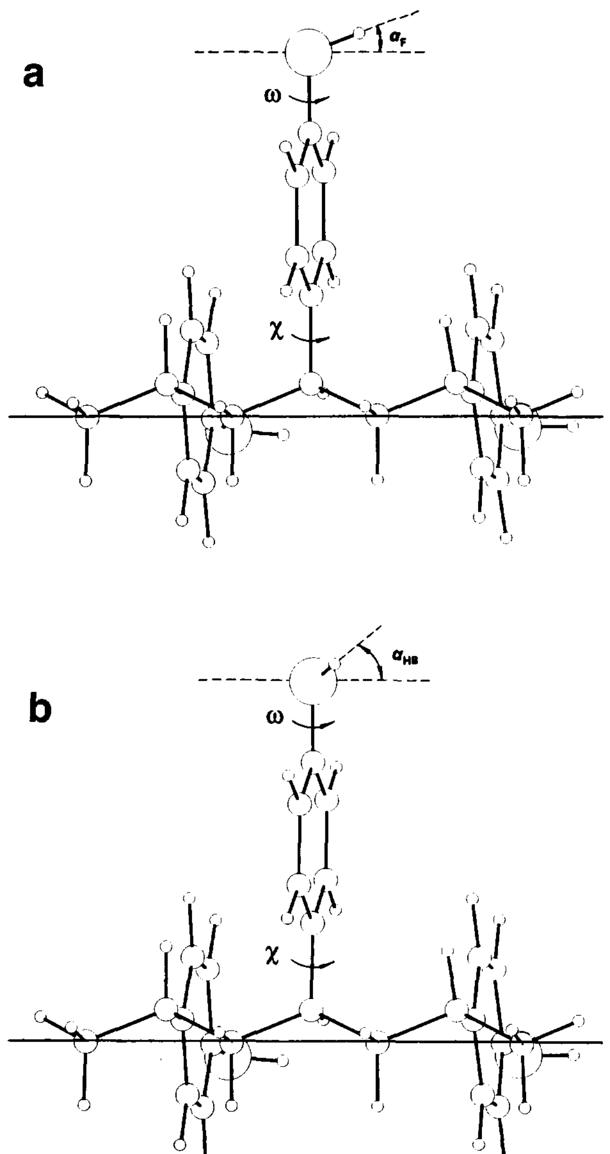

Figure 7 Proposed conformations for the hydroxyl groups in PVPh: (a) free OH; (b) hydrogen bonded OH

obtained for $\chi = 70°$ and $\omega = 90°$ (for the free OH groups), which yields the same value as that obtained from the experimental data, i.e. $\alpha = 26°$. Although this combination does not fit with one of the absolute minima of the map, it is within 0.3 kcal mol^{-1} of it, a small difference when considering the neglect of interchain interactions in the amorphous phase and uncertainties related to the force field. Other interactions present in the amorphous phase may also be responsible for this particular conformation.

For hydrogen bonded hydroxyl groups, it must be noted that the hydrogen bonds are able to adopt a distribution of geometries, which is reflected by the width of the observed vibration. The fact that $(R-1)/(R+2)$ varies linearly with $\langle P_2 \rangle$ suggests that the average α angle does not vary with orientation within the range of draw ratios that are studied here. Therefore, the α angle can be taken as an average value of the distribution of the geometry of the hydrogen bonds. The experimental α value of 65° can be reproduced by using values of $\chi = 60°$ and $\omega = 145°$. This value is close to an energy minimum. It can be surmised that, when hydrogen bonds form between chains, the OH group rotates away from the previous position, the energy barrier being very small, whereas the rotation of the phenyl ring remains virtually unchanged, with a variation of only $\sim 10°$. The proposed conformations for the free and hydrogen bonded OH groups are shown in *Figure 7*.

CONCLUSIONS

*FT*i.r. spectroscopy was used to investigate the uniaxial orientation of films of poly(vinyl phenol) (PVPh). The chain axis was taken as the axis passing through two consecutive CH_2 groups. Based on this assumption, the α angle of the CH in-plane bending of the aromatic ring was determined as 90°.

The orientation behaviour of PVPh, compared to that of PS, was not influenced by self-association through hydrogen bonding. This possibly results from the dissociation of hydrogen bonds at the draw temperature, which was above the T_g.

The OH valence vibration did not behave linearly with respect to the measured orientation. However, separation into its two components, namely free and hydrogen bonded hydroxyl groups, did yield linear relationships. Both types of groups behaved differently, which was attributed to changes in the conformation of the hydroxyl group upon formation of the hydrogen bonds, thus inducing a change in the α angle.

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