# FTIR and FT-Raman Studies of Partially Miscible Poly(methyl methacrylate)/Poly(4-vinylphenol) Blends in Solid States

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ABSTRACT: The miscibility of poly(4-vinylphenol) (PVPh) and poly(methyl methacrylate) (PMMA) blends has been investigated by FTIR and FT-Raman spectroscopy. Although both techniques provide evidence for the formation of hydrogen bonds between the hydroxyl group of PVPh and the ester group of PMMA, the blends show only a limited degree of hydrogen-bonding interactions when cast from tetrahydrofuran solutions. Comparison of the blends with those cast from a ketone solution and changes in the hydrogen-bonded fractions after thermal cycles indicate that the blends are partially miscible mixtures, in agreement with a previous NMR observation. During the thermally induced evolution of the miscibility, conformational transitions of side chain ester groups in the blend systems, analogous to the phenomenon occurring in PMMA homopolymers, were observed. With prolonged heating, the blends gradually approach the complete miscibility predicted by an association model. It may be concluded that even though the hydrogen bond between PVPh and PMMA favors their miscibility, phase separation still occurs due to the great difference in the two solvent−polymer interaction parameters, resulting in a nonequilibrium multiphase system that is effectively frozen.

## Introduction

A vast majority of studies have been performed to enhance the miscibility of polymer blends through incorporation into the blend components of local centers capable of participating in strong interactions.[1] These interactions include hydrogen bonding, ion−ion interactions, as well as a range of others, such as charge-transfer complexes, and ion−dipole interactions.[1] In particular, several investigations have been carried out with emphasis on hydrogen-bonding interactions as miscibility enhancers, and several systems have been the subjects of these studies, e.g., ethylene−methacrylic acid copolymer/poly(vinyl methyl ether),[2] poly(styrene−acrylic acid)/poly(methyl methacrylate),[3] phenoxy/poly(ϵ-caprolactone),[4] poly(vinylphenol)/poly(ϵ-caprolactone),[5] poly(vinylphenol)/polyethers.[6] These studies showed that the favorable hydrogen-bonding interactions are stronger than the dispersive interactions also present, which may oppose miscibility, and that immiscible blends may be converted to single-phase materials with the introduction of quite low levels of hydrogen bonding. Attempts at understanding the miscibility have been made by employing several spectroscopic techniques, such as NMR, FTIR, and fluorescence, where the frequency, intensity, and width of certain bands are sensitive to the strength and extent of hydrogen bonding. IR spectroscopy has been particularly useful for these studies because the strength of hydrogen bonding and the fraction of hydrogen-bonded groups can be directly investigated from the spectra, and a theory has been developed to predict the miscibility from IR data.[7,8]

It has been reported from IR studies that poly(4-vinylphenol) (PVPh) is miscible with poly(ethyl methacrylate) (PEMA) and poly(*n*-propyl methacrylate) (PPMA) over the entire composition range at temperatures between ambient and 200 °C, while PVPh/poly(n-butyl methacrylate) blends phase-separated at temperatures below 200 °C.[9] As for PVPh/poly(methyl methacrylate) (PMMA) blends, the trends observed in the FTIR spectra were similar to those for the PVPh/PEMA and PVPh/PPMA blends. However, due to the high glass transition temperatures ($T_g$) of both PVPh and PMMA, it was difficult to compare the experimental values of hydrogen-bonded fractions with theoretical ones based on an association model between the ester and phenol hydroxyl groups. A recent two-dimensional (2D) solid-state heteronuclear correlation (HETCOR) NMR study revealed the existence of intermolecular carbon−proton dipolar interaction resulting from the hydrogen bond between the carbonyl carbon of PMMA and the hydroxyl hydrogen of PVPh.[10] In contrast, another NMR investigation by using the $^{13}C$ cross polarization/magic angle spinning (CP/MAS) technique indicated that the PVPh/PMMA blend is immiscible and assumes a domain structure.[11] The contradictory observations may arise from the different solvents used for blend preparation. The implication here is that when ketones like methyl isobutyl ketone and methyl ethyl ketone are used as solvents, miscibility may be achieved, whereas a tetrahydrofuran (THF) cast blend is immiscible according to NMR data.

In the present study, FTIR and Raman spectroscopies are employed to explore the interactions occurring between PMMA and PVPh in the blends cast from THF, to verify the above discrepancy, and to seek a better understanding of the solvent effect on the miscibility and morphology involved in this system. It should be noted that the previous NMR studies of PVPh/PMMA[10,11] solely indicate whether a miscible phase exists, but not whether the whole system is miscible. Raman spectroscopy, regarded as a complementary technique to IR, has been underutilized for studying polymer blends. There have been few reports describing the potential usefulness of Raman spectroscopy in the studies of specific interactions in polymer blends,[12,13] even though the simplicity of sample preparation in Raman measurements allows us to access to more "realistic" blend specimen. We report here the effects of temperature on the molecular interactions revealed by both IR and Raman spectroscopies and the evolution of the miscibility induced by thermal annealing.

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## Experimental Section

Poly(methyl methacrylate) (PMMA) with molecular weight 120 000 and poly(4-vinyl phenol) (PVPh) with molecular weight 1500 were commercially available from Aldrich and Polyscience, respectively. Blends with varying compositions were prepared from the homopolymers by dissolving samples in THF (1−3 wt % solutions), mixing for 7 days, and casting at room temperature. The solvent was removed slowly under ambient conditions. All the samples were vacuum dried. Great care was taken to let the samples undergo the same thermal history for comparative purpose.

The IR spectra were obtained at a 2 $cm^{-1}$ resolution on a Nicolet Magna 550 FTIR spectrometer equipped with a cooled MCT detector. A minimum of 128 scans were coadded. The IR measurements at elevated temperatures were carried out with the assistance of a copper block device having a ceramic heater mounted inside the sample chamber. Temperature was regulated by an Omron E5T programmed thermocontroller, which has a temperature stability of better than ±0.1 °C. All the IR spectra were run in a transmission mode by casting the samples onto NaCl plates. The FT-Raman spectra were measured with a JEOL JRS-FT 6500N FT-Raman spectrometer equipped with a cooled InGaAs detector. An excitation wavelength at 1064 nm was provided by a cw Nd:YAG laser (Spectron SL 301 1355), and the laser power at the sample position was about 200 mW. The Raman data were collected at a spectral resolution of 4 $cm^{-1}$ and at least 300 scans were accumulated to achieve satisfactory signal-to-noise ratios. Various spectral data treatments were performed by Grams/386 (Galactic Industries Co.).

## Results and Discussion

If two polymers are completely incompatible, each individual polymer does not recognize, in IR spectral terms, the existence of the other in the blend. On the other hand, if the polymers are compatible, there should be considerable differences between the IR spectrum of the blend and the coaddition of the spectra of two components. These differences would be derived from chemical interactions resulting in band shifts, intensity changes, and broadening.

Figure 1 shows FTIR spectra in the range of 4000−2400 $cm^{-1}$ for PMMA/PVPh blends with various blend ratios. The peak frequency of a broad band due to hydrogen-bonded OH groups shifts to higher wavenumbers with increasing PMMA content. Meanwhile, the relative intensity of the non-hydrogen-bonded OH band near 3540 $cm^{-1}$ decreases and it is barely detected in the spectra of blends containing more than 50 wt % PMMA. This reflects the new distribution of hydrogen-bonded moieties resulting from the competition between hydroxyl−hydroxyl and hydroxyl−carbonyl specific interactions. It also indicates that, in PMMA-rich blends, the OH···O=C interaction predominates, so that a band at 3430 $cm^{-1}$ in the spectrum (F) may be due to the OH stretching vibration of the OH···O=C moiety. Thus, the OH···OH interaction is stronger than the OH···O=C interaction. Note that a weak band near 3426 $cm^{-1}$ in the spectrum of pure PMMA (Figure 1G) is due to the overtone of the C=O stretching mode.

Figure 2 presents FTIR spectra in the 1800−1650 $cm^{-1}$ region for the blends with different compositions. The relative intensities of the nonbonded and hydrogen-bonded carbonyl bands centered at 1730 and 1707 $cm^{-1}$, respectively, vary gradually in favor of the latter as the PVPh content in the blend increases. The C=O stretching band of pure PMMA appears asymmetrically, suggesting the presence of a self-aggregated state of PMMA chains in the THF cast films.[14] Quantitative estimation of the fraction of the hydrogen-bonded C=O groups can be undertaken by calculating the band areas of the two

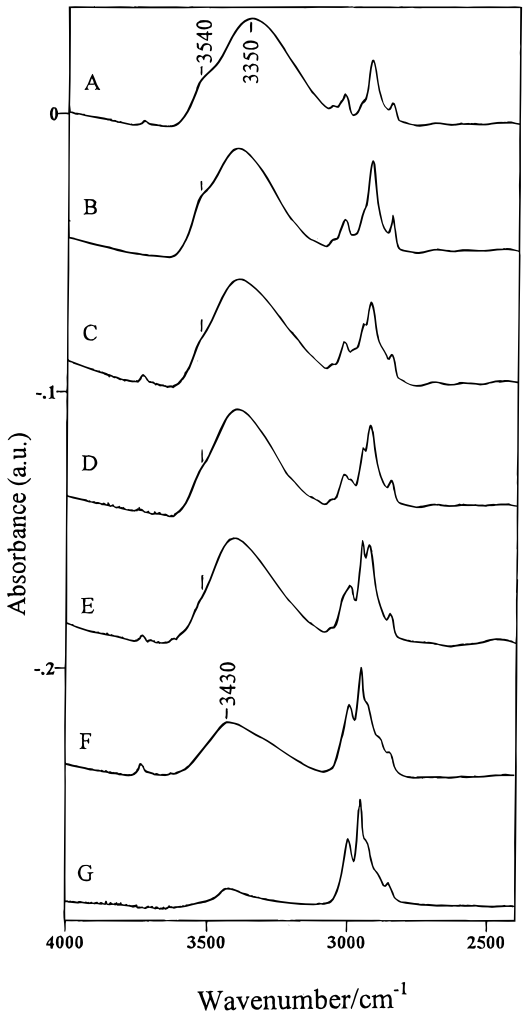


**Figure 1.** FTIR spectra in the 4000−2400 $cm^{-1}$ region of PVPh/PMMA blends in cast films: (A) 100, (B) 90, (C) 80, (D) 70, (E) 50, (F) 20, and (G) 0 wt % PVPh.

C=O stretching bands corrected for their absorptivity coefficient differences.[15] Here, an absorptivity ratio (the ratio of the absorptivity of the band assigned to hydrogen-bonded C=O groups to that of the band due to non-hydrogen-bonded C=O groups) of 1.5 was adopted since this value was previously confirmed and found to be acceptable for blends of PVPh or poly(styrene-*co*-vinyl phenol) with poly(methacrylates).[7,9]

Figure 3 shows a plot of the fractions of hydrogen-bonded C=O groups in percentage versus PMMA weight percent. With the increase in the PMMA content in the blend, the relative amount of the hydrogen-bonded C=O groups with respect to the total amount of C=O groups in the blend systems decreases throughout the entire composition range.

FT-Raman spectra in the 1800−1670 $cm^{-1}$ range of PMMA/PVPh blends with different compositions are shown in Figure 4. In this carbonyl stretching region, the spectra of the blends are dominated by a band at 1736 $cm^{-1}$, but a shoulder associated with the OH···O=C interaction is observed at lower wavenumbers near 1706 $cm^{-1}$. The Raman spectra also reflect the stoichiometry of hydrogen bonding. If there is no considerable difference between the Raman spectrum of the blend and the coadded spectra of the pure components, we cannot expect specific interactions within the blends. It should be noted that the appearance of a band at the lower wavenumber side of the C=O stretching region was once

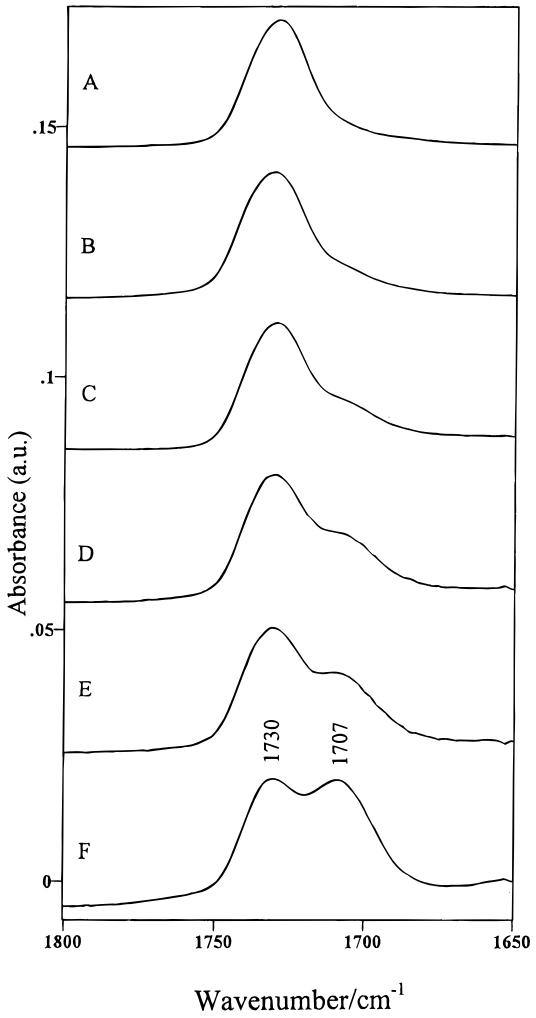


**Figure 2.** FTIR spectra in the 1800−1650 $cm^{-1}$ region for PVPh/PMMA blends with different compositions at 40 °C: (A) 100, (B) 80, (C) 50, (D) 30, (E) 20, and (F) 10 wt % PMMA.

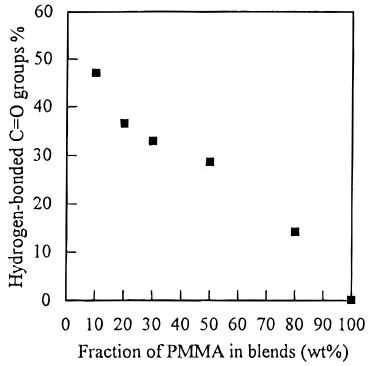


**Figure 3.** Fractions of hydrogen-bonded C═O groups in percentage *versus* PMMA weight percentage.

described by the effect of refractive index dispersion in the IR spectra.[16] When an immiscible blend with 10% of the carbonyl-containing polymer was treated as a multilayer film, Allara's calculation of the effect of refractive index dispersion on a hypothetical carbonyl stretching absorption in this blend indicated that the spectrum of the immiscible blend may differ by several percent from the pure polymer.[16] However, for most of the realistic samples, the effects of refractive index dispersion are appreciably smaller than the extreme case considered by Allara. On the other hand, in PMMA, which may exhibit an aggregated structure, the dipole−dipole interaction of the carbonyls which are

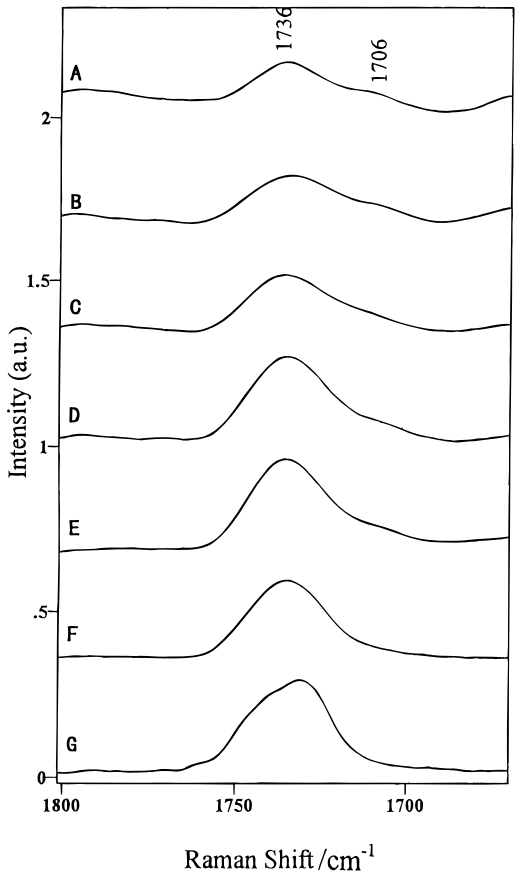


**Figure 4.** FT-Raman spectra in the 1800−1670 $cm^{-1}$ region of PVPh/PMMA blends: (A) 22, (B) 33, (C) 44, (D) 57, (E) 67, (F) 82, and (G) 100 wt % PMMA.

diluted by non-carbonyl-containing medium exists and may contribute to the appearance of a shifted sub-band near CO stretching.[14] The extent of this contribution is uncertain, making the IR observation controversial. However, in this work the consistent evidence from the Raman measurements corroborates the intermolecular interaction mechanism and lends support to the above IR observation that a definite amount of hydrogen-bonding interaction between PVPh and PMMA exists in the blend.

At a first glance, the above IR and Raman data are somewhat unique when compared with the previous $^{13}C$ CP/MAS NMR results.[11] It was argued that the down-field shifts of $^{13}C$ NMR resonances of the carbonyl CO of PMMA and the phenolic $^{\alpha}C$-OH of PVPh are not appreciable for the PMMA/PVPh blends. The blends from THF solutions have been considered to be at most partially miscible mixtures. However, the moderate degree of mixing at the molecular level and its composition dependence are clearly observed in the present IR and Raman measurements. To elucidate the limited degree of miscibility, we also made a comparison of a blend from THF solution with that from methyl isobutyl ketone (MIBK) solution with the same composition.

Figure 5 compares IR spectra of pure PMMA (A), a 80/20 PVPh/PMMA blend cast from THF (B), and that of the same composition cast from MIBK (C). Note that the stretching band near 1706 $cm^{-1}$ due to the C═O group hydrogen-bonded with an OH group is much more pronounced for the blend cast from MIBK than that from THF. The blend cast from THF provides a typical example that the appearance of bands associated with the OH···O═C bonding does not always result in miscibility.

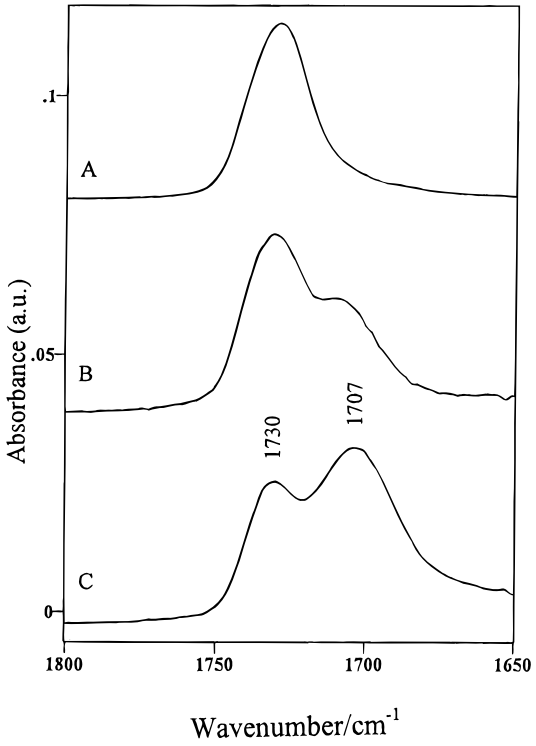


**Figure 5.** Comparison of FTIR spectrum of a partially miscible PVPh/PMMA blend with that of a completely miscible blend: (A) pure PMMA, (B) 80/20 PVPh/PMMA blend cast from THF, and (C) 80/20 PVPh/PMMA blend cast from MIBK.

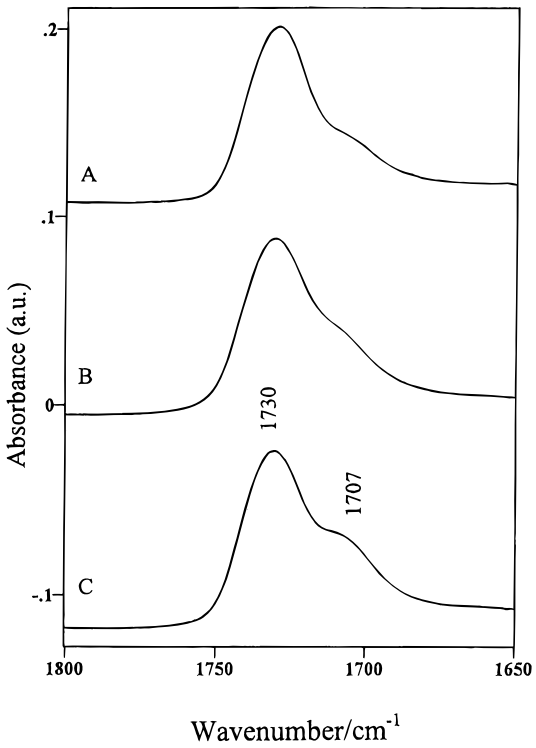


**Figure 6.** Scale-expanded FTIR spectra in the 1800 −1650 $cm^{-1}$ region of PVPh/PMMA 50/50 wt % blend: (A) before heating, (B) heating to 170 °C, and (C) cooling down to 40 °C.

Figure 6 depicts the annealing effect on the hydrogen-bonding interaction. As the temperature of the 50/50 blend is raised to 170 °C, the band near 1707 $cm^{-1}$ is increased, indicating the increase of the carbonyl groups bonded to OH groups (*vide infra*). During the course of slow cooling from 170 to 40 °C, the CO groups still tend to form new hydrogen bonds with OH groups, so the

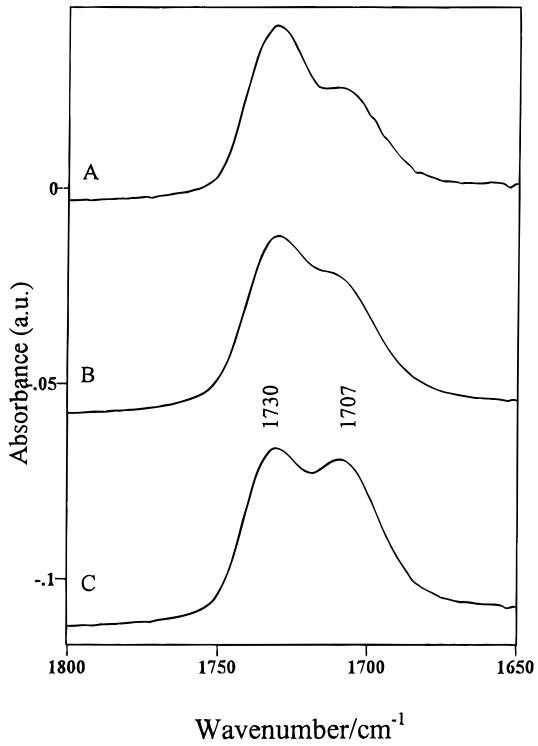


**Figure 7.** Scale-expanded FTIR spectra in the 1800 −1650 $cm^{-1}$ region of PVPh/PMMA 80/20 wt % blend: (A) before heating, (B) heating to 170 °C, and (C) cooling down to 40 °C.

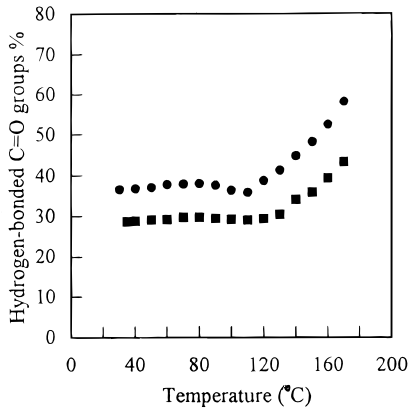


**Figure 8.** Fractions of hydrogen-bonded C=O groups in percentage versus temperature: (♦) 50/50 and (●) 80/20 wt % PVPh/PMMA blend.

amount of the hydrogen-bonded CO groups increases appreciably after the annealing. Similar phenomenon is observed for other blends. In Figure 7, the amount of hydrogen-bonded CO groups in the 80/20 blend is increased after heating to 170 °C, and this tendency does not stop during the course of slow cooling from 170 to 40 °C. Overall, more hydrogen-bonded CO groups are formed after the thermal cycle.

To describe the process quantitatively, we calculated the percentage of CO groups bonded with the OH groups *versus* temperature as shown in Figure 8. With increasing temperature, intermixing is induced by molecular motion of the side chain and backbone chain. On the other hand, dissociation may occur between the interassociated hydrogen bonds within the miscible phase as the temperature is raised. It is assumed that, as a whole, the newly formed hydrogen bonds between the nonbonded ester and OH groups are counterbalanced at the first stage of heating, and no significant change in mixing of unlike chains is observed below a

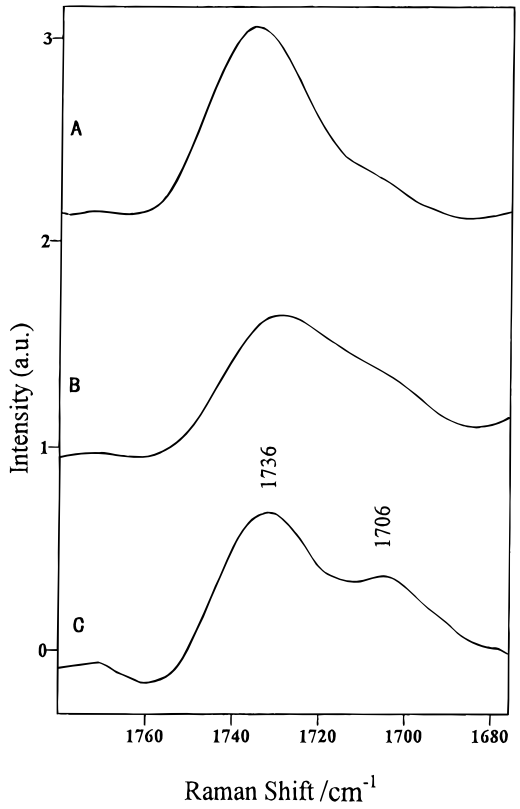


**Figure 9.** FT-Raman spectra of PVPh/PMMA 43/57 wt % blend: (A) before heating, (B) after heating to 130 °C for 3 h, and (C) after heating to 180 °C for 3 h.

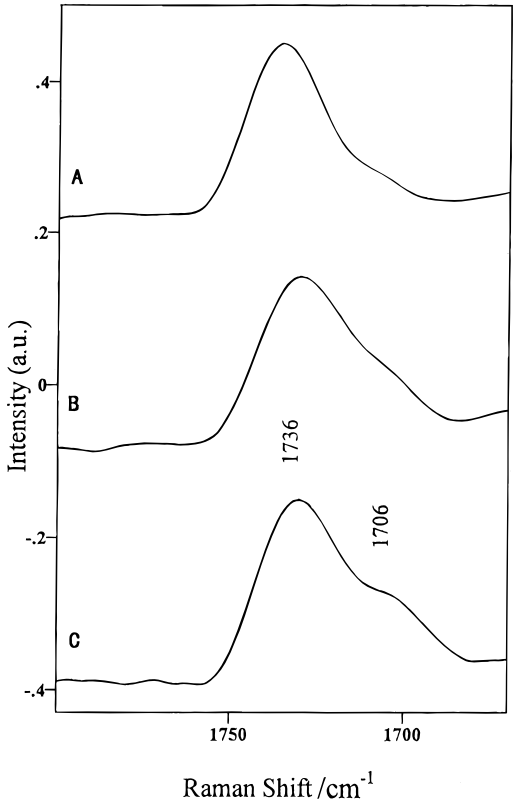


**Figure 10.** FT-Raman spectra of PVPh/PMMA 33/67 wt % blend: (A) before heating, (B) after heating to 130 °C for 3 h, and (C) after heating to 180 °C for 3 h.

temperature near the $T_g$ of PMMA. More intimate mixing level can be observed in FTIR measurements only after heating to temperatures above the $T_g$ of PMMA.

Figures 9 and 10 display FT-Raman spectra of 43/57 and 33/67 wt % PVPh/PMMA blends, respectively. The hydrogen-bonded C═O band near 1706 $cm^{-1}$ increases, after heating to 130 °C for 3 h, and continues to increase after heating to 180 °C for 3 h, in both Figures 9 and 10. Thus, with prolonged heating above $T_g$ of PMMA and PVPh, the blends gradually become more miscible, as predicted by an association model. [7,8]

Figure 11 shows the temperature dependencies of IR spectra in the region of 1650 −750 $cm^{-1}$ for the PVPh/PMMA 50/50 wt % blend. It can be seen from Figure 11 that bands at 1448 and 1172 $cm^{-1}$ exhibit pronounced temperature dependences. The intensity of the 1448 $cm^{-1}$ band decreases continuously as the temperature is increased. This band is attributed to an antisymmetric bending vibration of the methyl ester group ($OCH_3$) in PMMA.[17−20] The temperature-dependent change of this band indicates conformational transitions of the ester groups.[21] As *cis*, *trans*, and *gauche* orientations of the ester group can occur simultaneously, the temperature dependence reflects the population changes in various orientations; energetically more unfavorable conformations are realized at higher temperatures. The intensity of the 1172 $cm^{-1}$ band increases gradually with temperature. This band is due to an O−H in-plane bending mode of the phenol group of PVPh.[22] Its temperature dependent change suggests that the self-association between the phenol groups is reduced as temperature is raised.

Figure 12 shows the temperature dependence of IR spectra of the PVPh/PMMA 20/80 blend in the same region as in Figure 11. Again, we see that the intensity

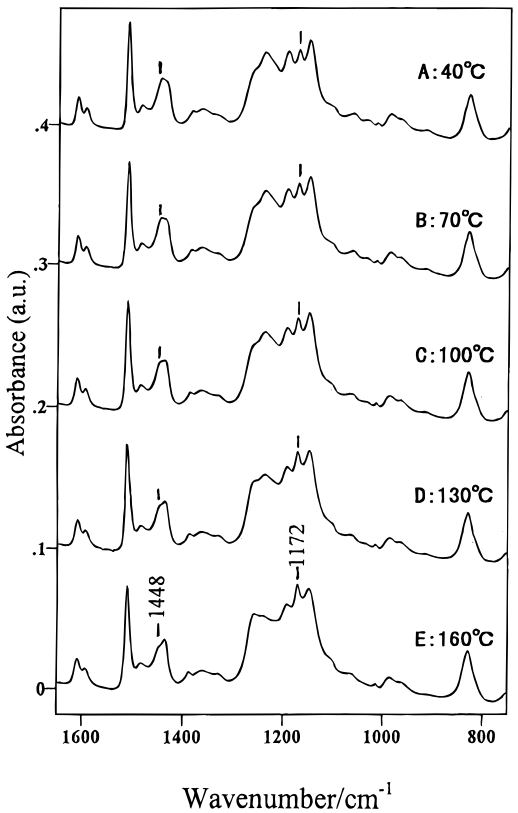


**Figure 11.** Scale-expanded FTIR spectra in the region of 1650 −750 $cm^{-1}$ for PVPh/PMMA 50/50 wt % blend at elevated temperatures.

of the band at 1449 $cm^{-1}$ decreases whereas that of the band at 1172 $cm^{-1}$ increases with increasing temperature. The former is also associated with the conforma-

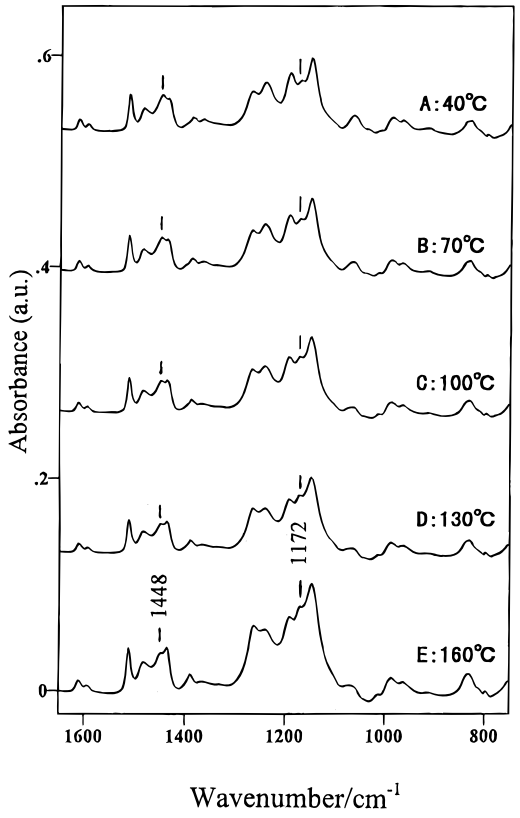


**Figure 12.** Scale-expanded FTIR spectra in the region of 1650 −750 $cm^{-1}$ for PVPh/PMMA 20/80 wt % blend at elevated temperatures.

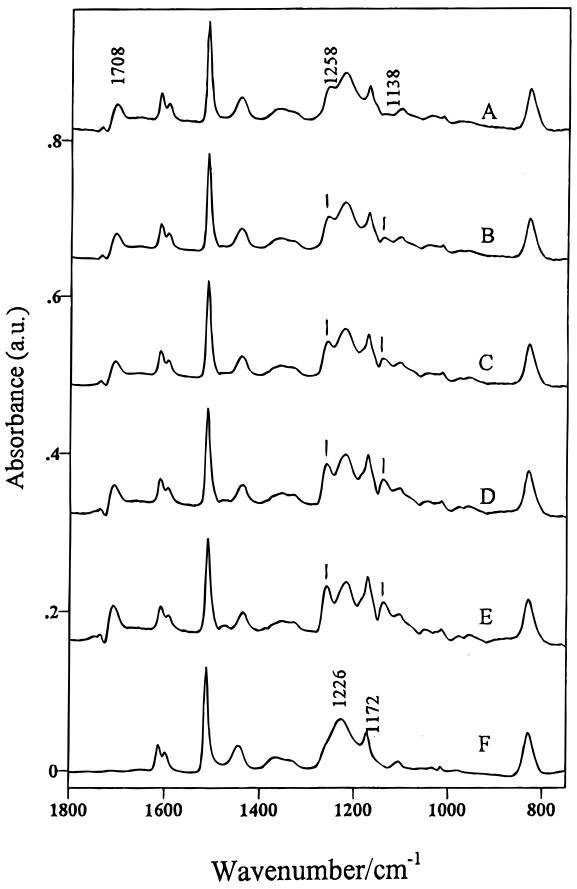


**Figure 13.** FTIR difference spectra of PVPh/PMMA 50/50 wt % blend over a temperature range of 50−170 °C: (A) 50, (B) 80, (C) 110, (D)140, and (E) 170 and (F) an IR spectrum of PVPh.

tional transitions in the side ester groups of PMMA while the latter is concerned with the reduction of the self-association of phenol groups of PVPh. Since the temperature-dependent change of the conformationally sensitive band at 1449 $cm^{-1}$ is very similar to that previously observed for pure PMMA films, [21] we assume that the main conformational structures of PMMA occurring in the blend systems are not perturbed by the presence of PVPh. This assumption is in agreement with the above observation that the blend has only a limited degree of miscibility and a multiphase structure exists in the blend systems.

The difference IR spectra of PVPh/PMMA blends at elevated temperatures obtained by subtracting the spectrum of PMMA are demonstrated in Figure 13. For comparison, an IR spectrum of PVPh is shown in Figure 13F. Besides the appearance of a hydrogen-bonded C═O band at 1708 $cm^{-1}$, two new bands are observed at 1258 and 1138 $cm^{-1}$ for which the intensities increase with temperature. It can be assumed that more interactions between the ester groups and OH groups are formed during the course of heating. The 1258 $cm^{-1}$ band can be attributed to a C−C−O antisymmetric stretching mode of the ester group hydrogen-bonded with an O−H group while the 1138 $cm^{-1}$ band can be assigned to a C−O−C antisymmetric stretching mode of the ester group hydrogen-bonded with the O−H group.[17]

The solvent effects on the miscibility and morphology of polymer blends have been investigated for several pairs of polymer blends, for example, polystyrene/poly(vinyl methyl ether).[1,23] However, most of the studies focused on blend systems where strong specific intermolecular interactions are seldom involved. For such solution-cast blend systems, it may be assumed that different miscibility is related to changes in the solvent−polymer interaction parameters ($\Delta\chi$). For a solvent with a high value of $\Delta\chi = |\chi_{12} - \chi_{13}|$, where $\chi_{12}$ and $\chi_{13}$ are solvent−polymer interaction parameters of the two constituent homopolymers, poor miscibility is observed, and *vice versa*. Therefore, it is appropriate to choose a solvent in which both polymers have nearly the same solvent-polymer interaction parameters. It seems that little has been studied on the effects of solvents on the phase separation dynamics and morphology of solution-cast blends with strong specific intermolecular interactions.[24] Light-scattering methods have been utilized to monitor the phase separation process during solvent evaporation of polymer A/polymer B/solvent tertiary systems,[25,26] but the investigations have been restricted to polymers without specific interactions. The presence of hydrogen-bond structure supplies the possibility of miscibility, but other factors, including solvent properties and steric hindrance, may also affect the phase structure of the blends obtained.

## Conclusions

FTIR and FT-Raman spectroscopies were utilized to explore the possible molecular interactions that induce miscibility in the blends of PMMA with PVPh. Even though the hydrogen bond between the hydroxyl groups in PVPh and the carbonyl groups in PMMA favors polymer miscibility, the blends show a limited degree of hydrogen-bonding interactions between them. In agreement with the previous NMR observations, the blends form a partially miscible mixture. The components are prevented from sufficient mixing due to severely restricted mobility. Phase separation is in-

duced as the polymer concentration gradually increases in the course of solvent evaporation. As a result, a nonequilibrium multiphase system is formed that is effectively frozen in. To drive the miscibility, heating produces two inverse trends for the interassociation between the ester and OH groups at an early stage. Molecular motion-induced intermixing and newly formed hydrogen bond may be counterbalanced by dissociation within the miscible phases when the temperature is raised. As a whole, no significant change in the mixing of unlike chains is observed below the $T_g$ of PMMA. A more intimate mixing level is observed in FT-IR and Raman after heating to the temperatures above the $T_g$ of PMMA. Thus, with prolonged heating, the blends gradually approach the complete miscibility predicted by an association model.

The present study has also provided an example that the existence of proton donor−acceptor groups for the potential formation of hydrogen bonds between these groups does not warrant the expected miscibility. Other factors, like the influence of the solvent−polymer interactions, should be considered, which otherwise make the specific interactions less prevalent in the polymers with strong polar groups.

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