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Application of Two-Dimensional Correlation Infrared Spectroscopy to the Study of Immiscible Polymer Blends

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ABSTRACT: Generalized two-dimensional correlation vibrational spectroscopy is potentially a powerful method for the study of interactions in polymer blends. This paper is the first in a series that systematically examines the utility of this technique and deals primarily with methodology. Normalization methods are discussed, and the effects of concentration errors and small bandwidth variations are considered. These often occur in immiscible systems because of sample preparation problems and lead to features in asynchronous spectra that can be misinterpreted.

Introduction

The recent introduction of generalized two-dimensional (2D) correlation spectroscopy as a result of the seminal work of Noda[1−3] has generated considerable interest and has led to a large number of vibrational spectroscopic studies. Of particular interest to us is the application of this technique to the study of polymer blends.[4−9] Essentially, the methodology allows the construction of synchronous and asynchronous correlation 2D plots from a set of spectra that change systematically with a variable such as time, temperature, or composition. Synchronous plots allow the identification of bands that change in a coupled or coordinated fashion, while asynchronous plots have generally been interpreted in terms of bands that change in an uncoordinated or independent manner with the chosen variable. Accordingly, 2D analysis should be a powerful tool in studying interactions in systems like polymer blends, and the work so far published also shows that the technique is capable of separating and identifying strongly overlapping bands. However, when attempting to apply this technique to a range of blends, we encountered various experimental problems and found that we disagreed with some of the interpretations of published data. We will discuss these problems in this and two following papers. In the first two papers, we will deal with non-hydrogen-bonded systems, as hydrogen-bonded blends present some separate and interesting issues. Here we will start by discussing immiscible systems, as this allows us to address some general problems we have found with methodology.

Experimental Section

The polymer samples used in this study are listed in Table 1. Blends were prepared by dissolving appropriate amounts of the components in THF to yield 4% (w/v) solutions. Thin films were obtained by casting these solutions onto KBr windows. The solvent was removed slowly under ambient conditions for a minimum of 24 h. The sample was then dried in a desiccator for an additional day. After that, the sample was placed in a vacuum oven to remove residual solvent.

Infrared spectra were obtained on a Digilab FTS-60 Fourier transform infrared (FTIR) spectrometer using a minimum of 64 co-added scans at a resolution of 2 cm^{-1}. All films were sufficiently thin to be within the absorbance range where the Beer−Lambert law is obeyed.

IR spectra were baseline-corrected and normalized to the same thickness based on the 1600 cm^{-1} band of polystyrene. Standard two-dimensional correlation analysis was carried out with a Matlab software program written in this laboratory. An experimental matrix is formed from the original IR spectra ordered in the direction of decreasing content of one of the polymer components, usually polystyrene. The average (or mean) spectrum of the spectra in the chosen set is then subtracted from each of the original spectra to obtain a set of "dynamic" difference spectra. Synchronous and asynchronous correlation spectra are then calculated from these dynamic spectra using the Hilbert transform suggested by Noda.[2] The spectra shown on the top and at the side of the 2D correlation maps are the average spectrum and/or the difference spectrum obtained from the highest concentration component in each set. In the 2D correlation plots, shaded regions indicate negative correlation intensities, while unshaded ones are positive.

Theory

The theory of generalized 2D correlation spectroscopy and calculation methodologies have been described in detail by Noda and co-workers,[1−3] but it is worth briefly reviewing key points here from the point of view of correlation and spectral density functions.[10] Correlation analysis has been classically used to determine the degree of *linear* dependence of, say, variables y and x. This is accomplished by calculating the average product of $x - \mu_x$ and $y - \mu_y$, where μ_x is the mean value of x and μ_y the mean value of y. If there are N paired measurements, x_i, y_i, $i = 1, 2, ..., N$, then for large N the covariance of x and y is defined as

$$\sigma_{xy} = \lim_{N\to\infty} \frac{1}{N}\sum_{i=1}^{N}(x_i - \mu_x)(y_i - \mu_y) \tag{1}$$

If the x, y data are unrelated, the sum of the positive products in eq 1 will equal the sum of the negative products and σ_{xy} will be zero. For a linear relationship σ_{xy} will be a maximum, corresponding to a correlation coefficient, $\sigma_{xy}/\sigma_x\sigma_y$, of 1. Note that a *nonlinear* systematic relationship, say $y = 1/x$, between the variables would result in a correlation coefficient of −1, while other nonlinear relationships (e.g., $y = x^2$) would result in values between −1 and 1.

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Table 1. Polymer Samples and Their Molecular Weights

name	abbreviation	MW[a]	source
polystyrene	PS	$M_w = 190\,000$	Scientific Polymer Production Inc.
polybutadiene	PB	$M_w = 200\,000$	Scientific Polymer Production Inc
poly(2,6-dimethyl-1,4-phenylene oxide)	PPO	$M_w = 50\,000$	Scientific Polymer Production Inc
poly(methyl methacrylate)	PMMA	$M_w = 120\,000$	Aldrich Chemical Co. Inc.

[a] Weight-average.

If both x and y are now functions of time (t), but there is a time delay,τ, between $x(t)$ and $y(t)$, a covariance function, $C_{xy}(\tau)$, can be defined as

$$C_{xy}(\tau) = \lim_{T\to\infty} \frac{1}{T}\int_0^T \{x(t) - \mu_x\}\{y(t+\tau) - \mu_y\}\,\mathrm{d}t = R_{xy}(\tau) - \mu_x\mu_y \quad (2)$$

where $R_{xy}(\tau)$ is the cross-correlation function.

$$R_{xy}(\tau) = \lim_{T\to\infty} \frac{1}{T}\int_0^T \{x(t)\,y(t+\tau)\}\,\mathrm{d}t \quad (3)$$

The cross-correlation function can be converted into the frequency domain (ω) by Fourier transformation to yield what is known in engineering applications as a spectral density function:

$$S_{xy}(f) = \int_{-\infty}^{\infty} R_{xy}(\tau)\mathrm{e}^{-i\omega t}\,\mathrm{d}t \quad (4)$$

This, in turn can be expressed in terms of real and imaginary components, which yield the synchronous and asynchronous plots obtained in 2D correlation vibrational spectroscopy. Before examining this, it is useful to switch to spectroscopic nomenclature, where we can consider a spectrum obtained at a time t. The intensity of this spectrum at a given wavenumber ν_1 is then given by $y(\nu_1,t)$. Instead of calculating the Fourier transform of the correlation function, as in eq 4, spectral density functions can also be obtained by direct Fourier transformation of the original data sets.[10] For example, if we take the intensity of the band at ν_1 as it varies with time, then

$$Y_1(\omega) = \int_{-\infty}^{\infty} y(\nu_1,t)\mathrm{e}^{-i\omega t}\,\mathrm{d}t = Y_1^{\mathrm{Re}}(\omega) + iY_1^{\mathrm{Im}}(\omega) \quad (5)$$

where $Y_1^{\mathrm{Re}}(\omega)$ and $Y_1^{\mathrm{Im}}(\omega)$ are the real and imaginary parts of the complex Fourier transform of $y(\nu_1,t)$.

In constructing the spectral density function from the Fourier transforms of the original data sets (spectra), it is necessary to obtain the conjugate of the data $y(\nu_2,t)$

$$\tilde{Y}_2{}^*(\omega) = \int_{-\infty}^{\infty} y(\nu_2,t)\mathrm{e}^{i\omega t}\,\mathrm{d}t = Y_2{}^{*\mathrm{Re}}(\omega) - iY_2{}^{*\mathrm{Im}}(\omega) \quad (6)$$

A correlation spectrum (cf. eq 3) can now be obtained from

$$\begin{aligned} X(\nu_1\nu_2) &= \langle y(\nu_1,t)\,y(\nu_2,t+\tau)\rangle \\ &= \frac{1}{\pi T}\int_{-\infty}^{\infty} Y_1(\omega)\,Y_2{}^*(\omega)\,\mathrm{d}\omega \\ &= \Phi(\nu_1,\nu_2) + i\Psi(\nu_1,\nu_2) \quad (7) \end{aligned}$$

where the two orthogonal components, $\Phi(\nu_1,\nu_2)$ and $\Psi(\nu_1,\nu_2)$, represent synchronous and asynchronous correlation intensities, respectively. As Noda[1−3] pointed out, this methodology applies to other variables that vary with a fixed interval, such as concentration. However, the point we wish to make here is that this procedure is simply a correlation analysis, which is classically used to determine the degree of *linear* dependence between variables, in this case intensities, at different wavenumbers. If all the intensities change in a linear fashion with the chosen variable, in this study we used concentration, then a synchronous plot will be obtained but the asynchronous plot should be zero (actually, it will show noise). However, an asynchronous plot will be produced not only if the intensity changes are unrelated *but also if they are related in a nonlinear fashion*.

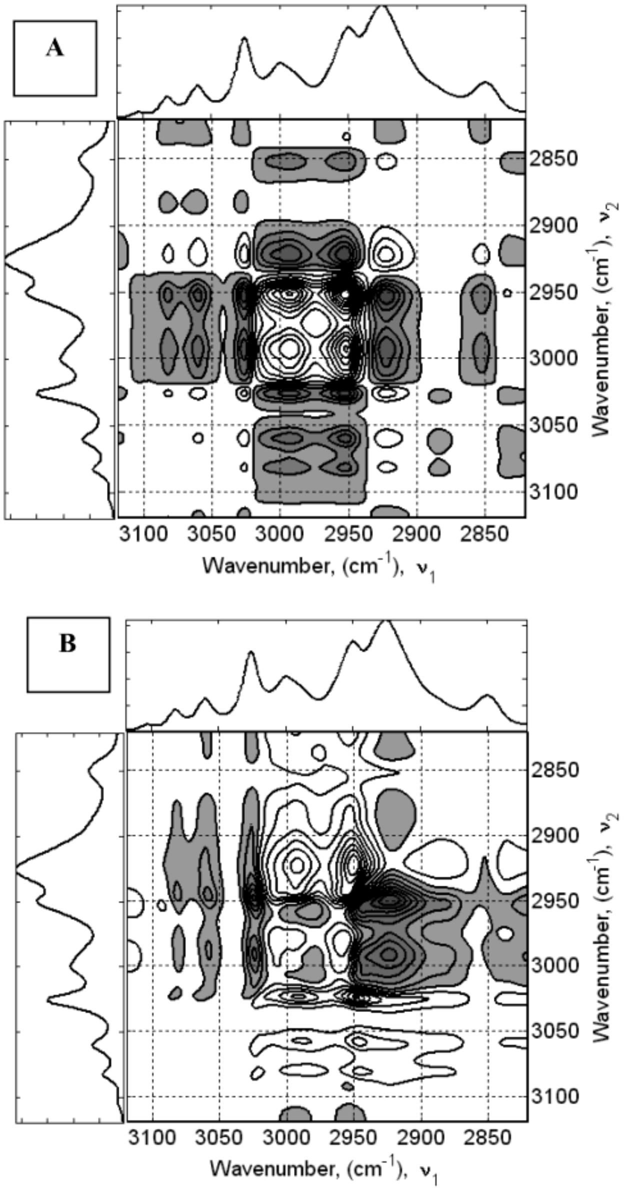

Figure 1. Synchronous (A) and asynchronous (B) contour plots in the region 3120−2820 cm^{-1} of the data obtained from five blends of composition (by weight): 90/10, 70/30, 50/50, 30/70, and 10/90 PS/PMMA.

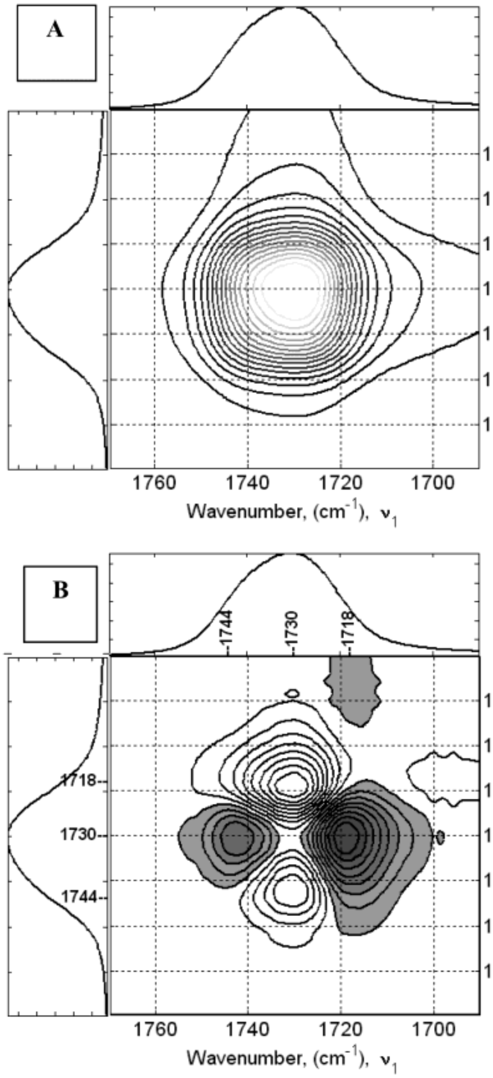

Figure 2. Synchronous (A) and asynchronous (B) contour plots in the region 1770−1690 cm^{-1} of the data obtained from five blends of composition (by weight): 90/10, 70/30, 50/50, 30/70, and 10/90 PS/PMMA.

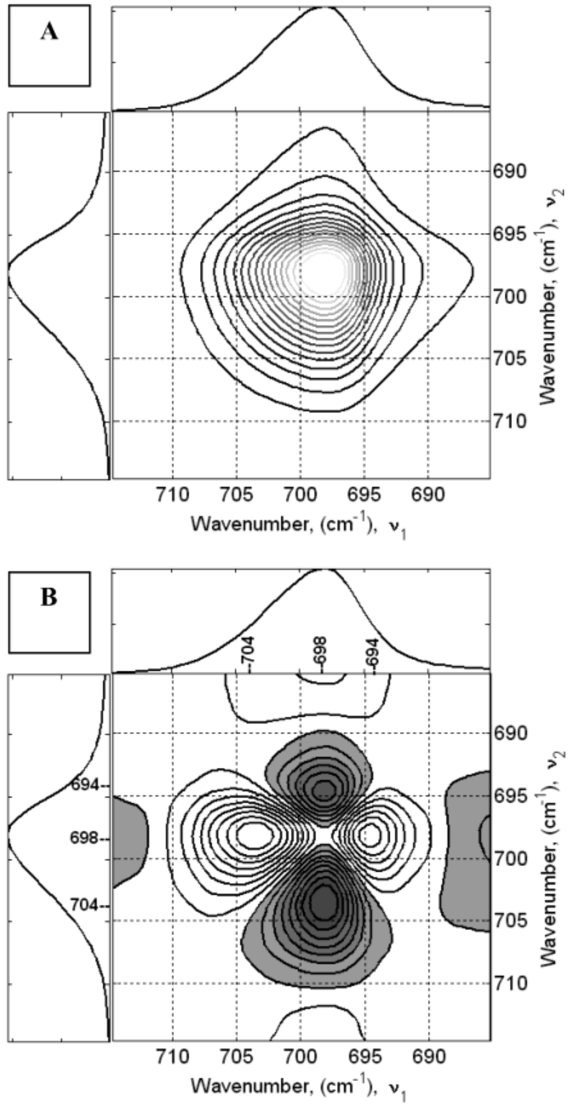

Figure 3. Synchronous (A) and asynchronous (B) contour plots in the region 715−685 cm^{-1} of the data obtained from five blends of composition (by weight): 90/10, 70/30, 50/50, 30/70, and 10/90 PS/PMMA.

Results and Discussion

If infrared spectra of immiscible mixtures with systematically varying compositions are obtained, we should expect to be able to calculate synchronous 2-D correlation maps or spectra, but not their asynchronous counterparts. This is because, in principle, there should be little or no interaction between the blend components and the intensities of all the bands in the spectra should change linearly with concentration. Matsushita et al.[5] studied blends of atactic polystyrene (PS) with poly(methyl methacrylate) (PMMA), where the concentration of the former varied systematically between 1% and 9%. They demonstrated that synchronous 2-D plots could be used to detect weak bands that are submerged under the much stronger contributions from PMMA. These authors did not present any asynchronous plots, however, simply noting that asynchronous peaks should only occur if intensity variations have dissimilar or uncoordinated trends. We were therefore surprised to find that we do, indeed, obtain asynchronous spectra from this blend system. Figures 1−3 show synchronous and asynchronous contour plots of the data obtained from five blends of composition (by weight): 90/10, 70/30, 50/50, 30/70, and 10/90 PS/PMMA. To keep the discussion simple, we show just three regions of the spectra: the C−H stretching region between 3120 and 2820 cm^{-1}; the carbonyl stretching region (PMMA) near 1700 cm^{-1}; and the aromatic C−H out-of-place bending mode (PS) near 700 cm^{-1}. The latter two regions are characteristic of the pure components. All of these plots were obtained by subtracting the “mean” spectrum, obtained in this case by simply adding all the spectra and dividing by 5, from each of the individual spectra. The resulting difference spectra are then used to calculate the synchronous and asynchronous contour plots. Note that each individual spectrum has also been concentration normalized initially so as to reflect as accurately as possible the change in composition of the blends (see Experimental Section). This is an important point because Sasic et al.[8] presented results showing that normalization procedures can strongly affect the analysis. We will return to this point later.

The synchronous plots are as we would expect them to be and can be interpreted according to the rules established by Noda[11] and applied to this system by Matsushita et al.[5] However, the fact that we obtained

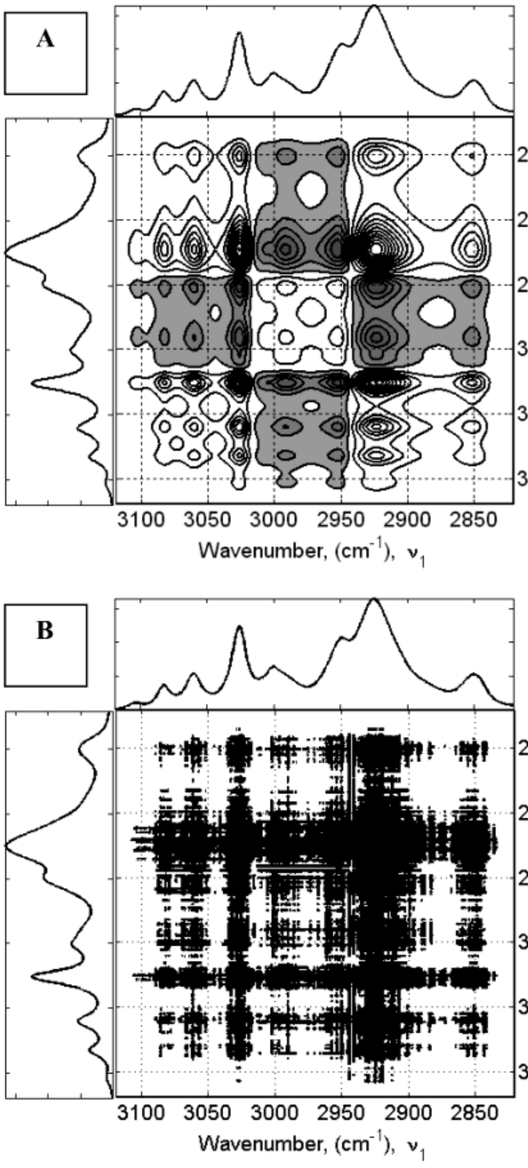

Figure 4. Synchronous (A) and asynchronous (B) contour plots in the region 3120−2820 cm^{-1} of the data obtained from five "synthetic" blends of composition (by weight): 90/10, 75/25, 50/50, 30/70, and 10/90 PS/PMMA.

asynchronous plots came as a surprise. Furthermore, the CH stretching region is complex, suggesting the presence of a large number of overlapping bands. We will defer discussion of this region of the spectrum until the following paper on miscible blends. Even in supposedly "simple" regions of the spectrum near 1730 and 700 cm^{-1}, however, the "standard" analysis of these asynchronous spectra would suggest the presence of three PMMA carbonyl bands, near 1744, 1730, and 1718 cm^{-1}, and three PS C−H out-of-plane bending modes, near 704, 698, and 694 cm^{-1}, as indicated on the plots. Some of the bands represented by these contour plots are negative while others are positive, reflecting how these modes change relative to one another as a function of concentration,[11] assuming that these results are not experimental artifacts of some kind. Clearly, it is important to determine whether results such as these represent real changes due to interactions or have some other origin.

First, it should be noted that if we simply add the spectra of the pure components in the correct proportions and then use these instead of the spectra of "real" blends, we do not obtain asynchronous spectra. We will consider this in more detail when we consider normalization procedures, but the point we wish to make initially is that these results are not a consequence of an erroneous calculation methodology on our part, so we looked for other possibilities. One such possibility is that the different phases do not consist of pure homopolymers. The solubility parameters of PS and PMMA are not that different [both near 9 (cal/cm^3)$^{0.5}$], and low molecular weight samples will actually form a single phase. We used high molecular weight samples, but even so, it is possible or even probable that minor amounts of one component dissolve in the other, thus perturbing the spectrum. We therefore also studied blends of high molecular weight polystyrene with polybutadiene (whose solubility parameters are very different) but obtained similar results. Asynchronous spectra were obtained, and bands such as the ones at 700 cm^{-1} appeared to have three components.

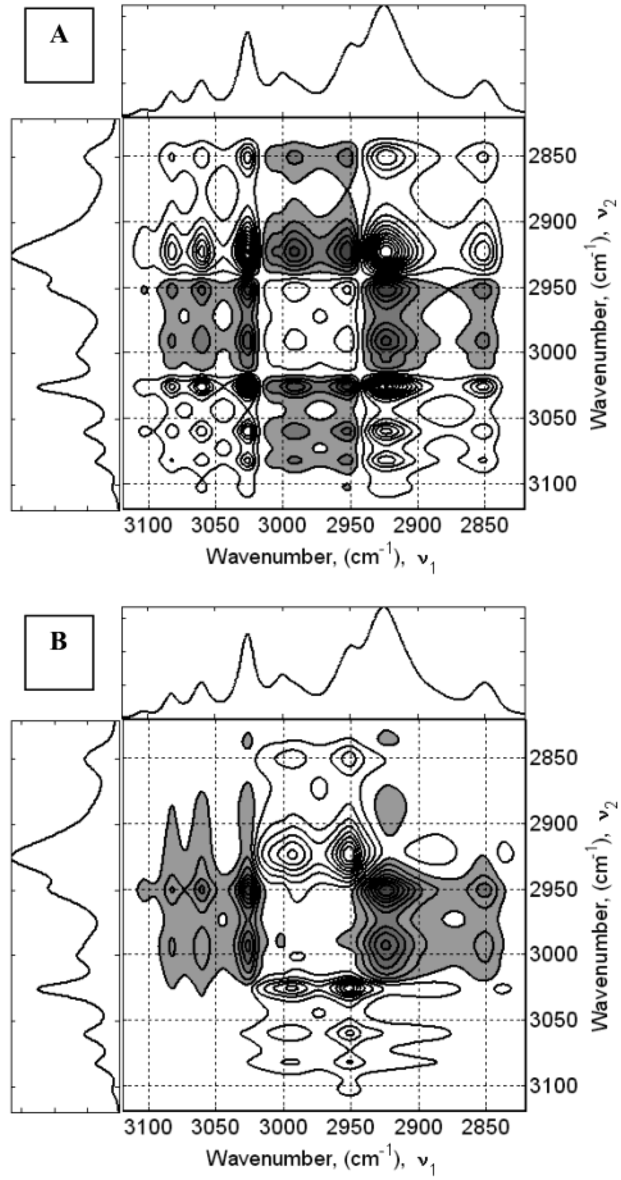

Figure 5. Synchronous (A) and asynchronous (B) contour plots in the region 3120−2800 cm^{-1} of the data obtained from five "synthetic" blends of composition (by weight): 90/10, 70/30, 50/50, 1.05*(30/70), and 10/90 PS/PMMA.

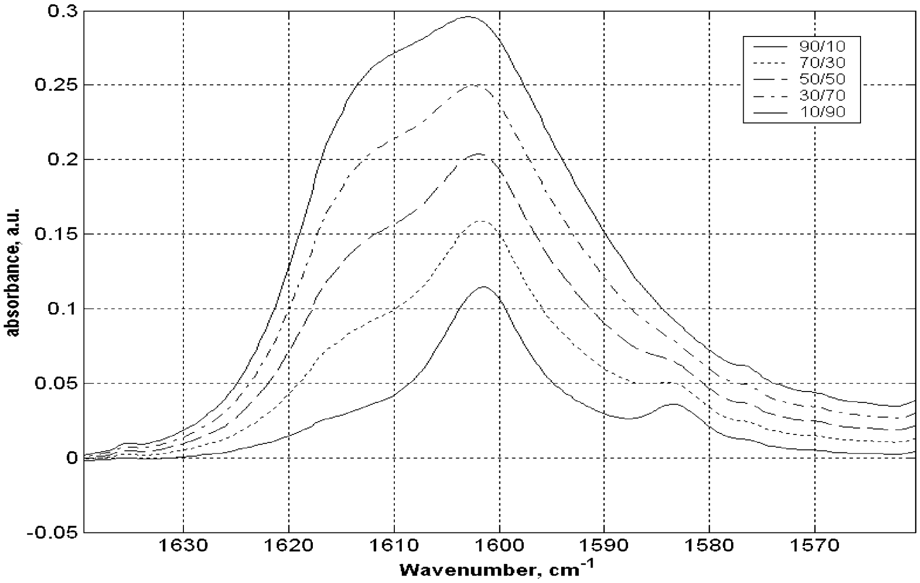

Figure 6. “Synthetic” spectra in the region 1640−1560 cm^{-1} of five blends of composition (by weight): 90/10, 70/30, 50/50, 30/70, and 10/90 PS/PPO.

A major problem with quantitative analysis of the spectra of cast films of polymers is obtaining films of even thickness and size. Films can be thicker in the middle than at the perimeter because solvent evaporates more quickly from the edges of a film, leaving a progressively more concentrated solution in the middle. In addition, a cast film may not fully cover the salt window used to support it, so that part of the infrared beam is not absorbed by the polymer, while part of it is. Such problems can lead to slight differences in bandwidth, small frequency shifts, and a nonlinear relationship between band intensities and concentration. We have discussed these experimental difficulties in detail elsewhere[12] and attempted to alleviate these as far as possible by the band normalization method described in the Experimental Section. Nevertheless, a nonlinear variation in band intensities as a function of concentration could well be responsible for our results. Furthermore, the correlation analysis approach developed by Noda[1−3] is thought to depend on having spectra that are evenly spaced in terms of the chosen variable, here concentration, so we first investigated the effect of these latter two factors.

We first obtained 2D contour plots by adding normalized spectra of pure PS and pure PMMA together to get simulated spectra of blends. We obtained no asynchronous spectra or, more precisely, noise from samples constructed with 90/10, 70/30, 50/50, 30/70, and 10/90 proportions. Changing the proportion of the second blend to 75/25, making the spacing of the blends slightly uneven, gave the plots shown in Figure 4 for the C−H stretching region. The asynchronous data are still essentially in the noise level. Even after we change the spacing drastically, to 75/25, 80/20, 60/40, 25/75, and 15/85 (but maintaining the correct concentration normalization of each “synthetic” blend spectrum), we still do not obtain asynchronous spectra, the results appearing as in Figure 4. As a result from the comments made by one of the reviewers of this paper, we now realize that, as long as the contributions to the blend spectrum from the original components add up to 100%, both the order in which the spectra are arranged and their spacing do not matter when calculating asynchronous plots from spectra where changes are linear with the chosen variable. This is because the resulting intensity values are all close to zero (in the noise level for “real” spectra), and there are no “positive” and “negative” trends to be revealed that would depend on ordering correctly.

However, if there are even minor errors in concentration that result in an incorrect normalization of the original spectra, then asynchronous spectra are produced. If we take our five original blend spectra (90/10, 70/30, 50/50, 30/70, and 10/90 compositions) and change the intensities of just one of these (the 30/70 spectrum) by 5% (by multiplying all the intensities by a factor of 1.05), then the contour plots shown in Figure 5 are produced. An asynchronous spectrum is clearly obtained and looks remarkably similar to the asynchronous spectrum shown in Figure 1 for the “real” blends.

The correlation analysis method used in most studies of blends relies on determining changes relative to a chosen reference spectrum, usually the mean. On the basis of a correspondence between correlation analysis and principal component analysis, Sasic et al.[8] called this mean centering. These authors presented results showing that changes in the synchronous spectra do not always portray concentration dynamics accurately if one of the components dominates the spectrum. Applying what they called a mean-column normalization or simply mean normalization to the spectra apparently improved the results considerably.[8] They also reported that mean centering alone resulted in the appearance of asynchronous peaks, but if the spectra are first mean normalized, the asynchronous spectra simply show noise, as they should for a sample where the bands are changing in a simple linear fashion with concentration. The blend system characterized by these authors was also a “model” or “synthetic” blend, in their case, obtained by adding the spectra of poly(2,6-dimethyl-1,4-phenylene ether) (PPO) and polystyrene (PS) in appropriate proportions. They obtained asynchronous spectra from a sample set *before* mean normalization. Their asynchronous spectra then disappeared after mean normalization. The former result obviously disagrees with what we obtained in our work, so we also investigated the spectra of model PS/PPO blends.

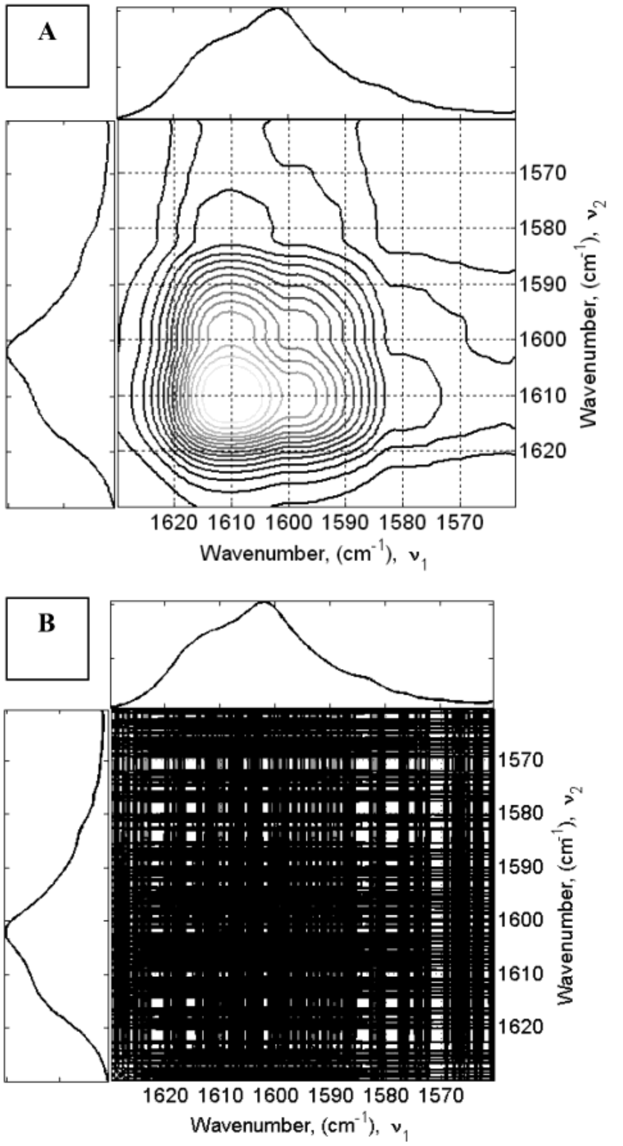

Figure 7. Synchronous (A) and asynchronous (B) contour plots in the region 1650−1560 cm^{-1} of the data from five "synthetic" blends of composition (by weight): 90/10, 70/30, 50/50, 30/70, and 10/90 PS/PPO.

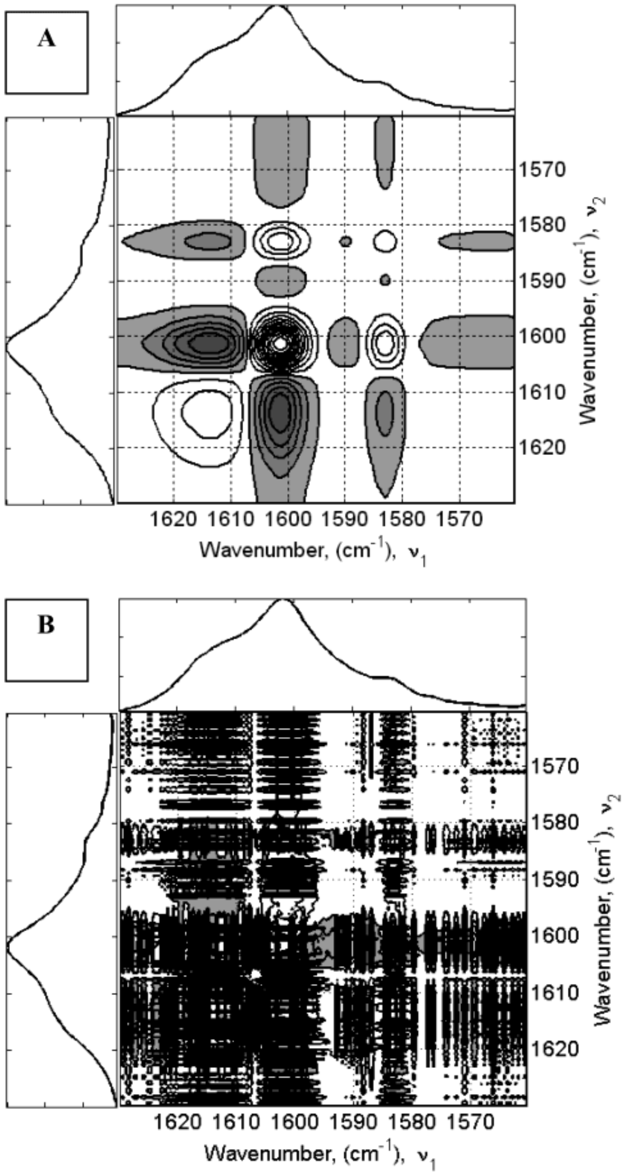

Figure 8. Synchronous (A) and asynchronous (B) contour plots in the region 1650−1560 cm^{-1} of the mean normalized data from five "synthetic" blends of composition (by weight): 90/10, 70/30, 50/50,30/70, and 10/90 PS/PPO.

"Real" blends of PPO and PS are, of course, miscible, and we should expect perturbations. But if we simply add the spectra of pure PS to that of pure PPO in appropriately weighted proportions, then we should have another model of an ideal immiscible system, as in the synthetic spectra of PS/PMMA blends discussed above. Figure 6 shows the 1640−1560 cm^{-1} region of the spectra of 90/10, 70/30, 50/50, 30/70, and 10/90 PPO/PS "synthetic" blends, where the pure component spectra were added in proportions weighted so as to reflect absorption coefficient differences, following Sasic et al.[8] These spectra are similar, but not identical, to those reported by these authors. The synchronous 2D plot obtained from these spectra, shown in Figure 7, also corresponds to the results they obtained. All the synchronous peaks are positive, and this plot does not accurately reflect concentration dynamics. Bands due to PPO should decrease, while those due to PS should increase. Mean normalization solves this problem, as Sasic et al.[8] demonstrated and reproduced here in the synchronous plots shown in Figure 8. Now both positive and negative peaks can be observed, reflecting the actual concentration dynamics. In neither case did we obtain asynchronous spectra, however, just noise, as also shown in Figures 7 and 8. Sasic et al.[8] obtained asynchronous spectra from their non-mean-normalized data. This may be a result of different concentration normalization procedures. Our concentration-normalized spectra did not appear to be the same as the ones reported by these authors. To match their spectra as closely as possible, we multiplied the intensities of the 90/10 PS/PPO blend by a factor of 1.25. Note that by doing this the contributions of the components to the blend exceed 100%, and in this sense the spectrum is no longer concentration-normalized. The resulting synchronous and asynchronous spectra are shown in Figure 9. Mean normalization of the spectra then gives the results reported by Sasic et al.;[8] synchronous spectra now reflect the correct concentration dynamics, while asynchronous plots just show noise.

These results now make physical sense if we recall that we are performing a linear correlation analysis.

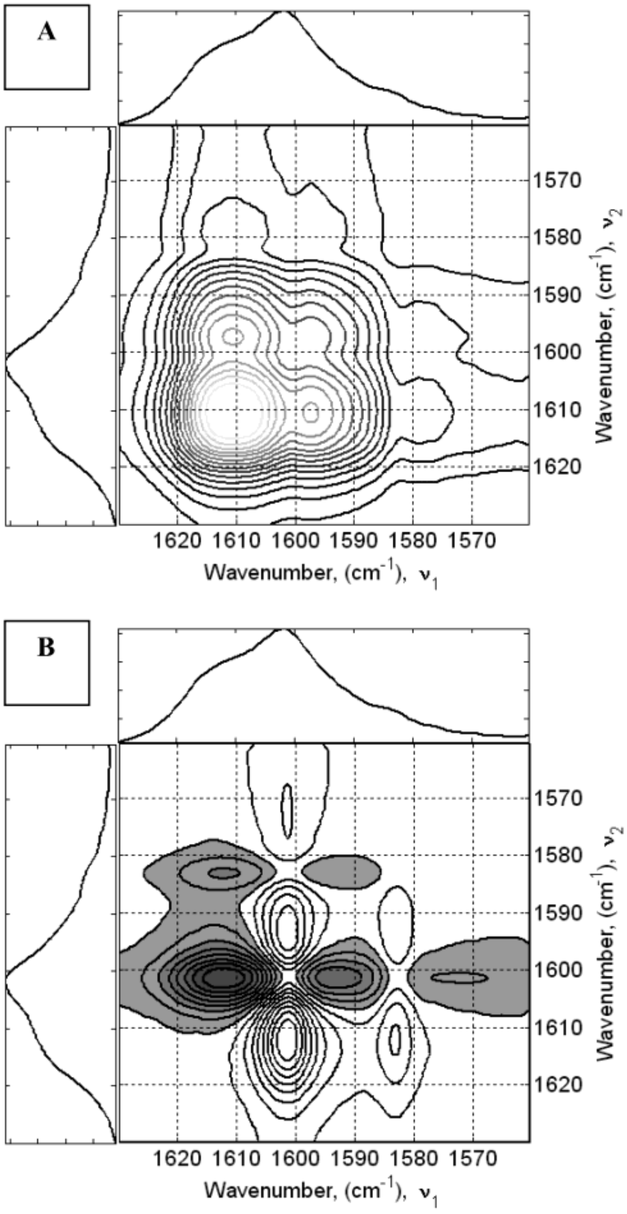

Figure 9. Synchronous (A) and asynchronous (B) contour plots in the region 1650−1560 cm^{-1} of five "synthetic" blends of composition (by weight): 1.25*[90/10], 70/30, 50/50, 30/70, and 10/90 PS/PPO.

Spectra that vary in a linear fashion should *never* have asynchronous spectra if they are concentration-normalized. We believe Sasic et al.[8] had a set of spectra that varied in a nonlinear fashion with concentration, possibly because their concentration normalization procedure was different to ours. Nevertheless, the mean normalization method employed by these authors is obviously useful, revealing the correct concentration dynamics in synchronous plots while minimizing effects due to errors in the asynchronous plots.

We can now return to examine the origin of the "new" bands apparently revealed in the asynchronous spectra of PS/PMMA, particularly in the 1730 and 700 cm^{-1} regions of the spectrum. To accomplish this, we carefully examined scale-expanded spectra in each of these regions shown in Figure 10. Each spectrum has been plotted to full scale, demonstrating that there are small bandwidth changes from spectrum to spectrum. These changes do not progress systematically with concentration, but are random, indicating they are a consequence of sample preparation problems of the type mentioned above (scattering, wedge effects, etc.). Because of this difference in bandwidth, lobes or points of inflection are generated in the difference spectra when the mean spectrum is subtracted from each of these. (It should be kept in mind that it is these difference spectra that are used to generate the 2D plots.) One such difference spectrum, obtained from subtracting the mean spectrum from that of the 50/50 PS/PMMA blend spectrum, is shown in Figure 11. Also shown in Figure 11 is a second derivative of the difference spectrum, clearly identifying the positive and negative lobes or humps near 703, 698, and 695 cm^{-1}. It is these difference bands that are responsible for the asynchronous bands that appear in Figures 2 and 3. They do not necessarily correspond to real infrared absorption bands at all but are often artifacts that result from subtracting bands of different half-width. (Subtracting a slightly thinner band from a broader one gives the type of difference spectrum shown

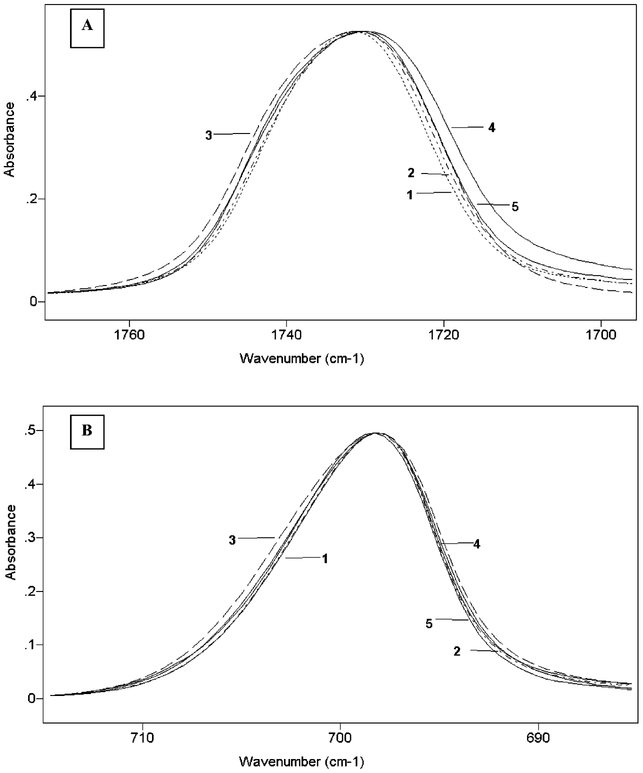

Figure 10. Random bandwidth change in the region of 1730 cm^{-1} (A) and 700 cm^{-1} (B) in the immiscible PS/PMMA blends: 1, 90/10; 2, 70/30; 3, 50/50; 4, 30/70; 5, 10/90.

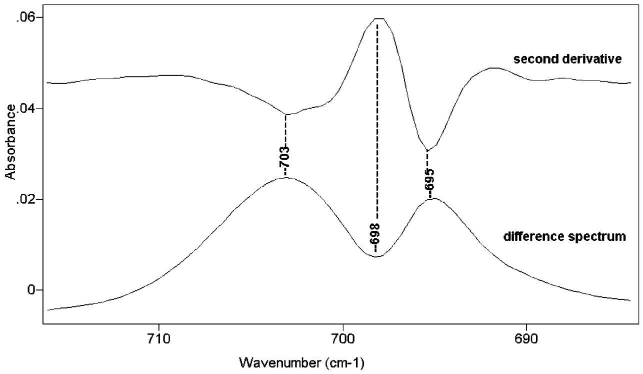

Figure 11. Difference spectrum at 700 cm^{-1} of a 50/50 PS/PMMA blend and its second-derivative spectrum.

Figure 11.) The resulting 45° rotated four-leaf clover like pattern is characteristic of systems with even small bandwidth changes, as shown previously in simulations reported by Czarnecki.[13]

Conclusions

In this study we have applied correlation infrared spectroscopy to a study of immiscible blends. Asynchronous spectra should not be obtained from such mixtures but usually are. This can be a consequence of concentration normalization errors, but most of the effects can be attributed to small differences in bandwidths. Band broadening can occur for a number of reasons. One is because the functional group involved is in a more homogeneous environment in one sample relative to another, and the observed broadening reflects subtle differences in environment. Because bandwidth changes are not systematic with concentration in these immiscible blends, we believe the origin is much more likely to be a consequence of sample preparation problems, however. We have mentioned above that it is very difficult to reproducibly obtain films of uniform thickness that completely cover a salt window. As a result, band intensities, particularly those associated with strongly absorbing modes, such as those at 1730 cm^{-1} (PMMA) and 700 cm^{-1} (PS), can appear to be within the Beer−Lambert law range when they are not, thus leading to an apparent change in width at half-height. Add to this the possibility of effects due to reflections, scattering in phase-separated systems, etc., and then it would be surprising if subtle spectroscopic changes were not observed. Asynchronous spectra appear to be very sensitive to these effects, and great care must be taken in the interpretation of features in these spectra. A careful examination of the original spectra and the difference spectra that are generated from these is usually sufficient to explain new features.

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Note added after ASAP Posting

This article was released ASAP on June 25, 2003. The following changes have now been made: Figure 1, changes were made to the alignment of the figure; Table 1, column 3, entry 4, 1 200 000 was changed to 120 000; second paragraph of the Results and Discussion section, sentence 5, “out-of-place” was replaced by “out-of-plane”. The correct version was posted on 09/15/2003.

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