Use of Fourier Transform Infrared and Second Derivative Ultraviolet Spectrometry in Determining Polystyrene–Poly(4-vinylpyridine) Blend Composition

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ABSTRACT: Polymer blend usage has increased in recent years as the blends provide a convenient means for modifying polymer properties. It is often necessary to be able to determine the percentages or ratios of polymers present in a blend. One blend of interest is the immiscible blend of polystyrene (PS) and poly(4-vinylpyridine) (P4VP). The percentages were determined by two methods: Fourier transform infrared (FTIR) spectroscopy and second derivative ultraviolet (UV) spectroscopy. The peak ratio versus percentage polymer technique was used in both methods. For FTIR, the ratio of the absorbance values of the out-of-plane C-H bending vibration of P4VP at 822 cm^{-1} and the aromatic C $=$ C stretch for PS at 1493 cm^{-1} were ratioed. For derivative UV, the vibrational structure of the aromatic secondary bands was used: 269 nm minimum for PS and the 271 nm maximum for P4VP. Both methods gave excellent and comparable results. The derivative UV determination had the advantage of requiring less sample due to its greater sensitivity. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2422–2426, 2005

Key words: blends; FTIR; UV–vis spectroscopy; polystyrene; poly(4-vinylpyridine)

INTRODUCTION

The use of polymer blends has increased in recent years since it provides a means for modifying polymer properties without the need for synthesizing new polymers. Properties such as chemical resistance, thermal stability, and mechanical strength may be enhanced by blending two or more existing polymers.[1,2]

Blends can be described as either miscible or compatible (homogeneous solid phase) or as immiscible or incompatible (multiphase systems). Regardless of miscibility, it is often necessary to determine the composition of the blend or to monitor composition during on-line processes. Analytical methods used in these determinations include IR, Fourier transform infrared (FTIR), NIR, and ^{13}C-NMR.[3–5]

In this work, the composition of blends of polystyrene (PS) and poly(4-vinylpyridine) (P4VP) will be ascertained. These polymers form an immiscible blend, as might be expected since there is no possibility of hydrogen bonding, dipole attraction, or aromatic stacking (π stacking).[6] Calculation of the Flory–Huggins chi value also indicates a high degree of incompatibility.[7] The immiscibility is also obvious from the work done here, which shows the FTIR spectra and the second derivative UV spectra of the blends simply to be superpositions of the spectra of the individual polymers. In this work, the composition of the blends was determined by two different methods: FTIR and second derivative UV spectroscopy.

EXPERIMENTAL

Materials

Polystyrene (M_w 190,000) and poly(4-vinylpyridine) (M_w 50,000) were from Scientific Polymer Products. Chloroform was certified ACS from Fisher Scientific. UV cells–demountable cells–quartz were from NSG Precision Cells. FTIR cells–Real Crystal IR card (NaCl) was from International Crystal Laboratories. The Real Crystal cards were used for several reasons. They are mounted on cards, which facilitates labeling. They are manufactured by a process that makes them impervious to atmospheric moisture, which allows long-term storage without desiccant. They are also considerably less expensive than standard NaCl windows. All materials were used as received.

Instruments

FTIR analysis was done with a Perkin-Elmer BX FTIR spectrophotometer. Four scans were made
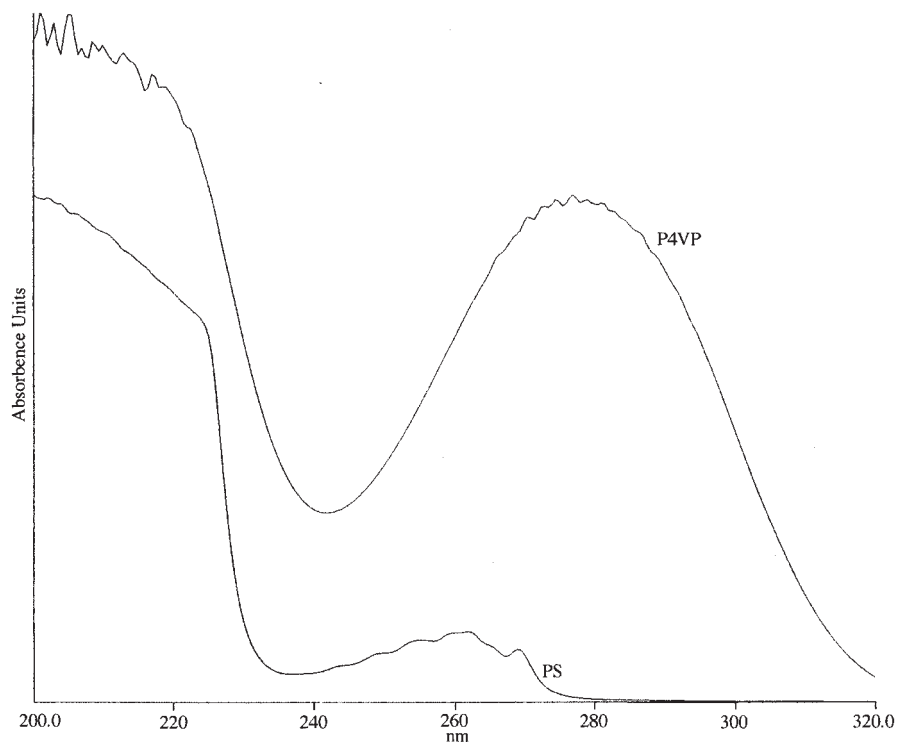

Figure 1 Zero-order UV spectra of PS and P4VP.

with a resolution of 4 cm^{-1}. Absorbance versus wavenumber (cm^{-1}) was recorded and the spectra were scanned from 4000 to 450 cm^{-1}. The out-of-plane C-H bending vibration of P4VP at 822 cm^{-1} and the aromatic C = C stretch for PS at 1493 cm^{-1} were chosen as peaks for ratioing. These peaks were chosen because there were no peaks from the other polymer in these areas. That is to say, PS had no significant peaks in the 822 cm^{-1} region and P4VP had no significant peaks in the 1493 cm^{-1} region. In addition, both peaks were sufficiently strong that they would not disappear at low concentration.

Zero-order UV spectroscopy could not be used because the individual polymers showed somewhat broad, featureless bands that overlapped each other, as seen in Figure 1. However, second derivative spectroscopy allowed enhancement of the vibrational structure such that individual peaks could be easily discerned.

Second derivative UV analysis was done with a Perkin-Elmer Lambda 2S UV–vis spectrophotometer with a 1-nm slit width, a photometric accuracy of ±0.005A (absorbance units) at 1A and a reproducibility of ±0.002A at 1A. The second derivative, $d^2A/d\lambda^2$, where A represents absorbance and λ wavelength in nanometers was plotted versus wavelength. This instrument generates derivative spectra through electronic differentiation of the spectrophotometer output data. Therefore, no exter-

nal computer or software is required. When using the peak-zero method (where the intensities are measured from the zero line) it does not matter whether both are maxima, both are minima, or one is a maximum and the other a minimum as long as they are proportional to the concentrations of the individual components.[8] Therefore, the 269-nm minimum for PS and the 271-nm maximum for P4VP were chosen for ratioing because they are both strong peaks that would not disappear at low concentration. The derivative spectra were scanned from 230 to 320 nm.

Sample preparation

The polymers were weighed out to give solutions of 90% P4VP–10% PS, 70% P4VP–30% PS, 50% P4VP–50% PS, 30% P4VP–70% PS, and 10% P4VP–90% PS. The total polymer weight was 0.1 g/10 mL (10 g/L). Each sample was dissolved in chloroform. Samples of 100% P4VP and 100% PS were also dissolved in chloroform at the same concentration (0.1 g/10 mL). FTIR spectra and second derivative UV spectra were run on all of the above. For FTIR work, the solutions were applied to Real Crystal IR cards (NaCl) and for the UV spectra to the nonrecessed window of a quartz demountable cell. The chloroform was allowed to evaporate and the spectra of the cast films

were recorded. Several solution applications were necessary to obtain appropriate absorbance values, with the FTIR cards of course requiring more layers due to the lower sensitivity of the method.
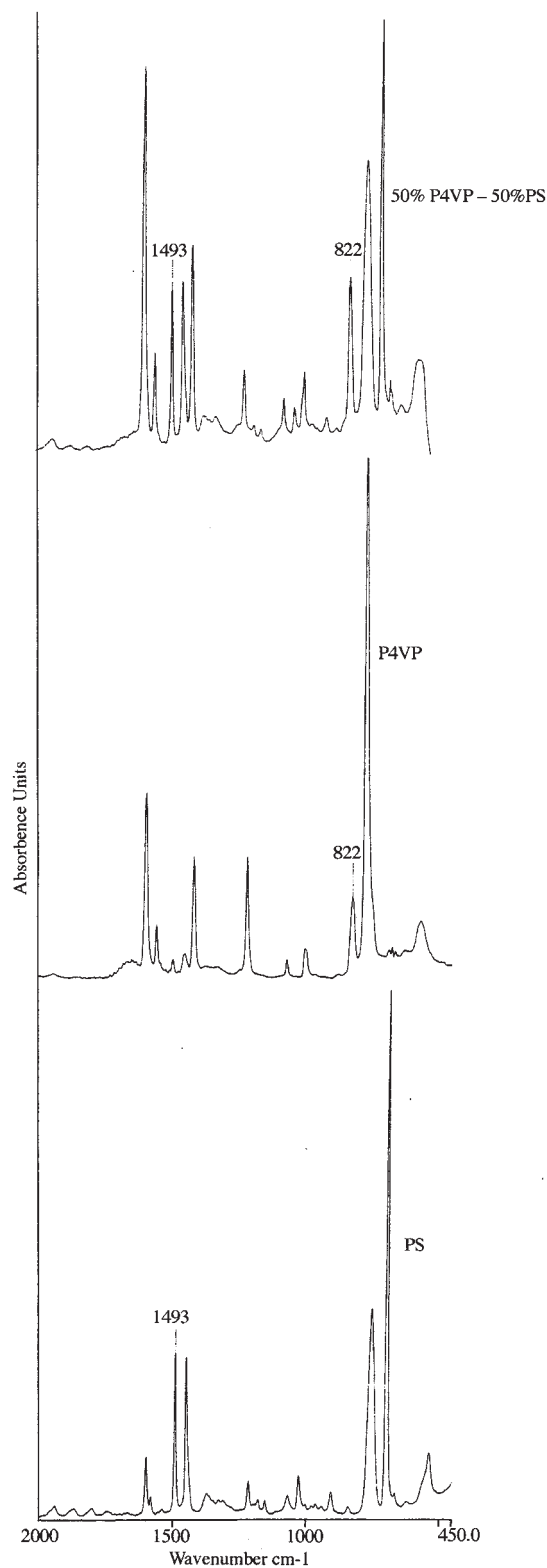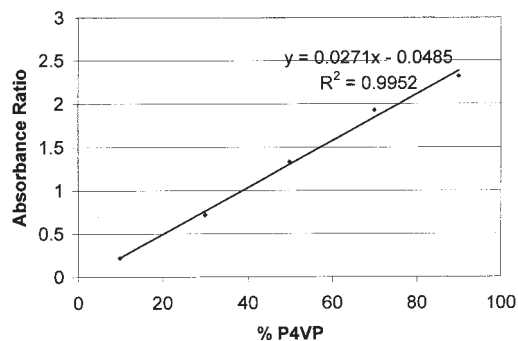

Figure 3 Plot of the FTIR absorbance ratios versus % P4VP.

RESULTS AND DISCUSSION

FTIR results

The out-of-plane C-H bending vibration for P4VP at 822 cm^{-1} and the aromatic C $=$ C stretch for PS at 1493 cm^{-1} were chosen as the peaks for which the absorption ratios would be calculated. Spectra for pure P4VP, pure PS, and a 50–50 blend of P4VP and PS, as seen in Figure 2, show that the spectrum of the immiscible blend is simply a superposition of the spectra of the individual polymers. Although the region was scanned from 4000 to 450 cm^{-1}, only the spectral region of interest is shown. The plot of the ratios of the absorbances of the 822 cm^{-1} peak to the 1493 cm^{-1} peak to the corresponding percentage compositions is shown in Figure 3.

Second derivative UV results

The second derivative UV spectra were scanned from 230 to 320 nm because this encompasses the entire aromatic secondary band. This band is often called the *B* band and corresponds to the 255-nm band of unsubstituted benzene.[9–11] This band shows fine or vibrational structure. The lower wavelength aromatic primary band, which corresponds to the unsubstituted benzene 204 nm band, usually does not show this type of fine structure.[10]

Vibrational structure from the aromatic secondary band was used for obtaining the second derivative intensity ratios. The 269-nm minimum for PS and the 271-nm maximum for P4VP were used. The second derivative spectra for PS, P4VP, and a 50–50 blend of PS and P4VP are shown in Figures 4, 5, and 6 respectively. Again, the spectrum of the blend is a superposition of the spectra of the individual polymers. The plot of the ratios of the 269-nm minimum to the 271-nm maximum to the corresponding percent compositions is shown in Figure 7.

Figures 3 and 7 show that plots from both types of data yield straight lines with R^2 values with a value of >0.99.
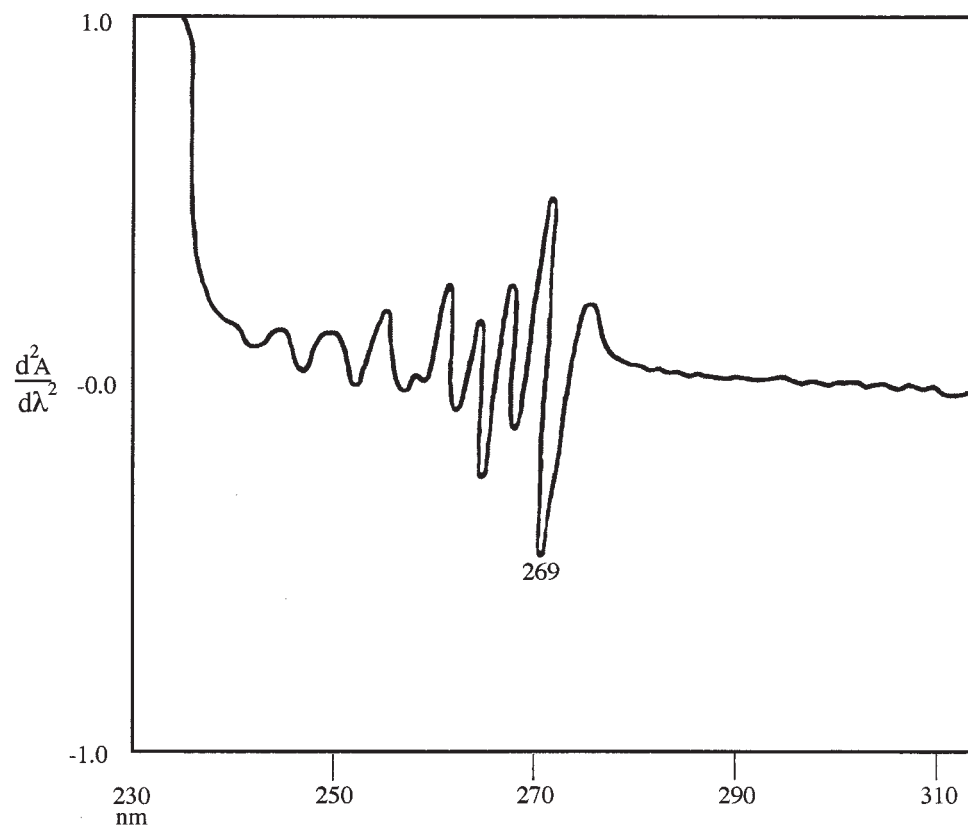

Figure 2 FTIR spectra of pure PS and P4VP and a 50% PS–50% P4VP blend.

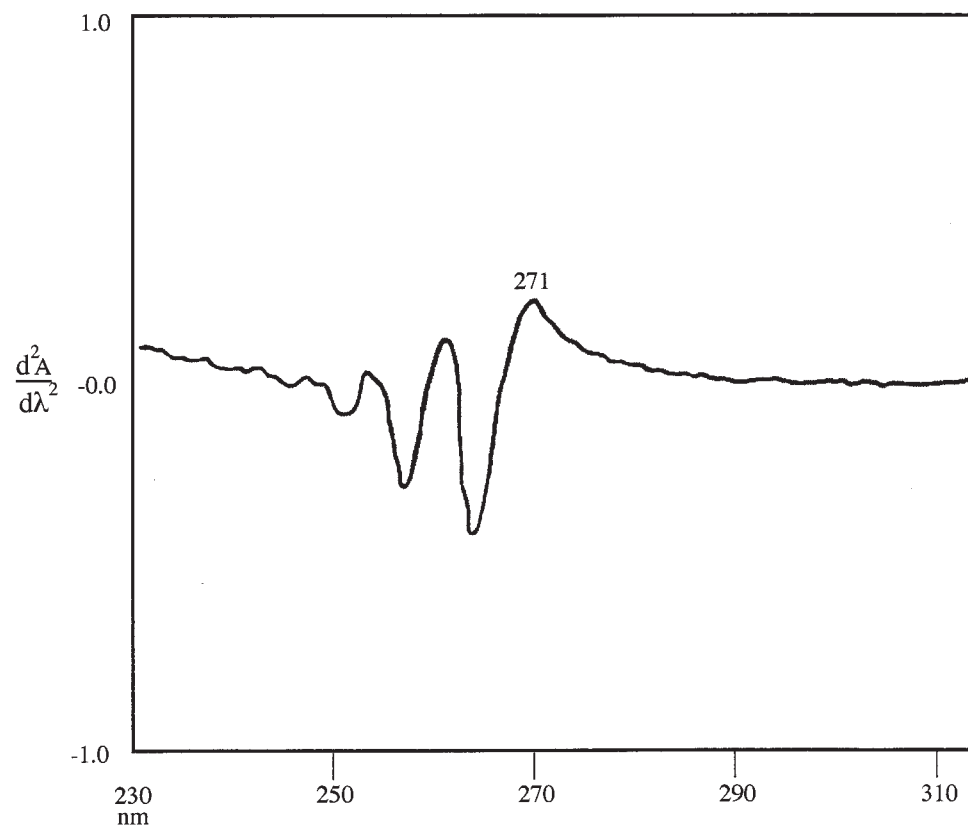**Figure 4**   Second derivative UV spectrum of PS.

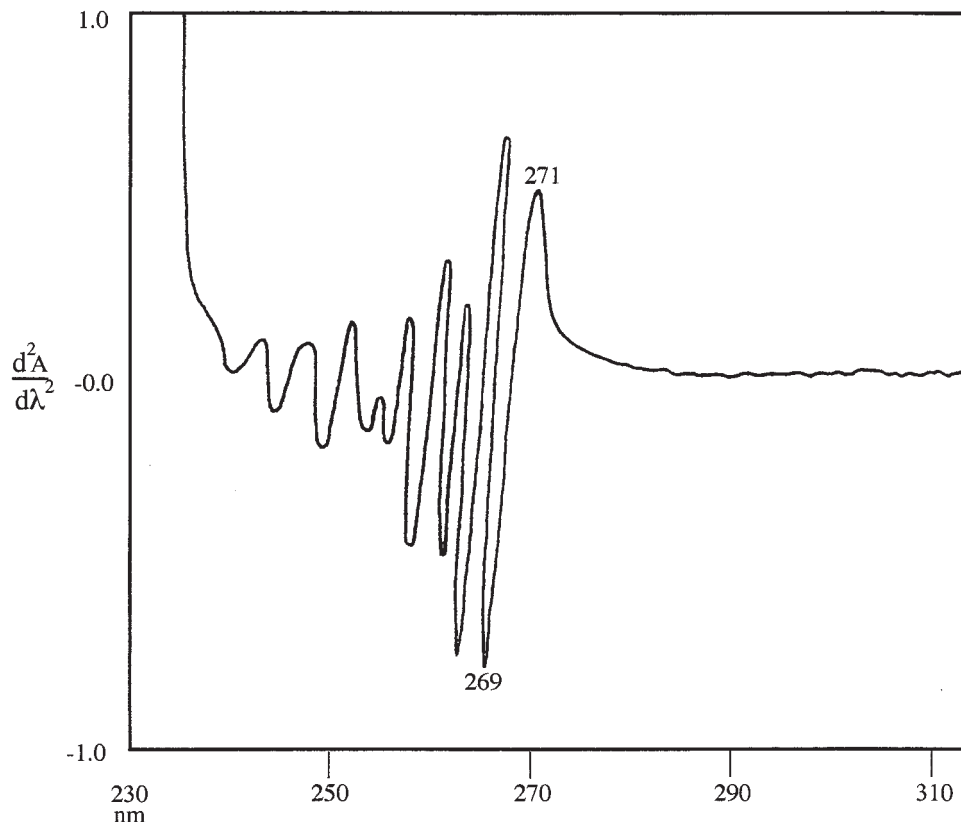**Figure 5**   Second derivative UV spectrum of P4VP.

Figure 6 Second derivative spectrum of a blend of 50% P4VP and 50% PS.

CONCLUSIONS

The data indicate that both the FTIR method and the second derivative UV method provide an excellent means for determining percentages in P4VP–PS blends. The results from both methods are comparable with similar R^2 values. Experimentally, both methods are simple and fast. The derivative UV method has the advantage of being much more sensitive than the FTIR technique and this can be important when the quantity of the sample is limited. In general, the UV deriv-

ative method can be used if both polymers in the blend have chromophores that lead to different features in the respective derivative spectra.

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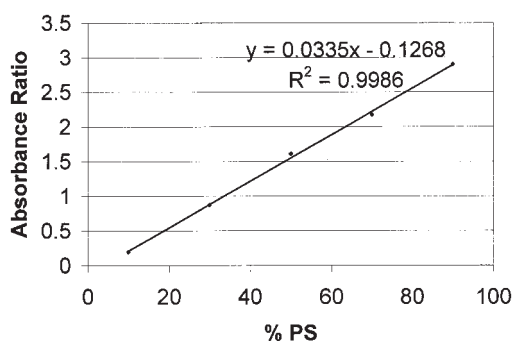11. Mohan, J. Organic Spectroscopy Principles and Applications; CRC Press: New York, 2000; Chapter 3.

Figure 7 Plot of the ratios of the second derivative UV 269 minimum to the 271 maximum versus % PS.