

# Fourier Transform Infrared and Second Derivative Ultraviolet Spectrometry in Determining Polystyrene-Poly(4-methylstyrene) 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 determine the percents or ratios of the polymers present in a blend. One blend of interest is the immiscible blend of polystyrene (PS) and poly(4-methylstyrene) (P4MS). The percentages were determined by two methods: Fourier transform infrared (FTIR) spectroscopy and second derivative ultraviolet (UV) spectroscopy. The peak ratio versus percent polymer technique was used in both methods. For the FTIR, the ratio of the absorbance values for the out-of-plane C—H *para*-substituted bending vibration of P4MS at 813 cm<sup>-1</sup> and the

out-of-plane monosubstituted C—H bending vibration for PS at 757 cm<sup>-1</sup> were ratioed. For derivative UV, the vibrational structures of the aromatic secondary bands were used: the 269 nm minimum for PS and 275 nm minimum for P4MS. The derivative UV method gave considerably better results and also had the advantage of requiring less sample due to its greater sensitivity. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3400–3403, 2006

**Key words:** blends; FTIR; UV-vis spectroscopy; polystyrene; poly(4-methylstyrene)

## INTRODUCTION

The use of polymer blends has increased in recent years since the blending provides a means of producing materials with improved properties. These properties include thermal stability, mechanical strength, and chemical resistance.<sup>1,2</sup>

Blends can be characterized as miscible or compatible (homogenous solid phase) or immiscible or incompatible (multiphase system). Regardless of miscibility, it is frequently necessary to determine the composition of the blend or to monitor composition during on-line processes. Methods used in these determinations include FTIR, NIR, and <sup>13</sup>C-NMR.<sup>3–5</sup>

In this work, the composition of blends of polystyrene (PS) and poly(4-methylstyrene) (P4MS) are determined. These two polymers form an immiscible blend as might be expected since there is little possibility of hydrogen bonding, dipole attraction, or aromatic stacking ( $\pi$  stacking).<sup>6</sup> It has also been established that these two polymers do not become miscible until an upper critical solution temperature of approximately 270°C and that polymer properties like tacticity and crystallinity do not affect the miscibility.<sup>7</sup> The immiscibility of this blend is also apparent in this work in

that the FTIR spectra and the second derivative UV spectra used for analysis of the blends were simply superpositions of the spectra of the individual polymers.

## EXPERIMENTAL

### Materials

Polystyrene ( $M_w$ , 190,000) and poly(4-methylstyrene) ( $M_w$ , 100,000) were from Scientific Polymer Products, Inc. Chloroform, certified ACS from Fisher Scientific. UV cells – demountable cells – quartz from NSG Precision Cells, Inc. FTIR cells – Real Crystal IR card (NaCl) 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 PerkinElmer BX FTIR spectrophotometer. Four scans were made with a resolution of 4 cm<sup>-1</sup>. Absorbance versus wavenumber (cm<sup>-1</sup>) was recorded and the spectra were scanned from 4000 to 450 cm<sup>-1</sup>. The out-of-plane *para*-substi-

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tuted C—H bending vibration of P4MS at  $813\text{ cm}^{-1}$  and the out-of-plane monosubstituted C—H bending vibration of PS at  $757\text{ cm}^{-1}$  were chosen as peaks for ratioing. These peaks were chosen because both peaks were sufficiently strong that they would not disappear at low concentration.

In addition, the ratios of other peaks showed little or no correlation to the percent composition. This was the case when the P4MS  $813\text{ cm}^{-1}$  peak was ratioed to the PS peaks at  $1493$  and  $692\text{ cm}^{-1}$ .

Zero-order UV spectroscopy could not be used because the individual polymers showed somewhat broad 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 PerkinElmer Lambda 2S UV-vis spectrophotometer with a  $1\text{ nm}$  slit width, a photometric accuracy of  $\pm 0.005A$  (absorbance units) at  $1A$  and a reproducibility of  $\pm 0.002A$  at  $1A$ . The second derivative,  $d^2A/d\lambda^2$  where  $A$  represents absorbance and  $\lambda$  represents wavelength in  $\text{nm}$ , was plotted versus wavelength. This instrument generates derivative spectra through electronic differentiation of the spectrophotometer output data. Therefore, no external 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 or both are minima or one is a maximum and the other is a minimum as long as they are proportional to the concentrations of the individual components.<sup>8</sup> Therefore, the  $269\text{ nm}$  minimum for PS and the  $275\text{ nm}$  minimum for P4MS were chosen for ratioing because they are both strong peaks that would not disappear at

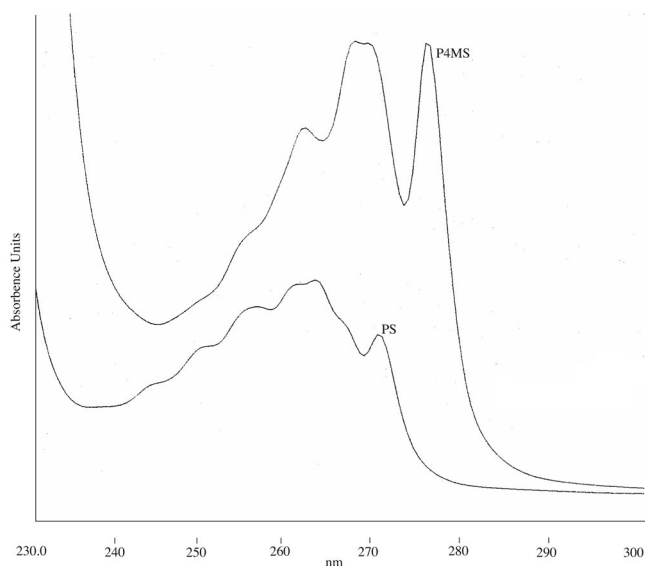


Figure 1 Zero-order UV spectra of PS and P4MS.

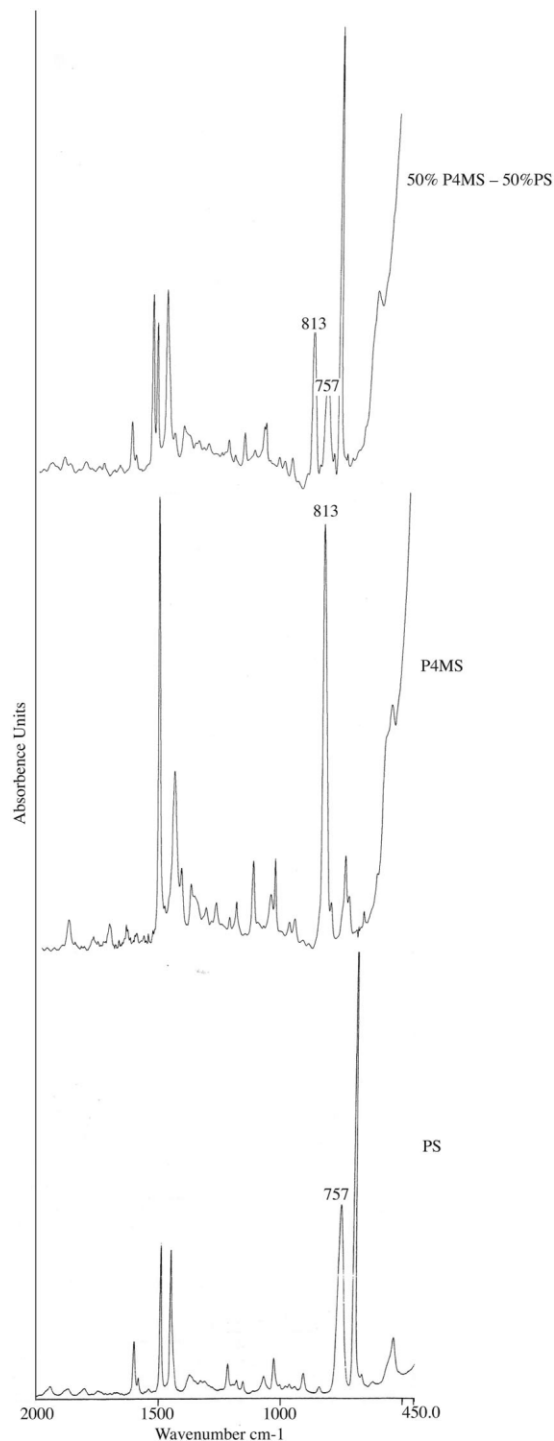
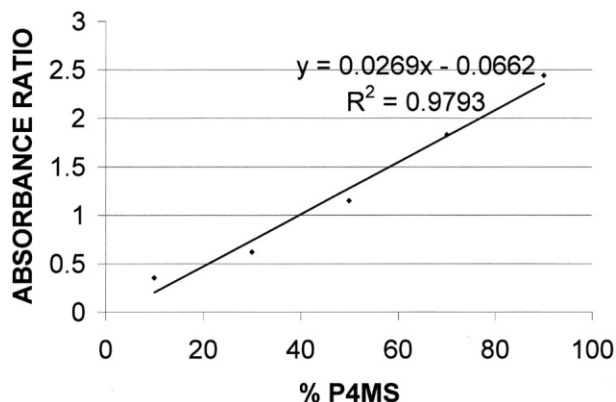


Figure 2 FTIR spectra of pure PS and P4MS and a 50% PS-50% P4MS blend.

low concentration. The derivative spectra were scanned from  $230$  to  $320\text{ nm}$ .

### Sample preparation

The polymers were weighed out to give solutions of  $90\%$  P4MS- $10\%$  PS,  $70\%$  P4MS- $30\%$  PS,  $50\%$  P4MS-



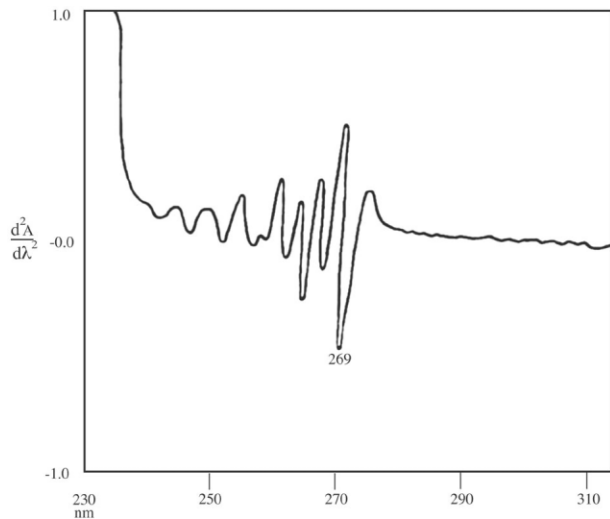
**Figure 3** Plot of the FTIR absorbance ratios versus % P4MS.

50% PS, 30% P4MS-70% PS, and 10% P4MS-90% PS. Total polymer weight was 0.1 g/10 mL (10 g/L). Each sample was dissolved in chloroform. Samples of 100% P4MS 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 the 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, the FTIR cards of course requiring more layers due to the lower sensitivity of the method.

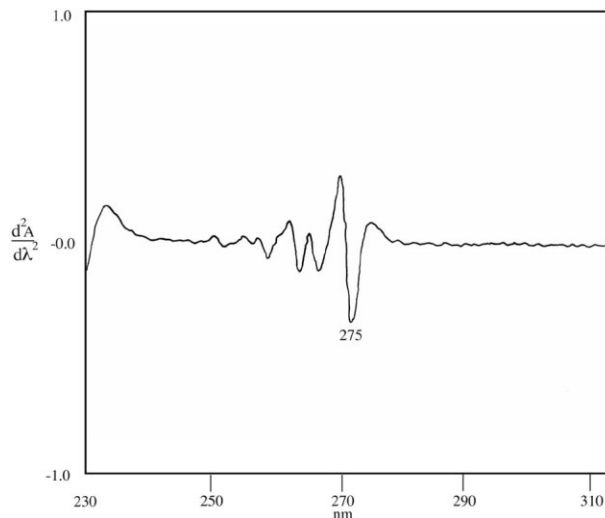
## RESULTS AND DISCUSSION

### FTIR results

The out-of-plane *para*-substituted C—H bending vibration for P4MS at  $813\text{ cm}^{-1}$  and the out-of-plane



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

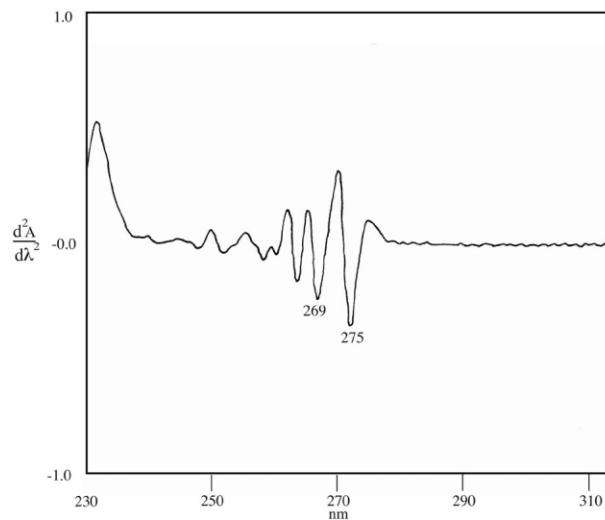


**Figure 5** Second derivative UV spectrum of P4MS.

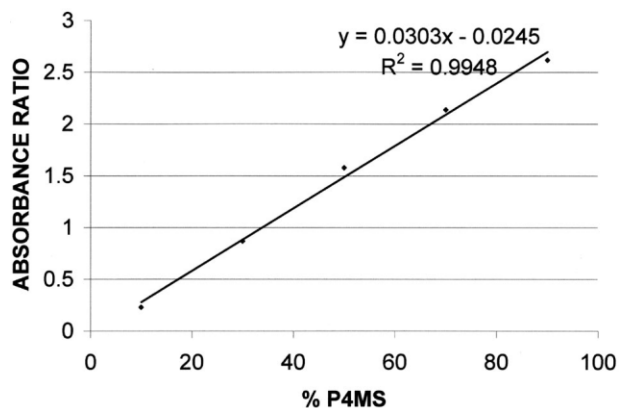
mono-substituted C—H bending vibration for PS at  $757\text{ cm}^{-1}$  were chosen as the peaks for which absorbance ratios would be calculated. Spectra for the pure P4MS, PS, and a 50/50 blend of P4MS and PS as seen in Figure 2 show that the spectrum of the immiscible blend is simply a superposition of the spectra of the individual polymers. Although the spectra were scanned from  $4000$  to  $450\text{ cm}^{-1}$ , only the spectral region of interest is shown. The plot of the ratios of the absorbances of the  $813\text{ cm}^{-1}$  peak to the  $757\text{ cm}^{-1}$  peak to the corresponding percent 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



**Figure 6** Second derivative spectrum of a blend of 50% P4MS and 50% PS.



**Figure 7** Plot of the ratios of the second derivative UV 269 minimum to the 275 minimum versus % P4MS.

aromatic secondary band. This band is also called the B band, and corresponds to the 255 nm band of unsubstituted benzene.<sup>9–11</sup> 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.<sup>9</sup>

Vibrational structure from the aromatic secondary band was used for calculating the second derivative intensity ratios. The PS 269 nm minimum and the P4MS 275 nm minimum were used. The second derivative spectra of PS, P4MS, and a 50/50 blend of the two are shown in Figures 4–6, respectively. As before the spectrum of the blend is a superposition of the spectra of the individual polymers. The plot of the intensity ratios of the 275 nm peak to the 269 nm peak

to the corresponding percent compositions is shown in Figure 7.

## CONCLUSIONS

Figures 3 and 7 indicate that the second derivative UV method gives somewhat better results since the UV method gives an  $R^2$  value of 0.9945 and the FTIR method gives an  $R^2$  value of 0.9793. The greater sensitivity of the derivative UV technique has the added advantage of requiring less sample. This is obviously important when the quantity of sample is limited. Both methods are simple and fast.

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