

Identification of Structurally Similar Polymers by Second Derivative Ultraviolet Spectroscopy

Infrared methods have been used extensively in the characterization and identification of polymers. These methods have been reasonably successful, even though problems often arise in sample preparation. The simplest technique, direct casting from solution, may leave a film of uneven thickness which may cause some distortion in the spectrum. Pyrolysis is quite time-consuming, whereas hot pressing is suitable only for making thicker films. It is often impossible to prepare KBr discs since many polymers are hard to disperse throughout the KBr.¹

Newer IR methods have overcome some of these sampling problems. Diffuse reflectance FTIR has been used in the characterization of poly(ethylene terephthalate).² Emission spectra of this polymer also have been recorded by using thin films at 100°C.³ External reflection spectroscopy (IR-ERS) has been utilized in characterizing poly(methyl methacrylate).⁴

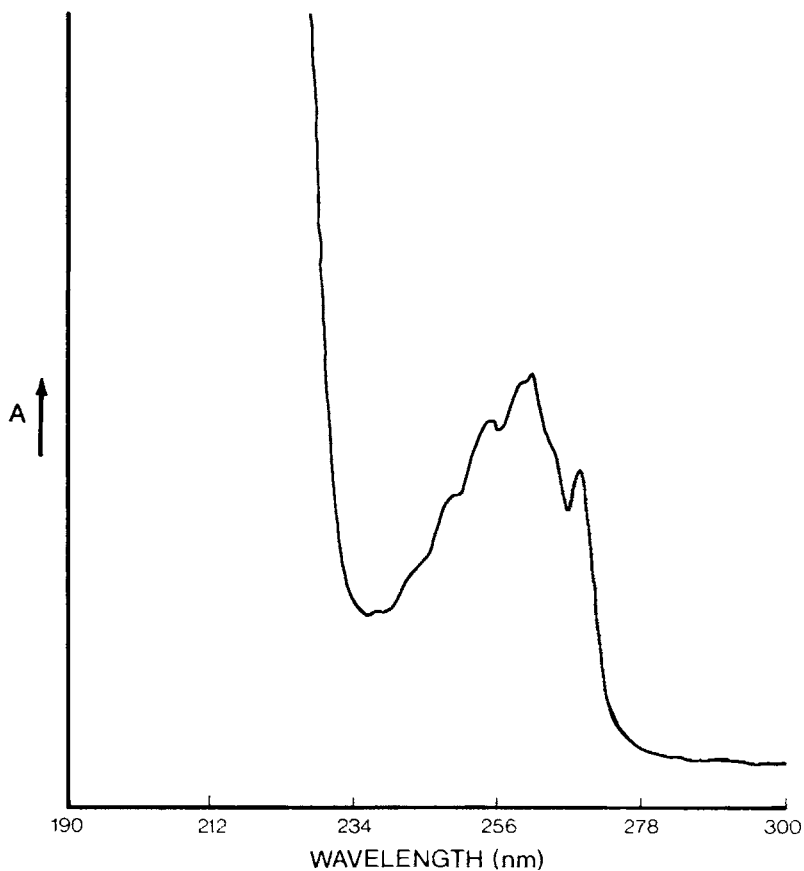


Fig. 1. Zero-order UV spectrum: polystyrene.

Other instrumental methods have been somewhat useful in qualitative studies of polymers. Poly(ethylene oxide) and polystyrene have given NMR CRAMPS (combined rotation and multiple pulse spectroscopy) spectra showing fine structure that is useful in qualitative analysis.⁵ Hyphenated and tandem techniques such as GC/MS⁶ and GC-IR-MS⁷ have also proven helpful.

Ultraviolet spectroscopy has not seen much use in polymer identification. This is to be expected since most polymers give rather featureless zero-order spectra. Furthermore, polymers of the same general type give zero-order spectra that are very similar or indistinguishable. This is not the case, however, with derivative spectra. Second derivative UV spectroscopy has been established as a valuable, qualitative method,⁸⁻¹¹ and first, second, and fourth derivative UV spectroscopy has been used in studying polymers with considerable structural differences.¹² This paper will describe the use of second derivative spectroscopy in characterizing and identifying polymers with similar structures utilizing a simple and rapid method for sample preparation. This technique does not require the expensive instrumentation or lengthy procedures necessary in the methods mentioned above.

EXPERIMENTAL

Reagents

Polystyrene (MW 280,000), poly(2,4,6-tribromostyrene) (MW 230,000), poly(4-methylstyrene) (MW not available), poly(α -methylstyrene) (MW 19,000), poly(styrene sulfonic acid), sodium

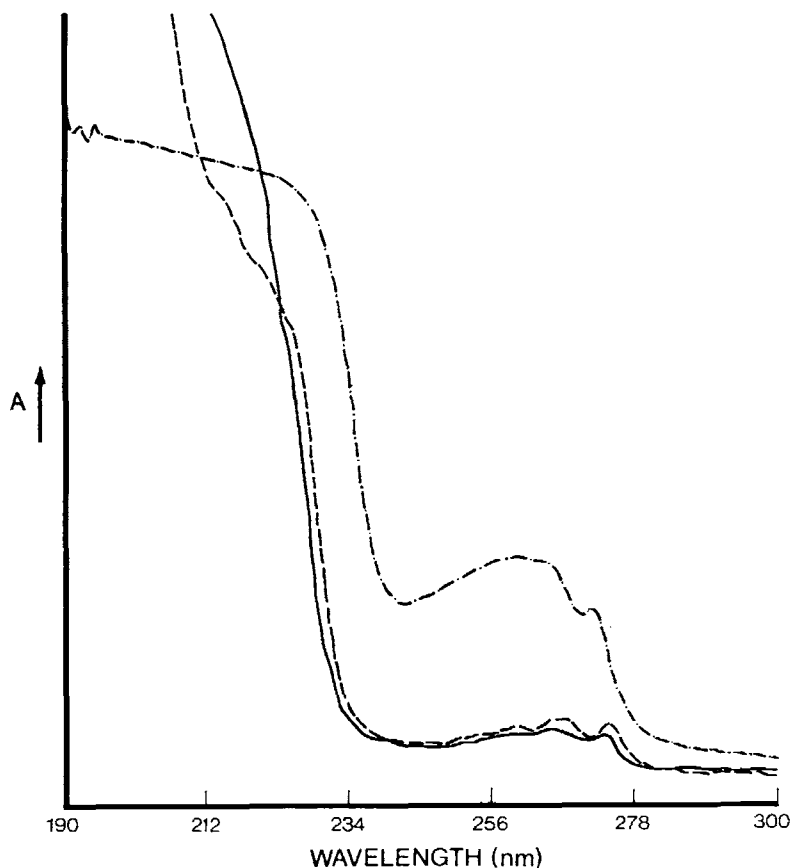


Fig. 2. Zero-order UV spectra: (---) poly(4-methylstyrene); (—) poly(vinyltoluene); (- · -) poly(α -methylstyrene).

salt (MW 500,000), poly(vinylbenzyl chloride) mixture of meta (60%) and para (40%) isomers (MW 53,000), poly(vinyl toluene) mixed meta and para isomers (MW 80,000), and poly(*p*-tert-butylstyrene) (MW 27,000) were all obtained from Sp² Scientific Polymer Products, Inc.

Apparatus

Spectral data were recorded with a Pye-Unicam, Model 8-100, recording UV-VIS spectrophotometer with first and second derivative accessory. The spectra were obtained with the following instrumental parameters: bandwidth, 1 nm; wavelength speed, 1 nm/s; chart speed, 5 s/cm; absorbance, 2. The derivative accessory was set for second derivative measurement at gain 3. This instrument generates derivative spectra through electronic differentiation of the spectrophotometer output data. Spectrophotometers which employ other means of differentiation may not be suitable for the type of work described here. The cells were 1 mm, quartz, divided cells from NSG Precision Cells, Inc.

Procedure

All of the polymers except poly(styrene sulfonic acid), sodium salt were dissolved in chloroform (Fisher Scientific, Certified ACS). Poly(styrene sulfonic acid), sodium salt was dissolved in a solution of 77% distilled water and 23% 2-propanone (Fisher Scientific, Certified ACS). Concentrations of the polymer solutions were approximately 5 g/L. The divided cells were disassembled,

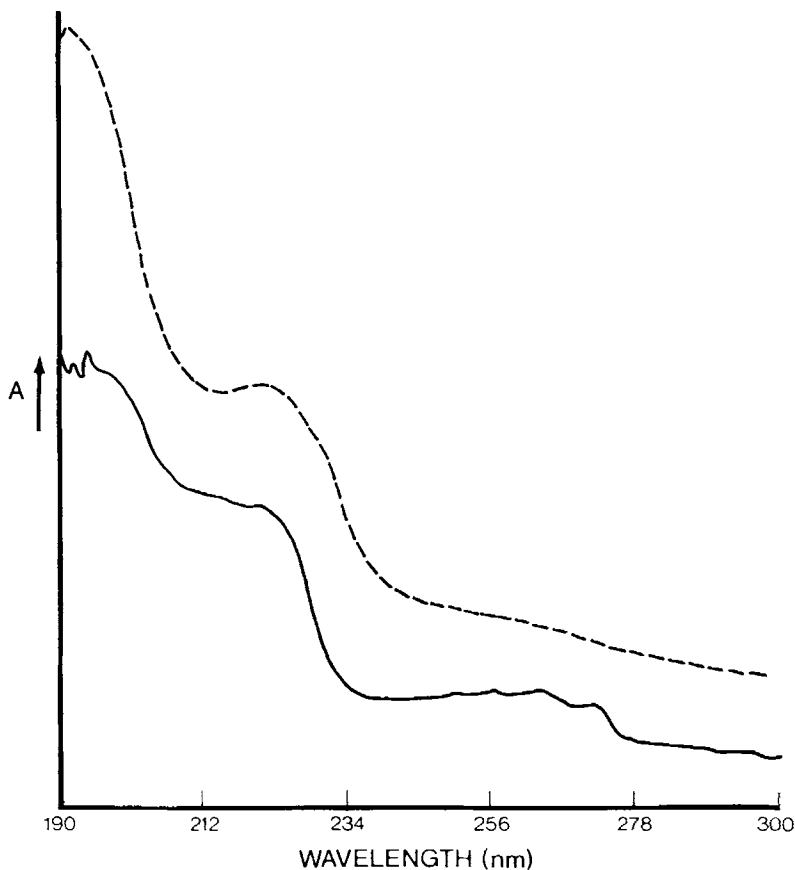


Fig. 3. Zero-order UV spectra: (---) poly(styrene sulfonic acid), sodium salt; (—) poly(*p*-tert-butylstyrene).

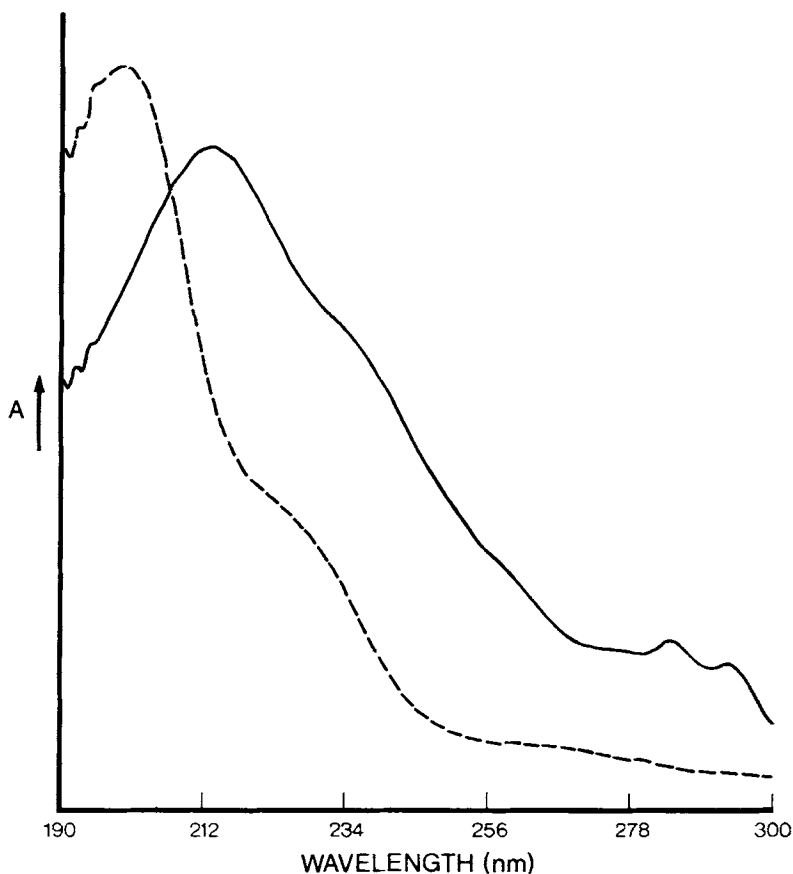


Fig. 4. Zero-order UV spectra: (—) poly(2,4,6-tribromostyrene); (---) poly(vinylbenzyl chloride).

and only the removable windows were used. The polymer solutions were applied to the windows with a Pasteur pipet and were allowed to dry in a hood at room temperature. The solvent evaporated in about 3 min leaving a thin film of polymer on the cell window. The window was inserted in the cell holder with the film either facing the light source or facing away from the light source. Identical spectra were produced with the window in either position. No reference was used. The ultraviolet

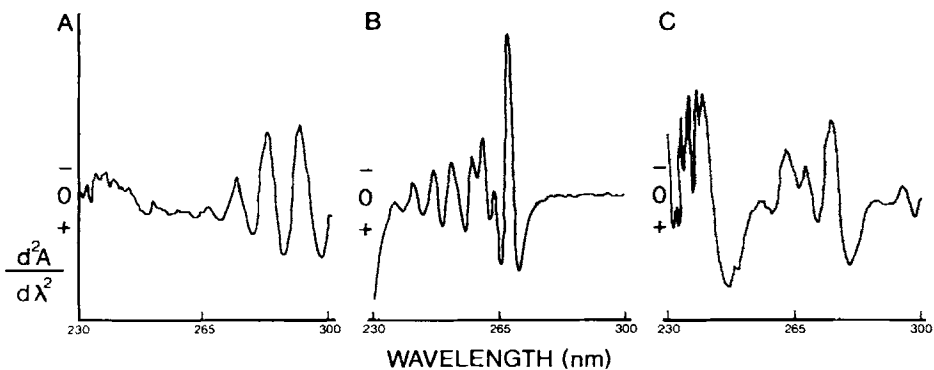


Fig. 5. Second derivative UV spectra: (A) poly(2,4,6-tribromostyrene); (B) polystyrene; (C) poly(vinylbenzyl chloride).

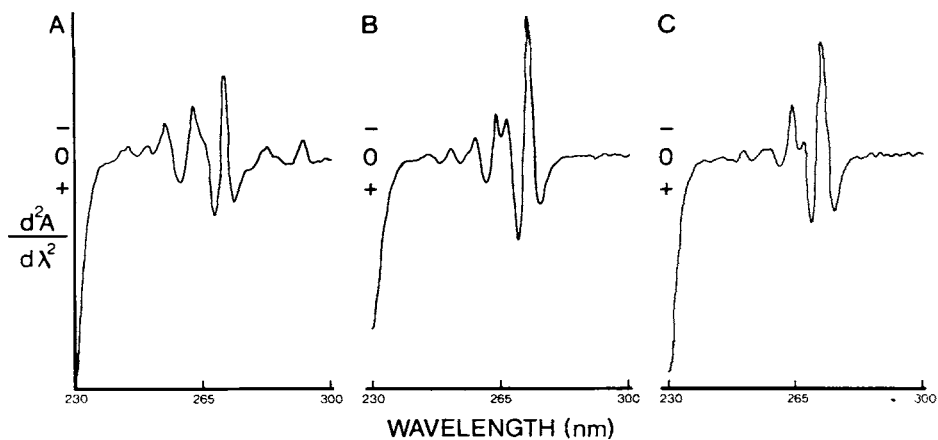


Fig. 6. Second derivative UV spectra: (A) poly(*p*-*tert*-butylstyrene); (B) poly(4-methylstyrene); (C) polyvinyltoluene.

region was scanned from 300 to 190 nm to obtain the zero-order spectra and from 300 to 230 nm for the second derivative spectra.

RESULTS AND DISCUSSION

The zero-order UV spectra of polystyrene, poly(2,4,6-tribromostyrene), poly(4-methylstyrene), poly(α -methylstyrene), poly(styrene sulfonic acid), sodium salt, poly(vinylbenzyl chloride), poly(vinyltoluene) and poly(*p*-*tert*-butylstyrene) are shown in Figures 1-4. With the exception of

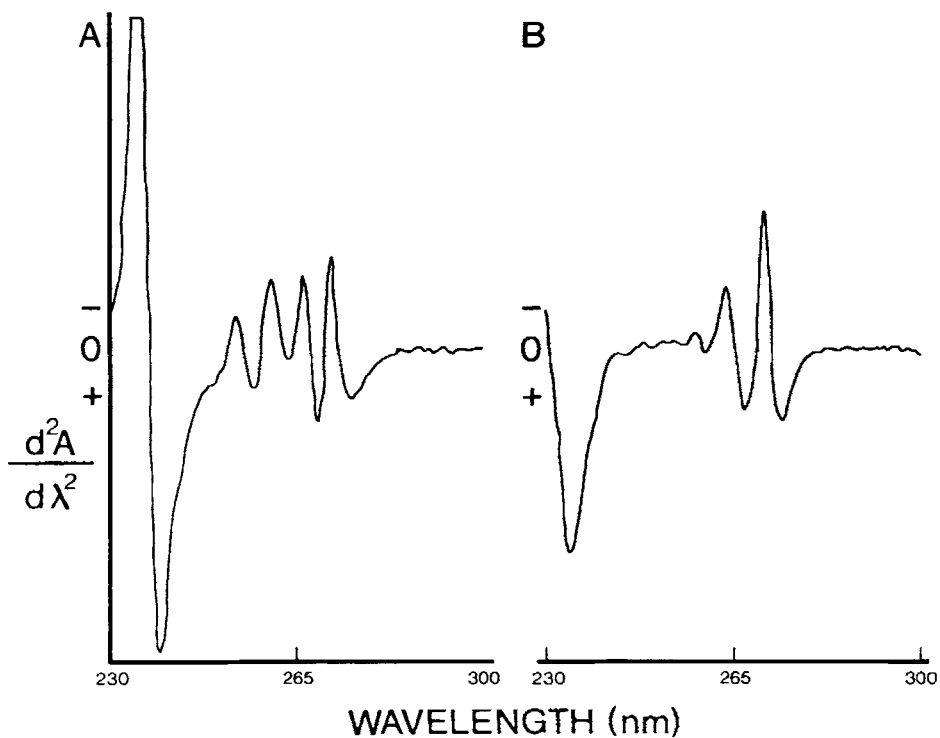


Fig. 7. Second derivative UV spectra: (A) poly(styrene sulfonic acid), sodium salt; (B) poly(α -methylstyrene).

polystyrene, none of the polymers give spectra with distinct fine structure, and that in the polystyrene spectrum is not sharp. In addition, some of the spectra are very similar. The polyvinyltoluene, the poly(4-methylstyrene), and the poly(α -methylstyrene) spectra show a close resemblance in the 245–280 nm area, while the sodium salt of poly(styrene sulfonic acid), and the poly(*p*-*tert*-butylstyrene) are similar in the region from 212–280 nm. Because of the broad, featureless bands and the similarities among the spectra, the zero-order spectra are not useful in identification of the polymers.

The second derivative UV spectra of the same polymers are shown in Figures 5–7. Even a cursory inspection of these spectra reveals that each is unique. The poly(2,4,6-tribromostyrene) spectrum [Fig. 5(A)] has strong maxima and minima in the 300–275 nm range. These strong peaks are not present in the other spectra. The polystyrene spectrum [Fig. 5(B)] is unique in that it does not show any minima at wavelengths higher than 268 nm. The strong maximum at 281 nm clearly differentiates the poly(vinylbenzyl chloride) spectrum [Fig. 5(C)] from the others, and only the poly(*p*-*tert*-butylstyrene) spectrum [Fig. 6(A)] shows weak maxima and minima in the 295–280 region. The remaining spectra all display maxima and minima in the 276–250 region. However, these spectra can be readily distinguished, since no two spectra have all of the maxima and minima at identical wavelengths. The two most similar spectra, poly(4-methylstyrene) [Fig. 6(B)] and polyvinyltoluene [Fig. 6(C)], show minima at 272, 267, and 264 nm and maxima at 276, 270, and 266 nm. However, the ratios of these peaks are quite different in each spectrum. The 267 and 264 nm peaks are of nearly equal intensity in the poly(4-methylstyrene) spectrum, whereas the 264 peak is considerably more intense than the 267 nm peak in the polyvinyltoluene spectrum. In addition, the 270 nm peak is more intense relative to the 276 nm peak in the poly(4-methylstyrene) spectrum. There are many other differentiating features apparent in the spectra in Figures 5–7. Those discussed in detail are the most notable and are more than sufficient for identifying and distinguishing the polymers. These results illustrate the value of second derivative UV spectra in the identification of these structurally similar polymers. Sample preparation is rapid, and only small amounts of polymer are required.

References

1. H. A. Willis, J. H. van der Maas, and R. G. J. Miller, *Laboratory Methods in Vibrational Spectroscopy*, 3rd ed., Wiley, New York, 1987, Chap. 9.
2. S. C. Pattacini and T. J. Porro, *Am. Lab.*, **20**(8), 24–32 (1988).
3. Reference 1, Chap. 20.
4. Marc D. Porter, *Anal. Chem.*, **60**, 1143A–1155A (1988).
5. Charles E. Bronnimann, Bruce L. Hawkins, Ming Zhang, and Gary E. Maciel, *Anal. Chem.*, **60**, 1743–1750 (1988).
6. Ray E. Clement, Francis I. Onuska, Gary A. Eiceman, Herbert H. Hill, Jr., *Anal. Chem.*, **60**, 279R–294R (1988).
7. Wayne P. Duncan, *Am. Lab.*, **20**(8), 40–46 (1988).
8. Jerry E. Cahill and Frank G. Padera, *Am. Lab.*, **12**(4), 101–112 (1980).
9. Larie Meal, *Anal. Chem.*, **55**, 2448–2450 (1983); **58**, 834–836 (1986).
10. L. G. Hargis and J. A. Howell, *Anal. Chem.*, **60**, 137R–138R (1988) (review).
11. J. A. Howell and L. G. Hargis, *Anal. Chem.*, **58**, 113R (1986) (review).
12. Sadao Mori, *J. Appl. Polym. Sci.*, **33**, 1923–1931 (1987).

LARIE MEAL

Chemical Technology Department
University of Cincinnati
Cincinnati, Ohio 45206

Received June 8, 1989

Accepted February 15, 1990