

Identification of Styrene Copolymers and a Terpolymer by Second Derivative Ultraviolet Spectroscopy

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SYNOPSIS

A method for distinguishing styrene copolymers and a terpolymer by second derivative ultraviolet spectroscopy will be described. The polymers were dissolved in chloroform except for one which was dissolved in 2-butanone. Concentrations of about 5 g/L were used. The polymer solutions were applied to the removable windows of divided, quartz cells and were allowed to dry to a thin film. The ultraviolet region was scanned from 300 to 230 nm. Then thinner films were used, and the 240–200 nm region was scanned. The second derivative spectra that resulted could be distinguished easily. This technique allows rapid, sample preparation and identification of these copolymers and the terpolymer.

INTRODUCTION

Polymers have been studied by infrared methods for a number of years. However, characterization and identification have been facilitated recently by newer IR methods that minimize some problems in sample preparation. Diffuse reflectance FTIR has been used in the characterization of poly(ethylene terephthalate).¹ External reflection spectroscopy (IR-ERS)² and emission spectra³ have also been employed.

Although IR studies involving polymers have been extensive, relatively little work has been accomplished in the characterization and identification of copolymers and terpolymers. Infrared studies of acrylonitrile/butadiene/styrene terpolymers have been successful both qualitatively and quantitatively. Butadiene and styrene characteristics are easily identified in these spectra. This provides not only qualitative information but also permits quantitative determination of the percent butadiene.⁴ IR spectra of polystyrene/butadiene copolymers have also been recorded using microtomed sections.⁵ Additional IR work with copolymers and terpolymers is rather sparse. Other methods commonly used in polymer characterization have found little use in the study of copolymers and terpolymers. These methods include GC/MS and GC-IR-MS.

Ultraviolet spectroscopy has not been utilized in the identification of copolymers and terpolymers. This is to be expected since many copolymers and terpolymers give rather featureless zero-order spectra. Furthermore, copolymers and terpolymers which contain a common polymer show zero-order spectra that are very similar or nearly identical. Derivative UV spectroscopy, however, permits the characterization and identification of some copolymers and terpolymers which contain a common polymer. Derivative UV spectroscopy has already been used to study polymers with significant structural differences⁶ and also to identify some that are structurally similar.⁷ This paper will describe the use of second derivative UV spectroscopy in characterizing and identifying some styrene copolymers and a terpolymer. A simple and rapid method for sample preparation will also be described. This technique does not require the expensive instrumentation or the lengthy procedures necessary in many of the methods mentioned above.

EXPERIMENTAL

Reagents

The following polymer, copolymers, and terpolymer were obtained from Sp² Scientific Polymers Products, Inc.:

1. Styrene (14%)/isoprene (86%) ABA block copolymer (MW 150,000)
2. Styrene/allyl alcohol copolymer, hydroxyl content 5.4–6.0% (MW 3000)
3. Styrene (30%)/butadiene (70%) ABA block copolymer
4. Styrene (50%)/butyl methacrylate (50%) (MW 135,000)
5. Polystyrene (MW 280,000)
6. Styrene (75%)/acrylonitrile (25%) copolymer (MW 165,000)
7. Styrene (28%)/ethylene-butylene (72%) ABA block copolymer (MW 118,000)
8. Styrene (50%)/maleic anhydride (50%) copolymer (MW 50,000)
9. Acrylonitrile/butadiene/styrene terpolymer (high butadiene content)

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 at gain 3. This instrument generates derivative spectra through electronic differentiation of the spectrophotometer output data. Spectrophotometers that 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 the styrene/maleic anhydride copolymer were dissolved in chloroform (Fisher Scientific, Certified, A.C.S.). The styrene/maleic anhydride copolymer was dissolved in 2-butanone (Fisher Scientific, Certified, A.C.S.). Concentrations of the polymer solutions were approximately 5 g/L. The divided cells were disassembled, 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 region

was scanned from 300 to 190 nm to obtain the zero-order spectra. Two separate scans were made in recording the second derivative spectra. One scan of the 300–230 nm region was recorded, while another scan was made of the more strongly absorbing 240–200 range. Thinner films were used in obtaining the second derivative spectra in the 240–200 nm region.

RESULTS AND DISCUSSION

The zero-order spectra of the copolymers of styrene with ethylene-butylene, isoprene, butadiene, butyl methacrylate, and allyl alcohol were all identical with the polystyrene spectrum (Fig. 1). The styrene/acrylonitrile spectrum (Fig. 1) was very similar to that of the polystyrene except for some subtle differences in the fine structure in the 278–234 nm band. This band is very weak and shows no fine structure in the acrylonitrile/butadiene/styrene spectrum (Fig. 2) or in the styrene/maleic anhydride spectrum (Fig. 2). This probably is due to the low styrene content in the acrylonitrile/butadiene/styrene terpolymer, and perhaps may be attributed to the more polar 2-butanone used in dissolving the styrene/maleic anhydride copolymer. It is obvious that the zero-order spectra cannot be used to distinguish these copolymers and the terpolymer. The spectra are either too similar or too featureless for identification purposes.

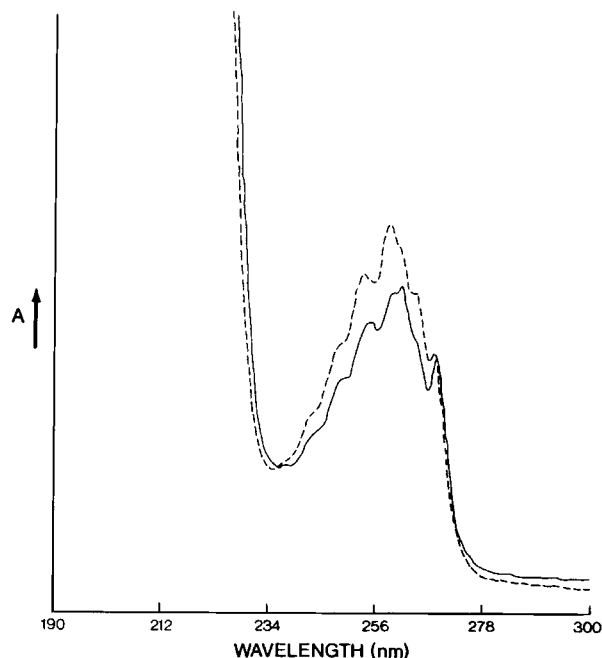


Figure 1 Zero-order UV spectra: (—) polystyrene; (---) styrene/acrylonitrile copolymer.

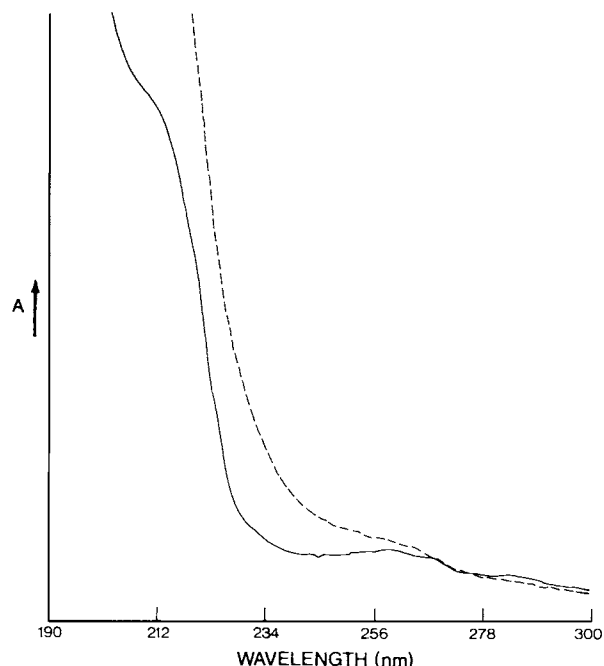


Figure 2 Zero-order UV spectra: (—) acrylonitrile/butadiene/styrene terpolymer; (---) styrene/maleic anhydride copolymer.

The second derivative spectra, however, show significant differences in certain regions. The spectra recorded in the 300–230 nm region will be examined first. The second derivative spectra of the copolymers of styrene with allyl alcohol, butadiene, isoprene, and ethylene-butylene are identical to that of polystyrene [Fig. 3(A)] in this region. They all show minima at 268, 264, 261, 257, 252, 247, 241, and 236 nm and maxima at 271, 265, 262, 259, 255,

249, 244, and 238 nm, with all the peaks in the same ratios in each spectrum. The styrene/butyl methacrylate spectrum [Fig. 3(B)] is different in that the 257 minimum is more intense than the 261 minimum, while the reverse is true in the polystyrene spectrum. The styrene/acrylonitrile spectrum [Fig. 4(A)] shows even more differences. Here the 257 nm peak is more intense than the 261 nm peak, but the ratio is much larger than in the styrene/butyl methacrylate spectrum. In addition, the 264 minimum is less intense than the 261 minimum in both the polystyrene and styrene/butyl methacrylate spectra, but this peak is much more intense than the 261 nm peak in the styrene/acrylonitrile spectrum. The acrylonitrile/butadiene/styrene spectrum [Fig. 4(B)] is identical to the styrene/acrylonitrile spectrum except that the 261 minimum appears only as a shoulder on the 257 minimum. The styrene/maleic anhydride spectrum [Fig. 4(C)] is significantly different from all the other second derivative spectra. The 261 minimum disappears completely and the 262 maximum is shifted to 259 nm. The minima at 268, 264, and 257 nm are more nearly equal in intensity than in the other spectra with the 257 nm peak being slightly more intense than the others.

It is evident then that the spectra shown in Figures 3 and 4 do not show enough differences to permit identification of all the copolymers and the terpolymer. Only the copolymers of styrene with butyl methacrylate, acrylonitrile, and maleic anhydride and the acrylonitrile/butadiene/styrene terpolymer can be distinguished and identified. It is, therefore, necessary to examine the second derivative spectra in the 240–200 nm region. The copolymer and ter-

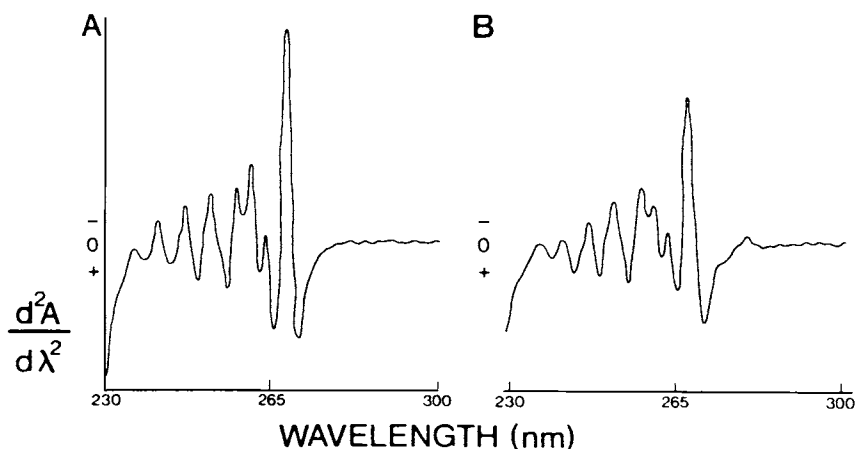


Figure 3 Second derivative UV spectra: (A) polystyrene; (B) styrene/butyl methacrylate copolymer.

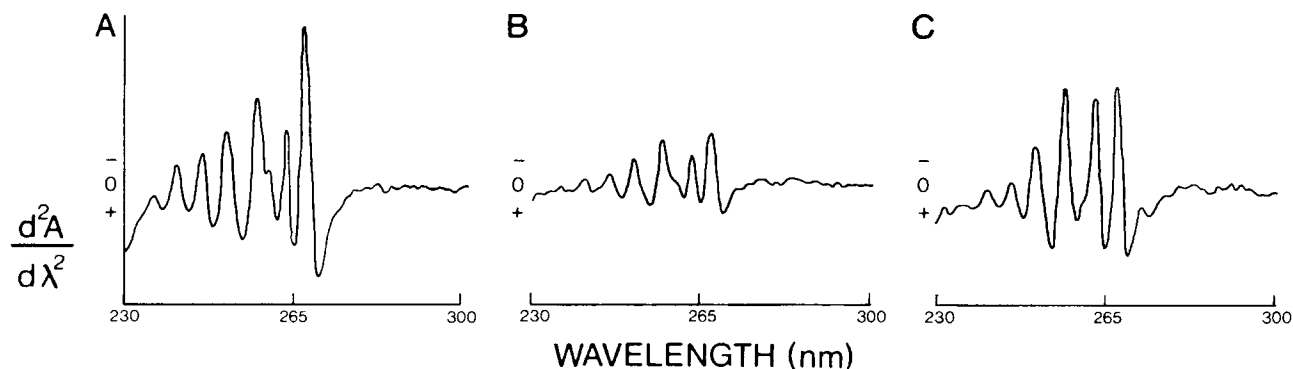


Figure 4 Second derivative UV spectra: (A) styrene/acrylonitrile copolymer; (B) acrylonitrile/butadiene/styrene terpolymer; (C) styrene/maleic anhydride copolymer.

polymers absorb much more strongly in this region, and thinner films must be used. If thin films are not used, some of the distinguishing, spectral features may be lost.

The polystyrene spectrum [Fig. 5(A)] shows minima at 220, 215, and 211 nm and maxima at 225, 217, and 214 nm. The styrene/ethylene-butylene [Fig. 5(B)] and the styrene/allyl alcohol [Fig. 5(C)] spectra also have maxima and minima at these wavelengths. In all three spectra, the order of intensity of the minima is $220 > 211 > 215$, while the order for the maxima is $225 > 217 > 214$. However, the spectra are not identical because the ratios of the peaks differ in each of the spectra. The ratios of the minima at 220, 211, and 215 nm are 5.3, 2.1, and 1.0 in the polystyrene spectrum, while they are 4.3, 2.5, and 1.0 in the styrene/ethylene-butylene spectrum. In the styrene/allyl alcohol spectrum the ratios are 3.9, 3.2, and 1.0. The ratios for the maxima at 225 and 217 nm are 25.5 and 1.0 in the polystyrene

spectrum and 30.0 and 1.0 in the styrene/ethylene-butylene spectrum. In the styrene/allyl alcohol spectrum, the ratios are 7.3 and 1. These copolymers can, therefore, be distinguished from each other and from polystyrene because the ratios of the maxima and minima show significant differences.

The styrene/butadiene spectrum [Fig. 6(A)] has minima at 220, 215, and 211 nm with the order of intensity being $220 > 215 > 211$. The maxima are at 225, 217, and 214 nm with the order of intensity being $225 > 214 > 217$. The styrene/butadiene spectrum is unique in having peaks at these wavelengths in these orders of intensity.

The styrene/butyl methacrylate spectrum [Fig. 6(B)] shows minima at 220, 215, and 211 nm with an order of intensity of $220 > 211 > 215$. The maxima at 225, 217, and 214 nm have an order of intensity of $225 > 214 > 217$. This spectrum is also different from the others because of the ratios of the maxima and minima. This copolymer also gave a

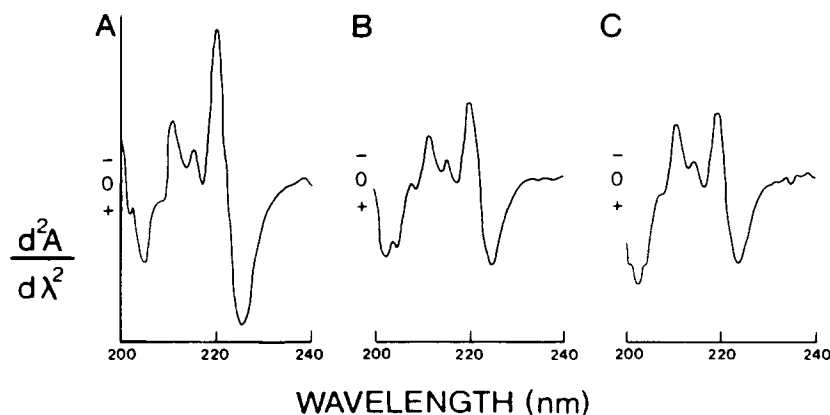


Figure 5 Second derivative UV spectra: (A) polystyrene; (B) styrene/ethylene-butylene copolymer; (C) styrene/allyl alcohol copolymer.

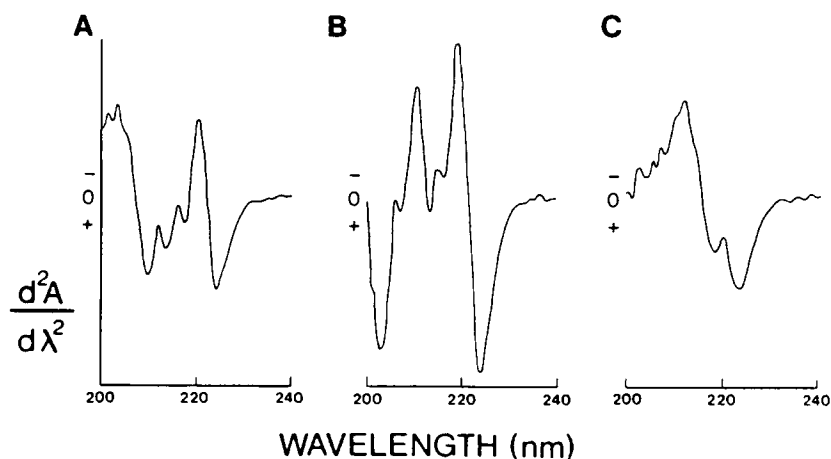


Figure 6 Second derivative UV spectra: (A) styrene/butadiene copolymer; (B) styrene/butyl methacrylate copolymer; (C) styrene/isoprene copolymer.

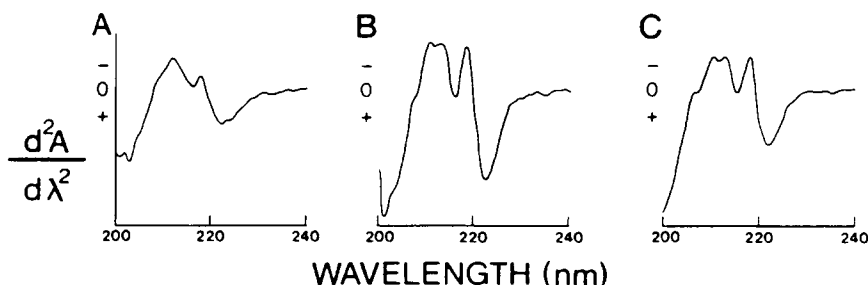


Figure 7 Second derivative UV spectra: (A) styrene/maleic anhydride copolymer; (B) styrene/acrylonitrile copolymer; (C) acrylonitrile/butadiene/styrene terpolymer.

distinctive second derivative spectrum in the 300–230 nm region.

The styrene/isoprene spectrum [Fig. 6(C)] gives minima at 220 and 212 nm and maxima at 224 and 218 nm. These wavelengths are close to those that appear in the styrene/maleic anhydride spectrum [Fig. 7(A)] with minima at 218 and 212 nm and maxima at 222 and 216 nm. However, the spectra can be easily distinguished by noting that the ratios are different and that the 220 nm minimum appears on the positive side of the zero line in the styrene/isoprene spectrum.

The spectra of the copolymers of styrene with maleic anhydride [Fig. 7(A)] and acrylonitrile [Fig. 7(B)] and the terpolymer with acrylonitrile and butadiene [Fig. 7(C)] are somewhat similar. The spectra all show minima at 218 and 212 nm with maxima at 222 and 216 nm. However, these copolymers and the terpolymer gave second derivative spectra in the 300–230 nm region that can be used to distinguish them from each other and from the other copolymers.

These results illustrate the value of second de-

riivative UV spectra in the identification of these styrene copolymers and terpolymer. Sample preparation is rapid, and only small amounts of polymer are required.

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Received April 27, 1990

Accepted January 3, 1991