Derivative Ultraviolet and Visible Spectrophotometry: Applications to Polymer Analysis

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Synopsis

First- to fourth-derivative spectra of humic acids, polystyrene, and mixtures of several prepolymers were measured and the advantage of derivative spectrophotometry such as resolution enhancement and background correction was discussed. Although the vis-absorption spectra for humic acids in pH solutions from pH 2.0 to 10.0 could be hardly discriminated, humic acids in solutions above pH 7.0 could be clearly distinguished from those in solutions below pH 6.0 by first-derivative spectrophotometry. Similarly, the first-derivative spectra of the copper-humic acid complex were different from those of free humic acids, though both absorption spectra resembled each other. UV absorption spectrum of a mixture of phenol-novolac resin and methylated methylol-melamine resin was similar to and the second-derivative spectrum was different from that of phenol-novolac resin. The difference of derivative spectra of a mixture of polycarbonate and epoxy resin was also discussed. Shoulder and unresolved peaks were clearly revealed by differentiation of absorption spectra and peak assignments from the fourth-derivative spectra were more accurate than those from the absorption spectra. This advantage was discussed by using polystyrene as an example.

INTRODUCTION

The derivative technique for absorption spectra is recognized as a resolution enhancement technique to facilitate the measurement of the wavelengths of poorly resolved components of a complex spectrum, and as a background correction technique to reduce the matrix background interferences. Theoretical aspects for derivative spectrophotometry has been reported.[1,2] However, until recently the technique has not been so popular in analytical spectrophotometry because of instrumental complexity and the lowering of the signal-to-noise ratio (increase in noise). The recent development of microcomputer technology enables the advent of microcomputer assisted ultraviolet (UV) and visible (VIS) spectrophotometers that have numerous benefits in terms of easy calculation and more accurate results. Derivative spectroscopy on a modern microcomputer-assisted instrument is now a standard feature. Differentiation of absorption spectra and the process of smoothing are not difficult by using this type of spectrophotometer.

Recently, second-derivative UV-VIS spectrometry has been established as a valuable qualitative method in some areas of forensic chemistry[3,4] and arson analysis.[5]

One of the classic analytical problems in the field of UV–VIS spectrophotometry is the resolution of a number of components in a mixture. The use of second- and fourth-derivatives offers considerable advantages. The derivative

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technique can also enhance spectral detail rather than straightforward UV-VIS spectrophotometry. In the present report, first- to fourth-order UV and VIS spectra of humic acids, polystyrene, and mixtures of phenol-novolac resin and methylol melamine resin, and epoxy resin and polycarbonate were measured and several useful results are summarized.

EXPERIMENTAL

Apparatus

A Jasco UV-VIS spectrophotometer Model UVIDEC-610C (Japan Spectroscopic Co., Ltd., Hachioji, Tokyo 192, Japan) was used. This spectrophotometer is operated with the assistance of a microcomputer and includes a cathode ray tube (CRT) monitor and a keyboard. With the use of the keyboard entry, any absorption and derivative spectra can be conveniently obtained on the CRT monitor and on the recorder chart. Two thousand data points at the wavelength interval of 1/50 of λ scale (a parameter of λ scale must be inputted through a keyboard) can be stored in memory. For example, when λ scale is 20 (nm/cm), then absorbance at intervals of 0.4 nm wavelength is stored up to 2000 data points. This spectrophotometer does not require any derivative accessory.

Instrumental specifications are as follows: spectral reproducibility, ±0.1 nm; accuracy of wavelength, ±0.3 nm; band width, 0.1–5 nm continuous. Other operational variables were as follows unless otherwise specified: band width, 2.0 nm; time constant, 0.4 s; scan speed, 20 nm/min; absorbance, 1.0; λ scale, 20 nm/cm, chart speed, 2 mm/min. Quartz cells of 1-cm path length were used.

Differentiation

Differentiation of spectra and the smoothing of derivative spectra were carried out by the scheme shown in Figure 1. Absorption spectra were magnified X times (5 or 10 times in this experiment) before differentiation. The magnified spectra were smoothed, differentiated, magnified, smoothed, and printed (for first-derivative spectra). For higher order-derivative spectra, a sequence of differentiation, magnification, and smoothing was performed for N-1 times. Here, N means the Nth order-derivative spectra. Symbols in parentheses, n and n', express the number of the interval of data points used. For example, "$n = 1$" means that every data point is used, "$n = 2$" means that differentiation or smoothing is made every two data points, and "$n = 3$" every three data points.

This instrument generates derivative spectra by a numerical method. The zero-order spectra are expressed as

$$A \text{ (absorbance)} = f(\lambda) \tag{1}$$

where λ is wavelength in nm. The first-order spectra are obtained by

$$dA/d\lambda = \lim_{\Delta\lambda \to 0} \frac{f(\lambda + \Delta\lambda) - f(\lambda)}{\Delta\lambda} \tag{2}$$

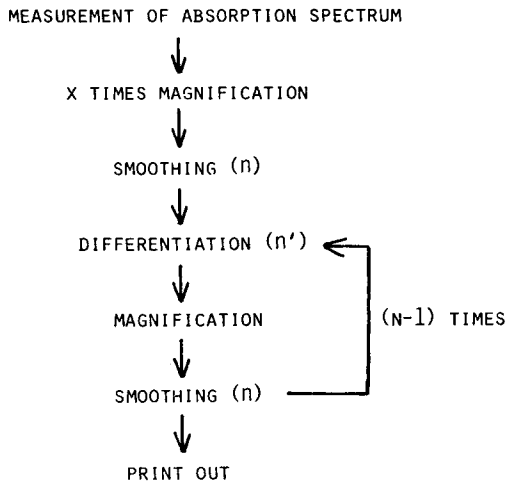

Fig. 1. Schematic diagram for differentiation of absorption spectra. Letters, n and n' in parentheses refer to the data point intervals.

As λ scale is 20 nm/cm, absorbance at every 0.4 nm is stored in memory. When $n' = 1$, then the first order spectra are calculated as

$$dA/d\lambda = \frac{f(\lambda + 0.4) - f(\lambda)}{0.4} \tag{3}$$

and when $n' = 2$, then

$$dA/d\lambda = \frac{f(\lambda + 2 \times 0.4) - f(\lambda)}{2 \times 0.4} \tag{4}$$

The second-derivative spectra are calculated from the stored first-derivative data using Eq. (3) or (4). The third- and fourth-derivatives are also performed similarly.

The process of smoothing is very important for the determination of derivative spectra, because the signal-to-noise ratio decreases rapidly as the derivative order increases. The number of times that the smoothing is passed through the data series is, in general, $N + 1$ passes of smoothing for the Nth derivative spectra.[1]

Samples

Humic acids were reagent grade (Wako Chemical Co., Japan) and were dissolved in a 0.01 M KOH solution at a 0.1% concentration. The solution was diluted to an appropriate concentration for spectrophotometric measurements and pH values of the sample solutions were adjusted between 2 and 10. The copper-humic acid complex was prepared by adding a dilute copper sulfate solution to the humic acid solution adjusted to pH 7. The resulting precipitate was washed with 0.01 M HCl and redissolved in a pH 10 solution. Polystyrene (NBS 706) was dissolved in chloroform at a 0.3% concentration. Polycarbonate, epoxy resin (EPIKOTE 1001), phenol-novolac resin, and methyl-

ated methylol-melamine resin were commercially available and were dissolved in chloroform at 0.2% concentration each.

RESULTS AND DISCUSSION

Spectra of Humic Acids

Figure 2 is VIS absorption spectra of humic acids dissolved in different pH solutions. The scale of the ordinate is arbitrary. Although absorption coefficients varied to some extent in different pH solutions, the shape of absorption spectra were extremely similar and the difference in spectra were hardly recognized. First-derivative visible spectra obtained by differentiating the spectra in Figure 2 are shown in Figure 3. Magnification was five times. Smoothing was made every two data points ($n = 2$) and differentiation every five data points ($n' = 5$). The spectra of humic acids in solutions of pH 10.0 and 8.0 have a broad peak between 420 and 530 nm and are different from the other three spectra. The ruggedness of the peak is probably due to noise. The spectra in a solution of pH 7.0, which is not shown here, were similar to those in solutions above pH 8.0. The peak at about 600 nm for humic acids in a pH 8.0 solution was not identified.

The VIS absorption and first-derivative spectra of the copper-humic acid complex are shown in Figure 4. The absorption spectrum in a pH 6.0 solution is similar to that of free humic acids in a solution of the same pH value, but their first-derivative spectra are different from each other. Hence, discrimination between free humic acid and the copper-humic acid complex is possible. The first-derivative spectrum of the complex in a solution of pH 6.0 is similar to those of free humic acids in solutions above pH 7.0. In other words, the spectra of the complex in solution above pH 7.0 cannot be distinguished from those of free humic acids in the same pH solutions.

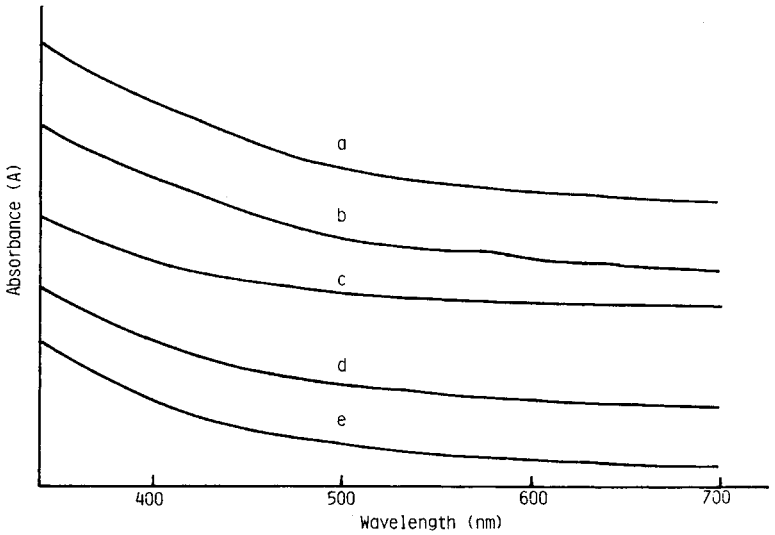

Fig. 2. Visible absorption spectra of humic acids in different pH solutions. (a) pH = 10.0; (b) pH = 8.0; (c) pH = 6.0; (d) pH = 4.0; (e) pH = 2.0.

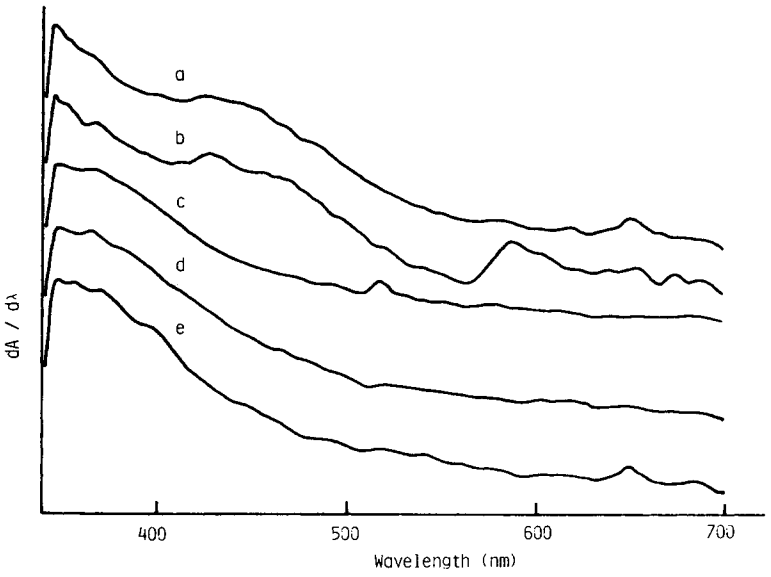

Fig. 3. First-derivative visible spectra of humic acids in different pH solutions. (a) pH = 10.0; (b) pH = 8.0; (c) pH = 6.0; (d) pH = 4.0; (e) pH = 2.0. Parameter settings: $n = 2$, $n' = 5$, $X = 5$.

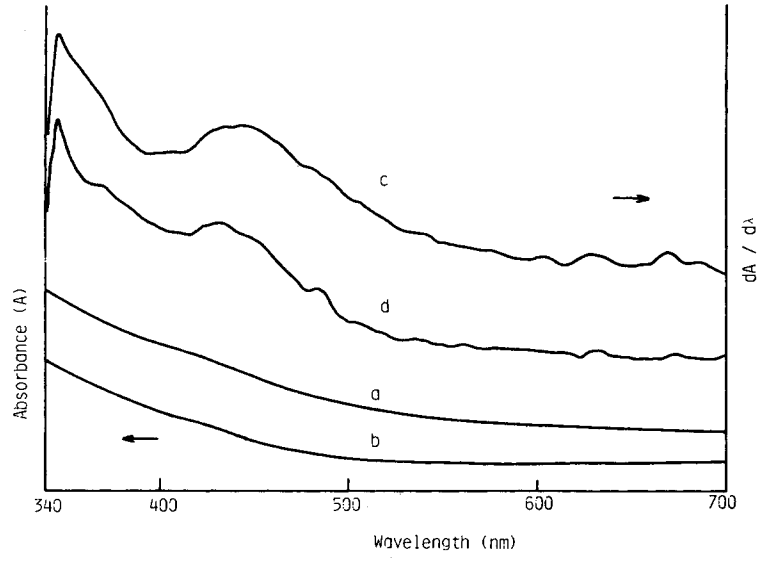

Fig. 4. Visible absorption spectra (a, b) and first-derivative visible spectra (c, d) of the copper-humic complex. (a), (c) in pH = 10.0; (b), (d) in pH = 6.0. Parameter settings: $n = 2$, $n' = 5$, $X = 5$.

The difference of first-derivative spectra of humic acids in different pH solutions is probably related to the difference in dissociation of carboxylic and phenolic hydroxyl groups of humic acids. At the higher pH region, carboxylic and phenolic hydroxyl groups of humic acids exist as anions and at lower pH region, most of these groups are neutral forms. The peak between 420 and 530 nm is suggestive of the structural difference of humic acids at different pH values and also of the similarity of the chemical form of the copper-humic acid complex to the dissociated free humic acids above pH 7.0.

Spectra of Prepolymers

Figure 5 shows UV absorption and first- and second-derivative spectra of polycarbonate and three prepolymers: epoxy resin, phenol-novolac resin, and methylated methylol-melamine resin. Samples were dissolved in chloroform. Except for the spectrum of methylated methylol-melamine resin, the spectra of the other three polymers are similar to each other and first-derivative

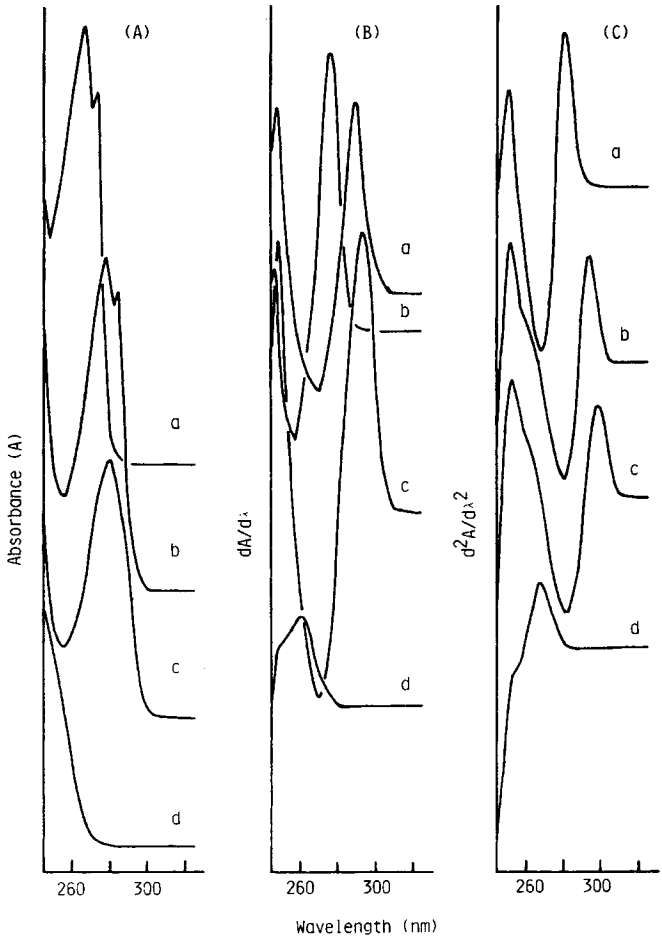

Fig. 5. Ultraviolet absorption (A), first-derivative (B), and second-derivative (C) spectra of polymers and prepolymers in chloroform. (a) Polycarbonate; (b) epoxy resin (EPIKOTE 1001); (c) phenol-novolac resin; (d) methylated methylol-melamine resin.

spectra of these polymers [Fig. 5(B)] are distinguishable from each other. Second-, [Fig. 5(C)], third-, and fourth-derivative spectra of epoxy resin and phenol-novolac resin are almost the same. They are distinguishable from polycarbonate and methylated methylol-melamine resin, the latter two polymers being also different from each other.

UV absorption spectrum of a mixture of phenol-novolac resin and methylated methylol-melamine resin shown in Figure 6(A, a) resembles that of one of constituents, phenol-novolac resin, but the second-derivative spectrum of the mixture can be clearly discriminated from that of phenol-novolac resin [Fig. 6(A, b)]. Therefore, differentiation of absorption spectra is a very useful technique for determining whether a spectrum is from a single component or a mixture.

Figure 6(B, a) is an absorption spectrum of a mixture of polycarbonate and epoxy resin. The absorption spectrum is different from that of either polycarbonate or epoxy resin. The derivative spectra [Fig. 6(B, b; B, c)] of the mixture are also different from those of the constituents. However, peak

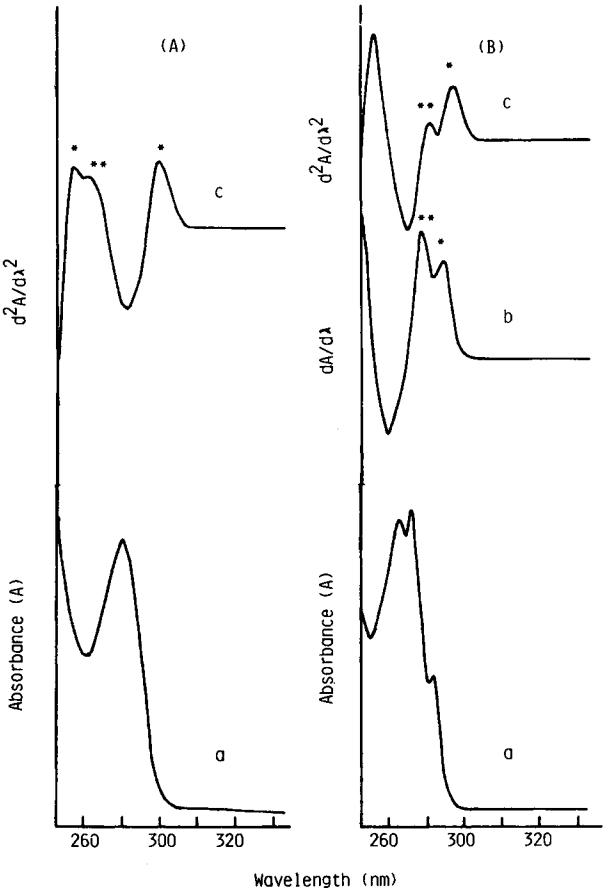

Fig. 6. Ultraviolet absorption (a), first-derivative (b), and second-derivative (c) spectra of mixtures of polymers. (A) a mixture of phenol-novolac resin and methylated methylol-melamine resin. (*) Specific for phenol-novolac resin; (**) specific for methylated methylol-melamine resin. (B) a mixture of polycarbonate and epoxy resin. (*) Specific for epoxy resin; (**) specific for polycarbonate.

positions designated with the asterisks are coincident with those of an individual component and therefore, components included in the mixture can be identified by differentiating the absorption spectra and by comparing them with derivative spectra of constituents.

Effects of Band Width

Band width influences resolution in addition to the signal-to-noise-ratio. Resolution increases and the signal-to-noise ratio decreases with a decrease in

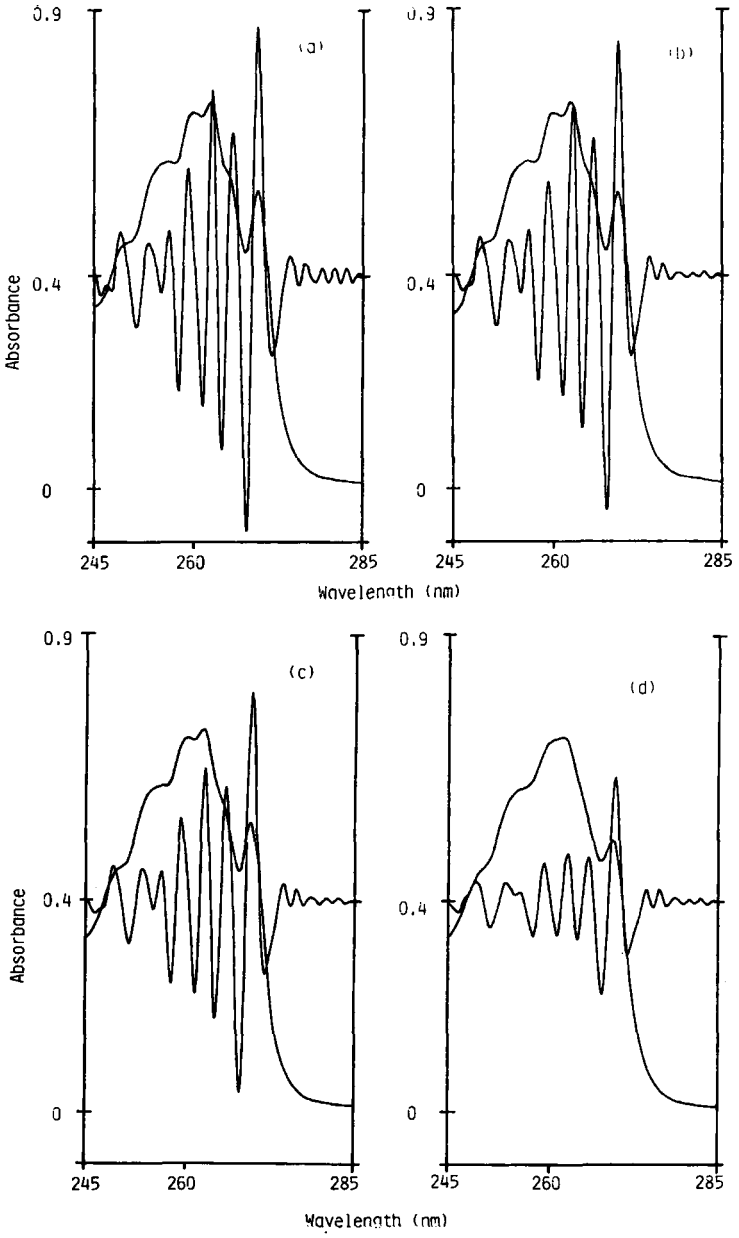

Fig. 7. Ultraviolet and fourth-derivative spectra of polystyrene in chloroform obtained at different band widths. Band width (nm): (a) 0.1; (b) 0.5; (c) 1.0; (d) 2.0.

TABLE I
Assignment of Peak Positions from Absorption and Fourth-Derivative Spectra for Polystyrene in Chloroform at Different Band Widths

Band width (nm)					
0.1	0.2	0.3	0.5	1.0	2.0
		From Absorption Spectra			
269.6	269.6	269.6	269.6	269.6	269.5
—	—	—	—	—	—
262.5	262.6	262.6	262.6	262.5	262.0
260.0	260.0	259.9	260.0	260.0	—
256.3	256.1	256.2	256.2	256.0	—
		From Fourth-Derivative Spectra			
269.6	269.6	269.6	269.7	269.7	269.9
266.0	265.9	265.9	266.0	266.0	265.9
262.8	262.8	262.8	262.9	262.8	262.7
259.2	259.2	259.3	259.3	259.4	259.5
256.3	256.3	256.3	256.3	256.2	255.5
254.0	253.1	253.1	253.2	253.4	253.5

band width. Therefore, a compromise must be often employed between using a wide band width for high S/N ratio and a narrow band width for high resolution.

Figure 7 shows UV absorption and fourth-derivative spectra of polystyrene in chloroform at different band widths. Light below 240 nm is totally absorbed by chloroform used as the solvent. When the band width is 0.1 nm, seven major peaks can be observed between 245 and 275 nm. However, the shoulder at 266 nm disappears and a bimodal peak at about 260 nm is combined in one peak at the band width of 2.0 nm. Peaks of fourth-derivative spectra of polystyrene at any band width correspond accurately to those of the absorption spectra. The shoulder peak and unresolved peaks are clearly revealed. Peak assignments from the absorption and the derivative spectra are listed in Table I. The results show that peak assignment from the derivative spectra are accurate irrespective of band width.

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