

The Effect of Composition, Sequence Length, and Tacticity on the UV Absorption Analysis of Styrene Copolymers in Solution

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Synopsis

As a first step in the elucidation of the microstructure of styrene copolymers using ultraviolet spectroscopy, the data available in the literature has been reviewed and reevaluated. It is shown by using simple error propagation analysis that the abnormalities observed in the extinction coefficients of styrene copolymers can be easily attributed to the experimental error. No significant deviations from the linear absorption behavior can be observed at the specific wavelengths reported in the literature (254–269 nm). As a result of this work, a useful set of correlations for the estimation of the copolymer composition have been obtained. These correlations appear to be adequate for copolymers of different microstructure.

INTRODUCTION

Recent studies on the absorption behavior of styrene containing copolymers^{1–7} have shown significant deviations from the standard assumptions of linearity of absorption with composition (Beer's law) and additivity of the responses of the individual components. These deviations have been attributed to the microstructure of the copolymer chains^{1,3–6} and in some cases to the conformation of the molecules in solution.^{2,7} There are, however, some discrepancies in the experimental results which warrant a review of the above assumptions. These discrepancies are as follows:

(1) Gallo and Russo² observed hypochromic effects on styrene–methyl methacrylate copolymers in solution. The extent of the hypochromism and the composition at which it appears are functions of the dielectric constant of the solvent, which suggests changes in conformation of the molecules in solution. This is in contrast with the observations made on the same copolymer by Stutzel et al.⁶ and O'Driscoll et al.,⁵ who correlated changes in the extinction coefficient of the copolymer with changes in the length of the styrene sequences.

(2) If the lengths of the styrene sequences are solely responsible for the hypochromic effects, then the extinction coefficient of styrene dyads, triads, etc., determined in the same solvent and wavelength, should be the same for all styrene copolymers regardless of the nature of the comonomer. This is not generally the case³ as it is shown in Table I for isolated styrene units (A) in BAB sequences.

(3) Recent H¹NMR data on styrene acrylonitrile copolymers³ indicates the presence of isotactic styrene sequences. This adds uncertainty to the hypothesis that the band shifts and intensity changes observed in the UV spectra of styrene copolymers are due solely to the length of the styrene sequences.

TABLE I
Molar Extinction Coefficient for Styrene in BAB Styrene-Centered Triads in THF at 25°C

Copolymer	Extinction coefficient ϵ_c/ϵ_{ps} (269 nm)	Reference
Styrene-acrylonitrile	0.593	3
Styrene-methyl methacrylate	0.342	6
Styrene- <i>n</i> -butyl acrylate	0.619	4
Styrene- <i>n</i> -butyl methacrylate	0.506	4

The standard procedure for the estimation of extinction coefficients is as follows: Polymer solutions of known concentrations (g/cc) are prepared in the desired solvent and absorbances at selected wavelengths are measured. If Beer's law is shown to be valid, the absorption and concentration are related by eq. (1), from which the extinction coefficient is estimated under the assumption of additivity of the responses of the components [eq. (2)]:

$$A_c(\lambda) = \epsilon_c(\lambda) \cdot l \cdot C_c \quad (1)$$

$$A_c(\lambda) = 1 \cdot C_c \sum_{i=1}^N \epsilon(\lambda)_i \cdot P_{iw} \quad (2)$$

An additional assumption normally made is that the only chromophore present in the copolymer is the phenyl ring in the styryl units.¹⁻⁷ This assumption has been justified on the basis that the homopolymers of the comonomers are transparent in the region where polystyrene absorbs. Based on this assumption, eq. (2) can be rewritten as

$$A_c(\lambda) = l \cdot C_c \cdot \epsilon_{ps}(\lambda) \cdot P_{1w} \quad (3)$$

If eq. (1) is used to estimate the extinction coefficient of polystyrene (ϵ_{ps}), then from eq. (3)

$$\epsilon_{ps}(\lambda) = \epsilon_c(\lambda) / P_{1w} \quad (4)$$

or in molar basis

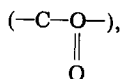
$$\epsilon_{ps}(\lambda) = \epsilon_c(\lambda) \cdot M_c / P_1 \quad (5)$$

where

$$M_c = M_s \cdot P_1 + M_i (1 - P_1)$$

There are four major objections to the estimation of extinction coefficients based on the aforementioned assumptions and equations:

(1) The most critical assumption in the analysis of styrene containing copolymers is that of the phenyl group being the only group responsible for the absorption behavior of the copolymer, for it is well known⁸ that esters



nitriles ($-\text{C}\equiv\text{N}$), and dienes ($-\text{C}=\text{C}-$) are also chromophores in other regions of the UV spectra. In addition, these groups are capable of hydrogen bonding and have unsaturated bonds capable of resonance and different ground ab-

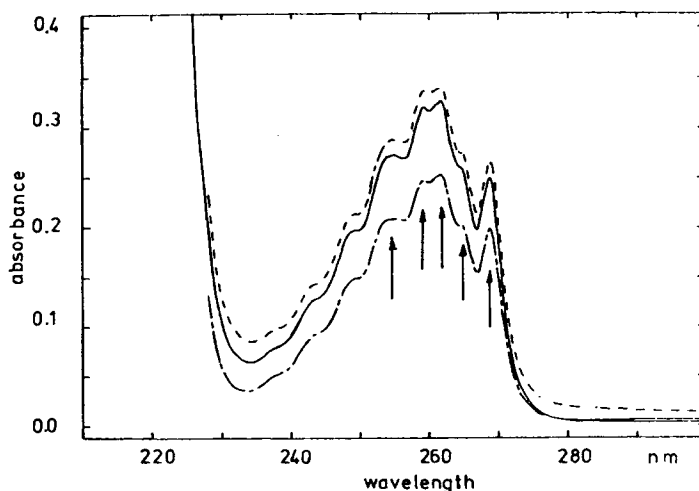


Fig. 1. Typical UV spectra of polystyrene in THF. Arrows indicate relevant absorption bands.

sorption stabilization. Such an effect would be expected to be a function of the dielectric constant of the solvent. The effect of the comonomer groups on the extinction coefficient may or may not be linear with respect to their concentration in the copolymer.

(2) Statistically, the effect of the comonomer on the absorption behaviour should be verified by estimating the extinction coefficients in eq. (2), testing the adequacy of the model and then the value of the parameters, to see if, given the experimental error, any of them is significantly different from zero. Comparison of the extinction coefficients of the homopolymers cannot be considered sufficient proof that there are no effects due to the concentration of the comonomer in the copolymer molecule.

(3) The use of eqs. (4) or (5) greatly propagates the errors in composition, as is shown in the Appendix and in Figure 5, creating sometimes apparent trends which could lead to erroneous conclusions.

(4) Most of the phenyl absorption bands in the ultraviolet are formed by overlapping peaks (Fig. 1). However, the spectra are not normally resolved in their components prior to or as part of the analysis. It is conceivable that the shifts and abnormal absorption behavior observed at some wavelengths are due to intensity changes in adjacent bands.

In order to exemplify the importance of the above objections, the data available in the literature¹⁻⁷ has been reinterpreted using the raw extinction coefficients as measurements (i.e., $\epsilon_c = \epsilon_{c \text{ reported}} \times P_{1w}$) since the original absorption data was not available. As a first step, the consistency of the data from several authors was investigated. Using polystyrene as reference, the extinction coefficients of the copolymers were normalized and compared (Figs. 2 and 3). No significant differences can be observed in the data obtained from different authors. In addition, a conservative estimate of the standard deviation in the measurement of extinction coefficients can be obtained from the data reported in the literature for which there are replicate measurements (Figs. 2 and 3). This value is $\sigma_{\epsilon_c} = 0.003 \times 10^6 \text{ Au} \times \text{cm}^2/\text{gmol}$. As a second step, the 95% confidence limits (2σ)

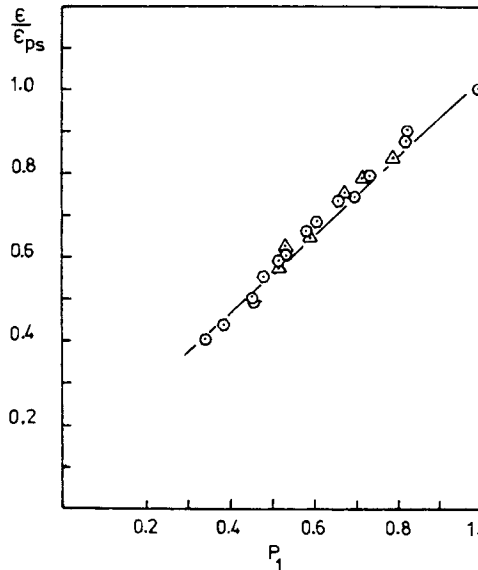


Fig. 2. Normalized extinction coefficient at 254 nm of styrene/acrylonitrile copolymers in THF. (O) Data from Ref. 1; (Δ) data from Ref. 3.

on the extinction coefficients estimated from eqs. (4) or (5) was estimated using simple error propagation techniques and standard deviations typical of composition measurements ($\sigma_{P_1} = 0.02$). As a third step the extinction coefficients for all polymer systems were estimated from equations

$$\epsilon_c(\lambda) = \epsilon_{ps}(\lambda) \cdot P_{1w} + \epsilon_i(\lambda) \cdot (1 - P_{1w}) \quad (6)$$

or

$$\epsilon_c(\lambda) = \epsilon_{ps}(\lambda) \cdot P_{1w} + \epsilon_i(\lambda) \cdot (1 - P_1) \quad (7)$$

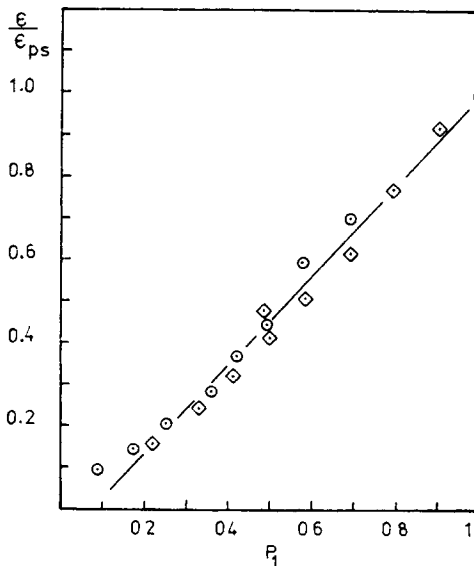


Fig. 3. Normalized extinction coefficients at 269 nm of styrene/methyl methacrylate copolymers. (O) Data from Ref. 2; (\diamond) data from Ref. 6.

depending on whether the extinction coefficients were reported on a weight or molar basis.

RESULTS AND DISCUSSION

An example of the dramatic effects of the use of eqs. (4) or (5) for the estimation of extinction coefficients and the dangers of the subsequent interpretation without the proper error analysis is shown in Figures 4 and 5. In Figure 4, the raw extinction coefficients (ϵ_c) and the extinction coefficients for the styrene units (ϵ_{ps}) are plotted as functions of the copolymer composition. The ϵ_{ps} values [eq. (5)] show a definite trend downwards as the styrene content in the copolymer decreases. Furthermore, a definite difference in the extinction coefficient between free radical, alternating and block copolymers is evident from the graph.

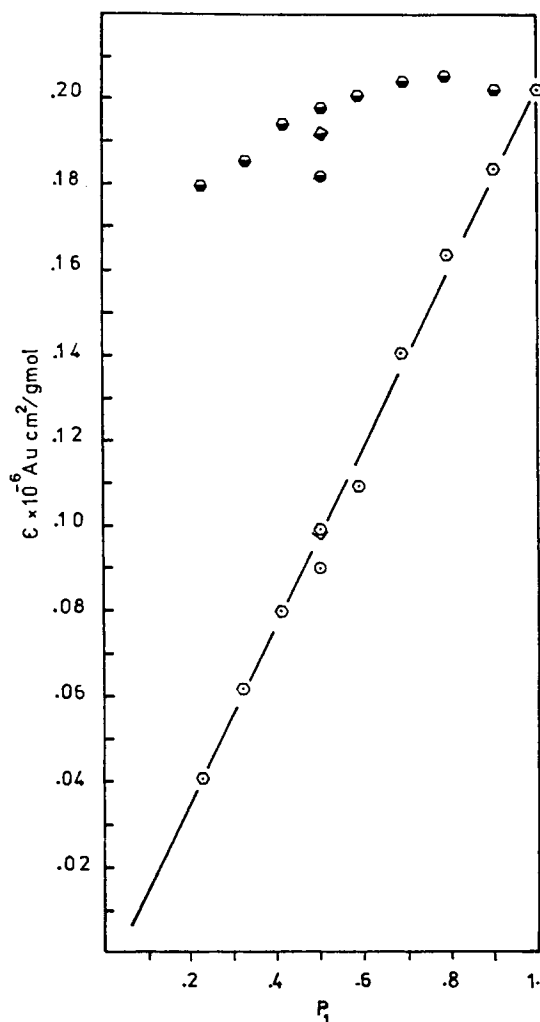


Fig. 4. Extinction coefficients of styrene/methyl methacrylate copolymers in THF at 259 nm. Open figures. Transformed data ($\epsilon_c = \epsilon_{c \text{ reported}} \times P_1$). Full figures original data as reported in Ref. 6. (\circ , \bullet) Free radical; (\odot , \ominus) alternating; (\diamond , \blacklozenge) block copolymers.

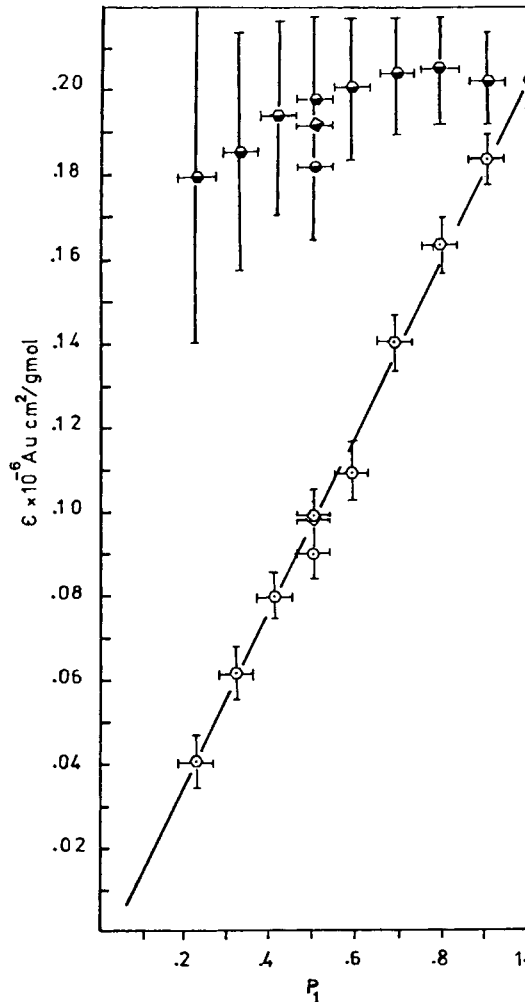


Fig. 5. 95% confidence limits on the extinction coefficients of styrene/methyl methacrylate copolymers in THF at 259 nm. For typical errors in the extinction coefficients ($\sigma_{\epsilon_c} = 0.003 \times 10^6 \text{ Au} \times \text{cm}^3/\text{g}\cdot\text{mol}$) and in composition ($\sigma_p = 0.02$) open figures. Transformed data ($\epsilon_c = \epsilon_c \text{ reported} \times P_1$) full figures original data as reported. (\odot , \bullet) Free radical; (\circ , \ominus) alternating; (\diamond , \blacklozenge) block; (\oplus , \ominus , \blacklozenge) specific values.

Therefore, these deviations have been attributed to differences in the microstructure of the copolymer molecules.⁶ The extinction coefficients for the copolymers (ϵ_c), on the other hand, appear to follow a linear dependence with respect to the copolymer composition. This apparent contradiction can be easily resolved if the approximate 95% confidence limits (2σ) are superimposed on both extinction coefficients ϵ_c and ϵ_{ps} (Figure 5). Clearly, the experimental errors have propagated significantly through eq. (5) (see Appendix) suggesting trends that cannot be unambiguously identified given the magnitude of the propagated experimental error. Therefore, it can be concluded that the differences in extinction coefficients for random, block, and alternating copolymers reported by Stutzel, Miyamoto, and Cantow⁶ appear to be within the experimental error typical of extinction coefficient measurements. In other words, there is not

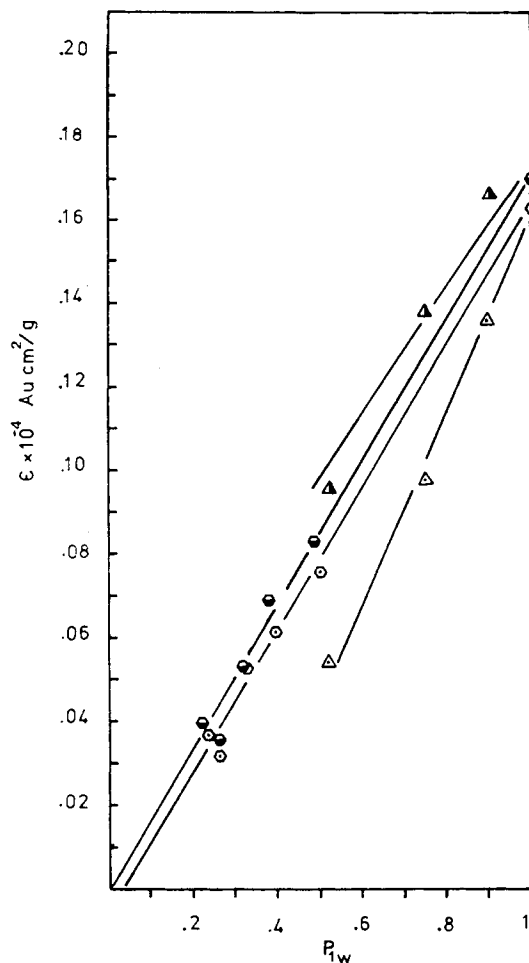


Fig. 6. Extinction coefficients of styrene copolymers at several wavelengths in THF. Data from Ref. 1: (O) styrene/butadiene copolymers; (Δ) styrene/maleic anhydride; (\bullet , \blacktriangle) 254 nm; (O, Δ) 269 nm.

enough evidence to assign the differences in extinction coefficients to differences in microstructure. The linear behavior of the extinction coefficient ϵ_c with respect to the copolymer composition (Figures 6 and 7) is adequately described by eqs. (6) or (7) (Table II) for a variety of styrene copolymers with different microstructure configurations indicating, therefore, that the coefficients reported in Table II can be used to estimate the composition of the corresponding copolymers independently of their microstructure.

The fact that some of the extinction coefficients estimated are negative can be explained on the basis of the interaction of the electronic configuration of the comonomer with the phenyl group and the solvent. This does not preclude sequence length effects and could also explain the relationship between the hypochromic effect and the solvent dielectric constant reported by Gallo and Russo.²

At this point, there is not enough evidence to account completely for the anomalous behavior of styrene containing copolymers across the UV spectra in

TABLE II
 Wave Length Region^a

System	269 nm	264 nm	261 nm	259 nm	254 nm	249 nm
Styrene/ acrylonitrile ($P_1^* = P_1$)	$\epsilon_c/\epsilon_{ps} =$ $m =$ $\rho =$	-0.099 ± 0.033 1.103 ± 0.04 0.995	-0.193 ± 0.036 1.194 ± 0.044 0.995	-0.099 ± 0.013 1.098 ± 0.016 0.999	0.127 ± 0.014 1.127 ± 0.017 0.999	-0.103 ± 0.028 1.112 ± 0.034 0.996
Styrene/ butadiene ($P_1^* = P_1$)	$\epsilon_c/\epsilon_{ps} =$ $m =$ $\rho =$	-0.020 ± 0.007 1.021 ± 0.010 0.999	-0.007 ± 0.006 1.007 ± 0.009 0.999	0.0002 ± 0.007 1.000 ± 0.009 0.999	-0.001 ± 0.007 1.002 ± 0.010 0.999	
Styrene/ maleic anhydride ($P_1^* = P_1$)	$\epsilon_c/\epsilon_{ps} =$ $m =$ $\rho =$	-0.435 ± 0.060 1.424 ± 0.066 0.994	-0.257 ± 0.016 1.259 ± 0.018 0.999	0.017 ± 0.039 0.991 ± 0.043 0.994	0.099 ± 0.052 0.911 ± 0.058 0.988	
Styrene/ methyl methacrylate ($P_1^* = P_1$)	$\epsilon_c/\epsilon_{ps} =$ $m =$ $\rho =$	-0.141 ± 0.020 1.138 ± 0.024 0.996	-0.078 ± 0.011 1.076 ± 0.013 0.999	-0.34 ± 0.007 1.036 ± 0.009 0.999		

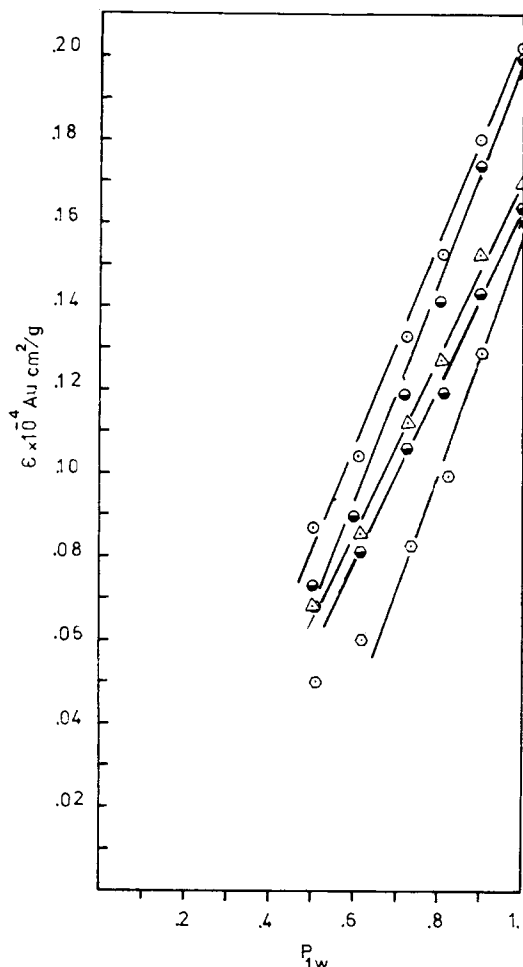


Fig. 7. Extinction coefficients of styrene/acrylonitrile copolymer at several wave lengths in THF. Data from Ref. 1: (○) 259 nm; (●) 261 nm; (△) 254 nm; (●) 264 nm; (○) 269 nm.

terms of composition, sequence length, tacticity, or the conformation of the molecules in solution most likely proceeding hand in hand with them. It is possible, however, by adequate treatment of the data, to select the experimental conditions (wavelengths, solvents, etc.) and to obtain useful correlations (Table II) which allow the use of UV spectrometers as mass and/or composition detectors in the analysis of styrene copolymers and eventually correlate the spectral information with the microstructure of the copolymer molecules.

APPENDIX

To show that errors in composition propagate significantly when eqs. (4) or (5) are used to calculate the extinction coefficients, the following simplifications are made:

- (1) $\epsilon_c(\lambda)$ is considered a measurement with variance, $\text{var}(\epsilon_c(\lambda))$.
- (2) P_1, P_{1w} are independent variables with variance, $\text{var}(P_1)$, $\text{var}(P_{1w})$.
- (3) The measurements of $\epsilon_c(\lambda)$ and P_{1w} and $\epsilon_c(\lambda)$ and P_1 are uncorrelated (i.e., $\text{cov}(\epsilon(\lambda), P_1) = 0$).

Under these conditions the variance of the extinction coefficient as estimated from eq. (4) is given by³

$$\text{var}(\epsilon_{\text{ps}}(\lambda)) = (1/P_{1w})^2 \text{var}(\epsilon_c(\lambda)) + (\epsilon_c(\lambda)/P_{1w})^2 \text{var}(P_{1w}) \quad (8)$$

and from eq. (5)

$$\text{var}(\epsilon_{\text{ps}}(\lambda)) = [(M_s - M)_i/P_1]^2 \text{var}(\epsilon_c(\lambda)) + (\epsilon_c(\lambda)/P_1)^2 \text{var}(P_1) \quad (9)$$

All the terms in eqs. (8) and (9) are always positive. Therefore,

$$\begin{aligned} \text{var}(\epsilon_{\text{ps}}(\lambda)) &> \text{var}(\epsilon_c(\lambda)) \\ \text{var}(\epsilon_{\text{ps}}(\lambda)) &> \text{var}(\epsilon_c(\lambda)) \end{aligned} \quad (10)$$

Clearly, the variance of the extinction coefficients as estimated from eqs. (4) or (5) will always be greater than the variance of the original estimates on eqs. (1) or (2). In addition, the transformation to molar basis will further increase the error variance in proportion to the difference in molecular weights of the monomer units [eq. (9)]. It is evident that if trends are going to be investigated they should be done by considering the appropriate variance (Figures 4 and 5). For example, even if it is assumed that $\text{var}(\epsilon_c(\lambda)) = 0$ [i.e., $\epsilon_c(\lambda)$ is estimated without error] but the standard deviation of the composition measurement is

$$\sigma_p = \sqrt{\text{var}(P_{1w})}$$

then from eqs. (4) and (8) the 95% confidence limits (2σ) are given by

$$\epsilon_{\text{ps}}(\lambda) = \frac{\epsilon_c(\lambda)}{P_{1w}} \left(1 \pm \frac{2\sigma_p}{P_{1w}} \right) \quad (11)$$

The uncertainty in the estimation of $\epsilon_{\text{ps}}(\lambda)$ will increase with decreasing styrene content.

NOMENCLATURE

$A_c(\lambda)$	absorbance measured at wavelength λ from a copolymer solution
Au	absorbance units
C_c	copolymer concentration (g/cm ³)
l	cell path length
M_c	copolymer molecular weight (g/gmol)
M_s	molecular weight of styrene
M_i	molecular weight of the comonomer
P_1	mol fraction of styrene in the copolymer
P_{1w}	weight fraction of styrene in the copolymer
$\epsilon_c(\lambda)$	copolymer extinction coefficient at wavelength λ (au \times cm ² /g)
$\epsilon_i(\lambda)$	comonomer extinction coefficient (au \times cm ² /g)
$\epsilon_{\text{ps}}(\lambda)$	polystyrene extinction coefficient (au \times cm ² /g)
$\epsilon_{\text{ps}}(\lambda)$	polystyrene extinction coefficient (au \times cm ² /gmol)

References

1. R. J. Brussau and D. J. Stein, *Angew. Makromol., Chem.* **12**, 59 (1970).
2. B. M. Gallo and S. Russo, *J. Macromol. Sci. Chem.*, **A8**(1), 521 (1974).
3. L. Garcia-Rubio, Ph.D., thesis, McMaster University (1981).
4. E. Gruber and W. Knell, *Makromol. Chem.*, **179**, 733, 1978.
5. K. F. O'Driscoll, W. Wertz, and A. Husar, *J. Polym. Sci.*, **A1**(5), 2159 (1967).
6. B. Stutzel, T. Miyamoto, and H. J. Cantow, *Polym. J.*, **8**(3), 247 (1976).
7. M. T. Vala, J. Haebig, and S. A. Rice, *J. Chem. Phys.*, **43**(3), 886 (1965).
8. R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds*, Wiley Interscience, New York, 1967.

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