Copolymer Analysis by UV Spectroscopy

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Synopsis

An extensive and detailed analysis of copolymers was made by developing a rapid spectrophotometric method. Successful analysis of composition in styrene-*p*-methoxystyrene, styrene-*p*-chlorostyrene, and styrene-*p*-fluorostyrene copolymers were performed by UV spectrometry. Their absorption bands were investigated either with respect to pure polystyrene or with respect to the homopolymer of the other constituent at the same wavelength. Attempts to analyze copolymers of styrene-4-vinylpyridine and styrene-*N*-vinylcarbazole by similar methods were unsuccessful.

INTRODUCTION

There are a number of methods for analysis of copolymers, including infrared spectroscopy, elemental analysis, NMR, differential index of refraction, and UV spectroscopy. While none is generally applicable, UV spectroscopy is an attractive choice when the following conditions can be met: (1) The backbone units must not have overlapping absorbance maxima; (2) solutions can be prepared in nonopaque solvents; (3) there are not major shifts in spectral intensity or position of one backbone unit due to the presence of the other.

Numerous examples of bias in polymer analysis have been reported in the literature, although apparently very little attention has been paid to this fact. Lewis et al.[1] studied the system, vinylidene chloride–acrylonitrile, and observed that their carbon, nitrogen, or chlorine analysis were not consistent with one another. Their chlorine analysis always resulted in a lower vinylidene chloride content than the other two methods. Although the nitrogen and carbon analysis did not agree, there was a consistency in the differences between them. Ritchey and Ball,[2] in studying the system styrene–acrylonitrile, noted that their Kjeldahl analyses were consistently about 4.5 mol % lower than their NMR analysis. Izumi and Kitagawa[3] found a definite consistent bias between their NMR and Kjeldahl results for acrylonitrile–methylacrylate copolymers, and infrared measurements agreed with neither. Tidwell and Mortimer[4] found that ^{14}C scintillation counting is not in quantitative agreement with microelemental analysis.

Gruber and Elias[5] analyzed several identical samples of styrene–methyl methacrylate copolymers by five different analytical methods. The least squares, $r_1 r_2$ values, calculated by each method are tabulated in Table I. It is

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TABLE I
Copolymerization Reactivity Ratios Calculated from the Data of Gruber and Elias[5]

Assay method	r_1	r_2
C, H, O	0.52	0.46
Infrared	0.60	0.45
Ultraviolet	0.23	0.48
NMR	0.49	0.26
dn/dc	0.56	0.40

noteworthy that their ultraviolet method gave a higher methyl methacrylate concentration in the copolymers in every instance than did either the infrared, NMR, or dn/dc methods. The dn/dc method was lower in every case than the combustion analysis for C, H, O. These results clearly show that bias in analytical procedures does exist and that it has a powerful influence on the $r_1 r_2$ values.[4,5]

Principal causes for the inconsistencies evident in the literature on reactivity ratios are the use of either biased polymer assay procedures or a model which fails to describe the copolymerization system used to create the polymer. Only those data taken at essentially the same reaction conditions were used to avoid the possibility that the reaction conditions might be responsible for the observed differences. In addition to differences in reaction conditions, there are other reasons why reactivity ratios differ significantly.

For copolymerization, if the same initial monomer conditions have not been selected, it can cause discrepancies. Tidwell and Mortimer[4] describe some methods for resolving discrepancies. The influence of reaction medium (solvent effects on both r_1 and r_2 which can be correlated to the variation in the dielectric constant of solvent) for the free radical copolymerization of styrene and methyl methacrylate have been evaluated by Bonta et al.[6] in different solvents.

Bamford et al.[7] already indicated the variation of reactivity ratios by changing the dielectric constant of the reaction medium. Quite recently, various papers were published related with the methods of calculating monomer reactivity ratios.[8-12] Joshi[9] has reviewed the various published methods of calculating r_1 and r_2. All the earlier methods are considered inadequate and obsolete, whereas new computer programs for minimizing errors lead to the maximum reliable information about monomer reactivity ratios.[7,13,14]

For many years UV has been used for the determination of the percentage of unpolymerized styrene in the homopolymer[15,16] and styrene residue in butadiene–styrene copolymer.[6,17] In spectroscopic analysis, the amount of unpolymerized monomer in polymerized styrene is determined by the following equation[15]:

$$A = [x/100]wE_m + [(100 - x)/100]wE_p \tag{1}$$

where x is the percent of unreacted monomeric styrene in the polymerizing mixture, w is the weight of the sample, and E_m, E_p, and A are the extinction coefficients of monomeric styrene, pure polystyrene, and optical density of the

monomer–polymer mixture, respectively. This equation is used by taking individual UV-absorption spectra of monomeric styrene, monomer-free polystyrene, and monomer–polymer mixture.

The mole fraction x of the styrene present in butadiene–styrene copolymer is determined by

$$x = (E - E_B)/(E_S - E_B) \qquad (2)$$

where E, E_S, and E_B are the specific extinction coefficients of copolymers, pure polystyrene, and pure polybutadiene, respectively.

In this work, UV-spectroscopy methodology was applied to the styrene–methyl methacrylate copolymers, and values almost identical to those obtained by elemental analysis were found.[18]

The analysis of the copolymers, styrene–4-vinylpyridine, styrene–N-vinylcarbazole, styrene–p-methoxystyrene, styrene–p-chlorostyrene, and styrene–p-fluorostyrene were performed by UV spectrophotometry by developing the previously proposed studies,[15–18] and results were compared with other methods. However, it should be pointed out that there were several restrictions to the use of this method for copolymer analysis:

1. The copolymer and the pure homopolymer of only one constituent must show absorption bands at the same wavelength. However, the homopolymer of the other constituent should not give an absorption band at this wavelength.

2. In some cases absorption is dominated by the solvent, and no sharp absorption due to polymer is observed. This fact limits the general application of the UV absorption method for every copolymeric system.

EXPERIMENTAL

Materials

All monomers were obtained either from K and K Rare and Fine Chemicals Laboratories, Inc. or Fluka A G Buch SSG Chemische Fabrik.

p-Chlorostyrene was removed from inhibitor by washing three times with 5% NaOH, then several times with water, dried overnight over $CaCl_2$, and distilled at 10^{-4}–10^{-5} mm Hg (or distilled under 3 mm Hg and fraction boiling between 53 and 54°C were collected).

p-Fluorostyrene was distilled at 4 mm Hg and 29–30°C.

p-Methoxystyrene was distilled at 5 mm Hg and the fraction at 55–56°C was collected.

4-Vinylpyridine was separated from inhibitor by distilling under vacuum shortly before use. The middle cut fraction at 59–60°C and 13 mm Hg was used.[19]

N-vinylcarbazole was purified by recrystallization from petroleum ether.[19] The melting point was found to be 64°C.

Styrene was distilled at 10^{-5} mm Hg at room temperature (or distilled under 10 mm Hg and the fraction boiling between 32–33°C was collected).

Methanol was obtained from Merck Dormstadt and used without further purification.

Chloroform was a product of Riedel-DeHaen AG Seelze-Hannover and was used without any further purification.

Benzoyl peroxide, which was used as an initiator, was an Eastman Kodak Company product and was recrystallized twice from ethyl alcohol.

The spectrometer used was an SP 800D UV Unicam Spectrophotometer.

PREPARATIONS OF COPOLYMERS

Monomer mixtures were weighted in Pyrex polymerization tubes in several molar ratios and about 0.1% (by weight) benzoyl peroxide was added to each as a catalyst. The tubes were evacuated to 10^{-4}–10^{-5} mm Hg and post-polymerized in constant temperature baths at 60–80°C for different time intervals. The copolymers were dissolved in toluene and precipitated twice in methanol by adding the solutions dropwise with constant stirring. They were then dried in a vacuum oven at 50°C. Homopolymers were prepared in the same manner from their monomers.

Post-polymerization conversions at 80°C were between 91 and 95%.

PROCEDURE

The polymers were dissolved in chloroform to obtain approximately 1 mg/mL solutions in order to have the same initial concentrations of each copolymeric and homopolymeric sample. A wavelength was sought at which one homopolymer and its copolymer showed a characteristic peak and the homopolymer of the other constituent did not absorb. By preparing solutions of various concentrations, different spectra were taken for each copolymer as well as its corresponding homopolymers. One of the homopolymers was chosen as a reference for analysis. The most convenient concentration was chosen to represent 100% concentration at this absorption region. A calibration curve was then obtained by plotting the absorbance values against percent concentrations of solutions of homopolymers. The absorbance values of the copolymeric samples at the same concentration were obtained from the spectra of the copolymers and the corresponding percentages of the desired residues were determined from the calibration curve.

RESULTS

UV Absorption of Polystyrene

UV absorption spectra for different concentrations of pure polystyrene were taken (Fig. 1). Using the data given in Table II, a graph was plotted of absorbance value of polystyrene at 37,100 cm^{-1} (269 nm) vs. percent concentration, assuming that the maximum peak at concentration 26.2 mg/25 mL (1.05 mg/mL) in chloroform represents 100% concentration (Fig. 2). This figure was used as a calibration curve for further analysis of copolymers. The solutions of copolymers were prepared at the highest concentration given in Table II, and by means of the calibration curve the percentage of styrene incorporated into the copolymers was determined.
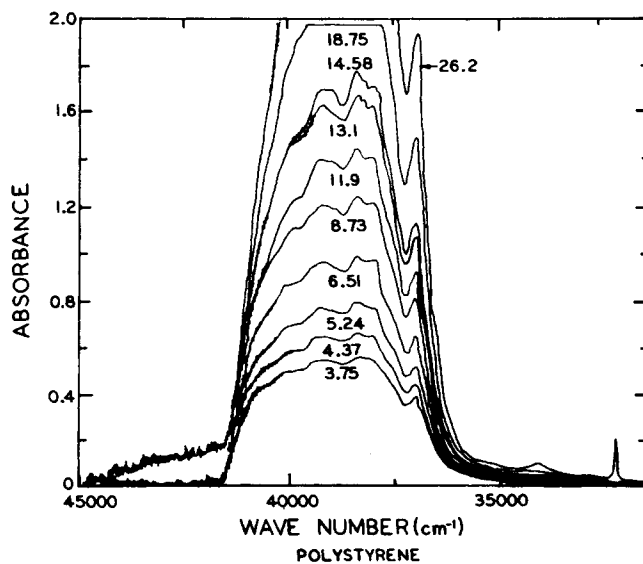
Fig. 1.   Absorption spectra for different concentrations of polystyrene homopolymer.

TABLE II
UV Absorption of Polystyrene

Concentration of solution (mg/mL)	Absorbance at 37,100 cm^{-1} (269 nm)	Concentration (%)
1.05	1.94	100.0
0.75	1.49	71.5
0.58	1.14	55.2
0.52	1.08	43.9
0.48	0.93	45.2
0.35	0.82	33.4
0.26	0.65	25.0
0.21	0.52	19.9
0.17	0.45	16.7
0.15	0.39	14.3

STYRENE–p-METHOXYSTYRENE COPOLYMERS

UV absorption spectra were taken for pure poly(p-methoxystyrene) and one of its copolymers with styrene (Figs. 3 and 4). The most convenient concentration for comparison was chosen as 3.75 mg/25 mL (0.15 mg/mL) in chloroform for all samples. Pure poly(p-methoxystyrene) also showed a certain amount of absorption where pure polystyrene gives a characteristic absorption band at 37,100 cm^{-1} (269 nm). As a result, the absorption peaks at this wavelength for styrene–p-methoxystyrene copolymers exceed the peak for pure polystyrene, due to overlapping.

Therefore, these copolymers were analyzed with respect to the p-methoxystyrene homopolymer. The peaks at 35,000 cm^{-1} (286 nm) are due only to

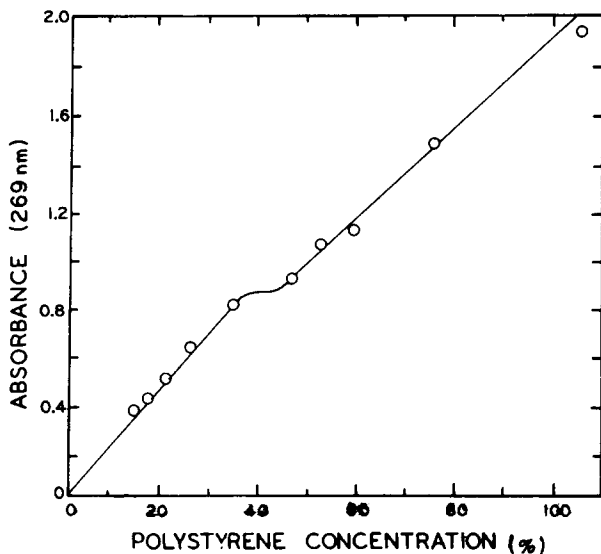Fig. 2.   Absorbance of polystyrene at 37,100 cm^{-1} (269 nm) vs. percent concentration [peak at 26.2 mL/25 mL (1.05 mg/mL) in chloroform represents 100% concentration].

the p-methoxystyrene incorporated into the copolymer. A calibration curve was obtained by plotting the absorbance values of pure poly(p-methoxystyrene) at 35,000 cm^{-1} (286 nm) vs. percent concentration, considering the concentration 3.75 mg/25 mL (0.15 mg/mL) in chloroform to have a maximum absorption (Fig. 5). The extinction coefficients for poly(p-methoxystyrene) and polystyrene homopolymers were 1.36 and 0.39, respectively, at this wavelength. The reactivity ratios calculated by Walling et al.[20] for

POLY - p - METHOXYSTYRENE
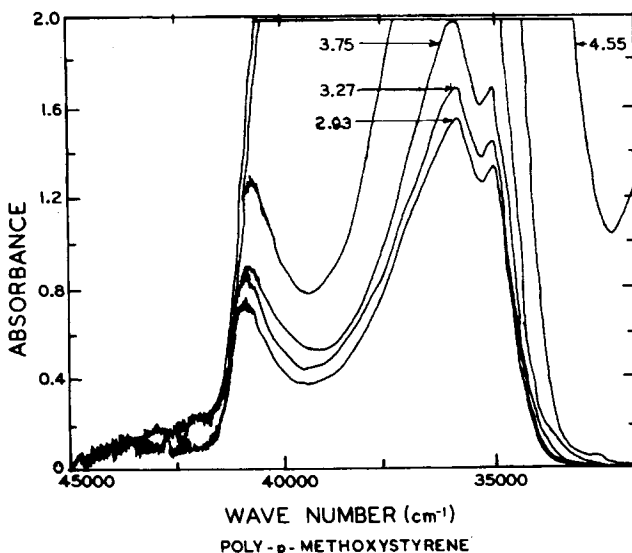
Fig. 3.   Absorption spectra for poly(p-methoxystyrene) homopolymer at different concentrations.
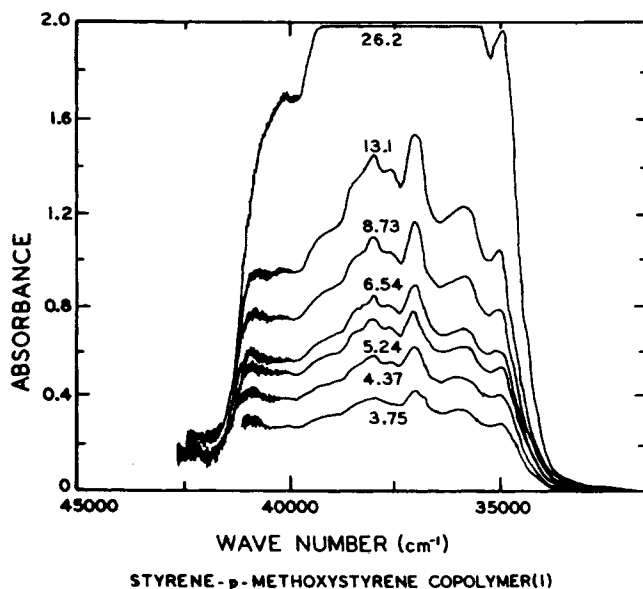
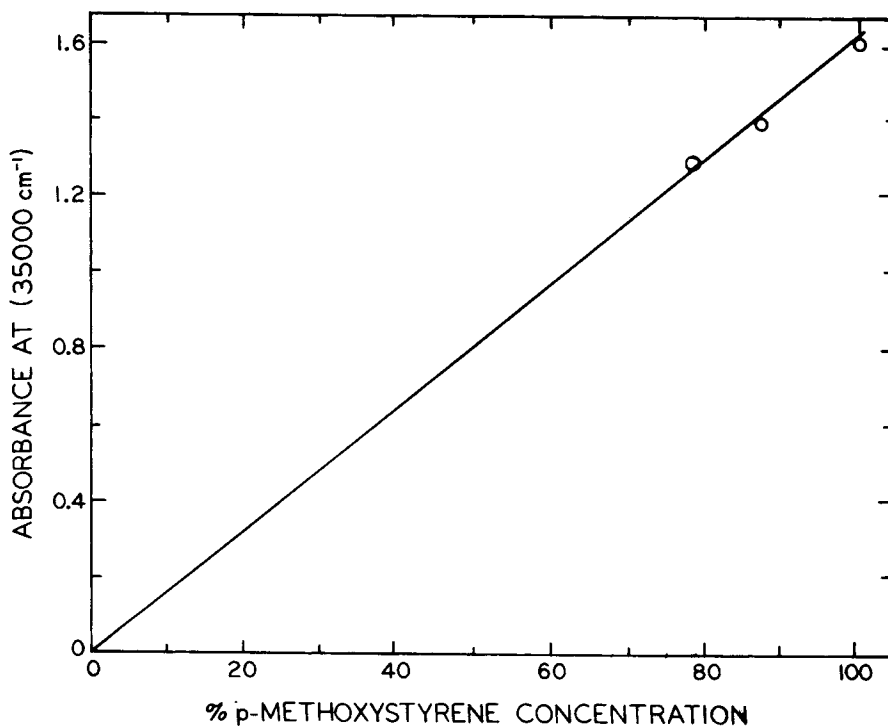Fig. 4.   Absorption spectra for styrene–*p*-methoxystyrene copolymer (1) at different concentrations.

Fig. 5.   Absorbance of poly(*p*-methoxystyrene) homopolymer at 35,000 cm⁻¹ (286 nm) vs. percent concentration [peak at 3.75 mg/25 mL (0.15 mg/mL) in chloroform represents 100% concentration].

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TABLE III
Copolymer analysis of Styrene–p-Methoxystyrene Copolymer[a]

Copolymer number	1	2	3	4	5
1	0.30	16.78	14.85	18.3	16.8
2	0.68	35.23	30.40	41.5	40.4
3	0.93	75.67	50.30	56.8	56.0
4	1.36	—	94.00	95.2	95.0
100% PMS	1.64	100.0	100.0	100.0	100.0
100% PS	0.03	—	—	—	—

[a] Concentration 0.15 mg/mL. PMS = poly(p-methoxystyrene), PS = polystyrene. Column headings: (1) absorbance at 35,000 cm^{-1} (286 nm); (2) PMS in monomer (mol %); (3) PMS in copolymer by Figure 5 (mol %); (4) PMS in copolymer by Figure 5 (wt %); (5) PMS in copolymer by eq. (2) (wt %).

styrene and p-methoxystyrene monomers were 1.16 and 0.82 at 60°C, respectively.

For different copolymers the weight percent of p-methoxystyrene residue was determined by using calibration curve (Fig. 5). The results are given in Table III.

The weight percents were also calculated by Newell's method [eq (2)]. The weight percent values calculated by using eq. (2), and those obtained by Figure 5, which was plotted by the method developed in this work, are in close agreement. Figure 6 shows the mole percent of p-methoxystyrene in monomer mixture vs. mole percent of polymerized p-methoxystyrene in the corresponding copolymer. Using the data given in Table III, the absorbance values at 35,000 cm^{-1} (286 nm) was plotted vs. weight percent of p-methoxystyrene residue in copolymer (Fig. 7). The curve gives a straight line which proves that Beer's law is observed by this copolymer.
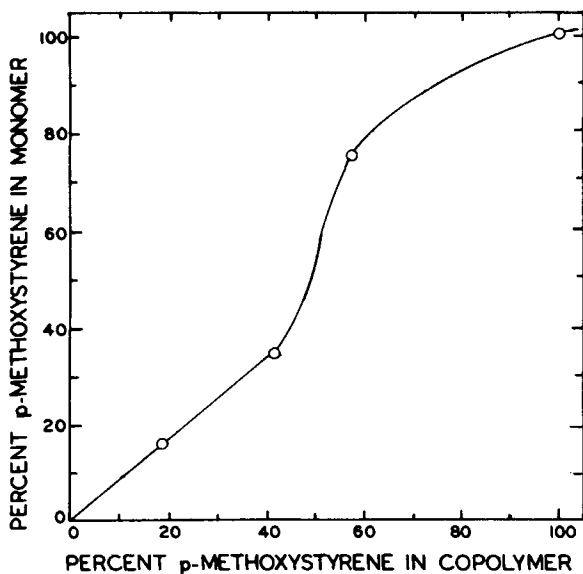

Fig. 6. Mole percent of p-methoxystyrene in styrene–p-methoxystyrene monomer mixture vs. mole percent of p-methoxystyrene in copolymer.
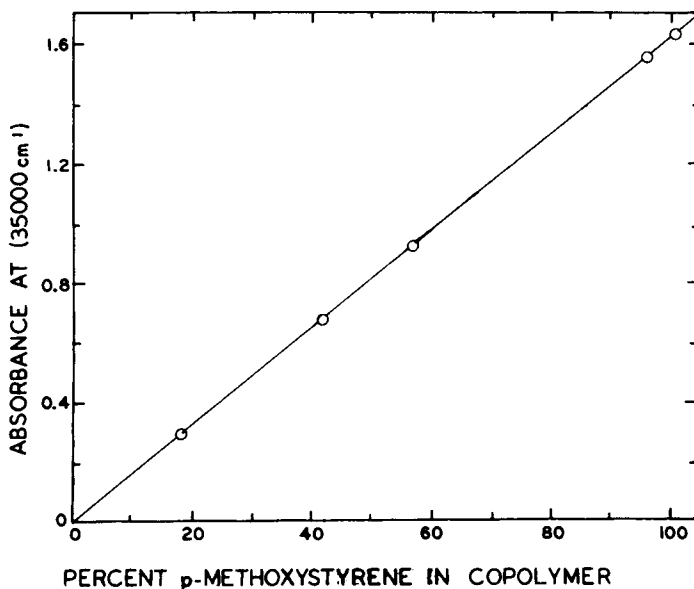
Fig. 7.   Absorbance at 35,000 cm^{-1} (286 nm) vs. weight percent of p-methoxystyrene residue in styrene–p-methoxystyrene copolymers.

STYRENE–p-CHLOROSTYRENE COPOLYMERS

The absorption spectra for various concentrations of pure poly(p-chlorostyrene), prepared by using 0.1 mol% benzoyl peroxide as an initiator, and one of its copolymers with styrene are shown in Figure 8 and 9, respectively. The absorption peaks of copolymers and p-chlorostyrene homopolymers were compared at the same wavelength, 35,900 cm^{-1} (278.5 nm). Pure polystyrene
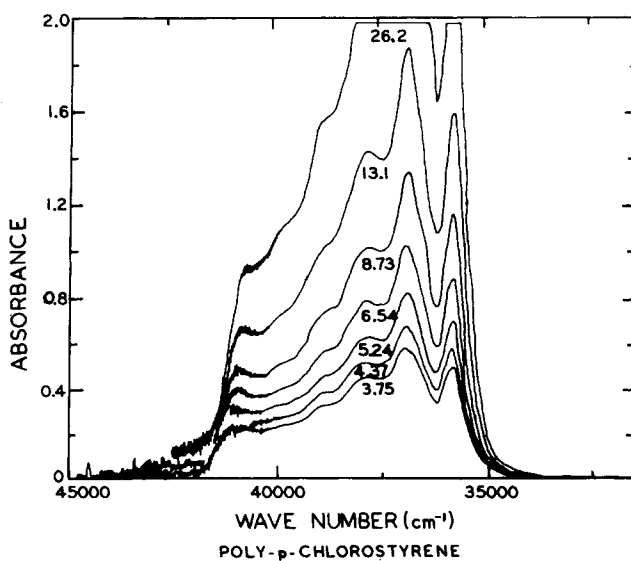

Fig. 8.   Absorption spectra for different concentrations of poly(p-chlorostyrene) homopolymer at different concentrations.
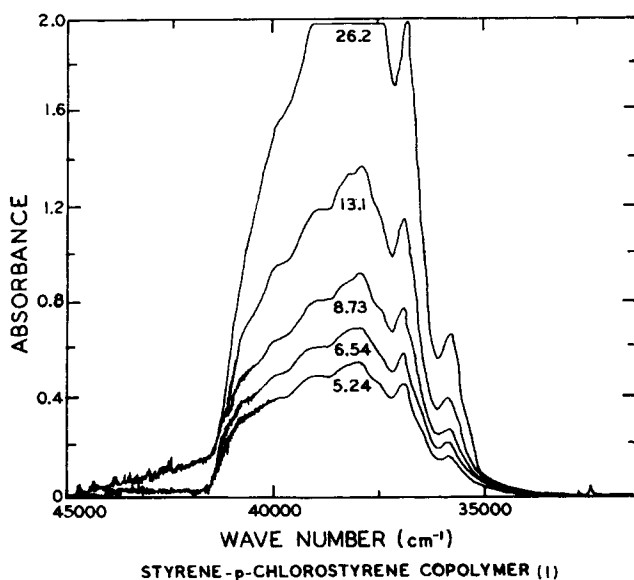
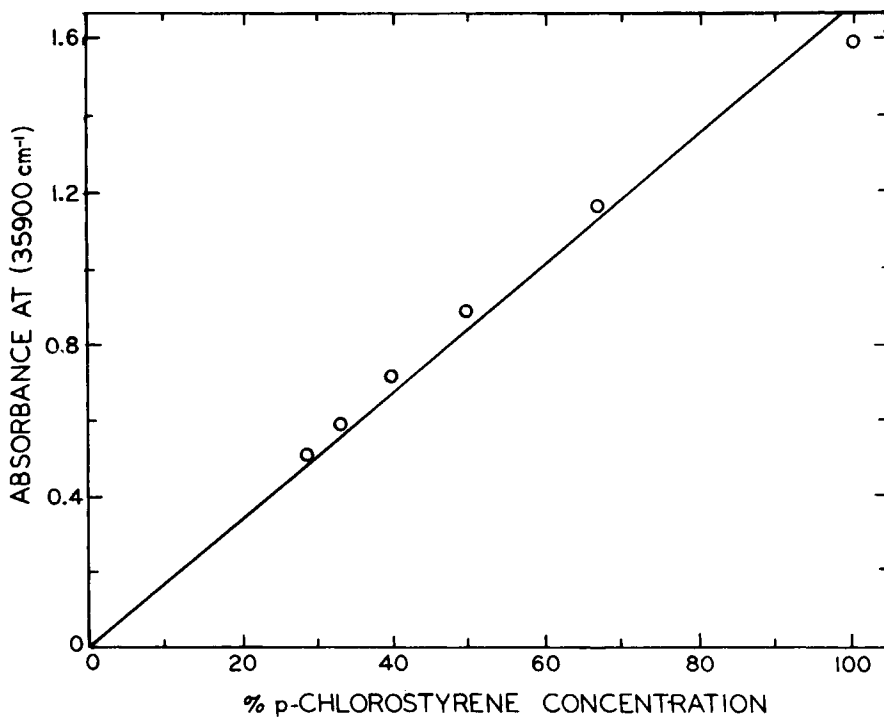Fig. 9.   Absorption spectra for styrene–p-chlorostyrene copolymer (1) at different concentrations.

Fig. 10.   Absorbance of poly(p-chlorostyrene) homopolymer at 35,900 cm^{-1} (278.5 nm) vs. percent concentration [peak at 13.1 mg/25 mL (0.52 mg/mL) in chloroform represents 100% concentration].

TABLE IV
Styrene–p-Chlorostyrene Copolymer Analysis[a]

Copolymer number	1	2	3	4	5
1	20	0.43	25.0	20.0	23.0
2	40	0.61	36.0	29.7	34.0
3	60	0.76	44.5	37.5	44.1
4	80	1.10	64.5	75.0	66.8
100% PCS	100	1.60	100.0	100.0	100.0

[a] Concentration 0.52 mg/mL. PCS = poly(p-chlorostyrene). Column headings: (1) PCS in monomer (mol %); (2) absorbance at 35,900 cm^{-1} (278.5 nm); (3) PCS in copolymer by Figure 10 (wt %); (4) PCS in copolymer by Figure 10 (mol %); (5) PCS in copolymer by eq. (2) (wt %).

has near zero absorbance at this wavelength (Fig. 1). The most convenient concentration for comparison was chosen to be 13.1 mg/25 mL (0.52 mg/mL) in chloroform.

Figure 10 represents a calibration curve of absorbance values at 35,900 cm^{-1} (278.5 nm) vs. percent concentration of pure poly(p-chlorostyrene), where absorbance at 0.52 mg/mL concentration corresponds to 100% concentration. From the corresponding absorbances of the copolymer at the same concentration and wavelength, the weight percent of p-chlorostyrene in the copolymer was determined by using the calibration curve. The results for four copolymeric samples are given in Table IV. The extinction coefficients of poly(p-chlorostyrene) and polystyrene homopolymers were 3.02 and 0.19, respectively, at this wavelength. The reactivity ratios calculated by previous workers[20,21] for styrene and p-chlorostyrene monomers were 0.74 and 1.03 at 60°C, respectively.[20,21]
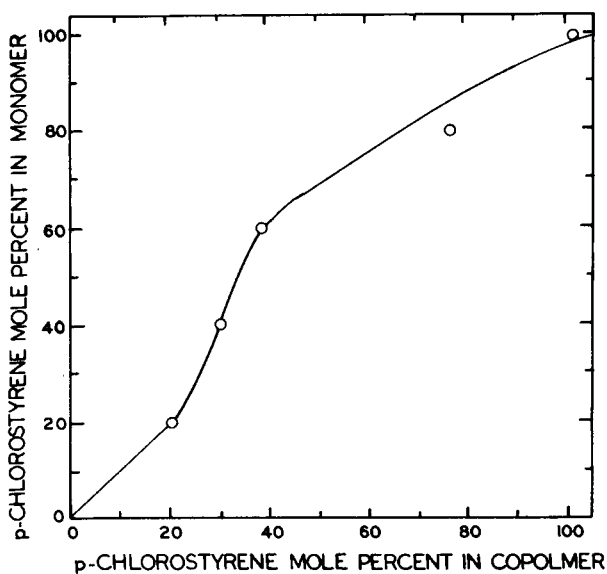

Fig. 11. Mole percent of p-chlorostyrene in styrene–p-chlorostyrene monomer mixture vs. mole percent of p-chlorostyrene residue in copolymer.
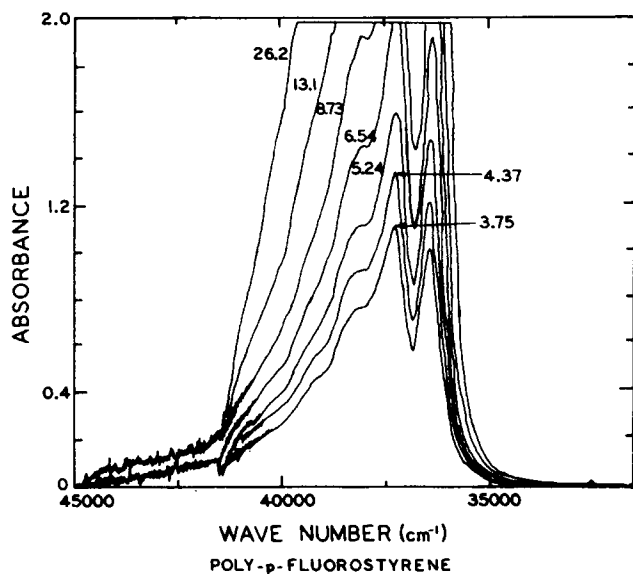
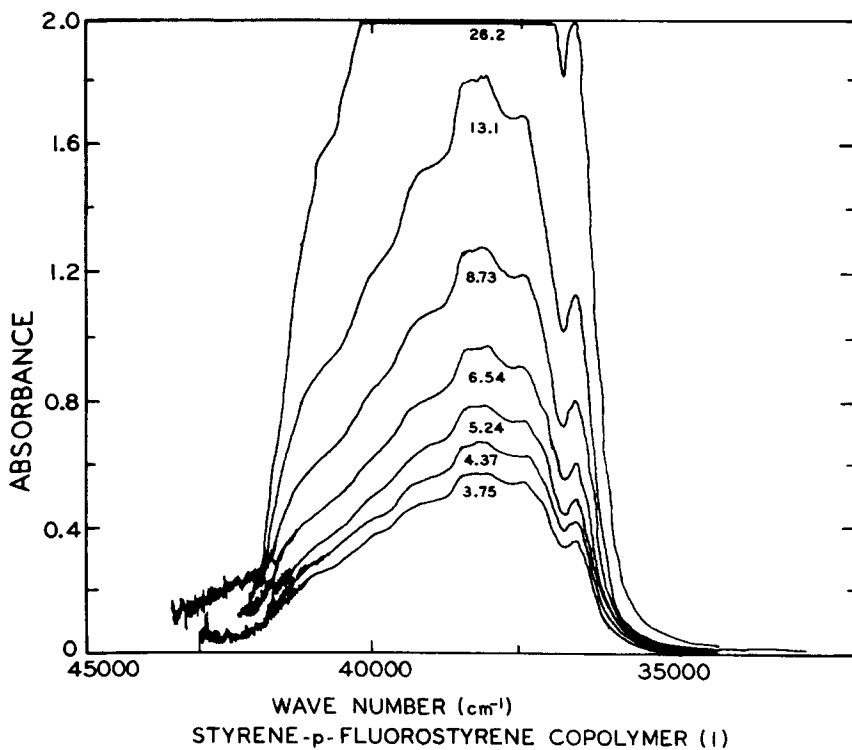Fig. 12.   Absorption spectra for poly(*p*-fluorostyrene) homopolymer at different concentrations.

Fig. 13.   Absorption spectra of styrene–*p*-fluorostyrene copolymer (1) at different concentrations.
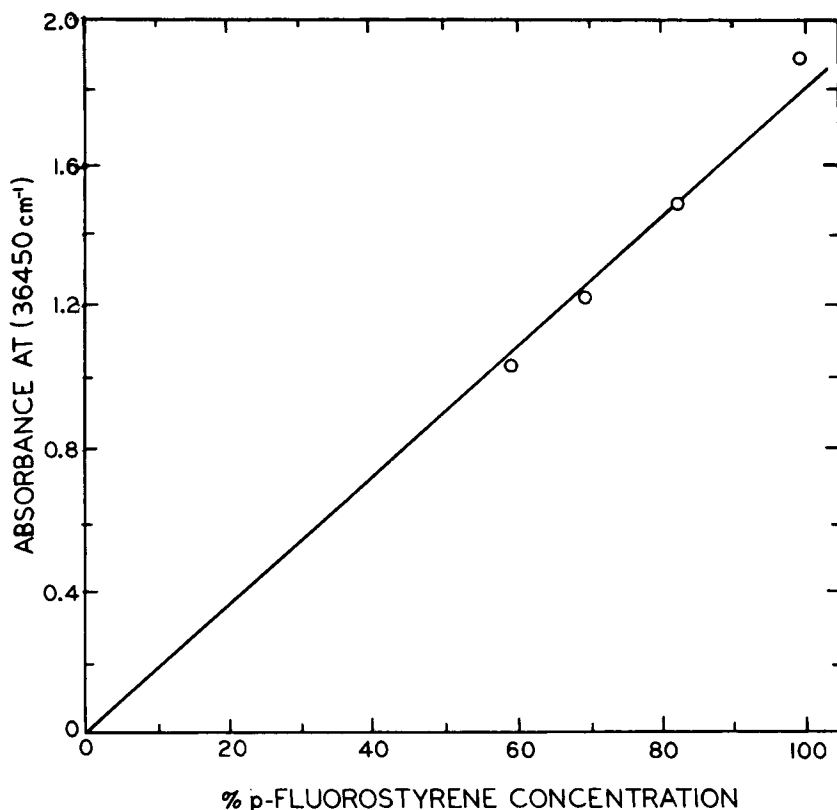
Fig. 14.   Absorbance of poly(p-fluorostyrene) at 36,450 cm^{-1} (274.5 nm) [peak at 6.54 mg/25 mL (0.26 mg/mL) in chloroform represents 100% concentration].

Figure 11 was plotted of mole percent of p-chlorostyrene in monomers vs. mole percent of p-chlorostyrene residue in copolymer.

STYRENE–p-FLUOROSTYRENE COPOLYMERS

The absorption spectra in Figures 12 and 13 are of poly(p-fluorostyrene) homopolymer and one of its copolymers with styrene. For comparison, the absorption bands at 36,450 cm^{-1} (274 nm) and a concentration of 6.54 mg/25

TABLE V
Styrene–p-Fluorostyrene Copolymer Analysis[a]

Copolymer number	1	2	3	4	5
1	20	0.60	33.5	30.09	23.15
2	40	0.99	55.5	51.10	46.00
100% PFS	100	1.92	100.0	100.00	100.00

[a] Concentration 0.26 mg/mL. PFS = poly(p-fluorostyrene). Column headings: (1) PFS in monomer (mol %); (2) absorbance at 36,450 cm^{-1} (274 nm); (3) PFS in copolymer by Figure 14 (wt %); (4) PFS in copolymer by Figure 14 (mol %); (5) PFS in copolymer by eq. (2) (wt %).
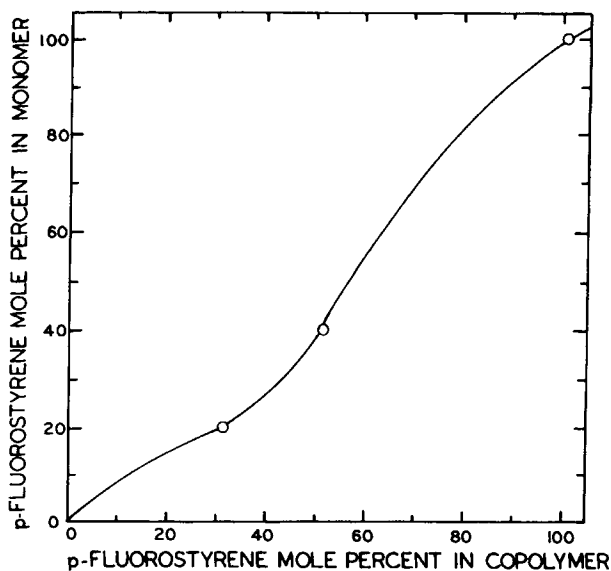
Fig. 15. Mole percent of p-fluorostyrene in styrene–p-fluorostyrene monomer mixture vs. mole percent of p-fluorostyrene residue in copolymer.

mL (0.25 mg/mL) in chloroform was chosen. Pure polystyrene does not absorb in this spectral region (Fig. 1). Figure 14 was plotted as a calibration curve of absorbance values at this wavelength vs. percent of poly(p-fluorostyrene) considering the absorption peak at 6.54 mg/25 mL corresponds to 100% concentration.

The copolymer analysis is given in Table V. Figure 15 represents mole percent of p-fluorostyrene in monomer vs. mole percent of p-fluorostyrene residue in copolymer. The extinction coefficients of pure poly(p-fluorostyrene) and polystyrene are 7.38 and 0.77 at this wavelength (36,450 cm^{-1}). According to other workers,[21–23] the calculated reactivity ratios for styrene and p-fluorostyrene monomers are 0.70 and 0.90 at 60°C, respectively.

STYRENE–4-VINYLPYRIDINE COPOLYMERS

Figure 16 shows an absorption spectrum of one styrene–4-vinylpyridine copolymer. No sharp peak was observed at 37,100 cm^{-1} (269 nm) where polystyrene gives a characteristic absorption band.

The absorption peaks for styrene and 4-vinylpyridine were overlapped, and there was no possibility for analysis with respect to styrene. However, the peak at 38,800 cm^{-1} (258 nm) could be due to the absorbtion of 4-vinylpyridine alone at this region.

STYRENE–N-VINYLCARBAZOLE COPOLYMERS

Absorbtion spectra taken for 1 mg/mL in chloroform of pure poly(N-vinylcarbazole) and its copolymers with styrene gave no sharp peak. There was no absorption band observed even for its tenfold diluted solutions. There was no possibility for the application of this method on this copolymer.
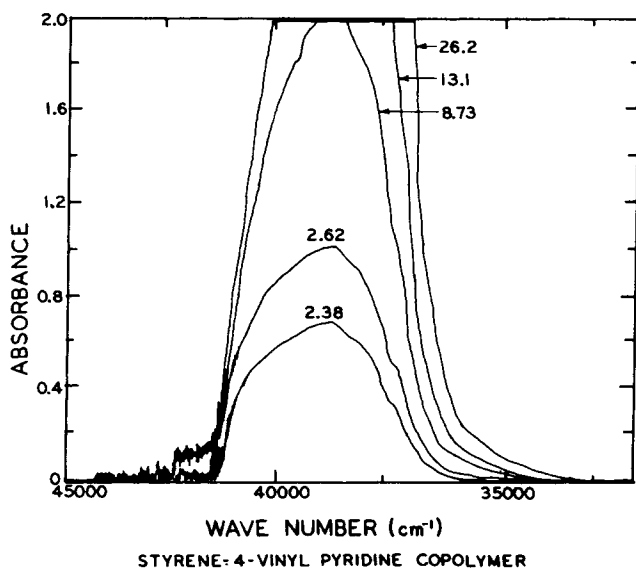
Fig. 16.   Absorption spectra of styrene–4-vinlypyridine copolymer (1) at different concentrations.

DISCUSSION

In this work a rapid method based on UV spectroscopy for the analysis of styrene–p-substituted styrene copolymers has been developed.

Copolymers of styrene–p-methoxystyrene, styrene–p-chlorostyrene, and styrene–p-fluorostyrene were prepared at different compositions. The plots indicating absorbances as a function of percent of homopolymer residue in copolymer are given for these three copolymer systems. These plots would be valuable for compositional analysis of the copolymers prepared from varying composition mixtures of the same monomers. In addition, the plots representing the percent of one of the monomers in initial solution as a function of percent residue of the same component in the copolymeric form are given. These later plots can be used to choose the proper initial monomer composition for the desired copolymer composition to be prepared.

Using the method developed in this work, attempts to analyze styrene–4-vinylpyridine and styrene–N-vinylcarbazole copolymers were not successful. As a result, it can be concluded that the method presented in this work appears to be feasible for the analysis of some, but certainly not all, systems.

In many cases the copolymerization was described by models considering both monomer reactivity and chain end reactivity. For these models the Alfrey–Mayo equation[24] is outstanding. However, for many studies of copolymers the r values were found to be dependent on the nature of the solvent,[25,26] pressure,[27] and temperature,[28] but it was assumed to be independent of conversion if the system is dilute and the conversions are moderate.

The most popular mathematical model for the description of copolymer kinetics in the literature is the differential copolymer composition equation.[24] Although the Mayo equation has been extensively used to estimate reactivity

ratios,[4,29] it is only applicable to copolymerizations carried to very low conversions. As the conversion becomes perceptible, bias is introduced because of the drift in feed composition. Integration of the Mayo equation results in the Meyer–Lowery equation.[30,31]

Johnson and co-workers[32] attributed the failure of the Mayo–Lewis equation in describing the data to the diffusion effects on the propagation reaction. Also, some recent workers[32-34] have shown that in some cases even the integrated Alfrey–Mayo model is inadequate to describe the copolymerization behavior up to high conversions.[32,33]

For the systems of styrene–ethyl methacrylate in bulk,[35] the experimental curves of monomer feed ratio vs. conversion deviates significantly from the expected values obtained from the integrated Alfrey–Mayo model (Meyer–Lowery equation). These results unambiguously indicate that the departures from this model occur before the onset of the gel effect, which is the moment at which a significant increase in conversion rate occurs. For the copolymerization of this system at moderately high conversions anomalous copolymerization behavior occurred.[35] Although the onset of the departure from the expected copolymerization behavior seems to be related to the onset of the gel effect, this relation did not hold when mimicking higher conversion by adding an amount of homopolymer. Therefore, the propagation reactions must not only be effected by changes in diffusion characteristics, but also by changes in other medium characteristics, e.g., interaction between monomeric and copolymer species.

The statistical procedures employed by O'Dristal on the Meyer–Lowery equation use an "error-in-all-variables" model which assumes that all observations are coming from some unknown true values plus measurement errors. Variable metric methods were used to obtain point estimates of the parameters which produced an approximation to the variance–covariance matrix of the resulting parameter estimates from which confidence regions were calculated. Johnson et al.[32] suggested that reactivity ratios were a function of conversion. This was rejected by Dionisio and O'Driscoll[33] on the basis that reactivity ratios, being ratios of propagation rate constants, should be affected by changes in the diffusional characteristics of the reaction medium. Penultimate unit effects, depropagation, and charge-transfer complex formation were also rejected. These mechanisms could not predict the data observed.[31] As a result, by assuming a correct model, the Meyer–Lowery-equation can adequately describe the high-conversion free-radical copolymerization.[30] When the resulting copolymer composition was determined by NMR and UV methods by applying this model, they both verified the consistency of the composition estimates, and independently their data were very consistent.

In order to develop a model that accurately describes the copolymerization system under observation, the data must be evaluated for possible inconsistencies and bias. To minimize errors, new methods have been developed by other workers.[4,8,13] Many of the earlier methods may be considered inaccurate due to lack of primary polymer standards. New computer programs for determining copolymerization reactivity ratios have been proposed.[4,13] A Fortran IV program is based on the curve fitting method.[8] The exact nature of the interaction of polymeric species with solvent is still unknown for many

systems, due to microphase separation, complex formation, and polarization of growing macroradicals.[36] Copolymerization rate and monomer reactivity ratios vary if the experimental corrections are not the same.

To describe the copolymerization system, a polymer assay procedure or a model has to be determined. To prevent bias and inconsistencies both in copolymer analysis and the reactivity ratios, primary polymer standards, that is, copolymers with exactly known composition, must be used in calibration of polymer assay. Also, alternative procedures such as mass or material balance[4] should be used to assure that these methods are accurate. To discover the primary bias in methods, independent methods can be used to determine the quantity of unreacted monomers and the composition of the copolymer.[37-39]

The detection of the failure of the system to be described by the assumed model can be done in two ways. First, replicate experimental runs should be made with sufficient care. These data can, then be employed to assure the adequacy of the model.[4,13] As further check, the residuals—the differences between the observed and computed polymer composition—should be graphed vs. the initial monomer concentration, the calculated polymer composition, and the experimental run order as an additional method of evaluating the agreement or lack of agreement between experimental results and the copolymerization model.[4] The use of a model[4] that fails to describe the system indicates that either the experimental practices are inappropriate or the assumptions made about the copolymerization scheme are not correct.

Although the complete explanation of the nature of the present anomalous copolymerization behavior at high conversions cannot be presented yet, the results obtained in this method for the copolymer analysis calculated from eq. (2) and by the calibration curves are in close agreement. The results certainly indicate that this method can be developed in the future even for high conversions considering one of the models[4,30,31] presented in the Discussion section. Further work in this area seems to be needed in the future.

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