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Bianca M. Gallo^a; Saverio Russo^a

^a Istituto di Chimica Industriale Università di Genova, Genoa, Italy

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Ultraviolet Absorption Spectra of Styrene Copolymers. I. Solvent Effects on the Hypochromism of Poly(styrene-co-methyl Methacrylate) at 2695 Å

BIANCA M. GALLO and SAVERIO RUSSO

Istituto di Chimica Industriale
Università di Genova
16132 Genoa, Italy

ABSTRACT

The use of a UV spectrometer for evaluating the chemical composition of styrene-methyl methacrylate random copolymers is conditioned by the presence of a marked hypochromism at 2695 Å.

The composition range where the hypochromic effect appears is strongly affected by the solvent employed. Optical densities at 2695 Å for copolymer solutions in chloroform, dichloroethane, tetrachloroethane, tetrahydrofuran, and dioxane have been determined and compared to the absorbance values of polystyrene solutions. A linear correlation between solvent dielectric constant and copolymer composition corresponding to the maximum hypochromism is found.

Implications involving gel permeation chromatography analyses of styrene copolymers are discussed.

INTRODUCTION

Polystyrene shows several absorption bands in the UV region, the principal ones being centered about 800, 1940, 2150, and 2600 Å [1]. As polymethyl methacrylate does not absorb appreciably above 2500 Å, it has been proposed by Tobolsky et al. [2] that the composition of styrene-methyl methacrylate copolymers be determined by measuring the absorbance of their chloroform solutions at 2690 Å.

A deviation from linearity in the plot of optical density vs styrene content in the copolymers has been observed and tentatively ascribed [3] to the different absorption coefficients of styrene units isolated between methyl methacrylate mers and those of two adjacent styrene mers. Several other styrene copolymers show an anomalous pattern of their UV spectra [4].

Indeed, considerable error might arise from the misuse of UV data through disregard of the comonomer effects on the extinction coefficient [5, 6]. This is the case, for instance, in gel permeation chromatography analyses of copolymers, where precise correlations between elution volumes and eluate composition are needed in order to give correct molecular weight distributions.

For copolymers containing comonomer units able to absorb in the UV region, a UV spectrometer has been proposed as a second detector for evaluating the copolymer composition [7-9], and the UV absorption has been assumed to depend only on the total concentration of chromophore units. The use of such a detector for styrene copolymers on the basis of the above assumption provides erroneous results and has recently been questioned [4, 10].

The present study accounts for the anomalous pattern in the UV spectra of styrene copolymers. Part I reports on the strong influence that solvents exert upon the UV extinction coefficient of styrene-methyl methacrylate random copolymers at 2695 Å.

EXPERIMENTAL

Materials

Copolymer samples were prepared by free-radical polymerization in bulk (initiator: α,α' -azobisisobutyronitrile) and were purified by double precipitation [11]. Number-average molecular weights (by osmometry) were in the range 80,000 to 380,000 [12]. Copolymer composition has been evaluated by elemental analysis [13] and confirmed by NMR spectroscopy. The solvents used were chloroform (Rudi Pont), tetrahydrofuran (Baker), p-dioxane (Baker), sym-dichloroethane (Carlo Erba), and sym-tetrachloroethane (Carlo Erba), all purified by the usual techniques.

Measurements

Optical density measurements have been carried out using a single-beam Zeiss spectrophotometer equipped with stoppered quartz cells, 10 mm long. All solutions were independently prepared on a weight basis. Polymer concentrations (in moles/liter) were computed by use of solvent densities as quoted in the literature. All the measurements were performed at a temperature of $20 \pm 0.05^\circ\text{C}$. No effect of molecular weight on the absorbance values has been found. The Lambert-Beer law was obeyed by every solution, at least up to a concentration of about 2 mg/ml. Absorbance data were referred to a total copolymer concentration of 1×10^{-2} mole/liter and plotted as functions of styrene molar content in the copolymer. Calibration curves for polystyrene in the concentration range from 0 to 1×10^{-2} mole/liter were also determined. It was considered unnecessary to introduce any correction for scattered light [14].

EXPERIMENTAL RESULTS

The optical densities for chloroform solutions of polystyrene and styrene-methyl methacrylate random copolymers have been determined at 2695 Å. The results, plotted as functions of styrene content, are reported in Fig. 1.

As far as copolymers are concerned, there are three different parts of the plot: Part a (from 0 to about 25 mole % styrene) and Part c (from about 80 to 100% styrene), where a single linear relationship between optical density and styrene concentration remains valid and the straight line coincides with the calibration curve for polystyrene, and the middle area b, related to a styrene content ranging from 25 to 75-80 mole %, where there is a sharp, almost symmetrical deviation from the calibration curve and from linearity. The maximum decrease of the extinction coefficient corresponds to a copolymer containing 50 mole % styrene.

Mechanical mixtures of polystyrene and polymethyl methacrylate, on the contrary, give absorbance values identical to the values obtained for polystyrene alone.

A check of the whole absorption band centered around 2695 Å (Fig. 2) reveals the existence of a real hypochromism, usually accompanied by a very small shift toward lower energies (bathochromism).

In order to investigate the possible causes of hypochromism and bathochromism, we have measured the optical densities of our samples in other solvents: p-dioxane, sym-tetrachloroethane, tetrahydrofuran, and sym-dichloroethane.

Solvent and comonomer effects on the wavelength of the maximum are reported in Table 1.

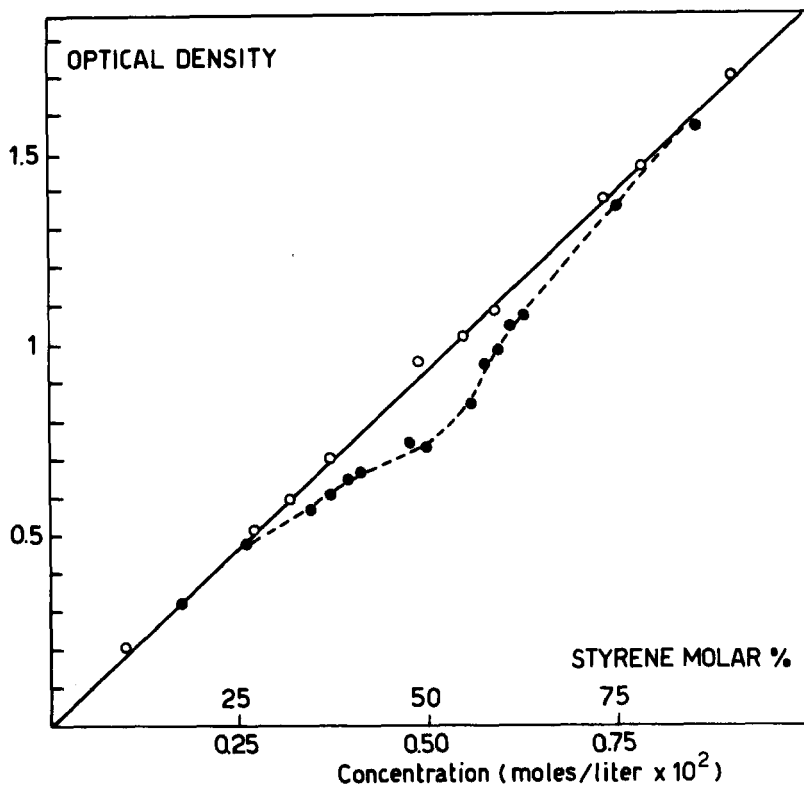


FIG. 1. Optical density of chloroform solutions at 2695 Å as a function of styrene molar content. (○) Polystyrene. (●) Poly(styrene-co-methyl methacrylate).

TABLE 1. Wavelength of the Lowest Energy Maximum of the Band around 2600 Å as a Function of the Solvent for Polystyrene and Poly(styrene-co-methyl Methacrylate).

Solvent	λ_{\max} (Å)	
	Polystyrene	Copolymer
Dichloroethane	2695	2695 - 2700
Tetrachloroethane	2695	2695
Tetrahydrofuran	2695	Very slight bathochromism
Chloroform	2695	2695 - 2702
Dioxane	2695	2695 - 2700

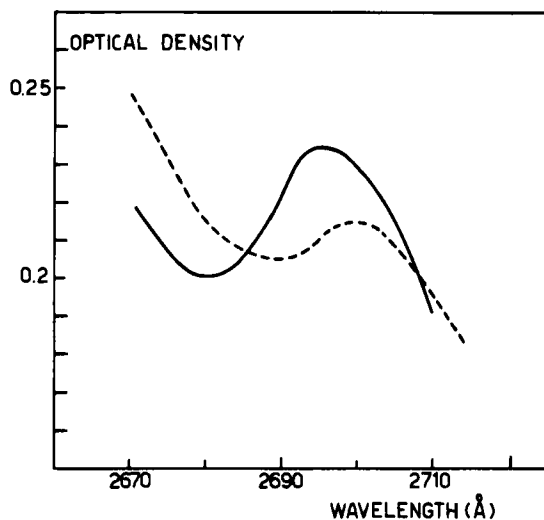


FIG. 2. UV absorption spectra of the band around 2695 Å. Solvent: chloroform. (—) Polystyrene. (--) Copolymer containing 50 mole % methyl methacrylate).

The wavelength shift is known to be caused by any increase in the interactions of groups and/or solvents with the chromophore units [15]. In our case, however, the shift is very small. Therefore a fixed wavelength (2695 Å) was chosen. It was also chosen because of the practical applications of UV spectrometry (GPC, etc). The implied errors were negligible.

The optical density values at 2695 Å as functions of styrene content are plotted in Fig. 3.

It appears that the optical densities of polystyrene solutions are only slightly affected by the solvents employed. For copolymers, on the contrary, the solvent effect is very strong: the same trend as in chloroform is found, with a very sharp hypochromism, but the composition range where hypochromism appears is a function of the solvent.

In Table 2 the composition ranges of Parts a, b, and c, as well as the copolymer composition corresponding to the maximum deviation from the calibration curve, are reported as functions of the solvent employed.

In Table 3 the decrease of absorption intensity per chromophore referred to the maximum hypochromism is reported.

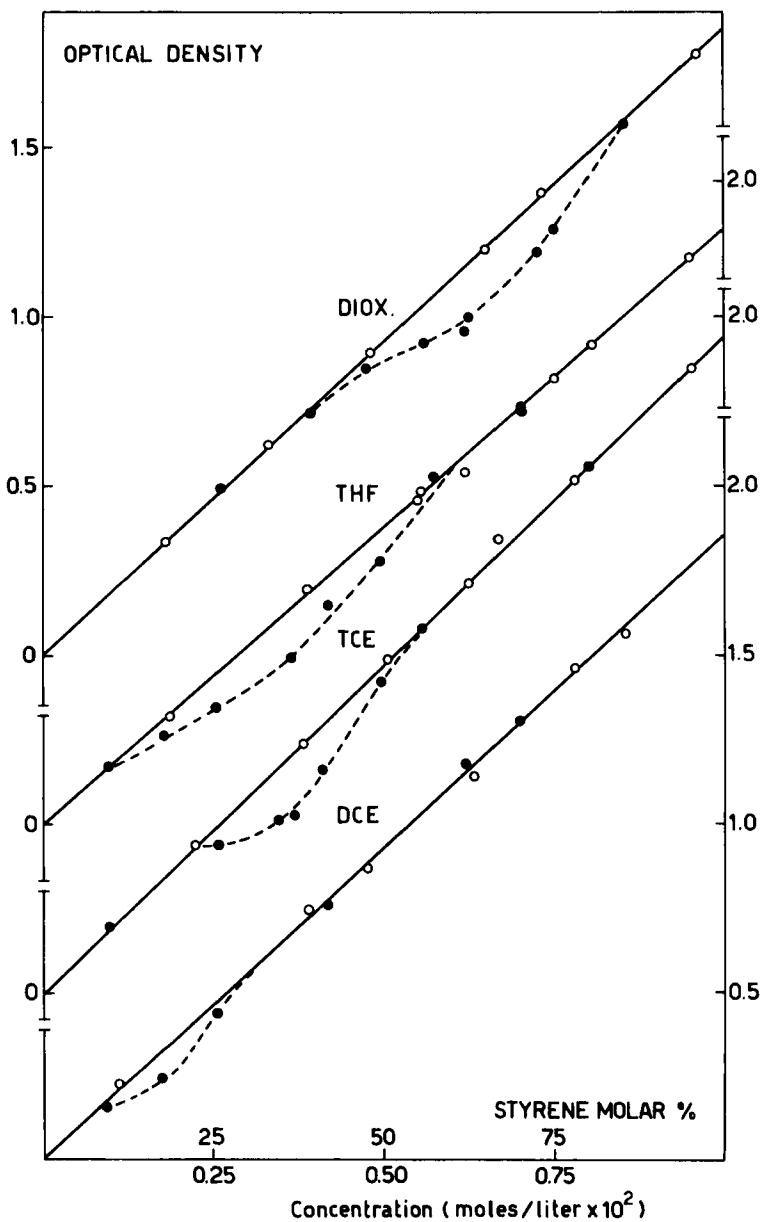


FIG. 3. Optical densities at 2695 Å as functions of styrene molar content. From the bottom: polymer solutions in dichloroethane, in tetrachloroethane, in tetrahydrofuran, and in dioxane. (○) Polystyrene. (●) Poly(styrene-co-methyl methacrylate).

TABLE 2. Solvent Effect on the Hypochromism of Poly(styrene-co-methyl Methacrylate)

Solvent	Styrene mole % in the copolymer			
	a (linear)	b (hypochromism)	Maximum hypochromism	c (linear)
Dichloroethane	0-7	7-28	~19	28-100
Tetrachloroethane	0-20	20-55	~34	55-100
Tetrahydrofuran	0-10	10-65	~36	65-100
Chloroform	0-25	25-80	~50	80-100
Dioxane	0-40	40-85	~63	85-100

DISCUSSION

The peak at 2695 Å is part of the fine vibrational structure of the band centered around 2600 Å, related to the lowest energy forbidden $\pi - \pi^*$ electronic transition of the phenyl ring ($A_{1g}' - B_{2u}'$ in benzene). It is more suitable than others for a calibration curve giving the styrene content in a copolymer, because the interactions of comonomer units seem weaker than those at lower wavelengths [16].

For styrene-methyl methacrylate random copolymers, despite the absence of any absorption above 2500 Å due to methyl methacrylate units, the optical densities at 2695 Å are not a linear function of the chromophore units.

Furthermore the hypochromism is not centered around a fixed copolymer composition, but moves about as a function of the solvent employed.

With our results it is possible to correlate the solvent effects on the hypochromism to their dielectric constants. A plot of the copolymer composition causing the maximum hypochromism as a function of the solvent dielectric constant is given in Fig. 4.

A linear dependence is evident. The intercept corresponding to ϵ_{Diel} equal to 1 (no interactions of the solvent) gives the copolymer composition truly responsible of the maximum hypochromism; i.e., the number of methyl methacrylate groups which do affect the UV absorption of styrene units at 2695 Å. Solvents only reduce the above interactions as their dielectric constants become higher.

These results suggest that the hypochromic effect is mainly due to electronic interactions between the ester group and the phenyl ring. A more detailed analysis of comonomer unit effects in terms of sequence length distribution will be given in Part II [16].

TABLE 3. Maximum Percent Hypochromism as a Function of Solvent

Solvent	Dichloroethane	Tetrachloroethane	Tetrahydrofuran	Chloroform	Dioxane
% Hypo- chromism	27.9 ± 1.3	24.8 ± 1.2	24 ± 1.2	19.2 ± 1.3	15.5 ± 1.3

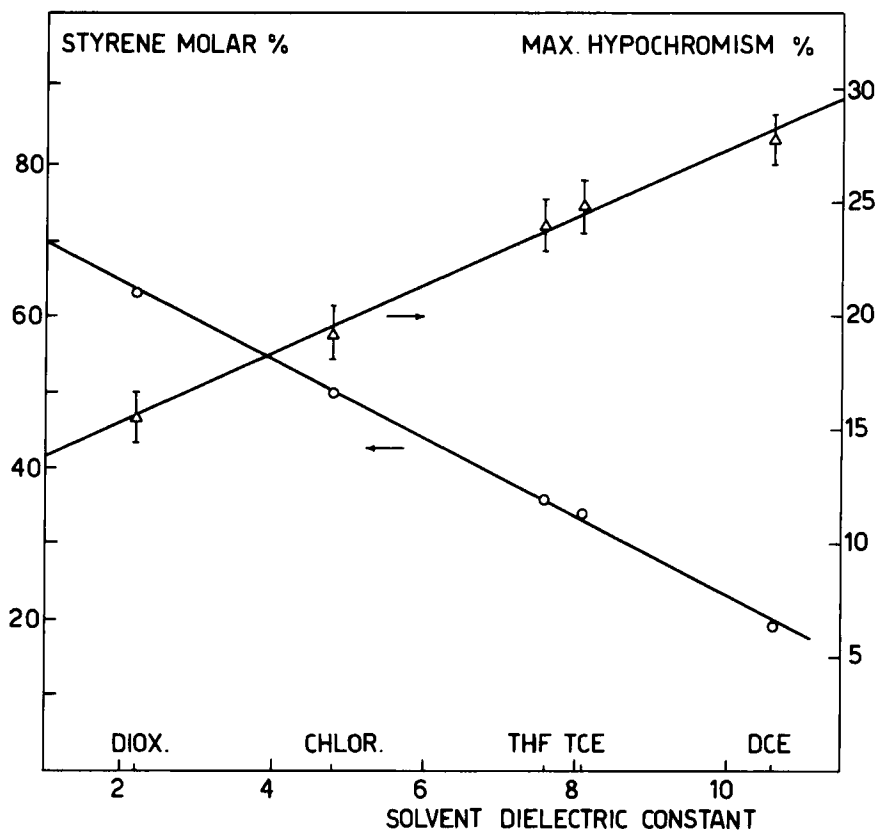


FIG. 4. Copolymer composition responsible of the maximum hypochromism (left) and maximum percent hypochromism (right) as functions of the solvent dielectric constant.

Also, the maximum percent hypochromism is a linear function of the solvent dielectric constant, as indicated in Fig. 4.

The extrapolation to $\epsilon_{\text{Diel}} = 1$ gives a maximum percent hypochromism of about 14%, due to about 30 mole % of methyl methacrylate units in the copolymer.

CONCLUSIONS

Through the proper choice of suitable solvent it is possible, in principle, to evaluate the composition of styrene-methyl methacrylate random copolymers in a composition range where there is no

hypochromic effect, i.e., where the calibration curves based on polystyrene are valid. Solvents such as sym-dichloroethane, characterized by relatively high dielectric constants, seem preferable for this purpose because the hypochromism is confined to copolymers with low styrene content.

A careful choice of solvent, therefore, can overcome criticism on the use of a UV spectrometer as a second detector for GPC analyses of styrene copolymers.

When the hypochromic effect is disregarded, the UV data give a styrene content which is lower than the true one, with a maximum difference well beyond experimental errors, ranging from -7.5% (dichloroethane) to -11.5% (chloroform) as a function of the solvent.

This seems to be the reason for the discrepancies in the composition values of styrene-methyl methacrylate random copolymers obtained by Gruber and Elias [5] from UV data in chloroform as compared to values from IR, NMR, and dn/dc .

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