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Ultraviolet Absorption Spectra of Styrene Copolymers. II. Studies on Model Compounds

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ABSTRACT

The hypochromism of styrene-methyl methacrylate random copolymers at 269.5 nm is attributed to strong interactions between the carbonyl groups of the ester and the phenyl rings. Support to this correlation is provided by model studies. Namely, the effect of several esters and other carbonylic solvents on the extinction coefficients of ethylbenzene and atactic polystyrene confirms the nature of the hypochromism. In order to eliminate the hypochromism of S-MMA copolymers, ester-type solvents are proposed. Indeed, when such solvents are used, a linear correlation between optical density at 269.5 nm and polystyrene content in the copolymers is found. Implications in gel permeation chromatography analysis are discussed.

INTRODUCTION

For styrene random copolymers the UV absorption band centered around 260 nm, corresponding to the symmetry forbidden transition ^1L_b of the phenyl ring, is frequently used for evaluating the styrene content [1-7]. Unfortunately, the extinction coefficient ϵ of the band maximum generally depends not only on the total concentration of the chromophores (i.e., on copolymer composition), but also on the sequence length distribution [8, 9]. Therefore, it is not usually possible to evaluate the composition from the simple determination of ϵ. On these grounds, the results obtained by dual detector-gel permeation chromatography (GPC), when an auxiliary UV spectrometer for determining the copolymer composition was used [6], have been strongly criticized [9, 10].

In the case of styrene-methyl methacrylate (S-MMA) random copolymers, a marked hypochromism with respect to atactic polystyrene can be observed [8, 11, 12] at 269.5 nm (a peak which is part of the fine vibrational structure of the secondary band).

As we have already reported [11, 12] the hypochromism of S-MMA copolymers seems to originate from quite different causes as compared to the well-known conformational hypochromism of isotactic polystyrene [10, 13, 14]. On the basis of experimental evidence, it is likely that the mutual disposition of phenyl rings (determining the hypochromism of isotactic polystyrene [15]) only plays a secondary role in the hypochromism of S-MMA copolymers. This effect seems rather to be produced by specific interactions between methyl methacrylate mers and styrene units.

The present study accounts for the physical origin of the hypochromism. For this purpose, solvents containing carbonyl groups and low molecular weight models were used. Indeed, we have investigated in detail the spectroscopic properties of atactic polystyrene, S-MMA random copolymers, and ethylbenzene (the model compound) with several esters as solvents. The results of these studies and their implications in GPC are discussed in the following.

EXPERIMENTAL

Materials

Synthesis, purification, and characterization of polystyrene and S-MMA copolymers have been described [11, 12].

The solvents used were purified with the usual techniques.

UV Spectrophotometry

A Zeiss single-beam spectrophotometer was used in this study. The cell compartment was carefully thermostated at 25°C during the measurements. All solutions were prepared with solute concentrations not higher than 10^{-2} mol/L. The molar extinction coefficients were determined at the wavelength corresponding to the absorption maximum for the peak centered around 269.5 nm.

TABLE 1. Molar Extinction Coefficients at 269.5 nm of Atactic Polystyrene in Esters and in Some Reference Solvents

Solvent	ϵ_{max} (L/mol·cm)
Methyl acetate	140
Propyl acetate	142
Isopropyl acetate	139
Butyl acetate	152
Isobutyl acetate	157
Amyl acetate	146
Isoamyl acetate	145
Butyl formate	140
Ethyl propionate	140
Dioxane [11, 12]	185
Chloroform [11, 12]	186
Tetrahydrofuran [11, 12]	175
Dichloroethane [11, 12]	185
Tetrachloroethane [11, 12]	192

RESULTS AND DISCUSSION

The optical densities of atactic polystyrene samples in ester-type solvents have been measured between 260 and 280 nm. The band maximum has always been found at 269.5 nm. In Table 1, ϵ_{max}, the molar extinction coefficient at λ_{max}, is given. The extinction coefficients in dioxane, chloroform, tetrahydrofuran, dichloroethane, and tetrachloroethane [11, 12] are quoted as references. As it can be seen, a sharp decrease of ϵ_{max} is present when an ester is used as solvent. The extent of the hypochromism is close to the values found for S-MMA random copolymers in various solvents [11, 12] (Table 2). This analogy suggests that the presence of an ester group in the close vicinity of the phenyl rings, either on the same macromolecule or as the solvating medium, very strongly affects the absorption intensity at 269.5 nm, causing a marked decrease of the extinction coefficient.

In order to elucidate the nature of this effect, the behavior of a model compound (ethylbenzene) in several solvents containing carbonyl groups has been investigated. Esters, aldehydes, acids, ketones,

TABLE 2. Maximum Hypochromism at 269.5 nm and Corresponding Compositions of S-MMA Random Copolymers

Solvent	Maximum hypochromism (%)	Styrene content in copolymer (mol%)
Dioxane	15.5	63
Chloroform	19.2	50
Tetrahydrofuran	24.0	36
Tetrachloroethane	24.8	34
Dichloroethane	27.9	19

acyl halides, and amides were used. In Table 3 the results of this study are quoted together with the values of ϵ_{max} for ethylbenzene in the last five solvents listed in Table 1. It can be seen that, for ethylbenzene, the hypochromic effect caused by an ester-type solvent is even greater than for polystyrene; clearly, when phenyl rings are part of a small molecule, they are available to interact with ester groups to a higher extent. Furthermore, from the data reported in Table 3, three remarkable aspects can be noticed: 1) not only esters but almost any carbonylic solvent gives rise to a marked decrease of the absorption intensity of the phenyl ring at 269.5 nm. 2) The specific structure of the carbonylic solvent does not appreciably affect ϵ_{max}. This is particularly evident for the ester series. 3) With the exception of acetyl chloride, the hypochromism seems to be related to the dipolar moment of the carbonyl group of the solvent. Indeed, it can be seen from Table 3 that the absorption intensity at 269.5 nm decreases in the solvent order

$$RCOCl > R'R''CO \simeq R'CONR''R''' > RCHO > R'COOR''$$

while the dipolar moment of the carbonyl group, deduced from reactivity data of the functional derivatives of carboxylic acids in the alkaline hydrolysis and from IR spectroscopic data, increases in the order

$$R'CONR''R''' < R'R''CO < RCHO < RCOOH < R'COOR'' < RCOCl$$

These observations suggest that hypochromism of ethylbenzene in carbonylic solvents is mainly due to specific interactions between carbonyl groups and aromatic rings. To the extent to which it is possible to admit that similar effects can take place in macromolecules

TABLE 3. Molar Extinction Coefficients at 269.5 nm of Ethylbenzene in Several Carbonylic Solvents and in Some Reference Solvents

Solvent	ϵ_{max} (L/mol·cm)
Methyl acetate	107
n-Butyl acetate	126
Isobutyl acetate	122
Isoamil acetate	108
Ethyl propionate	105
Propionic acid	122
Butyraldehyde	146
Dimethylformamide	157
N,N-Dimethylacetamide	175
Methyl ethyl ketone	158
Cyclohexanone	170
4-Heptanone	183
Acetyl chloride	197
Dioxane	193
Chloroform	185
Tetrahydrofuran	169
Tetrachloroethane	178
Dichloroethane	175

by intra- or intermolecular means, the observed spectral perturbations for S-MMA copolymers can also be ascribed to interactions between the carbonyl group of methyl methacrylate units and the phenyl ring.

On the basis of this hypothesis, no deviation from a linear relationship between optical density and styrene content is to be expected for S-MMA random copolymers when an ester is used as the solvent. Indeed, this behavior has been experimentally found, as shown in Fig. 1. In fact, the hypochromism of such copolymers can be basically regarded as a measure of the total amount (and intensity) of intra- and intermolecular interactions between the carbonyl group of methyl methacrylate mers and phenyl rings. The entity of these interactions, changing with the copolymer composition, gives rise to deviations from the linear dependence of optical density on styrene content. When an ester is used as solvent, it can be assumed that the phenyl rings are not engaged (but only to a minor extent) in interactions with the

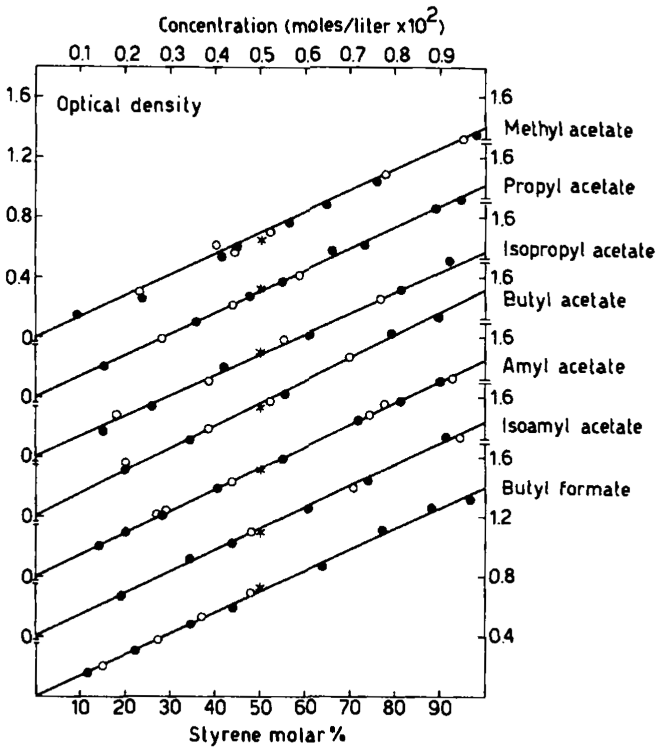

FIG. 1. Optical density vs styrene content in several ester-type solvents: (○) PS, (●) S-MMA random copolymers, (*) S-MMA alternating polymers.

carbonyl groups of the methyl methacrylate units because of the more favorable interactions with the carbonyls of the solvent. Concentration and conformational effects maximize these interactions, thus keeping constant ϵ_{max} as shown in Fig. 1. As an obvious consequence, no difference can be found in the extinction coefficients of polystyrene and random and alternating S-MMA copolymers when ester-type solvents are used.

CONCLUSIONS

Although the hypochromism of S-MMA copolymers is probably the result of several individual superimposed effects, the data reported in this work, on the whole, point out that the most important factor determining such phenomena consists of intra- and intermolecular interactions between carbonylic groups and phenyl rings. The global relevance of this effect is linked to both the number (governed by the copolymer sequence distribution) and intensity (affected by the dielectric constant of the solvent) of interactions. When the global effect reaches its maximum (random or alternating copolymers in ester-type solvents), the relationship between optical density and styrene content becomes linear. This means that in these solvents the styrene content of S-MMA copolymers can be directly calculated by applying Lambert-Beer's law. Implications in GPC analysis are evident.

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