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Spectrophotometric determination of the styrene content of alpha-methylstyrene – styrene copolymers

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Summary

The electronic absorption spectra of polystyrene and poly(alpha-methylstyrene) show a great difference in the extinction coefficient values at 226nm. On basis of this fact, it is shown that the styrene content of styrene - alpha-methylstyrene copolymers can be determined by ultraviolet spectrophotometry. The relationship between the extinction coefficient at 226nm and the polystyrene content in the mixture shows a linear dependence.

Introduction

The ultraviolet spectroscopy of styrene copolymers has been studied by several authors, who have concluded that the UV extinction coefficient depends not only on the population of the units able to absorb but also, in some cases, on the sequence length of copolymer chains. For example, copolymers derived from styrene and methyl methacrylate, (1-3) styrene and vinylpyridine, (4-5) styrene and butadiene (6) and others present a hypochromic or hyperchromic effect in their electronic absorption spectra when compared to the spectra of physical blends of the homopolymers.

This behavior is more pronounced in alternating copolymers and has been observed mainly when the two constituent monomers differ in their chemical nature or when one of the monomers is substituted in the ortho position relative to the main chain. Statistical copolymers of styrene and p- or m-substituted styrene, (7-8) do not show this phenomena.

Spectrometric studies involving styrene - alpha-methylstyrene copolymers have not been made, but we believe that the differences in the UV extinction coefficient with the sequence length of the chains are not so important because of the similarity in their chemical structure.

In this paper we would like to report an application of this method in determination of the composition of styrene - alpha-methylstyrene copolymers.

Experimental

Materials

Polystyrene, poly(alpha-methylstyrene) and styrene - alpha-methylstyrene copolymers were synthesized in liquid sulfur dioxide with m-chloroperbenzoic acid as initiator according to the method previously described. (9)

Dichloromethane used in UV absorption measurements were purified by refluxing it over fumming sulfuric acid (30% SO_3) and then distilled.

Measurements

The UV measurements were carried out on a Varian,Cary 17 Spectrometer, in the wavelength range of 200-400nm, using quartz cells, 10 mm long. The concentrations of styrene monomer units in solution changed from 5×10^{-3} to 1.0×10^{-4} mol/l. The extinction coefficients are given in l/(mol-styrene unit)cm.

The NMR spectra were obtained on a Varian, CFT-20 Spectrometer. The polymers were dissolved in carbontetrachloride, using dioxane as internal reference.

Results and Discussion

The UV absorption spectra of polystyrene, poly(alpha-methylstyrene) and some physical blends of these homopolymers are shown in Fig. 1. A notable change can be observed in the extinction coefficient at 226nm with increasing poly(alpha-methylstyrene) content in the mixture. The absorptions in the wavelength range of 240-300nm, normally used in polystyrene analysis, did not show significant variation, as exhibited by the data in Table 1. The strong hyperchromic effect observed in poly(alpha-methylstyrene) samples can be attributed to the high syndiotacticity of the polymer chain. This stereoregularity favors the corresponding transition. Thus, we have decided to employ the absorption at 226nm to study the relationship between extinction coefficient and polystyrene concentration in the mixture. We would like to emphasize that the Lambert-Beer law was obeyed by every solution. A plot of the extinction coefficient values at 226nm as a function of polystyrene content in the mixture is given in Fig. 2.

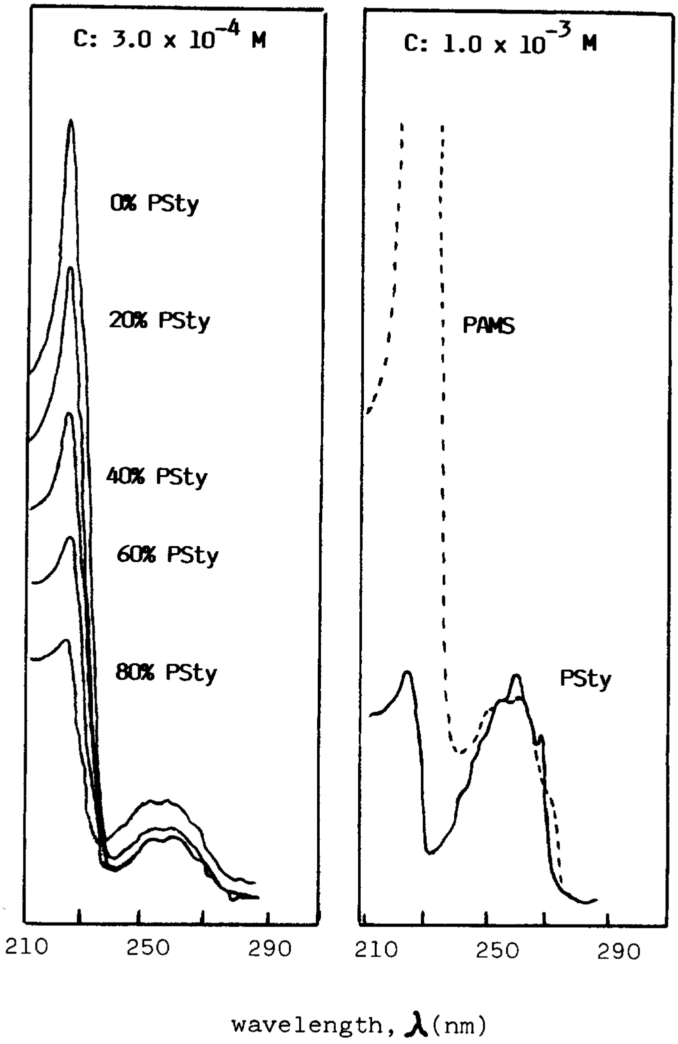

Figure 1. UV absorption spectra of polystyrene(PSty), poly (alpha-methylstyrene) (PAMS) and physical blends of these homopolymers (on the left). The polystyrene contents in the mixture and the concentrations of Sty monomer units in solutions are indicated.

In order to test this analytical method, some copolymers with the composition previously determined by NMR, were also analyzed by UV spectrophotometry. The results shown in Table 2 are considered to be in agreement by taking into account the error in delimiting the area of the aliphatic proton peaks in the NMR spectra.

TABLE 1

Wavelength λ and extinction coefficient ε at peak positions of physical blends of polystyrene and poly(alpha-methylstyrene) homopolymers

PSty contents in the mixture (%)	ε (l.mol^{-1}.cm^{-1}) at λ_{max}:				
	269nm	261.2nm	258nm	254.5nm	226nm
0	140	205	202	210	2940
20	148	208	230	210	2307
40	151	210	208	190	1820
50	155	210	210	185	1660
60	155	210	208	190	1400
80	160	220	210	195	900
100	162	218	215	190	210

TABLE 2

Chemical composition of some styrene - alpha-methylstyrene copolymers determined by UV and NMR spectrometry

sample	Sty mole fraction in the copolymer	
	UV (%)	NMR (%)
B-103 F3	25	22
B-124	65	62
B-102 F6	78	75
B-103	63	60
B-102 F3	58	60
B-121 F8	56	59
B-121 F7	42	40

Some other results concerning to the application of this method in random copolymers synthesized by free radical mechanism, as well as the effect of solvent polarity used in UV measurements on the extinction coefficient will be reported in

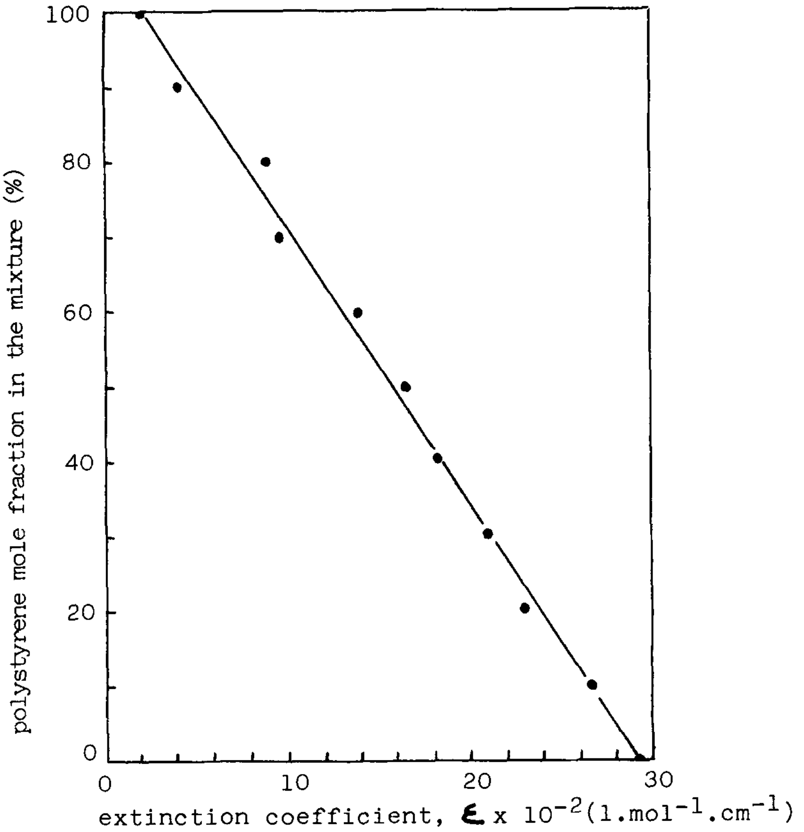

Figure 2. Plot of extinction coefficient at λ_{max}: 226nm against the polystyrene molar fractions in physical blends of polystyrene and poly(alpha-methylstyrene)homopolymers

a subsequent paper.

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References

1. O'Driscoll,K.F., Wertz,W., Husar,A., J. Polym. Sci., Part A-1, 2159 (1967)
2. Gallo,B.M., Russo,S., J. Macromol. Sci.-Chem., A8, 521, (1974)
3. Stutzel,B., Miyamoto,T., Cantow,H.J., Polym. J., 8, 247, (1976)
4. Noel,C., Monnerie,L., C. R. Acad. Sc. Paris, Groupe 7, t-260, 5270 (1965)
5. Schneider,C., Noel,C., Monnerie,L., C. R. Acad. Sc. Paris, serie C, t-265, 703 (1967)
6. Meehan,E.J., J. Polym. Sci., 1, 175 (1946)
7. Phillips,B.D., Hanlon,T.L., Tobolsky,A.V., J. Polym. Sci., Part A-2, 4231 (1964)
8. Noel,C., Monnerie,L., Polym. J., 8, 319, (1976)
9. Soares,B.G., Gomes,A.S., J. Polym. Sci., Polym. Chem. Ed., 25, 1105 (1987)

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