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Syntheses and Characterization of Various Polyisobutylene-Polystyrene Copolymers

2. Refractive Indices and UV-Spectra of Tri- and H-Block Copolymers

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SUMMARY

The overall compositions of various polystyrene PSt polyisobutylene PIB block copolymers and blends of homopolymers have been investigated by a variety of techniques. While ^{1}H NMR and IR spectroscopies gave reliable data, the UV/RI dual detector GPC method and static UV absorption method were found to be unsuitable for composition analysis of these block copolymers. The discrepancy in composition determination is due to strong hyperchromism exhibited by these novel block copolymers. The block copolymers showed significant absorption in the 280-350 nm range and their UV absorbances were much larger over the whole absorption region than those of blends of homopolymers with similar composition. In the absence of independent supporting data, e.g., NMR or IR spectroscopy, both the GPC method and UV spectroscopy yield unreliable high PSt content data. Hyperchromism of low molecular weight PSt-PIB block copolymers in solution may be due to a significant interpenetration of the PSt and PIB domains.

INTRODUCTION

According to Runyon et al.(1), UV-RI dual detector GPC could be used to calculate "point-by-point" composition of binary polymer systems. Subsequently, various authors (2-4) have used this method to determine point-by-point and overall compositions of styrene-containing polymers. However, this method of composition analysis has been strongly criticized by German authors (5,6), on account of peculiarities in the UV absorption spectra (hypo- and hyperchromism).

Hypochromism of polystyrene PSt solutions has been extensively studied (6,7-9). The extinction coefficient of PSt is affected by temperature, solvent and microstructure. Hypochromism was explained by assuming conformational changes of the PSt chain, specifically of phenyl rings.

In regard to copolymers, Harmon and Folt (2) obtained satisfactory PSt content data by the use of GPC for styrene-butadiene copolymers (SBR Ameripol Type 1502) and for blends of SBR with cis-1,4-polybutadiene. In contrast, Brüssau and Stein (5) found that the extinction coefficients of random styrene-butadiene copolymers were unexpectedly large (hyperchromism). Hypochromism of styrene-acrylnitrile copolymers (5) and styrene-

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methyl methacrylate copolymers (6, 10-12) has also been observed. By disregarding the hypochromic effect, the styrene content determined by UV spectroscopy is lower than the actual one. Recent observations on the hypochromic effect of various esters and other carbonyl group-containing solvents suggest that in styrene-methyl methacrylate copolymers hypochromism is due to intra- and intermolecular interactions between carbonyl groups and phenyl rings (13). It has been generally accepted that the UV extinction coefficient of copolymers is determined not only by the overall concentration of the chromophores (i.e., on copolymer composition), but also by the sequence length distribution (5,6); therefore, great care has to be exercised when determining the overall composition of UV chromophore-containing copolymers and composition information should not be generated by a simple UV extinction coefficient determination.

Of particular importance for this research is conflicting evidence in regard to block copolymers. Although Runyon et al. have used UV-RI dual detector GPC to obtain the composition of styrene-butadiene block copolymers, and this method has also been used to determine the compositions of styrene-isoprene (3) and styrene-methyl methacrylate (4) block copolymers, the presence of strong hyperchromism in a styrene-butadiene block copolymer observed by Brüssau and Stein (5) may invalidate these conclusions.

This paper concerns solution optical properties of the new styrene-isobutylene block copolymers (whose synthesis is the subject of the preceding communication (14)).

EXPERIMENTAL

Materials - Solvents were dried by refluxing over CaH_2 overnight and distilled. Synthesis, purification and characterization of styrene-isobutylene tri- and H-block copolymers P-1, P-2 and P-3, and their parent homopolymers PIB-1, PIB-2 and PSt_{800} have been described (14). Two additional standard PSt samples ($\bar{M}_n$=192,000 and 37,000) were also used in GPC experiments.

Measurements - A Waters Associates high pressure GPC instrument equipped with UV (at 254 nm) and RI detectors (THF as solvent), Perkin-Elmer 521 Grating Infrared Spectrophotometer (0.5 mm KBr cells, 2.5 wt % CCl_4 solution), Laser Differential Refractometer (Chromatrix KMX-16, 6330Å), Brice Phoenix Differential Refractometer (4358Å and 5461Å) and Perkin-Elmer 559 A UV/VIS Spectrophotometer (1 cm light-path length cells, 1 mg/ml solution) were used. GPC, IR and UV measurements were carried out at room temperature; refractive index increments (dn/dc) were measured at 35°C.

RESULTS AND DISCUSSION

Composition determination of PSt-containing binary polymer systems by the UV-RI dual detector GPC method is based on two assumptions: 1) The refractive index increments are additive and 2) The UV extinction coefficient of the PSt component in the binary system is identical to that of homopolystyrene under the given conditions. If these two conditions are met, the following expressions should hold over the entire PSt composition range:

$$H_{RI_i} = K_{PSt}\, C_{PSt_i} + K_2C_{2_i} \qquad (1)$$

$$H_{UV_i} = kC_{PSt_i} \qquad (2)$$

where H_{RI_i} and H_{UV_i} are the RI and UV responses for the i-th elution count in a GPC experiment; C_{PSt} and C_2 are the weight concentrations of PSt and the second polymer component; and K_{PSt}, K_2 and k are constants. Thus,

$$\left(\frac{H_{RI}}{H_{UV}}\right)_i = \frac{K_{PSt}}{k} + \frac{K_2}{k}\cdot\left(\frac{C_2}{C_{PSt}}\right)_i \qquad (3)$$

at each point along the elution count axis of a GPC experiment. The overall composition can be expressed by:

$$\frac{S_{RI}}{S_{UV}} = \frac{K_{PSt}}{k} + \frac{K_2}{k}\cdot\frac{C_2}{C_{PSt}} \qquad (4)$$

where S_{RI} and S_{UV} are the respective areas of the RI and UV responses. Thus a plot of S_{RI}/S_{UV} versus C_2/C_{PSt} should give a straight line with the intercept K_{PSt}/k and slope K_2/k.

According to our results, S_{RI}/S_{UV} versus C_{PIB}/C_{PSt} plots of a series of physical blends of PIB ($\bar{M}_{n_{PIB-1}}$=38,200, $\bar{M}_{n_{PIB-2}}$= 3,910) and PSt ($\bar{M}_n$=192,000 and 37,000) gave the expected linear correlation (Figure 1). Interestingly, however, the slope of this line is quite different from that obtained with our P-1 and P-2 triblock and P-3 penta (or H) block copolymers; the overall compositions of the latters were determined by ^{1}H NMR spectroscopy (14). As illustrated by the data in Table 1, the overall compositions obtained by ^{1}H NMR spectroscopy were independently confirmed by IR spectroscopy, however, those obtained by the GPC "calibration" plot constructed with a series of PIB/PSt blends gave unreasonably high PSt contents, i.e., do not accurately reflect the overall composition of these block copolymers.

The question immediately arises: What is the reason that GPC (i.e., UV plus RI) cannot be used to calculate the overall composition of PIB-PSt block copolymers?

First, we examined the operational validity of the first assumption, i.e., the additivity of the refractive index increments dn/dc. Table 2 shows dn/dc data of the block copolymers together with the parent homopolymers in three different solvents. It can be seen that the data of the block copolymers in toluene and CCl_4 follow ideal linearity, whereas in THF the data are slightly higher than expected. However, this deviation does not explain the composition discrepancies obtained by ^{1}H NMR and GPC (see Table 1).

Evidently, then, the observed discrepancy must be due to some unexpected UV absorption phenomenon of PSt-PIB block copolymers. Figure 2 shows representative UV spectra in THF of

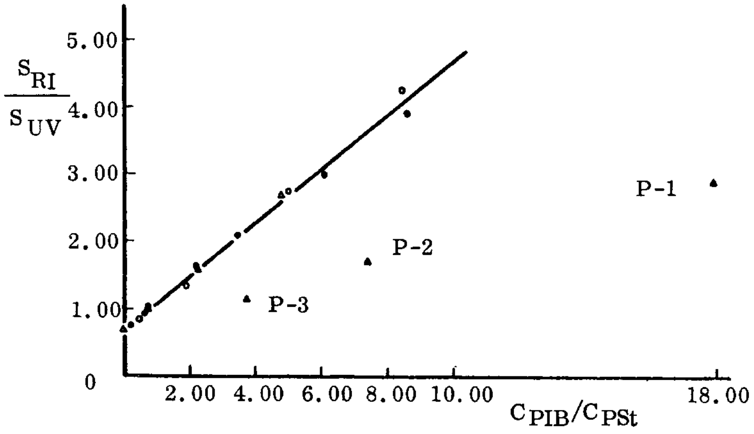


Fig. 1. A plot of S_{RI}/S_{UV} versus C_{PIB}/C_{PSt}
○ PIB-1/PSt$_{192,000}$ ● PIB-2/PSt$_{192,000}$
▲ PIB-1/PSt$_{37,000}$

TABLE 1

Composition of Block Copolymer Determined by by ^{1}H NMR, IR and GPC

Sample	PSt (wt %) content		
	^{1}H NMR	IR*	GPC
P-1 triblock	5.3	5.8	15.6
P-2 triblock	11.9	14.9	28.2
P-3 H-block	21.2	23.8	45.5

*Calculated average values from absorbance at 1380 and 3080 Å according to the equations: $A_{1380}=0.100 + 0.950$ (1-PS %); $A_{3080}=0.050 + 0.385$ PS %.

our block copolymers plus a PSt/PIB-1 blend containing 18.8 wt% PSt, i.e., in the range of the block copolymers. Significantly, the blend does not absorb above 280 nm whereas the block copolymers exhibit noticeable absorptions up to ∿350 nm and the UV absorptions of the block copolymers are higher over the whole scan region than that of a similar blend. Figure 3 further illustrates this hyperchromic phenomenon.

Similar observations have been made by the use of $CHCl_3$ and CCl_4 solvents. Figure 4 shows the data for the triblock copolymer P-2 (the scan in THF is identical to that shown in Figure 2). While differences in detail (i.e., extent of

TABLE 2

Refractive Index Increment of PIB-PSt Block Copolymers and Respective Homopolymers at 35°C

Sample	Toluene	Carbon Tetrachloride		THF	
	6330Å	4358Å	5461Å	4358Å	5461Å
PIB-1	0.0142	0.0572	0.0578	0.112	0.107
PIB-2	0.0118	0.0563	0.0560	0.113	0.111
PSt_{800}	0.0940	0.142	0.132	0.190	0.184
P-1	0.0228	0.0662	0.0658	0.126	0.126
P-2	0.0225	0.0683	0.0672	0.129	0.127
P-3	0.0310	0.0795	0.0776	0.133	0.131

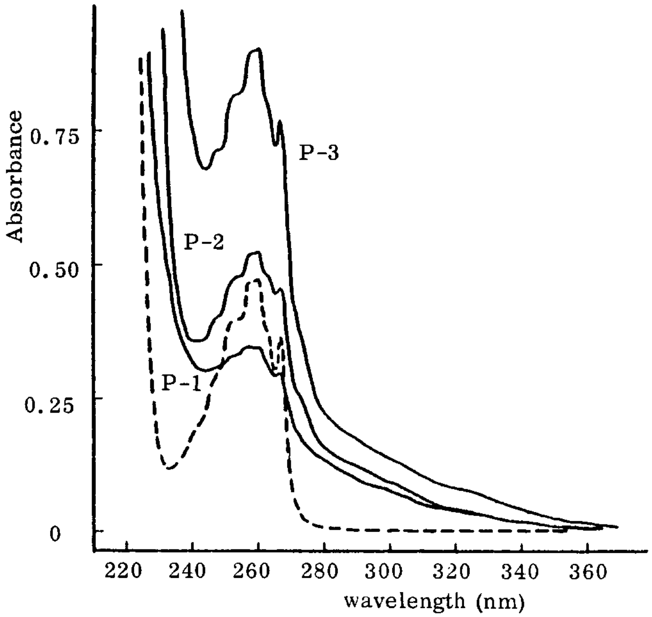


Fig. 2. UV absorption spectra of block copolymers and a blend of homopolymers(dotted line) containing 18.8% PSt

absorbance, overall shape) exist, the presence of significant absorptions in the critical region from 280 to 350 nm is again diagnostic of the hyperchromic effect.

In view of this effect great care must be exercised when determining the overall composition of PSt/PIB block and/or random copolymers by UV spectroscopy; indeed the composition of our PSt/PIB block copolymers in which the PSt was of low molecular weight cannot be determined by UV analysis.

Overall PSt composition data obtained by the use of "calibration" plots constructed with parent PSt/PIB blends at two wavelengths in three solvents (for example, the THF 268 nm plot is shown in Figure 3, and the other five plots were similar), are much higher than those we believe to be correct obtained by ^{1}H NMR spectroscopy (see Table 1 and 3).

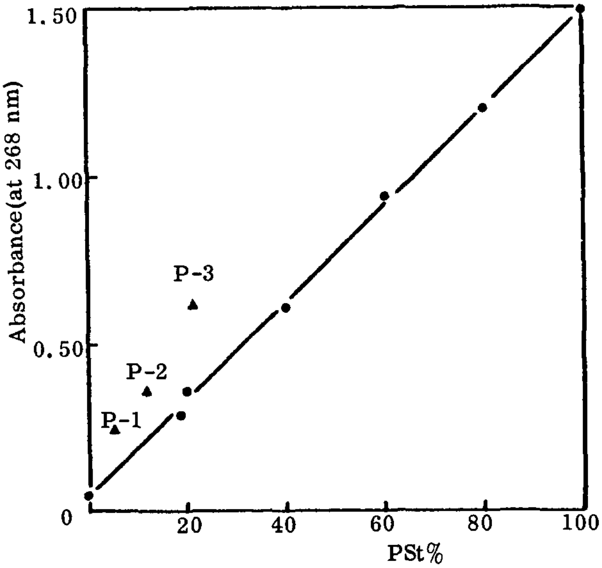
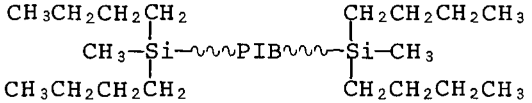


Fig. 3. A plot of UV absorbance versus composition of block copolymers and blends of homopolymers(●) in THF

Clearly, in the absence of independent supporting data, e.g., NMR or IR spectroscopy, UV spectroscopy or UV-RI dual detector GPC will yield unreliable composition data due to the hyperchromism of PSt-PIB tri- and H-block copolymers.

To ascertain that the hyperchromic effect is not an artifact or is caused by the Si atom connecting the PSt and PIB blocks, we have reacted a methyldichlorosilane-telechelic PIB ($\bar{M}_n$=38,200) with n-butyllithium and thus obtained:



$$(CH_3CH_2CH_2CH_2)_2(CH_3)Si\sim\sim\sim PIB\sim\sim\sim Si(CH_3)(CH_2CH_2CH_2CH_3)_2$$

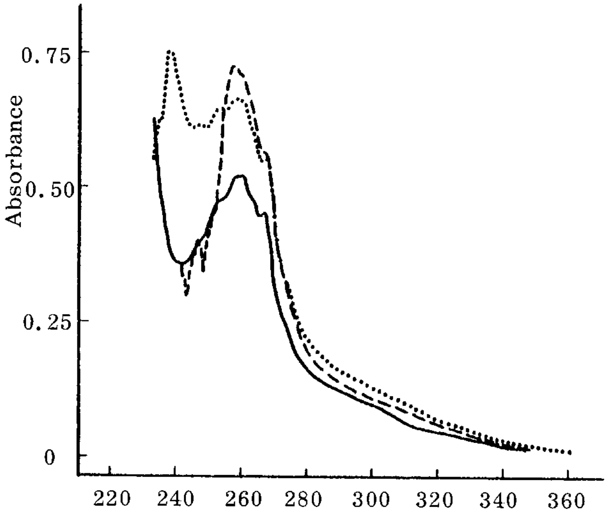


Fig. 4. UV absorption of block copolymer P-2 in THF(——), $CHCl_3$(·······) and CCl_4(– – –)

TABLE 3

PSt wt% of Block Copolymers by UV Absorption Spectroscopy*

Sample	THF		$CHCl_3$		CCl_3	
	260 nm	268 nm	260 nm	268 nm	260 nm	268 nm
P-1	12.0	13.5	14.0	15.5	15.0	14.5
P-2	19.5	21.5	23.0	25.5	25.5	24.5
P-3	35.0	39.5	36.0	40.5	44.0	43.5

*Static UV method using PE instrument (see Experimental).

The UV spectra of this material and its blends with various quantities of PSt did not show hyperchromism.

The discrepancy between the UV absorption spectra of PSt-PIB block copolymers and blends of the parent homopolymers cannot be explained by the model of diblock copolymer chains in dilute solution recently proposed by Tanaka et al.(15). Rather, hyperchromism is probably due to significant interpenetration of PSt and PIB domains in block copolymers, particularly in view of our low molecular weight PSt-PIB tri- and H-block copolymers.

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