

On the Colligative Nature of the Specific Refractive Increment for Statistical Copolymers

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In their theory for light scattering in copolymer solutions, Stockmayer et. al.¹ assume the specific refractive increment, (dn/dc) is a colligative property of the copolymer and independent of molecular weight. The light-scattering investigation of Bushuk and Benoit² and Krause³ on block, graft, and statistical copolymers agree with the light-scattering theory and thus justify this assumption. In addition, Bushuk and Benoit show the mole fraction of each mer in a single high conversion styrene-methyl methacrylate copolymer, as determined from the measured specific refractive increment, is within 2% of that obtained through chemical analysis.

However, a more thorough evaluation of the colligative nature of this property in statistical copolymer systems over a wider range of mer composition has not been reported. The additivity can be critically examined by comparing chemical analysis and specific refractive increment measurements on a series of statistical binary copolymers with a broad compositional range. Moreover, the mer mole fractions in the copolymer, as obtained from the specific refractive increment, can be used to determine the r_1, r_2 values for the copolymer system which can be compared with the r_1, r_2 values obtained through standard chemical analysis or other analytical techniques. For this study, the copolymer system styrene-methyl methacrylate was chosen because the refractive index difference of the two homopolymers is reasonably large and a considerable volume of data for comparative purposes is available.

Experimental

The monomers were washed with aqueous sodium hydroxide, then fractionally distilled; the middle

third of the distillate was retained for polymerization. The monomers were mixed, degassed, and sealed under vacuum into glass ampules. All polymerizations were performed in bulk at 60°C. with benzoyl peroxide as the initiator. Details of the copolymer mixtures are shown in Table I.

TABLE I
Preparation of Polymers

Polymer	M_2 mole fraction styrene	M_1 mole fraction methyl methacrylate	Time polymerized, hr.	Conversion, %
M	0	1.00	2.00	—
MS-2	0.761	0.239	2.25	1.68
MS-3	0.655	0.345	3.25	4.81
MS-5	0.393	0.607	3.00	4.05
MS-6	0.321	0.679	3.00	5.43
MS-8	0.196	0.804	2.00	3.84
S	1.00	0	2.00	—

The resulting low conversion copolymers were precipitated twice, then dried under vacuum at 100°C. to a constant weight. Specific refractive increment measurements were taken with a Brice-Phoenix differential refractometer at $25 \pm 0.1^\circ\text{C}$. The mercury green line (5460 Å.) was used throughout, and the instrument was calibrated to give the relationship $\Delta\eta = 0.978\Delta d$, where Δd is the difference reading on the instrument between solution and solvent and $\Delta\eta$ is the difference in the refractive index.

Results and Discussion

According to Bushuk and Benoit, the specific refractive increment for binary copolymers expressed as a colligative property takes the form:

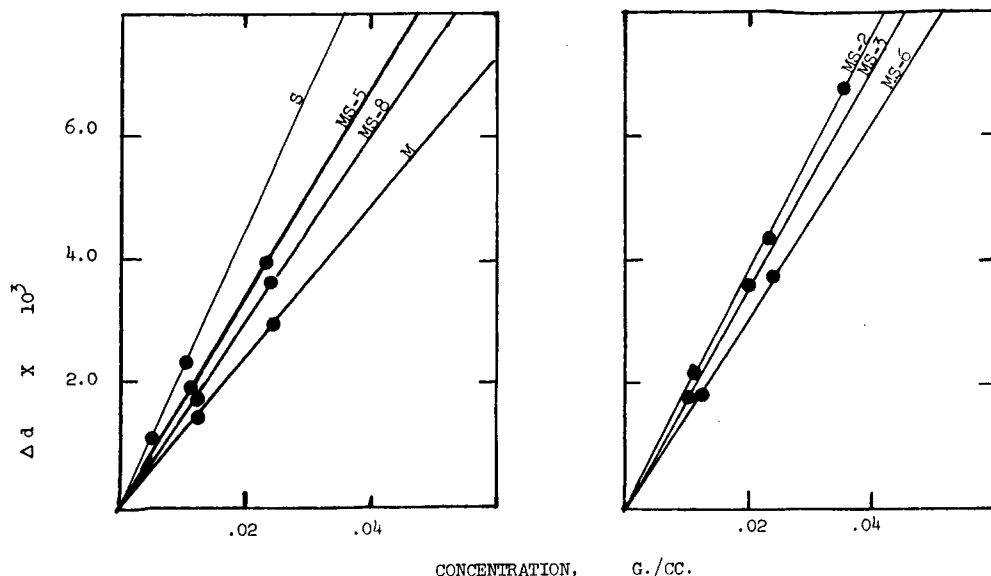


Fig. 1. Methyl methacrylate-styrene copolymers in ethyl acetate.

$$\nu = x_A\nu_A + (1 - x_A)\nu_B \quad (1)$$

where

$$\nu_A = (dn/dc)_A$$

$$\nu_B = (dn/dc)_B$$

$$\nu = (dn/dc)_{AB}$$

and

$$x_A = (c_A/c_A + c_B)$$

x_A being the weight fraction of component A where c is in grams/cubic centimeter and $x_A + x_B = 1$. Thus according to eq. (1), if the specific refractive increment for the two homopolymers is known in a given solvent, the weight fraction of both components can be calculated by determining ν for the copolymer (the equation should be equally useful for mixtures of two homopolymers). The mole fraction can be calculated from the weight fraction through the relationship:

$$M_A = x_A MW_B / (x_A MW_B + x_B MW_A) \quad (2)$$

where MW_A and MW_B are the molecular weights of the two monomers respectively.

The measured specific refractive increments for the homopolymers of methyl methacrylate and styrene and the copolymers in three solvents are shown in Table II. Also included is carbon content as obtained by commercial chemical analysis. A representative plot of Δd versus c is shown in Figure 1, and the mole fraction of styrene and methyl methacrylate in the copolymers as calculated

from eqs. (1) and (2) is given in Table III for the three different solvents and by carbon analysis.

Finally, these data are plotted according to the Ross-Fineman technique in Figure 2 and the r_1, r_2 values evaluated (Table IV). The least-squares

TABLE II
(dn/dc) of Polymers

Polymer	Carbon content, %	dn/dc in various solvents		
		Benzene	Ethyl acetate	Methyl ethyl ketone
M	60.0 (calc.)	0.0098	0.120	0.121
MS-2	81.9	0.0770	0.193	0.215
MS-3	79.3	0.0683	0.178	0.181
MS-5	76.2	0.0554	0.172	0.177
MS-6	71.4	0.1447	0.158	0.161
MS-8	69.3	0.0378	0.149	—
S	92.3 (calc.)	0.1086	0.226	0.250

TABLE III
Mole Fraction of Styrene (M_2) in the Styrene-Methyl Methacrylate Copolymers

	M_2 by chemical analysis	M_2 from dn/dc		
		Benzene	Ethyl acetate	Methyl ethyl ketone
MS-2	0.674	0.672	0.681	0.721
MS-3	0.595	0.582	0.537	0.455
MS-5	0.498	0.452	0.481	0.424
MS-6	0.351	0.344	0.349	0.301
MS-8	0.286	0.274	0.226	—

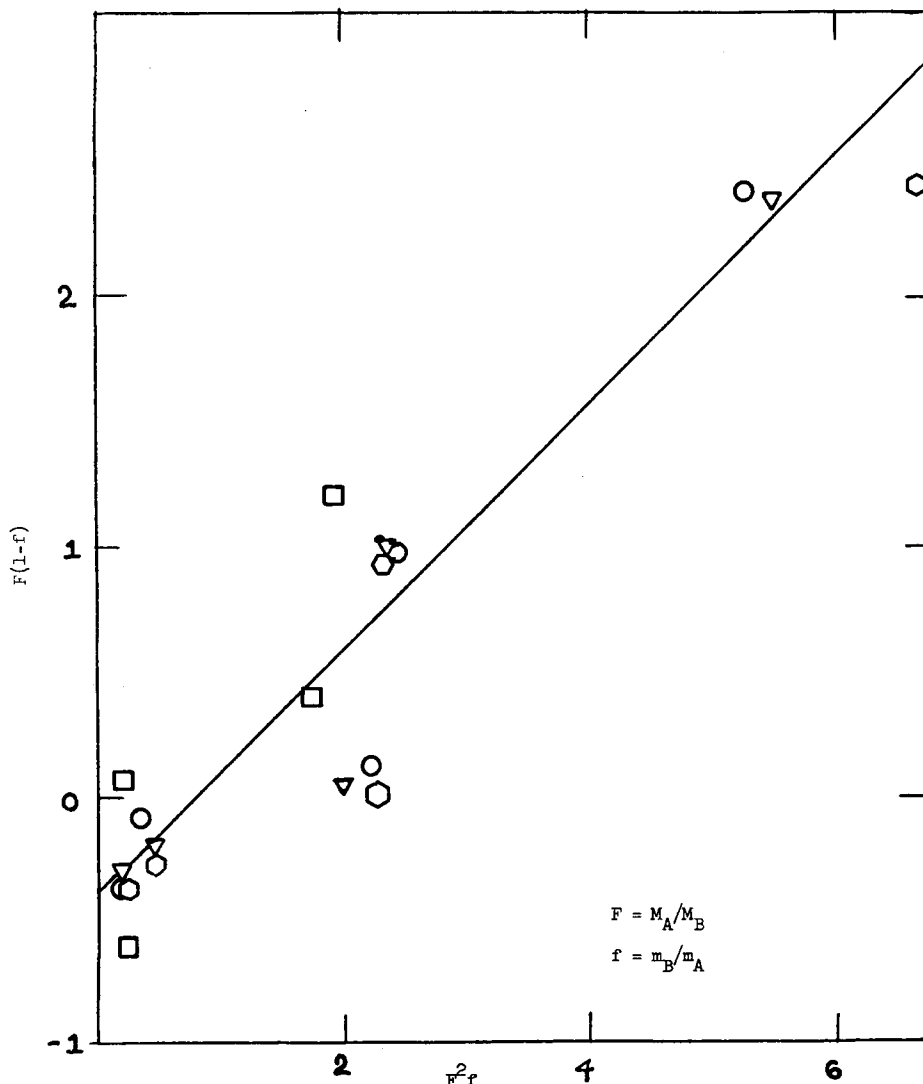


Fig. 2. Ross-Fineman plot for methyl methacrylate-styrene copolymers at 60°C.: *square*, in methyl ethyl ketone; *circle*, in ethyl acetate; *triangle*, in benzene; *hexagon*, by carbon analysis.

values for r_1 and r_2 taken from a combination of all solvent data given an average r_1 of 0.51 and an average r_2 of 0.46. These data are in reasonable agreement with r_1, r_2 values in the literature and that obtained by chemical analysis. The absolute magnitude of the r_1, r_2 values as determined by the refractive increment method are extremely sensitive to the (dn/dc) values for the homopolymers, whereas the scatter in the experimental points is determined by the chemical purity of the copolymers and the precision of the (dn/dc) values. In principle, therefore, the measurement of (dn/dc) for copolymers can be useful for determining the mole fraction of mers in either mixtures of homopolymers or for copolymer systems, and represents

TABLE IV
Reactivity Ratios for Styrene (M_2) and Methyl Methacrylates (M_1) from Ross-Fineman Plot

	r_1	r_2
Benzene	0.53	0.51
Ethyl acetate	0.52	0.49
Methyl ethyl ketone	0.48	0.38
Carbon analysis	0.43	0.41
All solvents (average)	0.51	0.46
Literature ^a	0.46 ± 0.03	0.52 ± 0.03

^aData of Walling et al.⁵

another useful technique for analyzing the composition of binary copolymers.

This technique for determining the composition

of copolymers may be especially useful where chemical or other methods of analysis are somewhat difficult or inaccurate. However, as the refractive indexes of the two homopolymers approach one another, the ability to resolve the specific refractive increment on commercial instruments becomes increasingly difficult. An attempt to analyze a copolymer with isomeric units (methyl acrylate-vinyl acetate copolymers), whose literature r_1, r_2 values show 100% error by a chemical technique, was unsuccessful because of the close approximation of the refractive index of the two homopolymers.

Previously, the colligative nature of the refractive index of films has been used to determine the mole fraction of mers in copolymers.⁴ This technique has limited use however, because of the temperature coefficient of the refractive index and the difficulty of measuring the refractive index of polymer films. In addition, polymers which crystallize at room temperature may be more readily examined in solution by the refractive index increment technique, which is less sensitive to small temperature fluctuations.

References

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Synopsis

The specific refractive increment for statistical copolymers is shown to be colligative in nature for copolymers of styrene-methyl methacrylate thus giving direct evidence to support the assumption of Stockmayer et al. on the theory for light scattering in copolymers. The determination of the mole fraction of mer composition in copolymers by specific refractive increment measurements is shown to be a useful technique and nearly as precise as chemical analysis for carbon. The technique is restricted to soluble systems and is limited by the resolution of the measuring instrument.

Résumé

On montre que l'incrément spécifique de réfraction pour des copolymères statistiques est colligatif pour des copolymères de styrène et de méthacrylate de méthyle, ce qui met directement en évidence l'hypothèse de Stockmayer, concernant la théorie de la diffusion lumineuse dans les copolymères. La détermination de la fraction molaire dans les copolymères par des mesures de cet incrément spécifique de réfraction est une technique utile et presque aussi précise que l'analyse chimique du carbone. La technique est limitée au cas de systèmes solubles et par le pouvoir de résolution des instruments de mesure.

Zusammenfassung

Es wird gezeigt, dass das spezifische Brechungsinkrement statistischer Copolymerer für Copolymere von Styrol und Methylmethacrylat kolligativer Natur ist; das bildet eine direkte Stütze für die von Stockmayer u.a. gemachte Annahme über die Theorie der Lichtstreuung von Copolymeren. Es wird gezeigt, dass die Messung des spezifischen Brechungsinkrements eine zur Bestimmung des Molenbruches der Monomereinheiten in den Copolymeren brauchbare Methode darstellt und fast ebenso genau wie eine chemische Kohlenstoffanalyse ist. Die Methode ist auf lösliche Systeme beschränkt und ihre Genauigkeit durch das Auflösungsvermögen des Messinstrumentes bestimmt.

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