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Dilute Solution Properties of Styrene-N-Butyl Methacrylate (65:35) Copolymer: Short- and Long-Range Interaction of the Polymer Chain

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ABSTRACT

Viscosity and light-scattering data on styrene-*n*-butyl methacrylate (65:35) in chloroform are presented and tested by the two-parameter theoretical relations. The short-range interactions K and A and the long-range interaction parameter B have been calculated by different equations, using intrinsic viscosity and second virial coefficient data. These are then compared to the values of the homopolymer polystyrene. The conformation or the steric factor for the polymer chain has also been calculated. The excluded volume parameter Z , which is related to both the short- and long-range parameters, has been evaluated along with the expansion factor α_η . The higher value of the short-range parameters and the conformation factor compared to the parent styrene homopolymer is attributed to the effect of unlike monomer interactions causing extension of the polymer chain. An increase in the restriction of the internal rotation of side chains about the C-C bonds is also suggested. The excess interaction parameter has a negative value. The expansion factor α_η has been related to the excluded volume

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factor Z and the coefficient C is in close agreement with the theoretically calculated value of Yamakawa and Tanaka.

INTRODUCTION

The properties of polymer solutions may be expressed in terms of two parameters, i.e., mean-square end-to-end distance $\langle r_0^2 \rangle$ of a chain in the theta state and the excluded volume parameter Z . The main problem in the theory of dilute solutions is to relate properties such as average molecular dimensions, second virial coefficients, and intrinsic viscosities with the two parameters. Both radius expansion factor α_s and the viscosity expansion factor α_η are related to the excluded volume factor Z . We have tried to correlate only the viscosity expansion factor α_η with Z . The excluded volume parameter Z is also related to the short- and long-range parameters in the following equations:

$$Z = (B/A^3)M_w^{1/2} \quad (1)$$

$$A^2 = \langle \bar{r}_0^2 \rangle / M_2 = \ell^2 / 6m_s \quad (2)$$

$$B = (1/4\pi)^{3/2} (\beta/m_s^2). \quad (3)$$

A and B represent the short-range and long-range interactions, respectively; M_w is the molecular weight of the polymer; ℓ^2 and m_s are the mean-square length and molecular weight of a segment of the statistical model; β is the binary cluster integral between any pair of segments and vanishes at $T = \theta$; and $\langle r_0^2 \rangle$ is the unperturbed mean-square end-to-end distance. The assumptions of the two-parameter theory have been adequately substantiated by experiments [4-8]. The interactions between chain elements greatly influence the dimensions of long-chain molecules in solution. Interactions between atoms and groups separated by only a small number of valence bonds are termed short-range interactions (A). Constant bond angles and torques that hinder internal rotations are a consequence of the short-range interactions. Interactions between nonbonded groups, which are separated in the basic chain structure by many valence bonds, are termed long-range interactions (B). They are, therefore, similar in nature and magnitude to van der Waals interactions between the parts of two different molecules. The two parameters A and B can be determined experimentally from the molecular weight dependence of the second virial coefficient A_2 [6, 9], the molecular weight dependence of

mean-square radius of gyration [3, 6], and the molecular weight dependence of intrinsic viscosity [3, 7, 9-11].

The two-parameter theory has been successfully extended to copolymer systems [12, 13]. In a binary copolymer there are unlike monomer contacts that are absent in either of the parent homopolymers. Usually the net effect is a repulsive interaction that expands the polymer coil. These repulsive interactions influence both the short- and long-range interactions. We have investigated the dilute solution properties of the random copolymer styrene-n-butyl methacrylate (65:35) as a continuation of a study of solution properties of homopolymers and copolymers. This is part of a series of investigations on copolymers which will include temperature and solvent effects on solution properties.

EXPERIMENTAL

Materials

Poly(styrene-n-butyl methacrylate): Styrene and n-butyl methacrylate monomers were purified and reacted using benzoyl peroxide as the initiator. The reaction was terminated at 10% conversion. The relatively low conversion in the toluene solution with varying amounts of benzoyl peroxide ensured a symmetrical distribution MWD of ~ 2.0 . The dispersity of samples was determined by gel permeation chromatography. All samples had a weight percent composition of polystyrene/n-butyl methacrylate of $65/35 \pm 1\%$ as determined by pyrolysis gas chromatography [24]. All measurements were carried out in chloroform with 1% ethanol preservative (Burdick and Jackson, Muskegon, Michigan).

Light Scattering

The weight-average molecular weights of the polymers were determined by light-scattering measurements using a Sofica (Model 71) light-scattering photometer over the angular range of $30-150^\circ$ with unpolarized light of 4356 \AA . The solvent chloroform and solutions were carefully filtered through a $0.2\text{-}\mu\text{m}$ Alpha Metrical membrane filter (Gelman Instrument Co., Ann Arbor, Michigan). The concentration was varied between $1-0.25 \text{ g/L}$. The refractive index increment (dn/dc) in chloroform was determined with a Brice-Phoenix differential refractometer at 4356 \AA (Phoenix Precision Instruments Co., Philadelphia, Pennsylvania).

Treatment of the Data

Light-scattering data were treated according to Zimm [25]. Plots of Kc/R_θ versus $\sin^2(\theta/2) + 100C$ were made and M_w was calculated

from the reciprocal of the ordinate intercept; the second virial coefficient A_2 was calculated from the slope of the concentration line extrapolated to a zero angle, and the mean square radius of gyration $(\bar{S}^2)_Z$ from the slope of the angular line was extrapolated to zero concentration. The Z average mean-square radius of gyration was converted to $(\bar{S}^2)_w$ according to the relation [26]

$$(\bar{S}^2)_w = (\bar{S}^2)_Z(h + 1)/(h + 2 + \beta) \quad (4)$$

where

$h = [(M_w/M_n) - 1]^{-1}$ in the Schulz-Zimm distribution and

$\beta = (2a - 1)/3$ (where a is the exponent in the Mark-Houwink equation).

The $(\bar{S}^2)_w$ is then converted to (\bar{r}^2) , the root mean-square end-to-end distance, by

$$(\bar{r}^2)_w = (\bar{S}^2)_w(2 + \beta)(3 + \beta) \quad (5)$$

Viscosity

Intrinsic viscosities of the solvent and solutions in the range of 0.25 to 2.0 g/dL were measured at 25°C in chloroform. Cannon-Ubbelohde-type capillary dilution viscometers were used. The viscometer constants ranged from 0.001186 to 0.0383. Measurements were made in a thermostatically controlled bath maintained at 25 ± 0.01°C. All solvents and solutions were filtered before use. The intrinsic viscosity was calculated from the reduced viscosity by means of the Huggins relationship [27]:

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2C \quad (6)$$

Viscosity and light-scattering data are provided in Table 1.

RESULTS AND DISCUSSION

Estimation of K

To evaluate the Mark-Houwink constant K from values of $[\eta]$ and \bar{M}_w , an account must be made of the polydispersity of the samples.

TABLE 1. Styrene-n-Butyl Methacrylate, Molecular Weight, Dispersity, Intrinsic Viscosity, and Mean-Square Radius of Gyration

\bar{M}_w	q_{MH}	Dispersity	$[\eta]$ (dL/g)	$[\eta]/q_{MH}$	Root-mean square radius of gyration $(\bar{S}^2)^{1/2}$ (Å)	Root-mean square end to-end distance $(\bar{r}^2)^{1/2}$ (Å)
24,600	0.89	2.72	0.162	0.181	15.8	30.98
37,300	0.89	2.73	0.226	0.253	56.3	110.28
39,000	0.90	2.60	0.230	0.256	68.6	135.21
66,000	0.91	2.30	0.299	0.328		
95,250	0.91	2.32	0.441	0.485	157.2	314.66
180,000	0.91	2.37	0.623	0.687	177.8	354.83
223,000	0.90	2.50	0.674	0.748	194.6	385.68
225,000	0.90	2.46	0.714	0.791		

For polydisperse samples for which the weight-average molecular weight has been determined, the Mark-Houwink relationship takes the form

$$[\eta]/q_{MH} = K\bar{M}_w^a \quad (7)$$

where q_{MH} is the polydispersity correction factor. If it is assumed that the samples have a logarithmic normal molecular weight distribution, the following relationship can be used [28]:

$$q_{MH} = (\bar{M}_w/\bar{M}_n)^{(a^2 - a)/2} \quad (7a)$$

Approximate values of K and a are first obtained from the uncorrected data. The a and polydispersity values are then used to calculate q_{MH} from Eq. (7a). In all subsequent calculations, the corrected value $[\eta]/q_{MH}$ is used. Values of \bar{M}_w and $[\eta]$ in dL/g and q_{MH} are provided in Table 1 and their relationship can be described as

$$[\eta] = 2.89 \times 10^{-4} \bar{M}_w^{0.634} \quad (8)$$

Figure 1 provides a graphical presentation of the data.

Values for corresponding homopolymers, e.g., polystyrene and *n*-butyl methacrylate [28], respectively, are

$$[\eta] = 1.12 \times 10^{-4} \bar{M}_w^{0.73} \quad (9)$$

and

$$[\eta] = 4.37 \times 10^{-3} \bar{M}_w^{0.80} \quad (10)$$

According to Flory [1], the exponent a in the Mark-Houwink equation must be between 0.5 and 0.8 for linear flexible chains without draining effects. The lower limit is for rather tightly coiled chains in theta solvents and the upper limit for highly swollen polymers in very good solvents. Increasing values of a have also been related to the "stiffness" of the molecules.

The Mark-Houwink equation, as well as others described below, are empirical expressions. To understand the expansion of polymers in solution, measurements must be carried out in a thermodynamically ideal solvent, i.e., a θ solvent. However, as an ideal solvent is not always readily available, the interaction parameters can be obtained from measurements in a nonideal solvent using extrapolation

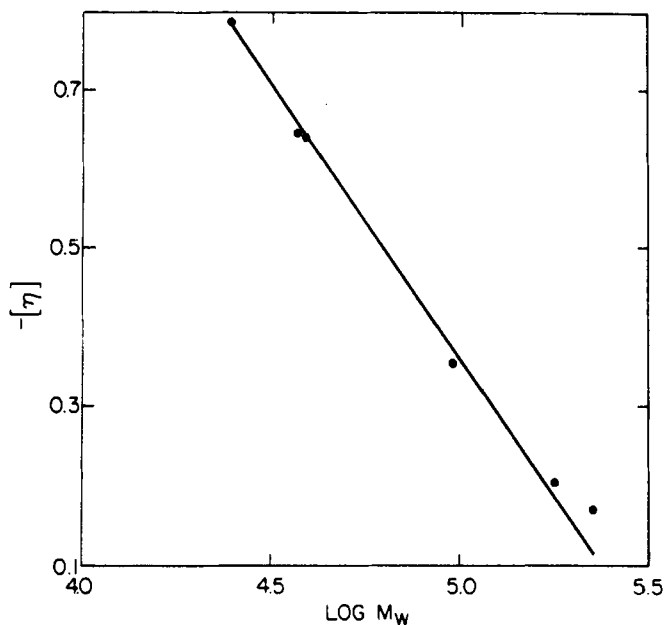


FIGURE 1.

techniques. Several investigators have proposed equations for the estimation of K , B , and A from $[\eta]$ in good solvents. These equations and their application are discussed below.

Fox-Flory [15]

$$[\eta]^{2/3} / M_w^{1/3} = K^{2/3} + 0.857K^{2/3} \phi_0 B M_w [\eta]^{-1} \tag{11}$$

where ϕ_0 = the universal Flory constant, 2.87×10^{21} . Plots of $[\eta]^{2/3} / M_w^{1/3}$ versus $M_w / [\eta]$ were linearly extrapolated, and value of K was calculated from the intercept and that of B from the slope.

Kurata- Stockmayer [3]

This is a modified form of Fox-Flory equation and is applicable to polymers dissolved in good and poor solvents. This equation was derived from the solution theory of Kurata, Stockmayer, and Roig [16]:

$$[\eta]^{2/3} / M_w^{1/3} = K^{2/3} + 0.363 \phi_0 B [g(\alpha_n) M_w^{2/3} / [\eta]^{1/3}] \tag{12}$$

where $g(\alpha_\eta)$ is a coefficient dependent on α_η , the expansion factor.

The $g(\alpha_\eta)$ can be obtained from the following equations:

$$[\eta]_\theta = KM_w^{1/2} \quad (13)$$

$$\alpha_\eta = [\eta]^{1/3} / [\eta]_\theta \quad (14)$$

$$g(\alpha_\eta) = 8\alpha_\eta^3 / (3\alpha_\eta^2 + 1)^{3/2} \quad (15)$$

Thus, from a knowledge of $[\eta]$ for samples of known molecular weights, K and $g(\alpha_\eta)$ can be evaluated. Plots of $[\eta]^{2/3} / M_w^{1/3}$ vs $g(\alpha_\eta)M_w^{2/3} / [\eta]^{1/3}$ provide the value of K from the intercept and that of B from the slope.

Stockmayer-Fixman [17]

A simpler form of equation has been proposed which is widely used:

$$[\eta] / M_w^{1/2} = K + 0.15B\phi_0 M_w^{1/2} \quad (16)$$

This is apparently inadequate at high α_η (exceeding ~ 1.5) and results in a nonlinear plot. The α_η values for our system are around 1.1. Again, a plot of $[\eta] / M_w^{1/2}$ vs $M_w^{1/2}$ provides K from the intercept and B can be calculated from the slope.

Inagaki-Ptitsyn [10, 18]

Inagaki, Suzuki, and Kurata [10] have proposed a viscosity equation based on the Ptitsyn [18] relation:

$$[\eta]^{4/5} / M_w^{2/5} = 0.786K^{4/5} + 0.454K^{2/15} \phi_0^{2/3} B^{2/3} M_w^{1/3} \quad (17)$$

The linear extrapolation of $[\eta]^{4/5} / M_w^{2/5}$ vs $M_w^{1/3}$ provides K from the intercept and B from the slope. Inagaki et al. [10] point out that this relationship provides an accurate value of K for systems for which $\alpha_\eta > 1.4$ and as such is complementary to Eq. (16).

Cowie [19]

$$[\eta] / M_w^{1/2} = K(\phi/\phi_0) + 0.0925(\phi/\phi_0)K(\langle r^2 \rangle / M_w)^{-21/20} B^{7/10} M_w^{7/20} \quad (18)$$

where $\langle r^2 \rangle$ is the mean-square end-to-end distance and ϕ can be obtained using the Ptitsyn-Eizner [20] approximation.

$$\phi = \phi_0(1 - 2.63\epsilon + 2.86\epsilon^2) \text{ dL cm}^{-3} \text{ mol}^{-1} \tag{19}$$

where $\epsilon = (2a - 1)/3$ and a is the exponent of the Mark-Houwink expression.

Values of K obtained from different equations along with their linear regression coefficients are provided in Table 2. Inagaki-Ptitsyn, Fox-Flory, Cowie, and Stockmayer-Fixman equations provide values that are within the experimental error. In all cases, the values of K are larger than those for polystyrene.

Short-Range Parameter A

This parameter can be calculated from the following:

$$A = (K/\phi_0)^{1/3} \tag{20}$$

where K is the constant discussed above and $\phi_0 = 2.87 \times 10^{21}$. Table 3 presents values for this parameter using K values calculated from various expressions.

Kurata et al. [8] have proposed an equation that relates the second virial coefficient A_2 to both the short-range parameter A and the long-range parameter B :

TABLE 2. Values of K Obtained from Different Equations

Equations	$K \times 10^4$	Linear regression coefficient, r^a
Mark-Houwink	2.89	0.90
Kurata-Stockmayer	10.87	0.84
Stockmayer-Fixman	10.07	0.90
Fox-Flory	14.82	0.82
Cowie	11.3	0.91
Inagaki-Ptitsyn	11.22	0.91

$$^a y = a + bx$$

$$\text{Correlation coefficient, } r = \frac{n\sum xy - (\sum x)(\sum y)}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2]}}$$

$$A_2 M_w^{1/2} = 1.65 \times 10^{23} A^3 + 0.968 \times 10^{23} B M_w^{1/2} \quad (21)$$

Thus a plot of $A_2 M_w^{1/2}$ vs $M_w^{1/2}$ provides A from the intercept and B from the slope (see Fig. 2). Berry [7] has proposed a relation that also relates the second virial coefficient to the parameter A:

$$1.42 \times 10^{-24} A_2 M_w^{1/2} = -A^3 + 6A(s^2)_z / M_w \quad (22)$$

A plot of $A_2 M_w^{1/2}$ vs $(s^2)_z / M_w$ provides the value of A from the intercept. The A values in Table 3 are in the range of 1.8 - 9.3×10^{-9} . There is no reported value of this parameter for polystyrene in chloroform. We have found the value of A in toluene to be 6.1×10^{-9} [13].

Unperturbed Dimensions and the Conformation Factor σ

Values of mean-square radius of gyration $(\bar{s}^2)_z^{1/2}$ and the root-mean-square end-to-end distance $(\bar{r}^2)_w$ are provided in Table 1.

The former were obtained from light-scattering measurements, while the latter were calculated using Eqs. (4) and (5). From the log-log plots, the $(\bar{s}^2)_z^{1/2}$ and $(\bar{r}^2)_w^{1/2}$ vs M_w relationships can be expressed as

$$(\bar{s}^2)_z^{1/2} = 1.8 \times 10^{-3} \bar{M}_w^{0.96} \quad (23)$$

$$(\bar{r}^2)_w^{1/2} = 2.99 \times 10^{-3} \bar{M}_w^{0.97} \quad (24)$$

TABLE 3. Values of Short-Range Parameter A and Long-Range Parameter B

Equations	A (cm)	B (cm ³)
Kurata-Stockmayer	7.29×10^{-9}	6.34×10^{-28}
Stockmayer-Fixman	7.05×10^{-9}	9.38×10^{-28}
Kurata et al.	9.3×10^{-9}	5.08×10^{-27}
Cowie	7.33×10^{-9}	4.0×10^{-27}
Fox-Flory	8.02×10^{-9}	4.6×10^{-28}
Inagaki-Ptitsyn	7.31×10^{-9}	2.13×10^{-28}
Berry	1.8×10^{-9}	

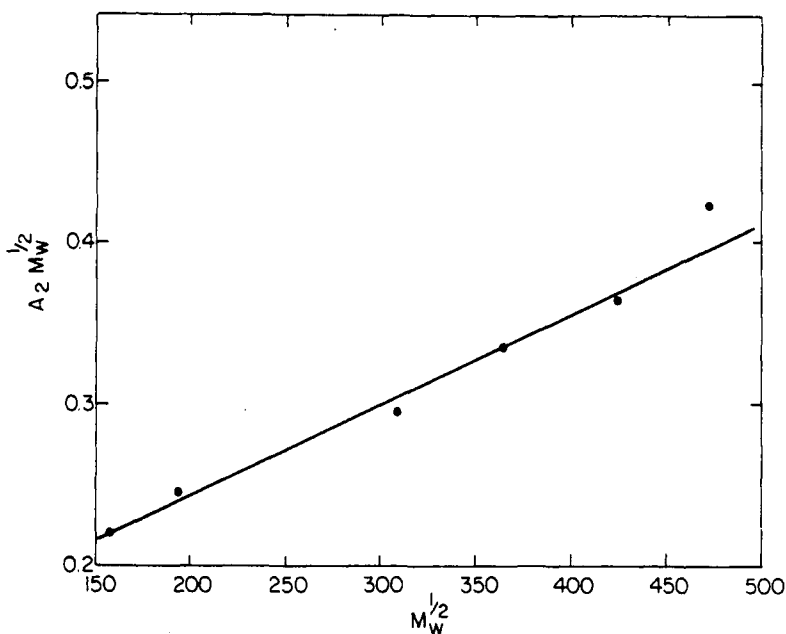


FIGURE 2.

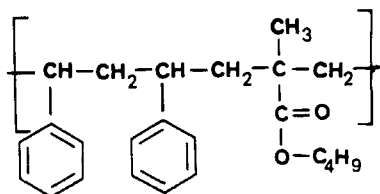
It should be noted that we are relating S_z , the z-average mean-square length to M_w , the weight-average molecular weight. The same polydispersity, therefore, makes the power dependence of M_w less than 1.2 as reported by Miyaki and co-workers [38].

The unperturbed mean-square end-to-end distance of a hypothetical chain $(r_{0f}^2)^{1/2}$ in which the internal rotation about the C-C bond is assumed to be completely free is given by

$$(r_{0f}^2/M) = [\ell^2/m(1 - \cos \theta)/(1 + \cos \theta)]^{1/2} \quad (25)$$

where ℓ is the C-C bond length and θ the valence angle. ℓ and θ are assumed for simplicity to be 1.54×10^{-8} cm and 109.5° , respectively; m = molecular weight of the repeating unit as shown on the following page. The styrene-n-butyl methacrylate copolymer has six C-C bonds in the backbone for the composition used. The mean-square end-to-end distance in the unperturbed state can be calculated from

$$(r_0^{-2}/M)^{1/2} = (K/\phi_0)^{1/3} \quad (26)$$



where $\phi = 2.87 \times 10^{21}$ and $K = 9.95 \times 10^{-4}$. The conformation parameter σ is defined as

$$\sigma = (r_0^{-2}/r_{0f}^{-2})^{1/2} \quad (27)$$

and is a measure of hindrance to internal rotation about the carbon-carbon single bond of the polymer chain. The values of $(r_0^2/M)^{1/2}$ and $(r_{0f}^2/M)^{1/2}$ are 8.47×10^{-9} and 3.55×10^{-9} , respectively. The value for σ , the conformation, or steric factor calculates to be 2.38. The reported value of σ for polystyrene is 2.22 [30] in various solvents. Chinai and co-workers [21-23] have reported σ values for a number of methacrylates and found that this value does not increase monotonically as the side chain varies from methyl to n-lauryl, but passes through a minimum for ethyl or for n-butyl ester. The σ value for n-butyl methacrylate is reported to be 2.09 [23]. The higher value of σ for styrene-n-butyl methacrylate compared to the component monomers suggests increase in the restriction about the C-C bonds.

The Second Virial Coefficient

Values for the second virial coefficient are provided in Table 4. This coefficient is a measure of thermodynamic nonideality of solutions per unit change of mole concentration. The A_2 gets smaller as the M_w increases and their relationship can be represented as

$$A_2 = 2.4 \times 10^{-2} \bar{M}_w^{-0.29} \quad (28)$$

The second virial coefficients were also calculated from the Orofino-Flory equation (Eq. 29)

$$A_2 = (2^{5/2} N \pi / 27 \phi) [[\eta] / M_w] \ln [1 \times (\pi^{1/2} / 2) (\alpha^2 - 1)] \quad (29)$$

where $\phi = 2.27 \times 10^{21}$, N = Avogadro's number, and α is computed from

TABLE 4. The Second Virial Coefficient A_2 . Experimental and Calculated Values

\overline{M}_w	$A_2 \times 10^{-4} \text{ cm}^3 \text{ mol/g}^2$	
	Experimental	Calculated
24,600	14.1	9.8
37,300	12.7	9.0
39,000	11.1	8.8
95,250	9.6	6.9
180,000	8.6	5.1
223,000	7.9	4.5
225,000	7.6	4.4

$$[\eta] = K_{\theta} M_w^{1/2} \alpha^{2.43} \tag{30}$$

There is reasonable agreement between the calculated and experimental values as shown in Table 4.

Long-Range Interaction Parameter B

The parameter B was calculated from viscosity equations of Fox-Flory (Eq. 11), Kurata-Stockmayer (Eq. 12), Stockmayer-Fixman (Eq. 16), Inagaki-Ptitsyn (Eq. 17), and Cowie (Eq. 18). It was also calculated from the second virial coefficient relationship of Kurata et al. (Eq. 21) and Berry (Eq. 22). These values are in the range 5.08×10^{-2} to 2.13×10^{-28} . This parameter for polystyrene in toluene has been reported by us [13] to be 1.21×10^{-28} . Kotaka et al. [12] contend that the estimation of B from the currently proposed theories is unsatisfactory and therefore the significance of these changes should be interpreted with caution.

The Excess Interaction Parameter

Stockmayer et al. [31] suggested that the parameter B for a random binary copolymer may be written as a quadratic function of composition as

$$B = m^2 B_1 + (1 - m)^2 B_2 + 2m(1 - m) B_{12} \tag{31}$$

where B_{12} is a parameter representing the long-range interactions between unlike monomers and m is the molal volume. As a zero-order approximation, the extra interaction term ΔB_{12} can be calculated from the short-range interaction values of styrene (B_1) and *n*-butyl methacrylate (B_2) using

$$\Delta B_{12} = B_{12} - (B_1 + B_2)/2 \quad (32)$$

The ΔB_{12} is supposed to be solvent-dependent through its molal volume (m) and is characteristic of the type of monomer species.

The terms B , B_1 , and B_2 in Eq. (31) were calculated from the viscosity data using the Stockmayer-Fixman equation [16]

$$[\eta]/M^{1/2} = K_0 + 1.55\theta_0' BM^{1/2} \quad (33)$$

The numerical constant 1.55 was chosen to attain agreement with the first-order perturbation theory [32, 33]. The value of θ_0' is related to viscosity according to Pyun and Fixman [34]

$$10^{-21}\theta_0' = 39.4[\eta] \text{ dL/g} \quad (34)$$

The B , B_1 , and B_2 have been found to be 22.7×10^{-30} , 39×10^{-30} , and 32.8×10^{-30} , respectively. The value for polystyrene in chloroform is in close agreement with the value obtained by Kotaka and co-workers [12] in 1-chloro-*n*-butane. The excess interaction term ΔB_{12} has a negative value of 14.8. Reddy and Kalpagam [35] have also reported negative values of ΔB_{12} for the styrene-methyl methacrylate copolymer in dimethylformamide and γ -butyrolactone, which are difficult to explain.

The Excluded Volume Factor Z and the Expansion Factor α_η

The excluded volume factor Z , which is related to both the short-range and long-range parameters A and B (Eq. 1), is a linear function of the molecular weight (Table 5). According to current theoretical treatment, the excluded volume effects on the equilibrium properties of dilute polymer solutions are expected to depend on the parameter Z , provided that the polymer is linear, flexible, and homogeneous both in molecular weight and molecular composition. Additionally, the solvent should be one component and the interaction between

TABLE 5. Values of Expansion Factor α_η and Excluded Volume Factor Z

M_w	α_η	Z
24,600	1.05	0.13
37,300	1.094	0.16
39,000	1.091	0.16
95,250	1.085	0.25
180,000	1.163	0.30
223,000	1.174	0.35

nonbonded segments of polymer should be short ranged and additive pairwise. The expansion factor α_η (Table 5) calculated from Eq. (14) takes into consideration the non-Gaussian character of the chain due to the excluded volume. The average value of α_η for the styrene-n-butyl methacrylate copolymer is 1.19 compared to our reported value of polystyrene as 1.44 [13]. Becerra, Radic, and Gargallo [30] have shown that for various methacrylates derivatives in benzene this factor is influenced by the substituents and, in some cases, by the solvent. They report higher σ (3.37) and lower α_η (1.0) for poly(pentachlorophenyl methacrylate) as compared to the unchlorinated poly(phenyl methacrylate), which has a σ value of 2.73 and an α_η value of 1.29. They conclude that the completely chlorinated phenyl group restricts internal rotation of the side chain about the C-C bond and results in the lowering of α_η and a rise in σ .

The expansion factor α_η has been related to the excluded volume factor Z. The Kurata-Yamakawa theory [32] appears to be quite satisfactory relating α_η to Z in the form $\alpha_\eta^3 = 1 + C_1 Z \dots$. However, experimental data compiled by Yamakawa [36] shows that C_1 varies from 1.05 to 0.87, depending on the value of α_η , as follows:

$$\alpha_\eta^3 = 1 + 1.05Z \text{ for } 0 < \alpha_\eta^3 < 1.6 \quad (35)$$

$$\alpha_\eta^3 = 1 + 0.87Z \text{ for } 0 < \alpha_\eta^3 < 2.5 \quad (36)$$

instead of the C_1 value of 1.55 predicted by the Kurata-Yamakawa theory [32]. Yamakawa and Tanaka [37] have theoretically calculated

the C_1 value to be 1.06, introducing exactly the excluded volume effect in the Zimm-Hearst theory. Our value of C_1 is 1.63 for the styrene-*n*-butyl methacrylate random copolymer, which is closer to the value predicted by Kurata-Yamakawa theory [32].

In summary, the higher value of the short-range parameters K and A and the conformation factor σ , and the lower value of α_η for styrene-*n*-butyl methacrylate copolymer compared to those for the parent styrene homopolymer can be attributed to the effect of unlike monomer interactions, causing a higher extension of the polymer chain. It also suggests an increase in restriction of internal rotation of side chains about the C-C bond. The excess interaction parameter has a negative value. The expansion factor α_η has been related to the excluded volume factor Z , and the coefficient C_1 is in close agreement with the theoretically analyzed value of Yamakawa and Tanaka [37].

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