Partial Volume of Copolymers in Mixed Solvents and Volume Contraction in Bulk-Copolymerization

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ABSTRACT: On the basis of a simple and unified phenomenological method for treating the excess volume of mixing in multicomponent systems, formulas were developed for the partial molar volume of a copolymer (or a mixture of two polymers) in a mixture of two solvents and for the volume contraction factor in the bulk-copolymerization of two monomers. The possible dependence of the "net" volume of a copolymer on its primary structure was taken into account. The proposed formulas were partly checked against some experimental data, and found satisfactory. The previously proposed formulas for the copolymerization contraction factor seem to be less generally applicable.

KEY WORDS Copolymers in Mixed Solvents / Partial Molar Volume / Copolymerization Contraction Factor / Primary Structure Dependence / Concentration Dependence /

Polymerization is usually accompanied by a negative volume change which is important for determining polymerization rates. The contraction factor Γ , expressed in units of mL mol^{-1} , is defined by

$$\Gamma = -(\partial U / \partial N_p) \quad (1)$$

where U is the volume of the system, and N_p is the number of moles of monomeric units converted to polymer molecules. The differentiation in eq 1 should be carried out by taking account of the conservation of mass. Given Γ , one can readily convert the rate of change in volume or density to the rate of polymerization.

There is considerable complexity in regard to the Γ factor for copolymerization, but this matter has never been adequately discussed. In the past, it was customarily assumed that Γ for a 1-2 binary copolymerization is given by a linear combination of the contraction factors Γ_1 and Γ_2 for the relevant homopolymerizations¹⁻³:

$$\Gamma = F_1\Gamma_1 + F_2\Gamma_2 \quad (2)$$

Here $F_1 (=1-F_2)$ is the mole fraction of monomeric unit 1 in the copolymer. The inadequacy of eq 2 soon became apparent,^{4,5} and Wittmer^{5,6} proposed the equation

$$\Gamma = F_{11}\Gamma_1 + F_{22}\Gamma_2 + F_{12}\Gamma_{12} \quad (3a)$$

or equivalently

$$\Gamma = F_1\Gamma_1 + F_2\Gamma_2 + F_{12}\Delta\Gamma_{12} \quad (3b)$$

$$\Delta\Gamma_{12} = \Gamma_{12} - (\Gamma_1 + \Gamma_2)/2 \quad (3c)$$

where F_{ij} is the population of i - j chemical bonds in the copolymer, $F_{ii} + (F_{12}/2) = F_i$ ($i=1$ or 2), and Γ_{12} and hence $\Delta\Gamma_{12}$ are constants independent of F_{ij} . The basic idea underlying eq 3 is equivalent to that of Inagaki *et al.*,^{7,8} who first noticed that the apparent molar volume of a copolymer in a single solvent differs from the composition average of those of the homopolymers by an amount proportional to F_{12} . More recently, Braun *et al.*^{9,10} and Disselhoff¹¹ employed an equation analogous to eq

3, but its physical meaning is not very clear.

In this paper, we present unified and theoretically more complete formulas for the partial molar volume of a binary copolymer in a binary mixture of solvents and for the Γ factor for the bulk-copolymerization of two monomers. These formulas are derived on the basis of the van Laar-Scatchard type equation of mixing, which takes into consideration all contributing factors toward the excess volume of mixing, and which provides reasonably adequate explanation of desired quantities as functions of concentration. The possible dependence of volume parameters on the primary structure of copolymers is also taken into account by introducing the diad approximation proposed by Inagaki^{7,8} and Wittmer.^{5,6}

Prediction of the Γ factor for a given copolymerization on the basis of this rather comprehensive treatment requires an independent determination of a certain number of parameters. If this number is too large, the use of the dilatometric method has little advantage. As for incipient copolymerizations, this number is only two, provided that Γ_1 , Γ_2 and the volumes of the monomer mixtures are known. In contrast, Wittmer's eq 3b includes the single parameter $\Delta\Gamma_{12}$. It is shown below that eq 3b is correct only in limited cases. Our formulas are compared with some published data to check validity.

THEORETICAL

Systems of Homopolymers and Solvents

We consider a system consisting of z components ($z \geq 2$), each of which may be either a homopolymer or a solvent. The volume U of the system is assumed to be given by the van Laar-Scatchard form¹²

$$U = U^* \left(1 + \sum_{m < n}^z \sum_{m < n}^z a_{mn} \phi_m \phi_n \right) \quad (4)$$

$$U^* = \sum_m^z N_m V_m \quad (5)$$

where N_m is the number of moles of component m having a molar volume V_m in the pure state (when the component is a polymer, N_m is the number of moles of monomeric units, and V_m is the molar volume per monomeric unit), ϕ_m is defined as a volume fraction before mixing, i.e., $\phi_m = N_m V_m / U^*$, and a_{mn} is the binary interaction parameter between

the components m and n .

Recently, Aminabhavi and Munk¹³ successfully treated the excess volume and polarizability of mixing of one polymer and two solvents, using a refined version of eq 4. Their equation includes a ternary interaction term as well as binary terms, but according to their own experimental results, the contribution from the ternary term was of minor importance.¹³ For simplicity, ternary interactions are not considered here. Generally, the interaction parameter a_{mn} is a function of the relative composition, $\phi_m / (\phi_m + \phi_n)$. As a crude approximation, we assume throughout this paper that all a_{mn} are constants, although it is not very difficult to incorporate the composition dependence of a_{mn} into the theory.

The partial molar volume $\bar{V}_i$ of component i is obtained by differentiating U with respect to N_i with all N_j ($j \neq i$) fixed constant:

$$\begin{aligned} \bar{V}_i &= (\partial U / \partial N_i)_{N_j} \\ &= V_i \left(1 + \sum_{m \neq i}^z a_{im} \phi_m - \sum_{m < n}^z \sum_{m < n}^z a_{mn} \phi_m \phi_n \right) \end{aligned} \quad (6)$$

Systems of One Copolymer and Two Solvents

Next we consider a system consisting of a 1-2 binary copolymer and two solvents (components 3 and 4). We assume that the interactions in this system are the same as in the system made up by mixing homopolymers 1 and 2 with solvents 3 and 4 in such a way that the volume fractions are the same as in the copolymer system. Thus we may write U as

$$U = U^* \left(1 + \sum_{n < m}^4 \sum_{n < m}^4 a_{mn} \phi_m \phi_n \right) \quad (7)$$

The reference volume U^* may be properly written

$$U^* = N_P V_P^* + N_S V_S^* \quad (8)$$

$$N_P = N_1 + N_2 \quad (9)$$

$$N_S = N_3 + N_4 \quad (10)$$

where V_S^* is a reference molar volume of the solvent mixture,

$$V_S^* = f_3 V_3 + f_4 V_4 \quad (11)$$

$$f_3 = 1 - f_4 = N_3 / N_S \quad (12)$$

and V_P^* is a reference molar volume (per monomeric unit) of the copolymer, which, as indicated

previously, is assumed to be given by

$$V_P^* = F_1 V_1 + F_2 V_2 + F_{12} \Delta V_{12} \quad (13)$$

$$F_1 = 1 - F_2 = N_1/N_P \quad (14)$$

where ΔV_{12} is a constant, and F_{12} is the relative population of 1-2 chemical bonds in the copolymer. All the equations for $\Delta V_{12}=0$ are identical with those for $F_{12}=0$, or the equations for the two-polymers-two-solvents system formulated in a previous section. In reality, copolymer systems, even if $\Delta V_{12}=0$, may be different from homopolymer systems. For example, phase-separation may occur in one system but not necessarily in another, and this brings about a certain difference in the two systems. Obviously, this contradiction arises from the basic assumption involved in eq 4 and 7 that all components mix with each other randomly. Care should be taken in this matter, when data for one system are compared with those for another.

Now, we introduce the volume fractions ϕ_P and ϕ_S of the copolymer and solvents, respectively, which are represented by

$$\phi_P = \phi_1 + \phi_2 = N_P V_P^* / U^* \quad (15)$$

$$\phi_S = \phi_3 + \phi_4 = N_S V_S^* / U^* \quad (16)$$

Clearly, $\phi_P + \phi_S = 1$. We further introduce the volume-based compositions X_i ($i=1$ or 2) and x_j ($j=3$ or 4) of the copolymer and the solvent mixture, respectively, which are represented by

$$X_1 = 1 - X_2 = \phi_1 / \phi_P \quad (17)$$

$$\begin{aligned} x_3 &= 1 - x_4 = \phi_3 / \phi_S \\ &= f_3 V_3 / V_S^* \end{aligned} \quad (18)$$

The copolymer volume composition X_1 may be legitimately given by

$$X_1 = \left[F_1 V_1 + F_{12} \Delta V_{12} \left(\frac{V_1}{V_1 + V_2} \right) \right] / V_P^* \quad (19)$$

We note that V_P^* defined by eq 13 is *not* the molar volume in the pure state. In the present treatment (cf. eq 7, 8, and 17), the pure-state volume V_P of the copolymer is given by

$$V_P = V_P^* (1 + a_{12} X_1 X_2) \quad (20)$$

Similarly, the molar volume of the solvent mixture (in the absence of a polymer) is given by

$$V_S = V_S^* (1 + a_{34} x_3 x_4) \quad (21)$$

The partial molar volume $\tilde{V}_P$ of the copolymer (per monomeric unit) is given as

$$\begin{aligned} \tilde{V}_P &= (\partial U / \partial N_P)_{X_1, N_3, N_4} \\ &= V_P^* [1 + A(X, x) \phi_S^2 - a_{34} x_3 x_4 \phi_S^2 \\ &\quad + a_{12} X_1 X_2 \phi_P (1 + \phi_S)] \\ A(X, x) &= a_{13} X_1 x_3 + a_{14} X_1 x_4 \\ &\quad + a_{23} X_2 x_3 + a_{24} X_2 x_4 \end{aligned} \quad (22)$$

Equation 22 can be expressed in terms of $\tilde{V}_{i,j}$, the partial molar volume of i in the i - j two-component system *having the same solvent fraction* ϕ_S . Referring to eq 6, we have $\tilde{V}_{i,j} = V_i (1 + a_{ij} \phi_j^2)$ with $\phi_j = 1 - \phi_i = \phi_S$. Thus,

$$\begin{aligned} \tilde{V}_P &= x_3 (F_1 \tilde{V}_{1,3} + F_2 \tilde{V}_{2,3}) + x_4 (F_1 \tilde{V}_{1,4} + F_2 \tilde{V}_{2,4}) \\ &\quad + F_{12} \Delta V_{12} - V_P^* [a_{34} x_3 x_4 \phi_S^2 \\ &\quad - a_{12} X_1 X_2 \phi_P (1 + \phi_S)] + \Delta \end{aligned} \quad (24)$$

where the last term Δ is a linear function of $a_{ij} \Delta V_{12}$, which is generally so small compared with other terms that it may be neglected. In a similar approximation, the V_P^* in the fourth term in eq 24 may be equated to $\tilde{V}_P$. We thus have

$$\begin{aligned} \tilde{V}_P &= \frac{x_3 (F_1 \tilde{V}_{1,3} + F_2 \tilde{V}_{2,3}) + x_4 (F_1 \tilde{V}_{1,4} + F_2 \tilde{V}_{2,4}) + F_{12} \Delta V_{12}}{1 + a_{34} x_3 x_4 \phi_S^2 - a_{12} X_1 X_2 \phi_P (1 + \phi_S)} \end{aligned} \quad (25)$$

In the present treatment, we have assumed ΔV_{12} and a_{12} to be constants independent of the solvents. To determine ΔV_{12} , it may be convenient to measure a copolymer in a single solvent, say solvent 3, in the dilute limit, *i.e.*, $\phi_P \rightarrow 0$. In this case, eq 25 reduces to

$$\tilde{V}_{P,3}^\circ = F_1 \tilde{V}_{1,3}^\circ + F_2 \tilde{V}_{2,3}^\circ + F_{12} \Delta V_{12} \quad (26)$$

Hereafter, the superscript “ $\circ$ ” denotes the dilute limit. Equation 26 is equivalent to the expression proposed by Inagaki *et al.*^{7,8} for the “apparent” molar volume of a copolymer in a solvent. The parameter a_{12} may be determined by the study of either a copolymer or a mixture of the homopolymers ($F_{12}=0$) in a single solvent at finite concentrations:

$$\tilde{V}_{P,3} = \frac{F_1 \tilde{V}_{1,3} + F_2 \tilde{V}_{2,3} + F_{12} \Delta V_{12}}{1 - a_{12} X_1 X_2 \phi_P (1 + \phi_S)} \quad (27)$$

Such a study has recently been carried out by Nagata *et al.*¹⁴ for a two-polymers-one-solvent system. Finally, the parameter a_{34} in eq 25 may be determined by the study of the solvent mixtures (*cf.* eq 21). The importance of this term has been demonstrated by Aminabhavi and Munk¹³ for one-polymer-two-solvents systems. Equation 25 (more rigorously eq 24) with $F_2 = F_{12} = \Delta V_{12} = \phi_P = 0$ reduces to their equation with the ternary interaction term omitted.

The Contraction Factor for Bulk-Copolymerization

In this section, we consider a system of a 1-2 binary copolymer and two monomers 1 and 2. The equations derived above are valid if solvents 3 and 4 are regarded as monomers 1 and 2, respectively.

However, some additional parameters may be necessary. In a copolymerization, monomers are continually converted to polymers, satisfying the following relations at any instant:

$$N_j^\circ = N_i + N_j; \quad (i, j) = (1, 3) \text{ or } (2, 4) \quad (28)$$

Here N_i is the total number of moles of monomer j converted to polymers, and N_j and N_j° are the numbers of moles of monomer j present at a given instant and at the onset of the polymerization, respectively. Since conversion rates are generally different for the two monomers, the compositions of the copolymer and the feed continually change. We let $\bar{F}_i$ be the average mole-composition for the copolymers that have been produced up to the instant in question, and F_i be the composition of the copolymer produced at that particular instant. Clearly,

$$\bar{F}_i = N_i / N_P \quad (29)$$

$$F_i = dN_i / dN_P \quad (30)$$

with $N_P = N_1 + N_2$, as before. The average and instantaneous values of all other relevant quantities are distinguished by attaching the symbol ' $\bar{}$ ' to the former. Clearly, the volume U of the system is given by eq 7 with U^* and all ϕ_m expressed in terms of the average quantities. For example, the reference volume of the copolymer to be used in eq 8 is $\bar{V}_P^*$ given by

$$\bar{V}_P^* = \bar{F}_1 V_1 + \bar{F}_2 V_2 + \bar{F}_{12} \Delta V_{12} \quad (31)$$

The contraction factor Γ , defined as a decrease in the volume of the system per unit mole of the

monomers polymerized, is obtained as

$$\begin{aligned} \Gamma &= -(\partial U / \partial N_P)_{N_3^\circ, N_4^\circ} \\ &= (F_1 V_3 + F_2 V_4 - V_P^*) [1 - a_{34} x_3 x_4 \phi_S^2 \\ &\quad - A(\bar{X}, x) \phi_S \phi_P - a_{12} \bar{X}_1 \bar{X}_2 \phi_P^2] \\ &\quad - \phi_S [A(X, x) V_P^* - a_{34} (x_4 F_1 V_3 + x_3 F_2 V_4)] \\ &\quad - \phi_P [a_{12} V_P^* (X_1 \bar{X}_2 + X_2 \bar{X}_1) \\ &\quad - \bar{X}_1 (a_{13} F_1 V_3 + a_{14} F_2 V_4) \\ &\quad - \bar{X}_2 (a_{23} F_1 V_3 + a_{24} F_2 V_4)] \end{aligned} \quad (32)$$

In the dilute limit of polymer concentration, eq 32 converges to

$$\begin{aligned} \Gamma^\circ &= (F_1 V_3 + F_2 V_4 - V_P^*) (1 - a_{34} x_3 x_4) \\ &\quad - A(X, x) V_P^* + a_{34} (x_4 F_1 V_3 + x_3 F_2 V_4) \end{aligned} \quad (33)$$

By neglecting trivial terms like $a_{ij} \Delta V_{12}$ and introducing the contraction factors Γ_1° and Γ_2° for the homopolymerizations, eq 33 can be written

$$\begin{aligned} \Gamma^\circ &= (F_1 \Gamma_1^\circ + F_2 \Gamma_2^\circ) (1 - a_{34} x_3 x_4) - F_{12} \Delta V_{12} \\ &\quad + x_4 F_1 (a_{34} V_3 - \Delta a_1 V_1) \\ &\quad + x_3 F_2 (a_{34} V_4 - \Delta a_2 V_2) \end{aligned} \quad (34)$$

$$\Delta a_1 = a_{14} - a_{13}; \quad \Delta a_2 = a_{23} - a_{24} \quad (35)$$

where use of the following relations have been made, from which Γ_i° is obtained by setting $\phi_i = 1 - \phi_j = 0$:

$$\Gamma_i = V_j - V_i + a_{ij} (\phi_i^2 V_j - \phi_j^2 V_i) \quad (36)$$

$$(i, j) = (1, 3) \text{ or } (2, 4); \quad \phi_i + \phi_j = 1$$

Equation 34 can be converted to a more useful form. If the terminal-model kinetics of copolymerization¹⁵⁻¹⁷ is valid,¹⁸ the well-known relations between the copolymer structure and feed composition hold, *e.g.*

$$F_1 = \frac{f_3(r_1 f_3 + f_4)}{f_3(r_1 f_3 + f_4) + f_4(r_2 f_4 + f_3)} \quad (37)$$

$$F_{12} = \frac{2f_3 f_4}{f_3(r_1 f_3 + f_4) + f_4(r_2 f_4 + f_3)} \quad (38)$$

where r_1 and r_2 are the reactivity ratios (in the usual notation, f_3 and f_4 are written as f_1 and f_2 , respectively, but to avoid confusion, we adopt the present notation). Use of eq 37 and 38 in eq 34 gives

$$\Gamma^\circ = (F_1 \Gamma_1^\circ + F_2 \Gamma_2^\circ) (1 - a_{34} x_3 x_4) + G(f) R(f) \quad (39)$$

$$G(f) = F_{12}/[f_3 + f_4(V_4/V_3)] \quad (40)$$

$$R(f) = I + Sf_3 \quad (41)$$

where I and S are constants independent of f_3 :

$$\begin{aligned} I = & -(V_4/V_3)\Delta V_{12} \\ & + (V_4/2V_3)(a_{34}V_3 - \Delta a_1V_1) \\ & + (r_2/2)(a_{34}V_4 - \Delta a_2V_2) \end{aligned} \quad (42)$$

$$\begin{aligned} S = & -[1 - (V_4/V_3)]\Delta V_{12} \\ & + (r_1 - 1)(V_4/2V_3)(a_{34}V_3 - \Delta a_1V_1) \\ & - [(r_2 - 1)/2](a_{34}V_4 - \Delta a_2V_2) \end{aligned} \quad (43)$$

Thus, the function R given by

$$R(f) = [\Gamma^\circ - (F_1\Gamma_1^\circ + F_2\Gamma_2^\circ)(1 - a_{34}x_3x_4)]/G(f) \quad (44)$$

is linear in f_3 (cf. eq 41). Provided that Γ_1° , Γ_2° , a_{34} and the elementary parameters in eq 40 are known, measurements of Γ° at two different values of f_3 suffice to predict Γ° at any other values of f_3 . For

this purpose, there is no need to know the individual parameters in eq 42 and 43. A similar simplification is possible for $\tilde{V}_P^\circ$ that can be obtained from eq 25.

To a crude approximation, we may set $V_3 \approx V_4$, and neglect the a_{34} -term in the first term in eq 39 (but not those in the other terms, whose contributions may be important unless a_{34} is very small). In special cases, e.g., $r_1 = r_2 = 1$, the equation thus derived becomes formally the same as eq 3b.

DISCUSSION

We have expressed $\tilde{V}_P$ and Γ in terms of the parameters a_{ij} and ΔV_{12} . Each of the six a_{ij} parameters is related to the excess volume of physically mixing components i and j , whereas ΔV_{12} is related to the excess volume of "chemically mixing" components 1 and 2, i.e., formation of 1-2 covalent bonds. To our knowledge, a_{ij} as well as $\Delta V_{12}/V_P^*$ may be of the order of 10^{-2} , and their contributions may possibly be equally important. The prediction of $\tilde{V}_P$ or Γ based on eq 22 (or 25) or 32 thus requires

Table I. Values of contraction factor and other relevant parameters for low-conversion copolymerizations (60°C)^a

ST-MMA:	$r_1 = 0.52$	$r_2 = 0.46$	$V_3 = 119.4$	$V_4 = 111.5$	$a_{34} = 0.00$
f_3	0	0.22	0.44	0.76	1
Γ°	29.77	26.58	26.13	23.79	20.30
BMA-ST:	$r_1 = 0.53$	$r_2 = 0.34$	$V_3 = 175.3$	$V_4 = 119.4$	$a_{34} = 0.004$
f_3	0	0.18	0.59	0.77	1
Γ°	20.30	22.94	25.18	27.49	33.66
BMA-MMA:	$r_1 = 1.06$	$r_2 = 0.83$	$V_3 = 175.3$	$V_4 = 111.5$	$a_{34} = -0.010$
f_3	0	0.11	0.39	0.76	1
Γ°	29.77	29.71	30.49	31.88	33.66
NVP-ST:	$r_1 = 0.08$	$r_2 = 24.2$	$V_3 = 110.2$	$V_4 = 119.4$	$a_{34} = -0.041$
f_3	0	0.20	0.50	0.80	1
Γ°	20.30	19.54	17.94	15.93	13.88
NVP-MMA:	$r_1 = 0.15$	$r_2 = 4.39$	$V_3 = 110.2$	$V_4 = 111.5$	$a_{34} = -0.020$
f_3	0	0.20	0.50	0.80	1
Γ°	29.32	20.13	24.00	27.52	13.88

^a Data from ref 9 and 10: In system A-B, components 1, 2, 3, and 4 are poly-A, poly-B, monomer A and monomer B, respectively; Γ° and V 's are in ml mol⁻¹; a_{34} is an average value.

Figure 1. Plot of function R vs. feed composition f_3 for incipient copolymerization of (1): ST-MMA (half-filled circles), (2): BMA-ST (filled circles), and (3): BMA-MMA (open circles). The data were taken from Table I. The solid lines are best-fit representations according to eq 41.

six a_{ij} and one ΔV_{12} . At present, we are not in a position to test the validity of these general equations, because the experimental data for these seven parameters are not available.

Some discussion can be made on the dilute limit eq 39. Table I shows the data of Braun *et al.*^{9,10} for low-conversion copolymerizations of (1): styrene (ST) and methyl methacrylate (MMA), (2): butyl methacrylate (BMA) and ST, (3): BMA and MMA, (4): *N*-vinylpyrrolidone (NVP) and ST, and (5): NVP and MMA. The authors determined Γ° by a direct measurement of the volume vs. conversion curves, but reported it in units different from mL mol^{-1} . To express their Γ° in units of mL mol^{-1} , we employed the parameter values provided by the same authors, and included them in Table I. Equation 39 can now be tested using the experimental data.

In Figure 1, the function R given by eq 44 is plotted against the feed composition f_3 for systems 1–3. The data points seem to fall on straight lines, as eq 41 predicts. In system 2, the slope of the line is fairly large, while small in system 3. According to Wittmer's eq 3b, the slope in an R vs. f_3 plot should be nearly zero. According to our equation, this occurs when $r_1 = r_2 = 1$, as has been pointed out. System 3, in fact, meets this condition approxi-

mately. However, these results do not immediately mean a superiority of one equation over the other: First, rather small experimental errors in Γ° may result in a large slope. Secondly, as far as these systems are concerned, eq 3b and 39 can reproduce the data nearly equally as well, if the parameter values are properly chosen. In this regard it is evident that eq 3b has an advantage over eq 39, since the former is a one-parameter theory, and the latter, a two-parameter theory.

More critical tests of these two equations can be made using the data for the remaining two systems. System 4 is particularly interesting, since the reactivity ratios for this system are $r_1 = 0.08$ and $r_2 = 24.2$, and the absolute value of the monomer-monomer interaction parameter a_{34} is fairly large ($a_{34} = -0.041$ on average). According to eq 42 and 43, the function R for this system is dominated by the terms involving r_2 multiplied by a_{34} . We thus expect that the intercept, $-I$, as well as the slope, S , should be anomalously large. According to eq 3b, on the other hand, R should be nearly independent of f_3 , and its magnitude should be "normal", *i.e.*, as small as in the previous examples. Figure 2 shows the data for this system. The large scale of the ordinate should be noted. The broken line in the figure has been calculated from eq 42 and 43 using the above values of r_i and a_{34} but neglecting all the terms that include the other parameters. It remarkably well reproduces the data points. System 5 is also characterized by relatively large values of r_2 ($=4.39$) and a_{34} ($=-0.020$ on average). In this example, nearly one half of the observed dependence of R on f_3 can be explained by the terms involving r_2 and a_{34} alone (the dot-dash line in Figure 2). Our equations are thus supported by these data.

Figure 3 illustrates the dependence of Γ° on copolymer composition F_1 predicted by various approximate theories. The three curves have been calculated according to eq 2 (broken line), eq 3b (dot-dash line) and eq 39 (full line) so as to give the best fit to the data points for system 4 (circles). It is noted that there are very large differences among the Γ° values predicted by different theories.

Now that the validity of our treatment seems to have been confirmed in part, we proceed to illustrate some behavior of a high-conversion system, for which the dilatometric method may show its greatest power. We take a ST-MMA system as a

Figure 2. Plot of function R vs. feed composition f_3 for incipient copolymerization of (4): NVP-ST (open circles) and (5): NVP-MMA (filled circles). The data were taken from Table I. The solid lines are best-fit representations according to eq 41. The broken and dot-dash lines were calculated from eq 41–43 with $\Delta V_{12} = \Delta a_1 = \Delta a_2 = 0$ (see the text).

Figure 3. Plot of contraction factor Γ° vs. copolymer composition F_1 for incipient copolymerization of NVP-ST, calculated according to eq 2 (broken line), eq 3b (dot-dash line), and eq 39 (full line) so as to give the best fit to the data points (circles).

model. Values of the basic parameters for this system are listed in Table II. The molar volumes V_1 and V_2 of PST (component 1) and PMMA (component 2) were tentatively taken from the literature data for the solids.^{19,20} The propriety of this choice will be discussed in a forthcoming paper.¹⁴ The values of a_{13} and a_{24} were obtained from the above-

Table II. Parameter values employed to calculate the contraction factor for high-conversion copolymerization of ST and MMA (60°C)^a

V_1^b	V_2^c	V_3^d	V_4^d	ΔV_{12}^e	r_1^d	r_2^d
100.0	85.4	119.4	111.5	-1.16	0.52	0.46
a_{12}^f	a_{13}^g	a_{14}^g	a_{23}^g	a_{24}^g	a_{34}^d	
0.00	-0.010	0.040	-0.079	-0.031	0.00	

^a Components 1, 2, 3 and 4 are PST, PMMA, ST, and MMA, respectively; V 's and ΔV_{12} are in ml mol⁻¹.

^b Reference 19; value for the solid.

^c Reference 20; value for the solid.

^d Reference 9.

^e Reference 8; value for 30°C.

^f Reference 14; value for 30°C.

^g Estimated from the data in ref 9.

cited data,⁹ which also enabled us to estimate a_{14} and a_{23} (cf. Figure 1 and eq 42 and 43). The value of a_{12} was taken from our results for a PS-PMMA-bromobenzene ternary system,¹⁴ and the ΔV_{12} -value from the study of Nakazawa *et al.* for ST-MMA copolymers in *p*-xylene.⁸ The other parameter values are as given in ref 9.

Based on eq 32, we are now able to compute Γ as a function of the feed-composition f_3 (at a given instant): all other variables in eq 32 are functions of f_3 only. For example, the average composition $\bar{F}_1$ and the average diad-population $\bar{F}_{12}$ are given by

$$\bar{F}_1 = (f_3^\circ - f_3)/C + f_3 \quad (45)$$

$$\bar{F}_{12} = C^{-1} \int_{f_3^\circ}^{f_3} \frac{(1-C)F_{12}}{f_3 - F_1} df_3 \quad (46)$$

where f_3° is the composition of the initial feed, and C is the mole-conversion, which is related to f_3 by²¹

$$C = 1 - (f_3/f_3^\circ)^\alpha (f_4/f_4^\circ)^\beta [(f_3^\circ - \delta)/(f_3 - \delta)]^\gamma \quad (47)$$

In eq 47, α , β , γ , and δ are known functions of r_1 and r_2 only (see ref 21). The integration in eq 46 seems difficult to perform analytically. For the present purpose, it suffices to approximate $\bar{F}_{12}$ by

$$\bar{F}_{12} = \frac{4\bar{F}_1\bar{F}_2}{1 + [1 + 4\bar{F}_1\bar{F}_2(r_1r_2 - 1)]^{1/2}} \quad (48)$$

which is correct for instantaneous copolymers.²² On the other hand, the volume of the system, U , is also a function of f_3 alone. It is thus possible to determine Γ as a function of U , or a relative change $\Delta U/U^\circ$, where U° is the initial volume, and $\Delta U =$

Figure 4. Plot of relative volume change $\Delta U/U^\circ$ vs. mole conversion C for ST-MMA copolymerization, calculated with the data in Table II for the values of initial ST-composition f_3° indicated in the figure.

Figure 5. Plot of contraction factor Γ vs. mole conversion C for ST-MMA copolymerization, calculated with the data in Table II for the values of initial ST-composition f_3° indicated in the figure.

$U^\circ - U$.

The calculated results for several values of initial ST-composition f_3° are presented in Figures 4 and 5. Figure 4 gives $\Delta U/U^\circ$ and Figure 5 gives Γ as a function of C . Although not too much importance

should be attached to the numerical results, since the parameter values employed may possibly contain errors (in particular, the values of a_{14} and a_{23} seem somewhat unreasonable), these figures serve to illustrate complicated, not easily predictable dependence of Γ on $\Delta U/U^\circ$ or C as well as on f_3° . No simple approximation such as those expressed by eq 2 and 3b seems valid at any level of conversion. A set of accurately estimated values of the parameters for the same system at 40°C will be reported elsewhere.²³

LIST OF SYMBOLS

General

- $\bar{Y}$ value of Y averaged over different copolymer species
- $\tilde{Y}$ partial value of Y in multicomponent solution
- Y^* value of Y under the ideal mixing
- Y° value of Y at vanishing polymer concentration

Individual

- A a function of a_{ij} , X_i , and x_j (eq 23)
- a_{ij} binary interaction parameter related to excess volume of mixing (eq 4)
- Δa_i difference between the binary interaction parameters (eq 35)
- C mole conversion
- F_i mole composition of i in the copolymer: $F_1 + F_2 = 1$ (eq 14)
- f_j mole composition of j in the solvent mixture: $f_3 + f_4 = 1$ (eq 12)
- F_{ij} population of i - j chemical bonds in the copolymer: $F_{11} + F_{22} + F_{12} = 1$
- N_i number of moles of component i
- N_p total number of moles of monomeric units in the copolymer (eq 9)
- N_s total number of moles of solvent molecules (eq 10)
- r_i copolymerization reactivity ratio
- U total volume of the system
- V_i molar volume of component i (in the pure state)
- $\tilde{V}_{i,j}$ value of $\tilde{V}_i$ in the i - j two component system
- V_p molar volume of copolymer per monomeric unit (in the pure state, eq 20)
- V_p^* reference molar volume of copolymer per monomeric unit (eq 13)
- V_s molar volume of the solvent mixture (eq 21)

- ΔV_{12} correction parameter related to V_p^* (eq 13)
 X_i volume composition of i in the copolymer:
 $X_1 + X_2 = 1$ (eq 17)
 x_j volume composition of j in the solvent mixture:
 $x_3 + x_4 = 1$ (eq 18)
 Γ molar contraction in copolymerization
 Γ_i molar contraction in homopolymerization of monomer i
 $\Delta \Gamma_{12}$ correction parameter related to Γ (eq 3b)
 ϕ_i volume fraction of component i in the system
 ϕ_P volume fraction of copolymer in the system (eq 15)
 ϕ_S volume fraction of solvents in the system (eq 16)

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