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# Light Scattering Study of Three-Component Systems. 1. Excluded Volume Effect of Poly(methyl methacrylate) in the Binary Mixture 1-Chlorobutane + 2-Methoxyethanol

**Mitsuo Nakata* and Naoko Numasawa[†]**

*Department of Polymer Science, Faculty of Science, Hokkaido University, Sapporo, Japan.*
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ABSTRACT: Light scattering measurements have been made on dilute solutions of poly(methyl methacrylate) ($M_w = 2.44 \times 10^6$) in the mixed solvent 1-chlorobutane (BuCl) + 2-methoxyethanol (MOEt) at 40 °C. On account of a very small refractive index difference between BuCl and MOEt, the light scattering data were analyzed as in the case of polymer solutions of a single solvent to determine the molecular weight $M_w$, the mean-square radius of gyration $\langle s^2 \rangle$, and the second virial coefficient $A_2$. The molecular weight obtained from zero-angle scattering was independent of the composition of the mixed solvent. $A_2$ and $\langle s^2 \rangle$, obtained as a function of the volume fraction $u_2$ of MOEt in the mixed solvent, showed a large maximum value at the same $u_2$. The behavior of the universal function $\Psi$ as a function of the expansion factor $\alpha$ showed the same trend as those observed in experiments with a single solvent. In the framework of the two-parameter theory, the excluded volume effect in the present ternary system did not show a clear difference from that in systems of a single solvent. From the magnitude of the excluded volume of the polymer segment, the mixed solvent was found to act as a good solvent for poly(methyl methacrylate).

## I. Introduction

Dilute polymer solutions in mixed solvents show different behavior from those in the constituent single solvents. The second virial coefficient $A_2$ and the intrinsic viscosity $[\eta]$ in mixed solvents have been found to be larger than those in the constituent single solvents.[1-6] Even nonsolvents for a polymer can become good solvents for the polymer when mixed.[5-8] The behaviors of dilute polymer solutions in a mixed solvent and in its constituent single solvents have been compared by evaluating excluded

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[†] Present address: Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan.

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volumes from viscosity data. The evaluation of the excluded volumes has been made with the aid of the two-parameter theory.[9] The second virial coefficients observed on single solvents and on their mixed solvent have been compared without the correction for the excluded volume effects. We are not aware of experimental studies to verify the two-parameter theory in mixed solvents. The lack of experimental data to test the two-parameter theory is caused by the fact that the evaluation of the mean-square radius of gyration from light scattering data had not been justified in mixed solvents before the theoretical study of light scattering by Yamakawa.[10] According to the distribution function theory for three-component systems, the mean-square radius of gyration of polymers in mixed solvents could be estimated from the angular dependence of the scattered light in the same manner as in the case of two-component systems, provided that the derivative of the refractive index of the solution with respect to the composition of the mixed solvent is very small. This condition can be easily fulfilled when the refractive indices of the component solvents are very close to each other. Nonetheless, light scattering studies on dilute polymer solutions in mixed solvents have not been made by taking advantage of the isorefractive solvent pair. It is interesting to know whether or not the behavior of dilute polymer solutions in mixed solvents is different from that in single solvents within the scope of the two-parameter theory. Furthermore, it is desirable to analyze the second virial coefficient $A_2$ in mixed solvents by the two-parameter theory in order to estimate quantitatively the solvent power and to compare it with lattice theories based on homogeneous segment distribution. Therefore, dilute polymer solutions in mixed solvents should be studied from the standpoints of both the excluded volume effect and the acquired solvent power.

In this paper, we report light scatering measurements on the ternary system poly(methyl methacrylate) (PMMA) + 2-methoxyethanol (MOEt) + 1-chlorobutane (BuCl). This system was employed for the following reasons. On account of a small refractive index difference between MOEt and BuCl the solvents can be taken as an isorefractive solvent pair. Secondly, an addition of a small amount of MOEt to the binary system PMMA + BuCl causes a large increase of the solvent power and the mixed solvent acts as a good solvent for PMMA, though BuCl is a poor solvent and MOEt is a moderate solvent for PMMA. We have analyzed the light scattering data in the framework of the two-parameter theory to investigate the excluded volume effect in the mixed solvent. In the subsequent paper, we will compare the observed second virial coefficients with a lattice theory by using the thermodynamic relation of the three-component system to analyze the enhanced solvent power of the mixed solvent.

## II. Experimental Section

**A. Materials.** PMMA was prepared by bulk polymerization of freshly distilled methyl methacrylate with 2,2-azobis(isobutyronitrile) (AIBN) of 0.03% weight fraction as initiator at 50 °C. The polymerization was carried out for 400 min to a conversion of 11.6%. The PMMA was fractionated into 18 fractions in the mixture toluene + methanol by the fractional solution technique and the ninth fraction was used as a sample for light scattering studies. For refractive index increment measurements another sample of PMMA was prepared with AIBN of 0.213% weight fraction at 50 °C. The PMMA was fractionated into 9 fractions and the fourth fraction with molecular weight $M_w = 7.6 \times 10^5$ was used for the measurements. MOEt was treated with anhydrous sodium carbonate and fractionally distilled in a 1.8 × 100 cm column packed with Raschig rings. A constant-boiling fraction within 0.1 K was used for the measurements. BuCl was washed with concentrated sulfuric acid, water, and 10% sodium carbonate solution. After being dried over calcium chloride BuCl was fractionally distilled and a fraction at constant temperature within 0.1 K was collected for a sample. The solvent samples were stored in the dark.

**B. Light Scattering and Refractive Index Increment Measurements.** A Shimadzu light scattering photomer of the Brice type was used. Scattered light intensity was measured at intervals of 15° in the range from 30° to 150° using unpolarized incident light at 436 nm of a mercury arc. The measurements were made at 40.0 ± 0.2 °C. The calibration of the photometer was made with benzene as standard, taking its Rayleigh ratio $46.5 \times 10^{-6}$ cm$^{-1}$ at 436 nm.[11]

PMMA solutions of 10-mL volume were flame-sealed in cylindrical glass cells of 19-mm i.d. The cells could float in a liquid in a centrifuge tube and underwent centrifugation at 10 000 rpm near 40 °C for optical clarification. After 1 h of centrifugation the cells were transferred into a light scattering cell filled with the solvent mixture. The back-reflections at the glass–air interface were eliminated as described elsewhere.[12] For each solvent mixture the light scattering measurments were carried out at five polymer concentrations in the range $c_3 < 2.0 \times 10^{-3}$ g/mL.

Refractive index increments $(\partial n/\partial c_3)_{u_2}$ were measured at 40.0 °C with a differential refractometer of the Brice type. The refractive index difference between the solvent mixture BuCl + MOEt and BuCl was also determined as a function of the composition by the differential refractometer.

## III. Experimental Results

In the light scattering theories of the ternary system solvent (1) + solvent (2) + polymer (3), two compositions are employed, that is, the polymer concentration $c_3$ and the volume fraction $u_2$ of component 2 in the mixed solvent. Light scattering measurements with mixed solvent depend on the quantity $\gamma$ defined by

$$\gamma = (\partial n/\partial u_2)_0/(\partial n/\partial c_3)_{u_2} \tag{1}$$

where $n$ is the refractive index of solutions as a function of $u_2$ and $c_3$. The partial derivative $(\partial n/\partial u_2)_0$ is taken at $c_3 = 0$. According to the distribution function theory for dilute polymer solutions in mixed solvent, the practical expression for light scattering at $\gamma = 0$ can be written as[10]

$$Kc_3/R_\theta = 1/M_3 + 2A_2(u_2)c_3 + (16\pi^2n^2/3\lambda^2)(\langle s^2(u_2)\rangle/M_3)\sin^2(\theta/2) + ... \tag{2}$$

where

$$K = (2\pi^2n^2/N_A\lambda^4)(\partial n/\partial c_3)_{u_2}{}^2$$

where $R_\theta$ is the excess scattering from polymer molecules, $M_3$ is the molecular weight of the polymer, $N_A$ is Avogadro's number, and $\lambda$ is the wavelength in a vacuum. $A_2(u_2)$ and $\langle s^2(u_2)\rangle$ are the second virial coefficient and the mean-square radius of gyration at the volume fraction $u_2$, respectively. Equation 2 means that $M_3$, $A_2(u_2)$, and $\langle s^2(u_2)\rangle$ can be evaluated from light scattering data in the same way as in the case of the system of polymer + single solvent, provided that $\gamma$ vanishes.

In the present ternary system, the components were assigned as BuCl (1), MOEt (2), and PMMA (3). Figure 1 shows the plot of the refractive index difference $\Delta n = n - n_1$ vs. the volume fraction $u_2$ of MOEt, where $n$ and $n_1$ are the refractive indices of the binary mixture BuCl + MOEt and BuCl, respectively. The refractive index difference between BuCl and MOEt is $2.3 \times 10^{-3}$ and the slope $(\partial n/\partial u_2)_0$ is very small, vanishing near $u_2 = 0.17$. The maximum slope is observed at $u_2 = 0$ as $-0.023$ and the typical slope could be taken near $u_2 = 1$ as $5.0 \times 10^{-3}$. On acount of the small value of $(\partial n/\partial u_2)_0$ we took the ternary system PMMA + BuCl + MOEt as a binary system in light scattering data analyses. Figure 2 shows the plot of the

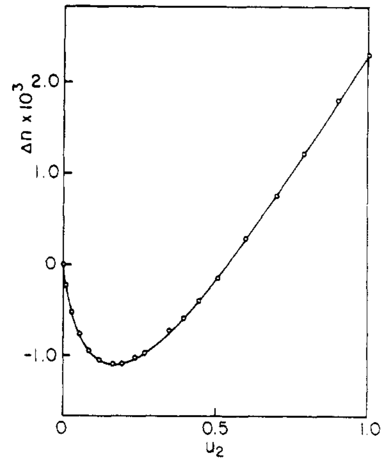

**Figure 1.** Refractive index difference $\Delta n$ ($=n - n_1$) between the binary mixture 1-chlorobutane (1) + 2-methoxyethanol (2) and 1-chlorobutane as a function of the volume fraction $u_2$ at 40 °C.

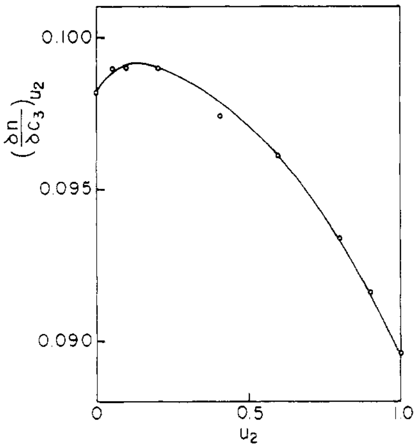

**Figure 2.** Refractive index increments $(\partial n/\partial c_3)_{u_2}$ cm$^3$/g for PMMA in the mixed solvent 1-chlorobutane (1) + 2-methoxyethanol (2) as a function of the volume fraction $u_2$ at 40 °C.

### Table I
### Light Scattering Data of Poly(methyl methacrylate) in the Binary Mixture 1-Chlorobutane + 2-Methoxyethanol at 40 °C

| $u_2$ | $M_w \times 10^{-6}$ | $A_2 \times 10^5$, cm$^3$ mol/g$^2$ | $\langle s^2 \rangle \times 10^{11}$, cm$^2$ | $A_2^0 \times 10^5$,[a] cm$^3$ mol/g$^2$ |
|---|---|---|---|---|
| 0 | 2.44 | 0 | 1.61 | 0 |
| 0.0096 | 2.64 | 1.9 | 2.02 | 2.5 |
| 0.0534 | 2.58 | 5.8 | 2.72 | 11.2 |
| 0.1018 | 2.50 | 7.6 | 2.88 | 17.4 |
| 0.1717 | 2.46 | 9.5 | 3.13 | 24.5 |
| 0.1959 | 2.43 | 9.7 | 3.03 | 27.9 |
| 0.3023 | 2.40 | 11.0 | 3.52 | 27.8 |
| 0.4020 | 2.40 | 11.6 | 3.54 | 30.6 |
| 0.5110 | 2.37 | 11.4 | 3.57 | 28.9 |
| 0.6000 | 2.40 | 11.2 | 3.59 | 27.8 |
| 0.7062 | 2.43 | 10.3 | 3.35 | 26.4 |
| 0.7982 | 2.33 | 9.8 | 3.19 | 25.5 |
| 0.8967 | 2.42 | 8.3 | 3.03 | 19.4 |
| 1.0000 | 2.44 | 7.0 | 2.72 | 16.4 |

[a] Calculated from the data of $A_2$ and $\langle s^2 \rangle$ by using eq 15.

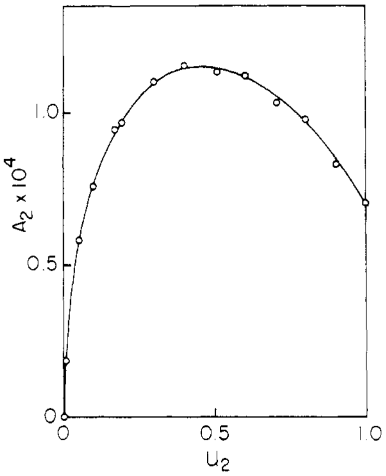

**Figure 3.** Second virial coefficient $A_2$ as a function of the volume fraction $u_2$ for PMMA in the mixed solvent 1-chlorobutane (1) + 2-methoxyethanol (2) observed at 40 °C.

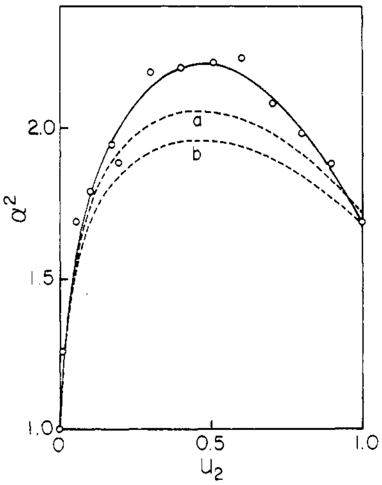

**Figure 4.** Expansion factor $\alpha$ as a function of the volume fraction $u_2$ for PMMA in the mixed solvent 1-chlorobutane (1) + 2-methoxyethanol (2) observed at 40 °C. Curves a and b were calculated with eq 11 and 10, respectively.

refractive index increment $(\partial n/\partial c_3)_{u_2}$ against $u_2$. In the analyses of the observed Rayleigh ratio $R_\theta$ due to polymer molecules, relevant values of $(\partial n/\partial c_3)_{u_2}$ were read from the graph in Figure 2.

The light scattering data was analyzed by using the Zimm plot of $(Kc_3/R_\theta)^{1/2}$ vs. $\sin^2(\theta/2)$ + constant × $c_3$ to determine the molecular weight $M_3$, the second virial coefficient $A_2$, and the $z$-average of the mean-square radius of gyration $\langle s^2 \rangle$. The plots of $(Kc_3/R_\theta)^{1/2}$ vs. $\sin^2(\theta/2)$ and $(Kc_3/R_\theta)^{1/2}$ vs. $c_3$ were represented by a straight line. The results of the light scattering measurements are given in Table I. Except in the range of $u_2 < 0.1$ $M_3$ shows a constant value as expected from the very small value of $\partial n/\partial u_2)_0$. As the molecular weight of the PMMA sample we employed $M_3 = 2.44 \times 10^6$. Since the slopes $(\partial n/\partial u_2)_0$ at $u_2 = 0.0096$ and 0.0534 are relatively large, −0.021 and −0.008, respectively, we tried to estimate the preferential adsorption coefficient $\lambda$, the definition of which is given in the subsequent paper. The results were $\lambda = 0.19$ and 0.35 at $u_2 = 0.0096$ and 0.0534, respectively. Since these values of $\lambda$ appear to be about 10 times larger than those observed on other systems of PMMA + mixed solvent,[5] the large values of $M_3$ in $u_2 < 0.1$ cannot be attributed to the preferential adsorption alone. At the small $u_2$, $A_2$ and $\langle s^2 \rangle$ increase rapidly with increasing $u_2$. It is inconceivable that this behavior is affected by the apparent values of $M_3$, though the reason for the high values is not clear. Since the second virial coefficient $A_2$ vanishes in the single solvent BuCl, the value $\langle s^2 \rangle_0 = 1.61 \times 10^{-11}$ cm$^2$ can be taken as the unperturbed mean-square radius of gyration. Figure 3 shows the behavior of the second virial coefficient $A_2$ as a function of $u_2$. In Figure 4 the expansion factor $\alpha^2 = \langle s^2 \rangle / \langle s^2 \rangle_0$ is plotted against $u_2$, where the solid curve illustrates the behavior of the experimental points.

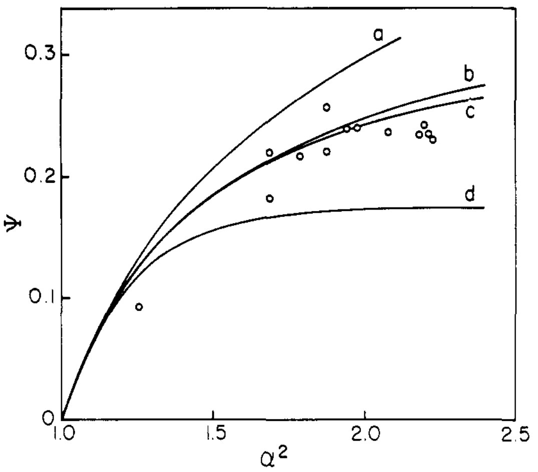

**Figure 5.** Plot of the universal function $\Psi$ against the square of the expansion factor $\alpha$. Curves a, c, and d are calculated, respectively, with eq 6, 9, and 8 combined with eq 10. Curve b is calculated with eq 7 and 11.

## IV. Comparison with Two-Parameter Theory

According to statistical theories of dilute polymer solution,[9] the second virial coefficient $A_2$ can be written in the form

$$A_2 = A_2^\circ h(z/\alpha^3) \tag{3a}$$

$$A_2^\circ = N_A r^2 \beta/(2M^2) \tag{3b}$$

where $\beta$ is the binary cluster integral, $r$ is the number of segments in a chain, and $z$ is the excluded volume parameter defined by

$$z = A_2^\circ M^{1/2}/[4\pi^{3/2}N_A(\langle s^2\rangle_0/M)^{3/2}] \tag{4}$$

The function $h(z/\alpha^3)$ decreases with increasing $z/\alpha^3$ and equals unity at $z = 0$. From eq 3 and 4 we can define the universal function $\Psi$ by

$$\begin{aligned}\Psi &= (4\pi^{3/2}N_A)^{-1}A_2M^2/\langle s^2\rangle^{3/2} \\ &= (z/\alpha^3)h(z/\alpha^3)\end{aligned} \tag{5}$$

Many theoretical equations have been presented for the function $h$ and the expansion factor. The typical ones for the function $h$ are the modified Flory–Krigbaum–Orofino theory[14,15]

$$h(z/\alpha^3) = [5.73(z/\alpha^3)]^{-1} \ln [1 + 5.73(z/\alpha^3)] \quad \text{(FKO.m)} \tag{6}$$

the Kurata–Yamakawa theory[9,16,17]

$$h(z/\alpha^3) = \{1 - [1 + 3.903(z/\alpha^3)]^{-0.4683}\}/[1.828(z/\alpha^3)] \quad \text{(KY)} \tag{7}$$

and the Casassa–Markovitz theory[18]

$$h(z/\alpha^3) = \{1 - \exp[-5.73(z/\alpha^3)]\}/[5.73(z/\alpha^3)] \quad \text{(CM)} \tag{8}$$

The semiempirical equation of Stockmayer[19]

$$h(z/\alpha^3) = 1/[1 + 2.865(z/\alpha^3)] \quad \text{(S)} \tag{9}$$

has been used because of its simple form and moderate behavior. In Figure 5 $\Psi$ is plotted against $\alpha^2$. Curves a, c, and d are described, respectively, by eq 6, 9, and 8 combined with the modified Flory equation for the expansion factor $\alpha$ given by[19,20]

$$\alpha^5 - \alpha^3 = 1.276z \tag{10}$$

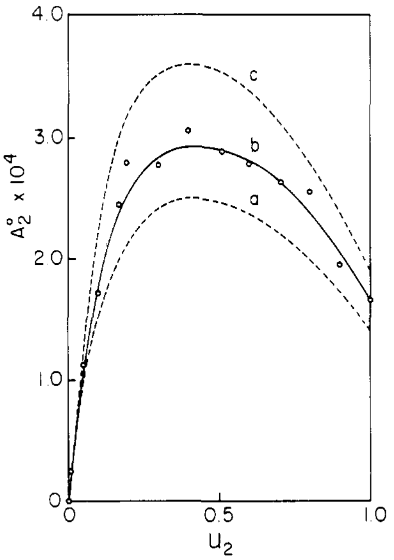

**Figure 6.** Plot of $A_2^\circ$, defined by eq 3, against the volume fraction $u_2$ of 2-methoxyethanol. Open circles were calculated from the experimental data by using eq 7 and their behavior is illustrated by solid curve b. Broken curves a and c are due to eq 6 and 9, respectively.

Curve b is illustrated by eq 7 and the Yamakawa–Tanaka equation[21]

$$\alpha^2 = 0.541 + 0.459(1 + 6.04z)^{0.46} \tag{11}$$

The relation between $\Psi$ and $\alpha$ has been studied by many experiments for polymer solutions in single solvents.[13,22–24] The data points in these experiments appear to fall between curves a and b in the region $\alpha^2 < 2$ and tend to scatter around curve b in the region $\alpha^2 > 2$. Although the two-parameter theory has been developed in the scope of dilute polymer solutions in single solvents, we tried the plot of $\Psi$ vs. $\alpha^2$ for the present data in the mixed solvent. The molecular weight $M_3 = 2.44 \times 10^6$ was used for the calculation of $\Psi$ at each $u_2$. The result is represented by the open circles in Figure 5. The experimental data points are fairly well represented by the Kurata–Yamakawa theory combined with eq 11 and the semiempirical equation of Stockmayer with eq 10. This behavior shows the same trend as the experimental data obtained for systems of polymer + single solvent. Therefore, we could not find a characteristic feature due to the mixed solvent in the plot of $\Psi$ vs. $\alpha^2$, though the precise behavior is obscure on account of the scattering of the data points. These results verify the use of the two-parameter theory for the present ternary system.

We tried to calculate the values of $A_2^\circ$ from the present experimental data. With the experimentally accessible quantity defined by

$$G = 2.865M^{1/2}/[2\pi^{3/2}N_A(\langle s^2\rangle/M)^{3/2}] \tag{12}$$

the quantity $z/\alpha^3$ in eq 3 can be written as

$$z/\alpha^3 = (1/5.73)GA_2^\circ \tag{13}$$

From eq 3, 13, and 6–9 we can express $A_2^\circ$ with $A_2$ and $G$ as

$$A_2^\circ = [\exp(GA_2) - 1]/G \quad \text{(FKO.m)} \tag{14}$$

$$A_2^\circ = [(1 - 0.319GA_2)^{-2.135} - 1]/(0.681G) \quad \text{(KY)} \tag{15}$$

$$A_2^\circ = -(1/G) \ln (1 - GA_2) \quad \text{(CM)} \tag{16}$$

$$A_2^\circ = A_2/(1 - GA_2/2) \quad \text{(S)} \tag{17}$$

These equations enable us to evaluate $A_2^\circ$ from the experimental data of $\langle s^2 \rangle$ and $A_2$. Since the value of $GA_2$ was found to exceed unity except at small $A_2$, eq 16 was discarded. This behavior of $GA_2$ is also observed in the data for the system polystyrene + decalin.[13] In Figure 6 $A_2°$ is plotted against $u_2$. The open circles were calculated with eq 15 and solid curve b illustrates their behavior. Broken curves a and c were obtained with eq 14 and 17, respectively. The different behavior of curves b and c in contrast to curves b and c in Figure 5 is caused by the use of the experimental data of $\langle s^2 \rangle$ instead of the theories of $\alpha$. Although curves b and c in the plot of $\Psi$ vs. $\alpha^2$ are very close to each other, curve b is more reasonable than curve c because of its consistent theoretical basis for the expansion factor $\alpha$ and the second virial coefficient $A_2$. Therefore, the value of $A_2°$ calculated with eq 15 could be taken as the most reliable one. Broken cuves a and c in Figure 6 could be considered as a measure of the uncertainty in determining $A_2°$. The values of $A_2°$ calculated with eq 15 are given in Table I. Broken curves a and b in Figure 4 were calculated with eq 11 and 10, respectively, where the parameter $z$ was calculated from the values of $A_2°$ read from curve b in Figure 6. As expected from Figure 5 eq 11 is close to the observed behavior. The discrepancy at large $\alpha$ is similar in magnitude to that observed for systems of polymer + single solvent.

Figure 6 shows that an addition of a small amount of MOEt to the binary system PMMA + BuCl causes a rapid increase in the solvent power. Around $u_2 = 0.5$ the mixed solvent acts as a good solvent for PMMA, though BuCl is a poor solvent and MOEt is a moderate solvent. This synergistic behavior of the mixed solvent can be compared with the cosolvent phenomenon, in which the mixture of two nonsolvents for a polymer behaves as a good solvent for the polymer.[5-8] As shown in the following paper we have analyzed the behavior of $A_2°$ by using the generalized expression of the Flory–Huggins equation.[25] It was found that the behavior of $A_2°$ can be explained by introducing a ternary function which depends on the volume fraction $u_2$ and the concentration $c_3$. According to the above analyses by the two-parameter theory, however, the relation between the expansion factor $\alpha$ and the second virial coefficient $A_2$ in the mixed solvent is the same as that for single solvents. Moreover, the preferential adsorption inevitable in mixed solvents does not appear to affect the relation between $A_2$ and $\alpha$ in the framework of the two-parameter theory.

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