# The Pressure and Temperature Dependences of the Second Virial Coefficients and the Chain Dimensions of Polydimethylsiloxane Solutions

Kenji Kubota, Kenji Kubo, and Kazuyoshi Ogino
*Department of Pure and Applied Sciences, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153*

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A new light-scattering optical cell was designed in order to perform light-scattering measurements at various temperatures and under pressures up to 400 kg/cm². The second virial coefficients and the radii of gyration were determined at high polymer dilutions for polydimethylsiloxane in cyclohexyl bromide at 27.0, 36.5, 47.2, and 56.2 °C, in benzene and toluene at 27.0 °C, and in chlorobenzene at 30.0 °C. The method employed to determine the dimensions of the polymer is described. By a series of measurements of polydimethylsiloxane solutions, it is shown that the second virial coefficients, the radii of gyration, and the fundamental thermodynamic properties of the solutions depend on the pressure. The correlation between values of $A_2$ and $\langle S^2\rangle^{1/2}$ shows that pressure influences these quantities through its effect on the polymer-solvent interaction parameter, $\chi$ or $z$. The values of the relative partial molar excess volume were calculated directly from the data. The obtained data were compared with the excluded volume theories and the corresponding state theories; the agreement was fair.

The most important thermodynamic variables of the systems are the composition, the temperature, and the pressure. For polymer solutions, a very extensive literature exists on the dependence of the chemical potential upon the composition and the temperature, but the pressure was generally held constant. Solution theories have traditionally emphasized an energetic difference in the chemical nature and intermolecular force. However, recent works[1–3] in polymer solution thermodynamics have shown the importance of a difference in free volume, or in degrees of thermal expansion and isothermal compressibility, between the polymer and the solvent.

By mixing the polymer and the solvent, the free volumes change towards an intermediate value characteristic of the mixture. These changes contribute strongly to the thermodynamic functions of the mixture: $\Delta H_M$, $\Delta S_M$, $\Delta G_M$ as well as $\Delta V_M$. In particular, the free volume contribution to the interaction parameter, $\chi$, is remarkable. Accordingly, a large difference in the free volume between the polymer and the solvent will influence the $\chi$ parameter strongly. This accounts for the existence of the lower critical solution temperature.[4]

The application of pressure will cause a change in the difference in the free volume through the difference of the compressibility between the polymer and the solvent and the corresponding effect on the $\chi$ parameter. Then, the effect of the pressure is remarkable. It is evident that the pressure effect on $\langle S^2\rangle$ and $A_2$ should be large. The pressure dependence of the critical solution temperature is negative near the upper critical solution temperature in the case of a negative value of $\Delta V_M$. This predicts that the Flory temperature will decrease with the pressure. The solvent becomes better for the polymer with an increase in the pressure, and $A_2$ and $\langle S^2\rangle$ should increase. Besides, the pressure dependence of the lower critical solution, where the free volume contribution is dominant, is particularly large.

Accordingly, a complete knowledge of the systems requires a knowledge of the effect of the pressure,[5] and the pressure should be included as an available independent variable.

Schulz and Lechner[5–7] studied the effect of the pressure on light scattering for polystyrene solutions. They measured up to 800 atm. The results are in semiquantitative agreement with a theoretical treatment of the pressure effects. An interesting change in the $A_2$ of polystyrene in *trans*-decalin with the pressure was observed.

Gaeckle and Patterson[8] studied the second virial coefficients and the radii of the gyration of polyisobutylene in 2-methylbutane and polystyrene in 2-butanone up to 110 atm. They showed that the corresponding state theories are good representations of the pressure effects.

McDonald and Claesson[9] examined the light-scattering properties of various pure solvents and the second virial coefficients of polystyrene in 4-methyl-2-pentanone up to 5000 atm. The polymer solution showed a limiting behavior above 2000 atm in terms of the magnitude of both the second virial coefficient and the radius of gyration.

In this work, polydimethylsiloxane in cyclohexyl bromide (theta solvant), benzene, toluene, and chlorobenzene (good solvents) were examined, using a modified Shimadzu light scattering photometer (PG-21) and a high-pressure optical cell which had been designed for this work. Polydimethylsiloxane was chosen since it has a very large thermal expansion coefficient and isothermal compressibility compared with other polymers.

## Thermodynamic Considerations

*Pressure and Temperature Dependence of* $A_2$. At low concentrations the following equation is valid:

$$-\Delta\mu_1/RT = cV_1/M + A_2c^2V_1 \qquad (1)$$

Here, $V_1$ is the molar volume of the pure solvent at the experimental temperature and pressure and $c$ is the usual concentration, *i.e.*, the weight of the polymer per volume of the solution. The second virial coefficient is related to the excess chemical potential of the solvent:

$$A_2 = -\Delta\mu_1{}^{\mathrm{E}}/RTc^2V_1 \qquad (2)$$

According to the Gibbs-Helmholtz equation, the excess chemical potential of the solvent is split into an enthalpy term, $\Delta\bar{H}_1$, and an entropy term, $\Delta\bar{S}_1{}^{\mathrm{E}}$. Thus, two corresponding terms are obtained for the second virial coefficient:

$$A_2 = A_{2,\mathrm{H}} + A_{2,\mathrm{S}} \qquad (3)$$

$$A_{2,\mathrm{H}} = -\Delta\bar{H}_1/RTc^2V_1 \qquad (4)$$

$$A_{2,\mathrm{S}} = \Delta\bar{S}_1{}^{\mathrm{E}}/Rc^2V_1 \qquad (5)$$

Then, from the temperature dependence of $A_2$ at a constant pressure and weight fraction, the values of $A_{2,\mathrm{H}}$ and $A_{2,\mathrm{S}}$ can be calculated:

$$A_{2,\mathrm{H}} = \alpha TA_2 - T(\partial A_2/\partial T)_{\mathrm{P}} \qquad (6)$$

$$A_{2,\mathrm{S}} = A_2(1-\alpha T) + T(\partial A_2/\partial T)_{\mathrm{P}} \qquad (7)$$

By combining Eqs. 4 and 5 with Eqs. 6 and 7, we obtain:

$$\Delta\bar{H}_1/RT = c^2V_1T((\partial A_2/\partial T)_{\mathrm{P}}-\alpha A_2) \qquad (8)$$

$$\Delta\bar{S}_1{}^{\mathrm{E}}/R = c^2V_1((1-\alpha T)A_2+T(\partial A_2/\partial T)_{\mathrm{P}}) \qquad (9)$$

On the other hand, from the pressure dependence of $A_2$ at a constant temperature and weight fraction, the relative partical molar excess volume is obtained:

$$\Delta\bar{V}_1/V_1 = c^2RT(-(\partial A_2/\partial P)_{\mathrm{T}}-\beta A_2) \qquad (10)$$

Here, $\alpha$ and $\beta$ are the thermal expansion coefficient and the isothermal compressibility of the solvent respectively.

*Excluded Volume Effects and the $\chi$ Parameter.* Equations 8 and 10 give $\Delta\bar{H}_1$ and $\Delta\bar{V}_1$ in the dilute region where the solution is nonuniform according to the excluded volume effect. These values cannot be directly compared with the usual heat and volume measurements made at higher concentrations where the polymer molecules interpenetrate and the solution is uniform. Consequently, in order to estimate the free energy parameter, $\chi$, from the value of $A_2$ obtained from the light-scattering measurements, the evaluation of the excluded volume effect is necessary.

According to the dilute solution theories, the nonuniformity of the solution gives rise to the penetrating function, $\Phi(z)$, in the expression of $A_2$:[10)]

$$A_2 = 4\pi^{3/2}N_{\mathrm{A}}\langle S^2\rangle^{3/2}\Phi(z)/M^2$$

$$= 4\pi^{3/2}N_{\mathrm{A}}\langle S^2\rangle^{3/2}zh(z)/M^2 \qquad (11)$$

$$z = (1/4\pi)^{3/2}(v_{2,\mathrm{sp}}^2/N_{\mathrm{A}}V_1)M^2(1-2\chi)/\langle S^2\rangle_0{}^{3/2} \qquad (12)$$

Here $z$ is the excluded volume parameter, while $v_{2,\mathrm{sp}}$ and $<S^2>_0{}^{1/2}$ are the specific volume of the polymer and the unperturbed mean-square radius of the gyration of the polymer.

Direct thermodynamic measurements of the heats and volumes of mixing leading to the values of $\Delta\bar{V}_1$ and $\Delta\bar{H}_1$ have been made between 20—80% of a polymer in general. If the values of $A_2$ of dilute polymer solutions were available for use in finding the chemical potential of the solvent for high concentrations, the values of $\Delta\bar{V}_1$ and $\Delta\bar{H}_1$ could be predicted from Eqs. 8 and 10.[8,11)] In comparison with the Flory-Huggins equation, the theoretical expression of $A_2$ at a sufficiently high concentration is written as follows:

$$A_2{}^{\mathrm{c}} = v_{2,\mathrm{sp}}^2(1/2-\chi)/V_1 \qquad (13)$$

In this equation, the excluded volume effect function $h(z)$ is absent. Therefore, $A_2{}^{\mathrm{c}}$, the second virial coefficient at a high concentration, can be obtained from the experimental values of a dilute solution through division by $h(z)$:

$$A_2{}^{\mathrm{c}} = A_2/h(z) \qquad (14)$$

Moreover, $h(z)$ can be evaluated from $<S^2>$ using excluded volume effect theories, and then $A_2{}^{\mathrm{c}}$ or $\chi$ can be estimated. Transforming the concentration into volume fraction, we obtain:

$$\phi_2 = cv_{2,\mathrm{sp}} \qquad (15)$$

A change in the volume on mixing, $\Delta V_{\mathrm{M}}$, is symmetrical in the volume fractions of the components, *i.e.*:

$$\Delta V_{\mathrm{M}}/V = D\phi_1\phi_2 \qquad (16)$$

By differentiating Eq. 16 with the number of the solvent, we obtain:

$$\Delta\bar{V}_1/V_1 = D\phi_2{}^2 \qquad (17)$$

Consequently, from Eqs. 10 and 17 we obtain:

$$D = (RT/v_{2,\mathrm{sp}}^2)(-(\partial A_2{}^{\mathrm{c}}/\partial P)_{\mathrm{T}}-\beta A_2{}^{\mathrm{c}}) \qquad (18)$$

On the other hand, by combining Eqs. 13 and 14 we obtain:

$$\chi_{1,\mathrm{H}} = -T(\partial\chi/\partial T)_{\mathrm{P}} = T(\partial(V_1TA_2{}^{\mathrm{c}}/v_{2,\mathrm{sp}}^2)/\partial T)_{\mathrm{P}}$$

$$= (V_1T/v_{2,\mathrm{sp}}^2)((\partial A_2{}^{\mathrm{c}}/\partial T)_{\mathrm{P}}-\alpha A_2{}^{\mathrm{c}}) \qquad (19)$$

Thus, the pressure dependence of the parameters can be obtained from the second virial coefficients for dilute solutions.

## Experimental

*Materials.* The polydimethylsiloxane is from the Shinetsu Chemical Co., with $50\times10^4$ CS and $10\times10^4$ CS. The $M_{\mathrm{V}}$ values of these polymers are $14.6\times10^4$ (1) and $10.6\times10^4$ (2) respectively.[12)] The polydimethylsiloxane (PDMS)-(1) was fractionated by means of the fractional solution method into 13 fractions, using benzene (good solvent) and methanol (poor solvent). The 12th fraction (1F12) of $M_{\mathrm{W}}=57.8\times10^4$ ($M_{\mathrm{W}}/M_{\mathrm{N}}<1.02$) was used in this work. The PDMS-(2) was fractionated in the same way into 8 fractions, and the 3rd fraction (2F3) of $M_{\mathrm{W}}=7.30\times10^4$ was used. All the solvents (cyclohexyl bromide, benzene, toluene, and chlorobenzene) were reagent-grade and were further purified before use.

*Apparatus.* A high pressure optical cell was constructed. The cell, of a cylindrical form, was made of brass (Fig. 1). The windows were made of quartz (12 mm×5 mm) and were

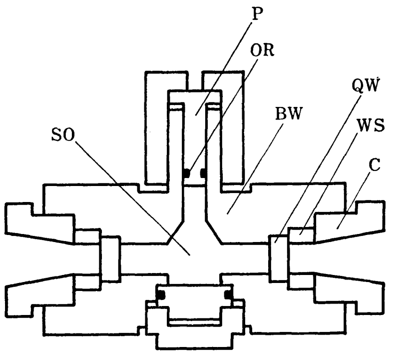

Fig. 1. High pressure optical cell (side view): (P) piston; (B) body; (CP) cap; (OR) O-ring gasket; (QW) quartz window; (WS) window spacer; (SO) solution.

tightened using the conventional unsupported area technique.[13] The capacity of the cell was *ca.* 5 cm$^3$. All the O-rings were of Teflon, were stored in pure solvents for about 1 month prior to use, and were cleaned with an ultrasonic cleaner before measurement. The dimensions of the cell were designed so that the cell could be used for the Shimadzu light-scattering photometer (PG-21) without any modification. The pressure was generated by compressing the polymer solutions directly. The pressure was determined by a solid-front pressure gauge (Heise Bourdon Gauge).

*Procedure.* The polymer solution was made up to approximately the required concentration and was cleared of dust by ultracentrifugation. The optical cell was connected to the pressure tube (1/16″ o.d. and 0.5 mm i.d.) and heated to the required temperature, and the solution was compressed to the required pressure. About one hour was necessary for the solution to become homogeneous and for the pressure gradient to be got rid of before measurements. The concentration of the solution was determined by weighing the solution and the polymer after measurements. The scattered light intensity was measured at the angle of 90°.

*Determination of the Optical Constant,* K, *at High Pressures.* In order to determine the absolute scattered intensity, a relative method was employed. The intensity of the solution was measured under the same conditions as those of the solvent.

The radius of the gyration of the polymer is determined by measurements of the wavelength dependence or the scattering-angle dependence or disymmetry of the scattered intensity. In this work, the following method was employed in order to determine $P(90)$, the value of the scattering function at the angle of 90°. It is assumed that the molecular weight of the polymer is constant as a function of the pressure; that is, no aggregation or decomposition happens.

According to Debye,[14] the following equation in terms of the Rayleigh ratio is yielded:

$$Kc/R_{90} = 1/MP(90) + 2A_2c \qquad (20)$$

As this relation is still valid at high pressure,

$$K^*c/R_{90} = 1/MP(90) + 2A_2c \qquad (21)$$

where $K^* = Kf$. $K$ is the optical constant at 0 kg/cm$^2$. The factor, $f$, which indicates the change in $K$ with the pressure has a magnitude less than unity.

Substitution and rearrangement give:

$$Kc/R_{90} = 1/MP(90)f + 2A_2c/f \qquad (22)$$

Here, the direct measurable quantities as a function of the pressure are $R_{90}$ and $c$. Plotting $Kc/R_{90}$ *vs.* $c$ gives an intercept value which is $1/MP(90)f$ and a slope of $2A_2/f$. In the case of $\langle S^2\rangle^{1/2} \ll \lambda$, $P(90)$ is unity, and as the optical constant, $K$, does not vary with the molecular weight of the polymer, by measuring the scattered intensity of the solution of the polymer with the radius of gyration, which is much smaller than the wavelength of the light, $f$ is determined from the intercept value to be as is expressed in Eq. 23:

$$Kc/R_{90} = 1/Mf + 2A_2c/f \qquad (23)$$

Using this value of $f$, $P(90)$ can be determined from the intercept and $A_2$ can be determined from the slope obtained from Eq. 22. With this value of $P(90)$, $\langle S^2\rangle$ is determined. PDMS (2F3) is used in order to determine $f$. The radius of the gyration of 2F3 is obtained by extrapolating the data given by Schulz and Haug;[15] it gives *ca.* 60Å for $\langle S^2\rangle_0^{1/2}$. This is much smaller than the wavelength of the light, and the assumption $P(90) = 1$ is reasonable.

## Results

The absolute Rayleigh ratio of cyclohexyl bromide as a function of the pressure is shown in Fig. 2 as an example, while the $f$-factor of PDMS in cyclohexyl bromide are shown in Fig. 3. The Rayleigh ratio decreases linearly with the pressure. This can be intuitively expected, for an increase in the pressure tends to produce a more ordered state.[9] The magnitude of the decrease is variable, depending on the solvents. The changes in the Rayleigh ratio of the solvents, $(\partial \ln R^\circ_{90}/\partial P)_T$, are $2.76\times10^{-4}$, $3.81\times10^{-4}$, $3.38\times10^{-4}$, and $1.01\times10^{-4}$ 1/kg cm$^{-2}$ for cyclohexyl bromide, benzene, toluene, and chlorobenzene respectively. It seems that there is a correlation between the magnitude of compressibility and that of the decrease in the Rayleigh ratio for the solvents.

The values of $A_2$ obtained for each solvent are summarized in Table 1. The values of $A_2$ are shown in Figs. 4 and 5 as a function of the pressure for PDMS (1F12) and of $\langle S^2\rangle^{1/2}$ in Fig. 6 as a function of the temperature under various pressures for 1F12 in cyclohexyl bromide. These values under 0 kg/cm$^2$ agree well with the results obtained by Schulz and Haug.[15] The unperturbed dimensions of the polymer were

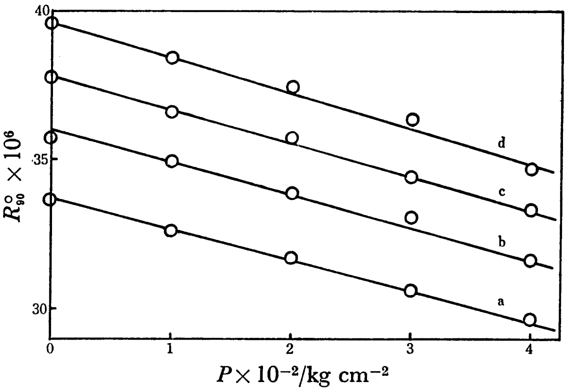

Fig. 2. Absolute Rayleigh ratio of cyclohexyl bromide as a function of pressure at 27.0 °C (a), 36.5 °C (b), 47.2 °C (c), and 56.2 °C (d).

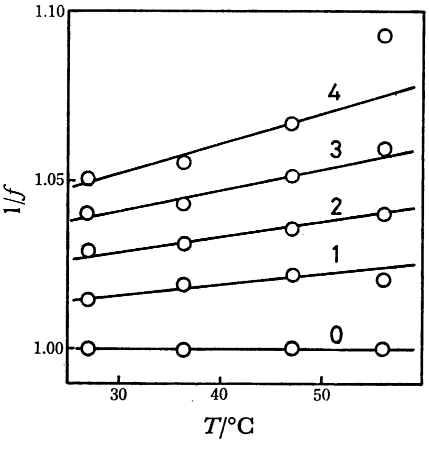

Fig. 3. $f$-Factor for PDMS in cyclohexyl bromide as a function of temperature unde 0(0), 100(1), 200(2), 300(3), and 400(4) kg/cm$^2$.

Table 1. Second virial coefficients of polydimethylsiloxane solutions

| Pressure (kg/cm$_2$) | $A_2\times 10^5$ cm$^3$ mol/g$^2$ | | | |
|---|---|---|---|---|
| | Cyclohexyl bromide | | | |
| | 27.0 °C | 36.5 °C | 47.2 °C | 56.2 °C |
| 0 | −0.158 | 3.62 | 6.57 | 9.54 |
| 100 | 0.258 | 4.37 | 7.39 | 10.0 |
| 200 | 0.538 | 5.04 | 7.94 | 10.4 |
| 300 | 0.782 | 5.48 | 8.20 | 10.7 |
| 400 | 0.995 | 5.76 | 8.52 | 11.1 |
| | Benzene | Toluene | Chlorobenzene | |
| | 27.0 °C | 27.0 °C | 30.0 °C | |
| 0 | 29.5 | 45.0 | 10.4 | |
| 100 | 30.2 | 44.6 | 11.0 | |
| 200 | 30.2 | 46.3 | 11.6 | |
| 300 | 30.3 | 46.7 | 12.1 | |
| 400 | 30.0 | 46.7 | 12.5 | |

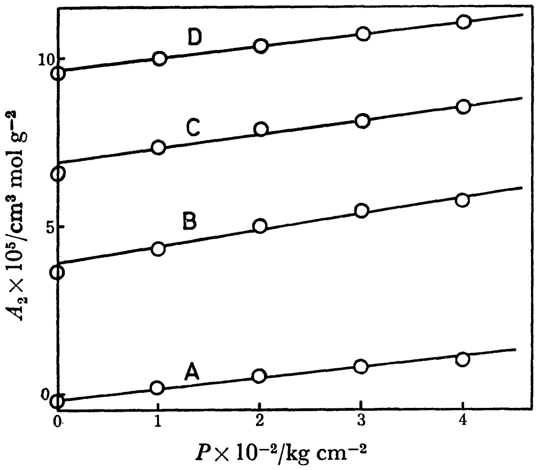

Fig. 4. The second virial coefficient, $A_2$, as a function of pressure for PDMS (1F12) in cyclohexyl bromide at 27.0 °C (A), 36.5 °C (B), 47.2 °C, and 56.2 °C (D).

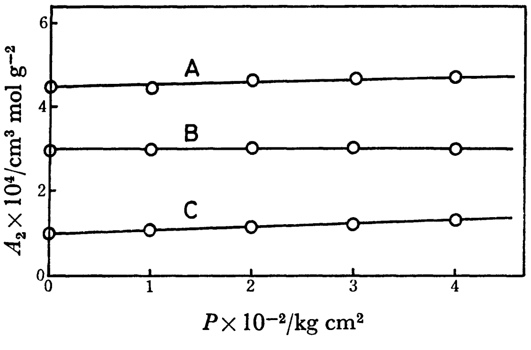

Fig. 5. The second virial coefficient, $A_2$, as a function of pressure for PDMS (1F12) in toluene at 27.0 °C (A), in benzene at 27.0 °C (B), and in chlorobenzene at 30.0 °C (C).

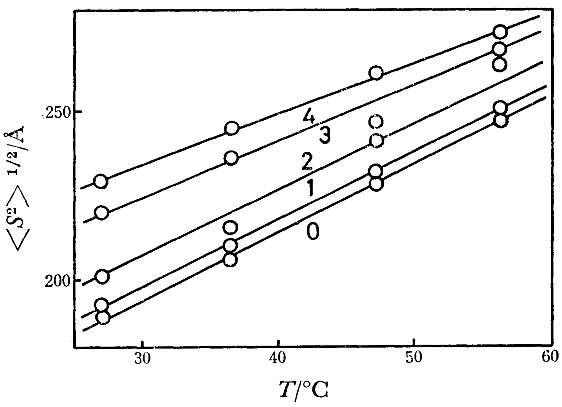

Fig. 6. The radius of gyration, $<S^2>^{1/2}$, as a function of temperature for PDMS (1F12) in cyclohexyl bromide under 0(0), 100(1), 200(2), 300(3), and 400(4) kg/cm$^2$.

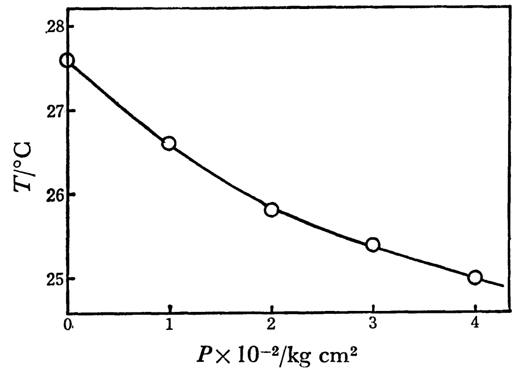

Fig. 7. $\theta$-Temperature as a function of pressure for PDMS in cyclohexyl bromide.

determined by reading off the $<S^2>^{1/2}$ *vs.* temperature plot at the temperature of $A_2=0$. In Fig. 7, the $\theta$-temperatures for various pressures determined in this way are shown. $\theta$-Temperature decreases with the pressure and decreases more slowly as the pressure increases. $\theta$-Temperature seems to have a tendency to reach a limiting value at high pressures. Both $A_2$ and $<S^2>^{1/2}$ increases with the pressure, in accord with negative values of $\Delta V_m$. The change in $<S^2>^{1/2}$ with the pressure is more rapid than that of $A_2$. The dimension increases about 20% under 400 kg/cm$^2$. Accordingly, the effect of the pressure makes the solvent better for the polymer.

Using Eqs. 6 and 7, $A_2$ can be separated into $A_{2,H}$ and $A_{2,S}$. These values are summarized in Table 2. At $\theta$-temperature $-A_{2,H}$ and $A_{2,S}$ (these cancel each other out) increase considerably with the pressure and the solvent becomes more endothermal. At higher temperatures, however, $-A_{2,H}$ decreases with the pressure and the solvent becomes less endothermal. From this fact and from the fact that $A_2$ increases with the pressure, it is evident that the contribution of the entropy term is larger than the enthalpy term.

In polar solvents, cyclohexyl bromide and chlorobenzene, the extent of the change in $A_2$ with the pressure is larger than in good solvents, benzene and toluene. In particular, $A_2$ in benzene seems to be independent of the pressure.

From the pressure dependence of $A_2$ and Eq. 10, the values of the relative partial molar excess volume were obtained; they are tabulated in Table 3. It is evident from this table that the volume contracts on mixing for all solvents.

TABLE 2. $A_{2,\mathrm{H}}$ AND $A_{2,\mathrm{S}}$ OF PDMS IN CYCLOHEXYL BROMIDE

| Pressure (kg/cm²) | $A_{2,\mathrm{H}}\times10^3$ cm³ mol/g² | | | | $A_{2,\mathrm{S}}\times10^3$ cm³ mol/g² | | | |
|---|---|---|---|---|---|---|---|---|
| | θ-point | 35 °C | 45 °C | 55 °C | θ-point | 35 °C | 45 °C | 55 °C |
| 0 | −1.26 | −1.05 | −0.859 | −0.779 | 1.26 | 1.08 | 0.924 | 0.871 |
| 100 | −1.34 | −1.10 | −0.851 | −0.679 | 1.34 | 1.14 | 0.920 | 0.775 |
| 200 | −1.43 | −1.16 | −0.824 | −0.642 | 1.43 | 1.20 | 0.897 | 0.742 |
| 200 | −1.45 | −1.17 | −0.838 | −0.627 | 1.45 | 1.21 | 0.906 | 0.732 |
| 400 | −1.52 | −1.20 | −0.818 | −0.600 | 1.52 | 1.25 | 0.899 | 0.709 |

TABLE 3. RELATIVE PARTIAL MOLAR EXCESS VOLUMES OF SOLVENTS IN PDMS SOLUTIONS

| $\Delta\bar{V}_1\times10^6$ cm³/mol ($c$=0.01 g/cm³) | | | |
|---|---|---|---|
| Cyclohexyl bromide | | | |
| 27.0 °C | 36.5 °C | 47.2 °C | 56.2 °C |
| −14.1 | −15.2 | −16.3 | −16.4 |
| Benzene | Toluene | Chlorobenzene | |
| 27.0 °C | 27.0 °C | 30.0 °C | |
| −6.28 | −21.5 | −16.5 | |

## Discussion

*Absolute Rayleigh Ratio of the Solvents.* The values in Fig. 2 are the absolute Rayleigh ratios of the solvents obtained in the manner described above. The experimental values of this ratio were reproducible within the limit of experimental error. The isotropic Rayleigh ratio is defined as follows:[16]

$$R_{\mathrm{iso}} = (2\pi^2/\lambda_0^4)kT(\tilde{n}(\partial\tilde{n}/\partial P))^2/\beta \tag{24}$$

By experiments, the total Rayleigh ratio is measured. Since a statistical independence is assumed for the assorted fluctuation phenomena,

$$R_{\mathrm{total}} = R_{\mathrm{iso}} + R_{\mathrm{aniso}} \tag{25}$$

The anisotropic component of the Rayleigh ratio is defined using the degree of depolarization, $\rho_{\mathrm{u}}$, and $R_{\mathrm{total}}$ is written as follows:

$$R_{\mathrm{total}} = R_{\mathrm{iso}}(6+6\rho_{\mathrm{u}})/(6-7\rho_{\mathrm{u}}) \tag{26}$$

According to McDonald and Claesson,[9] $R_{\mathrm{aniso}}$ is nearly independent of the pressure. The change in $R_{\mathrm{total}}$ with the pressure is determined by the contribution of the $R_{\mathrm{iso}}$ term in Eq. 25; therefore, the degree of depolarization increases with the pressure, and the contribution of $R_{\mathrm{aniso}}$ to $R_{\mathrm{total}}$ increases. This means that the refractive index of the solvent increases with the pressure, but the $(\partial\tilde{n}/\partial P)_{\mathrm{T}}$ term decreases more rapidly with the pressure. Since the anisotropic characteristics are related to the structural properties of the liquids, a further examination is warranted. The refractive index of benzene under high pressures is available,[17] and the calculation of the depolarization can be done. The pressure dependence of the Rayleigh ratio of benzene was examined by McDonald and Claesson.[9] Their results are in good agreement with the above.

*The Pressure Dependence of the θ-Temperature.* In the PDMS+cyclohexyl bromide solution, the θ-temperature decreases with the pressure. At the θ-temperature, $A_2$ becomes zero and $\mathrm{d}\theta/\mathrm{d}P$ is expressed by the following equation:

$$\mathrm{d}\theta/\mathrm{d}P = -(\partial A_2/\partial P)_{\mathrm{T}}/(\partial A_2/\partial T)_{\mathrm{P}} \tag{27}$$

From the values of $A_2$ tabulated in Table 1, $(\partial A_2/\partial T)_{\mathrm{P}}$ and $(\partial A_2/\partial P)_{\mathrm{T}}$ are obtained. Under 0 kg/cm² the θ-temperature is 27.6 °C. The value of $(\partial A_2/\partial T)_{\mathrm{P}}$ at 27.6 °C and under 0 kg/cm² is $4.72\times10^{-6}$, while that of $(\partial A_2/\partial P)_{\mathrm{T}}$ is $4.5\times10^{-8}$, which gives $\mathrm{d}\theta/\mathrm{d}P=-0.95\times10^{-2}$ deg/kg cm$^{-2}$. The value of the corresponding $\mathrm{d}\theta/\mathrm{d}P$ obtained from the experiments (Fig. 7) is $-0.96\times10^{-2}$ deg/kg cm$^{-2}$. These values are consistent.

The pressure coefficient of a critical solution temperature is given by the relation:[18]

$$\mathrm{d}T_{\mathrm{c}}/\mathrm{d}P = T(\partial\Delta\bar{V}_1/\partial\phi_2)_{\mathrm{c}}/(\partial\Delta\bar{H}_1/\partial\phi_2)_{\mathrm{c}} \tag{28}$$

In the vicinity of the upper critical solution temperature, the process of mixing is endothermal, and $(\partial\Delta\bar{H}_1/\partial\phi_2)_{\mathrm{C}}$ must be negative. A negative value of the volume change on mixing is obtained (see Table 3), so $(\partial\Delta\bar{V}_1/\partial\phi_2)_{\mathrm{C}}$ is positive. Consequently, $\mathrm{d}T_{\mathrm{C}}/\mathrm{d}P$ must be negative. This is in good agreement with the negative value of $\mathrm{d}\theta/\mathrm{d}P$. The pressure coefficient of the upper critical solution temperature of PDMS in cyclohexyl bromide must be small, of the order of $10^{-2}$. According to Gaeckle and Patterson,[8] the pressure dependence of $A_2$ in the vicinity of the lower critical solution temperature, polyisobutylene in 2-methylbutane, is very large, and $(\partial A_2/\partial P)_{\mathrm{T}}$ is $2.2\times10^{-6}$ cm³ mol g$^{-2}$ bar$^{-1}$. The $\mathrm{d}T_{\mathrm{C}}/\mathrm{d}P$ of the lower critical solution temperature is 0.44 deg/bar, in contrast to PDMS in cyclohexyl bromide. This behavior is due to the difference in the pressure contribution. At the lower critical solution temperature, the free volume contribution is dominant and the pressure dependence is large. At the upper critical solution temperature, polystyrene in cyclohexane,[19] $\mathrm{d}T_{\mathrm{C}}/\mathrm{d}P$ is in the order of $10^{-3}$ and changes in sign depending on the molecular weight. These are reflected in the extent of $(\partial A_2/\partial P)_{\mathrm{T}}$.

*Pressure and Temperature Dependence of* $\langle S^2\rangle_0$. The values of $\langle S^2\rangle^{1/2}$ at the θ-temperature give the unperturbed chain dimensions of the polymer. The radius of gyration is related to the coil expansion coefficient, α:

$$\langle S^2\rangle = \langle S^2\rangle_0\alpha^2 \tag{29}$$

The coil expansion coefficient, α, is changed through pressure and temperature. For PDMS in cyclohexyl bromide at different temperatures and pressures, the α's were plotted against the corresponding values of $A_2$, as is shown in Fig. 8. A single curve was obtained. This shows that the effect of the pressure on the chain dimension is not at all different from that of the temperature and that $\langle S^2\rangle_0$ is a function of the pressure. According to Schulz and Lechner,[5–7] the radius of gyration changes with the pressure, although $A_2$ remains nearly constant, and the unperturbed dimensions are influenced by the pressure. Moreover, if the pressure dependence of the unperturbed dimension is not included in the estimation of $\alpha$, the plot of $\alpha$ against $A_2$ does not give a single curve.[8] Therefore, it must be concluded that $<S^2>_0$ is influenced by the pressure.

For the same value of $A_2$ under various pressures, $<S^2>^{1/2}$ for PDMS in cyclohexyl bromide increases with the pressure. This indicates that the unperturbed dimension is an increasing function of the pressure. The unperturbed chain dimension, $<S^2>_0^{1/2}$, was determined by interpolating the $\theta$-temperature in the $<S^2>^{1/2}$ plot against the temperature under various pressures, as is shown in Fig. 6. These values were 191, 193, 200, 216, and 227 Å for 0, 100, 200, 300, and 400 kg/cm² respectively. The increase in the dimensions with the pressure reaches *ca.* 20% at 400 kg/cm². On the other hand, the temperature dependence of the unperturved chain dimension $(\partial \ln <R^2>_0/\partial T)_P$ of PDMS is $0.75\times10^{-3}$ l/deg. Since $\theta$-temperature decreases with the pressure, the increase in the unperturbed chain dimension is directly due to the pressure. As Gaeckle and Patterson have shown, this result indicates the pressure effect of the solvent packing on the population of conformations or rotational isomers of polymer. It is usually believed that the solvent has little effect on the unperturbed dimensions of a polymer, but in the present case it should not be disregarded. Even a small effect of solvent packing on the rotational isomer equilibrium would have important consequences in the polymer solution thermodynamics. In the case of PDMS, this effect is large. PDMS has, as an irregular form, pendant $CH_3$ groups spaced by comparatively long Si–O and Si–C bonds. The irregularity in the cross section of the chain will make the effect of the solvent packing large.[20]

These results show that $\alpha$ should be determined considering the pressure effect on the unperturbed chain dimension and that the excluded volume effect should be examined by including the pressure effect as well as the temperature.

*Pressure and Temperature Dependence of* $A_2$ *and* $<S^2>$. The excluded volume effect was examined at different temperatures and pressures using Eq. 11 and the corresponding value of $A_2$ given in Table 1, while the values of $zh(z)$ were calculated for PDMS in cyclohexyl bromide. Figure 8 shows the relation between $\alpha$ and $zh(z)$; it may be seen that the points for different temperatures and pressures do approximately fall on a single curve, as expected from the theory. This is not changed even by the effects of polydispersity on the values of $A_2$ and $<S^2>^{1/2}$, as has examined by Gaeckle and Patterson.[8]

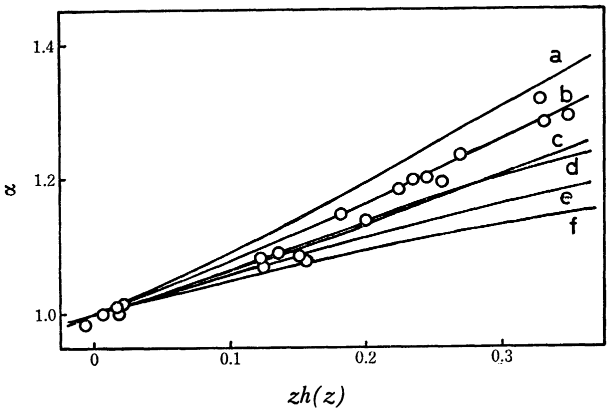

Fig. 8. The coil expansion factor, $\alpha$, for PDMS (1F12) in cyclohexyl bromide at various temperatures and pressures. Curves a, b, and c are given by the Fixman-Stockmayer expression for $\alpha$, Eq. 30, and the KCKR theory for $A_2$ with $\rho$ equal to 0, 0.4, and 1, respectively. Curves d, e, and f are given by the Flory-Stockmayer modification, Eq. 31, and the KCKR theory for $A_2$ with $\rho$ equal to 0, 0.4, and 1, respectively. The abscissa, $zh(z)$, is proportional to $A_2$.

A number of closed expressions for the expansion factor, $\alpha$, of the polymer relating to $A_2$ or $z$ are also presented. In the usual treatment, the penetrating function, $\Phi$, is plotted against $\alpha$. In this work, however, in order to estimate $A_2{}^c$ or $\chi$, $\alpha$ was plotted against $zh(z)$. This plot makes clear the tendency of the change in $\alpha$. The abscissa in Fig. 8, $zh(z)$, was obtained from the Krigbaum-Carpenter-Kaneko-Roig (KCKR) theory[21] with three values of the $\rho$-parameter: 0, 0.4, and 1. The $\rho$-parameter depends on the ratio of the total number of intramolecular contacts to the number of long-range contacts. The evaluation of $z$ from $\alpha$ was obtained by using the Fixman-Stockmayer expression[22] and the Flory-Stockmayer modification[23]:

$$\alpha^3 - 1 = 2z \tag{30}$$

$$\alpha^5 - \alpha^3 = 1.276z \tag{31}$$

The resulting six curves of $\alpha$ against $zh(z)$ are shown in Fig. 8. It is noticeable that $zh(z)$ is equal to $\alpha^3\Phi$. The experimental data are well expressed by Eq. 30 and $\rho=0.4$.

The penetrating function, $\Phi$, was also examined. Five conjugate closed expressions were compared with the experimental data. These were the Flory[24]-Flory, Krigbaum, Orofino:[25] Flory, Stockmayer modification[23]-Flory, Krigbaum, Orofino modification;[23] Fixman[22]-Kurata;[26] Yamakawa-Tanaka;[27] and Casassa[28] equations. The experimental points were in better agreement with the Casassa equation than the others. The Casassa equation corresponds to the KCKR theory with the $\rho$-parameter equal to 0. These results show that pressure effect on the excluded volume effect is quite similar to the temperature effect.

*Relative Partial Molar Excess Volumes and Heats of the Solvent.* In order to evaluate the volumes and heats of dilution, Eqs. 8 and 10 were used. In Table 2, $A_{2,H}$ and $A_{2,S}$ are shown, while in Table 3, the $\Delta \bar{V}_1$ values are tabulated.

For all the solvents the $\Delta \bar{V}_1$ values were negative, and the absolute value of $\Delta \bar{V}_1$ for cyclohexyl bromide decreases with the temperature. Throughout the pressure range of the experiment, $(\partial A_2/\partial P)_T$ was nearly constant, and the pressure dependence of $\Delta \bar{V}_1$ was not remarkable. However, according to McDonald and Claesson,[9] $A_2$ reaches a limiting value at a high pressure. Consequently, $(\partial A_2/\partial P)_T$ becomes zero and the volume of dilution at a high pressure is directly related to the limiting value of $A_2$. Their results show that the change in the volume on mixing at a high pressure decreases and reaches a limiting value.

The value of $\Delta\bar{V}_1$ varies depending on the solvent. However, the values for the polar solvents, cyclohexyl bromide and chlorobenzene, are very similar. The value of $\Delta\bar{V}_1$ for cyclohexyl bromide depends mainly on $(\partial A_2/\partial P)_T$. On the contrary, those of the good solvents, benzene, toluene, and chlorobenzene, depend mainly on the term of $\beta A_2$ in Eq. 10. This is because the value of $A_2$ is about ten times larger than that for the $\theta$-solvent. In the case of polyisobutylene in 2-methylbutane, $(\partial A_2/\partial P)_T$ term is much larger than $\beta A_2$ term. For $\theta$-solvent the $(\partial A_2/\partial P)_T$ term is dominant over $\Delta\bar{V}_1$.

In comparing $A_{2,S}$ with $A_{2,H}$, the contribution of $A_{2,S}$ is larger to $A_2$ and the pressure effect is effectively reflected in the entropy term.

The KCKR theory was used to obtain the $h(z)$ function in order to furnish values of $A_2^c$ for use in Eqs. 18 and 19. In this theory, the values of the ρ-parameter equal to 0, 0.2, and 1 give results corresponding to the well-known Casassa,[28] Kurata-Yamakawa,[26] and Flory-Krigbaum[29] theories respectively. In accordance with the KCKR[21] and Gaeckle and Patterson,[8] and from a comparison with the experimental results shown in Fig. 8, an intermediate value of 0.4 was used for the ρ-parameter in evaluating $h(z)$. Then the $h(z)$ function was calculated from the KCKR theory, and $A_2^c$ was obtained from the values of $A_2$ in a dilute solution. From Eq. 13 the χ-parameter was obtained. The χ-parameter decreases with the temperature and the pressure.

The values of $D$ at the temperature of 27.0, 36.5, 47.2, and 56.2 °C for PDMS in cyclohexyl bromide in Eq. 18 were obtained; they were $-1.08\times10^{-3}$, $-1.26\times10^{-3}$, $-1.00\times10^{-3}$, and $-0.878\times10^{-3}$ respectively.

From the change in $A_2$ at zero pressure, values of the enthalpic parameter, $\kappa$, were obtained for PDMS cyclohexyl bromide. They were 0.197 at 27.0 °C and 0.178 at 56.2 °C. The corresponding values of the entropic parameter, $\psi$, were 0.196 at 27.0 °C and 0.194 at 56.2 °C.

*Comparison of the Pressure Dependence of* A$_2$ *with the Predictions of Newer Theories.* The second virial coefficient is related to the polymer-solvent interaction parameter, χ, through Eqs. 11 and 12. The pressure dependence of χ can be predicted using a newer theory of polymer solution. The following equations were used to predict the pressure dependence of χ and that of $A_2^c$ in the concentrated range of the polymer solution:

$$\chi_1/c_1 = -\tilde{U}_1\nu^2/\tilde{T}_1 + (1/2)\tilde{C}_{p,1}(\tau+\pi\tilde{P}_1\tilde{V}_1^2/(\tilde{P}_1\tilde{V}_1^2+1))^2 \quad (32)$$

$$\chi_1 = (P_1^*V_1^*/\tilde{V}_1RT)(A^2\alpha T/2+Y) - V_1^*Q/R(s_1/s_2)^2 \quad (33)$$

$$\chi_1/c_1 = (1/\tilde{V}_1\tilde{T}_1)(1-(P_2^*/P_1^*)^{1/2}(\tilde{V}_1/\tilde{V}_2))^2 + \delta \quad (34)$$

Equations 32, 33, and 34 are given by the Patterson theory, the Flory theory, and the solubility parameter theory respectively.

Here $\tilde{U}_1$ and $\tilde{C}_{P,1}$ are the reduced configurational energy and the heat capacity of the pure solvent. $\tilde{P}_1$, $\tilde{V}_1$, and $\tilde{T}_1$ are the reduced pressure, the volume, and the temperature of the solvent. $P_1^*$, $V_1^*$, and $T_1^*$ are the characteristic pressure, volume, and temperature of the solvent. $A$ and $Y$ are defined as follows;

$$A = (1-T_1^*/T_2^*)(P_2^*/P_1^*) - (s_2/s_1)(X_{12}/P_1^*) \quad (35)$$

$$Y = (X_{12}/P_1^*)(s_2/s_1)^2 \quad (36)$$

The Flory theory essentially predicts these quantities, using a van der Waals model of the liquid state and a partition function similar to the Hirschfelder-Eyring cell partition function.[30] Then,

$$\tilde{U}_1 = -\tilde{V}_1^{-1} \quad (37)$$

$$\tilde{C}_{p,1}^{-1} = (1-(2/3)\tilde{V}_1^{-1/3}) -2(1-\tilde{V}_1^{1/3})/(\tilde{P}_1\tilde{V}_1^2+1) \quad (38)$$

The τ-parameter is related to the difference between the thermal expansion coefficient of the solvent and the polymer, and is defined by:

$$\tau = 1 - T_1^*/T_2^* \quad (39)$$

The $\nu^2$-parameter is related to the difference in cohesive energy and size between the solvent and the polymer segment. The π-parameter is similarly related to the difference between the reduction parameter, $P^*$, of the components and is defined by:

$$\pi = P_1^*/P_2^* - 1 \quad (40)$$

$c_1$ is the number of external degrees of freedom of the solvent molecule. This is calculated from the relation:

$$c_1 = P_1^*V_1^*/RT_1^* \quad (41)$$

In the Flory theory, the $X_{12}$ parameter measures the interchange energy on the formation of contacts between the solvent and the polymer, $Q$ is analogously defined to represent the entropy arising from the interchange of neighboring molecules, and $s_1$ and $s_2$ denote the number of surface sites for segments of the respective species.

In treating the thermodynamics of the PDMS solutions, the $\tau$, $\pi$, and $c_1$ parameters were determined from Eqs. 39, 40, and 41. Moreover, $\nu^2$, $X_{12}$, $Q$, and $\delta$ were decided to fit with the zero pressure data of $A_2$.

The pressure dependence of $A_2$ was predicted from Eqs. 32, 33, and 34 using the parameters decided as above. The evaluation of $A_2$ from χ was done by means of the KCKR theory.

The values of $(\partial A_2/\partial P)_T$ predicted by Eq. 34 were all overestimated. Equation 34 was obtained by combining the solubility parameter theory with the corresponding state theory. In the solubility parameter theory, the Berthelot relation is assumed for the energy of the (1—2) contacts relative to the (1—1) and (2—2) contacts. Also, the parameter $\delta$ expresses the correction of entropy. In PDMS solution, the contribution of the entropy is unusually large. Consequently, the error from $\delta$ may be large. Besides, as Flory has described,[31] the Berthelot relation is not a good assumption for the polymer solutions.

For cyclohexyl bromide and chlorobenzene solutions, the values of $A_2$ predicted by Eqs. 32 and 33 were underestimated. Also, the negative values of $(\partial A_2/\partial P)_T$ were obtained. The reason for this is that these solvents are both polar solvents, and that the configurational energy is not expressed in the form of $1/V$ which was assumed by Flory[2] for liquids. Especially, for chlorobenzene $(\partial U/\partial V)_T$ is an increasing function of the volume at a constant temperature.[32] Therefore, the equation of state defined by Flory is not in conformity with the polar solvents.

For benzene and toluene, the curves of $A_2$ predicted by Eq. 32 are a little underestimated compared with the experimental results. The fitted $v^2$ parameter is small, corresponding to $X_{12}=4.54$ and 3.72 cal/cm$^3$ respectively, as obtained from the relation of $X_{12}=v^2P_1^*$. The slopes predicted from Eq. 32 are $-4.0\times10^{-8}$ and $-1.0\times10^{-8}$ cm$^3$ mol g$^{-2}$/kg cm$^{-2}$ at 27.0 °C for benzene and toluene. The predicted values of $\chi$ at 27.0 °C under zero pressure are in good agreement with the results reported by Kuwahara.[33] They are 0.48 for benzene and 0.46 for toluene at 25.0 °C; on the other hand, in this experiment 0.47 and 0.44 were found respectively.

The $c_1v^2$ term in Eq. 32 increases with the pressure, and the interchange energy contribution increases. However, the $\tilde{C}_{P,1}$ term decreases with the pressure, and the effect of the pressure on the free volume or the equation of state term makes the polymer more soluble to the solvent. This suggests the significance of the contribution of the free volume. Indeed, the $\chi_{1,H}$ term predicted from Eq. 32 decreases with the pressure. In the Patterson theory, the $Q$ term in the Flory theory is neglected. For PDMS solutions the contribution of the $Q$ term to $\chi$ is usually large;[34] consequently, the entropy term of $\chi$ in the Patterson theory was overestimated and $(\partial A_2/\partial P)_T$ was underestimated. However, this behavior of $\chi_{1,H}$ is in agreement with the behavior of $A_{2,H}$ of the cyclohexyl bromide solution at higher temperatures.

For benzene the curve of $A_2$ predicted from Eq. 33 was also examined. The $(\partial A_2/\partial P)_T$ predicted from Eq. 33 using values of $X_{12}$ and $Q$ parameter equal to 5.26 cal/cm$^3$ and $-0.01$ cal/cm$^3$ deg obtained by Flory and Shih[34] was underestimated and negative. The predicted value of $(\partial A_2/\partial P)_T$ was $-2.5\times10^{-8}$ cm$^3$ mol g$^{-2}$/kg cm$^{-2}$ at 27.0 °C. $\chi_{1,H}$ which is given by the $\chi_{1,H}=-T(\partial\chi/\partial T)$ relation; $\chi$ is defined by Eq. 33 and decreases with the pressure. Also, the free volume term of $\chi$ in Eq. 33 decreases with pressure. However, for a benzene solution the free volume term or the equation of state term contribution to the free energy predicted from Eq. 33 is unusually small and the interchange energy contribution is large. PDMS has an extremely large thermal expansion coefficient and isothermal compressibility compared to the other polymers, for example, polystyrene; it corresponds to the small values of $P^*$ and $T^*$. Consequently, the $A$ parameter (Eq. 35) is small. Because of this, the contribution of $X_{12}$ to $\chi$ is dominant.

For polyisobutylene in 2-methylbutane, which gives a $\theta$-temperature associated with the lower critical solution temperature of 45 °C, the free volume contribution is dominant and the $(\partial A_2/\partial P)_T$ predicted from Eq. 32 is positive and large. Its value is $2.2\times10^{-6}$ and $3.4\times10^{-6}$ cm$^3$ mol g$^{-2}$/kg cm$^{-2}$ at 24 and 57 °C respectively. These values are in good agreement with the results of Gaeckle and Patterson.[8] This means that the pressure effect is well explained when the free volume contribution is dominant. In the vicinity of the upper critical solution temperature, the energy contribution is predominant over the free volume contribution, and the energy contribution predicted from the corresponding state theory is overestimated.

This discrepancy in the PDMS solution may be related to the discrepancy of the excess volume predicted from the corresponding state theory against the experiment.[34] Especially the estimation of the excess volume of mixing is important in considering the pressure effect. The behavior of $A_2$ for polystyrene in *trans*-decalin is related to the volume change on mixing.[19] At a high pressure $A_2$ shows a limiting behavior and the excess volume depends on the pressure. However, the corresponding state theory gives a qualitative prediction of the pressure contribution.

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## References

1) I. Prigogine, "The Molecular Theory of Solutions," North Holland Publishing Co., Amsterdam (1957).

2) P. J. Flory, *Discuss. Faraday Soc.*, **49**, 7 (1970).

3) D. Patterson and G. Delmas, *Trans. Faraday Soc.*, **65**, 708 (1969).

4) D. Patterson, *Macromolecules*, **2**, 672 (1969).

5) G. V. Schulz and M. Lechner, *J. Polym. Sci.*, *Part A-2*, **8**, 1885 (1970).

6) M. Lechner and G. V. Schulz, *Eur. Polym. J.*, **6**, 945 (1970).

7) G. V. Schulz and M. Lechner, in "Light Scattering from Polymer Solutions," M. B. Huglin, Ed., Academic Press, New York, N. Y. (1971).

8) D. Gaeckle and D. Patterson, *Macromolecules*, **5**, 136 (1972).

9) C. J. McDonald and S. Claesson, *Chemica Scripta*, **4**, 155 (1973).

10) M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolym. Forsch.*, **3**, 196 (1963).

11) K. Kubo and K. Ogino, *Bull. Chem. Soc. Jpn.*, **44**, 997 (1971).

12) Shin-Etsu technical data, T6-4.

13) P. W. Bridgman, "Physics of High Pressure," Bell and Sons, London (1949).

14) P. Debye, *J. Appl. Phys.*, **15**, 338 (1944).

15) G. V. Schulz and A. Haug, *Z. Phys. Chem. Neue Folge.*, **34**, 328 (1962).

16) C. I. Carr, Jr. and B. H. Zimm, *J. Chem. Phys.*, **18**, 1616 (1950).

17) F. E. Gibson and J. F. Kincaid, *J. Am. Chem. Soc.*, **60**, 511 (1938).

18) I. Prigogine and R. Defay, "Chemical Thermodynamics," Longmans, Green and Co., London (1954).

19) S. Saeki, N. Kuwahara, M. Nakata, and M. Kaneko, *Polymer*, **16**, 445 (1975).

20) Hsiang Shih and P. J. Flory, *Macromolecules*, **5**, 758 (1972).

21) W. R. Krigbaum, D. K. Carpenter, M. Kancko, and A. Roig, *J. Chem. Phys.*, **33**, 921 (1960).

22) M. Fixman, *J. Chem. Phys.*, **23**, 1656 (1955).

23) W. H. Stockmayer, *Makromol. Chem.*, **35**, 54 (1960).

24) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).

25) T. A. Orofino and P. J. Flory, *J. Chem. Phys.*, **26**, 1067 (1957).

26) M. Kurata, M. Fukatsu, H. Sotobayashi, and H. Yamakawa, *J. Chem. Phys.*, **41**, 139 (1964).

27) H. Yamakawa, *J. Chem. Phys.*, **48**, 2103 (1968).

28) E. F. Casassa and H. Markovitz, *J. Chem. Phys.*, **29**, 493 (1958).

29) P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**,

1086 (1950).
30) H. Eyring and J. O. Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937).
31) A. Abe and P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1838 (1965).
32) R. E. Gibson and O.H. Loeffler, *J. Am. Chem. Soc.*, **61**, 2515 (1939).
33) N. Kuwahara, *J. Polym. Sci.*, *A*, **1**, 2395 (1963).
34) P. J. Flory and Hsiang Shih, *Macromolecules*, **5**, 761 (1972).