In conclusion, it is apparent that a further investigation of the application of the sedimentation velocity method is certainly warranted. Precision of experimental data recording seems especially critical and is most in need of improvement. The value for the parameter β must be obtained before meaningful conversion of the sedimentation constant distribution to molecular weight distribution can be accomplished. Finally, a comparison with a molecular weight distribution obtained from an independent experimental technique is desirable.

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Effect of Pressure on the Second Virial Coefficient and Chain Dimensions in Polymer Solutions

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ABSTRACT: Second virial coefficients and radii of gyration at pressures up to 110 bars were determined at high polymer dilution for polyisobutylene in 2-methylbutane at 24, 57, and 64° and for polystyrene in 2-butanone at 22°, using SOFICA light-scattering equipment and a pressure-resistant cell. The results permit a calculation of the pressure dependence of the lower critical solution temperature of the polyisobutylene + 2-methylbutane system which is in good agreement with direct measurement. The pressure and temperature dependence of A_2 are consistent with newer theories of polymer solution thermodynamics. The dependences may be used to obtain relative partial molar volumes, $\Delta\bar{V}_1$, and heats, $\Delta\bar{H}_1$, of the solvent. Excluded-volume theories allow a comparison of $\Delta\bar{V}_1$ and $\Delta\bar{H}_1$ with literature values determined at high polymer concentration; agreement is fair. A correlation between values of $\langle S^2\rangle^{1/2}$ and A_2 shows that pressure influences these quantities through its effect on the polymer–solvent interaction parameter χ or the z parameter.

Solution theories have traditionally emphasized an energetic contribution to the mixing functions arising from the relative weakness of contacts between molecules of different chemical nature and intermolecular force fields. Recent work[1,2] in polymer solution thermodynamics shows the importance of a difference of free volumes, or degrees of thermal expansion, between the polymer and the solvent. During the mixing process, the free volumes move toward an intermediate value characteristic of the mixture. These changes produce major contributions (termed structural[1] or equation of state[2]) to the thermodynamic mixing functions, ΔH_M, ΔS_M, and ΔG_M as well as ΔV_M. The free volume contribution to ΔG_M and the interaction parameter, χ, is predicted to be positive. It accounts[3] for the existence of the lower critical solution temperature occurring in polymer solutions at high temperature, where there is a large difference in free volume between polymer and solvent. The application of pressure will normally compress the solvent to a much greater extent than the polymer, thus reducing the free volume difference between them, and the corresponding contribution to ΔG_M and χ. Pressure does in fact markedly increase[4] the value of the LCST, with a corresponding enhancement of polymer solubility. It is evident that pressure should have a large effect on quantities which reflect the polymer–solvent interaction, in particular the second virial coefficient, A_2, and the radius of gyration of the macromolecule, $\langle S^2\rangle^{1/2}$. Where the free volume contribution is dominant, *i.e.*, at higher temperature or in systems where the disparity of intermolecular forces between the polymer and solvent is small, A_2 and $\langle S^2\rangle^{1/2}$ should increase with pressure. This would correspond to a decrease of ΔG_M, or to a negative value of ΔV_M. At low temperature, however, approaching the upper critical solution temperature, the free volume contribution may be of less importance. Then the second virial coefficient and the polymer dimensions could decrease with pressure, corresponding to a positive value of ΔV_M.

Schulz and Lechner[5-7] have pioneered in the study of the effect of pressure on light scattering in polymer solutions. Using a high-pressure optical cell and special instrumentation, they have made measurements up to 800 atm on a number of systems: polystyrene + *trans*-decalin, + toluene, + cyclohexane, and + chloroform. The results have been shown to be in qualitative and semiquantitative agreement with a theoretical treatment[8] of pressure effects. In particular, $(\partial A_2/\partial P)_T$ for polystyrene + *trans*-decalin[5,6] is negative near the UCST ($\Theta = 19°$) corresponding to $\Delta V_M > 0$. However, at higher temperature, $(\partial A_2/\partial P)_T$ becomes positive (for small pressures), indicating that $\Delta V_M < 0$. The present work is an investigation of polyisobutylene (PIB) + 2-methylbutane and polystyrene (PS) + 2-butanone at lower pressure, using the standard SOFICA light-scattering equipment, and with new features of interpretation.

Thermodynamic Considerations

Relationship between the Pressure and Temperature Dependence of A_2 and the Partial Molar Volumes and Heats of the

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Solvent. The following relation is valid at low concentration of polymer

$$\frac{\Delta\mu_1}{RT} = -\frac{\pi V_1}{RT} = \frac{cV_1}{M} + A_2c^2V_1 \qquad (1)$$

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.*, weight of polymer per volume of solution. The relative partial molar volumes and enthalpies of the solvent (volumes and heats of dilution), $\Delta\bar{V}_1$ and $\Delta\bar{H}_1$, are obtained through the pressure and temperature dependences of A_2 at constant weight fraction, w_2, or mole fraction, rather than constant concentration. We have, at low concentration

$$\frac{\Delta\bar{V}_1}{V_1} = \frac{1}{V_1}\left[\frac{\partial(\pi V_1)}{\partial P}\right]_{\mathrm{T,w_2}} = c^2RT\left[-\left(\frac{\partial A_2}{\partial P}\right)_{\mathrm{T}} - \beta_1A_2\right] \qquad (2)$$

$$\frac{\Delta\bar{H}_1}{RT} = T\left[\frac{\partial(\pi V_1/RT)}{\partial T}\right]_{\mathrm{P,w_2}} = c^2V_1T\left[\left(\frac{\partial A_2}{\partial T}\right)_{\mathrm{P}} - \alpha_1A_2\right] \qquad (3)$$

Here β_1 and α_1 are the isothermal compressibility and the thermal expansion coefficient of the solvent. In the present work, the terms in β_1 and α_1 are negligible compared with the pressure and temperature variation of A_2. Equation 3 for $\Delta\bar{H}_1$ has been given by Schulz and Lechner.[5,6] Their expression for $\Delta\bar{V}_1$, however, is apparently incorrect, and would give infinite values as $P \to 0$. An error was incurred through equating energy changes at constant pressure and volume in their[6] eq 9.

Comparison of Relative Partial Molar Heats and Volumes of the Solvent in Dilute and Concentrated Solution. Equations 2 and 3 give $\Delta\bar{V}_1$ and $\Delta\bar{H}_1$ in the dilute region where the solution is nonuniform due to the excluded-volume effect. These values presumably 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. In dilute solution theories, solution nonuniformity gives rise to the $h(z)$ function in the A_2 expression[9]

$$A_2 = {}^1\!/_2N_ABh(z) = 1.52N_AA^3M^{-1/2}zh(z) \qquad (4)$$

where B and z are the long-range, polymer–solvent interaction parameters[9]

$$B \equiv 2({}^1\!/_2 - \chi)/N_AV_1\rho^2 \qquad (5)$$

$$z \equiv 0.330BM^{1/2}/A^3 \qquad (6)$$

$$A \equiv (\langle L_0^2\rangle/M)^{1/2} \qquad (7)$$

The quantities ρ and $\langle L_0^2\rangle$ are respectively the density of the polymer and the mean-square unperturbed end-to-end distance of the macromolecule. Direct thermodynamic measurements of volumes and heats of mixing leading to values of $\Delta\bar{V}_1$ and $\Delta\bar{H}_1$ are usually made at high concentrations, between 20 and 80% of polymer. Equations 2 and 3 could be used to predict these values of $\Delta\bar{V}_1$ and $\Delta\bar{H}_1$ if values of A_2 were available for high polymer concentration (A_2^{conc}). At a sufficiently high concentration, which is probably no more than ~5%, the theoretical expression for A_2 still corresponds to eq 4, but the excluded volume function $h(z)$ is absent. We therefore obtain A_2^{conc} for use in eq 2 and 3 from experimental dilute-solution values of A_2 through division by $h(z)$, *i.e.*

$$A_2^{\mathrm{conc}} = A_2/h(z) \qquad (8)$$

In work in the concentrated range, the traditional composition variable has been the volume fraction ϕ_2, related to the concentration by

$$\lim_{c\to 0}(\phi_2/c) = v_{2,\mathrm{sp}} \qquad (9)$$

where $v_{2,\mathrm{sp}}$ is the specific volume of the pure polymer. It has been usual to obtain the volume of mixing, ΔV_{M}, rather than $\Delta\bar{V}_1$, and it is found that ΔV_{M} is symmetrical in the volume fractions of the components, *i.e.*[10]

$$\Delta V_{\mathrm{M}}/V = k_{\mathrm{V}}\phi_1\phi_2 \qquad (10)$$

leading to

$$\Delta\bar{V}_1/V_1 = k_{\mathrm{V}}\phi_2^2 \qquad (11)$$

Similarly, the heat of dilution is given by

$$\Delta\bar{H}_1/RT = \kappa\phi_2^2 \qquad (12)$$

Combining eq 2 and 3 with 11 and 12, we have

$$k_{\mathrm{V}} = \frac{RT}{v^2_{2,\mathrm{sp}}}\left[-\left(\frac{\partial A_2^{\mathrm{conc}}}{\partial P}\right)_{\mathrm{T}} - \beta_1A_2^{\mathrm{conc}}\right] \qquad (13)$$

$$\kappa = \frac{V_1T}{v^2_{2,\mathrm{sp}}}\left[-\left(\frac{\partial A_2}{\partial T}\right)_{\mathrm{P}} - \alpha_1A_2^{\mathrm{conc}}\right] \qquad (14)$$

Recently, the segment fraction (designated here as ϕ_2') has been used[2] as a composition variable. Then

$$\lim_{c\to 0}(\phi_2'/c) = v_{2,\mathrm{sp}}\tilde{V}_2/\tilde{V}_1 \qquad (15)$$

where $\tilde{V}$ is the reduced volume of the pure components. Values of κ' found in terms of the segment fractions are then given by

$$\kappa'/\kappa = (\tilde{V}_2/\tilde{V}_1)^2 \qquad (16)$$

Experimental Section

Materials. Light scattering gave an M_{w} value of 1.02×10^6 for the Esso Vistanex PIB fraction which we used, while $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.45$ from gel permeation chromatography. The polystyrene fraction was from Pressure Chemical Co. (Pittsburgh, Pa.), with a nominal molecular weight of 8.6×10^5 and an $M_{\mathrm{w}}/M_{\mathrm{n}}$ value given as less than 1.15. Our value of M_{w}, determined by light scattering, was 9.75×10^5, and a determination by gel permeation chromatography was consistent with this value. Values of $M_z/M_{\mathrm{w}} \sim 1.10$ have been obtained[11] for the series of Pressure Chemical Co. polystyrene fractions. They are thus very sharp. The 2-methylbutane was Phillips "pure grade" (99.0% pure), and the 2-butanone was a Fisher Certified Reagent. Both solvents were subjected to column fractionation. The purity of the 2-butanone was tested by gas–liquid chromatography and impurities were found to be less than 0.1%.

Apparatus. The optical cell was made of a heavy-wall Pyrex tube, clamped between stainless-steel blocks and sealed with Teflon and rubber O rings. The capacity of the cell was *ca.* 6 cm^3. The dimensions were designed so the cell could be used in the standard SOFICA photogoniodiffusometer without any modification of the instrument. A tube led from the top block to a valve, by means of which the cell was closed off. The volume of the tube from the cell to the valve was known. This space was accessible to the polymer solution whose total volume was constant, apart from thermal expansion of the whole system. Behind the valve, the pressure line contained a high-pressure filter (Millipore), and then connected to the pressure generator (High Pressure Co., Erie, Pa.) and to a solid-front pressure gauge (Heise Bourdon Gauge Co., Newton, Conn.). Pure solvent constituted the pressure medium.

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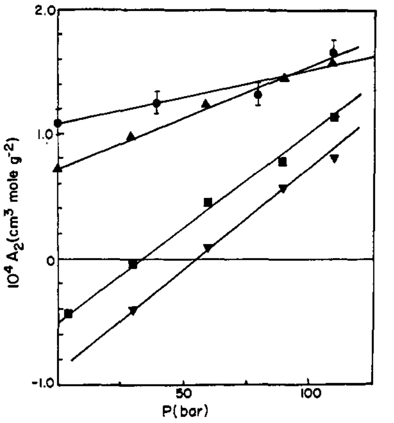

Figure 1. The second virial coefficient, A_2, as a function of pressure for polyisobutylene + 2-methylbutane at 24 (▲), 57 (■), and 64° (▼) and for polystyrene + 2-butanone at 22° (●).

Procedure. The polymer solution was made up to approximately the required concentration and was cleared of dust by ultracentrifugation at low temperature. The cell was filled, connected to the pressure line, and brought to the required temperature. Expansion of the solution could take place into the tube between the cell and the valve, so that polymer was not lost. The solvent was forced in to complete the known volume up to the valve. The concentration could be thus calculated. About 2 hr was allowed for the solution to become homogeneous before measurements were undertaken. Pressure was applied by forcing more solvent into the known volume, passing through the high-pressure filter to clear it of dust. Thus, the value of the concentration did not change as the pressure was raised.

Light intensities obtained with the pressure cell were corrected by comparison with those obtained using a conventional cell furnished with the instrument. This was done at each concentration of the system and for each angle of measurement. The corrections to the light intensity, established at room temperature and atmospheric pressure, did not exceed 5%, and were used at other temperatures and pressures. A benzene standard was used for calibration at each temperature, in the manner described in ref 12.

The angle-dependence technique (Zimm plot) was employed for the determination of M_w, A_2, and $\langle S^2\rangle^{1/2}$. The intensities of scattered light of λ 5461 Å were measured at seven angles from 45 to 135° and at six concentrations ranging from $\sim 3 \times 10^{-4}$ to $\sim 30 \times 10^{-4}$ g/cm³. The equation used for obtaining M_w and A_2 was[12]

$$0.506 I_B^{25}\left(\frac{dn}{dc}\right)^2\left(\frac{c}{I}\right)_{\substack{\theta=0\\ c\to 0}} = \frac{1}{M_w} + 2A_2c \qquad (17)$$

based on a value of the Rayleigh ratio for benzene at 25°, $R_B = 16.3 \times 10^{-6}$ for λ 5461 Å. I_B^{25} is the scattered intensity for the benzene standard at 25° and at a 90° angle, while dn/dc is the refractive index increment at the experimental temperature and pressure.

The radius of gyration was found in the usual manner from the ratio of the slope of $(c/I)_{\theta\to 0}$ at $c = 0$ to the intercept of c/I at zero concentration and angle

$$\langle S^2\rangle^{1/2} = \frac{\sqrt{3}\lambda}{4\pi n}\left[\text{slope}\left(\frac{c}{I}\right)_{\substack{\theta\to 0\\ c=0}} \Big/ \left(\frac{c}{I}\right)_{\substack{\theta=0\\ c=0}}\right]^{1/2} \qquad (18)$$

We have also used the modified procedure due to Berry,[13] in which $(c/I)^{1/2}$ is plotted against $\sin^2(\theta/2)$ and c. The results for M_w, A_2, and $\langle S^2\rangle^{1/2}$ are very similar to those obtained with the Zimm plot.

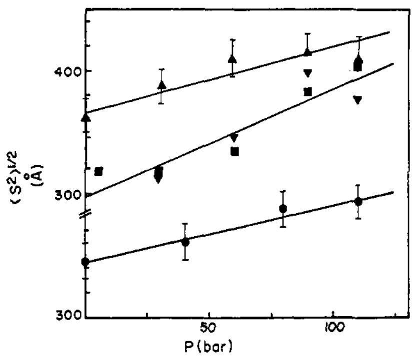

Figure 2. The radius of gyration $<S^2>^{1/2}$ as a function of pressure for polyisobutylene + 2-methylbutane at 24 (▲), 57 (■), and 64° (▼) and for polystyrene + 2-butanone at 22° (●).

Determination of Refractive Index Increments. Schulz and Lechner note the inconvenience of determining dn/dc for a system under pressure. In the case of the PIB + 2-methylbutane system, light-scattering measurements were made at temperatures considerably above the normal boiling point; dn/dc measurements with conventional instruments would also be inconvenient in this temperature range. Two procedures for obtaining dn/dc were used.

(1) An experimental value of dn/dc was obtained at 5461 Å for the system at a single temperature and at atmospheric pressure. For PS + 2-butanone, dn/dc is well known.[14] For PIB + 2-methylbutane, a value at 25° was measured using a Rayleigh differential refractometer and found to be 0.188 cm³/g. Next, the values of M_w for the PIB and PS fractions were measured by light scattering, giving the values listed in the Materials section. These values of M_w were then taken to be idependent of P and T, *i.e.*, the macromolecules are assumed not to aggregate. Thus, at each value of P and T, a light-scattering determination of the intercept $(c/I)_{\theta=0}$ at $c = 0$ allows a value of dn/dc to be calculated from the known value of M_w.

(2) A number of expressions[15] relate the refractive index of a liquid to its density. The variation of density with P and T may be calculated using the recent, and accurate, Flory equation of state[2] for a polymeric[16] or a small-molecule liquid. Thus, using, for instance, the Lorentz–Lorenz expression, the variation of n_1 and n_2 may be found. The simple relation

$$dn/dc = (n_2 - n_1)/\rho_2 \qquad (19)$$

has been found[12] to give a reasonable approximation for dn/dc as a function of temperature for PIB + butyl ether. For the PS + 2-butanone system, the known value of dn/dc[14] at 25° and atmospheric pressure was used to calculate n_2 for the polymer in the liquid state at 25°. Thus, values of dn/dc for other pressures could be calculated with eq 19. For PIB + 2-methylbutane, dn/dc was calculated using $n_2(25°) = 1.515$.[12] This gave a value of dn/dc = 0.177 cm³/g, *i.e.*, 6% lower than found experimentally. Values of dn/dc at various P and T (24, 57, and 64° and pressures up to 100 bars) were computed from eq 19 with $n_2(25°) = 1.515$. They were then increased by 6%. The values of dn/dc found in this way were in reasonable agreement with those calculated with the first method, which assumed M_w to be constant. The largest difference was 6%.

Values of A_2 were calculated from the light-scattering data, using values of dn/dc obtained with the above two methods, and were found to agree to within experimental error. The points in Figure 1 were obtained with the second method for dn/dc.

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Results and Discussion

Figures 1 and 2 show the values of A_2 and $\langle S^2\rangle^{1/2}$ as a function of pressure for PIB + 2-methylbutane at 24, 57, and 64° and for PS + 2-butanone at 22°. The heat of dilution of the PS + 2-butanone system is found[17] by calorimetry to be exothermic, but very small; A_2 and $\langle S^2\rangle^{1/2}$ should therefore be almost independent of temperature for this system, and the light-scattering measurements were confined to the one temperature. Both A_2 and $\langle S^2\rangle^{1/2}$ increase with pressure for both systems, in accord with negative values of ΔV_M.

The Berry $(c/I)^{1/2}$ plot was used for two extreme values of the pressure in the case of the PS + 2-butanone system and the PIB + 2-methylbutane system at 24°. In the former case, the values of M_w, A_2, and $\langle S^2\rangle^{1/2}$ were respectively decreased by 3%, increased by 4%, and decreased by 5%. In the latter case, the corresponding changes were a decrease of 1%, a decrease of 2%, and an increase of 6%. These changes were ignored, however, since they are within the experimental error.

LCST Values in the PIB + 2-Methylbutane System. Values of the LCST have been obtained[4] for different molecular weights of PIB in 2-methylbutane at the saturated vapor pressure. Extrapolation to infinite molecular weight gives a Θ temperature, associated with the LCST, of 45°. This is consistent with the present results, where A_2 is positive at 24° and zero pressure but decreases to negative values at 57 and 64°. Assuming $(\partial A_2/\partial T)_P$ to be constant through this temperature range, one finds that, under zero pressure conditions, $A_2 = 0$ at $\Theta = 43°$. This value of the Θ temperature is in good agreement with that found from the LCST measurements. Studies have been made of the effect of pressure on the LCST of PIB + 2-methylbutane, *i.e.*, of the (P, T) projection of the critical line. For a fraction of PIB which gives an LCST at 50° under zero pressure, one has[4b] $(\mathrm{d}T/\mathrm{d}P)_c = 0.44$ deg/bar. From the thermodynamic analysis[18] of critical solution points, we have

$$(\mathrm{d}T/\mathrm{d}P)_c = T(\partial^2V/\partial x_2^2)_c/(\partial^2H/\partial x_2^2)_c = T(\partial\Delta\tilde{V}_1/\partial x_2)c/(\partial\Delta\tilde{H}_1/\partial x_2)_c \tag{20}$$

Neglecting β_1 and α_1 in eq 2 and 3, eq 20 becomes

$$(\mathrm{d}T/\mathrm{d}P)_c = -(\partial A_2/\partial P)_T/(\partial A_2/\partial \mathrm{T})_P \tag{21}$$

The values of the LCST as a function of pressure thus correspond to a constant value of A_2. For a polymer of infinite molecular weight, $A_2 = 0$ along the critical line and all points along this line correspond to Θ temperatures, unperturbed polymer dimensions, and Gaussian distribution of segments. Values of A_2 at 24 and 64° at $P = 0$ gave $(\partial A_2/\partial T)_P$ at the mean temperature of 44°. This value and a corresponding mean value of $(\partial A_2/\partial P)_T$ were used in eq 14, which gives $(dT/dP)_c = 0.3$ deg/bar, in good agreement with the value of 0.44 deg/atm obtained from the pressure dependence of the LCST.

Relative Partial Molar Volumes and Heats of the Solvent. The Krigbaum–Carpenter–Kaneko–Roig (KCKR) theory[19] was used to obtain the $h(z)$ function in order to furnish values of A_2^{conc} for use in eq 13 and 14. In this theory, values of the ρ parameter equal to 0, 0.2, and 1 give results corresponding respectively to the Casassa–Markovitz,[20] Kurata–Fukatsu–Sotobayashi–Yamakawa,[21] and Flory–Krigbaum[22] theories. We used an intermediate value of 0.4, which was originally favored[19] on the basis of a comparison with experiment. The following values[9] of the parameter A were used in conjunction: PIB, 740×10^{-11}; PS, 670×10^{-11}. The $h(z)$ function given by the KCKR theory then allowed A_2^{conc} to be calculated from values of A_2 obtained in the dilute concentration range. Its pressure dependence was used in eq 13 to yield the following values of k_V for the PIB + 2-methylbutane system: 24°, -3.5×10^{-2}; 57°, -4.6×10^{-2}; and 64°, -4.5×10^{-2}. Direct measurements of ΔV_M have not, to our knowledge, been reported. However, comparison can be made with ΔV_M values[23] for PIB with the isomer *n*-pentane at 25°. The values are symmetrical in volume fraction, with $k_V = -5.0 \times 10^{-2}$. For the PS + 2-butanone system, we find $k_V = -3.6 \times 10^{-2}$. Values of $\Delta V_M/V$ have been obtained by Flory and collaborators,[2] whose results are consistent with a value of $k_V = -3.3 \times 10^{-2}$.

From the change of A_2 at zero pressure between 24 and 57°, we calculate a value of the enthalpic parameter $\kappa = -0.12$ with $\rho = 0.4$ in the KCKR theory. Experimental heats of dilution are not available for this system. However, heats of mixing PIB with 2-methylbutane to great dilution of the polymer have been measured and are very similar to those measured for PIB in *n*-pentane, where heats of dilution are available.[24] The quantity κ defined by eq 12 is found to be independent of concentration for PIB–*n*-pentane. In terms of the volume fractions, $\kappa = -0.14$. It seems that fairly accurate values of the volumes and heats of dilution may be obtained from the light-scattering measurements.

Comparison of the Pressure Dependence of A_2 with Predictions of Newer Theories. The second virial coefficient, A_2, is related to the polymer–solvent interaction parameter, χ, through eq 4 and 5. The following equation has been used to predict the pressure and temperature dependence of χ at low concentration of polymer, but still in the "concentrated" range, *i.e.*, assuming interpenetration of the macromolecules.

$$\chi(P, T) = c_1\left[-\frac{\tilde{U}_1}{\tilde{T}_1}\nu^2 + \frac{1}{2}\tilde{C}_{\mathrm{p},1}(P_1, T_1)\left\{\tau + \frac{\tilde{P}_1\tilde{V}_1^2}{\tilde{P}_1\tilde{V}_1^2 + 1}\pi\right\}^2\right] \tag{22}$$

The quantities $\tilde{U}_1$ and $\tilde{C}_{\mathrm{p},1}$ are the reduced configurational energy and heat capacity of the pure solvent. The Flory theory[2] 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. Then $\tilde{U}_1$, $\tilde{C}_{\mathrm{p},1}$, and $\tilde{T}_1$ are given in terms of the reduced quantities $\tilde{P}_1$ and $\tilde{V}_1$ of the solvent. The τ parameter is a measure of the difference in degrees of thermal expansions or free volumes of the two components

$$\tau = 1 - T_1^*/T_2^* \tag{23}$$

The temperature reduction parameters T^* may be obtained from the equation of state quantities of the pure components following, for instance, the prescription of Flory and collaborators. The ν^2 parameter expresses the difference of chemical nature of the components which results in a weakness of the energy of the (1–2) contacts relative to the (1–1) and (2–2) contacts. It is identical with the ratio X_{12}/P_1^* of the Flory

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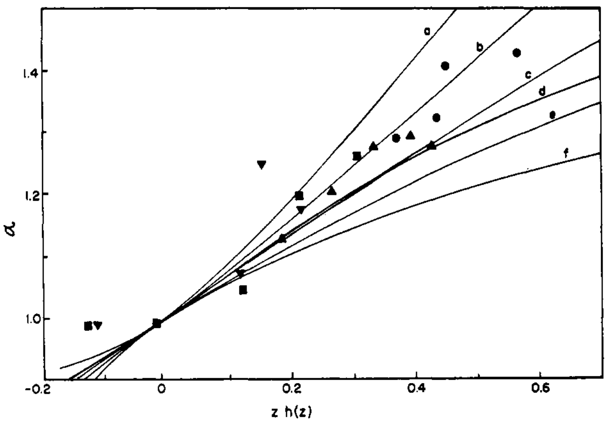

Figure 3. The coil expansion factor, α, for the polymer–solvent systems at various pressures and temperatures (symbols as in Figures 1 and 2). The abscissa, $zh(z)$, is proportional to A_2 as in eq 4. Theoretical curves a, b, and c are given by the Fixman-Stockmayer expression for $\alpha(z)$, eq 25, and the Krigbaum–Carpenter–Kaneko-Roig theory for A_2 with ρ equal to respectively 0 (Casassa-Markovitz), 0.4, and 1 (Flory-Krigbaum). Theoretical curves d, e, and f are given by the Stockmayer modification of the Fox-Flory expression, eq 26, and the KCKR theory with ρ equal to respectively 0, 0.4, and 1.

theory. The π parameter expresses a difference in P^* reduction parameters similar to eq 23: $\pi = P_1^*/P_2^* - 1$, and the parameter $3c_1$ is the number of external, volume-dependent degrees of freedom of the solvent molecule. At zero pressure, eq 22 becomes the Flory theory expression for χ (eq 49–51 of ref 25a), except that the Flory parameter s_2/s_1 is set equal to unity and only second powers of the quantities τ and ν are retained. In treating the thermodynamics of the PIB + n-pentane system at 25°, Eichinger and Flory[25b] fit their theory to heats of solution in order to evaluate the $\nu^2 = X_{12}/P_1^*$ parameter and then predict χ (at zero pressure). At low polymer concentration the predicted $\chi = 0.65$, which would erroneously give large negative values of A_2. We have decided to fit both the ν^2 and τ parameters with the zero-pressure data for A_2, and then use the theory to predict the pressure dependence of A_2. Thus, for the PIB + 2-methylbutane system at zero pressure we take $A_2 = 0$ at $\Theta = 44°$, where $\kappa = -T(\partial X/\partial T)_P = -0.12$ calculated for the "concentrated" solution as described in the preceding section. The fitted ν^2 parameter is small, as expected from the close chemical similarity of the polymer and solvent; it corresponds to a value of $X_{12} = 1.8$ cal/cm^3. The fitted τ parameter was 30% smaller than the value calculated from the T^* parameters obtained from equation of state data. The predicted A_2 increases with pressure, the curve being slightly concave downward. In the 0–100-bar range, however, it is virtually a straight line. The slopes (cm^3 mol g^{-2} bar^{-1}) are 2.2×10^{-6} (24°) and 3.4×10^{-6} (57°). This is in fair agreement with values of $(\partial A^{\text{conc}}/\partial P) = 1.7 \times 10^{-6}$ and 2.1×10^{-6} cm^3 mol g^{-2} bar^{-1} found experimentally for the PIB + 2-methylbutane system (using the KCKR excluded volume theory with $\rho = 0.4$ to give $h(z)$).

An analogous calculation was performed for the polystyrene + 2-butanone system. Values of ν^2 and τ were obtained by fitting eq 22 to the value of $A_2^{\text{conc}} = 1.9 \times 10^{-4}$ cm^3 mol g^{-2} at 22° and zero pressure. Calorimetric measurements[16] show that the heat of dilution is negative but very small, and we took $\kappa = 0$ at 22°. The value of the fitted ν^2 parameter was small, corresponding to $X_{12} = 1.8$ cal/cm^3, while τ was approximately equal to the value calculated from equation of state data. The predicted pressure dependence of A_2 at 22° is 0.9×10^{-6} cm^3 mol g^{-2} bar^{-1}, which is again in fair agreement with the experimental value of $\partial A^{\text{conc}}{}_2/\partial P = 1.3$ cm^3 mol g^{-2} bar^{-1}. We conclude that the theoretical eq 22 gives reasonable, if not quantitative, agreement with experiment.

Pressure and Temperature Dependence of the Radius of Gyration. Values of $\langle S^2\rangle^{1/2}$ for the PIB molecules in 2-methylbutane at different temperatures and pressures were plotted against the corresponding values of A_2. A single curve was obtained, showing that the effect of pressure on the chain dimensions is similar to that of temperature. Both act through the polymer–solvent interaction parameters B and z, which also bring about the change of A_2. The radius of gyration

$$\langle S^2\rangle^{1/2} = \langle S_0^2\rangle^{1/2}\,\alpha(z) \tag{24}$$

is the same whether the expansion coefficient, $\alpha(z)$, is changed through P or T. On the other hand, the results of Schulz and Lechner[6] (in their Table 4) for PS in *trans*-decalin and toluene do not give a single curve of the radius of gyration at different P and T against A_2. For the same A_2, $\langle S^2\rangle^{1/2}$ values are lower when obtained at higher pressures, indicating that the unperturbed dimension $\langle S_0^2\rangle^{1/2}$ is a decreasing function of pressure, as noted.[6] This result may indicate an effect of the solvent packing on the population of conformations or rotational isomers of the polystyrene. It is usually believed that the solvent has little effect on the unperturbed dimensions of the macromolecule, but the possibility[26] should not be disregarded. Even a small effect of solvent packing on the rotational isomer equilibrium would have important consequences in polymer solution thermodynamics.

Values of $\alpha(z)$ were obtained from $\langle S^2\rangle^{1/2}$ with a value of $\langle S_0^2\rangle^{1/2}$ of PIB equal to 320 Å, read off the $\langle S^2\rangle^{1/2}$ *vs.* A_2 plot at $A_2 = 0$. For PS + 2-butanone, an approximate value of $\langle S_0^2\rangle^{1/2} = 260$ Å was obtained by extrapolation, and $\alpha(z)$ was determined. Using eq 4 and the values of A given in the preceding section, values of $zh(z)$ were computed from A_2 for both systems. Figure 3 shows $\alpha(z)$ against $zh(z)$, where it may be seen that the points for both systems and for different T and P do approximately fall on a single curve, as expected from theory. This result does not change on considering the effects of polydispersity on the values of $\langle S^2\rangle^{1/2}$ and A_2 (see below).

A number of similar closed expressions[9] relate the expansion factor α of the polymer coil to z, *i.e.*, they give the ordinate in Figure 3. We have used the Fixman–Stockmayer expression

$$\alpha^3 - 1 = 2z \tag{25}$$

and the Stockmayer modification of the Flory–Fox relation

$$\alpha^5 - \alpha^3 = (134/105)z \tag{26}$$

The abscissa of Figure 3, $z(hz)$, was obtained through the KCKR theory with the three values of the ρ parameter, 0, 0.4, and 1. Figure 3 shows the resulting six curves of $\alpha(z)$ against $zh(z)$. We note that the $zh(z)$ function is the same as $\psi\alpha_s^3$ used in some other treatments.[27]

The PIB + 2-methylbutane data are consistent with either of the two $\alpha(z)$ formulas. However, the difference in pre-

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dictions for $\alpha(z)$ becomes more marked at large z, and the PS + 2-butanone data are in better agreement with the Fixman–Stockmayer than with the modified Flory–Fox prescription.

We have also calculated α against $zh(z) \equiv \psi\alpha_s^3$ for three other combinations of theories for A_2 and α. These were as given by eq 17–22 of ref 27, and corresponded to the original Flory–Krigbaum–Orofino A_2 expression combined with the original Flory α expression, the combination of the modified expressions, and the Kurata–Fukatsu–Sotobayashi–Yamakawa A_2 combined with the Yamakawa–Tanaka α expressions. The first and third recipes gave curves of α against $zh(z)$ close to curves c and d in Figure 3, while the second gave a lower curve toward e. The experimental points lie slightly above these three curves, but the difference is probably within experimental error.

Effects of Polydispersity. We have used the Yamakawa–Kurata treatment[28] to assess the effect of polydispersity on the value of A_2. Their series expansion for $h(z)$ is

$$h(z) = 1 - 2.865Q_w'z_w \ldots \tag{27}$$

Here z_w is the value of z corresponding to the weight-average molecular weight of the sample and Q_w' is a parameter greater than unity in the case of polydispersity. For the present polydisperse PIB sample, characterized by $h \simeq 2.2$, Figure 1 of ref 26 indicates that $Q_w' \simeq 1.07$. Following eq 27, we have replaced z in the closed expressions for $h(z)$ with the product $Q_w'z_w$. We find that a monodisperse fraction of the same M_w would have values of A_2 approximately 4% higher than those found experimentally with our polydisperse sample. The treatment of Casassa[29] also indicates that the change in A_2 would be very small, and it seems reasonable to ignore it.

In the case of the coil expansion factor α, Kurata and Stockmayer[9] give the series expansion

$$\alpha^2 - 1 = (134/105)q_sz_w + \ldots \tag{28}$$

where the factor introduced by polydispersity, q_s, is 1.257 for $h = 2.2$. Following ref 9, we have assumed that the product q_sz_w may be used in the closed expressions, *i.e.*, eq 25 and 26, in order to correct the values for α for the polydispersity of the PIB sample. We find that the difference between the value of α and unity is decreased by approximately 15%. The points in Figure 3 for the PIB + 2-methylbutane system would be lowered and fall closer to curve c than to b. It seems, however, that the general conclusions of the last section would remain, particularly since the points in Figure 3 for the polystyrene + 2-butanone system would be virtually unchanged, corresponding to the very low polydispersity of this polymer sample.

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A Revised Version of the Integrodifferential Equation in the Zimm Theory for Polymer Solution Dynamics

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ABSTRACT: Some of the viscoelastic quantities provided by the bead–spring model theory of Zimm have been reevaluated with the use of a new version of the integrodifferential equation, revising the numerical solutions of Tschoegl for intermediate degrees of hydrodynamic interaction. Comparison for low numbers of submolecules (N) with the result of the exact solution of Zimm's eigenvalue problem by Lodge and Wu reveals that the revised version (in contrast with the original) gives almost identical results for dynamic-mechanical properties and intrinsic viscosity. Numerical results showed that the quantities previously regarded as determined solely by the hydrodynamic interaction parameter h depend also on N even if N is not very small. An apparent "non-free-draining" effect is expected for the intrinsic viscosity irrespective of the value of h if $h/N^{1/2}$ is close to 0.25.

The bead–spring model theory of Zimm[1] is extremely important in determining the viscoelastic properties of dilute polymer solutions. Recently, it was pointed out by Lodge and Wu[2] that the use of the approximate integrodifferential equation given by Zimm[1] may cause a serious error for some cases. This led us to a closer examination of the integrodifferential equation. It turned out that the approximate version is good only for the free-draining or non-free-draining limits and not for intermediate degrees of hydrodynamic interaction. A revised equation, with an additional term, gives results in satisfactory agreement with the exact numerical solution (without the use of the integrodifferential equation)[2] for low values of N, the number of submolecules in a molecule. Since the integrodifferential equation is a better approximation for larger values of N, this is expected to give an almost mathematically exact evaluation of the Zimm theory for large values of N. In this paper, we report numerical results for some viscoelastic quantities as evaluated from the revised equation for the Zimm theory.

Theory and Method of Calculation

The problem this paper is concerned with is the solution of the eigenvalue problem

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