The pressure effect on the thermodynamic properties of polystyrene—*trans*-decalin solution

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The viscosity of a solution of polystyrene in *trans*-decalin was measured over pressure and temperature ranges from atmospheric pressure to 400 kg/cm^2 and 20° to 40°C. The viscosity measurements at elevated pressure were made by the use of a rolling-ball type viscometer, and the validity of this method was confirmed by comparing with the calibrated Ubbelohde viscometer at atmospheric pressure. Values of the interaction parameter, χ, were obtained from the coil expansion coefficients on the assumption of the fifth-power rule of the Flory theory for the expansion of the polymer molecules in the solution. χ_1 increases with increasing pressure. The pressure coefficient of the theta-temperature calculated from the pressure and the temperature derivatives of χ_1 is in good agreement with the result of Schulz *et al.* The values of χ_1 were compared with those calculated from the new Flory theory and the Patterson theory for polymer solutions. At lower pressure these theories predict the behaviour of χ_1 well, but at higher pressure the prediction becomes inaccurate.

INTRODUCTION

The importance of the effect of pressure on the thermodynamic properties of a solution has been recognized by recent investigatons, and many interesting characteristics of the pressure effect have become evident[1–11]. The characteristics of a polymer solution have been qualitatively explained by the well known Flory–Huggins theory[12], where the free energy of mixing comprises a combinatorial entropy and an exchange enthalpy. The existence of the lower critical solution temperature[13] and the contribution of the volume change on mixing to the mixing functions[14,15] are beyond the scope of the Flory–Huggins theory. Recent work in polymer solution thermodynamics shows the importance of the effect of the free volume difference between the polymer and the solvent[16]; the application of pressure normally compresses the solvent rather than the polymer, and the pressure effect on the free volume difference is large, which for the interaction parameter is of great importance.

Recently, Flory[17] has formulated a new theory for liquid mixtures of chain molecules taking into account the thermal expansion coefficients and the thermal pressure coefficients based on the principle of corresponding states[18]. Patterson[19,20] has also presented a new theory and has explained the existence of the lower critical solution temperature in polymer solutions of non-polar molecules. In both theories, the thermodynamic properties are subjected to the free volume contribution as well as to the contact energy contribution.

The pressure effect on the thermodynamic properties of the polymer solutions has been investigated mainly by light scattering[1–4], the second virial coefficient, the radii of gyration, the phase diagram, or the upper and lower critical solution temperature[5–11]. Previously, we presented the pressure dependence of the viscosity of poly(dimethyl siloxane in cyclohexyl bromide[21] and examined the pressure effect on the expansion coefficient of the polymer molecule and the interaction parameter χ.

In this work, we investigated the effect of pressure on the thermodynamic properties of polystyrene in *trans*-decalin by the viscosity at elevated pressure by use of the results of Schulz and Lechner[1]. Theta-temperature increases with increasing pressure in contrast to the case of poly(dimethyl siloxane)–*trans*-decalin. The values of the interaction parameter, χ, were calculated on the assumption of the fifth-power rule[22] for the expansion of the polymer molecule in the solution and were compared with those predicted from the new Flory theory and the Patterson theory.

EXPERIMENTAL

Polystyrene was obtained from the Pressure Chemical Co. The viscosity-average molecular weight was determined from the relation of $[\eta] = 8.2 \times 10^{-4} M^{1/2}$ in cyclohexane[23] at 34°C, and was 17.9×10^4. *Trans*-decalin was obtained by converting a mixture of *cis*- and *trans*-isomers into the *trans*-form using aluminium chloride, washing with water and drying over calcium chloride. The purification was carried out by fractional distillation under reduced pressure[24]. The purity of the *trans*-decalin was examined by gas chromatography and the *cis*-form could not be found.

The density of *trans*-decalin at atmospheric pressure was obtained by Nakata *et al.*[24], and represented as a function of t(°C) by:

$$\rho(\text{g/cm}^3) = 0.88463 - 7.338 \times 10^{-4} t - 0.191 \times 10^{-6} t^2 \tag{1}$$

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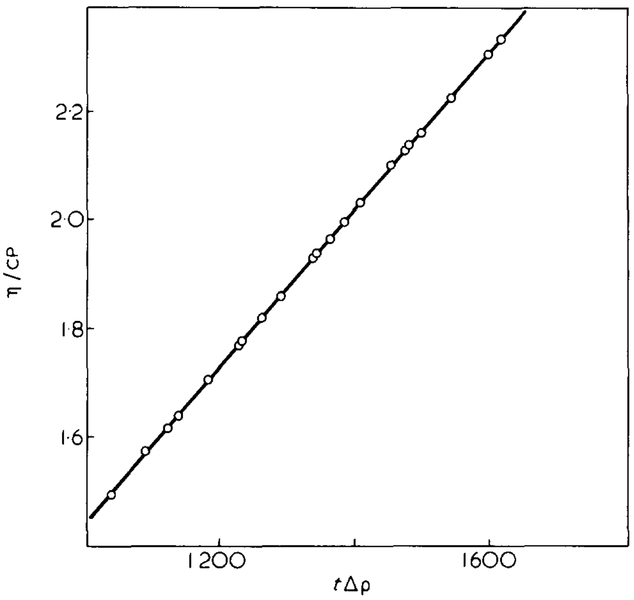

Figure 1 The calibration curve of the rolling-ball viscometer. t is the rolling down time of the steel ball and $\Delta\rho$ is the difference of the density between the steel ball and the solution. The slope of this line is K of equation (9)

This expression gives the thermal expansion coefficient:

$$\alpha(\text{deg}^{-1}) = 8.295 \times 10^{-4} + 1.119 \times 10^{-6}t + 1.107 \times 10^{-9}t^2 + 1.16 \times 10^{-12}t^3 \quad (2)$$

The relative volume of *trans*-decalin as a function of pressure was given by Schulz and Lechner[1], and these isotherms were arranged by the well known Tait equation:

$$1 - V_P/V_0 = C\ln(1 + P/B) \quad (3)$$

where C is a constant, P the pressure, and B is expressed as a function of temperature t (°C) by:

$$B(\text{kg/cm}^2) = b_1 \exp(-b_2 t) \quad (4)$$

where b_1 and b_2 are constants. From the data reported by Schulz and Lechner, C, b_1, and b_2 were found to be 0.068, 1089 kg/cm^2, and 6.467×10^{-3} (°C)$^{-1}$, respectively. From equations (1)–(3), the characteristic parameters of the new Flory theory at elevated pressure were calculated.

The density of polystyrene at atmospheric pressure was obtained by Flory[25] and represented by the following equation:

$$\rho(\text{g/cm}^3) = 1.0865 - 6.19 \times 10^{-4}t + 1.36 \times 10^{-7}t^2 \quad (5)$$

The expression for the thermal expansion coefficient obtained from equation (5) is:

$$\alpha(\text{deg}^{-1}) = 5.70 \times 10^{-4} + 0.75 \times 10^{-7}t \quad (6)$$

The relative volume of liquid polystyrene was given by Simha[26] by use of the Tait equation and is expressed by:

$$1 - V_P/V_0 = 0.0894 \ln(1 + P/B) \quad (7)$$

$$B(\text{kg/cm}^2) = 2.212 \times 10^3 \exp(-3.32 \times 10^{-3}t) \quad (8)$$

These equations were obtained for liquid polystyrene above the glass-transition temperature, and were extrapolated to the experimental temperature range.

The viscosity measurements at elevated pressure were carried out by use of a self-made rolling-ball type viscometer up to 400 kg/cm^2. The viscosity is determined from the rolling down time for the steel ball (2 mm diameter) in the high pressure tube (2.11 mm i.d.) between two pick-up coils. The details of the apparatus are described elsewhere[21]. The rolling down time was read off to 0.01 sec.

In the present work, the simplified relation developed by Sage[27] under limiting Reynolds number was used:

$$\eta = Kt\Delta\rho \quad (9)$$

where η is the viscosity, K a constant, t the rolling down time, and $\Delta\rho$ the difference in density between the solution and the steel ball. The density of the steel ball was calculated from the expression in degrees Celcius and kg/cm^2:

$$\rho(\text{g/cm}^3) = 7.8835/(1 + 3.5 \times 10^{-5}t)(1 - 6.3 \times 10^{-7}[P - 1]) \quad (10)$$

The relation of equation (9) was examined by measuring the rolling down time of a liquid with known viscosity. The specific viscosity of the solution at elevated pressure was determined by:

$$\eta_{sp} = \eta^{\circ}_{rel}([t\Delta\rho]^{P}_{soln}/[t\Delta\rho]^{\circ}_{soln})/([t\Delta\rho]^{P}_{solv}/[t\Delta\rho]^{\circ}_{solv}) - 1 \quad (11)$$

where η°_{rel} is the relative viscosity of the solution at atmospheric pressure, and *soln* and *solv* signify the values of solution and solvent, respectively.

The pressure was generated by compressing the solution directly. The viscometer was placed in a water bath regulated to within ±0.05°C. The pressure was determined by a calibrated Bourdon-type pressure gauge and controlled within ± 1 kg/cm^2. The concentration of the solution was determined by weighing the solution and the polymer after measurements.

RESULTS AND DISCUSSION

The rolling time ranged from about 150 to 420 sec. Repeatibility of the experiment was found to be better than 0.1% over the whole range. The viscometer was calibrated at atmospheric pressure using polystyrene–*trans*-decalin solution, whose viscosity was determined using the calibrated Ubbelohde viscometer over the experimental temperatures. The calibration curve is shown in *Figure 1*. Equation (9) holds well. The constant, K, was found to be 1.446×10^{-3} cp/gcm^{-3} sec. With increasing pressure, the rolling down time and the viscosity increase. A plot of η_{sp}/c against concentration at 400 kg/cm^2 is shown in *Figure 2* as an example. The values of the intrinsic viscosity of polystyrene in *trans*-decalin are tabulated in *Table 1*.

Flory[22] showed the fifth-power rule for the expansion of the polymer molecule in the solution as follows:

$$[\eta] = KM^{1/2}\alpha^{2.43} \qquad K = \Phi(\langle R^2\rangle_0/M)^{3/2}$$

$$\alpha^5 - \alpha^3 = 2Cf(1/2 - \chi_1)M^{1/2}$$

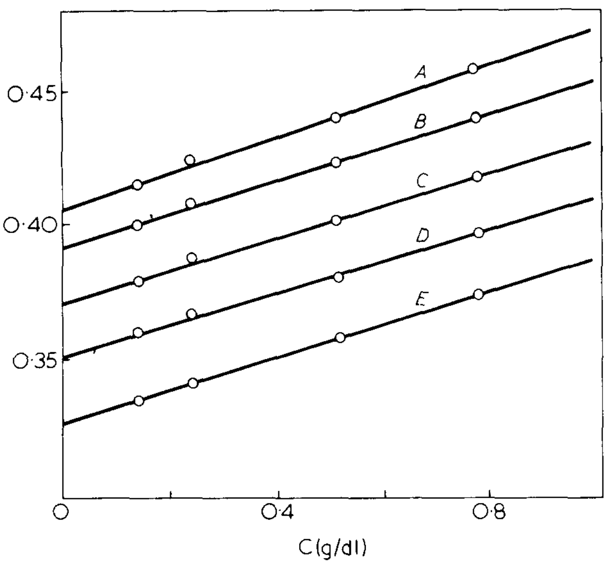

Figure 2 η_{sp}/c *versus c* relationships for polystyrene—*trans*-decalin at 400 kg/cm^2 at temperatures, A – 40°C, B – 33°C, C – 30°C, D – 25°C and E – 20°C

Table 1 Intrinsic viscosity of polystyrene in *trans*-decalin, [η] (dl/g)

Temperature (°C)	Pressure (kg/cm^2)				
	0	100	200	300	400
10.0	0.3282	0.3276	0.3270	0.3265	0.3260
25.0	0.3508	0.3507	0.3506	0.3505	0.3504
30.0	0.3703	0.3705	0.3708	0.3712	0.3718
35.0	0.3888	0.3891	0.3895	0.3904	0.3915
40.0	0.4044	0.4050	0.4057	0.4064	0.4074

$$C = 1.423 \times 10^{-24}(\bar{v}^{-2}/V_1)(\langle R^2\rangle_0/M)^{-3/2} \qquad (12)$$

where α is the expansion factor arising from the intramolecular interaction, Φ a universal constant, $\bar{v}$ the specific volume of the polymer, V_1 the molar volume of the solvent, and $\langle R^2\rangle_0$ the unperturbed end-to-end distance of the polymer molecule. The factor f is 0.4913 according to Stockmayer[28] from the perturbation theory for the excluded volume effect. The θ-temperature at elevated pressure was obtained from the results of Schulz and Lechner[1]. Values of K, $[\eta]_\theta/M^{1/2}$, were calculated from the intrinsic viscosity at the θ-temperature, and increase a little with increasing pressure. The expansion coefficient of the polymer molecule was calculated from the relation $\alpha^{2.43} \doteq [\eta]/[\eta]_\theta$, assuming K to be constant for the experimental temperature range. Values increased with increasing temperature and decreased with increasing pressure. In *Figure 3*, the intrinsic viscosity as a function of pressure is shown and the pressure derivative is negative at lower temperature, but is positive at higher temperature. The interaction parameter, χ_1, was deduced from equation (12). The pressure and the temperature dependence of χ_1 are shown in *Figure 4*. χ_1 increased with increasing pressure and the compatibility became worse.

χ_1 can be resolved into enthalpy and entropy terms by:

$$\chi_1 = \chi_{H,1} + \chi_{S,1} = 1/2 - \psi_1 + \kappa_1 = 1/2 - \psi_1(1 - \theta/T) \qquad (13)$$

where ψ_1 is the entropy parameter and κ_1 is the enthalpy parameter. This implies that $(1/2 - \chi_1)$ is linear for the reciprocal of temperature. The plot of $(1/2 - \chi_1)$ vs. $1/T$ shows that the linearity is well reproduced for each pressure: thus the entropy parameter was determined from the intercept as shown in *Figure 5*. ψ_1 increased with increasing pressure.

According to the excluded volume theory[29], the second virial coefficient is related to χ_1 by the relation

$$A_2 = (v_2^2/V_1)(1/2 - \chi_1)h(z/\alpha^3) \qquad (14)$$

where v_2 is the specific volume of the polymer and z is the well known excluded volume parameter and $h(z/\alpha^3)$ is defined by Flory as:

$$h(z/\alpha^3) = \ln(1 + 5.73[z/\alpha^3])/5.73[z/\alpha^3] \qquad (15)$$

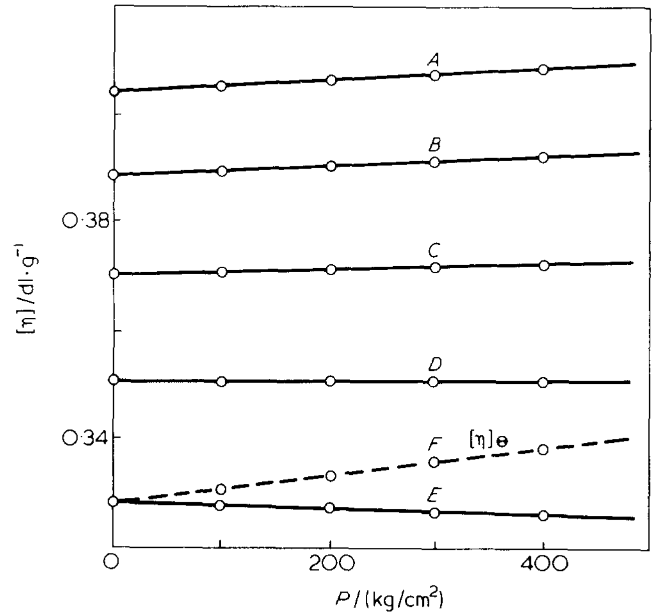

Figure 3 The intrinsic viscosity as a function of pressure at temperatures: A – 40°C, B – 35°C, C – 30°C, D – 25°C, E – 20°C, F – θ-temperature

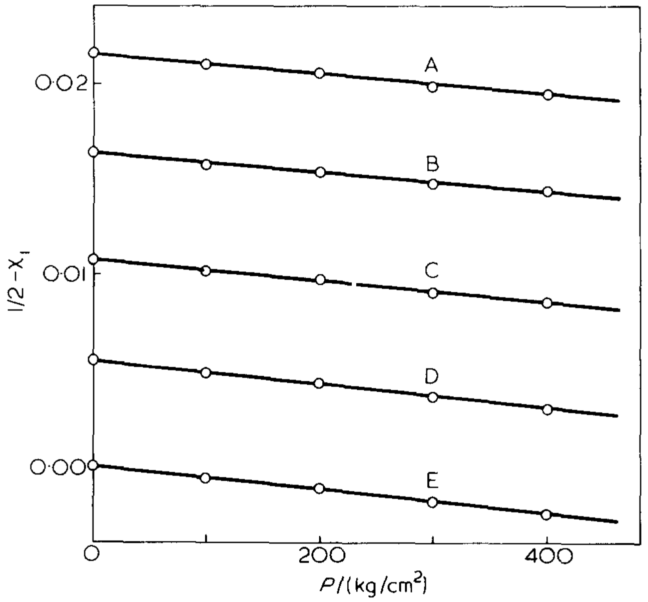

Figure 4 Plots of $(1/2 - \chi_1)$ *versus* pressure at various temperatures for polystyrene—*trans*-decalin determined from the fifth power rule for the coil expansion. A – 40°C, B – 35°C, C – 30°C, D – 25°C, E – 20°C

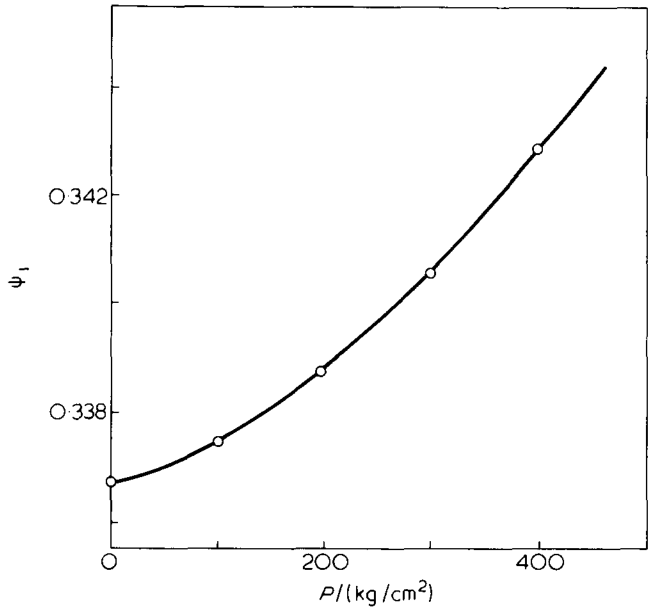

Figure 5 The entropic parameter, ψ_1, as a function of pressure. Those were determined from the intercept of the plots of $(1/2 - \chi_1)$ *versus* $1/T$

From the intrinsic viscosity, the values of A_2 calculated were compared with the values obtained by Schulz and Lechner[1], and they were in good agreement, within 10%, over the whole range. The pressure derivative of A_2 at 20°C was -3.3×10^{-8} and 3.6×10^{8} for the calculated value and for the results of Schulz, respectively. Schulz reported that the excluded volume theory fits well with the experimental results and this is also shown in the viscometric results. The pressure effect on the excluded volume at high pressure is the same as at atmospheric pressure and is quite similar to that caused by the temperature change. A negative pressure derivative of A_2 implies positive volume change on mixing and corresponds to the positive pressure coefficient of the upper critical solution temperature or corresponding θ-temperature.

At the θ-temperature, χ is 0.5, and neglecting $\chi_2\phi_2^2$ and higher orders of the series expansion of ϕ_2, the segment fraction for χ is:

$$d\theta/dP = -(\partial\chi_1/\partial P)_T/(\partial\chi_1/\partial T)_P \qquad (16)$$

In the vicinity of the upper critical solution temperature, the process of mixing is endothermic and $(\partial\chi_1/\partial T)_P$ is negative[30], and the sign of the pressure coefficient of the θ-temperature is the same as that of the volume change on mixing, or $(\partial\chi_1/\partial P)_T$. The positive excess volume of mixing was observed by Schulz and the pressure derivative of the θ-temperature should be positive. The observed positive excess volume of mixing corresponds to the existence of the lower critical solution pressure.

According to Schultz and Lechner[1], the pressure dependence of the θ-temperature is 20.0, 20.8, 22.3, 23.8, and 24.6 for 1, 200, 400, 600, and 800 atm, respectively. We obtained values at the experimental pressure by interpolation. The value of $d\theta/dP$ at atmospheric pressure is 5.8×10^{-3} deg/kgcm^{-2}. From the values of χ_1 the pressure and the temperature derivatives of χ_1 were calculated and were 6.25×10^{-6} cm^2/kg and -1.08×10^{-3} deg^{-1} respectively at atmospheric pressure and 20°C (θ-temperature). These give $d\theta/dP = 5.79 \times 10^{-3}$ deg/kgcm^{-2}. This value is in good agreement with the result of Schulz *et al.*

The value of $d\theta/dP$ of polystyrene in *trans*-decalin is much lower than -0.30 deg/atm of polystyrene in t-butyl acetate and is comparable to the pressure dependence of the upper critical solution temperature of polystyrene in cyclohexane observed by Saeki[10]. This value is mainly determined by the magnitude of $(\partial\chi_1/\partial P)_T$ and/or by the excess volume of mixing. The large difference in these values between *trans*-decalin and t-butyl acetate is due to the magnitude of the excess volume and large difference of the characteristic temperature. Thus, the sign of excess volume differs between the two solvents, and the magnitude of the contribution of the free volume effect is very different. This effect is related to the behaviour with temperature change, that is, for polystyrene in *trans*-decalin, the θ-temperature corresponding to the lower critical solution temperature or cloud point is not observed even above 360°C[10], but for polystyrene in t-butyl acetate the θ-temperature corresponding to the lower critical solution temperature is observed at a very low temperature of about 86°C and the difference between the lower and the upper critical solution temperature is small[10]. In the t-butyl acetate system, the free volume effect and/or the equation-of-state term contribution through $\alpha/\tilde{v}$, is comparable to the exchange term and contributes greatly to the interaction parameter. Therefore, for pressure changes the contribution of free volume is of great importance and the thermodynamic properties of the polymer solutions are subject to the properties of their respective components as is expected by the new Flory theory and the Patterson theory.

According to the new Flory theory[17], the interaction parameter, χ_1, is expressed by:

$$\chi_1 = (P_1^* V_1^*/RT\tilde{V}_1)\,[A^2\alpha_1 T/2 + X_{12}/P_1^*(s_1/s_2)^2]$$
$$- V_1^* Q_{12}/R(s_1/s_2)^2 \qquad (17)$$

$$A = (1 - T_1^*/T_2^*)(P_2^*/P_1^*) - (X_{12}/P_1^*)(s_2/s_1) \qquad (18)$$

and the reduced residual partial molar enthalpy, $\chi_{H,1} = \chi_1 - \chi_{S,1}$ is expressed by:

$$\chi_{H,1} = (P_1^* V_1^*/RT\tilde{V}_1)(1 + \alpha_1 T)\,[X_{12}/P_1^*(s_1/s_2)^2$$
$$- (2/3)(A\alpha_1 T)^2] \qquad (19)$$

where the asterisk and tilde signify respectively the characteristic and reduced quantities; χ_{12} characterizes the energetic weakness of the (1 – 2) contacts relative to (1 – 1) and (2 – 2) and is the exchange interaction parameter for the enthalpy exclusively and Q_{12} is the corresponding parameter for the exchange entropy. s_1/s_2 is the ratio of surface areas per unit characteristic volume for solvent and polymer. For polystyrene–*trans*-decalin solution, Nakata *et al.*[24] obtained these parameters from the osmotic pressure measurements as $X_{12} = 18.7$ J/cm^3, $Q_{12} = 0.0004$ J/cm^3 deg, and $s_1/s_2 = 1.52$. Q_{12} reflects the contribution from an inaccuracy in the combinatorial entropy of random mixing. These values well reproduce the behaviour of χ_1 at atmospheric pressure determined from the intrinsic viscosity. Equations (17) and (18) were used for predicting the pressure and the temperature dependence of χ_1. The characteristic parameters of solvent and polymer determined from the equation of state of the new Flory theory at various pressures are listed in *Table 2*. They change a little with pressure and temperature because of the shortcoming of the new Flory theory, but this influence may be reduced by using the values of the charac-

Table 2 Characteristic parameters for polystyrene and *trans*-decalin at 20°C and elevated pressure determined from the equation-of-state of the new Flory theory

		P^* (kg/cm^2)	V^* (cm^3/g)	T^* (K)	$\tilde{V}$
Polystyrene	0	5612	0.8092	7389	1.1504
	100	5459	0.8088	7364	1.1466
	200	5307	0.8084	7332	1.1429
	300	5157	0.8080	7294	1.1394
	400	5008	0.8075	7251	1.1361
trans-Decalin	0	5174	0.9473	5694	1.2135
	100	5196	0.9460	5666	1.2068
	200	5217	0.9448	5633	1.2010
	300	5241	0.9435	5598	1.1959
	400	5266	0.9420	5561	1.1914

teristic parameters at the same pressure and temperature as the viscosity measurements for the solutions.

Using equations (17) and (18), the pressure and the temperature derivatives of χ_1 were calculated and listed in *Table 3*. (1) were calculated considering the pressure and the temperature dependences of the characteristic parameters of solvent and polymer and (2) were not. From these values, the pressure coefficient of the θ-temperature was calculated. The predicted value of $(\partial\chi_1/\partial P)_T$ of (1) agrees well with that of the experimental, but (2) is about one and half times greater than the experimental. The predicted values of $(\partial\chi_1/\partial T)_P$ of (1) and (2) are almost the same as each other. The pressure coefficient of the θ-temperature predicted from (1) is smaller than that from (2) reflecting the magnitude of $(\partial\chi_1/\partial P)_T$, but both give comparatively good prediction for $d\theta/dP$. This implies that by considering the pressure and the temperature dependences of the characteristic parameters not only the θ-temperature but also the behaviour of χ_1 are well represented by the new Flory theory as is observed by osmotic pressure and cloud point curves at atmospheric pressure[24].

In equation (17), χ_1 comprises three terms: the equation-of-state term related to the thermal expansion coefficient; the X_{12} term relating to the exchange energy, and the Q_{12} term. The Q_{12} term does not directly affect the pressure and the temperature dependence of χ_1. The equation-of-state term reflects the contribution from the difference in thermodynamic properties of polymer and solvent. The contribution of equation-of-state term to $(\partial\chi_1/\partial P)_T$ has inverse sign, as large as that of the X_{12} term, but the former contribution to $(\partial\chi_1/\partial T)_P$ is much smaller than the latter. The contribution of the equation-of-state is inverse for pressure and temperature. The pressure effect on the equation-of-state is a large and negative contribution to χ_1 as predicted. This is also shown in the behaviour of $\chi_{H,1}$ or $\chi_{S,1}$. Experimental $\chi_{H,1}$ was 0.3367 at 20°C, and the predicted $\chi_{H,1}$ by equation (19) was 0.375. The experimental pressure derivative of $\chi_{H,1}$ was obtained to be 1.38×10^{-5} and the predicted one was 7.92×10^{-5}. The contribution of equation-of-state term is about half of that of the χ_{12} term and is an important part in the pressure effect.

According to Patterson[19], the interaction parameter, χ_1, is expressed by:

$$\chi_1/c_1 = (-\tilde{U}_1/\tilde{T}_1)\nu^2 + (1/2)\tilde{C}_{P.1}[\tau + \pi\tilde{P}_1\tilde{V}_1^2/(\tilde{P}_1\tilde{V}_1^2 + 1)]^2 \tag{20}$$

where c_1 is the external degree of freedom of solvent, $\tilde{U}_1$ the reduced internal energy, $\tilde{C}_{P,1}$ the reduced heat capacity. The τ parameter is a measure of the difference in degrees of thermal expansion or free volume of the components and is defined as:

$$\tau = 1 - T_1^*/T_2^* \tag{21}$$

The π parameter expresses a difference in P^* reduction parameters similar to equation (21):

$$\pi = P_1^*/P_2^* - 1$$

Using the equation-of-state of the new Flory theory[17] $\tilde{U}_1$ and $\tilde{C}_{P,1}$ are given by:

$$\tilde{U}_1 = -\tilde{V}^{-1} \quad \tilde{C}_{P,1}^{-1} = [1 - (2/3)\tilde{V}_1^{-1/3}] - 2(1 - \tilde{V}_1^{-1/3})/(\tilde{P}_1\tilde{V}_1^2 + 1) \tag{22}$$

The ν^2 parameter expresses the difference of chemical nature of the components corresponding to X_{12} in the new Flory theory. This representation of χ_1 contains the pressure effect explicitly and it is able to be compared with the values at elevated pressure directly. The ν^2 parameter was determined to give 0.5 for χ_1 at the θ-temperature. It is 0.01572 at atmospheric pressure and decreases a little with increasing pressure (about 4% at 400 kg/cm^2).

Using equations (20)–(22), the pressure and the temperature derivatives of χ_1 were calculated and listed in *Table 3*. (1) and (2) signify similarly as in the case of the new Flory theory. (1) gives good prediction of both $(\partial\chi_1/\partial P)_T$ and $(\partial\chi_1/\partial T)_P$, but in the case of (2) the predicted value of $(\partial\chi_1/\partial P)_T$ is much larger than the experimental one. The predicted pressure coefficient of the θ-temperature was in good agreement for (1) but was too large for (2). Therefore, it is necessary to consider the pressure and temperature dependence of the characteristic parameters for respective components in solution thermodynamics. The behaviour of the ν^2 or interaction term and the equation-of-state term is the same as in the new Flory theory, though the magnitude of pressure derivatives of the ν^2 term and equation-of-state term are smaller by one order than that in the new Flory theory. The pressure dependence of χ_1 at several temperatures, predicted from equations (20)–(22) was examined and is shown in *Figure 6*. As is shown, near the θ-temperature and at lower pressure, agreement is good, but at higher pressure and temperature, agreement becomes worse. These deficiences may partly be due to the uncertainty from the extrapolating isotherm of liquid polystyrene above the glass-transition temperature, but the theoretical prediction gives (qualitatively) reasonable agreement with the experiment. From the investigation of the thermodynamic properties at elevated pressure, it is noted that the free volume contribution is large and is of great importance.

Table 3 Pressure and temperature derivatives of χ_1 at atmospheric pressure and theta temperature and pressure dependence of theta-temperature

	$\partial\chi_1/\partial P \times 10^6$ (kg^{-1} cm^2)	$\partial\chi_1/\partial T \times 10^3$ (deg^{-1})	$d\theta/dP \times 10^3$ (deg dg^{-1} cm^2)
Experimental	6.25	−1.08	5.79
Flory (1)	6.17	−1.28	4.82
Flory (2)	9.01	−1.34	6.72
Patterson (1)	5.15	−0.95	5.42
Patterson (2)	58.4	−1.29	45.2

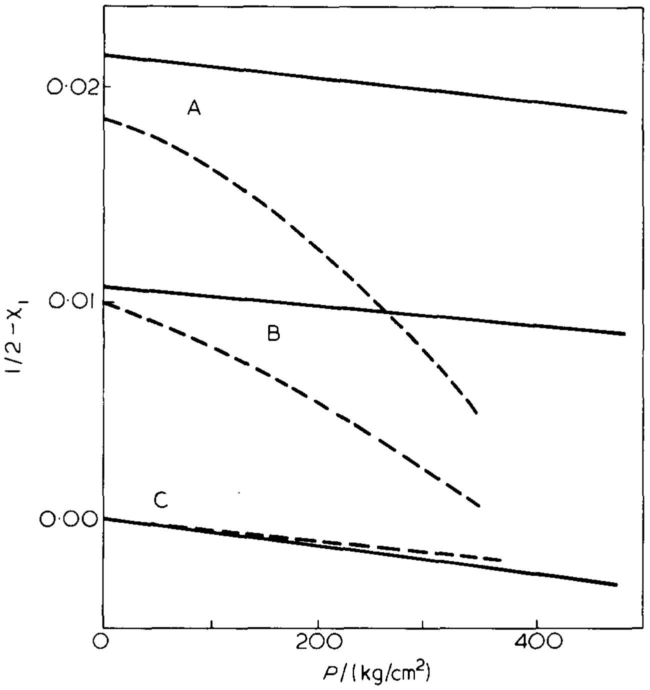

Figure 6 The comparison between experimental results and the theoretical prediction by the Patterson theory, equation (20), for ($1/2-\chi_1$) *versus* pressure at various temperatures, A — 40°C, B — 30°C, C — 20°C. ——, experimental; — — —, theoretical results

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