(19) The data of molecular weight reported by Fukuda et al.[10] on the same samples are all smaller than the present data, and the difference increases with molecular weight. The descrepancy was found to originate from the error in their concentration determination. The solution on which the concentration had been determined was filtered through a Millipore filter, and the light-scattering measurements were carried out on the filtrate. Therefore, the concentration was overestimated due to the retention of some material on the filter. The higher the sample molecular weight becomes the larger is the amount of the retained material. Their data of A_2 may also involve some error. The data of $\langle S^2 \rangle$ may be least affected because the relative concentration suffices for the measurement. Indeed, reevaluation of $10^{18}\langle S^2 \rangle_0/M$ (*trans*-decalin, 20.4 °C) with use of molecular weight obtained here yields a constant 7.28 irrespective of molecular weight within 3%. However, for the sake of clarity we used in the later analysis a value of 7.60 as reported by Berry.[7] A similar experimental procedure was employed for the concentration determination by Kato et al. on the study of poly(α-methylstyrene): T. Kato, K. Miyaso, I. Noda, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **3**, 777 (1970).

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Equation of State of Poly(dimethylsiloxane) up to 800 kg/cm^2

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ABSTRACT: Isotherms of poly(dimethylsiloxane) (molecular weight 5.10×10^4) were measured at various temperatures and up to 800 kg/cm^2. The P–V–T relations were described by the Tait equation. The pressure dependence of the characteristic parameters of the equation of state of the Flory theory was examined from these P–V–T relations. Pressure dependences were comparatively large. At high pressure the equation of state of the Flory theory cannot adequately represent the P–V–T behavior of the polymer system.

The present investigation was undertaken with the objective of examining the properties of the equation of state and the applicability of the Flory theory[1] to polymers under pressure. During the last 10 years, the theory of polymer solutions developed by Flory,[1,2] Patterson,[3] and the others[4,5] has clarified the importance of "equation-of-state" effects. These effects can be attributed to the free volume difference between the solvent and the polymer. The equation-of-state characteristics of bulk amorphous polymer are of intrinsic interest apart from the analysis of the properties of the solutions. Especially, poly(dimethylsiloxane) has an extraordinarily large thermal expansion coefficient and isothermal compressibility compared with other polymers. Many investigations about temperature dependences of equation-of-state parameters of polymers are reported, but data on the pressure dependences of these under elevated pressure are scarce.

In this work, from the density of poly(dimethylsiloxane) at various temperatures, the pressure dependence of the characteristic parameters of the equation of state of the Flory theory were examined, and various premises of the Flory theory were examined at elevated pressure.

Experimental Section

Poly(dimethylsiloxane) (PDMS) was from the Shin-Etsu Chemical Co., with 6000 CS. The viscosity average molecular weight determined by the equation of Barry[6] ($\log \eta_{CS}{}^{25\,°C} = 1.00 + 0.0123M^{0.5}$) was 5.10×10^4. PDMS was sufficiently evacuated before measurements in order to remove volatile constituents.

The P–V isotherms were measured by a piston–cylinder type high-pressure cell. The cell is made of beryllium–copper alloy and its capacity is ca. 10 cm^3. Pressure was applied by compressing the test sample directly, and the volume change was determined from the piston displacement, the accuracy of which was $\pm 2 \times 10^{-3}$ cm^3 (0.02%). The pressure cell was immersed in a silicon oil bath, and the temperature was regulated to within 0.01 °C. Pressure was measured using a manganin gauge and a home-made Kelvin double bridge. The temperature of the test sample in the pressure cell was checked by a platinum wire resistor.

The isothermal compressibility of benzene was measured for calibration and was compared with the data of Gibson et al.[7] The largest discrepancy was 1% in the range of 20–60 °C.

This apparatus yields only the volume change relative to that at atmospheric pressure. Therefore, it is necessary to know the specific volume of PDMS at atmospheric pressure, and the data of Shih and Flory[8] were used for this purpose.

Results and Discussion

Relative volumes were measured as a function of pressure and temperature over the range of 1–800 kg/cm^2 and 29–60 °C. Five isotherms (29.0, 32.5, 38.4, 49.0, and 60.0 °C) were obtained. The changes in volume relative to those at atmospheric pressure at various temperatures are given in Table I, and some of them are shown in Figure 1.

At all temperatures, the observed P–V behavior can be represented by the equation proposed by Tait,

$$V/V_0 = 1 - C \ln (1 + P/B) \qquad (1)$$

where V is the specific volume at pressure P and temperature T, V_0 is the specific volume at atmospheric pressure and the same temperature T, C is a dimensionless constant, and B is a volume-independent function of temperature. The theoretical basis of this equation has been discussed[9] and it is

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Table I
The Change in Volume at Elevated Pressure Relative to Atmospheric Pressure of Poly(dimethylsiloxane)

Pressure, kg/cm^2	(V/V_0)				
	29.0 °C	32.5 °C	38.4 °C	49.0 °C	60.0 °C
0	1.0000	1.0000	1.0000	1.0000	1.0000
100	0.9888	0.9886	0.9882	0.9873	0.9865
200	0.9784	0.9781	0.9774	0.9758	0.9745
300	0.9691	0.9686	0.9677	0.9656	0.9637
400	0.9604	0.9600	0.9588	0.9566	0.9539
500	0.9525	0.9521	0.9508	0.9482	0.9457
600	0.9452	0.9447	0.9434	0.9407	0.9377
700	0.9385	0.9380	0.9367	0.9336	0.9302
800	0.9322	0.9315	0.9299	0.9268	0.9234
$\sigma \times 10^{4}$[a]	4.58	1.58	1.11	1.68	2.03

[a] σ is the root-mean-square deviation of the relative volume as calculated from the Tait equation described in the text.

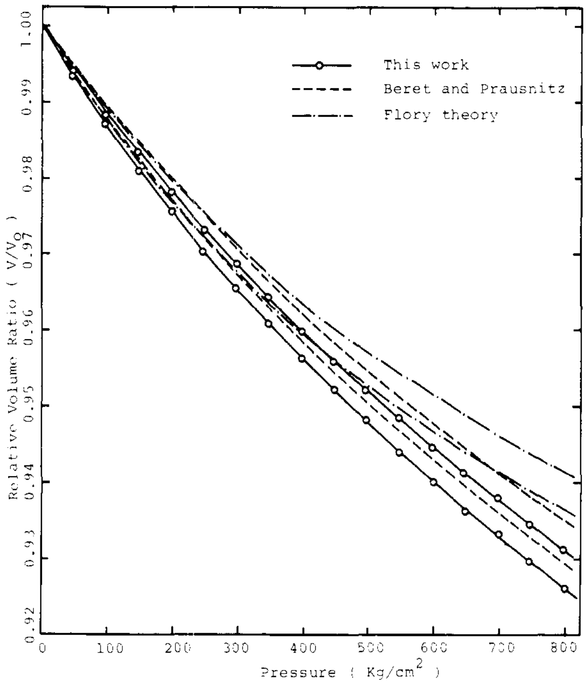

Figure 1. Relative volumes of poly(dimethylsiloxane) at 29.0 °C (upper) and at 49.0 °C (lower). The curves of Beret and Prausnitz are obtained using their Tait equation constants of ref 12. The curves predicted from the Flory theory are calculated using the values for P^*, V^*, and T^* at 29.0 and 49.0 °C and at atmospheric pressure.

found that the adjustable parameter C of the Tait equation appears to be temperature independent.[10]

The parameter B which reflects the repulsive pressure is expressed by the following equation,[11]

$$B = b_1 \exp(-b_2 T) \tag{2}$$

where b_1 and b_2 are empirical constants.

Table II
Comparison of Isothermal Compressibility of Poly(dimethylsiloxane) at Atmospheric Pressure ($\times 10^{-4}$ kg/cm^2)

	30 °C	40 °C	50 °C	60 °C
This work[a]	1.205	1.283	1.372	1.456
Prausnitz[b]	1.133	1.202	1.274	1.351
Flory[c]	1.209	1.284	1.364	1.449

[a] Interpolated values from measurements. [b] Calculated values from Table III of ref 12. [c] Calculated values from thermal expansion coefficients and thermal pressure coefficients of Table II of ref 8.

From the P–V isotherms at various temperatures, by the method of least squares, C, b_1, and b_2 were found to be 0.09883, 5.088 × 10^3 kg/cm^2, and 6.035 × 10^{-3} K^{-1}. Beret and Prausnitz[12] reported them to be 0.100916, 1.0407 × 10^3 bar, and 5.8507 × 10^{-3} K^{-1}, respectively. Simha et al.[13] set the dimensionless constant C in eq 1 equal to 0.0894 for high molecular weight hydrocarbons and for several polymers. However, this constant is here allowed to vary from one polymer to another. In Figure 1 the isotherms calculated from the Tait parameters of Beret and Prausnitz and ours are shown in comparison. On the other hand, Shih and Flory[8] obtained thermal expansion coefficients and thermal pressure coefficients of PDMS at atmospheric pressure. Isothermal compressibility at atmospheric pressure was calculated from those. A comparison of isothermal compressibility among the three sets of data is given in Table II. The values of Prausnitz are somewhat lower than both ours and Flory's.

Flory[1] and co-workers proposed a theory using an intermolecular energy of the van der Waals form, and his equation of state can be regarded as one in which the configurational energy is added as a perturbation to the equation of state for hard spheres.[14] Flory's equation of state relates reduced pressure to reduced volume and temperature by the following equation,

$$\tilde{P}\tilde{V}/\tilde{T} = \tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1) - 1/\tilde{V}\tilde{T} \tag{3}$$

where $\tilde{P}$, $\tilde{V}$, and $\tilde{T}$ are P/P^*, V/V^*, and T/T^*, respectively. Here P^*, V^*, and T^* are characteristic parameters determined from density, thermal expansion coefficient, and thermal pressure coefficient of the substance. According to eq 3, each characteristic parameter is determined by the following equations derived by differentiating eq 3,

$$\tilde{V}^{1/3} = 1 + \tfrac{1}{3}[1 + 1/\alpha T - 2P/(P + P_i)]^{-1} \tag{4}$$

$$\tilde{T} = (\tilde{V}^{1/3} - 1)(P/P_i + 1)/\tilde{V}^{4/3} \tag{5}$$

$$P^* = P_i \tilde{V}^2 \tag{6}$$

$$P_i = T\gamma - P \tag{7}$$

where α is the thermal expansion coefficient and γ is the thermal pressure coefficient at T and P. The quantity P^* is a measure of the mean intermolecular energy per unit volume corrected for the density of packing in the liquid. The characteristic parameters determined by eq 4, 5, and 6 are listed in Table III.

PDMS has very low values of P^* compared with other polymers.[8] They are comparable or smaller than those of low molecular weight liquids. The intermolecular energy of PDMS is extraordinarily low and the intermolecular degree of freedom is large. These suggest that PDMS would have a large free volume and a high compressibility.

All characteristic parameters, especially P^*, decrease with increasing pressure. According to the Flory theory, $P^*V^* = ckT^*$, where c measures the number of external degrees of freedom and should presumably be a molecular constant. The constancy of c or P^*V^*/T^* is thus regarded as a measure of applicability of the Flory theory. We find that P^*V^*/T^* decreases with pressure as well as temperature. Generally speaking, the change of c for the polymer is a little larger than that for a low molecular weight liquid; for example, the change in P^*V^*/T^* of benzene is 4% at 30 °C from atmospheric pressure to 600 kg/cm^2. The large change in P^*V^*/T^* of PDMS with pressure, 10% at 50 °C in the same pressure range, means that PDMS has a large free volume, and the pressure effect is strong. These correspond to the other peculiar

Table III
Pressure Dependence of the Characteristic Parameters of the Flory Theory at 50 °C

Pressure, kg/cm^2	P^*, kg/cm^2	V^*, cm^3/g	T^*, K
0	3358	0.8468	5700
200	3152	0.8413	5546
400	2963	0.8369	5355
600	2782	0.8307	5136
800	2603	0.8258	4896

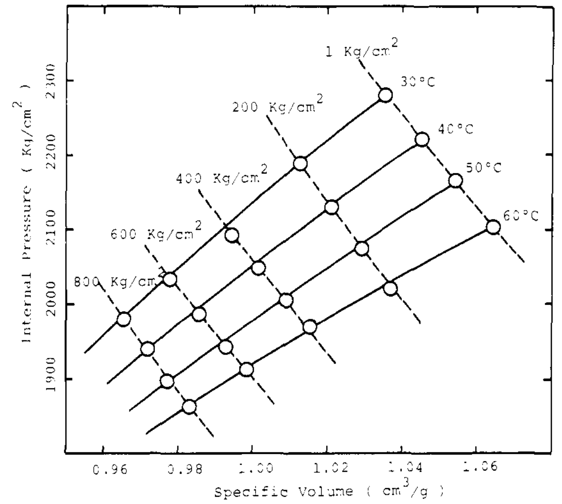

Figure 2. The internal pressure of poly(dimethylsiloxane) as a function of specific volume.

properties of PDMS, i.e., low viscosity and its large pressure coefficient and low temperature coefficient. Thus, it is necessary to examine the pressure dependence of the internal pressure of PDMS. (See Figure 2.)

According to the Flory theory, it is assumed that the internal energy U is only a volume-dependent function and is proportional to the reciprocal volume, i.e., internal pressure $(\partial U/\partial V)_T$ is proportional to V^{-2}. In many low molecular weight liquids this relation is satisfied.[15] When liquids are expanded and the repulsive term of the potential becomes negligible, the internal energy can be represented by the attractive term only. As is expected, this approximation by the attractive term a/V^n becomes inadequate for more complex molecules, or for higher pressure and lower temperature. In fact, $V^2(\partial U/\partial V)_T$ of PDMS varies greatly with pressure, though its temperature dependence is small. The internal pressure of PDMS is not only a volume function, but depends on both volume and temperature. Olabisi and Simha[16] obtained the reduced internal pressure for several oligomers and polymers using the reduced Tait equation. And using the equation of state derived in the hole theory, they reported that the reduced internal pressure can be represented by an exponential relation, i.e., $\tilde{P}_i = 0.5332/\tilde{V}^{2.869}$. But this is at atmospheric pressure. The reduced internal pressure of PDMS at atmospheric pressure also lies almost on the curve of eq 16b of ref 16. If the pressure is changed, the relation of the reduced internal pressure to the reduced volume cannot be represented by a pure volume function, as is shown in Figure 6 of ref 16 or Figure 2 of this paper. PDMS has very small P^* and T^* in the hole theory as well as in the Flory theory. And P^* and T^* are outside the range for which eq 7 of ref 17 or eq 12 of ref 16 were established and show significant departures. Therefore, in the case of PDMS, the tendency described above appears distinctly.

Following Gibson and Loeffler,[10] we assume that the contributions to the internal pressure P_i due to the intermolecular attractive forces in the liquid can be equated to the quantity $T\gamma$ + B. A plot of ln $(T\gamma + B)$ vs. ln $\overline{V}$ (Figure 3) is linear. As is shown, $T\gamma + B$ for PDMS depends only on volume and from the slope $T\gamma + B$ is found to be proportional to $1/\overline{V}^{2.4}$. The exponent 2.4 is smaller than the values obtained by Gibson and Loeffler. They reported the exponents 3, 2.70, 2.69, 2.78, and 2.78 for benzene, aniline, nitrobenzene, bromobenzene, and chlorobenzene, respectively.[18]

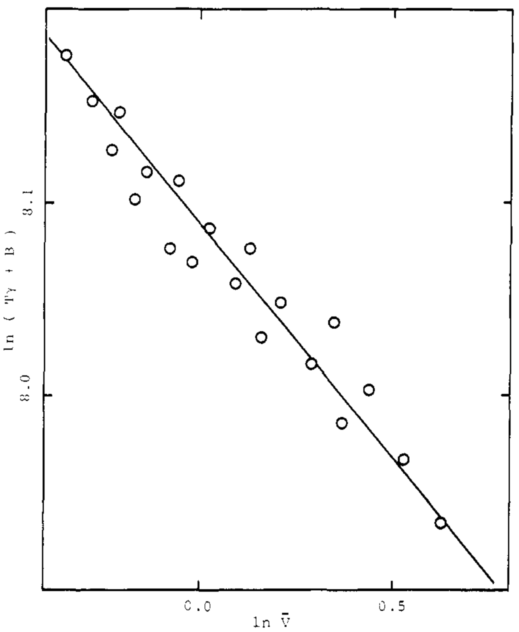

Figure 3. The logarithm of the attractive internal pressure as a function of the logarithm of the specific volume. Experimentals at different pressure and temperatures lie nearly on one line, the slope of which is 2.4.

As is expected from the pressure dependence of the internal pressure of PDMS at constant temperature, the repulsive term is predominant for the change of pressure, and the volume dependence of the repulsive term cannot be approximated by a hard-core potential. It thus appears that Flory's equation of state is not suitable for use at high pressure in this system.

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