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Pressure-Volume-Temperature Relations of Supercooled Liquid and Glass of Triphenylchloromethane/*o*-Terphenyl Mixture

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Volumetric data on the supercooled liquid state and on the glassy state are reported for a binary mixture of triphenylchloromethane and *o*-terphenyl. In the supercooled liquid state, the thermal expansivity, the isothermal compressibility, and their temperature dependences of the mixture are much samller than those of simple molecular liquids and are almost the same order of magnitude as those of polymer liquids. The glass of the mixture also closely resembles polymer glasses in the apparent thermodynamic properties. Some representative lattice-like liquid theories are applied to the pressure-volume-temperature relations of the supercooled liquid sample, with the aid of the principle of corresponding states.

Supercooling and glass transition phenomena are general in all sorts of molecules.[1] Since polymer liquids can easily be supercooled and vitrified, many experimental and theoretical studies on the glass transition of polymers have been proposed.[2,3] The polymer glass transition has been interpreted as arising from a large decrease in the intramolecular conformational entropy of the liquid as the temperature decreases.[3,4] The models adopted in the theory above, however, may not be appropriate for simple molecular liquids.

Recent molecular dynamic simulation studies give some insight into properties of supercooled liquids and glasses,[5] but the one-component monatomic glasses to be studied by such computer experiments are usually extremely difficult to prepare experimentally.

While many accurate measurements of volumetric properties of supercooled liquids and glasses of polymers have been reported,[6–12] such measurements are few for simple molecular liquids due to their low glass transition temperature and poor stabilities of the supercooled liquid states. It is well known that *o*-terphenyl[13] and its mixtures[14] can be supercooled and vitrified. The supercooled liquid of a mixture of triphenylchloromethane (TPCM) and *o*-terphenyl (oTP), TPCM/oTP, was found to be still more stable oTP alone.[15] In this paper, we attempt to measure the pressure-volume-temperature (*P-V-T*) relations of TPCM/oTP below the melting temperature up to 78.5 MPa. The volumetric properties thus obtained are compared with some simple liquid theories.

Experimental

Sample. Triphenylchloromethane (TPCM, the melting temperature $T_m = 113$ °C) and *o*-terphenyl (oTP, $T_m = 55.5$ °C) were purchased from Tokyo Chemical Industry Co. and were used without further purification. A mixture of TPCM/oTP with composition of 25/75 in weight ratio was used in the present study.

The supercooled sample contained in Pyrex test tube was stable over one month at room temperature, but, when the sample was in contact with mercury, it crystallized after about one week. In the present dilatometric experiments, the sample is contained in a small pouch made of thin natural rubber vulcanizate to avoid evolutions of internal stress in the glassy sample as the sample vitrifies. When the sample contained in the rubber pouch was in contact with mercury, it crystallized after about two weeks.

Equipment. Measurements of the *P-V-T* relations were carried out in a Pyrex dilatometer set in a pressure vessel which was immersed in an ethylene glycol/water bath controlled to an accuracy of ±0.02 K by use of a refrigerator (CC-100, Neslab). The temperature was controlled within ±0.004 K in the pressure vessel which was outlined elsewhere.[12] Silicone oil (KF-94, Shin-Etsu Chemical Co.) was used to transmit the hydrostatic pressure. The pressure was measured by a Heise bourdon tube gauge with an automatic compensator (Dresser Industries) and the temperature by a calibrated alumel-chromel thermocouple inserted in the pressure vessel.

A schematic diagram of the pressure dilatometer is shown in Fig. 1. The sample was separated from mercury and Pyrex glass chamber by a thin pouch made of natural rubber vulcanizate. When the sample was directly in contact with the chamber, the dilatometer was almost always broken due to strong adhesion of the sample to the chamber wall as the sample vitrified. Even if the dilatometer was not broken, a high internal stress stored in the glassy sample would result in a poor reproducibility of the volumetric data.

Variations of the sample volume in the dilatometer with temperature and pressure were obtained from changes in the mercury level in the dilatometer, which was read by measuring the emf of a variable transformer (150-9, Shinko Electric Co.)

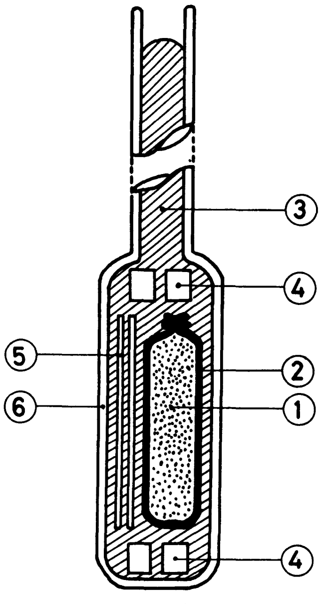

Fig. 1. Schematic diagram of pressure dilatometer.
1: Sample, 2: rubber pouch, 3: mercury, 4: pyrex stopper, 5: pyrex capillary, 6: pyrex chamber.

induced by a piece of Permalloy set on the top of mercury column. Pressure effects on the emf were negligibly small up to 100 MPa, but temperature effects were not.[12] The P-V-T data for mercury taken from Refs. 16 and 17 and a mercury-filled dilatometer were used to calibrate the temperature variation of the emf and to calculated the specific volume of the sample. Details of the pressure cell used and the treatments of data are given elsewhere.[12]

Experimental Procedure and Operations. TPCM and oTP were mixed at 130 °C. The sample was loaded in the rubber pouch at 70 °C, being degassed in slight vacuum. Then the sample was sealed by fastening the pouch with a band made of natural rubber vulcanizate. The rubber pouch and band had previously been purified by repeated sweeling with benzene and toluene and deswelling with methanol and acetone. Mercury was loaded in the dilatometer *in vacuo* at about −30 °C.

The density of the sample was measured at 30 °C by use of a picnometer of volume 25 ml. An isobaric cooling experiment to obtain T_g and the atmospheric V-T relation was carried out at about 1 K intervals in the liquid state and at about 0.5 K intervals in the glassy state with a continuous cooling rate of 0.24 K min^{-1} from 310 to 238 K. Then a heating experiment was carried out with a rate of 0.24 K min^{-1} from just above T_m of mercury (235.28 K) to 273 K.

Isothermal experiments in the supercooled liquid region were carried out to obtain the P-V-T relations at about 4 K intervals over a temperature range of 240—308 K. The pressure was changed in increments of 5.9 MPa in the 0.1—19.6 MPa region and in increments of 9.8 MPa in the 19.6—78.5 MPa region.

V-P relations of the glass vitrified by continuous cooling at a rate of 0.24 K min^{-1} were measured at about 1.5 K intervals from 235.5 K to 249.6 K. At lower temperatures, V-P relations under high pressures were not obtained due to crystallization of mercury. On the other hand, since the sample relaxed toward the equilibrium liquid state and slight retardations were observed in the volume at lower pressures near T_g, the pressure was not released in order to avoid the progressive retardation. The experiments for the glassy state were conducted as quick as feasible.

Although the sample penetrates into the natural rubber pouch, the excess mixing volume between TPCM/oTP and the pouch was ignored in the calculation of the specific volume v of the sample:

$$v_{\mathrm{app}}(w+w_r) = wv + w_r v_r, \tag{1}$$

where v_{app} is the apparent average specific volume of the sample and the rubber pouch and band, v_r the specific volume of the pouch and band,[18] w the mass of the sample (1.1181 g), and w_r the total mass of the pouch and band (0.2653 g).

Results

Supercooled Liquid State. The results of the P-V-T experiments are summarized in Fig. 2. Each atmospheric isobar of the liquid volume from the heating experiment exactly falls on that from the cooling experiment above 254 K. The liquid state specific volume v is expressed by a quadratic equation in temperature T at each pressure P:

$$v = a_0 + a_1 T + a_2 T^2. \tag{2}$$

Values of a_0, a_1, a_2, and the standard deviation σ obtained by the least-squares method are listed in Table 1. The second derivatives a_2 are very small and the isobars of TPCM/oTP are very close to being linear in the supercooled liquid region. Thus the thermal expansivity α, $\alpha \equiv (\partial \ln v/\partial T)_p$, decreases with increasing temperature at all pressures in the present temperature region. Some examples of v and α calculated from Eq. 2 are shown in Figs. 3 and 4, respectively.

The P-T isochores calculated from Eq. 2 are shown

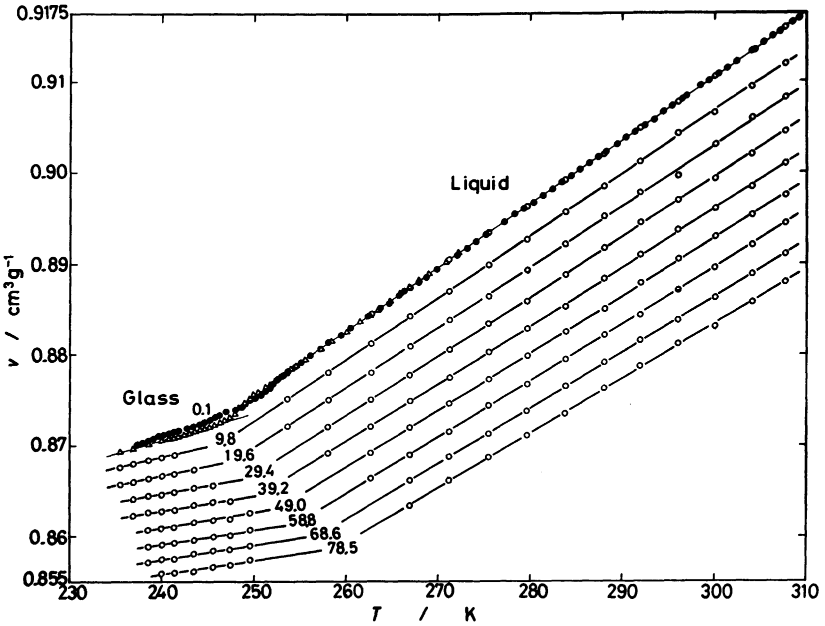

Fig. 2. Summary of P-V-T relations.
Open circles: isothermal experiments, closed circles: isobaric cooling experiment, triangles: isobaric heating experiment, lines: Eq. 2. Numbers in the figure are the pressures in MPa.

Table 1. Specific volume of the liquid

P MPa	a_0 cm^3 g^{-1}	$a_1\times 10^4$ K^{-1} cm^3 g^{-1}	$a_2\times 10^7$ K^{-2} cm^3 g^{-1}	$\sigma\times 10^5$ cm^3 g^{-1}	Region K
0.1	0.71261	6.1650	1.440	2.6	254—310
4.9	0.71932	5.622	2.298	26.6	254—307
9.8	0.70905	6.331	0.860	13.2	254—307
14.7	0.71832	5.602	2.053	12.1	254—307
19.6	0.71907	5.528	2.002	22.9	254—307
29.4	0.71476	5.721	1.450	15.7	258—307
39.2	0.71765	5.432	1.708	16.2	258—307
49.0	0.70645	6.117	0.310	15.1	263—307
58.8	0.71507	5.376	1.467	10.7	263—307
68.6	0.70281	6.119	0	15.5	267—307
78.5	0.70314	6.009	0	17.9	267—307

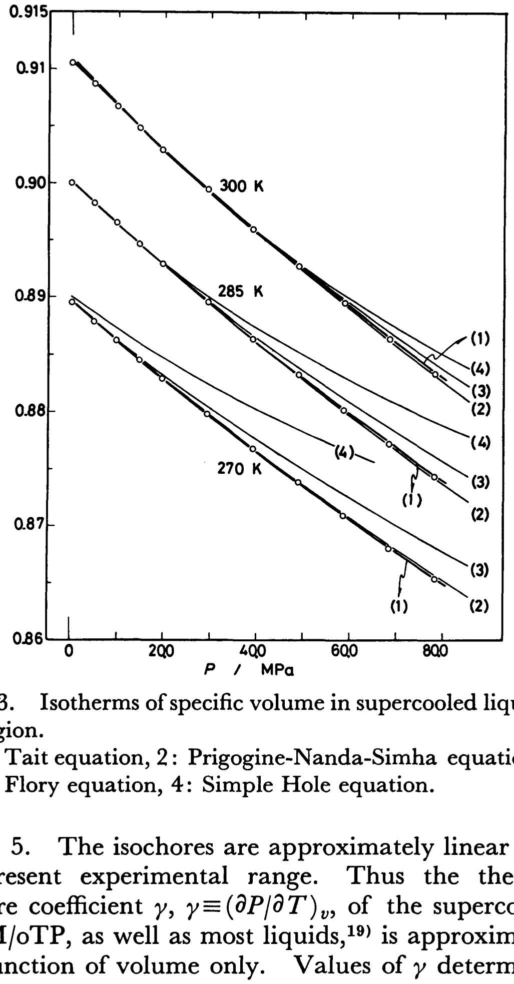

Fig. 3. Isotherms of specific volume in supercooled liquid region.
1: Tait equation, 2: Prigogine-Nanda-Simha equation, 3: Flory equation, 4: Simple Hole equation.

in Fig. 5. The isochores are approximately linear over the present experimental range. Thus the thermal pressure coefficient γ, $\gamma\equiv(\partial P/\partial T)_v$, of the supercooled TPCM/oTP, as well as most liquids,[19] is approximated as a function of volume only. Values of γ determined from slopes of the isochores are shown in Fig. 6. The variation of γ with volume is well represented by a linear equation:

$$\gamma = 11.159 - 10.350\,v \quad (\mathrm{K^{-1}\,MPa}), \tag{3}$$

with the standard deviation being 0.0033 K^{-1} MPa.

The isothermal compressibility β, $\beta\equiv-(\partial \ln v/\partial P)_T$, can be calculated from

$$\beta = \frac{\alpha}{\gamma}, \tag{4}$$

with α from Eq. 2 and γ from Eq. 3. The results are plotted as a function of pressure in Fig. 4. The values

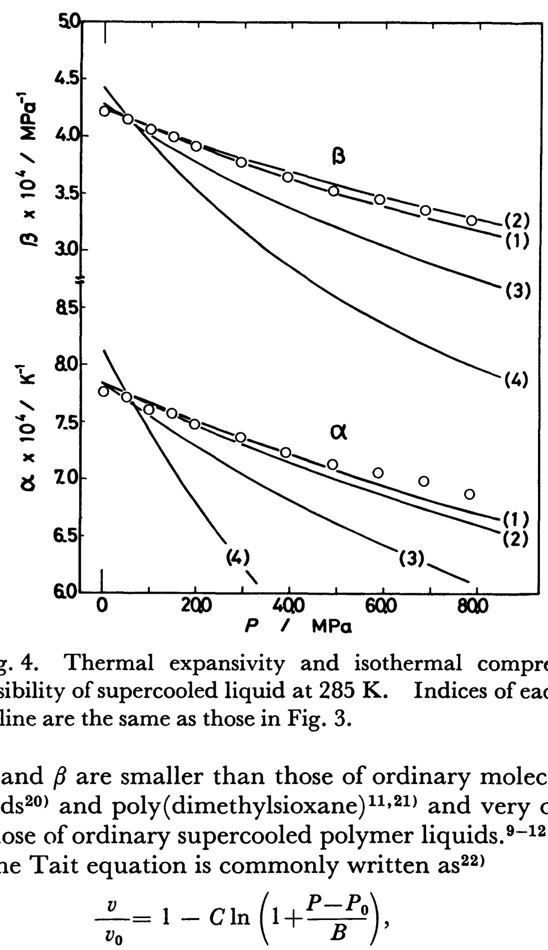

Fig. 4. Thermal expansivity and isothermal compressibility of supercooled liquid at 285 K. Indices of each line are the same as those in Fig. 3.

of α and β are smaller than those of ordinary molecular liquids[20] and poly(dimethylsioxane)[11,21] and very close to those of ordinary supercooled polymer liquids.[9–12]

The Tait equation is commonly written as[22]

$$\frac{v}{v_0} = 1 - C\ln\left(1+\frac{P-P_0}{B}\right), \tag{5}$$

where v_0 is the specific volume at the reference pressure P_0. Simha *et al.*[7,24] have shown that C can be assumed to have the universal value of 0.0894 and B can be expressed by

$$B = b_1 \exp\left(-b_2 T\right). \tag{6}$$

Values of b_1 and b_2 calculated by the least-squares

Table 2. Tait parameters

	C	b_1 MPa	$b_2\times 10^3$ K^{-1}
Liquid	0.0894	577.3	3.5428
Glass	0.0894	8852	13.096

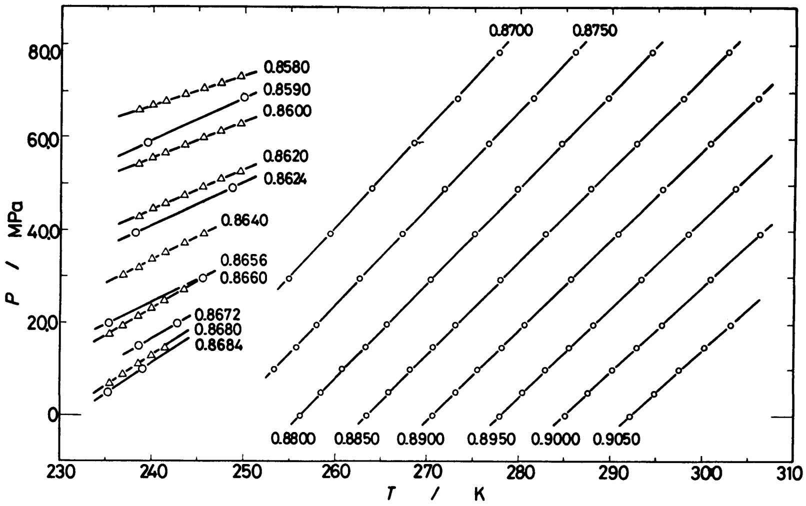

Fig. 5. Isochores of supercooled liquid and glass. The numbers in the figure are the specific volume in $cm^3\ g^{-1}$. Circles: from V-T relation, Eq. 2; triangles: from Tait equation, Eqs. 5 and 6.

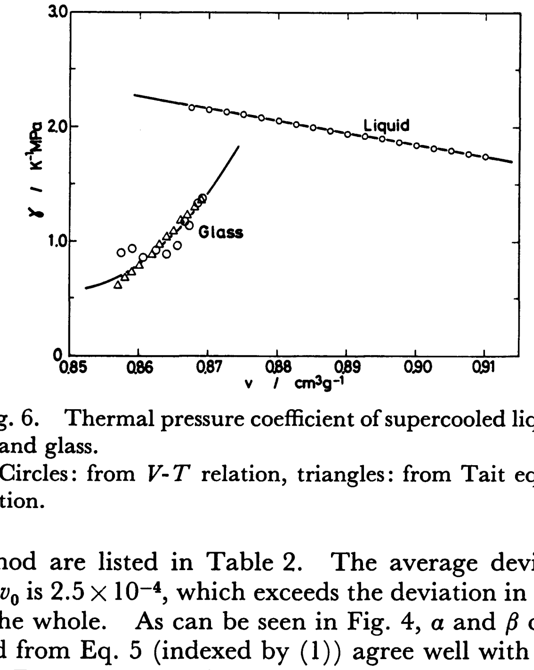

Fig. 6. Thermal pressure coefficient of supercooled liquid and glass.

Circles: from V-T relation, triangles: from Tait equation.

method are listed in Table 2. The average deviation in v/v_0 is 2.5×10^{-4}, which exceeds the deviation in Eq. 2 on the whole. As can be seen in Fig. 4, α and β calculated from Eq. 5 (indexed by (1)) agree well with those from Eqs. 2, 3, and 4 (circles).

Glassy State. In the glassy and glass transition regions, *i.e.*, 239—254 K Each atmospheric V-T isobar from the cooling experiment does not fall on that from the heating experiment, as shown in Fig. 2. In this region, the relation time is very long and the cooling isobar may not attain the one of the thermal steady state due to bulkiness of the sample. The atmospheric glass transition temperature obtained from the intersection point of the heating isobar and the liquid isobar (Eq. 2) is 244.2 K.

We have calculated the glass volume at elevated pressures based on the heating isobar. The glassy state specific volume were also expressed by Eq. 2 at each pressure. Values of the constants and the standard deviation in Eq. 2 obtained by the least-squares method are shown in Table 3, where isobars at elevated pressures are approximated by linear expressions, since the numbers of the experimental points are not sufficient. Volumetric properties of the glass calculated from Eq. 2 are summarized in Fig. 7.

The Tait equation was also applied for the glassy state and the average deviation was obtained to be 3.5×10^{-4}. The P-T isochores calculated from the isobars, Eq. 2, and from the isotherms, Eq. 5, are shown in Fig. 5.

Table 3. Specific volume of the glass

P / MPa	a_0 / $cm^3\ g^{-1}$	$a_1\times10^4$ / $K^{-1}\ cm^3\ g^{-1}$	$a_2\times10^7$ / $K^{-2}\ cm^3\ g^{-1}$	$\sigma\times10^5$ / $cm^3\ g^{-1}$	Region / K
0.1	0.84550	−0.758	7.504	3	234.4—245.2
4.9	0.80650	2.630	—	1	235.5—240.0
9.8	0.81196	2.361	—	4	235.5—241.4
14.7	0.81459	2.205	—	4	235.5—241.4
19.6	0.81609	2.104	—	7	235.5—243.5
29.4	0.82180	1.784	—	8	236.9—245.6
39.2	0.82264	1.670	—	15	236.9—247.5
49.0	0.81897	1.746	—	15	238.5—249.6
58.8	0.82214	1.539	—	11	238.5—249.6
68.6	0.81865	1.614	—	12	238.5—249.6
78.5	0.81893	1.533	—	17	240.0—249.6

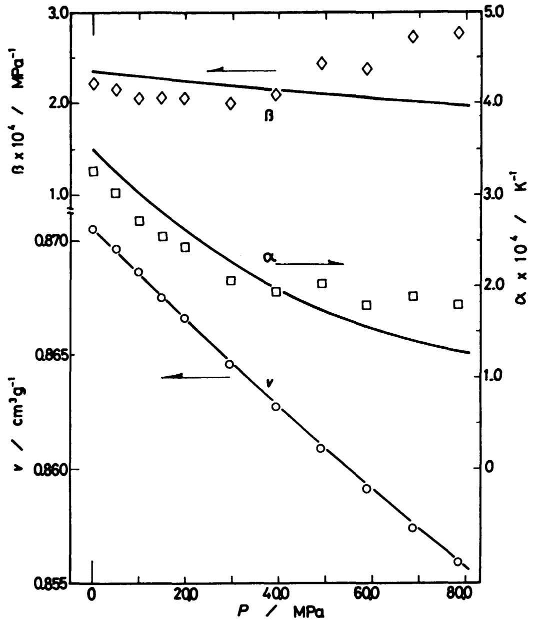

Fig. 7. Isotherms of specific volume (○), thermal expansivity (□), and isothermal compressibility (◇) in glassy state. Lines are calculations from Tait equation.

Values of γ determined from slopes of the isochores are shown in Fig. 6. Gamma from the isobars does not precisely agree with γ from the isotherms. A quadratic equation is applied to γ by the least-squares method:

$$\gamma = 1482.67 - 3489.57\,v + 2054.02\,v^2 \quad (\mathrm{K^{-1}\,MPa}), \tag{7}$$

where the standard deviation is 0.066 $\mathrm{K^{-1}}$ MPa.

As shown in Fig. 7, α calculated from Eqs. 5, 7, and 4 (solid line) approximately agrees with that from Eq. 2 (lozenges), but β from Eqs. 2, 7, and 4 (lozenges) considerably deviates from that from Eq. 5 (solid line). This implies the inconsistency involved in the empirical equations, Eqs. 2, 5, and 7. The inconsistency may arise from slow volumetric retardations of the glass towards an equilibrium liquid state.

Discussion

Comparison with Some Simple Equations of State for Supercooled Liquid. For the condensed liquid region, as an *empirical* or an *useful* equation of state, lattice-like liquid theories rather than more strict theories have widely used due to their simplicity and their quantitative success in liquids[24] and liquid mixtures.[25]

Prigogine, Trappeniers, and Mathot derived an equation of state for polymer liquids based on the Lennard-Jones and Devonshire cell model.[26,27] Its simplest form with a square-well approximation introduced by Nanda and Simha[28] is expressed as

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{1}{1-2^{-1/6}\tilde{v}^{-1/3}} + \frac{\tilde{v}^{-4}-\tilde{v}^{-2}}{\tilde{T}}, \tag{8}$$

wihch is hereafter referred to as the PNS equation. $\tilde{P}$, $\tilde{v}$, and $\tilde{T}$ are the reduced quantities related to the ordinary configurational quantities such as P, v, and T through characteristic reduction parameters (with asterisk):

$$\tilde{P} = \frac{P}{P^*},\ \tilde{v} = \frac{V}{V^*},\ \tilde{T} = \frac{T}{T^*}. \tag{9}$$

Using Tonks' free volume[29] and a van der Waals type intermolecular potential energy, Flory, Orwall, and Vrij presented an equation of state:[30]

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{1}{1-\tilde{v}^{-1/3}} - \frac{1}{\tilde{v}\tilde{T}}, \tag{10}$$

which is hereafter referred to as the Flory equation.

Hole theories, which usually lead to equations of state of complex form, generally improve the cell theories in the low density region, but not in the high density region.[31] In the well condensed region such as the supercooled liquid state, little is expected for such hole theories without some adjustable parameters.[32] Therefore, we do not discuss them here.

Apart from the cell theories, the most primitive hole theory is constructed by adopting a random-mixing assumption on the distribution of occupied cells and empty cells:

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \tilde{v}\ln\frac{1}{1-\tilde{v}^{-1}} - \frac{1}{\tilde{T}\tilde{v}}. \tag{11}$$

This is hereafter referred to as the Simple Hole equation. Based on this equation, Sanchez and Lacombe have proposed an equation of state for polymer liquids, which gives some qualitative success in polymer solution.[33]

From Eq. 9, αT and βP^* are expressed by

$$\alpha T = \left(\frac{\partial \ln \tilde{v}}{\partial \ln \tilde{T}}\right)_{\tilde{P}}, \tag{12}$$

$$\beta P^* = \left(\frac{\partial \ln \tilde{v}}{\partial \tilde{P}}\right)_{\tilde{T}}. \tag{13}$$

If the principle of corresponding states is applicable, αT and βP^* should be universal functions of the reduced quantities. At zero pressure, therefore, the theoretical αT *vs.* log $\tilde{v}$ curves should be shifted parallel to the log v axis to the experimental αT *vs.* log v curve. The shift factor corresponds to v^*. Similarly, the superposition of the theoretical αT curves parallel to the log T axis should give T^*. When T^* obtained above is employed, the superposition of the theoretical log βP^* curves parallel to the log β axis should give P^*. Results are summarized in Table 4.

The PNS equation approximately describes the variation of the thermal expansivity with pressure, *i.e.*, the variation of the compressibility with temperature, as shown in Fig. 4. This accordance can clearly be seen in Fig. 3. The PNS equation represents satisfactorily the *V-P* isotherms, while the Flory equation, as often demonstrated,[21,34] predicts appreciably less compressible than the experiments.

The Simple Hole equation, as naturally anticipated from its model which consists of gas-like molecules and

TABLE 4. CHARACTERISTIC PARAMETERS FOR THE LIQUID

Theory	v^* / $\mathrm{cm^3\,g^{-1}}$	T^* / K	P^* / MPa
Prigogine-Nanda-Simha	0.75431	2129.6	754.74
Flory	0.75388	5934.7	743.19
Simple Hole	0.85467	944.7	577.96

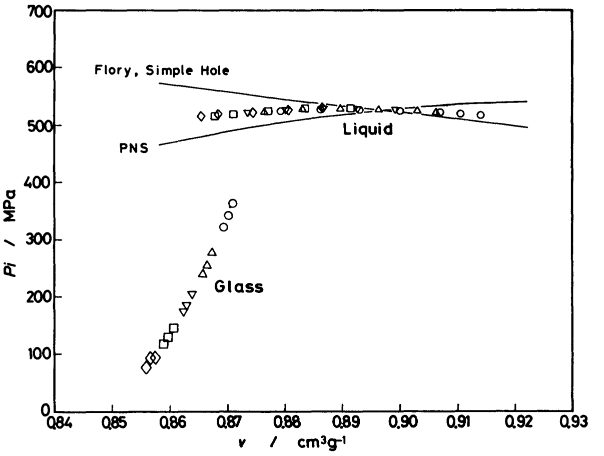

Fig. 8. Internal pressures of supercooled liquid and glass. Lines are theories.
○: 0.1, △: 19.6, ▽: 39.2, □: 58.8, ◇: 78.5 MPa.

vacuous cells, overestimates considerably the second and third derivatives of the thermodynamic free energies. The model might be suitable for the liquid state in a tolerably high temperature region.

In Fig. 8, the internal pressure P_i, $P_i = T_\gamma - P$, calculated from Eq. 3 is shown as a function of volume. P_i has a maximum at about 0.89 cm^3 g^{-1}. The maximum can be predicted by the Lennard-Jones potential (PNS equation), but a quantitative agreement with the experiments in the location of the maximum is not given. The van der Waals type potential seems to be appropriate in somewhat higher temperature region.

Glassy State. Several equations of state for glasses have been proposed.[12] However, the present experimental temperature range is considered to be too narrow to make a significant comparison with those theories.

The internal pressure P_i of the glass calculated from Eq. 7 is shown in Fig. 8. Values of P_i determined by using α from Eq. 2 and β from Eq. 5 are somewhat larger than those in Fig. 8 in the lower volume region, but the qualitative shape of the figure is unchanged. P_i of the glass is much smaller than that of the supercooled liquid. The glass P_i increases significantly with increasing volume. This behavior cannot be described by the van der Waals type potential. The Lennard-Jones potential may be appropriate for the TPCM/oTP glass as well as for the poly(vinyl chloride) glasses.[12]

Conclusion

The present study offers, probably for the first time as far as we know, the detailed data on the *P-V-T* relations in the supercooled liquid state and the glassy state of a relatively simple, global molecular liquid constituted by the triphenylchloromethane/*o*-terphenyl (25/75 in weight ratio) mixture.

The thermal expansivity, the compressibility, the thermal pressure coefficient, and their variations with temperature and pressure in the supercooled liquid region are apparently similar in magnitude to those of polymer liquids, rather than to those of simple molecular liquids above the melting temperature. The *P-V-T* relations of the supercooled liquid are fairly well represented by the Prigogine-Nanda-Simha equation of state. The lattice-like liquid model might be appropriate for the well condensed liquid state of normal liquids such as the supercooled liquid state.

The apparent thermodynamic properties of the TPCM/oTP glass are also very similar in magnitude to those of polymer glasses.

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