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Effects of Pressure on Dielectric Relaxation in Supercooled Triphenylchloromethane-*o*-Terphenyl Solution

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Dielectric measurements have been made as a function of frequency, temperature, and pressure on a binary mixture of triphenylchloromethane and *o*-terphenyl in its supercooled liquid region. Since the distribution of relaxation time is independent of temperature and pressure in the present experimental range, the time-temperature-pressure superposition is accurately applied. The activation parameters such as the activation enthalpy at constant pressure, H^*_P, the activation enthalpy at constant volume, H^*_V, and the activation volume V^* are obtained as a function of temperature and pressure. H^*_V is only half H^*_P unlike polymer liquids and associated liquids such as alcohols. V^* as well as the pressure coefficient of temperature at constant relaxation time τ, $(\partial T/\partial P)_\tau$, is similar in magnitude to that of polymer liquids and larger than that of associated liquids. These facts have revealed the contributions of inter- and intramolecular interactions to the molecular mobility in the supercooled liquid. $(\partial T/\partial P)_\tau$ coincides with the pressure coefficient of the glass transition temperature, $\mathrm{d}T_g/\mathrm{d}P$. This gives a statement that the glass transition temperature in simple normal liquids, as well as in polymer liquids, is an isorelaxation-time state.

The molecular mobility associated with the Brownian motion in simple liquids or with the micro-Brownian motion in polymer liquids is observed as a relaxation process at the audio- and radio-frequency range in the supercooled liquid region. The molecular mobility in the supercooled liquids is closely related to the glass transition[1,2] and the glassy state,[3–5] and the study of the relaxation process may make an important contribution to our understanding of the liquid state.

The secondary relaxation process pertaining to the local mode of motions governed by the localized energy field exists in the liquid state as well as in the glassy state,[6,7] and it merges the primary process pertaining to the Brownian motion at high frequency in elevated temperature region.[8,9] In the supercooled liquid region, however, the two processes are well separated from each other and their relaxation spectra can readily be obtainable.[6]

The introduction of pressure as a variable to the study in the molecular mobility makes primarily the role of volume in the relaxation process clear.[10] Analyses of the pressure effects on the dielectric relaxation have been reported in large numbers for associated liquids such as alcohols[11] and polymer liquids,[12–15] but a few for simple normal liquids such as short alkanes and benzene derivatives.[16] From the analysis of the viscosity of many liquids under elevated pressures above the melting temperature, MacKenzie has obtained that the activation enthalpy at constant volume, H^*_V, is only a small fraction of the activation enthalpy at constant pressure, H^*_P, in simple normal liquids, but H^*_V is almost equivalent to H^*_P in associated liquids.[17] H^*_P is given by

$$H^*_P = R\left[\frac{\partial \ln \tau}{\partial (1/T)}\right]_P, \tag{1}$$

as far as the empirical activation equation:

$$\tau = A \exp\left(\frac{G^*}{RT}\right), \tag{2}$$

is obeyed, and H^*_V is defined by

$$H^*_V = R\left[\frac{\partial \ln \tau}{\partial (1/T)}\right]_V, \tag{3}$$

Here, τ is the relaxation time, G^*, the activation Gibbs energy, R, the gas constant, and A, a constant independent of temperature T and pressure P. The ratio H^*_V/H^*_P prepresents the direct contribution of temperature to the temperature dependence of the relaxation time and gives a rough estimation of the magnitudes of the energetic or entropic contribution to the relaxation process. It may be very interesting to know H^*_V/H^*_P for simple normal liquids in the supercooled liquid region.

Many dielectric studies on the *o*-terphenyl solutions have been presented,[18,19] since *o*-terphenyl and its solutions can easily be vitrified at a relatively high temperature.[20–22] We now wish to clarify the effects of pressure on the dielectric relaxation process in the supercooled triphenylchloromethane/*o*-terphenyl solution as an example of simple normal liquids and to elucidate some intrinsic contributions to the molecular mobility in the supercooled liquid state.

Experimental

Sample. Triphenylchloromethane (TPCM) and *o*-terphenyl (oTP) were purchased from Tokyo Chemical Industry Co. and were used without further purification. In order to perform dielectric measurements without any apprehension of crystallization during the experimental period (about 3 d), crystallizability of the mixture of TPCM/oTP was preliminary tested. TPCM and oTP in various concentrations were mixed in test tubes at 130 °C. Then the mixtures were slowly cooled down to room temperature and were stored in a desiccator. Samples containing TPCM more than 50 wt% crystallized within 5 h. In samples containing TPCM less than 10 wt%, a slight crystallization peak was detected by a differential scanning calorimeter, Model DSC-1B (Perkin-Elmer Corporation) after 3 d. Any crystallization was not observed in samples containing 20—40 wt% of TPCM for one month, and we used the mixture TPCM/oTP in weight ratio of 25/75 in dielectric measurements.

Equipment. A General Radio 1620-A Capacitance Measuring Assembly, in conjunction with a General Radio 1310-B Oscillator employed to make small changes in frequency near dielectric loss peaks, was used for dielectric

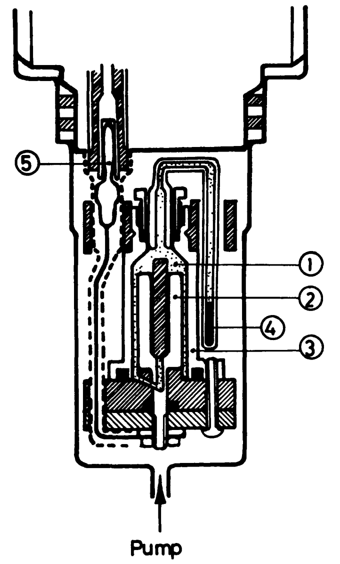

Fig. 1. Diagram of dielectric cell.
1: Sample, 2: main electrode, 3: sub electrode, 4: mercury seal, 5: electric terminal.

measurements in a frequency range of 0.03—100 kHz. The cell shown in Fig. 1 has a nominal geometric capacitance of about 15 pF with a small stray capacitance. Corrections for the stray capacitance and the change in the geometric capacitance with temperature and pressure were made by measuring the capacitance of the cell with air and with benzene (uvasol grade, Merck) in each measurement. The dielectric data of benzene were taken from those of Vij and Scaife.[23] Silicone oil (KF-94, Shin-Etsu Chemical Co.) was used to transmit the hydrostatic pressure. The pressure was measured by a Nikkiso bourdon gauge calibrated by a Heise bourdon gauge. The temperature was measured by a calibrated alumel-chromel thermocouple inserted near the sub electrode.

Experimental Procedure. The mixture (TPCM/oTP, 25/75) was prepared at 130 °C and was applied into the electrode at 70 °C. The dielectric cell was set in the pressure vessel heated previously up to 70 °C. After the pressure being increased to a desired value P_1, the temperature was lowered to the glass transition temperature T_g at P_1, $T_g(P_1)$. The dielectric measurements at P_1 were isobarically carried out at about 2 K intervals with increasing temperature to a temperature at which the frequency of dielectric loss maximum exceeded 100 kHz. This experimental operation (from the sample set to the isobaric measurements) was repeated for each pressure, *i.e.*, 1, 200, 400, 600, and 800 kg cm^{-2}. (1 kg cm^{-2}= 0.09807 MPa). The operation recurred twice for 1, 600, and 800 kg cm^{-2}.

Crystallization of the sample during the experimental period could easily be detected as a precipitous decrease in the capacitance and loss. We have excluded all the dielectric data of the experimental opetation in which the indication of the crystallization was recognized at any temperature.

Results

Some examples of the dielectric dispersion are shown in Fig. 2. The shapes of the loss curves at every temperature and pressure are all similar, being asymmetric to the high frequency side of the dispersion. The limiting low- and high-frequency dielectric constants, *i.e.*, ε_0 and ε_∞, respectively, were determined by extrapolation of the Cole-Cole plots. The plots appear to be well represented by the Davidson-Cole equation of a skewed-arc behavior,[24] but we do not discuss the parameter in the Davidson-Cole equation. It should be noted, however, that its asymmetric factor is independent over the present experimental range.

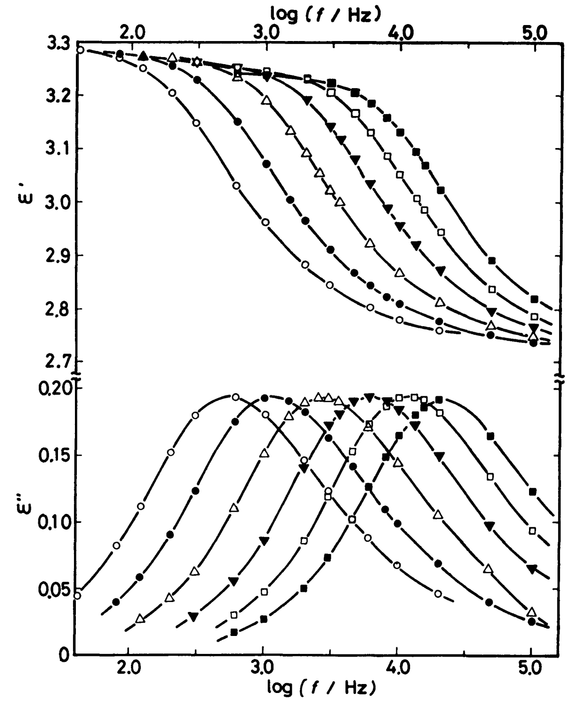

Fig. 2. Diectric dispersion at 800 kg cm^{-2}.
○: 285.92 K, ●: 288.24 K, △: 290.56 K, ▲: 293.05 K, □: 295.56 K, ■: 297.26 K.

Table 1. Static dielectric constants at log $\tau=-4$

P kg cm^{-2}	ε_0	ε_∞	$\varepsilon_0-\varepsilon_\infty$
1	3.260 ± 0.017	2.673 ± 0.005	0.587 ± 0.019
200	3.265 ± 0.037	2.685 ± 0.008	0.580 ± 0.042
400	3.283 ± 0.010	2.698 ± 0.005	0.585 ± 0.012
600	3.279 ± 0.009	2.715 ± 0.004	0.564 ± 0.010
800	3.273 ± 0.009	2.736 ± 0.004	0.537 ± 0.010

Values of ε_0 and ε_∞ interpolated to log $\tau=-4$ are listed in Table 1. Influences of pressure on ε_0, ε_∞, and the relaxation intensity represented by $\varepsilon_0-\varepsilon_\infty$ are very little. ε_0 is almost independent of pressure in the experimental errors, when ε_0 is plotted against $T-T_g$. ε_∞ increases with pressure in correspondence with the increase in density. Consequently, $\varepsilon_0-\varepsilon_\infty$ decreases slightly with pressure. The rather large experimental errors in ε_0 and ε_∞ values may be due to the experimental procedure that the electrode cell was reassembled for each pressure. These errors, however, exert no influence upon the following analysis, in which only the shape of the dispersion curve, the maximum loss, ε''_{max}, and the frequency of the maximum loss, f_{max}, are significant.

Figure 3 shows a master curve obtained by superposition of reduced dielectric loss, $\varepsilon''/\varepsilon''_{max}$, at every temperature and pressure to the reference one at 286.74 K and 600 kg cm^{-2}. The relaxation spectrum of the α relaxa-

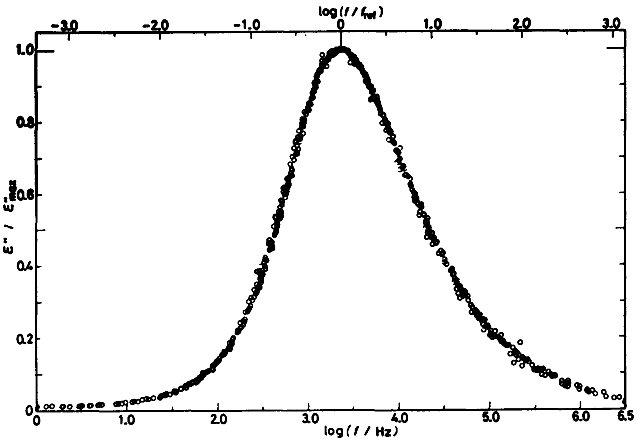

Fig. 3. Master curve of reduced dielectric loss. The reference temperature and pressure are 286.74 K and 600 kg cm^{-2}, respectively.

tion process in TPCM/oTP is typical in shape as Williams *et al.* demonstrated for oTP solutions and many polymers.[25] The value of the half width of the master curve of TPCM/oTP is 1.67 decade in frequency. This value is equal to that of anthrone/oTP solutions[18a] and smaller than those of other oTP solutions[18b] and decalin solutions.[6c]

The susperposition gives the shift factor $a_{T,P}$ at any temperature and pressure:

$$a_{T,P} = \frac{\tau}{\tau\,(T_r, P_r)}, \tag{4}$$

where τ is the characteristic relaxation time at T and P and $\tau(T_r,P_r)$, that at the reference temperature and pressure. The value of $\tau(T_r,P_r)$ was obtained from $f_{\max}$ at 286.74 K and 600 kg cm^{-2} by using

$$\tau(T_r,P_r) = \frac{1}{2\pi f_{\max}(T_r,P_r)}, \tag{5}$$

Variations of log $a_{T,P}$ or log τ with reciprocal temperature, *i.e.*, the Arrhenius plots, are shown in Fig. 4.

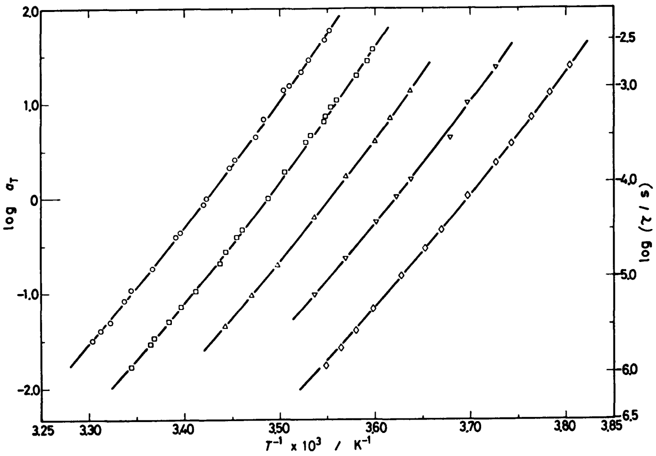

Fig. 4. Arrhenius plots of logarithmic shift factor and characteristic relaxation time. Lines: VFTH equation, Eq. 6.
◇: 1 kg cm^{-2}, ▽: 200 kg cm^{-2}, △: 400 kg cm^{-2}, □: 600 kg cm^{-2}, ○: 800 kg cm^{-2}.

The log τ isobars are well represented by the Vogel-Fulcher-Tammann-Hesse (VFTH) equation:[26]

$$\log\tau = -A + \frac{B}{T-T_0}, \tag{6}$$

which is transformable into the WLF equation for polymer liquids.[27] Values of the VFTH parameters A, B, and T_0 obtained to minimize the standard deviation σ by the least-squares regression are listed in Table 2. Since the experimental frequency range is limited, the temperature range where the dielectric loss reaches maximum is rather narrow. Consequently, long extrapolation of Eq. 6 may lead to a large uncertainty and there is no point in discussing about physical significance of B and T_0. The VFTH equation is utilized only for precise interpolation of τ to every temperature.

The T—P relations at constant τ calculated from Eq. 6 are shown in Fig. 5, in which values of the glass transition temperature T_g obtained by isobaric cooling experiments[28] are also plotted. The slope of the isochronal T—P relation is very similar to that of T_g—P relation shown in the same figure. The isothermal

Table 2. VFTH parameters

$\frac{P}{\text{kg cm}^{-2}}$	A	$\frac{B}{\text{K}}$	$\frac{T_0}{\text{K}}$	σ
1	21.565	1803.9	166.82	0.008
200	20.494	1629.4	176.35	0.014
400	20.238	1594.0	182.29	0.024
600	20.731	1713.7	183.34	0.030
800	23.179	2372.1	167.34	0.016

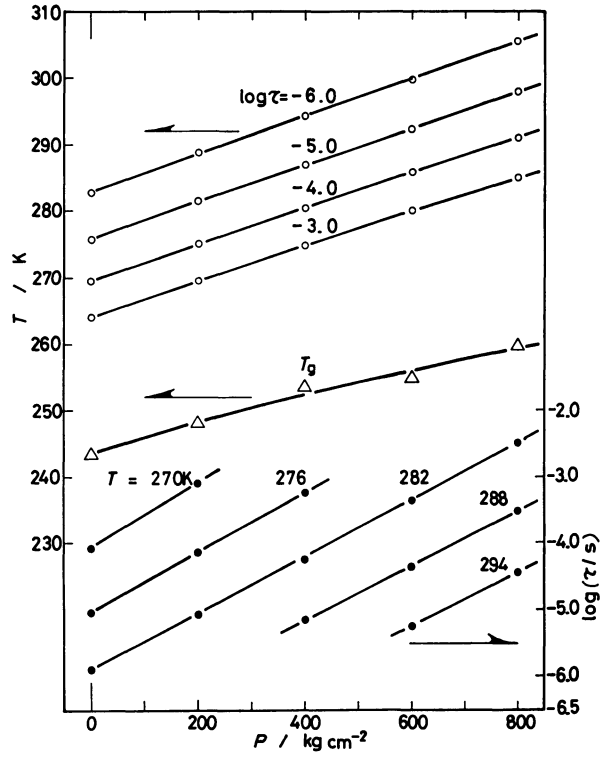

Fig. 5. Isochronal T—P relation (open circles), pressure dependence of T_g (triangles), and isothermal variations of log τ with pressure (solid circles).

dependences of τ on pressure are also shown in Fig. 5. Pressure effects on the slope of $\log \tau - P$ relation are scarcely observed due to the narrowness of the experimental frequency range.

Discussion

Activation Parameters. The activation enthalpy at constant pressure, H^*_P, given by Eq. 1 was obtained by differentiating the VFTH equation, Eq. 6:

$$\frac{\partial \ln \tau}{\partial(1/T)} = \frac{BT^2}{(T-T_0)^2}, \qquad (7)$$

Values of H^*_P are plotted as a function of $T-T_g$, in Fig. 6 where the value of T_g was calculated from the least-squares quadratic equation for the pressure dependence of T_g.[28] H^*_P depends on temperature and pressure. The pressure effects on H^*_P cannot be reduced by an exchange of the temperature scale from T to $T-T_g$ only. This situation remains unchanged when $T-T_g$ is replaced by T/T_g. This may be evidence for the fact that the glass transition temperature is not the corresponding point for the molecular mobility in the supercooled liquid.

The activation volume V^* given by

$$V^* = RT\left[\frac{\partial \ln \tau}{\partial P}\right]_T, \qquad (8)$$

is shown in Fig. 6. The pressure effects on V^* seem to be almost reduced in the experimental errors when V^* is plotted as a function of $T-T_g$ instead of T. V^* of TPCM/oTP is equal in magnitude to that of chlorinated diphenyl,[16] similar to that of polymer liquids which ranges from 50 to 400 cm^3 mol^{-1},[14a,15] and larger than that of associated liquids.[11]

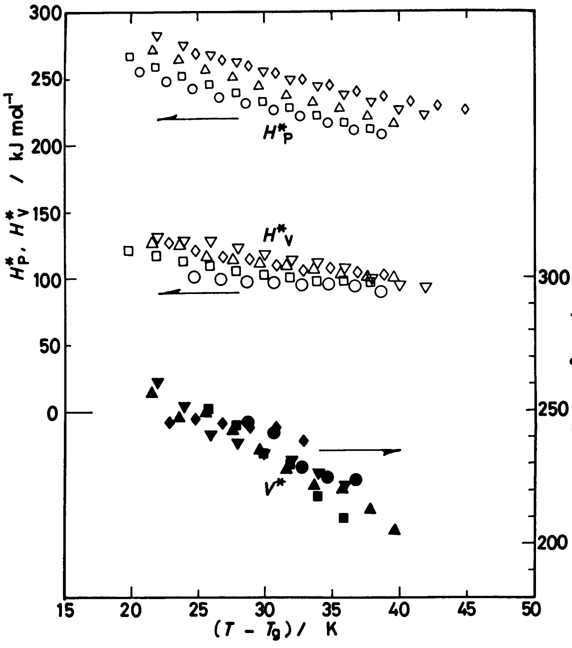

Fig. 6. Activation enthalpies at constant pressure and volume (open symbols) and activation volume (closed symbols) as a function of $T-T_g$.
○: 1 kg cm^{-2}, □: 200 kg cm^{-2}, △: 400 kg cm^{-2}, ▽: 600 kg cm^{-2}, ◇: 800 kg cm^{-2}.

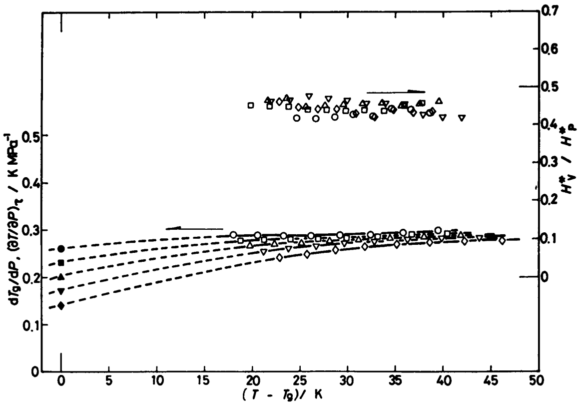

Fig. 7. Variations of H^*_V/H^*_P, $(\partial T/\partial P)_\tau$, and dT_g/dP with $T-T_g$. Symbols are the same as those in Fig. 6.

The activation enthalpy at constant volume, H^*_V, defined by Eq. 3 can be obtained from Eqs. 1 and 8 as

$$H^*_V = H^*_P - T\gamma V^*, \qquad (9)$$

where γ is the thermal-pressure coefficient, $(\partial P/\partial T)_V$. From dilatometric measurements, γ of TPCM/oTP is obtained as a function of the specific volume v:[28]

$$\gamma = 11.1587 - 10.3500\,v \qquad (\mathrm{K^{-1}\,MPa}). \qquad (10)$$

H^*_V, which is often called as the *true* energy of activation,[29] calculated from Eqs. 9 and 10 is plotted as a function of $T-T_g$. The pressure effects on H^*_V seem not to be well-reduced by the $T-T_g$ scale. The second term in Eq. 9 is comparatively large as H^*_V and H^*_V is much smaller than H^*_P.

In Fig. 7, the ratio H^*_V/H^*_P is shown as a function of $T-T_g$. The ratio has a value of about 0.45 and is almost independent of temperature and pressure. This value is equal to those of simple normal liquids near their melting temperatures obtained by viscosity measurements,[17] and is much smaller than those of polymer liquids[30,31] and associated liquids.[17]

Pressure Coefficient of Temperature at Constant Relaxation Time. The tangent of the $T-P$ relation at constant τ, $(\partial T/\partial P)_\tau$, is expressed by

$$\left(\frac{\partial T}{\partial P}\right)_\tau = -\left(\frac{\partial \ln \tau}{\partial P}\right)_T \Big/ \left(\frac{\partial \ln \tau}{\partial T}\right)_P. \qquad (11)$$

Values of $(\partial T/\partial P)_\tau$ calculated from this equation are plotted in Fig. 7. Effects of pressure on $(\partial T/\partial P)_\tau$ diminish as the temperature increases. At lower temperature, $(\partial T/\partial P)_\tau$ approaches the pressure coefficient of the glass transition temperature, dT_g/dP, shown in the same figure, *i.e.*,

$$\left(\frac{\partial T}{\partial P}\right)_\tau \simeq \frac{dT_g}{dP}. \qquad (12)$$

This supports the argument that the glass transition temperature is an isorelaxation-time state or an isoviscose state.[3-5] The argument has been proposed[32,33] and been supported[34] by the time-temperature-pressure superposition for polymer liquids. It may be stated that, irrespective of molecular weight, the T_g trace in the PVT space is identical with the isorelaxation-time trace.

$(\partial T/\partial P)_\tau$ of TPCM/oTP is equal in magnitude to

Table 3. Representative values of H^*_V/H^*_P, $(\partial T/\partial P)_\tau$, and $\mathrm{d}T_g/\mathrm{d}P$

Substance	H^*_V/H^*_P	$(\partial T/\partial P)_\tau$ / K MPa^{-1}	$\mathrm{d}T_g/\mathrm{d}P$ / K MPa^{-1}
Simple normal liquids			
CCl_4	0.40[a]	—	—
oTP	—	—	0.26[b]
TPCM/oTP	0.42	0.288	0.26
Polymer liquids			
Poly(vinyl acetate)	0.73[c]	0.20[c]	0.212[d]
Poly(vinyl chloride)	0.86[e]	0.19[e]	0.19[e]
Associated liquids			
1-Propanol	0.86[a]	—	0.07[f]
Glycerol	0.95[g], 0.86[a]	0.029[g]	0.04[f]

a) Values near the melting temperature (Ref. 17). b) Ref. 35. c) Ref. 32. d) Ref. 4. e) Ref. 34. f) Ref. 36. g) Ref. 11d.

$\mathrm{d}T_g/\mathrm{d}P$ of oTP,[35] almost the same as $(\partial T/\partial P)_\tau$ of polymer liquids,[15,30,32,36] much larger than $\mathrm{d}T_g/\mathrm{d}P$ of associated liquids.[35,36] In terms of V^*, $(\partial T/\partial P)_\tau$ can be expressed as

$$\left(\frac{\partial T}{\partial P}\right)_\tau = T\frac{V^*}{H^*_P}. \tag{13}$$

The small value of associated liquids is due to the smallness of V^*. In the molecular mobilities in such liquids, the arrangements of the free space or the free volume, *i.e.*, the formation of holes, are scarcely of importance, and the rearrangements of the number of the hydrogen bonds only are significant.

It is very interesting to compare the results above on $(\partial T/\partial P)_\tau$ with that on the ratio H^*_V/H^*_P. Representative values of H^*_V/H^*_P, $(\partial T/\partial P)_\tau$, and $\mathrm{d}T_g/\mathrm{d}P$ are listed in Table 3. With respect to the magnitude of H^*_V/H^*_P, liquids can be classified into two categories: the one (polymer liquids and associated liquids) whose H^*_V/H^*_P is larger than 0.7 and the other (simple normal liquids) whose H^*_V/H^*_P is smaller than 0.5. Whereas, with respect to the magnitudes of $(\partial T/\partial P)_\tau$ and $\mathrm{d}T_g/\mathrm{d}P$, the another classification applies: the one (simple normal liquids and polymer liquids) whose $(\partial T/\partial P)_\tau$ or $\mathrm{d}T_g/\mathrm{d}P$ is larger than 0.15 K MPa^{-1} and the other (associated liquids) whose $(\partial T/\partial P)_\tau$ or $\mathrm{d}T_g/\mathrm{d}P$ is smaller than 0.10 K MPa^{-1}.

$(\partial T/\partial P)_\tau$ is related to H^*_V/H^*_P through the following equation.

$$\frac{H^*_V}{H^*_P} = 1 - \gamma\left(\frac{\partial T}{\partial P}\right)_\tau \tag{14}$$

If one disregards differences in magnitude of γ, one finds from Eq. 14 that large(small) $(\partial T/\partial P)_\tau$ corresponds to the small(large) H^*_V/H^*_P. This is the case for simple normal liquids and associated liquids.

In polymer liquids, the contribution of the intramolecular conformational entropy is very large to the liquid entropy.[37] From the thermodynamic Maxwell relation

$$\gamma = \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T, \tag{15}$$

i.e., the thermal pressure coefficient is related to the dependence of the entropy S on volume. The intramolecular conformational entropy is regarded to be independent of volume.[37] Therefore, the magnitude of γ in polymer liquids is usually smaller than that of simple normal liquids. This is the reason for the large values of H^*_V/H^*_P in polymer liquids.

Conclusion

From the analysis on the isochronic pressure coefficient of temperature, $(\partial T/\partial P)_\tau$, we have found the fact that the glass transition temperature can be regarded as an isorelaxation-time state in the simple normal liquid as well as in polymer liquids. Therefore, the correspondence of the α relaxation process to the glass transition temperature is independent of the length of the molecules, *i.e.*, the molecular weight. The molecular mobility represented by the characteristic relaxation time, however, is significantly influenced by the molecular types such as simple normal liquids, polymer liquids, and associated liquids. The length of the molecules, regardless whether the bonds between molecules are covalent or hydrogen bonds, affects the magnitude of the ratio H^*_V/H^*_P, but not that of $(\partial T/\partial P)_\tau$. On the other hand, the kind of the intermolecular interactions such as the short range one (London potential) and long range one (coulomb potential) affects the magnitude of $(\partial T/\partial P)_\tau$ and $\mathrm{d}T_g/\mathrm{d}P$, but not that of H^*_V/H^*_P. These properties of the molecular mobilities obtained by the time-temperature-pressure superpositions of the dielectric α relaxation process are very similar to the properties of the viscosity above the melting temperature.[17] A more detailed investigation of the molecular mobility in the supercooled liquid state will be given in a succeeded paper.

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