Correlation between the equation of state and the temperature and pressure dependence of thermal conductivity of polymers and simple liquids

S. Saeki, M. Tsubokawa and T. Yamaguchi
Department of Materials Science and Engineering, Fukui University, Fukui 910, Japan
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A correlation between the equation of state and the temperature dependence of thermal conductivity λ for polymers such as natural rubber and poly(ethyl methacrylate) and simple liquids such as argon, n-heptane, and water and pressure dependence of λ for polymers such as poly(methyl methacrylate) and polystyrene and simple liquids as n-pentane, methanol and water has been examined by using the experimental data presented by Eiermann and Hellwege[13] and Barker, Chen and Frost[5] for polymers and Bridgeman[3] and other authors for simple liquids based on the equation of state derived in a previous work. The expression for λ obtained for the liquid state is given by $\ln(\lambda/\lambda_c)=\ln[1+A_0\{\ln(T_c/T)\}^{n_0}]+B_0(T)(P+P_0(T))^{m_0}$ where λ_c is a value at the critical temperature T_c, n_0, m_0 and A_0 are constants determined experimentally and $B_0(T)$ and $P_0(T)$ are functions of temperature. Values of n_0 for simple liquids range from 0.68 to 1.2 with an average $\bar{n}_0=0.87$ for simple liquids and $\bar{n}_0=0.326$ for water, while m_0 ranges from 0.02 to 0.44 for simple liquids with an average $\bar{m}_0=0.22$ and $\bar{m}_0=0.56$ for polymers. In the case of polymers, it is expressed by $\lambda\sim T^{-n_0}$ and values of n_0 range from -0.02 to -1.0 for the temperature range of $(\partial\lambda/\partial T)_P>0$, while $\bar{n}_0$ is 1.62 over $(\partial\lambda/\partial T)_P<0$. A strong correlation has been found between the thermal conductivity and thermal pressure coefficient in simple liquids including water and polymers. This suggests a mechanism of thermal conduction in solid and liquid state.

(Keywords: thermal conductivity; equation of state; polymer; simple liquid; thermal pressure coefficient; Debye phonon model)

INTRODUCTION

The thermal conductivity for polymers and simple liquids is the most fundamental quantity in understanding of the basic molecular process in the heat conduction and its temperature and pressure dependence is of practical importance. Investigation of the thermal conductivity has been carried out by many authors theoretically and experimentally. Choy[1] reviewed the thermal conductivity of polymers over the wide range of temperature 0.2–350 K, while McLaughlin[2] discussed that of liquids and dense gases. Bridgeman[3] investigated the pressure dependence of thermal conductivity of liquids over the pressure range up to 12 kbar and Andersson *et al.*[4] and Baker *et al.*[5] measured the pressure dependence of thermal conductivity of polymers. Most of the experimental data on liquid thermal conductivity are given in ref. 6. On the other hand, the theoretical and empirical expressions for λ are derived by Debye[7], McLaughlin[8], and Bridgman[3]. A main purpose of this work is to establish an empirical equation for λ based on the equation of state derived in the previous works[9,10] which can explain the experimental behaviour of λ over a wide range of temperatures ranging from 1 K to the gas–liquid critical temperature and at pressures over 12 kbar. The physical meaning of the empirical equation of λ is discussed based on the theories of Debye[7] and McLaughlin[2].

DERIVATION OF AN EMPIRICAL EQUATION FOR λ

In 1968, Baily and Kellner[11] published data for the thermal conductivity of liquid and gaseous argon over a wide range of temperature and pressure. These data are replotted in *Figure 1* as the pressure P *versus* the inverse of the thermal conductivity λ^{-1}. It is shown that P–λ^{-1} lines are quite similar to the P–V isotherm in the vicinity of the critical point, although a disagreement is observed over the lower pressure corresponding to gaseous region where a transition from positive $(\partial\lambda^{-1}/\partial T)_p$ to negative with decreasing pressure or an intersection point is observed. From the rough correlation between P–λ^{-1} and P–V it is shown that

$$\lambda \propto V^{-1} \tag{1}$$

The next step is to express V^{-1} as a function of temperature and pressure. In previous work[9], the following equation was derived

$$(\alpha_p T)^{-1}=c_0 X^{\beta_0} \tag{2}$$

where X is defined by

$$X=(V_c-V)/V \tag{3}$$

Here α_p is the thermal expansion coefficient, V is the molar volume, and V_c is V at the critical temperature T_c and c_0 is a constant. From equation (2) using the

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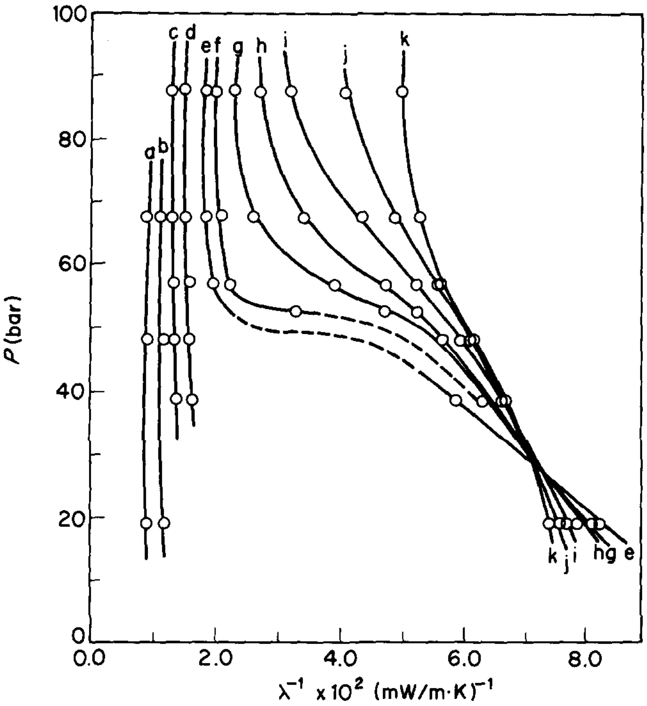

Figure 1 P vs. λ^{-1} (mW/mK)$^{-1}$ plot for argon at constant temperatures; curve a, 100 K; curve b, 120 K; curve c, 130 K; curve d, 140 K; curve e, 150 K; curve f, 155 K; curve g, 160 K; curve h, 165 K; curve i, 170 K; curve j, 180 K; curve k, 200 K. The data are taken from ref. (11)

approximation

$$\int_{V_c}^{V} X^{\beta_0}/V\,\mathrm{d}V \sim -X^{n+1}$$

we arrive at

$$V_c/V = 1 + c_0\{\ln(T_c/T)\}^{1/(n+1)} \qquad (4)$$

The pressure dependence of V is also derived using[10]

$$\ln(V/V_0) = -D(T)(P + P_0(T))^{m_0^{\delta}} + C(T) \qquad (5)$$

where V_0 is V at 1 atm, $D(T)$, $P_0(T)$ and $C(T)$ are functions of temperature. The expression for λ is derived using equations (1), (4) and (5) by

$$\ln(\lambda/\lambda_c) = \ln[1 + A_0\{\ln(T_c/T)\}^{n_0}] + B_0(T)(P + P_0)^{m_0} \qquad (6)$$

In the case of polymers where $T_c \gg T$, it is assumed that

$$\ln\lambda = \ln(C_1 + A_2 T^{-n_0}) + B_0(T)(P + P_0)^{m_0} \qquad (7)$$

where C_1 and A_2 are constants.

RESULTS

Typical plots for the temperature and pressure dependence of the thermal conductivity for polymers and simple liquids based on equations (6) and (7) are shown in *Figures 2–5* where a linearity is observed. The source of data, indices and constants such as n_0 and m_0 are summarized in *Tables 1* and *2*, where the values of m_0 in $\ln\lambda \sim \{P + P_0(T)\}^{m_0}$ in equation (6) are 0.02–0.44 for simple liquids and 0.3–0.7 for polymers, while the values of n_0 in $\lambda \sim \{\ln(T_c/T)\}^{n_0}$ in equation (6) are 0.6–1.2 for simple liquids and 0.1–0.5 for water; n_0 for polymers are −0.02 to −1.0 for the temperature range $\mathrm{d}\lambda/\mathrm{d}T > 0$ and 1.5–1.7 for $\mathrm{d}\lambda/\mathrm{d}T < 0$. Determination of the indices and constants has been carried out by the best fitting

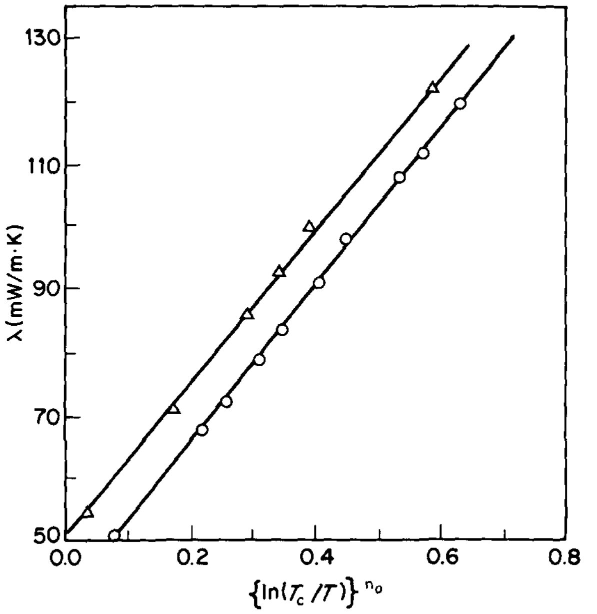

Figure 2 λ (mW/mK) vs. $\{\ln(T_c T)\}^{n_0}$ plot for argon at pressures of 48.0 bar with $n_0 = 0.685$ (○) and 67.6 bar with $n_0 = 0.793$ (△). Data are taken from ref. (11)

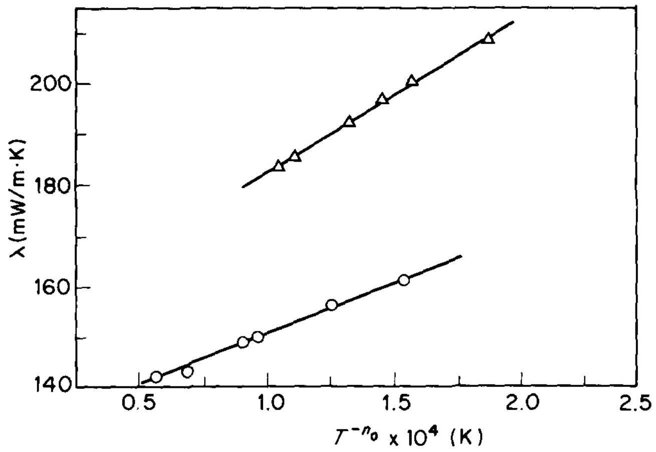

Figure 3 λ (mW/mK) vs. T^{-n_0} plot for polymers Vulkollan[13] (△, $n_0 = 1.58$) and natural rubber[13] (○, $n_0 = 1.66$) where $\lambda \propto T^{-n_0}$ is used

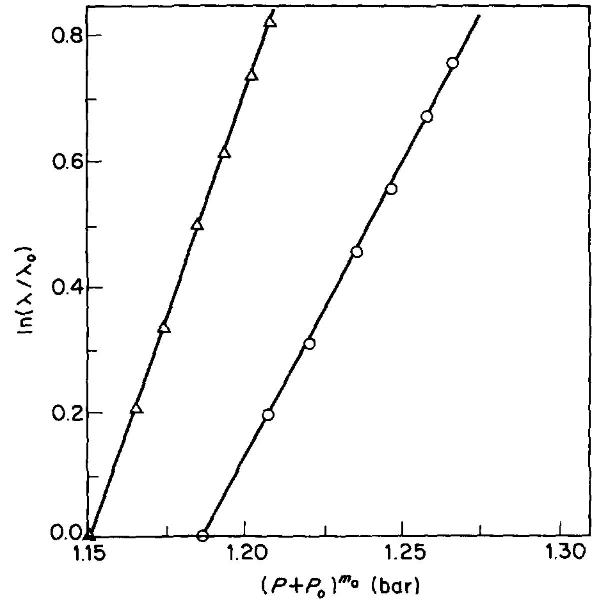

Figure 4 $\ln(\lambda/\lambda_0)$ vs. $(P + P_0)^{m_0}$ plot for ethanol at temperatures of 30° (○) and 75°C (△) where λ_0 is λ at 1 bar. Values of m_0 and P_0 are 0.025 and 916 bar for 30°C and 0.020 and 1078 bar for 75°C. Data are taken from ref. (3)

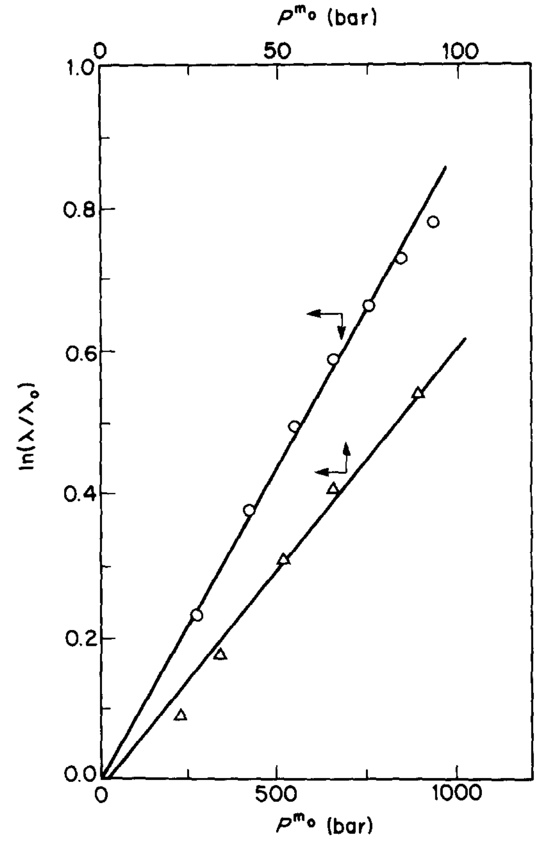

Figure 5 $\ln(\lambda/\lambda_0)$ vs. P^{m_0} plot for polymers polymethyl methacrylate[4] (○, $m_0=0.653$) and polyethyl methacrylate[5] (△, $m_0=0.609$)

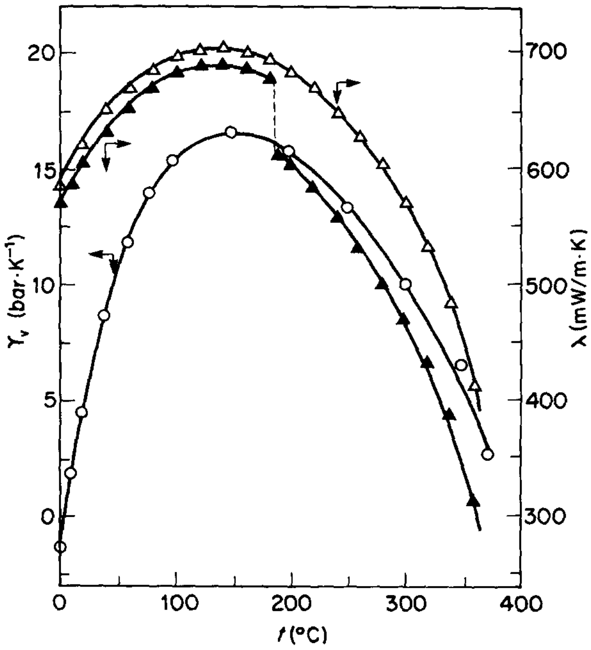

Figure 6 Temperature dependence of γ_v (○)[27] and λ for water[6] at pressures of saturation vapour pressure (▲) and 200 bar (△)

with the experimental data and therefore values of λ calculated agree with the observed ones within an error of 2% or less.

The temperature dependence of λ for water is shown in *Figure 6* where the temperature dependence of thermal pressure coefficient γ_v is also plotted. In *Figure 7* the thermal pressure coefficient of polymers calculated from the data of Simha[12] is plotted against specific volume. This plot indicates that γ_v decreases with increasing temperature above the glass transition temperature T_g but increases with temperature below T_g, which can compare with the temperature dependence of λ with a maximum[5,13,14] around T_g.

DISCUSSION

It is very interesting to discuss the correlation between the equation of state and the temperature and pressure dependence of thermal conductivity for polymers and simple liquids. In previous work[10] it has been shown that the thermal pressure coefficient γ_v is expressed by

$$\gamma_v = c_1(X^{\beta_0}/V)\exp(\alpha_0^{-1}I_0) \qquad (8)$$

where I_0 is defined by

$$I_0 = \int_{V_c}^{V} X^{\beta_0}/V\,dV$$

and

$$\gamma_v = C(T)\{P + P_0(T)\}^{\beta_0/(2\beta_0+1)} \qquad (9)$$

where T is constant. The temperature dependence of γ_v is also expressed by

$$\gamma_v \sim \{\ln(T_c/T)\}^{\beta_0/(n+1)} \qquad (10)$$

where P is constant. In the critical region equation (10) is given by

$$\gamma_v \sim \{(T_c - T)/T\}^{\beta_0/(n+1)} \qquad (11)$$

It is shown that $\gamma_v \sim (P+P_0)^{0.4}$, $\gamma_v \sim \{\ln(T_c/T)\}^{0.66}$ or $\gamma_v \sim (T_c - T)^{0.66}$ with $\beta_0 = 2.0$ and $n = 2.0$, which can compare with $\lambda \propto (P+P_0)^{m_0}$ with $\bar{m}_0 = 0.40$ for argon and $\bar{m}_0 = 0.56$ for polymers and $\lambda \sim \{\ln(T_c/T)\}^{n_0}$ with $\bar{n}_0 = 0.723$ for argon.

Riedel proposed an equation for λ at a temperature above the boiling point, which is expressed by[6]

$$\lambda = A\{1 + 6.667(1 - T/T_c)^{0.667}\} \qquad (12)$$

and is essentially the same as equation (11) with $\beta_0 = n = 2.0$ near T_c. As is shown in *Figures 6* and *7* the correlation between γ_v and λ is also observed in water and polymers. The correlation does not contradict $\lambda \propto V^{-1}$ in equation (1) because the variable X in γ_v in equation (8) is proportional to V^{-1} through $X = (V_c - V)/V \sim V_c/V$.

There is another general behaviour of λ that a sign of $(\partial\lambda/\partial T)_P$ changes from positive to negative with increasing temperature[3,15]. This can be explained by variation of state from a solid-like state $(\partial\lambda/\partial T)_P > 0$ and $(\partial\gamma_v/\partial T)_P > 0$ to a liquid state with $(\partial\lambda/\partial T)_P < 0$ and $(\partial\gamma_v/\partial T) < 0$ with increasing temperature or volume as is shown in *Figures 6* and *7* for water and polymers. It is also pointed out that the temperature dependence of γ_v with a maximum at a certain temperature, T_g, is quite general behaviour because γ_v approaches zero at the limit of 0 K and γ_v is negligible at the critical temperature T_c. Choy[1] reviewed the polymer thermal conductivity based on the experimental data over the wide temperature range and found that $\lambda \propto T^{2.0}$ in the amorphous solid below 0.5 K and it becomes independent of T between 5 and 15 K and becomes proportional to the heat capacity at constant volume C_v above 60 K, while λ for semicrystalline polymers normally exhibits a T^1 to T^3 dependence between 0.1 and 20 K which is similar to the temperature

Table 1 Constants in $\lambda = A_1\{\ln(T_c/T)\}^{n_0} + B_1$ in equation (6) at constant pressure*. λ is in mW/mK

Liquid	n_0	A_1	B_1	Pressure (bar)	Ref.
Argon	0.685	125.6	40.5	48.0	11
	0.793	123.6	50.1	67.6	11
	0.793	113.2	56.7	98.0	11
	0.627	102.6	60.7	196.0	11
	0.753	99.0	75.9	294.0	11
	0.684	94.4	80.9	391.0	11
n-pentane	1.10	102.0	73.5	49.0	6
n-hexane	0.891	91.7	78.2	50.0	6
n-heptane	0.886	85.6	77.7	50.0	6
hept-1-ene	0.881	78.3	77.3	50.0	6
octane	0.823	85.0	80.0	50.0	6
oct-1-ene	0.829	72.7	78.0	50.0	6
n-nonane	1.13	76.0	78.6	98.0	6
n-tridecane	1.21	69.0	84.9	49.0	6
methyl acetate	0.954	121.3	86.4	98.0	6
water	0.345	715.0	124.0	1.0	6
(200°–360°C)	0.184	855.0	−9.5	200.0	6
	0.281	515.0	326.0	300.0	6
	0.369	473.0	390.0	400.0	6
	0.451	410.0	463.0	500.0	6

$\lambda = A_2 T^{-n_0} \times 10^4 + B_2$ (equation (7))

Polymer	n_0	A_2	B_2	Pressure (bar)	Ref.
Vulkollan	1.58	0.78	3.61	1.0	13
Natural rubber	1.66	0.50	3.11	1.0	13

$A_1 = A_0 B_0^* \lambda_c$; $B_1 = B_0^* \lambda_c$ where $B_0^* = \exp\{B_0(T)(P+P_0)^{m_0}\}$; $B_2 = C_1 + B_0(P+P_0)^{m_0}$

$\lambda = A_3 T^{-n_0} + B_3$

Polymer	n_0	A_3	B_3	Pressure (bar)	Ref.
PVC[a]	−0.023	26.75	−26.7	1.0	13
PEMA[b]	−1.0	0.456	8.07	1.0	5

$\lambda = A'_2\{\ln(T/277.2)\}^{n'_0} + B'_2$

Liquid	n'_0	A'_2	B'_2	Pressure (bar)	Ref.
Water	0.400	262.5	523.0	1.0	6
(10°–100°C)	0.380	265.0	522.0	100.0	6
	0.333	270.0	515.0	200.0	6
	0.284	275.0	506.0	300.0	6
	0.310	265.0	525.0	400.0	6
	0.385	250.0	557.0	500.0	6

[a] Polyvinyl chloride
[b] Poly(methyl methacrylate)

dependence of heat capacity of amorphous solids $C_v = AT + BT^3$ (ref. 16). It is interesting to examine whether the behaviour of λ in the vicinity of 0 K is explained by the present formulation. It is well known that the thermodynamic Grüneisen parameter for a solid is related to γ_v by[17]

$$\gamma_v = \gamma_G C_v / V \tag{13}$$

where γ_G is the Grüneisen parameter. In the case of γ_G = constant, γ_v is approximately proportional to C_v and it is derived $\lambda \propto C_v$ from $\lambda \propto \gamma_v$ and equation (13). However, the behaviour $\lambda \propto T^2$ observed below 0.5 K cannot be predicted in the present work. The phenomena of $\lambda \approx T^2$ at low temperatures are discussed in terms of phonon boundary scattering[16,18,19], morphology[16] and resonant scattering by tunnelling states[20].

The correlation between λ and γ_v suggests that thermal conduction is controlled dominantly by a variation of pressure ΔP with a small change of temperature ΔT under constant volume or the entropy change due to a small change of volume at constant temperature, which comes from $\gamma_v = (\partial P/\partial T)_v = (\partial S/\partial V)_T$. In other words, an excess pressure necessary to maintain a constant volume of liquid or solid against the thermal expansion of volume transfers to a direction to lower temperature and the pressure conducts the thermal energy. It is very interesting to refer to theoretical works on the thermal conductivity. The Debye treatment of thermal conductivity, the phonon model, is expressed by[7]

$$\lambda \sim C_v \rho U L \tag{14}$$

where ρ is density, U is the velocity of elastic wave or sound velocity and L an average free path length. Here U is related to the adiabatic compressibility β_S by

$$U^2 = V/M\beta_S \tag{15}$$

where M is the molar mass. The expression can predict the temperature dependence of λ with a maximum around T_g for polymers[14] and it is possible to explain the divergence of λ near T_c if $C_v U$ diverges in the vicinity of T_c (ref. 21). An empirical equation proposed by Bridgman[3] is given by

$$\lambda = 2\alpha U/\delta^2 \tag{16}$$

Table 2 Constants in $\ln \lambda = A_0^* + B_0(T)(P+P_0(T))^{m_0}$ in equation (6) at constant temperature where $A_0^* = \ln \lambda_c + \ln[1 + A_0\{\ln(T_c/T)\}^{n_0}]$. λ is in mW/mK

Liquid	m_0	P_0 (bar)	A_0^*	$B_0(T)$	Temp. (K)	Max. P (bar)	Ref.
Argon	0.435	85.3	4.31	0.0347	108.7	490	11
	0.440	0.0	4.23	0.0357	121.5	490	11
	0.440	−19.6	3.88	0.0510	140.5	490	11
	0.280	−37.2	3.48	0.196	149.6	490	11
n-pentane	0.315	284.0	4.48	0.0709	303.2	5 580	3
	0.298	274.0	4.38	0.0903	348.2	11 760	3
methanol	0.085	1019.0	2.28	1.707	303.2	11 760	3
	0.085	1019.0	2.05	1.822	348.2	11 760	3
ethanol	0.025	916.0	−5.86	9.315	303.2	11 760	3
	0.020	1078.0	−10.96	14.02	348.2	11 760	3
n-butyl alcohol	0.215	691.0	4.32	0.197	303.2	11 760	3
	0.265	363.0	4.62	0.0999	348.2	11 760	3
Isopropyl alcohol	0.180	730.0	3.90	0.347	303.2	11 760	3
	0.135	686.0	3.37	0.681	348.2	11 760	3
Isoamyl alcohol	0.185	848.0	3.89	0.318	303.2	11 760	3
	0.354	348.0	4.69	0.038	348.2	11 760	3
ether	0.050	676.0	−0.781	4.12	303.2	11 760	3
Water	0.165	3675.0	4.92	0.383	303.2	8 820	3
	0.165	3969.0	4.87	0.411	348.2	11 760	3

$\ln \lambda = A_1^* + B_0(T)P^{m_0}$ in equation (7) with $A_1^* = C_1 + A_2 T^{-n_0}$, $P_0 = 0$

Polymer	m_0	A_1^*	$B_0 \times 10^2$	Temp. (K)	Max. P (bar)	Ref.
PMMA[a]	0.653	–	0.0886	300.0	35 000	4
PS[a]	0.653	–	0.0886	300.0	35 000	4
PEMA	0.609	4.82	0.620	253.2	1 563	5
PIBMA[b]	0.390	3.93	7.25	273.2	938	5
PNBMA	0.529	4.85	3.93	233.2	625	5
PMMA	0.536	5.06	0.76	293.2	2 030	5

[a] $\ln(\lambda/\lambda_0) = A_1^* + B_0 \times 10^2 P^{m_0}$ for PMMA and PS (ref. 4)

[b] Polyisobutyl methacrylate

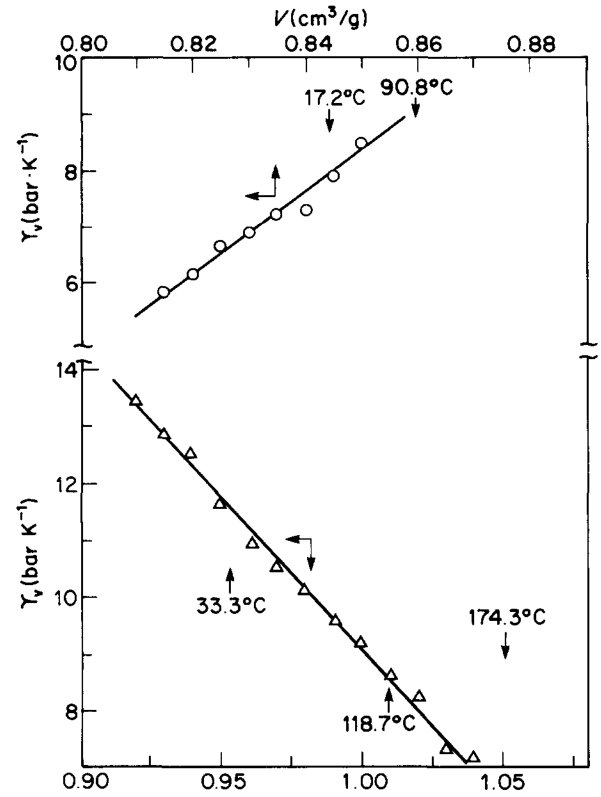

Figure 7 γ_v vs. V (cm³/g) plot for polymethyl methacrylate (PMMA) (○) at temperatures below T_g ($T < T_g$) and poly(n-butyl) methacrylate (PNBMA) (△) at $T > T_g$. Values of γ_v are obtained from data of Simha[12]. Values of T_g are 105 to 126°C for PMMA and −24 to 27°C for PNBMA[14]

where α is the gas constant, δ the mean distance of separation between the centres of molecules. This equation suggests that λ decreases monotonously with increasing temperature in the vicinity of T_c and δ^{-2} is a controlling factor. In both equations (14) and (16), the sound velocity is included, suggesting the adiabatic process in the thermal conductivity, while the correlation $\lambda \sim \gamma_V = \alpha_P/\beta_T$ indicates an importance of the isothermal process through β_T.

Horrocks and McLaughlin[8] derived an expression for λ that

$$\lambda = 2PvC_v/a \tag{17}$$

where P is the probability that energy is transferred on each collision, v the vibrational frequency, C_v the heat capacity associated with the transfer process, and a the nearest neighbour distance, which leads to

$$(\partial \ln \lambda/\partial T)_P = -\{1/3 - (\partial \ln v/\partial \ln V)_P\}\alpha_P \tag{18}$$

If it is assumed that the Grüneisen constant $\gamma_G = -(\partial \ln v/\partial \ln V)_P$ is constant, equation (18) is simplified as

$$\lambda \propto V^{-k_0} \tag{19}$$

where $k_0 = 1/3 + \gamma_G$. Equation (19) can be compared with $\lambda \sim \gamma_v$ and equation (8) so that

$$\lambda \sim \gamma_v \sim \{(V_c - V)/V\}^{\beta_0} \sim V^{-\beta_0} \tag{20}$$

Note that $\lambda \sim \gamma_v$ cannot predict the divergence of λ in the vicinity of the critical temperature[21,22] and $\lambda \propto T^2$ over the temperature region lower than 0.5 K. The other interesting point is that equation (8), expressed by a function of $X = (V_c - V)/V$, cannot predict the experimental behaviour $(\partial \gamma_v/\partial T) > 0$ in a solid. This may be solved by introducing a new variable characterizing the free volume in a solid, such as $X' = (V - V_0)/V$ where V_0 is a V at the limit of 0 K.

Michels *et al.*[23] and Rosenbaum *et al.*[24] discussed the relation between λ and γ_v for argon based on the Enskog theory[25] and found experimentally that there is a linear relation between λ and γ_v for dense gaseous region and a slight deviation from the straight line occurs in the liquid state. Frost *et al.*[26] discussed the pressure dependence of λ based on the hole theory of liquids.

We conclude in this work that there is a strong correlation between the thermal conductivity and thermal pressure coefficient in polymers and simple liquids.

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