ELSEVIER

PII: S0032-3861(96)00910-X

Polymer Vol. 38 No. 14, pp. 3485-3492, 1997

0032-3861/97/$17.00 + 0.00

Temperature and pressure dependence of thermal expansion coefficient and thermal pressure coefficient for amorphous polymers

F. Wang, S. Saeki* and T. Yamaguchi
Department of Materials Science and Engineering, Fukui University, Fukui 910, Japan
(Received 4 July 1996; revised 9 September 1996)

The simple P–V relation $V_x(P,T) = V_x(P_0,T)/[A_x\{P + P_x(T)\}^{m_x}]$ and T–V relation $\ln T = C[\{V_x(P,T) - V(P,0)\}/V_x(P,T)]^{n_x}$ derived in previous works have been used to calculate the compressibility and thermal expansion coefficient by $\beta_T = m_x/\{P + P_x(T)\}$ and $\alpha_p = \{V_x(P,T) - V(P,0)\}/\{V(P,0)n_x T \ln T\}$. The subscript x means a state of material such as $x = g$ for glass state and $x = l$ for liquid state, m_x, A_x and n_x are constants and $P_x(T)$ is a function of temperature. The $V_x(P_0,T)$ is the specific volume at constant pressure P_0 and temperature T, and $V(P,0)$ is the specific volume at pressure P and absolute zero temperature 0 K. The values of m_x for 18 amorphous polymers range from 0.0744 to 0.1382, with an average $\overline{m_g} = 0.1101$ in the glass state and from 0.0709 to 0.1190 with an average $\overline{m_l} = 0.0953$ in the liquid state. The values of n_x for the polymers range from 0.0214 to 0.4526 with an average value $\overline{n_g} = 0.1145$ in the glass state and from 0.0283 to 0.8700 with an average value $\overline{n_l} = 0.1947$ in the liquid state. Values of γ_V have the maximum point against temperature at glass transition temperature (T_g) at which $P_x(T)$ decreases rapidly by 1–4 kbar. The Ehrenfest equation at T_g has been examined based on the experimental data of $\Delta\beta$ and $\Delta\alpha$ at T_g, and it is found that $\mathrm{d}T_g/\mathrm{d}P \neq \Delta\beta/\Delta\alpha$ for seven polymers. © 1997 Elsevier Science Ltd.

(Keywords: equation of state; thermal expansion coefficient; thermal pressure coefficient)

INTRODUCTION

The thermodynamic coefficients such as compressibility β_T, thermal expansion coefficient α_p, and thermal pressure coefficient γ_V are important quantities in characterizing the thermodynamic properties of polymeric materials. An accurate determination of these coefficients is very difficult because these values are very small in order of $10^{-5}\,\mathrm{bar}^{-1}$ for β_T and $10^{-4}\,\mathrm{K}^{-1}$ for α_p for polymers. These coefficients have been evaluated by using empirical polynomials[1–8], the Tait equation[9–14] and other equations[15,16]. The specific volumes of polymers under pressure from 0 to as high as 10 kbar have also been determined experimentally by many researchers[17–26]. In present work we have examined the P–V and T–V relations derived in the previous works[27–30] based on the experimental data over the wide ranges of pressure and then evaluated the coefficients such as β_T, α_p and γ_V accurately. We have also examined the Ehrenfest equation at T_g based on the experimental data of β_T and α_p extrapolated to T_g.

DERIVATION OF BASIC EXPRESSIONS FOR COMPRESSIBILITY AND THERMAL EXPANSION COEFFICIENT

We have used the function

$$f(V,T) = aV(\partial f/\partial V)_T Z^b + g(T) \tag{1}$$

where a and b are constants, $g(T)$ is a function of temperature, $Z = \{V - V(0)\}/V$ and $V(0)$ is the volume at 0 K. The P–V relation at constant temperature is derived using equation (1) by[27–30]

$$V_x(P,T) = V_x(P_0,T)/[A_x\{P + P_x(T)\}^{m_x}] \tag{2}$$

and T–V relation at constant pressure is by[27–30]

$$\ln T = C[\{V_x(P,T) - V(P,0)\}/V_x(P,T)]^{n_x}, \quad T > 1\,\mathrm{K} \tag{3}$$

Here $V_x(P_0,T)$ is the specific volume at constant pressure P_0 such as atmospheric pressure and temperature T, $V_x(P,T)$ is the volume at P and T, $P_x(T)$ is a function of temperature, $V(P,0)$ is the volume at $T = 0\,\mathrm{K}$ and P and m_x, n_x and C are constants. The subscript x means a state such that $x = g$ for the glass state and $x = l$ for the liquid state. The expressions for β_T and α_P can be obtained from equations (2) and (3), respectively

$$\beta_T = m_x/\{P + P_x(T)\} \tag{4}$$

$$\alpha_P = \{V_x(P,T) - V(P,0)\}/\{V(P,0)n_x T \ln T\} \tag{5}$$

The value of the thermal pressure coefficient is obtained by the following thermodynamic relation that

$$\gamma_V = \alpha_P/\beta_T \tag{6}$$

The values of m_x, n_x and C, and functions of $P_x(T)$ and

---

* To whom correspondence should be addressed

Table 1 Constants and indices in equation (2) for polymers at constant temperature[a]

Polymer	T (K)	State[b]	m_x[c]	$P_x(T)$ (bar)	$V(P_0, T)$ (cm^3 g^{-1})	P_0 (bar)	$P_{\max}$ (Kbar)	ΔV_{av} (cm^3 g^{-1})	Ref.
PC	301.7	*g*	0.1368	5565	0.8373	0	1.8	0.0001	24
	371.3	*g*	0.1382	4987	0.8515	0	1.8	0.0001	24
	393.2	*g*	0.1301	4264	0.8573	0	1.8	0.0001	24
	416.4	*g*	0.1010	3009	0.8628	0	1.8	0.0001	24
	493.0	*l*	0.1020	1518	0.9017	0	1.8	0.0001	24
	513.7	*l*	0.0964	1315	0.9141	0	1.8	0.0001	24
	533.6	*l*	0.0972	1218	0.9260	0	1.8	0.0000	24
	553.5	*l*	0.0969	1097	0.9397	0	1.8	0.0003	24
	589.8	*l*	0.1015	1001	0.9600	0	1.8	0.0003	24
PA	326.8	*g*	0.1312	5268	0.8300	0	1.8	0.0001	24
	373.0	*g*	0.1376	5025	0.8388	0	1.8	0.0001	24
	417.8	*g*	0.1271	4170	0.8480	0	1.8	0.0002	24
	504.7	*l*	0.1164	1866	0.8833	0	1.2	0.0002	24
	526.6	*l*	0.1005	1460	0.8934	0	1.8	0.0002	24
	544.6	*l*	0.0989	1331	0.9033	0	1.8	0.0002	24
	584.1	*l*	0.1008	1191	0.9231	0	1.8	0.0002	24
PS	280.9	*g*	0.1172	4366	0.9557	1	2.0	0.0001	21
	294.2	*g*	0.1170	4307	0.9582	1	2.0	0.0000	21
	348.6	*g*	0.0949	2976	0.9707	1	2.0	0.0000	21
	388.6	*l*	0.1041	1666	0.9855	1	0.4	0.0001	21
	403.0	*l*	0.1001	1581	0.9928	1	0.8	0.0001	21
	429.0	*l*	0.0955	1356	1.0061	1	1.8	0.0003	21
	446.7	*l*	0.0986	1330	1.0152	1	2.0	0.0003	21
	458.1	*l*	0.0982	1278	1.0212	1	2.0	0.0002	21
	468.8	*l*	0.0990	1243	1.0269	1	2.0	0.0003	21
POMS	302.3	*g*	0.1225	4593	0.9807	1	2.0	0.0001	21
	309.5	*g*	0.1097	3935	0.9826	1	2.0	0.0001	21
	322.9	*g*	0.0886	2882	0.9860	1	2.0	0.0002	21
	338.8	*g*	0.0833	2529	0.9903	1	2.0	0.0001	21
	422.6	*l*	0.0717	1095	1.0172	1	0.6	0.0002	21
	432.4	*l*	0.0733	1057	1.0225	1	0.8	0.0001	21
	460.8	*l*	0.0812	1025	1.0380	1	1.8	0.0002	21
OR-25	298.2	*l*	0.1057	2485	1.0288	0	10.0	0.0007	17
OR-15	298.2	*l*	0.0940	2087	1.0373	0	10.0	0.0007	17
Neoprene	298.2	*l*	0.1024	2837	0.8818	0	10.0	0.0007	17
Thiokol ST	298.2	*l*	0.1190	3716	0.7704	0	10.0	0.0001	17

[a] Values of m_x and $P_x(T)$ for 18 polymers were determined, but only parts of them are listed here for saving space. We can give the data which are useful to evaluate β_T at arbitrary pressure if asked

[b] *g*, glass state; *l*, liquid state

[c] The average values of $\overline{m_g}$ and $\overline{m_l}$ for each polymer are given by: PC ($\overline{m_g} = 0.1265, \overline{m_l} = 0.0988$); PA (0.1320, 0.1042); PH (0.1015, 0.0977); PS (0.1097, 0.0993); POMS (0.1010, 0.0754); PMMA (0.1031, 0.0990); PCHMA (0.1001, 0.1038)

$V(P, 0)$ in equations (2) and (3) have been determined. The detailed procedures are given in the Appendix.

RESULTS

Accuracy of the P–V *equation (2)*

The values of m_x and $P_x(T)$ in equations (A1) and (A2), and n_x, $V(P, 0)$ and C in equations (A4), (A5) and (A6) (see the Appendix) have been determined by the experimental data for various polymers and are listed in *Tables 1* and *2*. The values of specific volume calculated by equation (2) with the m_x and $P_x(T)$ in *Table 1* are in good agreement with the experimental data and the average deviation is 0.0001 cm^3 g^{-1} for 18 polymers. *Figure 1* shows that values of m_x in the glass state are larger than those in the liquid state and are in the vicinity of 0.1 for various polymers. The average value of m_x is $\overline{m_g} = 0.1101$ for seven polymer glasses and $\overline{m_l} = 0.0953$ for 18 polymer liquids, and the individual average values of m_x for each of the seven polymers are given in *Table 1*. It is assumed that $\overline{m_g} = 0.1101$ for polymer glasses, and $\overline{m_l} = 0.0953$ for polymer liquids. Equation (2) is simplified to

$$V_x(P, T) = V_x(P_0, T)/[A_x\{P + P_x(T)\}^{\overline{m}_x}] \qquad (7)$$

where $P_x(T)$ is only one adjustable parameter because of $A_x\{P_0 + P_x(T)\}^{\overline{m}_x} = 1$. The specific volumes calculated by equation (7) agree with the experimental data within an absolute accuracy of 0.0000–0.006 cm^3 g^{-1}.

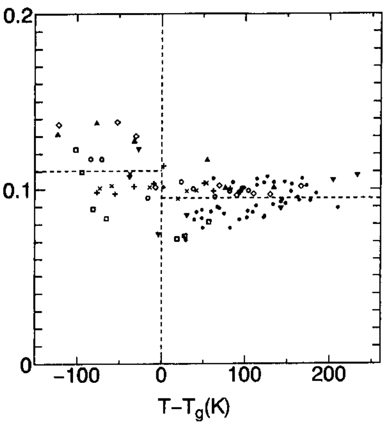

Figure 1 Temperature dependence of m_x in equation (2) for seven polymer glasses and 18 polymer liquids. ○, PS; □, POMS; ◇, PC; △, PA; ▽, PH; ×, PMMA; +, PCHMA; ●, other 11 polymer liquids

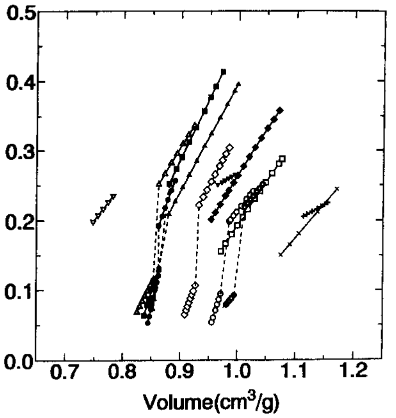

Figure 2 Volume dependence of α_pT for polymer glasses and liquids at atmospheric pressure (dashed lines correspond to glass transition). ○, PS; ●, PMMA; □, PVME; ■, PC; △, PA; ▲, PH; ◇, PCHMA; ◆, PNBMA; ▽, PECH; ▼, PCL; ◎, POMS; +, rubber; ×, PIB

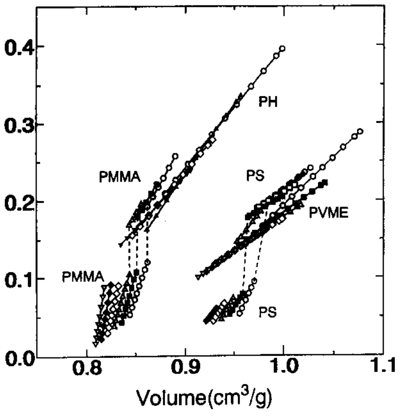

Figure 3 Volume dependence of α_pT for PS, PH, PVME, and PMMA at various pressures (dashed lines correspond to glass transition). ○, P = 0 bar; ●, P = 100 bar; □, P = 200 bar; ■, P = 400 bar; ▲, P = 600 bar; △, P = 800 bar; ◇, P = 1200 bar; ◆, P = 1600 bar; ▼, P = 1800 bar; ▽, P = 2000 bar

Empirical expressions for α_P and γ_V

A linearity between $\alpha_P T$ and V is obtained for various polymers at atmospheric pressure in *Figure 2* and various pressures in *Figure 3* and is expressed by

$$\alpha_P T = h_1 + k_1 V \tag{8}$$

The linearity between $\alpha_P T$ and V can be explained by equation (5) such that

$$\alpha_P T = -1/(n_x \ln T) + V/\{V(P,0)n_x \ln T\} = h_1 + k_1 V \tag{9}$$

where $h_1 = -1/(n_x \ln T)$ and $k_1 = 1/\{V(P,0)n_x \ln T\}$ are assumed to be constant because ln T is approximately constant over the narrow temperature range in the present work. The values of $\alpha_P T$ for various pressures concentrate on one straight line over the temperatures above T_g for PH, etc. as shown in *Figure 3*. This suggests that $\alpha_P T$ is a function of volume only for these polymers.

The relation between γ_V and volume below T_g for polymers is not linear at atmospheric pressure in *Figure 4*. The linear volume dependence of γ_V above T_g is observed in *Figure 5* and is expressed by

$$\gamma_V = h_2 + k_2 V \tag{10}$$

In *Figure 4* values of γ_V increase with increasing volume below T_g but decrease above T_g in *Figure 5*, which suggests that γ_V does not change drastically or discontinuously in the vicinity of T_g. However, α_P changes discontinuously at T_g as is shown in *Figures 2* and *3*. The values of h_1, k_1, h_2 and k_2 in empirical equations (8) and (10) are listed in *Table 3*. They are used to evaluate α_P and γ_V for various polymers in the temperature range in present work.

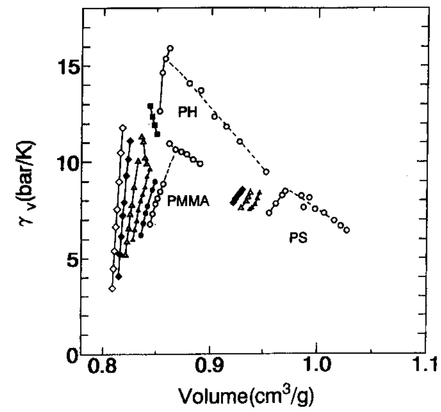

Figure 4 Volume dependence of γ_V for polymer glass at various pressures (dashed decrease lines correspond to the tendency above T_g at atmospheric pressure for comparison easily). ○, $P = 0$ bar; ●, $P = 400$ bar; ■, $P = 600$ bar; ▲, $P = 800$ bar; △, $P = 1200$ bar; ◆, $P = 1600$ bar; ◇, $P = 2000$ bar

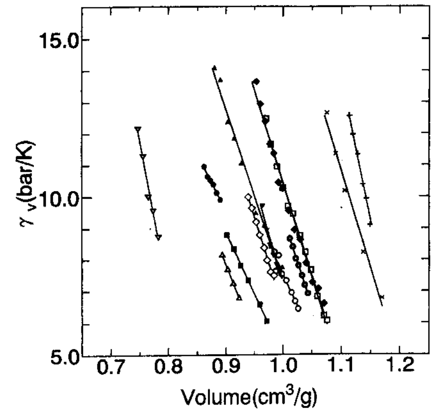

Figure 5 Volume dependence of γ_V for polymer liquids at atmospheric pressure. ○, PS; ●, PMMA; □, PVME; ■, PC; △, PA; ▲, PH; ◇, PCHMA; ◆, PNBMA; ▽, PECH; ▼, PCL; ◎, POMS; +, rubber; ×, PIB

Table 2 Constants and indices in equation (3) for polymers at constant pressure[a]

Polymer	Pressure (bar)	n_x	C	$V(P,0)$ (cm^3 g^{-1})	Temperature range (K)	State	ΔV_{av} (cm^3 g^{-1})	Ref.
PC	0	0.0743	7.4808	0.8153	300–420	*g*	0.0003	24
		0.1106	7.5545	0.7520	450–610	*l*	0.0008	24
	600	0.1594	9.0170	0.7787	300–420	*g*	0.0002	24
		0.4429	9.1825	0.5129	450–610	*l*	0.0005	24
	1200	0.1553	9.0861	0.7746	300–420	*g*	0.0001	24
	1800	0.1298	8.7287	0.7752	300–420	*g*	0.0002	24
PA	0	0.1128	8.1725	0.7905	300–440	*g*	0.0002	24
		0.1450	7.8484	0.7042	460–590	*l*	0.0003	24
	600	0.1392	8.7512	0.7760	300–400	*g*	0.0002	24
		0.2428	8.6053	0.6295	480–590	*l*	0.0002	24
	1200	0.1066	8.3420	0.7816	300–400	*g*	0.0002	24
		0.2977	9.0511	0.5965	500–590	*l*	0.0001	24
	1800	0.1895	9.9757	0.7529	300–400	*g*	0.0002	24
		0.0612	7.4580	0.7772	500–590	*l*	0.0003	24
PH	0	0.0320	6.5651	0.8417	300–340	*g*	0.0000	24
		0.1220	7.5819	0.7644	370–580	*l*	0.0004	24
	600	0.1172	8.2701	0.8078	300–340	*g*	0.0001	24
		0.1040	7.5820	0.7830	370–580	*l*	0.0006	24
	1200	0.3884	13.5385	0.7451	300–340	*g*	0.0001	24
		0.1270	7.8819	0.7582	370–580	*l*	0.0003	24
	1800	0.0729	7.6260	0.8121	300–340	*g*	0.0001	24
		0.1418	8.1213	0.7453	370–580	*l*	0.0001	24
PMMA	1	0.0521	7.0467	0.8311	290–374	*g*	0.0000	23
		0.0862	7.2963	0.7849	386–432	*l*	0.0000	23
	400	0.0468	6.9937	0.8263	290–374	*g*	0.0000	23
		0.0878	7.3938	0.7793	386–432	*l*	0.0001	23
	800	0.0476	7.0549	0.8196	290–386	*g*	0.0001	23
		0.0890	7.4778	0.7740	397–432	*l*	0.0002	23
	1200	0.0388	6.8923	0.8158	290–386	*g*	0.0002	23
	1600	0.0298	6.6962	0.8118	290–397	*g*	0.0002	23
	2000	0.0256	6.6131	0.8071	290–397	*g*	0.0002	23
PCHMA	1	0.0803	7.5476	0.8832	291–371	*g*	0.0002	23
		0.1171	7.5276	0.8074	383–472	*l*	0.0002	23
	400	0.1502	8.8925	0.8544	291–371	*g*	0.0001	23
		0.1104	7.6335	0.8191	395–472	*l*	0.0003	23
	800	0.1176	8.4406	0.8615	291–383	*g*	0.0002	23
		0.2346	8.7703	0.7271	407–472	*l*	0.0002	23
	1200	0.0690	7.5076	0.8692	291–396	*g*	0.0006	23
		0.1533	8.2940	0.7851	420–472	*l*	0.0002	23
	1600	0.0703	7.6296	0.8654	291–396	*g*	0.0005	23
		0.2411	11.3139	0.8282	420–472	*l*	0.0004	23
	2000	0.4526	16.9227	0.7942	290–407	*g*	0.0005	23
		0.0937	8.0156	0.8358	440–470	*l*	0.0001	23
PNBMA	1	0.1351	7.5122	0.8252	307–422	*l*	0.0002	23
	400	0.1745	7.9634	0.7950	307–472	*l*	0.0003	23
	800	0.0276	6.4002	0.9087	285–307	*g*	0.0000	23
		0.2436	8.5919	0.7475	319–472	*l*	0.0003	23
	1200	0.0214	6.2674	0.9011	285–307	*g*	0.0000	23
		0.3100	9.1900	0.7118	333–472	*l*	0.0003	23
	1600	0.0258	6.4212	0.8931	285–319	*g*	0.0003	23
		0.4536	10.2149	0.6482	333–472	*l*	0.0004	23
	2000	0.3024	10.6340	0.7803	285–355	*g*	0.0002	23
		0.3757	9.9695	0.6859	355–472	*l*	0.0003	23

Table 2 continued

Polymer	Pressure (bar)	n_x	C	$V(P,0)$ ($\mathrm{cm^3\,g^{-1}}$)	Temperature range (K)	State	ΔV_{av} ($\mathrm{cm^3\,g^{-1}}$)	Ref.
PS	1	0.0637	7.2613	0.9377	280–348	*g*	0.0000	21
		0.1670	8.0546	0.8227	388–468	*l*	0.0000	21
	400	0.0880	7.7825	0.9215	280–348	*g*	0.0001	21
		0.2360	8.7101	0.7707	388–468	*l*	0.0000	21
	800	0.0773	7.6343	0.9186	280–348	*g*	0.0001	21
		0.1062	7.7898	0.8719	403–468	*l*	0.0001	21
	1200	0.0890	7.9196	0.9085	280–348	*g*	0.0001	21
		0.0447	7.0553	0.9155	413–468	*l*	0.0002	21
	1600	0.1109	8.4192	0.8967	280–348	*g*	0.0000	21
		0.0283	6.7872	0.9173	429–468	*l*	0.0001	21
	2000	0.1626	9.5037	0.8775	280–348	*g*	0.0000	21
POMS	1	0.1685	8.9212	0.9112	302–355	*g*	0.0000	21
		0.1659	8.0119	0.8307	412–470	*l*	0.0000	21
	400	0.0470	7.0132	0.9594	302–355	*g*	0.0004	21
		0.3729	9.5445	0.7023	422–470	*l*	0.0003	21
	800	0.0938	7.9911	0.9349	302–355	*g*	0.0001	21
		0.0541	7.1863	0.9378	432–470	*l*	0.0001	21
	1200	0.0617	7.3961	0.9390	302–355	*g*	0.0001	21
	1600	0.1375	9.0949	0.9135	302–355	*g*	0.0000	21
	2000	0.2440	11.3411	0.8819	302–355	*g*	0.0000	21

[a] Values of n_x, $V(P,0)$ and C were determined for 14 polymers, but only parts of them are given here to save space. We can give the data which are useful in evaluating α_p at arbitrary temperature if requested

Table 3 Constants used in equations (8), (10), (20) and (21)

Polymer	State[a]	h_1	k_1	h_2	k_2	$-h_3$	k_3	$h_4 \times 10^5$	$k_4 \times 10^7$
PC	*l*	−1.287	1.750	43.48	−38.47	11.78	0.00441	21.97	7.60
	g	−2.127	2.616	−12.21	25.21	11.39	0.00258	−4.46	8.58
PA	*l*	−0.939	1.382	49.01	−45.75	11.65	0.00391	43.14	2.49
	g	−1.325	1.688			11.29	0.00210	14.82	2.59
PH	*l*	−1.167	1.566	61.68	−54.36	11.66	0.00409	32.85	6.31
	g	−5.242	6.232	−273.71	336.46	13.08	0.00716	−102.81	41.70
PS	*l*	−0.826	1.040	46.90	−39.38	10.80	0.00289	49.02	0.53
	g	−2.557	2.732	−63.20	73.84	11.45	0.00320	−14.18	11.81
POMS	*l*	−0.823	1.029	64.95	−55.63	11.32	0.00403	50.16	0.66
	g	−0.859	0.957			11.73	0.00407	27.54	−0.44
PMMA	*l*	−1.766	2.273	41.97	−36.03	11.10	0.00318	0.70	13.58
	g	−3.132	3.773	−105.39	133.17	11.44	0.00312	−30.47	16.70
PCHMA	*l*	−1.247	1.576	64.73	−58.28	11.80	0.00520	29.61	7.40
	g	−1.962	2.232	6.50	2.74	11.71	0.00378	−0.52	7.87
PNBMA	*l*	−1.074	1.337	69.81	−59.39				
PVME	*l*	−1.047	1.241	69.15	−58.71				
PECH	*l*	−0.568	1.026	83.87	−96.10				
PCL	*l*	−0.204	0.471	73.99	−66.84				
NR	*l*	−0.309	0.462	112.57	−89.82				
PIB	*l*	−0.909	0.985	78.40	−61.43				

[a] *l*, liquid state; *g*, glass state

DISCUSSION

Volume dependence of thermal pressure coefficient

The volume dependence of γ_V over temperature range including T_g at constant pressure can be expressed by the temperature dependence of γ_V through a transformation of volume to temperature under constant pressure by using P–V–T relation. The γ_V is obtained from equation (2) by

$$\gamma_V = (\partial P/\partial T)_V = -\mathrm{d}P_x(T)/\mathrm{d}T \qquad (11)$$

The slopes of $P_x(T)$ against temperature in *Figure 6*

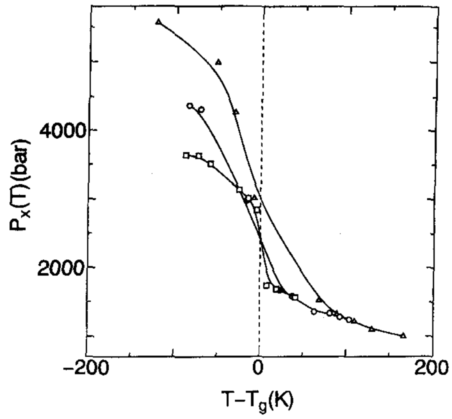

Figure 6 Temperature dependence of $P_x(T)$ in equation (2) for PS (○), PMMA (□), and PC (△)

change drastically at T_g. The absolute values of the slopes which give γ_V have the maximum at T_g, which means that γ_V shows the maximum value in the vicinity of T_g. The similar behaviour of γ_V with respect to temperature was obtained by Simha [13] and Hartmann[31,32]. Hartmann's equation of state is given by

$$\overline{P}\,\overline{V}^5 = \overline{T}^{3/2} - \ln \overline{V} \qquad (12)$$

where $\overline{P} = P/B_0$, $\overline{V} = V/V_0$, and $\overline{T} = T/T_0$ and B_0, V_0 and T_0 are reducing parameters. The γ_V is calculated from equation (12) by

$$\gamma_V = (3B_0 V_0^5 T^{1/2})/(2T_0^{3/2} V^5) \qquad (13)$$

Equation (13) gives the tendency that γ_V increases with increasing temperature below T_g and decreases above T_g. This is due to the fact that $T^{1/2}$ increases faster than V^5 with increasing temperature below T_g because of a very slow increasing rate of V in the glass state, while V^5 increases faster than $T^{1/2}$ above T_g due to a fast increasing rate of V in the liquid state.

Relation between equation (2) and the Tait equation

It is interesting to compare the expression for β_T yielded from equation (2) with that from the Tait equation. The Tait equation is written as

$$V(P,T) = V(0,T)[1 - 0.0894 \ln\{1 + P/B(T)\}] \qquad (14)$$

Here $B(T)$ is the so-called Tait parameter and is given by

$$B(T) = B_0 \exp(-B_1 T) \qquad (15)$$

The β_T from the Tait equation is expressed by

$$\beta_T = -(1/V_0)(\partial V/\partial P)_T = 0.0894/\{P + B(T)\} \qquad (16)$$

The Tait equation can be regarded as the typical case of equation (2) (see below).

Rewriting the Tait equation as

$$V(P,T) = V(0,T)[C - 0.0894 \ln\{P + B(T)\}] \qquad (17)$$

where $C = 1 + 0.0894 \ln B(T)$ is a constant when temperature is constant. On the other hand, equation (2) can be rewritten by

$$\ln\{V_x(P,T)/V_x(P_0,T)\} = -\ln A_x - m_x \ln\{P + P_x(T)\} \qquad (18)$$

and

$$V_x(P,T) = V_x(P_0,T)[C' - m_x \ln\{P + P_x(T)\}] \qquad (19)$$

where an approximation that $\ln\{V_x(P,T)/V_x(P_0,T)\} = \{V_x(P,T) - V_x(P_0,T)\}/V_x(P_0,T)$ is used, and $C' = 1 - \ln A_x$ is a constant. One can say that the Tait equation (17) is essentially the same as equation (19) derived from equation (2). The parameter m_x in equation (19) is an empirical parameter but in the Tait equation, $m_x = 0.0894$ is a constant. In fact, the average values of m_x in the liquid state $\overline{m}_l = 0.0953$ is about equal to 0.0894 for the Tait equation, but the values of $\overline{m}_g = 0.1101$ in the glass state is larger than 0.0894. This means that the P–V function in the liquid state is slightly different from that in the glass state, although in the Tait equation both functions are assumed to be the same.

Examination of the Ehrenfest relation at glass transition

Many researchers[21,23,24,31] have examined the Ehrenfest relations at the glass transition. Zoller defined a typical transition line and concluded that the Ehrenfest relations must hold according to his definition of transition line[24,33].

The values of β_T and α_P at T_g have been determined by using the following empirical equations in the present work

$$\ln \beta_T = h_3 + k_3 T \qquad (20)$$

and

$$\alpha_P = h_4 + k_4 T \qquad (21)$$

The values of h_3, k_3, h_4 and k_4 in equations (20) and (21) are also listed in *Table 3*. From equations (20) and (21), we evaluated the quantities of β_T and α_P at T_g by extrapolation and defined $\beta_l = \lim_{T \to T_g + 0} \beta_T$, $\beta_g = \lim_{T \to T_g - 0} \beta_T$, $\alpha_l = \lim_{T \to T_g + 0} \alpha_P$, and $\alpha_g = \lim_{T \to T_g - 0} \alpha_P$. The results determined above were compared with those calculated by Zoller for PC, PA, and PH[24], by Olabisi and Simha for PMMA, and PCHMA[23], and by Quach and Simha for PS and POMS[21] (see *Table 4*). It is expected that the results of β_l, β_g, and $\Delta\beta$ obtained in this work agree with those of Zoller, Olabisi and Simha and Quach and Simha because they calculated β_T by using the Tait equation, which is intrinsically identical with our equation discussed above. But the differences in α_l, α_g and $\Delta\alpha$ are obvious. It is noted that Zoller[24] calculated α_g by

$$\alpha_P = a_1/(a_0 + a_1 T) \qquad (22)$$

which derived from

$$V(0,T) = a_0 + a_1 T. \qquad (23)$$

According to equation (22), α_P decreases with increasing temperature which is contrary to general behaviour that α_P increases with increasing temperature. Zoller made an assumption that the α_P in the liquid state is a constant over a temperature range of 100°C above T_g, which is also contrary to the general tendency of α_P for liquid. According to equation (21) and the values of k_4 listed in *Table 3* for α_P in the present work, α_P increases with increasing temperature. The facts mentioned above can explain why our values of α_l are smaller

]]>

Table 4 Evaluation of the Ehrenfest equation

Polymer		$\alpha_l \times 10^4$ (K^{-1})	$\alpha_g \times 10^4$ (K^{-1})	$\Delta\alpha \times 10^4$ (K^{-1})	$\beta_l \times 10^5$ (bar^{-1})	$\beta_g \times 10^5$ (bar^{-1})	$\Delta\beta \times 10^5$ (bar^{-1})	$\Delta\beta/\Delta\alpha$ (K bar^{-1})	T_g (K)	$\mathrm{d}T_g/\mathrm{d}P$ (K bar^{-1})
PC	This work	5.42	3.19	2.23	4.97	3.36	1.61	0.0722	423.6	0.0520
	Zoller[24]	5.99	2.55	3.44	5.24	3.35	1.88	0.0547		
PA	This work	5.43	2.65	2.78	5.07	3.23	1.84	0.0662	450.0	0.0533
	Zoller	5.89	2.30	3.59	5.36	3.38	1.98	0.0552		
PH	This work	5.44	3.95	1.49	3.50	2.39	1.11	0.0745	341.2	0.0231
	Zoller	6.27	2.97	3.30	3.28	2.41	0.87	0.0264		
PMMA	This work	5.21	3.27	1.94	5.02	3.50	1.52	0.0784	378.2	0.0236
	Olabisi[23]	5.30	2.95	2.35	4.81	3.52	1.29	0.0549		
PCHMA	This work	5.77	2.94	2.83	5.44	3.47	1.97	0.0696	380.2	0.0224
	Olabisi	5.91	2.53	3.38	5.29	3.27	2.02	0.0598		
PS	This work	5.09	2.89	2.20	5.65	3.43	2.22	0.1009	365.0	0.0742
	Quach[21]	5.13	2.16	2.97	5.59	3.33	2.26	0.0761		
POMS	This work	5.28	2.58	2.70	6.19	4.15	2.04	0.0756	404.0	0.0730
	Quach	5.31	2.60	2.71	5.85	3.95	1.90	0.0701		

than and α_g are larger than those given by Zoller and the values of $\Delta\beta/\Delta\alpha$ in the present work are larger than those of Zoller. It is found in this work that $\Delta\beta/\Delta\alpha \neq \mathrm{d}T_g/\mathrm{d}P$ at the glass transition for seven amorphous polymers.

CONCLUSIONS

Three new results are obtained in this work.

1. The values of m_x for amorphous polymers in equation (2) are in the vicinity of 0.1 and the average value $\overline{m}_g = 0.1101$ in the glass state is slightly larger than $\overline{m}_l = 0.0953$ in the liquid state. It is suggested that the $P-V$ function in the liquid state is slightly different from that in the glass state although in the Tait equation both functions are assumed to be the same. The actual values of m_x can be used to reproduce the experimental data with an average accuracy 0.0001 cm^3 g^{-1} for 18 polymers and the maximum deviation is 0.0008 cm^3 g^{-1} for OR-25 in the pressure range from 0 to 10 kb.
2. The values of γ_V increase with increasing volume below T_g, while they decrease with increasing volume linearly at constant pressure above T_g over the volume range in this work and $P_x(T)$ decreases rapidly in the vicinity of T_g. The γ_V has the maximum point in the vicinity of T_g.
3. The Ehrenfest equation was examined by experimental data and a relation $\Delta\beta/\Delta\alpha \neq \mathrm{d}T_g/\mathrm{d}P$ was found for seven polymers. The Ehrenfest equation for the second order does not satisfy at the glass transition temperature for the seven polymers in this work.

ACKNOWLEDGEMENT

The authors thank Mr Tsubokawa for his assistance.

REFERENCES

1. Foster III, G. N., Waldman, N. and Griskey, R. G., *J. Appl. Polym. Sci.*, 1966, **10**, 201.
2. Orwoll, R. A. and Flory, P. J., *J. Amer. Chem. Soc.*, 1967, **89**, 6814.
3. Eichinger, B. E. and Flory, P. J., *Macromolecules*, 1968, **1**(3), 285.
4. Hocker, H., Blake, G. J. and Flory, P. J., *Trans. Faraday Soc.*, 1971, **67**, 2251.
5. Quach, A. and Simha, R., *J. Appl. Phys.*, 1971, **42**, 4592.
6. Shih, H. and Flory, P. J., *Macromolecules*, 1972, **5**, 758.
7. Barlow, J. W., *Polym. Eng. and Sci.*, 1978, **18**(3), 238.
8. Uriarte, C., Eguiazabal, J. I., Llanos, M., Iribarren, J. I. and Iruin, J. J., *Macromolecules*, 1987, **20**, 3038.
9. Cutler, W. G., McMickle, R. H., Webb, W. and Schiessler, R. W., *J. Chem. Phys.*, 1958, **29**(4), 727.
10. Zoller, P., *J. Appl. Polym. Sci.*, 1977, **21**, 3129.
11. Zoller, P., *J. Appl. Polym. Sci.*, 1979, **23**, 1051.
12. Zoller, P., *J. Appl. Polym. Sci.*, 1979, **23**, 1057.
13. Jain, R. K. and Simha, R., *Polym. Eng. and Sci.*, 1979, **19**(12), 845.
14. Gee, G., *Polymer*, 1966, **7**, 177.
15. Simha, R. and Wilson, P. S., *Macromolecules*, 1973, **6**(6), 908.
16. Olabisi, O. and Simha, R., *J. Appl. Polym. Sci.*, 1977, **21**, 149.
17. Weir, C. E., *J. Research NBS*, 1951, **46**(3), 207, RP2192.
18. Robert R. Matheson, Jr., *Macromolecules*, 1987, **20**(8), 1847.
19. Jain, R. K. and Simha, R., *J. Polym. Sci.: Polym. Phys. Ed.*, 1979, **17**, 1929.
20. Ougizawa, T., Dee, G. T. and Walsh, D. J., *Macromolecules*, 1991, **24**, 3834.
21. Quach, A. and Simha, R., *J. Appl. Phys.*, 1971, **42**(12), 4592.
22. Rodgers, P. A., *J. Appl. Polym. Sci.*, 1993, **48**, 1061.
23. Olabisi, O. and Simha, R., *Macromolecules*, 1975, **8**(2), 206.
24. Zoller, P., *J. Polym. Sci.: Polym. Phys. Ed.*, 1982, **20**, 1453.
25. Hellwege, K. H., Knappe, W. and Lehmann, P., *Kolloid-Z.*, 1962, **110**, 183.
26. Breuer, H. and Rehage, G., *Kolloid-Z.*, 1967, **159**, 216.
27. Saeki, S., Tsubokawa, M., Yamanaka, J. and Yamaguchi, T., *Polymer*, 1991, **32**(17), 3170.
28. Saeki, S., Tsubokawa, M. and Yamaguchi, T., *Polymer*, 1988, **29**, 123.
29. Saeki, S., Tsubokawa, M. and Yamaguchi, T., *Polymer*, 1989, **30**, 672.
30. Saeki, S., Tsubokawa, M., Yamanaka, J. and Yamaguchi, T., *Polymer*, 1992, **33**(3), 577.
31. Hartmann, B. and Haque, M. A., *J. Appl. Phys.*, 1985, **58**(8), 2831.
32. Hartmann, B. and Haque, M. A., *J. Appl. Polym. Sci.*, 1985, **30**, 1553.
33. Zoller, P., *J. Polym. Sci.: Polym. Phys. Ed.*, 1978, **16**, 1261.

APPENDIX

Determination of parameters in equations (2) and (3)

In order to determine m_x, $P_x(T)$ and A_x, three sets of P, V data at constant temperature and in the same phase region such as above or below P_g are selected, and the following relation can be established by equation (2):

$$\frac{\{1/V(P_1,T)\}^{1/m_x}-\{1/V(P_2,T)\}^{1/m_x}}{\{1/V(P_2,T)\}^{1/m_x}-\{1/V(P_3,T)\}^{1/m_x}}=\frac{P_1-P_2}{P_2-P_3} \quad \text{(A1)}$$

By equation (A1) m_x can be determined easily by computer and so can $P_x(T)$ and A_x by equations (A2) and (A3):

$$P_x(T)=\frac{\{V(P_3,T)/V(P_1,T)\}^{1/m_x}P_3-P_1}{1-\{V(P_3,T)/V(P_1,T)\}^{1/m_x}} \quad \text{(A2)}$$

$$A_x=\frac{1}{\{P_0+P_x(T)\}^{m_x}} \quad \text{(A3)}$$

In determination of n_x, $V(P,0)$, and C, three sets of T, V data at constant pressure in the same phase region are selected. The following relation is established by equation (3):

$$\frac{(\ln T_1)^{1/n_x}-(\ln T_2)^{1/n_x}}{\ln T_2)^{1/n_x}-(\ln T_3)^{1/n_x}}=\frac{\{1/V(P,T_2)\}-\{1/V(P,T_1)\}}{\{1/V(P,T_3)\}-\{1/V(P,T_2)\}} \quad \text{(A4)}$$

n_x can be determined by equation (A4) and so can $V(P,0)$ and C by equations (A5) and (A6):

$$V(P,0)=\frac{(\ln T_1/\ln T_2)^{1/n_x}-1}{\{1/V(P,T_2)\}(\ln T_1/\ln T_2)^{1/n_x}-\{1/V(P,T_1)\}} \quad \text{(A5)}$$

$$C=\frac{\ln T_1}{[\{V(P,T_1)-V(P,0)\}/V(P,T_1)]^{n_x}} \quad \text{(A6)}$$

Abbreviations

PC	Polycarbonate
PA	Polyarylate
PH	Phenoxy
PMMA	Polymethyl methacrylate
PCHMA	Polycyclothexyl methacrylate
PNBMA	Poly *n*-butyl methacrylate
PECH	Polyepichlorohydrin
PCL	Poly(ε-caprolactone)
PVC	Polyvinyl chloride
a-PP	Atactic polypropylene
PS	Polystyrene
POMS	Polyorthomethyl styrene
PVME	Polyvinyl methyl ether
NR	Natural rubber
OR	Raw rubber
PIB	Polyisobutylene