

# A new isothermal equation of state for polymers

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A new isothermal equation of state for polymers in the solid and the liquid is given by

$$P = B(T, 0)/(n - m) \{ [V(T, 0)/V(T, P)]^{n+1} - [V(T, 0)/V(T, P)]^{m+1} \}$$

where  $n = 6.14$  and  $m = 1.16$  are general constants for polymer systems. Comparison of the equation with experimental data is made for six polymers at different temperatures and pressures. The results predict that the equation of state describes the isothermal compression behaviour of polymers in the glass and the melt states, except at the transition temperature.

(Keywords: equation of state; polymer; high pressure; Tait equation)

## INTRODUCTION

Semi-empirical or empirical equations, such as the Tait equation, are usually adopted to describe the relation between pressure, volume and temperature<sup>1-4</sup>. However, the Tait equation does not adapt to describing the isothermal compressive behaviour of polymers in the glass state<sup>5-12</sup>. Theoretical studies of the equation of state for polymers in the liquid state have been carried out using equilibrium thermodynamics. Some interesting results have been obtained<sup>13</sup>, but the thermodynamic behaviour of polymers in the glass and crystalline states which are not in equilibrium are hardly described by equilibrium thermodynamics. Therefore, theoretical studies on the equation of state for polymers in the glass and the crystalline states have seldom been reported<sup>14,15</sup>.

In this paper, we report a new equation of state for polymers. In the derivation of the equation, we assume that the compression of the volume under external pressure  $P$  is due to changes in chain segment separation, and that the dynamic equilibrium conditions of the system under  $P$  is that the internal pressure  $P_1$ , determined by the change of the internal energy resulting from the thermal motions of chain segments, is equal to  $P$ .

## DERIVATION OF THE EQUATION OF STATE

From the above, it is assumed that for dynamic equilibrium conditions of a system under  $P$ :

$$P = P_1 \quad (1)$$

From a study of  $P_1$ , Pastin<sup>16</sup> considered that  $P_1$  was the sum of two terms, the pressure due to internal energy and thermal pressure:

$$P_1 = -(\mathrm{d}U/\mathrm{d}V)_{T=0} + P_T(V, T) \quad (2)$$

The first term is the pressure along the absolute zero temperature isotherm and is governed by the internal energy. The second term is the additional pressure generated by thermal motions. However, at constant temperature,  $P_1$  relies mainly on the value of  $(\mathrm{d}U/\mathrm{d}V)_T$ . Therefore, we consider that  $P_1$  is determined approximately by the change in the internal energy resulting from the change in volume. The effect of thermal motions of the chain segments on  $P_1$  is ascribed to changes in the internal energy and the volume at zero pressure with temperature:

$$P_1 = -(\partial U/\partial V)_T \quad (3)$$

According to Barkev's theory<sup>15</sup>, molecular interaction energy adopts the Mie potential. The relation between the internal energy and the volume is:

$$U(V, T) = -A/V^m + R/V^n \quad (4)$$

where  $A$  and  $R$  are determined by chain configurations.

Equations (1), (3) and (4) lead to

$$P = -mA/V^{m+1} + nR/V^{n+1} \quad (5)$$

$$\begin{aligned} B_T &= -V(\partial P/\partial V)_T \\ &= -m(m+1)A/V^{m+1} + n(n+1)R/V^{n+1} \quad (6) \end{aligned}$$

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$$\begin{aligned}
 B_T(\partial B_T/\partial P)_T &= -(\partial B_T/\partial V)_T \\
 &= -m(m+1)^2 A/V^{m+1} \\
 &\quad + n(n+1)^2 R/V^{n+1} \quad (7)
 \end{aligned}$$

where  $B_T$  is the bulk modulus and  $V(T, P)$  and  $U(T, P)$  are the molar volume and the interaction energy, respectively. According to the above equation, then

$$B(T, 0) = nmU(T, 0)/V(T, 0) \quad (8)$$

$$(\partial B_T/\partial P)_T = n + m + 2 - (n+1)(m+1)P/B_T \quad (9)$$

Equation (8) relates  $B_T$  and the internal energy density of the polymer at zero pressure.

Setting

$$(m+1)(n+1)P/B_T = 0$$

it can be shown that

$$P = B(T, 0)/(m+n+2)\{[V(T, 0)/V(T, P)]^{m+n+2} - 1\} \quad (10)$$

Equation (10) is the Murnaghan equation.

Setting

$$\begin{aligned}
 (m+1)(n+1)P/(m+n+2)B_T \\
 = 1 - V(T, P)/V(T, 0)
 \end{aligned}$$

then

$$\begin{aligned}
 1 - V(T, P)/V(T, 0) \\
 = 1/(m+n+3) \ln[1 + (m+n+3)P/B(T, 0)] \quad (11)
 \end{aligned}$$

This is the Tait equation. This demonstrates that the Murnaghan and Tait equations are two approximate solutions of equation (9).

Solving equation (9) then

$$B(T, P) = B(T, 0)[V(T, 0)/V(T, P)]^{m+1} + (n+1)P \quad (12)$$

and

$$B(T, P) = B(T, 0)V(T, 0)/V(T, P)^{n+1} + (m+1)P \quad (13)$$

Combining equations (12) and (13):

$$\begin{aligned}
 B(T, P) = B(T, 0)/(n-m) \\
 \times \{(n+1)[V(T, 0)/V(T, P)]^{n+1} \\
 - (m+1)[V(T, 0)/V(T, P)]^{m+1}\} \quad (14)
 \end{aligned}$$

$$\begin{aligned}
 P = B(T, 0)/(n-m) \\
 \times \{[V(T, 0)/V(T, P)]^{n+1} \\
 - [V(T, 0)/V(T, P)]^{m+1}\} \quad (15)
 \end{aligned}$$

Equation (14) compares with Broadhurst's equation (13). Equation (15) is a new isothermal equation of state for polymers.

## DISCUSSION

In this paper a comparison of the predictions of the equation of state has been made with experimental data for crystalline and amorphous polymers. Six polymers were studied: poly(methyl methacrylate), poly(hexamethyl methacrylate) in the glass state, and three polyethylenes in the crystalline state and poly(*n*-butylene methacrylate) in the liquid state. The data<sup>4</sup> generally cover the pressure range 0–2 kbar.

In comparing the equation with experimental data, the parameters  $B(T, 0)$  and  $V(T, 0)$  were determined by fitting the experimental data. Using this procedure, values of  $B(T, 0)$  and  $V(T, 0)$  were determined for the polymers in the glass and the melt at different temperatures. Fitting the experimental data, we found that the parameters  $n$  and  $m$  were effectively constant:

$$n = 6.14 \quad m = 1.16 \quad (16)$$

The parameters  $n$  and  $m$  can be set constant for polymers, and equation (15) becomes

$$\begin{aligned}
 P = B(T, 0)/4.98 \\
 \times \{[V(T, 0)/V(T, P)]^{7.14} \\
 - [V(T, 0)/V(T, P)]^{2.16}\}
 \end{aligned}$$

A quantitative comparison between theory and experiment was made for each polymer using the  $B(T, 0)$  and  $V(T, 0)$  obtained by fitting the experimental data<sup>4</sup>. The theoretical values were then calculated from equation (17). The experimental data and calculated theoretical values are listed in *Tables 1–4* for four polymers. The results listed in *Tables 1* and *2* show that the equation accurately describes the isothermal compression behaviour of polymers in the glass state. The average error in the absolute values of the specific volume between experimental and calculated values is  $\sim 0.0001 \text{ cm}^3 \text{ g}^{-1}$ , and within experimental error. The results listed in

**Table 1** Comparison between the experimental and calculated values of the specific volume under pressure for poly(methyl methacrylate) ( $\text{cm}^3 \text{ g}^{-1}$ )

$B(T, 0)$ (bar)	$T$ (°C)		$P$ (bar)											
			100	200	300	400	600	800	1000	1200	1400	1600	1800	2000
38 394	17.2	Exp.	0.8420	0.8399	0.8378	0.8358	0.8319	0.8281	0.8246	0.8212	0.8180	0.8149	0.8119	0.8091
		Calc.	0.8420	0.8399	0.8379	0.8359	0.8320	0.8283	0.8247	0.8213	0.8181	0.8149	0.8119	0.8090
36 684	31.9	Exp.	0.8443	0.8420	0.8399	0.8378	0.8337	0.8298	0.8261	0.8226	0.8192	0.8160	0.8129	0.8110
		Calc.	0.8443	0.8421	0.8400	0.8379	0.8338	0.8299	0.8263	0.8227	0.8193	0.8161	0.8130	0.8099
34 903	45.9	Exp.	0.8467	0.8444	0.8421	0.8399	0.8357	0.8316	0.8278	0.8242	0.8206	0.8173	0.8141	0.8110
		Calc.	0.8468	0.8445	0.8422	0.8400	0.8358	0.8317	0.8279	0.8242	0.8207	0.8173	0.8140	0.8109
33 834	56.8	Exp.	0.8488	0.8463	0.8440	0.8417	0.8373	0.8331	0.8292	0.8255	0.8219	0.8185	0.8152	0.8121
		Calc.	0.8488	0.8464	0.8441	0.8418	0.8374	0.8333	0.8293	0.8256	0.8219	0.8185	0.8152	0.8120
31 464	80.1	Exp.	0.8539	0.8512	0.8487	0.8462	0.8415	0.8371	0.8329	0.8289	0.8252	0.8216	0.8181	0.8148
		Calc.	0.8539	0.8513	0.8488	0.8464	0.8417	0.8373	0.8330	0.8290	0.8252	0.8215	0.8180	0.8147
30 386	90.8	Exp.	0.8567	0.8539	0.8513	0.8487	0.8439	0.8393	0.8350	0.8308	0.8269	0.8234	0.8199	0.8164
		Calc.	0.8567	0.8540	0.8514	0.8489	0.8441	0.8395	0.8351	0.8310	0.8271	0.8233	0.8197	0.8163
29 579	100.9	Exp.	0.8591	0.8563	0.8536	0.8509	0.8460	0.8412	0.8368	0.8327	0.8287	0.8249	0.8213	0.8179
		Calc.	0.8591	0.8564	0.8537	0.8511	0.8461	0.8414	0.8370	0.8328	0.8287	0.8249	0.8212	0.8177

**Table 2** Comparison between the experimental and calculated values of the specific volume under pressure for poly(hexamethyl methacrylate) ( $\text{cm}^3 \text{g}^{-1}$ )

$B(T, 0)$ (bar)	$T$ (°C)		$P$ (bar)											
			100	200	300	400	600	800	1000	1200	1400	1600	1800	2000
40 665	18.6	Exp.	0.9060	0.9039	0.9018	0.8997	0.8957	0.8920	0.8881	0.8845	0.8815	0.8784	0.8753	0.8723
		Calc.	0.9061	0.9039	0.9018	0.8997	0.8958	0.8920	0.8884	0.8849	0.8815	0.8783	0.8752	0.8721
38 970	30.3	Exp.	0.9085	0.9063	0.9041	0.9020	0.8978	0.8938	0.8901	0.8865	0.8830	0.8797	0.8764	0.8735
		Calc.	0.9086	0.9063	0.9042	0.9020	0.8979	0.8939	0.8902	0.8865	0.8830	0.8797	0.8765	0.8733
37 814	41.0	Exp.	0.9108	0.9085	0.9062	0.9040	0.8998	0.8957	0.8918	0.8881	0.8846	0.8811	0.8779	0.8750
		Calc.	0.9109	0.9086	0.9063	0.9041	0.8999	0.8958	0.8919	0.8882	0.8846	0.8812	0.8779	0.8747
36 654	52.0	Exp.	0.9134	0.9109	0.9085	0.9063	0.9018	0.8976	0.8936	0.8899	0.8862	0.8828	0.8794	0.8763
		Calc.	0.9133	0.9109	0.9086	0.9063	0.9019	0.8978	0.8938	0.8900	0.8863	0.8828	0.8794	0.8761
35 453	64.0	Exp.	0.9159	0.9134	0.9110	0.9085	0.9040	0.8998	0.8956	0.8918	0.8881	0.8844	0.8809	0.8778
		Calc.	0.9160	0.9135	0.9111	0.9087	0.9042	0.8999	0.8958	0.8918	0.8881	0.8844	0.8810	0.8876
34 246	74.3	Exp.	0.9181	0.9155	0.9130	0.9105	0.9058	0.9014	0.8972	0.8932	0.8894	0.8856	0.8821	0.8788
		Calc.	0.9182	0.9156	0.9131	0.9106	0.9060	0.9015	0.8973	0.8932	0.8894	0.8857	0.8821	0.8787
32 485	84.5	Exp.	0.9203	0.9177	0.9150	0.9123	0.9074	0.9026	0.8982	0.8942	0.8903	0.8865	0.8828	0.8793
		Calc.	0.9204	0.9177	0.9151	0.9125	0.9076	0.9023	0.8985	0.8943	0.8903	0.8864	0.8827	0.8791

**Table 3** Comparison between the experimental and calculated values of the specific volume under pressure for branched polyethylene ( $\text{cm}^3 \text{g}^{-1}$ )

$B(T, 0)$ (bar)	$T$ (°C)		$P$ (bar)											
			100	200	300	400	600	800	1000	1200	1400	1600	1800	2000
32 184	19.1	Exp.	1.0686	1.0653	1.0621	1.0589	1.0533	1.0477	1.0425	1.0377	1.0334	1.0282	1.0249	1.0205
		Calc.	1.0687	1.0655	1.0625	1.0595	1.0537	1.0483	1.0431	1.0382	1.0334	1.0289	1.0246	1.0204
29 801	29.0	Exp.	1.0739	1.0704	1.0668	1.0636	1.0573	1.0515	1.0458	1.0405	1.0359	1.0317	1.0278	1.0231
		Calc.	1.0741	1.0706	1.0673	1.0641	1.0579	1.0521	1.0465	1.0413	1.0363	1.0315	1.0269	1.0226
27 134	41.4	Exp.	1.0806	1.0766	1.0727	1.0693	1.0619	1.0555	1.0499	1.0448	1.0394	1.0351	1.0305	1.0258
		Calc.	1.0808	1.0770	1.0733	1.0698	1.0631	1.0568	1.0508	1.0451	1.0400	1.0345	1.0298	1.0251
24 348	51.2	Exp.	1.0877	1.0833	1.0791	1.0751	1.0673	1.0604	1.0541	1.0482	1.0425	1.0375	1.0330	1.0279
		Calc.	1.0879	1.0837	1.0796	1.0757	1.0683	1.0614	1.0549	1.0487	1.0429	1.0374	1.0322	1.0272
19 338	68.5	Exp.	1.1056	1.1002	1.0947	1.0899	1.0805	1.0721	1.0642	1.0572	1.0510	1.0449	1.0394	1.0345
		Calc.	1.1059	1.1006	1.0955	1.0907	1.0816	1.0732	1.0654	1.0581	1.0513	1.0449	1.0388	1.0331

**Table 4** Comparison between the experimental and calculated values of the specific volume under pressure for poly(*n*-butyl methacrylate) ( $\text{cm}^3 \text{g}^{-1}$ )

$B(T, 0)$ (bar)	$T$ (°C)		$P$ (bar)											
			100	200	300	400	600	800	1000	1200	1400	1600	1800	2000
17 886	73.5	Exp.	0.9726	0.9674	0.9626	0.9579	0.9494	0.9417	0.9345	0.9278	0.9217	0.9161	0.9105	0.9057
		Calc.	0.9728	0.9678	0.9630	0.9584	0.9499	0.9421	0.9349	0.9281	0.9219	0.9160	0.9105	0.9052
16 838	82.3	Exp.	0.9782	0.9728	0.9676	0.9627	0.9537	0.9457	0.9381	0.9310	0.9247	0.9188	0.9219	0.9079
		Calc.	0.9783	0.9730	0.9679	0.9631	0.9541	0.9459	0.9384	0.9313	0.9248	0.9187	0.9219	0.9075
15 772	94.5	Exp.	0.9858	0.9800	0.9743	0.9692	0.9598	0.9511	0.9432	0.9358	0.9291	0.9231	0.9173	0.9121
		Calc.	0.9860	0.9803	0.9749	0.9697	0.9603	0.9516	0.9436	0.9363	0.9294	0.9231	0.9171	0.9114
15 110	105.6	Exp.	0.9932	0.9871	0.9813	0.9759	0.9660	0.9571	0.9490	0.9415	0.9346	0.9282	0.9222	0.9166
		Calc.	0.9935	0.9875	0.9818	0.9765	0.9666	0.9576	0.9494	0.9418	0.9347	0.9281	0.9220	0.9162
14 179	118.7	Exp.	1.0025	0.9966	0.9898	0.9839	0.9735	0.9639	0.9554	0.9476	0.9407	0.9341	0.9280	0.9220
		Calc.	1.0028	0.9964	0.9904	0.9847	0.9742	0.9647	0.9561	0.9481	0.9408	0.9339	0.9275	0.9215
13 020	133.1	Exp.	1.0121	1.0051	0.9982	0.9920	0.9807	0.9707	0.9617	0.9531	0.9457	0.9390	0.9323	0.9264
		Calc.	1.0125	1.0055	0.9989	0.9928	0.9815	0.9714	0.9622	0.9538	0.9460	0.9388	0.9321	0.9258
12 203	146.4	Exp.	1.0215	1.0140	1.0067	0.9999	0.9884	0.9778	0.9681	0.9596	0.9517	0.9447	0.9375	0.9312
		Calc.	1.0219	1.0144	1.0074	1.0009	0.9890	0.9783	0.9687	0.9599	0.9518	0.9443	0.9373	0.9308
11 361	160.2	Exp.	1.0312	1.0229	1.0151	1.0081	0.9956	0.9841	0.9741	0.9653	0.9568	0.9496	0.9432	0.9365
		Calc.	1.0316	1.0236	1.0161	1.0091	0.9965	0.9852	0.9751	0.9659	0.9574	0.9496	0.9424	0.9356
10 488	174.3	Exp.	1.0414	1.0321	1.0239	1.0167	1.0024	0.9906	0.9799	0.9707	0.9627	0.9541	0.9479	0.9412
		Calc.	1.0417	1.0330	1.0249	1.0175	1.0040	0.9920	0.9813	0.9716	0.9628	0.9546	0.9471	0.9400
9 774	187.5	Exp.	1.0505	1.0408	1.0319	1.0237	1.0098	0.9974	0.9864	0.9770	0.9677	0.9593	0.9514	0.9448
		Calc.	1.0511	1.0417	1.0331	1.0251	1.0108	0.9983	0.9871	0.9770	0.9677	0.9598	0.9513	0.9441
9 173	199.5	Exp.	1.0599	1.0493	1.0400	1.0314	1.0163	1.0032	0.9919	0.9817	0.9727	0.9641	0.9565	0.9492
		Calc.	1.0602	1.0502	1.0411	1.0327	1.0177	1.0045	0.9929	0.9823	0.9727	0.9640	0.9559	0.9484

Tables 3 and 4 show that the equation also describes the isothermal compression behaviour of branched polyethylene in the crystalline state and poly(*n*-butylene methacrylate) in the liquid state. The average error in the absolute values of the specific volume is  $\sim 0.0007 \text{ cm}^3 \text{ g}^{-1}$ . The average error is larger than in the

glass state, since the thermal pressure  $P_T(V, T)$  determined by the thermal motions makes a large contribution to  $P_1$ . Equation (2) was reduced to equation (3) and this introduced an error in the liquid state. The average error for poly(*n*-butylene methacrylate) is  $\sim 0.0004 \text{ cm}^3 \text{ g}^{-1}$  at  $73.5^\circ\text{C}$ . As the temperature

increases, the greater is the average error in the absolute values of specific volume ( $0.0009 \text{ cm}^3 \text{ g}^{-1}$  at  $199.5^\circ\text{C}$ ). Despite these effects, the equation describes the isothermal compression behaviour of polymers in the solid and the melting states and the deviation between calculated and experimental values is within experimental accuracy.

## CONCLUSIONS

Considering the interaction energy of chains in a polymer system, we have derived a new equation of state for polymers:

$$P = B(T, 0)/(n - m) \\ \times [V(T, 0)/V(T, P)]^{n+1} \\ - [V(T, 0)/V(T, P)]^{m+1}$$

We found that the parameters  $n$  and  $m$  are universal constants for polymers ( $n = 6.14$  and  $m = 1.16$ ). Without transition, the equation adapts to describe the isothermal

compression behaviour of polymers in the glass and the melt states.

## REFERENCES

- 1 Curro, J. G. *J. Macromol. Sci., Rev. Macromol. Chem.* 1974, **C11**, 321
- 2 Simha, R. *J. Chem. Phys.* 1964, **41**, 1884
- 3 Hartmann, B. and Haque, M. A. *J. Appl. Polym. Sci.* 1985, **30**, 1553
- 4 Olabisi, O. and Simha, R. *Macromolecules* 1975, **8**, 206
- 5 Quach, A. and Simha, R. *J. Appl. Phys.* 1971, **42**, 4592
- 6 Quach, A. and Simha, R. *J. Macromol. Sci.* 1974, **B9**, 533
- 7 McKinney, J. E. and Simha, R. *Macromolecules* 1974, **7**, 894
- 8 Simha, R., Wilson, P. S. and Olabisi, O. *Koll. Z. Z. Polym.* 1973, **251**, 402
- 9 Olabisi, O. and Simha, R. *Koll. Z. Z. Polym.* 1975, **8**, 206
- 10 Zoller, P. *J. Appl. Polym. Sci.* 1978, **22**, 633
- 11 Zoller, P. *J. Appl. Polym. Sci.* 1979, **23**, 1051
- 12 Zoller, P. *J. Appl. Polym. Sci.* 1977, **21**, 3129
- 13 Simha, R. and Somcynsky, T. *Macromolecules* 1969, **2**, 342
- 14 Broadhurst, M. G. and Mopsik, F. I. *J. Chem. Phys.* 1967, **52**, 3634
- 15 Barker, R. E. *J. Appl. Phys.* 1967, **38**, 4234
- 16 Pastin, D. J. and Warfield, R. W. *Polymer* 1981, **22**, 1754