

# The Effects of Pressure and Temperature on the Densities of Liquid Polymers

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An equation is given which relates the pressure  $p$ , density  $d$  and absolute temperature  $T$  of unassociated liquids. This equation, in the following form, can be used for polymeric liquids (with c.g.s. units):

$$1.9 \times 10^6 p \left( \frac{T_c' - T}{T_c'} \right)^{0.9} = \left( \frac{21P'd}{M'} \right)^9 - \left[ \frac{8.24 \times 10^5 (T_c' - T)}{T_c'} \right]^{2.7}$$

$P'$  is the parachor and  $M'$  is the molecular weight for the repeating unit and both can be calculated readily. For a given polymer,  $T_c'$  is a constant and equals the temperature-reducing parameter proposed by A. Bondi. A considerable number of well known polymers of high molecular weight have almost the same value of  $T_c'$  which seems to depend upon the molecular flexibility.

A RELATIONSHIP<sup>1</sup>, between the isothermal compressibility  $\kappa_0$  and density  $d_0$  (both at zero pressure, or at a pressure sufficiently low to have negligible effect on these properties) of liquids, has been shown<sup>2</sup> to apply to liquid polymers, for which one can write:

$$\frac{21P'}{M'} = \frac{1}{d_0 \kappa_0^{1/6}} \quad (\text{c.g.s. units}) \quad (1)$$

$P'$  is the parachor and  $M'$  is the molecular weight for the repeating unit in the liquid polymer. We now propose to consider how densities and compressibilities at other pressures and temperatures can be estimated.

Tait<sup>3</sup> put forward one of the earliest relationships between the pressure and volume of a liquid but his equation is usually misquoted<sup>4</sup>. An alternative and related equation (2) between the pressure  $p$  and the isothermal compressibility  $\kappa_T$  at constant temperature appears to have been first suggested by Murnaghan<sup>5</sup>.

$$(1/\kappa_T) = (1/\kappa_0) + Cp \quad (2)$$

Others<sup>6-13</sup> have put forward the same relationship; some of them have given the integrated form—equation (3)—and have found the constant  $C$  to be about 9.

$$Cp = \frac{1}{\kappa_0} \left( \frac{d}{d_0} \right)^C - \frac{1}{\kappa_0} \quad (3)$$

Here,  $d$  is the density at pressure  $p$ . When the pressure change is small, the exact value taken for  $C$  is unimportant. Previously<sup>1</sup>, it was found that with  $C=6$ , equation (3) could be used for polymeric and other liquids at low pressures (up to a few hundred atmospheres) but now with the value of  $C=9$  preferred by most investigators, it is possible to predict densities and

compressibilities of liquid polymers at much higher pressures. Equations (1) and (2) give

$$\frac{1}{\kappa_T} = \left( \frac{21P'd_0}{M'} \right)^6 + 9p \quad (4)$$

and equations (1) and (3) give

$$9p = [21P'd_0/M']^6 [(d/d_0)^9 - 1] \quad (5)$$

In equation (5), the pressure is equated to the difference between two terms; a positive term which varies as the ninth power of the density and a negative term which is constant at a given temperature. If the equation were to hold at negative pressures, the density might drop sufficiently for the positive term to be neglected, so that the negative term might be a measure of the stress required to cause cavitation of the liquid, i.e.

$$\text{Stress for cavitation} = (1/9)(21P'd_0/M')^6 \text{ or } 1/9\kappa_0 \quad (6)$$

Briggs<sup>14</sup> has used a centrifugal method in attempts to measure the breaking stresses of some liquids and his values are between a quarter and a tenth those calculated from the densities or isothermal compressibilities using equation (6). The agreement is not too bad, however, since breaking stresses are difficult to measure. Random thermal movements of molecules can produce small regions of weakness from which a break can spread (see Thomson<sup>15</sup>) so that the breaking stress will normally increase as the time of the test decreases. Some reported breaking stresses<sup>16,17</sup> for polymers at high loading rates are between one half and one tenth those calculated from equation (6). This is not too disappointing: for one thing, the loading rates may not have been fast enough. Further, some of the polymers would be partly crystalline and the crystalline parts may have been anisotropic in some cases. The parts of a material, which are anisotropic, or of lower than average density, would be expected to be relatively more sensitive to changes of pressure than the material as a whole, and hence to be weaker.

The equations given above will, however, hold for solutions which are isotropic homogeneous liquids. If we have a solution of  $y$  parts by weight of a compound or polymer molecular weight  $M_1$  and parachor  $P_1$  dissolved in  $1-y$  parts of a compound or polymer with molecular weight  $M_2$  and parachor  $P_2$ , the ratio  $P:M$  for the mixture can be obtained from the ratios  $P_1:M_1$  and  $P_2:M_2$  since

$$P/M = yP_1/M_1 + (1-y)P_2/M_2 \quad (7)$$

This equation can be extended to solutions with more than two components and with the value found for  $P/M$ , equations (1), (4), (5) and (6) can be used for solutions such as liquid polymers containing plasticizers. In *Table I* are given some isothermal compressibilities  $\kappa_0$  and densities  $d_0$  of liquid polymers measured by P. Lamb and F. N. Cogswell in these laboratories. The values of  $1/\kappa_0^{1/6}d_0$  should equal  $21P'/M'$  according to equation (1). Equation (7) has been used to calculate  $21P'/M'$  for the poly(vinyl chloride) containing dioctyl phthalate. It will be seen that the addition of the plasticizer (which has  $21P/M$  equal to 51.9) has had the expected effect upon

## DENSITIES OF LIQUID POLYMERS

Table 1. Isothermal compressibilities and densities of some liquid polymers

Polymer	Temperature °C	$1/\kappa_0$ $\times 10^{-9}$ (dyne/cm <sup>2</sup> )	$d_0$ (g/cm <sup>3</sup> )	$\frac{1}{\kappa_0^{1/6}d_0}$	$\frac{21P'}{M'}$
Low density polyethylene	150	10.3	0.78	59.8	
	190	9.0	0.76	60.0	
	230	7.7	0.74	60.0	59.8
	270	6.2	0.72	59.5	
Poly(vinyl chloride) plasticized with 50% by wt. dioctyl phthalate	150	12.5	1.10	43.8	45.2
Poly(vinyl chloride) plasticized with 24% by wt. dioctyl phthalate	150	17.0	1.25	40.6	
	190	12.0	1.22	39.2	41.8
Poly(vinyl chloride) unplasticized	150	19.0	1.41	36.6	38.5
Fluorinated hydro- carbon polymer (65.4% fluorine)	150	9.5	1.65	27.9	
	190	8.4	1.60	28.2	27.0

$1/\kappa_0^{1/6}d_0$  for poly(vinyl chloride). Since isomers with the same number of bonds have the same value for  $21P'/M'$ , it is not necessary for the use of the equations that the exact structure be known. In Table 1, figures are given for low density polythene which is a hydrocarbon polymer and for a hydrocarbon polymer substituted with fluorine. The  $21P'/M'$  figure calculated from the fluorine content (65.4%) is in good agreement with the observed value of  $1/\kappa_0^{1/6}d_0$ .

The following equation has already been put forward<sup>1,18</sup> for the variation of isothermal compressibility of liquids  $\kappa_0$ , with temperature ( $T$  in °K).

$$(1/\kappa_0)^{5/9} = K(T_c' - T)/P^{2/3} \quad (8)$$

where again  $P$  is the parachor.

At the critical point  $1/\kappa_0$  becomes zero and  $T_c'$  would be the critical temperature if the liquid obeyed equation (8) up to this temperature. However, near the critical temperature the liquid begins to take on properties of the vapour and  $T_c'$  for unassociated liquids is lower than the critical temperature. For a given compound  $K$  is a constant but  $K$  increases with the size of the molecules. It has now been found that for unassociated liquids, the slopes and the intercepts of the linear plots of  $(1/\kappa_0)^{5/9}$  against  $T$  are related. If the associated liquids—water, methanol, ethyl alcohol and aniline<sup>19</sup>—are neglected, the examples in the previous communication<sup>18</sup> give

$$(1/\kappa_0)^{5/9} = 8.24 \times 10^5 [1 - (T/T_c')] \quad (9)$$

Equation (9) can be applied to polymers and if it is combined with equation (1), it gives equation (10) which is generally more useful.

$$[21P'd_0/M']^{10/3} = 8.24 \times 10^9 [(T_c' - T)/T_c'] \quad (10)$$

The elimination of  $d_0$  between equation (10) and equation (5) gives (11)

$$1.9 \times 10^6 p [(T_c' - T)/T_c']^{0.9} = [21P'd/M]^9 - [8.24 \times 10^5 (T_c' - T)/T_c']^{2.7} \quad (11)$$

This general expression (11) which relates the pressure ( $p$ ), the temperature ( $T$ ) and the density ( $d$ ) of liquids incorporates equations (1) to (6), (9) and (10) and summarizes a great deal of information. From it, for example, expressions for  $(\partial V/\partial T)_p$  and  $(\partial p/\partial T)_v$  can be derived.

In equation (11), the value taken for  $P'/M'$  is important since this ratio is raised to the ninth power. It is sometimes convenient to write the equation as equation (12) with two constants  $T_c'$  and  $K'$  and without a calculated value for  $P'/M'$

$$p = \frac{K'd^9}{[1 - (T/T_c')]^{0.9}} - 4.95 \times 10^9 [1 - (T/T_c')]^{1.8} \quad (12)$$

In Table 2, the densities of liquid polystyrene given by Hellwege, Knappe and Lehmann<sup>20</sup> are compared with values for  $d$  calculated from equation (12) with  $T_c' = 995.2^\circ\text{K}$  and  $K' = 1.25 \times 10^9$ . A computer was used to obtain these constants which gave the best fit. The calculated figures agree well with the

Table 2. Densities of liquid polystyrene

(a) Experimental<sup>20</sup>

Pressure $\times 10^{-8}$ (dyne/cm <sup>2</sup> )	Temperature ( $^\circ\text{K}$ )										
	373.8	379.9	388.6	399.2	409.0	418.4	435.5	451.9	476.0	502.2	522.1
0	1.009	1.006	1.001	0.995	0.990	0.985	0.975	0.965	0.951	0.937	0.927
1.961	1.019	1.016	1.011	1.006	1.000	0.996	0.987	0.977	0.965	0.952	0.943
3.923	1.029	1.027	1.022	1.017	1.011	1.007	1.000	0.990	0.979	0.968	0.959
5.884	—	1.036	1.031	1.027	1.021	1.018	1.011	1.002	0.992	0.981	0.973
7.845	—	—	1.040	1.036	1.031	1.028	1.021	1.013	1.002	0.993	0.985
9.807	—	—	—	1.044	1.039	1.036	1.030	1.022	1.012	1.003	0.996
11.768	—	—	—	—	1.047	1.045	1.038	1.031	1.021	1.013	1.007
13.729	—	—	—	—	—	1.052	1.046	1.039	1.029	1.022	1.016
15.691	—	—	—	—	—	—	1.054	1.047	1.037	1.031	1.025
17.652	—	—	—	—	—	—	—	1.055	1.046	1.039	1.034
19.613	—	—	—	—	—	—	—	—	1.054	1.048	1.042

(b) Estimated from equation (12) with  $T_c' = 995.2^\circ\text{K}$  and  $K' = 1.25 \times 10^9$

Pressure $\times 10^{-8}$ (dyne/cm <sup>2</sup> )	Temperature ( $^\circ\text{K}$ )										
	373.8	379.9	388.6	399.2	409.9	418.4	435.5	451.9	476.0	502.2	522.1
0	1.012	1.009	1.004	0.999	0.994	0.989	0.980	0.972	0.959	0.944	0.932
1.961	1.022	1.019	1.015	1.010	1.005	1.000	0.992	0.984	0.972	0.958	0.947
3.923	1.031	1.028	1.024	1.019	1.015	1.011	1.003	0.995	0.983	0.970	0.960
5.884	—	1.037	1.033	1.029	1.024	1.020	1.012	1.005	0.994	0.981	0.972
7.845	—	—	1.041	1.037	1.033	1.029	1.022	1.014	1.004	0.992	0.983
9.807	—	—	—	1.045	1.041	1.037	1.030	1.023	1.013	1.001	0.992
11.768	—	—	—	—	1.048	1.045	1.038	1.031	1.021	1.010	1.002
13.729	—	—	—	—	—	1.052	1.045	1.039	1.029	1.018	1.010
15.691	—	—	—	—	—	—	1.053	1.046	1.037	1.026	1.018
17.652	—	—	—	—	—	—	—	1.053	1.044	1.034	1.026
19.613	—	—	—	—	—	—	—	—	1.050	1.040	1.033

experimental ones. The value of  $K'$  corresponds to  $21P'/M' = 51.1$  which is close to 50.9 given previously<sup>2</sup>.

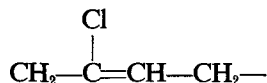
The densities of other liquid polymers have not been studied to the extent that those of polystyrene have. Values of  $T_c'$  have, however, been obtained for a number of the better known polymers and are given in *Table 3*. Values

*Table 3.* Constants for polymers

<i>Polymer</i>	$\frac{21P'}{M'}$	$T_c'$	$\theta$
Polyethylene	59.8	800	726
Polypropylene	59.8	780	695
Poly(butene-1)	59.8	780	—
Polyisobutylene	59.8	1 140	936
Polystyrene	50.9	995	855
Poly(dimethylsiloxane)	47.1	520	490
Poly(methyl methacrylate)	46.3	1 150	1 140
Poly(ethyl acrylate)	46.3	870	—
Poly(ethylene oxide)	46.0	770	—
Poly(vinyl acetate)	44.1	850	786
Terephthalic acid, ethylene glycol polyester	40.9	1 180	—
Poly(vinyl chloride)	38.5	—	—
Poly(trifluorochloroethylene)	23.4	800	888

of  $P'/M'$  were obtained from the calculated parachor<sup>21</sup> and  $T_c'$  was then obtained (largely from the densities given in a recent collection<sup>22</sup> and from references therein), with the help of equation (11).

The parachor is used as a measure of the molecular volume and a simple method has been given for its calculation<sup>21</sup>. Atomic parachors for each atom in the molecule are added together. The number of covalent bonds is found, but the different kinds of covalent bonds are not distinguished, and this number, multiplied by a factor, is subtracted from the sum of the atomic parachors to give the required parachor. The atomic parachors for some common elements are: hydrogen (24.7), carbon (46.35), nitrogen (40.8), oxygen (35.25), fluorine (29.7), silicon (76.05), phosphorus (70.5), sulphur (64.95), chlorine (59.4), bromine (74.3) and iodine (97.9). For a bond, regardless of whether it is a single bond, double bond, triple bond or aromatic bond, 18.6 is subtracted. Thus for the repeating unit of chloroprene



the parachor  $P'$  is  $(5 \times 24.7) + (4 \times 46.35) + 59.4 - (10 \times 18.6) = 182.3$ . The molecular weight  $M'$  of the unit is 88.54 which is the same as the monomer and so  $21P'/M'$  is 43.24. This simple method of calculation seems to be quite adequate for organic compounds with molecules free from strain and from over-crowding. Unless the parachor is easily calculated, it loses its value. Bond parachors have sometimes been used instead of atomic parachors. Benson and Buss<sup>23</sup> point out that the number of types of bonds can be very large and that the bond system represents a higher degree of

approximation than one based on atomic values. Moreover, Exner<sup>24</sup> has observed that no physical meaning can be attributed to bond increments for the parachor and other similar properties.

From a single density and equation (11),  $T_c'$  can be found for a liquid polymer and then densities can be estimated for other temperatures and pressures. In some cases, however, it is unnecessary to have even a single density. Gubler and Kovacs<sup>25</sup> found that the densities of liquid polyethylenes were independent of the presence and type of branching and this has been confirmed by other investigators<sup>26, 27</sup>. Polypropylene, poly(butene-1) and poly(4-methyl-pentene-1) give liquids of the same density as polyethylene at the same temperature: all these have the same  $P'/M'$  value and so must have almost the same  $T_c'$  values. Moreover, it appears that most polymers made up of units  $-\text{CH}(\text{R})-\text{CH}_2$  where R contains neither quaternary substituted carbon atoms nor rings have  $T_c'$  values near 800°K (see Table 3). This value of  $T_c'$  can be used for a large number of the known polymers. Polyisobutylene which has the same  $P'/M'$  value as polyethylene and polypropylene has  $T_c'$  about 1 140°K, which is considerably above 800°K. This polymer contains quaternary carbon atoms and the overcrowding of the groups in it would reduce the molecular flexibility and hence, according to Bondi (see below) raise  $T_c'$ . Methacrylates are another important class of polymer in which quaternary carbon atoms are present and the  $T_c'$  values for these also are high. Aromatic rings also raise  $T_c'$  and examples are polystyrene with  $T_c'$  equal to 995°K and the polyester of ethylene glycol with terephthalic acid with  $T_c'$  equal to 1 180°K. Poly(dimethyl siloxane) seems to have a low  $T_c'$  (about 520°K). This would seem to arise from the presence of silicon since in other polymers the replacement of  $-\text{CH}_2-$  groups by  $-\text{O}-$  still leaves  $T_c'$  at about 800°K. In homogeneous isotropic solids and glasses, molecular movements are restricted but it seems that the equations given above can still be used provided a new and higher value is taken for  $T_c'$ . An equation similar to equation (10) has been shown<sup>28</sup> to apply to the simple solids  $S_8$  and  $\text{P}_4$ .

Various relationships between the properties of polymers have been suggested in the past and it is worthwhile to compare some of these with the general equation (11). Flory, Orwell and Vrij<sup>29</sup> have used an equation based on the principle of corresponding states. In the equation, the temperature divided by a characteristic temperature is related to the volume divided by a characteristic volume and to the pressure divided by a characteristic pressure. In equation (11), the temperature is divided by  $T_c'$  and the molecular volume ( $M'/d$ )<sub>n</sub> is divided by the parachor ( $P'$ )<sub>n</sub> which is a standard volume. The introduction of a pressure characteristic of each polymer seems to be unnecessary. The most serious defect in the treatment of Flory *et al* is that the characteristic parameters are not independent of temperature<sup>30</sup>: the parachor  $P'$  and  $T_c'$  are, however, both independent of temperature. Other workers have used relationships based upon free volume which is a measure of the difference between the molecular volume and the actual volume of the molecules and is therefore again a function of the ratio of the molecular volume to the parachor. The Williams-Landel-Ferry<sup>31</sup> equation for viscosity is an example of a relationship of this kind. The most interesting

relationship is that suggested by Bondi and Simkin<sup>33</sup>. They used a reduced density  $V_w/V$  where  $V$  is the molecular and  $V_w$  is a standard constant molecular volume calculated from bond distances and van der Waals radii<sup>33</sup>. For high boiling liquids if  $V_w/V$  is plotted against a reduced temperature  $T/\theta$ , a general curve is obtained. Such a curve is just what would be expected from equation (10) and indeed,  $\theta$  should equal  $T_c'$ . Considerable changes in  $T_c'$  (or  $\theta$ ) have quite a small effect on density and so these constants are not known at all accurately but it will be seen from *Table 3* that the two constants<sup>34</sup> are approximately equal. Bondi<sup>35</sup> has attempted to estimate  $\theta$  for polymers and has found that for polymers composed of flexible molecules,  $\theta$  is lower than for those containing stiffer molecules. The curve which Bondi and Simkin<sup>33</sup> obtained as described above was found by them to fit the expression

$$V_w/V = 0.726 - 0.249(T/\theta) - 0.019(T/\theta)^2 \quad (13)$$

Now the values of  $V_w$  given by Bondi<sup>33</sup> are approximately one quarter of the parachors and when  $T/T_c'$  is small

$$\left[ \frac{T_c' - T}{T_c'} \right]^{3/10} \text{ is approximately } \left[ 1 - \frac{3T}{10T_c'} \right]$$

so that from equation (10)

$$\frac{V_w}{V} = \frac{P'd_0}{4M} = \frac{(8.24 \times 10^5)^{3/10}}{4 \times 21} \left[ 1 - \frac{3T}{10T_c'} \right]$$

$$\text{i.e.} \quad V_w/V = 0.708 - 0.212(T/T_c') \quad (14)$$

The resemblance between equation (14) and the empirical equation (13) is striking since the last term of equation (13) can be neglected if  $T/\theta$  is small. Bondi<sup>36</sup> and others have noted that the density (not the specific volume) is nearly linear with temperature over a wide range, as required by equations (13) and (14). It should be noted that  $T_c'$  (and  $\theta$ ) measures the flexibility of the molecule under thermal motion and not the flexibility for permanent deformation, such as might be necessary for ring formation.

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