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Pressure dependence of $T_{ee}$

II. Isotactic PMMA*)

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With 6 figures and 1 table

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Introduction

We have recently examined several bodies of $P$-$V$-$T$ data listed in table 1, for the primary purpose of a) trying to locate the weak $T_{ee}$ transition in the $V$-$P$ plane; and b) measuring the pressure dependence of $T_{ee}$. Incidentally, we locate the presence of other secondary transitions such as $T_B$.

For present purposes we note several facts about $T_{ee}$, taken from recent reviews (15–17).

1. $T_{ee}$ is usually observed in amorphous polymers and copolymers having no or only low degrees of cross-linking.

2. It has been observed, like $T_g$, both by kinetic methods (dynamic mechanical loss) and by thermodynamic methods ($V$-$T$ and $C_p$-$T$), all at atmospheric pressure.

3. It appears to be a third order transition in the Ehrenfest sense, with a discontinuity in the second derivative of heat content or volume with respect to temperature. $T_{ee}$ behaves in many ways like $T_g$:

   a) It is an activated process with an apparent enthalpy of activation, $\Delta H_a$ about half of that for $T_g$.

   b) It is an isofree volume state at $P = 1$ with a value about 20% greater than that for $T_g$.

Table 1. Polymers studied *) and values of $dT_{ee}/dP$

<table>
<thead>
<tr>
<th>No.</th>
<th>Polymer</th>
<th>Reference</th>
<th>$T_g$ (K)</th>
<th>$T_{ee}$ (K)</th>
<th>$T_{ee}/T_g$</th>
<th>$dT_{ee}/dP$ in K/kbar</th>
<th>Ref. for $dT_{ee}/dP$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Thermal PS</td>
<td>(1, 2)</td>
<td>368</td>
<td>436</td>
<td>1.18</td>
<td>65</td>
<td>(12)</td>
</tr>
<tr>
<td>2.</td>
<td>Anionic PS, $M_a = 20,200$</td>
<td>(3)*</td>
<td>368</td>
<td>436</td>
<td>1.18</td>
<td>65</td>
<td>(12)</td>
</tr>
<tr>
<td>3.</td>
<td>PVAc</td>
<td>(4)</td>
<td>298</td>
<td>343</td>
<td>1.15</td>
<td>72</td>
<td>(12)</td>
</tr>
<tr>
<td>4.</td>
<td>PVAc</td>
<td>(5, 6)</td>
<td>298</td>
<td>343</td>
<td>1.15</td>
<td>72</td>
<td>(12)</td>
</tr>
<tr>
<td>5.</td>
<td>PIB</td>
<td>(4)</td>
<td>200</td>
<td>264</td>
<td>1.32</td>
<td>120</td>
<td>(12)</td>
</tr>
<tr>
<td>6.</td>
<td>Ph BMA</td>
<td>(7, 8)</td>
<td>293</td>
<td>358</td>
<td>1.22</td>
<td>75</td>
<td>(12, 13)</td>
</tr>
<tr>
<td>7.</td>
<td>$P$ cyclohexyl MA</td>
<td>(7, 8)</td>
<td>380</td>
<td>438</td>
<td>1.15</td>
<td>50</td>
<td>(13)</td>
</tr>
<tr>
<td>8.</td>
<td>iso PMMA</td>
<td>(9, 10)</td>
<td>320 (10)</td>
<td>383*</td>
<td>1.20</td>
<td>70</td>
<td>*</td>
</tr>
<tr>
<td>9.</td>
<td>a-PMMA</td>
<td>(11)*</td>
<td>373</td>
<td>435</td>
<td>1.16</td>
<td>66</td>
<td>*</td>
</tr>
</tbody>
</table>

*) This is not a complete set of published PVT data. It represents the extent of our studies to date.

* The PVT data except for references (9) and (11).

Tabulated data supplied by Günther Rehage.

V – T data at $P = 1$.

DSC data at $P = 1$ and $P = 136$ bars.

Present report. Note: Values of $T_g$ from (12) and (13) except for iso PMMA from (10).

Dedicated to Prof. Dr. G. Rehage on the occasion of his 60th birthday.
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c) It is an isoviscous state with log $\eta_0$ about 4.5 poise instead of the value of about 11 at $T_g$.
d) Its intensity increases with annealing just below $T_{ee}$.

4. The ratio, $T_{ee}/T_g(K/K)$, is $1.20 \pm 0.05$, at $P = 1$, depending on molecular weight, test method and test frequency.

5. Values of $dT_{ee}/dP$ have not hitherto been reported except for paper 1 of this series (12), and a single determination by Panke and Wunderlich (11) using DSC on a-PMMA.

6. Throughout, we use the convention that coefficient of expansion, $\alpha$, or compressibility, $\kappa$, carry the subscript $\ell$, $\ell'$ or L, L above $T_{ee}$, or L below $T_{ee}$ but above $T_g$.

Discussion

We first tried to determine $dT_{ee}/dP$ by regression analysis of isobaric $V$-$T$ data. However, the expansivity, $\alpha_{ee} - \alpha_e$, at $T_{ee}$ quickly approached zero as $P$ exceeded several hundred bars (see ref. (12) for an example). Of course, $\alpha_{ee} - \alpha_e$ decreases with pressure at $T_g$ but is still measurable, as seen in the PVAc data of reference (5). We then turned to a study of the isothermal $V$-$P$ plane (12, 13).

We assumed that $\alpha_{ee} - \alpha_e \to 0$ at $T_{ee}$ was a direct consequence of a compensating step change in isothermal compressibility at $T_{ee}$. Step changes, $\kappa_{ee} - \kappa_e$, at $T_g$ are well known as, for example, in the PS data of Rehage and Breuer (18), and more recently of Oels and Rehage (3).

We quickly realized that isothermal $V$-$P$ data indeed provided a much better opportunity to determine the temperature variation of $T_{ee}$ with pressure and hence numerical values of $dT_{ee}/dP$. From the work of Simha and his collaborators (1, 2, 7, 8, 10), we were aware of the usefulness of the Tait equation, and of Wood’s variation of it (19), in analyzing $P$-$V$-$T$ data. But both seemed to present certain problems. We have therefore employed (12) simple approximations to the Tait equation which is commonly written as:

$$\frac{1 - V}{V_0} = C' \ln \kappa_{ee} \times (1 + P/b) \quad [1]$$

where $V$ is the volume at pressure $P$, and $V_0$ is a reference volume at $P = 0$. $C'$ and $b$ are constants. A pertinent discussion of equation [1] with numerical values for $C'$ and $b$ has been given by Simha, Wilson and Olabisi (20). They assign to $C'$ a universal value of 0.0894, but Beret and Prausnitz prefer to calculate a value specific to each polymer (4). The range in $C'$ is $\pm 10\%$ (4). They (20) report numerical values of the temperature-dependent parameter, $b$, for PS, PVC and PMMA. $b$ has a value of about 3000–4000 bars in the glassy state, decreasing to about 1000 bars at $T_{ee}$. $b$ undergoes a step increase at each pressure-induced transition in the $V$–$P$ plane. This increase is relatively small at weak secondary relaxations such as $T_{ee}$. For PVAc we found $b = 1567$ bars above $T_{ee}$, 2391 bars below $T_{ee}$ but above $T_g$. The change at the liquid to glass transition is substantial, such as a factor of two. It can be noted later from equations [4] and [5] that $b = C' \bar{K}_0$ where $\bar{K}_0$ is the bulk modulus at $P = 0$.

Figure 1 is a plot of $1/V/V_0$ calculated from the Vsp data of Quach, Wilson and Simha (10) as a function of $P$ at 138.2°C. The results appear to consist of three straight line sections intersecting at pressures $P_1$ and $P_2$. We tentatively identify these pressure-induced transitions as follows: $P_1 = T_{ee}$; $P_2 = T_g(LP)$. $T_g(LP)$ is a low pressure glass transition, a term introduced and defined by Quach and Simha (2) who gave numerical values of it for PS as a function of $P$.

![Fig. 1. Isothermal V-P data for iso PMMA at 138.2 °C. Values of 1- V/V_0 were calculated from Vsp data in reference (10). P_1 is T_{ee}, P_2 is T_g(LP)](image)

The slope changes at $P_1$ and $P_2$ presumably resulted from step jumps in the Tait parameter, $b$, at each pressure-induced transition. We were at first puzzled by the seeming linearity of the segments for data said by its authors to follow equation [1], especially at values of $P/b$ close to unity. We now discuss the generalized form of equation [1] when several successive transitions are involved as $P$ increases and $b$ changes.