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## Dependence of Polymer Glass Transition Temperatures on Heating Rate

TECHNIQUES such as Differential Scanning Calorimetry and Differential Thermal Analysis allow the measurement of the glass transition temperatures ($T_G$) of polymers on small samples (10 to 20 mg) provided that fairly high heating rates are used (8 to 64 deg./min). The $T_G$ so measured is usually considerably higher ($\sim$ 10 to 30 deg. K) than that found by dilatometry at a low heating rate ($\sim$0·06 deg./min), so that a method of relating $T_G$ to experimental heating rate would be very useful for providing comparative data.

The molecular processes that occur in a polymer at the $T_G$ are undoubtedly complex[1-4], but it has been found that the time dependence of the glass to liquid transformation can be treated to a good approximation as a simple first-order kinetic process with a single relaxation time[5,6], and the following treatment is based on this approach.

If the glass transition is considered to be a first-order kinetic process, the rate of transformation of 'glass' to 'liquid' molecules on heating through the $T_G$, is given by

$$-\mathrm{d}n/\mathrm{d}t = kn \qquad (1)$$

where $n$ is the mole fraction of 'glass' at any given instant, and $k$ is the rate constant. This equation can be written in the form

$$-\mathrm{d}n/n = (k/\phi)\,\mathrm{d}T \qquad (2)$$

where $\phi = \mathrm{d}T/\mathrm{d}t$, the linear heating rate.

Integration of equation (2) gives

$$\ln (n_0/n_t) = (1/\phi) \int_{T_0}^{T_t} k\,\mathrm{d}T \qquad (3)$$

where the subscripts 0 and $t$ refer to the state of the system at time zero and time $t$. If $T_G$ is defined as the temperature corresponding to the half-life of the process, so that $n_0/n_t = 2$, then

$$\ln 2 = (1/\phi) \int_{T_0}^{T_G} k\,\mathrm{d}T \qquad (4)$$

For two different heating rates $\phi_A$ and $\phi_B$, equation (4) gives

$$\phi_B/\phi_A = \int_{T_0}^{T_B} k\,\mathrm{d}T \Big/ \int_{T_0}^{T_A} k\,\mathrm{d}T \qquad (5)$$

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where $T_B$ and $T_A$ are the observed $T_G$s for heating rates $\phi_B$ and $\phi_A$. This equation can be derived by defining $T_G$ as the temperature corresponding to any fixed fractional degree of transformation. It can be shown that if $k$ is written in the Arrhenius form, $A \exp (-E/RT)$, where $A$, $E$ and $R$ are constants, $E$ being the activation energy and $R$ the gas constant, the integrated form of equation (5) is given by

$$\frac{\phi_B}{\phi_A} = \frac{T_B^2 \exp(-E/RT_B) - T_0^2 \exp(-E/RT_0)}{T_A^2 \exp(-E/RT_A) - T_0^2 \exp(-E/RT_0)} \tag{6}$$

Equation (6) is obtained by putting each of the integrals of equation (5) in a form involving the difference between two exponential integrals and taking the first two terms of the series expansions of these. The numerical error involved in this approximation is very small ($<0{\cdot}1$ per cent).

Expression (6) may be simplified for the inequality

$$T_B^2 \exp (-E/RT_B) \gg T_0^2 \exp (-E/RT_0) \ll T_A^2 \exp (-E/RT_A) \tag{7}$$

when, to a good approximation,

$$\phi_B/\phi_A = [T_B^2 \exp (-E/RT_B)]/[T_A^2 \exp (-E/RT_A)] \tag{8}$$

Taking logarithms in equation (8) gives

$$\ln [(\phi_B/\phi_A)(T_A/T_B)^2] = (E/R)[(1/T_A) - (1/T_B)] \tag{9}$$

If $\phi_B = \phi$, $T_B = T$, and $\phi$ and $T$ are variables, while $\phi_A$ and $T_A$ are fixed reference values, equation (9) can be written in the form:

$$\ln (\phi/T^2) = C - E/RT \tag{10}$$

where $C$ is a constant for a given polymer, and $T$ is the apparent $T_G$ corresponding to the linear heating rate $\phi$. When $\ln T^2 \simeq$ constant, equation (10) becomes

$$\ln \phi = C' - E/RT \tag{11}$$

Equations (10) and (11) are heating rate analogues of the Arrhenius activation energy equation for the dependence of $T_G$ on frequency in dynamic mechanical measurements[7].

The heating rate dependence of $T_G$ was investigated for poly(5-n-ethylresorcinol isophthalate) (PERI). The PERI sample was a high molecular weight fraction with $\eta_{\text{inh.}} = 1{\cdot}06$ dl/g (0·5 per cent in 40:60 w/w tetrachlorethane/phenol at 30°C)[8]. $T_G$ measurements at high heating rates (16 to 64 deg. K/min) were made using a Perkin–Elmer differential scanning calorimeter, model DSC-1B. The temperature scale of the instrument was calibrated at different heating rates with tin, indium, benzoic acid, stearic acid, diphenyl, and n-octane as melting point standards. Samples of the polymer ($\sim$ 20 mg) were encapsulated in aluminium pans and scanned at different heating rates under a nitrogen atmosphere. The samples were pre-conditioned by heating for about 30 minutes at a temperature about 50 deg. K above the $T_G$ and then either quenched in liquid nitrogen or cooled slowly at constant rate of 2 deg. K/min. The $T_G$ was

taken to be the point of inflection in the plots of differential heat capacity versus temperature for scans on the quenched sample.

The apparent activation energy ($E$) was determined by scanning the slow-cooled sample at 32 deg. K/min and analysing the peak in the heat capacity/temperature curve by the method of Ellerstein[6]. It was found that $E = 86\cdot3$ kcal/mole. The apparent $T_G$ at 32 deg. K/min ($T_B$) was 421 deg. K. From these data and equations (6) or (9) it is possible to calculate $T_A$ corresponding to the heating rate $\phi_A = 0\cdot06$ deg. K/min as used in the dilatometric measurement[9].

For equation (9) to apply it is necessary that the inequalities (7) should hold. For PERI, $T_0 \simeq 300°$ K, $T_A = 393°$ K (experimental dilatometric value)[9], and $T_B = 421°$ K, which gives

$$1\cdot3 \times 10^{-45} \gg 9\cdot0 \times 10^{-59} \ll 1\cdot5 \times 10^{-45}$$

The value of $T_A$ which satisfies equation (9) is 397° K, which is 4 deg. K greater than the experimental dilatometric $T_G$[9].

For the variation in apparent $T_G$ with heating rate, on the quenched sample, equation (10) should apply. *Figure 1* shows the data as a plot of
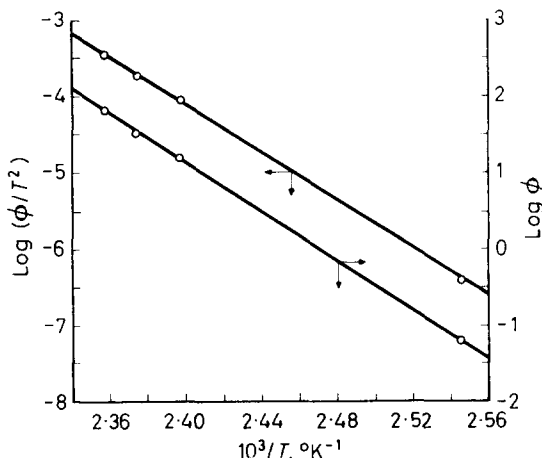


*Figure 1*—Plots of log ($\phi/T^2$) and log $\phi$ versus $10^3/T$ for poly(5-ethylresorcinol isophthalate)

log ($\phi/T^2$) versus $1/T$, and the dilatometric value is included. The plot is linear with a least squares slope corresponding to $E = 72\cdot5$ kcal/mole. The value of log $T^2$ varies from $5\cdot19$ at $0\cdot06$ deg. K/min to $5\cdot25$ at 32 deg. K/min, or about $1\cdot2$ per cent, and equation (11) is a good approximation as shown by the linear plot of log $\phi$ versus $1/T$, also given in *Figure 1*. The least squares slope corresponds to $E = 74\cdot2$ kcal/mole.

In conclusion, the proposed theory gives reasonable agreement with experiment, and provides a means of estimating dilatometric $T_G$s from data obtained at high heating rates. Work is in progress to test the method by application to a wide range of polymers.

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## *Molecular Weights by Gel Permeation Chromatography: Unperturbed Dimensions Calibration for Polyisoprene*

IN a recent paper[1], it was proposed that the unperturbed dimensions $\langle L_0^2 \rangle$ of a polymer can be used as the universal calibration parameter in gel permeation chromatography (GPC). Our experimental studies in chloroform gave the same molecular weight calibration for fractions of polystyrene, poly(methyl methacrylate) and poly(dimethyl siloxane). These polymers have very similar unperturbed dimensions. When literature calibration data[2-7] are placed on an unperturbed dimensions plot, reasonable universal curves are obtained[1]. To check the proposed procedure further, we have studied the calibration of polystyrene and polyisoprene which have different values for the unperturbed dimensions.

A Waters Associates GPC instrument with chloroform as solvent was used as described previously[1]. The injected weight for both polystyrene and polyisoprene was 5 mg. The polystyrene samples were the calibration standards supplied by Waters Associates. A smooth curve drawn through the peak molecular weight and elution volume (counts) data for polystyrene is shown on a semi-logarithmic plot in *Figure 1*. The microstructure of the polyisoprene samples 60, 66, 67 and 78, determined by nuclear magnetic resonance (n.m.r.), was 70–75 per cent *cis*-1,4-units, the remainder being almost entirely *trans*-1,4-units. The polyisoprene GPC elution curves are shown in *Figures 2* and *3*. Number average molecular weight $\bar{M}_n$ measurements were made with a Mechrolab membrane osmometer, using toluene as solvent at 37°C. Weight average molecular weight $\bar{M}_w$ measurements were made with a Sofica light scattering instrument, using cyclohexane as solvent at 30°C.

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