Thermochimica Acta, 118 (1987) 159–181
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A COMPARATIVE STUDY OF THE KINETIC AND THERMODYNAMIC APPROACHES TO THE GLASS TRANSITION PHENOMENON IN HIGH POLYMERS

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(Received 3 February 1987)

ABSTRACT

The effect of thermal history on the glass transition temperature T_g of polystyrene, polyvinylchloride and polyethyleneterephthalate was studied using differential scanning calorimetry (DSC). Parameters such as the hole energy E_h, the activation energy E_j for the disappearance of holes, the activation enthalpies $\Delta h1^*$ and $\Delta h2^*$ for structural relaxation and the activation energy E for the glass transition process were calculated. The increase in E_h value with increasing T_g showed that there exists a distribution of hole sizes. The E_j value calculated according to Wunderlich's treatment, the $\Delta h1^*$ parameter obtained using Moynihan's procedure and the E value derived from Barton and Critchley's method agreed with one another for polystyrene and polyvinylchloride. The $\Delta h2^*$ quantity obtained using Moynihan's formula increased as the rate of heating was increased, a result similar to the variation in E_h value with heating rate. The validity of the ΔC_p–T_g criteria proposed by Wunderlich and by Simha and Boyer were also investigated for the three polymers concerned. The variations in kinetic parameters such as ΔHa, the cohesive energy density (CED) and the thermodynamic quantity $\Delta\mu$ (Adam–Gibbs) were also calculated and their variation is discussed in the light of structure–property relationships.

INTRODUCTION

Polymers usually exhibit phase transitions, involving striking changes in many of their properties, at temperatures below their melting points. The most distinct transition is customarily referred to as the glass transition temperature T_g. In the glass transition region, many thermodynamic, physical, mechanical, electrical and other properties of polymers undergo consid-

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erable changes [1–5]. As the glass transition temperature largely determines the end uses to which the polymer may be put, it is of paramount importance in determining the physical properties of high polymeric materials.

The glass transition process in polymers occurring at the temperature T_g (K) marks the freezing-in (on cooling) or unfreezing (on heating) of micro-Brownian motion of chain segments 20–50 carbon atoms in length. This micro-Brownian motion is a semi-cooperative action involving torsional oscillation and/or rotation about backbone bonds in a given chain as well as in neighbouring chains. Torsional motion of side groups about the axes connecting them to the main chain may also be involved [5].

One difficulty in understanding the glassy phase lies in the definition of a glassy structure or, better, the lack of a generally accepted formalism. In order to understand fully the glassy phase and the phenomenon of glass transition and to be able to derive theories to describe this process, a proper understanding of the nature of the liquid state is a prerequisite, since the glass may be considered to be a metastable form of a liquid. Since concepts of liquids are themselves rather vague, it is hardly surprising that theories of glasses have not yet achieved the level of crystal or gas theories.

The glass transition phenomenon has traditionally been approached from three standpoints, namely free-volume factors, kinetic and relaxation effects and thermodynamic parameters. The one outstandingly successful approach to this problem to date has been the free-volume theory advocated initially by Fox and Flory [6,7].

The best-known experimental evidence in support of the kinetic theory of the glass transition is that when the transition is measured in a cooling run, T_g decreases with a decrease in the cooling rate [1]. Upon heating samples previously cooled at different rates, one observes a hysteresis phenomenon [8], which can be only explained on the basis of a kinetic glass transition. Other evidence comes from dynamic results, either mechanical or dielectric: when the frequency of measurement is decreased, the peak moves to lower temperatures. A detailed relaxation theory of vitrification was proposed by Volkenshtein and Ptitsyn [9]. Thereafter Wunderlich and co-workers [10–14] have discussed it in the light of Hirai–Eyring hole theory [15,16]. These theories regarded the vitrification process as a chemical reaction involving the passage of kinetic particles from one energy level to another. Using a model of structural relaxation in glasses, Moynihan and co-workers [17,18] developed theories to explain the kinetics of the glass transition process.

While the "hole" volume model in the Hirai–Eyring [15,16] model required no thermodynamic input, Gibbs and DiMarzio [19,20] approached the problem in terms of *PVT* variables and arrived at the conclusion that the glass transition is "in fact, the experimental manifestation of the second-order transition, T_2, in the Ehrenfest [21] sense". However, Adams and Gibbs [22] took into account both the rate effect and the equilibrium behaviour of the second-order transition.

Though detailed overviews on glass transition phenomena in high polymers, including discussions of theoretical aspects, have been published [23–25], no reported work to date has highlighted the similarities present in the results derived from different theoretical approaches. In the present work, three industrially important polymers (polystyrene, polyvinylchloride and polyethyleneterephthalate) are studied using differential scanning calorimetry (DSC).

C_p–T plots are constructed from which T_g and related quantities are derived for a wide variety of thermal histories. From the acquired data, a detailed study of the various kinetic parameters and thermodynamic quantities which characterize the glass transition phenomenon is presented. Finally, a comparison of different parameters, derived by various workers in the field and based on a number of different models explaining this industrially and theoretically important transition, is attempted and the results are discussed.

EXPERIMENTAL

Materials

The materials used for the investigation were polystyrene (PS) (M_w 170,900; NBS-705), polyvinylchloride (PVC) (M_w 160,000; Chemplasts Ltd., Madras, India) and polyethyleneterephthalate (PET) (M_w 22,000; Indian Organic Chemicals Ltd., Madras, India).

Methods

The specific heat (C_p) measurements were carried out using a Perkin-Elmer DSC-1B instrument with alumina as the enthalpy calibrant. The calorimeter temperature was raised from a steady value, T_1, to another, T_2, where $T_1 < T_g < T_2$, in the sequence: (i) empty, (ii) reference and (iii) sample. The results of (i) and (ii) gave the area-to-enthalpy conversion factor and reference data for the specific heats. The above data in combination with (i) and (iii), made it possible to calculate the total enthalpy change in the sample and the specific heats of the sample in the temperature interval T_1–T_2.

A computer program [26] based upon the calculation procedure developed by Richardson et al. [27,28] transformed the DSC output into specific heat values (cal deg^{-1} g^{-1}). First of all, the DSC thermograms obtained from the empty, reference and sample measurements in the temperature region T_1–T_2 were reduced to the same baseline. Then the isothermal temperature correction and a correction (derived from the sample curve itself) for the thermal lag caused by the finite heating rate were carried out. High purity calibrants

TABLE 1

Thermal lag factor obtained using various heating rates for the three polymers studied [a]

Material	Heating rate (deg min^{-1})					
	2	4	8	16	32	64
PS	0.6	0.9	2.5	6.0	10.2	–
PVC	1.1	1.0	2.6	3.9	7.3	14.4
PET	0.8	1.3	2.1	4.8	9.9	–

[a] PS, polystyrene; PVC, polyvinylchloride; PET, polyethyleneterephthalate.

used for the isothermal temperature correction were *N*-methylacetamide, diphenylamine, azobenzene, benzil, benzoic acid and indium. The specific heat values for the alumina reference were taken from Ginnings and Furukawa [29].

A known amount of PS was placed in the aluminium sample holder and heated in the DSC cell to about 420 K in an atmosphere of dry, oxygen-free nitrogen, with the dual purpose of removing any residual low molecular weight impurities and giving a stable sample geometry for the subsequent experiments. The polymer was transformed into the glassy state by cooling through T_g at a rate of 0.5° min^{-1} to 323 K. Then the specific heat run was made, employing a heating rate of 2° min^{-1} ($T_1 = 323$ K, $T_2 = 413$ K). This procedure was repeated for other cooling rates (1, 2, 4, 8, 16, 32 and 64° min^{-1}). Similar experiments were also carried out for other heating rates, namely 8, 16 and 32° min^{-1}.

For PVC the pretreatment was done at 399 K. As in the case of PS, for each particular heating rate, eight different cooling rates were employed. In this way, specific heat measurements were carried out for heating rates of 2, 4, 8, 16, 32 and 64° min^{-1}. In the case of PVC, $T_1 = 309$ K and $T_2 = 399$ K.

Owing to the occurrence of a cold crystallization exotherm around 400 K in the case of PET, the higher heating rates (32 and 64° min^{-1}) were not employed for this substance and T_2 was also changed depending upon the heating rate employed ($T_1 = 309$ K throughout; $T_2 = 366$ K for 4° min^{-1}, 371 K for 8° min^{-1} and 379 K for 16° min^{-1}). For each heating rate, eight different cooling rates were used. The thermal lags observed for the samples at various heating rates are shown in Table 1.

RESULTS AND DISCUSSION

Kinetic parameters and related quantities

Effect of thermal history on T_g

The effect of different cooling rates on the specific heat of PS at the 4° min^{-1} heating rate is shown in Fig. 1a and the T_g values obtained at various

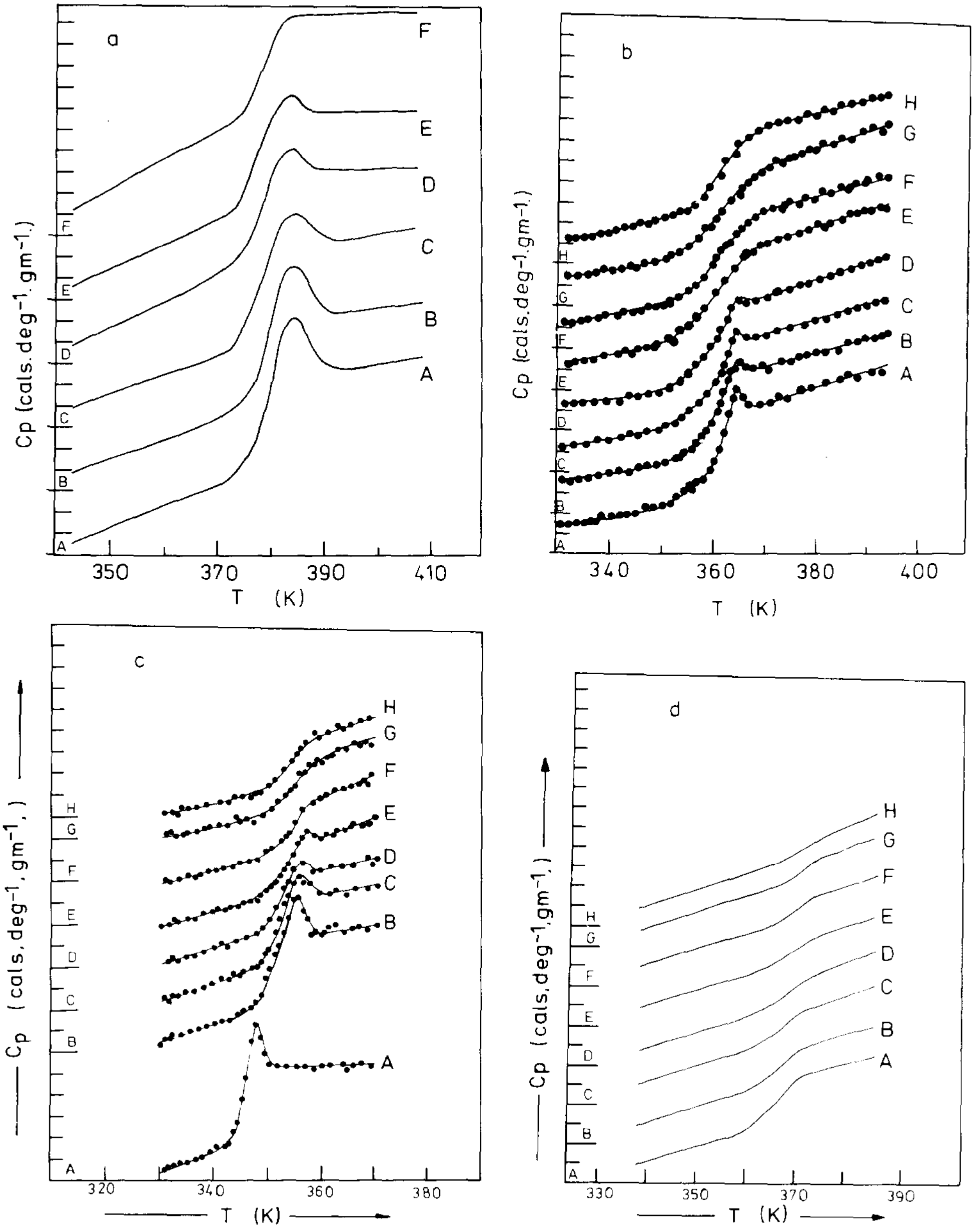

Fig. 1. Effects of various cooling rates on C_p and T_g. Each division on the C_p axis corresponds to an increment of 0.010 cal deg^{-1} g^{-1}. Curves B, C, D, E, F, G and H are shifted in the ordinate by distances $\overline{AB}$, $\overline{AC}$, $\overline{AD}$, $\overline{AE}$, $\overline{AF}$, $\overline{AG}$ and $\overline{AH}$, respectively. (a) Polystyrene: heating rate, 4° min^{-1}; the C_p axis starts at 0.380 cal deg^{-1} g^{-1}; cooling rates, A, 0.5; B, 1; C, 2; D, 4; E, 8 and F, 16° min^{-1}. (b) Polyvinylchloride: heating rate, 8° min^{-1}; the C_p axis starts at 0.270 cal deg^{-1} g^{-1}; cooling rates, A, 0.5; B, 1; C, 2; D, 4; E, 8; F, 16; G, 32 and H, 64° min^{-1}. (c) Polyethyleneterephthalate: heating rate, 4° min^{-1}; the C_p axis starts at 0.200 cal deg^{-1} g^{-1}; A, material as heated; cooling rates, B, 0.5; C, 1; D, 2; E, 4; F, 16; G, 32 and H, 64° min^{-1}. (d) Polyethyleneterephthalate: heating rate, 16° min^{-1}; the C_p axis starts at 0.250 cal deg^{-1} g^{-1}; cooling rates, A, 0.5; B, 1; C, 2; D, 4; E, 8; F, 16; G, 32 and H, 64° min^{-1}.

TABLE 2

Effects of thermal history on T_g

Cooling rate (deg $\min^{-1}$)	Glass transition temperature T_g (K) at the following heating rates					
	2° $\min^{-1}$	4° $\min^{-1}$	8° $\min^{-1}$	16° $\min^{-1}$	32° $\min^{-1}$	64° $\min^{-1}$
Polystyrene						
0.5	366.2		371.1	380.0	390.0	
1.0	367.0		371.9	380.5	391.1	
2.0	367.6		372.6	381.3	391.7	
4.0	368.4		373.3	381.6	392.9	
8.0	369.2		373.9	382.5	391.9	
16.0	–		374.9	383.6	–	
32.0	–		–	–	394.2	
Polyvinylchloride						
0.5	349.8	350.1	349.4	356.9	365.2	376.2
1.0	—	350.9	350.9	357.8	366.1	377.2
2.0	351.6	351.7	351.6	358.5	366.8	377.8
4.0	352.8	352.3	352.3	359.4	367.5	378.5
8.0	353.5	353.4	353.1	360.0	368.2	379.1
16.0	353.9	–	353.9	360.9	369.1	380.0
32.0	354.8	–	354.6	361.2	368.3	380.7
64.0	355.7	–	355.1	361.3	369.1	380.8
Polyethyleneterephthalate						
0.5		348.0	349.6	361.0		
1.0		348.8	350.2	361.9		
2.0		349.6	351.0	362.8		
4.0		350.4	351.8	363.4		
8.0		–	352.6	364.4		
16.0		351.6	353.4	365.4		
32.0		352.4	354.2	366.4		
64.0		353.0	355.0	367.2		

heating and cooling rates are listed in Table 2. Similarly, Fig. 1b shows the C_p–T curves for PVC, cooled at various rates and heated at 8° $\min^{-1}$. All the T_g values derived for a variety of heating and cooling rates are included in Table 2. Figures 1c and 1d present the C_p–T details in the glass transition region of PET, obtained for various cooling rates and then reheating at rates of 4 and 16° $\min^{-1}$, respectively. The T_g values for various thermal histories are presented in Table 2.

From Table 2 it may be seen that, for PS, PVC and PET at a constant heating rate, when the cooling rate was increased T_g also increased. A similar result was observed when the heating rate was increased for material which had previously cooled at a constant cooling rate. The reason for this is not difficult to see if one notes that isobaric heating or cooling at a constant rate is the limit as $\Delta T \rightarrow 0$ of a series of instantaneous, small temperature changes ΔT, each of which is followed by an isothermal hold of duration

$$\Delta t = \Delta T/q \tag{1}$$

where q is the heating or cooling rate

$$q = \mathrm{d}T/\mathrm{d}t = \Delta T/\Delta t \tag{2}$$

The three regions of the transition roughly correspond to the following conditions

$$\text{Liquid} \qquad \Delta t \gg \tau \tag{3}$$

$$\text{Transition region} \qquad \Delta t \approx \tau \tag{4}$$

$$\text{Glass} \qquad \Delta t \ll \tau \tag{5}$$

where τ is the relaxation time. From eqn. (1) it is evident that if the heating or cooling rate q is increased in magnitude, then the relaxation time τ must be correspondingly smaller for eqn. (4) to hold good and the transition is shifted to higher temperature.

When the T_g values obtained at different cooling rates for a constant heating rate were plotted against the logarithm of the cooling rate employed, the T_g values showed a linear dependence (Figs. 2a (PS), 2b (PVC) and 2c (PET)). An extrapolation of the T_g values to a very slow cooling rate (0.01° min^{-1}) gave the cooling rate-independent T_g value for a constant heating rate. The values thus obtained for different heating rates are presented in Table 3.

These cooling rate-independent T_g values at a constant heating rate shifted to higher temperatures as the heating rate was increased (Table 3). In order to obtain the heating *and* cooling rate-independent T_g value, i.e. the "true" glass transition temperature of each material, these cooling rate-independent T_g values were plotted against the logarithm of the heating rate utilized (Figs. 2a, curve E (PS) and 2b, curve E (PVC)). For both PS and PVC, the dependence was not exactly linear: the plot showed a curvature in that T_g was not very much affected at slower heating rates, whereas at faster heating rates it shifted rapidly to higher temperatures. A similar type of non-linear relation was obtained by Blanchard et al. [30] and by Hutchinson and Kovacs [31].

The WLF equation

The widely-used definition of the free volume of polymeric glasses arises from the important work of Williams et al. [32]. The empirical relationship developed by Williams, Landel and Ferry (the WLF equation) gives a_T, the ratio of relaxation times at temperature T and at the transition temperature T_g, for a polymer in the temperature interval T_g to $T_g + 100°$

$$\log a_T = -\frac{C_1(T - T_g)}{C_2 + T - T_g} \tag{6}$$

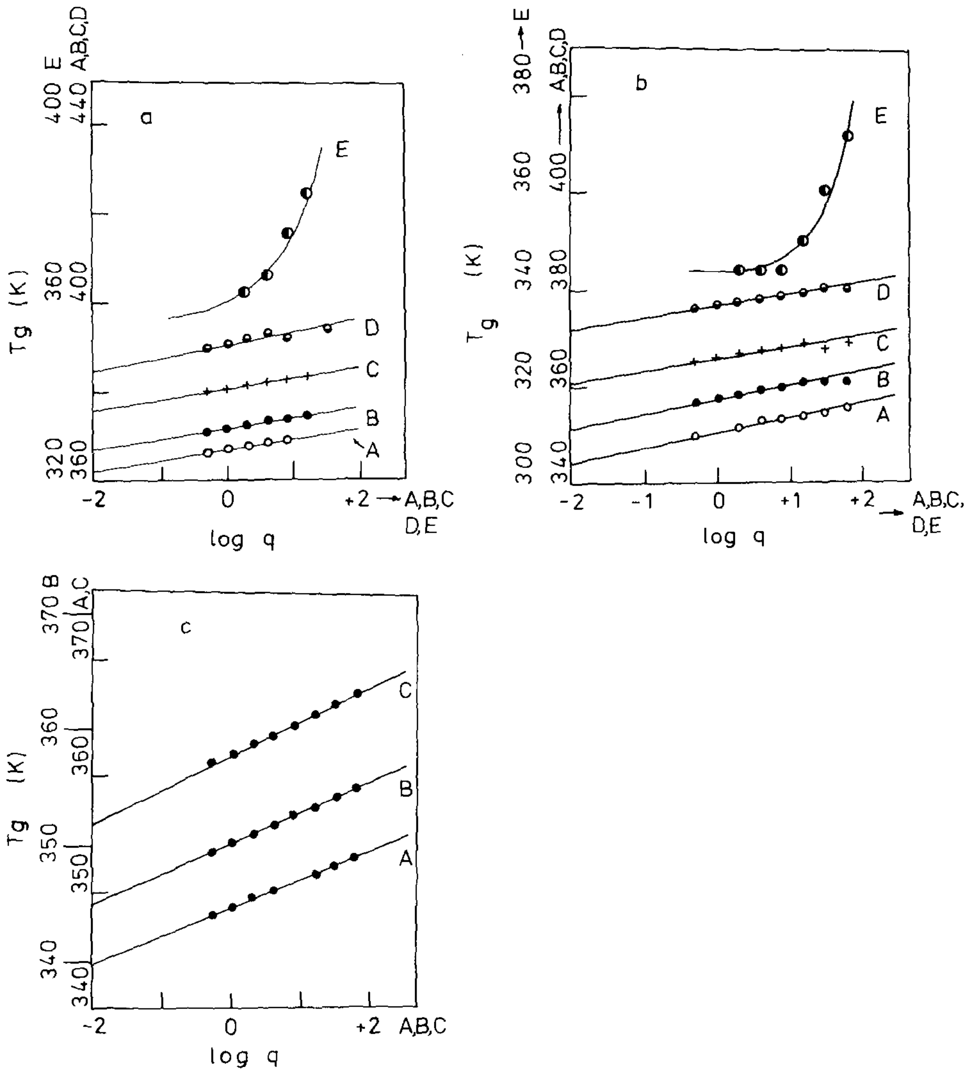

Fig. 2. Effects of thermal history on the glass transition temperature T_g. (a) Polystyrene: for lines A, B, C and D, log q is the cooling rate (heating rates, A, 2; B, 8; C, 16 and D, 32° min^{-1}); for curve E, log q is the heating rate. (b) Polyvinylchloride: for lines A, B, C and D, log q is the cooling rate (heating rates, A, 2, 4 and 8; B, 16; C, 32 and D, 64° min^{-1}); for curve E, log q is the heating rate. (c) Polyethyleneterephthalate: log q is the cooling rate (heating rates, A, 4; B, 8 and C, 16° min^{-1}).

This empirical relationship has achieved the status of a unique cornerstone to which all subsequent theoretical treatments have been related.

On differentiating the WLF equation, Ferry [33] reported the following relation

$$(\mathrm{d}\Delta T_g/\mathrm{d}\log a_T) \approx 3° \qquad (7)$$

TABLE 3

Effects of heating rate on various kinetic parameters [a]

Heating rate (deg $\min^{-1}$)	T_g at nearly zero cooling rate (K)	d ΔT_g/d log a_T	$\Delta h2^*$ (kcal mole^{-1})	E_h (cal mole^{-1})
Polystyrene				
2.0	362.2	2.50	239.3 (1.1)	2073
8.0	366.9	2.53	254.6 (1.0)	2100
16.0	375.7	2.39	278.5 (2.8)	2150
32.0	384.6	2.32	291.5 (7.2)	2201
Polyvinylchloride				
2.0	344.2	2.81	203.6 (1.2)	1970
4.0	344.2	2.75	204.4 (0.4)	1970
8.0	344.2	2.71	211.3 (1.4)	1970
16.0	351.3	2.66	255.3 (2.5)	2010
32.0	360.7	2.60	295.3 (5.4)	2064
64.0	371.8	2.53	280.3 (1.9)	2128
Polyethyleneterephthalate				
4.0	343.9	2.38	232.0 (0.8)	1968
8.0	345.1	2.57	214.3 (0.4)	1975
16.0	355.8	2.95	202.0 (0.5)	2036

[a] Values in parentheses are standard deviations.

which indicates that the glass transition temperature would change by roughly 3° if the cooling rate (log a_T) were changed by a factor of 10 at a constant heating rate.

The present experimental results on PS involving varying the cooling rate at a constant heating rate showed a shift in T_g of 2.32–2.53 (Table 3), in reasonable agreement with the relation proposed by Ferry [33]. For PVC and PET this value was found to lie in the ranges 2.53–2.81 and 2.38–2.95, respectively (Table 3). In all cases, the observed value is slightly smaller than that theoretically expected. The reasons for this discrepancy and also the very rapid shift in T_g at the higher heating rates have been dealt with in detail elsewhere [31].

Wunderlich's hole theory

According to hole theory, the two most important parameters characterizing the holes are E_h (the hole energy) and E_j (the activation energy for the disappearance of a hole). Considering the large number of different polymers studied, with T_g values ranging from 150 to 500 K, the correlation between E_h and T_g is exceptionally good [25]. Numerical evaluation of the data shows that

$$E_h/RT_g = 2.88 \pm 0.22 \tag{8}$$

Using this expression and the cooling rate-independent T_g values (Table 3),

E_h values were evaluated for PS. The values obtained, also shown in Table 3, clearly demonstrate that as T_g increases, the E_h value increases from 2073 to 2201 cal mol^{-1}. This indicates that with increasing energy input into the material, the cooperatively rearranging ensemble during the transition process increases, which is reflected in the E_h values, thus demonstrating the existence of a hole size distribution and/or holes with different relaxation behaviour in the same sample. Furthermore, the E_h values thus calculated are of the same order as the previously reported values [25] for PS, namely 1867–2153 cal mol^{-1}.

The E_h values calculated in the same way for PVC are shown in Table 3. The overall trend of the variation of E_h with T_g is the same as in the case of PS. However, comparison of the E_h values for PS and PVC at a constant heating rate shows that the former are greater than the latter. Since the molecular weights of the PS and PVC samples employed in the present investigation are nearly the same, one may conclude from the molecular architecture that the phenyl group movement needs more energy compared to that of the chlorine atom. The E_h values for PET also show the same trend as has been discussed above.

Wunderlich and co-workers [10,12,13] derived the expression

$$\log q = \text{constant} - 0.4343(E_j/RT_{max}) \tag{9}$$

where q is the heating rate and T_{max} is the position of the peak temperature in the C_p–T curve obtained in the glass transition region. The derivation is based upon the hole theory proposed by Hirai and Eyring [15,16]. Therefore, one easy procedure for evaluating E_j is to plot loq q vs. $1/T_{max}$. The variations in T_{max} values with various heating and cooling rates for PS and PVC are shown in Table 4. Similarly, plots of log q vs. $1/T_{max}$ are shown in Figs. 3a and 3b. The E_j value for PS was found to be 28.2 kcal mol^{-1}. Since the E_h value increases with heating rate, it is reasonable to expect a similar variation in the E_j values. However, the procedure suggested by Wunderlich gives only the overall or average E_j values for the material at various heating rates.

The actual E_j values for PVC obtained from the T_{max} values derived at various heating rates, after previous cooling at 0.5, 1 and 2° min^{-1}, are 27.8 ± 0.6, 22.5 ± 0.6 and 30.4 ± 0.5 kcal mol^{-1}, respectively, giving an average value of 26.9 ± 0.5 kcal mol^{-1}. As with the E_h values, the E_j values for PS are approximately 2 kcal mol^{-1} higher than those for PVC.

Moynihan's relaxation theory

On the basis of the kinetic and thermodynamic parameters controlling the evolution of enthalpy during the structural relaxation process occurring at the glass transition, Moynihan et al. [34] derived the following expression

$$\mathrm{d} \ln q/\mathrm{d}(1/T_g) = -\Delta h1^*/R \tag{10}$$

TABLE 4

Variation in T_{max} values with heating and cooling rates

Heating rate (deg min^{-1})	T_{max} (K) at the following cooling rates			
	0.5° min^{-1}	1° min^{-1}	2° min^{-1}	4° min^{-1}
Polystyrene				
2.0	375.2	375.4	373.4	–
8.0	384.0	384.0	384.4	391.4
16.0	392.0	389.0	393.6	384.0
32.0	403.6	404.6	403.0	–
Polyvinylchloride				
2.0	361.2	–	360.0	
4.0	361.4	361.9	362.0	
8.0	364.6	364.6	364.4	
16.0	370.2	367.0	372.0	
32.0	378.4	377.6	378.0	
64.0	392.8	393.4	390.0	

The equation is valid only for the T_g values measured from heat capacity cooling curves for which cooling was started well above the transition region, or from heat capacity heating curves obtained by reheating the glass from a temperature well below the transition region after it had previously been cooled through the transition region at a rate q equal to the heating

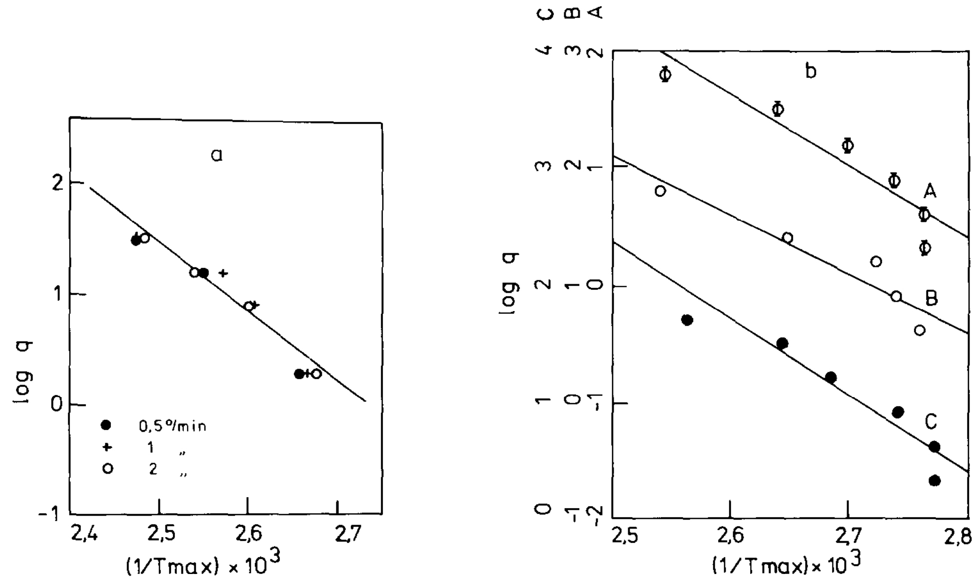

Fig. 3. Plots of log q (heating rate) vs. $1/T_{max}$ to obtain E_j. (a) Polystyrene. (b) Polyvinylchloride (cooling rates, A, 0.5; B, 1 and C, 2° min^{-1}).

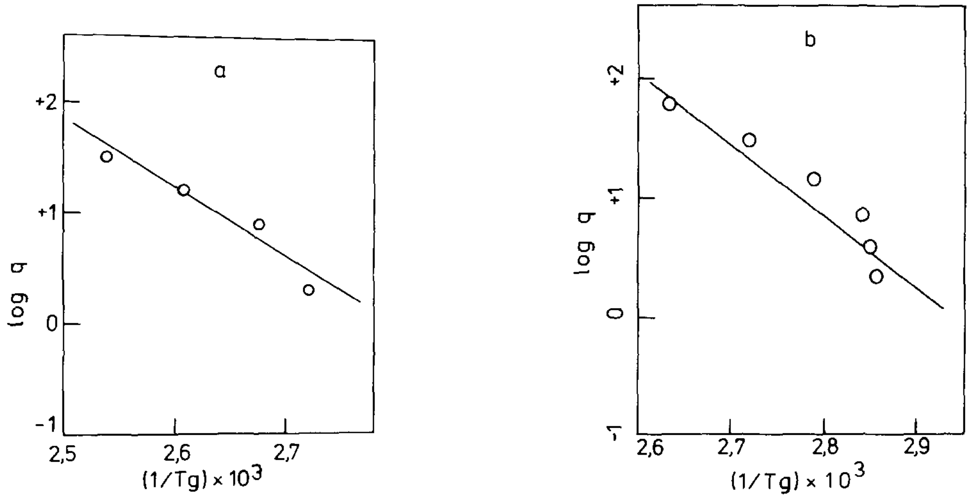

Fig. 4. Plots of log q (heating rate = cooling rate) vs. $1/T_g$ to determine $\Delta h l^*$. (a) Polystyrene. (b) Polyvinylchloride.

rate. The quantity $\Delta h l^*$ in eqn. (10) is the activation enthalpy for the relaxation times controlling the structural enthalpy or volume relaxation.

Thus, the T_g values for constant heating and cooling rate, e.g. 2° min^{-1} heating and 2° min^{-1} cooling, were taken from Table 2 and a plot of log q vs. $1/T_g$ was made for both PS and PVC, as shown in Fig. 4. From the slope of the straight line, the $\Delta h l^*$ values obtained for PS and PVC are 28.2 ± 0.6 and 27.8 ± 0.6 kcal mol^{-1}, respectively. The E_j value obtained from Wunderlich's treatment based on the hole theory is in excellent agreement with the $\Delta h l^*$ value derived from Moynihan's procedure.

A closer look into eqns. (9) and (10) and simple mathematical manipulation of eqn. (10) clearly shows that E_j and $\Delta h l^*$ are one and the same. From eqn. (10), one can write

$$2.303 \log q \approx -\Delta h l^*/R \times 1/T_g \tag{11}$$

$$\log q \approx -\Delta h l^*/2.303R \times 1/T_g \tag{12}$$

i.e.

$$\log q \approx -0.4342(\Delta h l^*/RT_g) \tag{13}$$

Hence, eqns. (9) and (10) are formally equal when $1/T_{max}$ in one is replaced by $1/T_g$ in the other. Once T_g shifts to higher temperatures, T_{max} automatically also shifts to higher temperature, with a magnitude that is nearly the same [34]. Therefore plots of log q vs. $1/T_{max}$ and of log q vs. $1/T_g$ must have the same slope. Taking into consideration the foregoing argument, it may be inferred that the Wunderlich hole theory and the relaxation theory proposed by Moynihan for the glass transition phenomenon are leading to the same conclusions.

Using the model of structural relaxation in glasses developed by Narayanaswamy [35], Gardon and Narayanaswamy [36] and Ritland [37], Moynihan and co-workers [17,18,38–40] developed the relation

$$\mathrm{d}\ln q/\mathrm{d}(1/T_g) = -\Delta h2^*/R \qquad (14)$$

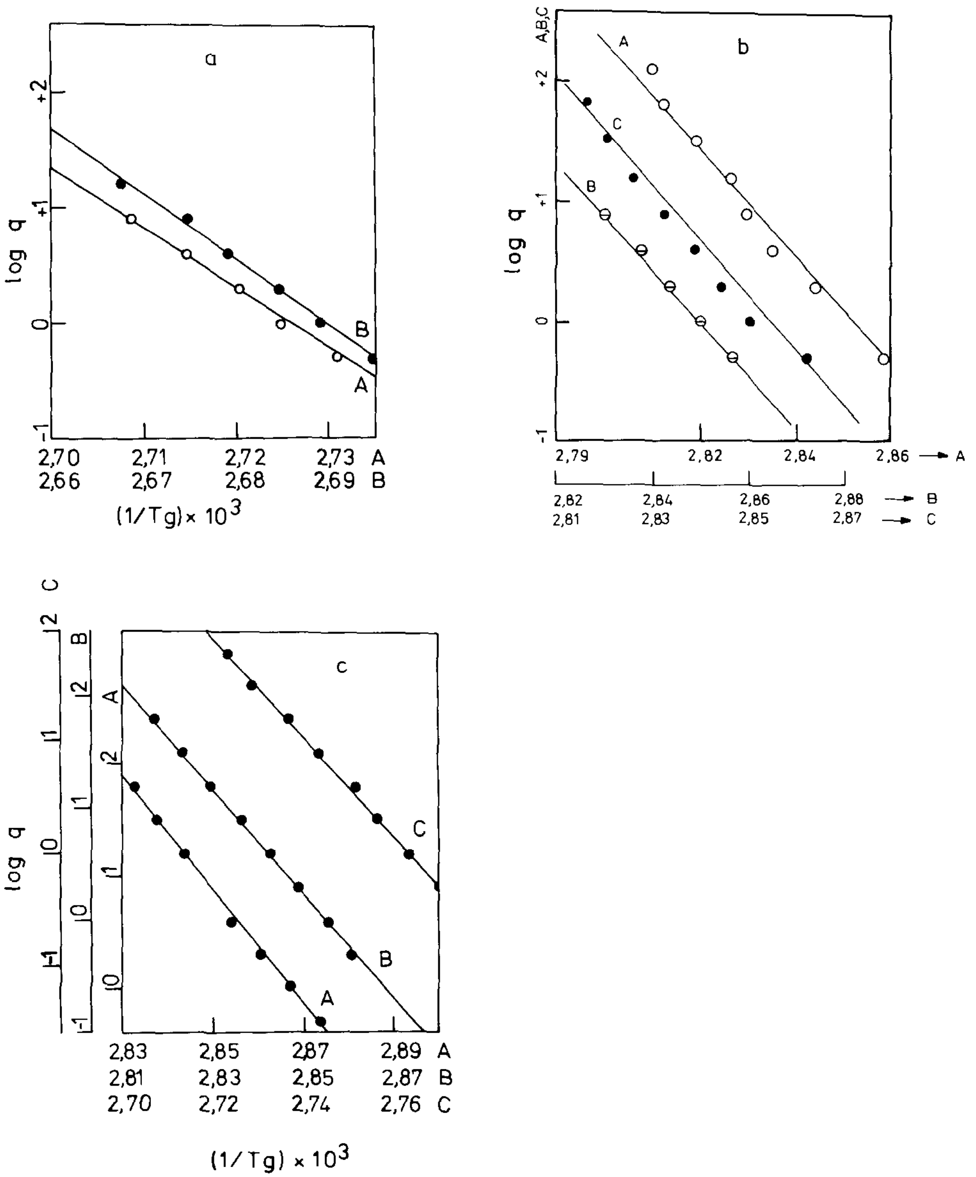

Fig. 5. Plots of log q (cooling rate) vs. $1/T_g$ to obtain $\Delta h2^*$. (a) Polystyrene: heating rates, A, 2 and B, 8° min^{-1}. (b) Polyvinylchloride: heating rates, A, 2; B, 4 and C, 8° min^{-1}. (c) Polyethyleneterephthalate: heating rates, A, 4; B, 8 and C, 16° min^{-1}.

where q is the cooling rate and $\Delta h2^*$ is the activation enthalpy for the structural relaxation. Employing the T_g values for various cooling rates but a constant heating rate, plots of log q vs. $1/T_g$ were made for PS, PVC and PET (Figs. 5a, 5b and 5c, respectively) and the estimated $\Delta h2^*$ values are presented in Table 3. For PS and PVC, $\Delta h2^*$ increases as the heating rate is increased, indicating that as the input energy is increased the size of the moiety rearranging during the transition process also increases. Another interesting observation is that the change in $\Delta h2^*$ values on going from one heating rate to the next higher rate for PS are of the same magnitude as the E_j values of Wunderlich or the $\Delta h1^*$ values of Moynihan. But for PVC, although $\Delta h2^*$ increases with heating rate the difference between the values does not correspond to either the $\Delta h1^*$ or the E_j values; however, the order of magnitude does not vary too much.

The $\Delta h2^*$ values calculated for PET, however, decrease with increasing heating rate. PET is a more easily crystallizable polymer than both PS and PVC. The stiffness of the backbone chains due to the *p*-phenylene rings and the polarity conferred by the ester groups, resulting in some possibility of local chain alignment, are among the factors which complicate the situation in PET. The effects of crystallization during the C_p measurements are well exemplified in Figs. 1c and 1d. In the C_p–T curves, the C_p discontinuities in the T_g region decrease as the heating rate is increased. A possible explanation for the decrease in $\Delta h2^*$ with increased heating rate is that the increased crystallinity of the samples results in a lowering of the activation energy, since the amorphous regions of the polymer contribute less to the enthalpy changes in the T_g region (owing to the cold crystallization phenomenon in PET, this type of complication occurs).

The Barton–Critchley method

Barton and Critchley [41] gave the relation

$$\ln\left[(\phi/\phi_g)(T_g/T_i)^2\right] = (E/R) \times \left(T_g^{-1} - T_i^{-1}\right) \tag{15}$$

where T_i is the "apparent" T_g corresponding to the heating rate ϕ, T_g corresponds to the value obtained at a standard heating rate ϕ_g and E is the activation energy. By taking ϕ_g as 2° min^{-1} and T_g as 362.2 K for PS, application of eqn. (15) to the different cooling rate-independent but heating rate-dependent T_g values (T_i) gave different E values (see Table 5). The value of E decreases with increasing heating rate.

When these $1/T_i$ values were plotted against the logarithm of the heating rate and extrapolated to a heating rate of 0.05° min^{-1}, the T_g obtained for PS was 335.6 K. Now using these values as ϕ_g and T_g, the E values for different heating rates ϕ are calculated and they are found to be in the order of 34.25 kcal mol^{-1}. Furthermore, E is remarkably constant for different heating rates. Yet another interesting result is that E calculated by the

TABLE 5

Activation energy E for the glass transition process following the procedure of Barton and Critchley

ϕ (deg min^{-1})	T_i [a] (K)	E (kcal mol^{-1})
Polystyrene: $\phi_g = 2°\ \mathrm{min}^{-1}$, $T_g = 362.2$ K		
8	366.9	76.43
16	375.7	40.18
32	384.6	32.78
Polyvinylchloride: $\phi_g = 2°\ \mathrm{min}^{-1}$, $T_g = 344.2$ K		
16	351.3	68.98
32	360.7	40.05
64	371.8	30.51

[a] The T_i represent T_g values at nearly zero cooling rate (see Table 3).

Barton–Critchley method has nearly the same order of magnitude as the E_j and $\Delta h l^*$ values discussed earlier.

Similarly for PVC, if ϕ_g is taken as 2° min^{-1} and T_g as 344.2 K, the value of E is found to decrease as the heating rate is increased (Table 5). If ϕ_g is taken as 0.05° min^{-1} and T_g as 319.4 K, then for various heating rates of 2, 4, 8, 16, 32 and 64° min^{-1} the E values obtained were around 32.90 kcal mol^{-1}. Once again, the E values have nearly the same order of magnitude as the E_j and $\Delta h l^*$ values. The E value for PVC is less than that of PS by approximately 2 kcal mol^{-1}.

If 0.05° min^{-1} is taken as the standard heating rate then it is reasonable to assume that the glass at 335.6 K (for PS) will be nearly ideal. Therefore the activation energy needed for this glass to undergo transition will be almost independent of the heating rate and the glass will be very near to the true second-order transition temperature T_2, as stated in thermodynamic theories of the glass transition process. From this ideal glassy state, the material takes up only the minimum amount of energy needed to surmount the potential energy barrier to go to the liquid state, irrespective of the heating rate. But if 2° min^{-1} is taken as the standard heating rate, it is obvious that the material at this point will be far removed from the equilibrium glassy state.

Therefore, there will be a wider distribution of holes and/or free volume, the farther the state is removed from equilibrium. Because of the non-equilibrium characteristics of this process, an apparent activation energy is found (see Table 5), reflecting the fact that different substates for the "liquid state" have been reached. From the discussions so far it is evident that an exact activation energy for the glass transition process can only be calculated from the Barton–Critchley relation if the ϕ_g and T_g values are appropriately chosen. The values of E_j, $\Delta h l^*$ and E for PET were not calculated in the present work because the material was taken to different T_2 values for different heating rates (cf. Experimental section earlier).

ΔC_p–T_g *criteria*

According to the operational definition for the glass transition

$$\Delta C_p = 2.7 \pm 0.5 \text{ cal deg}^{-1} \text{ (mole of beads)}^{-1} \tag{16}$$

and

$$\Delta C_p \times T_g = 27.5 \text{ cal g}^{-1} \tag{17}$$

These two empirical relations, reported by Wunderlich [42] (eqn. (16)) and by Simha and Boyer [43,44] (eqn. (17)) were tested in the present work for

TABLE 6

Effect of thermal history on ΔC_p and related parameters

Heating rate 8° min^{-1}				Cooling rate 0.5° min^{-1}			
Cooling rate (deg min^{-1})	ΔC_p (cal deg^{-1} g^{-1})	ΔC_p (per mole of beads)	$\Delta C_p T_g$ (cal g^{-1})	Heating rate (deg min^{-1}	ΔC_p (cal deg^{-1} g^{-1})	ΔC_p (per mole of beads)	$\Delta C_p T_g$ (cal g^{-1})
Polystyrene							
0.5	0.0445	2.32	16.51				
				2	0.0365	1.90	13.37
1.0	0.0450	2.34	16.74				
				8	0.0445	2.32	16.51
2.0	0.0455	2.37	16.95				
4.0	0.0460	2.40	17.17	16	0.0465	2.42	17.67
8.0	0.0465	2.42	17.39				
				32	0.0485	2.53	18.92
16.0	0.0470	2.45	17.62				
Polyvinylchloride							
0.5	0.0320	1.00	11.18				
				2	0.0305	0.95	10.67
1.0	0.0360	1.13	12.63				
				4	0.0292	0.91	10.22
2.0	0.0310	0.97	10.90				
				8	0.0320	1.00	11.18
4.0	0.0327	1.02	11.52				
				16	0.0315	0.98	11.24
8.0	0.0330	1.03	11.65				
				32	0.0350	1.09	12.78
16.0	0.0335	1.05	11.86				
				64	0.0405	1.27	15.24
32.0	0.0340	1.06	12.06				
64.0	0.0345	1.08	12.25				

PS, PVC and PET. The bead value of PS was taken [45] as 52.07. Between different cooling rates and at a constant heating rate of 8° min^{-1}, the ΔC_p values showed a variation of 2.32–2.45 cal deg^{-1} (mole of beads)$^{-1}$ (see Table 6), agreeing well with eqn. (16). But the $\Delta C_p \times T_g$ values were in the range 16.51–17.62 cal g^{-1}, greatly different from those suggested by relation of Simha and Boyer [43,44]. Wunderlich's data [42] were taken and inserted in eqn. (17). The $\Delta C_p \times T_g$ and ΔC_p values thus calculated were 19.10, 20.64 and 18.51 cal g^{-1} and 2.92, 3.12 and 2.71 cal deg^{-1} (mole of beads)$^{-1}$, respectively, for the various T_g and ΔC_p values used. Thus, the values agree well with eqn. (16) but deviate markedly from those derived from eqn. (17).

The values of T_g and ΔC_p reported by Richardson and Savill [27] for PS were also substituted into the two relationships, eqns. (16) and (17). For the values of T_g and ΔC_p considered, the ΔC_p and $\Delta C_p \times T_g$ parameters are calculated as 3.80, 3.74, 3.59 and 3.44 and 27.08, 26.73, 25.64 and 24.55, respectively. Thus the results obey eqn. (17) but do not fit eqn. (16).

The previously reported values [25] of ΔC_p and T_g for PVC were 0.068, 0.0710 and 0.0661 cal deg^{-1} g^{-1}, corresponding to T_g values of 355, 352 and 343 K. Employing these data, the calculated ΔC_p (cal deg^{-1} (mole of beads)$^{-1}$) and $\Delta C_p \times T_g$ (cal g^{-1}) values were 2.15, 2.22 and 2.07 and 24.14, 24.99 and 22.67, respectively. Thus the reported values agreed well with both eqn. (16) and eqn. (17). The present work (Table 6) shows that in the case of PVC, both parameters are low compared to the values theoretically expected. The bead value taken for PVC was 31.25 [45]. One possible explanation for the low values of ΔC_p (cal deg^{-1} g^{-1}) for PVC is that in the present investigation the samples were cooled to 309 K, whereas the previous work involved quenching of the samples. Molecular motions are not frozen out at 309 K to the same extent as they are at the quenching temperatures, resulting in different heat capacities.

Using 38.54 as the bead value for PET [42,45] 348.0 K as the T_g value (heating rate, 4° min^{-1}; cooling rate, 0.5° min^{-1}) and 0.034 cal deg^{-1} g^{-1} for ΔC_p, the values obtained from relations (16) and (17) were 1.30 and 11.83, respectively. As in the case of PVC, there is a large deviation from both empirical equations (16) and (17).

The Lewis and Hayes relations

Lewis [46] and Starkweather [47] gave the following two relationships, which form the basis of a method for estimating the activation energy $\Delta H\text{a}$ for the glass transition process

$$\Delta H\text{a} = (46.4T_g - 955)/(1.043 - 2.35 \times 10^{-3}T_g) \tag{18}$$

for sterically restricted polymers and

$$\Delta H\text{a} = (77.6T_g - 3030)/(0.94 - 1.55 \times 10^{-3}T_g) \tag{19}$$

for sterically unrestricted polymers. On the basis of the Lewis equation, and using the T_g value 362.2 K for PS (Table 2), the ΔHa value was calculated as 80.53 kcal mol^{-1}, indicating that PS is a sterically restricted polymer in agreement with conclusions drawn from dielectric studies [48]. Following a similar procedure for PVC, a ΔHa value of 73.16 kcal mol^{-1} ($T_g = 344.2$ K, from Table 2) was calculated, agreeing well with the previously reported value of 70 kcal mol^{-1}. Finally, PET was found to have a ΔHa value of 62.53 kcal mol^{-1}, indicating that it is a sterically restricted polymer ($T_g =$ 343.9 K, from Table 2).

The cohesive energy density (CED) can be calculated on the basis of the Hayes [49] relation

$$Hc = 0.5nRT_g - 25n \tag{20}$$

where Hc is the CED and n is a number, usually in the range 25–75, which is analogous to the degrees of freedom in expressions of kinetic energy. Using the same T_g values for PS, PVC and PET as were used in the Lewis equation, the CED values were calculated as 7701, 5071 and 14,440 cal, respectively, agreeing well with the previously reported values of 8090, 5380 and 14,250 cal. Thus, the value for PS is greater than that for PVC, which is a much more flexible polymer, but it is lower than that for PET, which is a semi-crystalline polymer. Furthermore, the CED values are in phase with the stiffness parameter reported elsewhere in solution property studies.

Thermodynamic parameters

The Prigogine–Defay ratio

When a liquid at equilibrium solidifies to a glass the second derivatives of the isobaric heat capacity C_p, the coefficient of thermal expansion α, and the isothermal compressibility β show discontinuities. The behaviour of these thermodynamic quantities along the line of transition is described by the Ehrenfest [21] relations

$$\mathrm{d}T_{tr}/\mathrm{d}P = \Delta\beta/\Delta\alpha \tag{21}$$

$$\mathrm{d}T_{tr}/\mathrm{d}P = TV\Delta\alpha/\Delta C_p \tag{22}$$

where T_{tr} is the transition temperature and represents the discontinuity. For the case in which a single order parameter together with T and P is sufficient to specify the state of the system, Prigogine and Defay [50] showed that the following condition must hold

$$\pi \equiv \Delta C_p \Delta\beta/TV(\Delta\alpha)^2 = 1 \tag{23}$$

where π is the Prigogine–Defay ratio. From the ΔC_p values obtained in the present study, together with data from McKinney and Simha [51] and Goldstein and co-workers [52–55], the value of π is 2.6 for PS and 1.55 for PVC. Hence the description of the glass transition process for PS and PVC must involve a number of order parameters; the microscopic significances of the order parameters are at present not unambiguously specified, but they may correspond to such things as the number of "holes", the number of "flexed bonds", etc. Owing to a lack of sufficient data, calculation of π for PET is not yet possible.

The Adam and Gibbs theory

Some difficulties arise from a purely kinetic view of the glass transition phenomenon. Kauzmann [56] showed that if the thermodynamic behaviour observed experimentally in material above its T_g is extrapolated through and below the T_g value in order to obtain the supposed equilibrium behaviour at these lower temperatures, absurd results such as negative entropies are obtained. Gibbs and DiMarzio [19] and Gibbs [57] resolved the "thermodynamic catastrophies" of Kauzmann and showed that at T_2 (the thermodynamic second-order transition temperature), the configurational entropy change vanishes. Below T_2, the configurational entropy remains, of course, zero rather than going to meaningless negative values. But the theory failed to provide a satisfactory relation between T_g and T_2. Such a type of relation was, however, developed by Adam and Gibbs [22] employing the molecular kinetic theory.

The Adam–Gibbs relation

$$T_g/T_2 = \exp\left[\left(T_g/C_2'\right) - 1\right]^{-1} \tag{24}$$

was employed to estimate T_2. With T_g as 371.1 K (8° min^{-1} heating and 0.5° min^{-1} cooling) and C_2' equal to 50° [33], T_g/T_2 was found to be 1.17 for PS. This agrees reasonably well with the Adam–Gibbs theoretical predictions

$$T_g/T_2 = 1.30 \pm 8.4\% \tag{25}$$

$$T_g - T_2 = 55 \pm 10.9\% \tag{26}$$

The value of $T_g - T_2$ obtained for PS is 53.9 K: thus, T_2 lies approximately 53.9 K below the observed value of T_g.

From the Adam–Gibbs theory [22] it is also possible to calculate $\Delta\mu$ (the potential energy hindering the cooperative rearrangement per monomer segment) by using the equation

$$\Delta\mu s_c^*/k = C_1' T_g \Delta C_p(T_g) \log T_g/T_2 \tag{27}$$

where s_c^* is the critical configurational entropy which is given by $s_c^* = k \ln 2$. By using the $\Delta C_p(T_g)$ value obtained in our experiments (0.0445 cal deg^{-1} g^{-1}) and the C_1' value reported in the literature (13.7°) [33], $\Delta\mu$ was calculated as 2.31 kcal deg (mole of segments)$^{-1}$ for PS.

Using the T_g value for PVC of 349.4 K (heating rate, 8° $\min^{-1}$; cooling rate, 0.5° $\min^{-1}$), the C_1' value of 17.44° [33], the C_2' value of 51.6° [33] and the $\Delta C_p(T_g)$ value of 2.00 cal $\deg^{-1}$ mole^{-1}, T_2 was calculated as 296.1 K and $\Delta\mu$ as 1.3 kcal deg (mole of segments)$^{-1}$. In the case of PET, the application of the Adam–Gibbs relation [22] (eqn. (24)), led to a T_g/T_2 ratio of 1.19, in good agreement with the theoretical predictions of eqn. (25). The T_g value used for the calculation was 348.0 K (heating rate, 4° $\min^{-1}$; cooling rate, 0.5° $\min^{-1}$) and C_2' was taken as 51.6° [33]. In order to derive $\Delta\mu$ using the eqn. (27), $\Delta C_p(T_g)$ was taken as 0.034 cal $\deg^{-1}$ g^{-1} and C_1' as 17.44° [19]. $\Delta\mu$ is of the order of 4.3 kcal deg (mole of PET segments)$^{-1}$.

The reported values of flexing energy for PS and PVC were 1.43 and 1.16 kcal (mole of segments)$^{-1}$, respectively. These values clearly show that the energy needed for the monomeric units in the PS molecule to go from one conformation to the other is greater than that needed in the case of PVC. From the present results, the $\Delta\mu$ values are in the order PET > PS > PVC. Taking into account the molecular architecture of these polymers, it is evident that, due to the presence of *p*-phenylene units in the backbone of PET, $\Delta\mu$ should be greater for PET than for either PS or PVC. These results show that the structure–property relationship can be estimated from Adam–Gibbs theory.

CONCLUSIONS

All of the kinetic and thermodynamic parameters calculated for PS, PVC and PET from C_p–T measurements in the glass transition temperature region are listed in Table 7. From the foregoing results and discussion we arrive at the following conclusions.

(i) The theoretical prediction of Ferry that $d\Delta T_g/d \log a_T \approx 3°$, derived on the basis of the WLF equation, agrees remarkably well with the experimental results.

(ii) The variation in the E_h values with increasing heating rate indicates that the size of the rearranging moiety is itself varying with heating rate.

(iii) The E_j values calculated following Wunderlich's procedure, the $\Delta h1^*$ parameter calculated using Moynihan's method and the E value calculated from the equation of Barton and Critchley agree well with one another in the cases of PS and PVC, proving the basic soundness of these various approaches. In other words, a definite amount of energy is required for the formation and destruction of particular structural units, usually identified as holes or free volume.

(iv) The increase in $\Delta h2^*$ values with increased heating rates, calculated on the basis of a modified version of Moynihan's treatment, were found to be of the same order of magnitude as E_j, $\Delta h1^*$ or E for PS and PVC. Thus

TABLE 7

Overall comparison of various kinetic and thermodynamic parameters for the glass transition process in the three polymers studied

Theory	Parameter	PS	PVC	PET
Ferry [33]	$\frac{\mathrm{d}\,\Delta T_g}{\mathrm{d}\log a_T}$	2.44	2.68	2.63
Wunderlich et al. [10], Wrasidlo [25]	E_h (cal mol^{-1})	2,131	2,019	1,993
	E_j (kcal mol^{-1})	28.2	26.9	–
Moynihan et al. [34]	$\Delta h1^*$ (kcal mol^{-1})	28.2 ± 0.6	27.8 ± 0.6	–
	$\Delta h2^*$ (kcal mol^{-1})	291.0 ± 3.0	241.7 ± 2.1	216.1 ± 0.6
Barton and Critchley [41]	E (kcal mol^{-1})	34.25	32.90	–
Wunderlich [42]	ΔC_p (cal deg^{-1} (mole of beads)$^{-1}$)	2.32–2.53	0.91–1.27	1.30
Simha and Boyer [43,44]	$\Delta C_p \times T_g$ (cal g^{-1})	16.51–17.62	10.22–15.24	11.83
Lewis [46]	ΔHa (kcal mol^{-1})	80.53	73.16	62.50
Hayes [49]	CED (cal)	7701	5071	14,440
Prigogine and Defay [50]	π	2.60	1.55	–
Adam and Gibbs [22]	T_g/T_2	1.17	1.18	1.19
	$T_g - T_2$	53.9	53.3	55.6
	$\Delta\mu$ (kcal deg (mole of segments)$^{-1}$)	2.31	1.30	4.30
Stiffness parameter [58]	σ	2.20	2.08	1.20–1.40

all the current kinetic theories exhibit very subtle similarities, a conclusion which has previously not been reported in the literature.

(v) The potential energy barrier hindering molecular motions was calculated to be highest for PET, intermediate for PS and lowest for PVC. Furthermore, the Adam–Gibbs predictions about the value of T_2 have been tested and found to be correct.

ACKNOWLEDGEMENTS

We thank Dr. Ramasamy (Chemplasts) and Dr. Subbaraman (I.O.C.L.) for providing PVC and PET samples, and Professor M.J. Richardson for providing the basic details needed for the computer programming. Thanks are also due to Professors B. Wunderlich, R.F. Boyer, R. Simha, C.T. Moynihan and M. Goldstein and Dr. N.S. Viswanathan for sending innumerable reprints pertaining to the glass transition phenomenon. One of us (C.T.V.) thanks the U.G.C., New Delhi, India for the award of a Junior Research Fellowship.

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