Relationships between melting temperature, maximum crystallization temperature and glass transition temperature

Norimasa Okui
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguroku, Tokyo, Japan

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Empirical prior rules in melting temperature, T_m, maximum crystallization temperature, T_{cmax}, at which crystal growth rate is maximum, and glass transition temperature, T_g, were investigated to find a phenomenological and theoretical background. Relationships among T_m, T_{cmax} and T_g were formulated as $T_{cmax}/T_m = C/(C+1)$ and $T_g/T_m = (C-1)/(C+1)$ on the bases of an iso-volume state model and a crystallization theory. In general, C varies from 3 to 9 and the mean value is about 5. That is, the ratio of T_g/T_m changes from 1/2 to 4/5 and the mean value is 2/3. The ratio of T_{cmax}/T_m changes from 3/4 to 9/10 and the mean value is 5/6.

(Keywords: melting; glass transition; crystallization; temperature; iso-volume)

INTRODUCTION

There are many characteristic temperatures commonly observed on a mechanical relaxation spectrum, d.s.c. and other methods. Such characteristics are melting temperature (T_m), glass transition temperature (T_g), β-relaxation temperature (T_β), liquid–liquid relaxation temperature ($T_{l,l}$), crystalline dispersion temperature ($T_{\alpha c}$) and maximum crystallization temperature (T_{cmax}) at which crystal growth rate is maximum. Also, there are second order transition (T_2) predicted by Gibbs–DiMarzio theory[1] and the temperature at which a free volume is zero (T_0). Although they are hypothetical temperatures, T_0 is identical with T_2. Among these characteristics, there are several empirical rules. For example, the ratio of T_{cmax}/T_m shows an almost constant value for a wide variety of materials[2–5] including metals, inorganic substances, organic compounds and polymers. Experimental results of T_{cmax}/T_m reported in the literature for many polymers have been summarized by Godovskii[3], where T_{cmax}/T_m (in K) lies between 0.82–0.83. This relationship has been pointed out first by Mandelkern *et al.*[3]. Constancy of the ratio T_g/T_m is also widely known as Boyer–Beaman rule[6,7]. Boyer classified polymers into two groups as symmetrical and unsymmetrical. However, in an extensive study of 132 polymers, there is no sharp division between the ratios of T_g/T_m observed for symmetrical polymers and those for unsymmetrical polymers and the average value for all polymers is about 2/3 (ref. 8). It is interesting to note that the ratio of T_g/T_m is found to be about 2/3 not only for polymers but also for inorganic substances[7,9] and organic compounds[7,10]. Moreover, a similar relationship between T_{cmax} and T_g is found as $T_{cmax}/T_g = 1.25–1.33$ (refs 11, 12). According to the above empirical rules, $2T_{cmax} = T_g + T_m$ was found by van Krevelen[10]. This means that T_{cmax} appears in the middle of T_m and T_g.

It is also interesting to note that the ratio of T_β/T_g shows the constant value of 0.75 (ref. 13) and T_0/T_g is about 0.77–0.80 (refs 14, 15). Thus it might be thought that T_β appears at almost the same temperature range as T_0. In addition, the ratio of $T_{l,l}/T_g$ is also found to be about 1.2 (ref. 13), which coincides with the value of $T_{\alpha c}/T_g$ or T_{cmax}/T_g. This may suggest that there is some correlation between the molecular motion at $T_{l,l}$ in the amorphous state and $T_{\alpha c}$ in the crystalline state. These characteristic temperatures may be based on a similar mechanism associated with large molecular motions in the amorphous or crystalline states.

According to the above empirical rules, the following interesting relationship can be derived.

$$T_g - T_0 = T_{cmax} - T_g = T_m - T_{cmax} \qquad (1)$$

This means that each characteristic temperature appears at the same temperature intervals. Although these relationships come from totally empirical backgrounds, these characteristic temperatures could be highly intercorrelated. The purpose of the present paper is to find a phenomenological and theoretical background to the relationships between T_m, T_g and T_{cmax}.

PHENOMENOLOGICAL ASPECTS

First it is necessary to consider the background of these temperatures. T_m is the thermodynamic equilibrium temperature and T_{cmax} and T_g are the temperatures based on kinetics. Temperature dependence of crystal growth rate (G) shows that the G increases as temperature decreases from T_m and passes through the maximum value (G_{max}) at some intermediate temperature (T_{cmax}) and subsequently decreases. That is, only one T_{cmax} is found in each polymer and T_{cmax} shows no time dependence. On the other hand, T_g shows obvious time dependence, however, such dependence could be assumed to be small. Therefore the relationships between T_m, T_{cmax} and T_g are worthy of further consideration without time dependence.

In order to find a phenomenological clue to the relationships between T_m, T_{cmax} and T_g, consider the thermal expansion model shown in *Figure 1*. The

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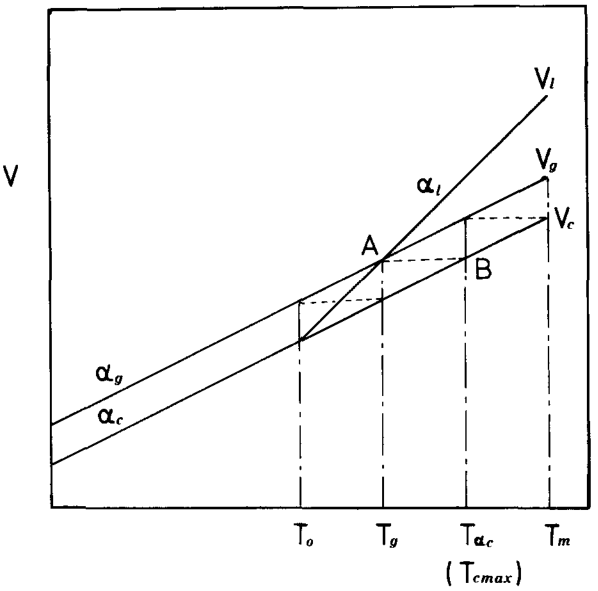

Figure 1 Schematic illustration of molar volume relations and relationships among several characteristic temperatures based on an iso-volume state model. Relationship between A and B represents one of the iso-volume state. V and α are the molar volume and the thermal expansion coefficient, respectively. Subscripts g, c and l denote, respectively, glassy, crystalline and supercooled liquid states

volume–temperature curves for glassy state (V_g) and crystalline state (V_c) are assumed to be straight lines with slopes of α_g and α_c, respectively. The straight line with slope of α_l can be drawn above T_g for undercooled liquid V_l (ref. 16). Intersections of V_l line with the V_g and the V_c lines give, respectively, the temperatures of T_g and T_0. It is widely known that T_g represents a frozen-in process of large molecular motions in an amorphous state or an iso-free volume state. Here, an iso-volume state model is proposed instead of an iso-free volume state model in order to find some rules in the above characteristic temperatures. The iso-volume state is defined when a molar volume in a glassy state at T_1 is equal to one in a crystalline state at T_2: $V_g(T_1) = V_c(T_2)$. In the iso-volume state, it is assumed that certain relaxation/transition temperatures are found both at T_1 in an amorphous state and at T_2 in a crystalline state. For example, if T_1 is assumed to be T_g at which a motion of a large number of sections of a polymer chain occurs in an amorphous state, such a large molecular motion may likewise arise at T_2 in a crystalline state. That is, T_2 could be thought of as a crystalline dispersion temperature $T_{\alpha c}$. The $T_{\alpha c}$ depends on the frequency because $T_{\alpha c}$ is an activated process. However, $T_{\alpha c}/T_m$ is found to be a constant with values of 0.82–0.83 at very low frequencies[13]. It is interesting to note that the ratio of $T_{\alpha c}/T_m$ is almost equal to that of T_{cmax}/T_m. This means that the maximum crystal growth rate occurs in the vicinity of $T_{\alpha c}$. Kinetic characteristics of T_{cmax} and $T_{\alpha c}$ may originate in the similar process associated with large molecular motions. Extrapolation of V_g at T_g to the V_c line holding the iso-volume state gives an intercept $T_{\alpha c}$ and T_m which is represented in the iso-volume state with V_g at $T_{\alpha c}$ as seen in *Figure 1*. From the geometrical relationship in *Figure 1*, the following relationships are found.

$$(T_g - T_0) = (\alpha_c/\alpha_g)(T_{cmax} - T_g) = (\alpha_c/\alpha_g)^2(T_m - T_{cmax}) \quad (2)$$

In the iso-volume state, α_l is expressed as $\alpha_l = \alpha_g + \alpha_c$. Here, the experimental data suggest that α_c is almost equal to α_g and the ratio of α_l/α_g is approximately 2 (refs 10, 17). This suggests that each characteristic temperature appears at the same temperature intervals. This is in accord with the relationship given by equation (1).

THEORETICAL ASPECTS

The ratio of T_{cmax} to T_m has been formulated previously as equation (3)[4] on the basis of a crystallization theory.

$$T_{cmax}/T_m = C/(C+1) \quad (3)$$

$$C = \sqrt{1 + \Delta E/K} \quad (4)$$

where ΔE is the activation energy of migration through the nucleus-melt interface and K is the nucleation parameter associated with the mean surface energy ($\bar{\sigma}$) and the heat of fusion (ΔH_m): $K = n\bar{\sigma}^2/\Delta H_m$, $\bar{\sigma} = (b_0\sigma_e\sigma_u)^{1/2}$ where n is a parameter of a mode of nucleation, b_0 is the thickness of the depositing growth layer and σ_e and σ_u are the end and the lateral surface energies, respectively. The greater the ratio of $\Delta E/K$ the greater is the ratio of T_{cmax}/T_m. However, a large variation in $\Delta E/K$ in its high value regions causes little change in T_{cmax}/T_m as seen in *Figure 2*. The minimum value of C is 1 when the activation energy ΔE is zero, that is, the minimum ratio of T_{cmax}/T_m is 1/2. The average value of $\Delta E/K$ is about 23 ($C = 4.9$) in most polymers[4]. Then T_{cmax}/T_m yields 0.83 which fits very well with the value reported by Godovskii[3] and Mandelkern *et al.*[2]. In general, C varies from 3 to 9 (ref. 4) and the mean value can be approximated to roughly 5. Combination of equations (2) and (3) leads to the following equation.

$$T_g/T_m = (C - \alpha_c/\alpha_g)/(C+1) \quad (5)$$

If the ratio of α_c/α_g is assumed to be 1,

$$T_g/T_m = (C-1)/(C+1) \quad (6)$$

The ratio of T_g/T_m changes from zero to 1 as seen in *Figure 2*. This means that the distribution in T_g/T_m is much larger than that in T_{cmax}/T_m. In fact, the plots of T_g against T_m show large distribution as seen in *Figure 3*

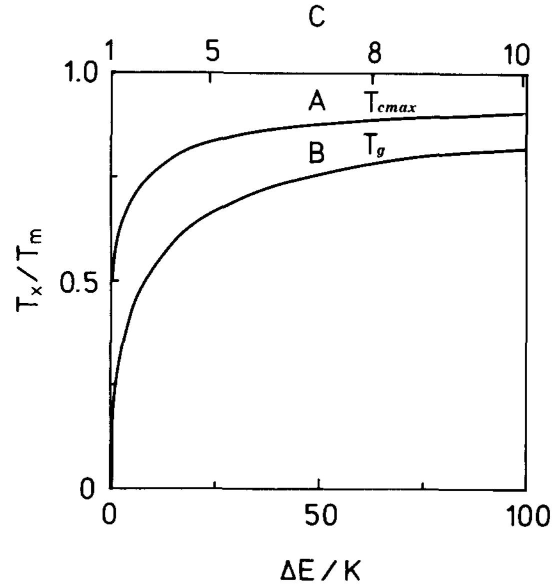

Figure 2 Plots of the ratios of T_{cmax}/T_m (curve A) and T_g/T_m (curve B) against C and $\Delta E/K$. C is a function of the ratio of the activation energy for transport (ΔE) to the nucleation parameter (K): $C = (1 + \Delta E/K)^{1/2}$

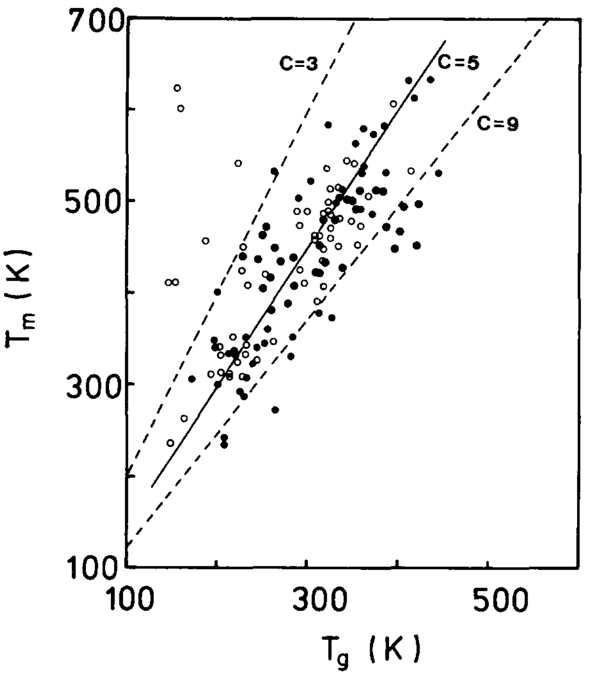

Figure 3 Relationship between T_m and T_g. The ratio of T_g/T_m varies in the range of 1/2–4/5 ($C=3$–9) with the average value of 2/3 ($C=5$) for symmetrical (○) and unsymmetrical (●) polymers. The figure is based on data from references 6 and 8

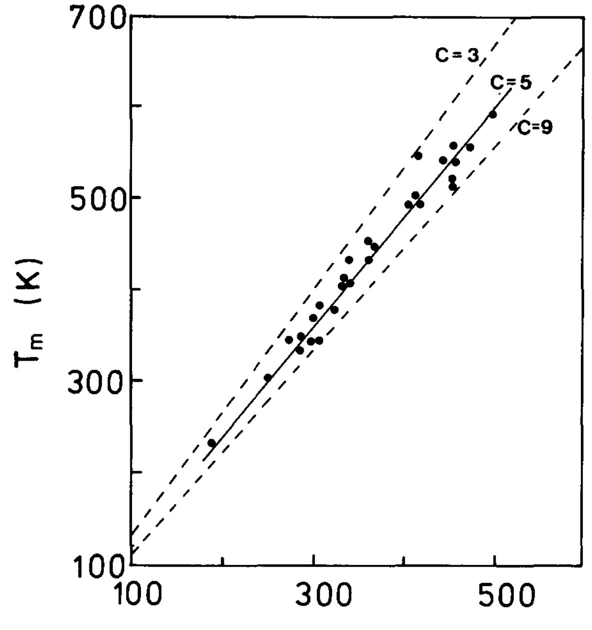

Figure 4 Relationship between T_m and T_{cmax}. The ratio of T_{cmax}/T_m varies in the range 3/4–9/10 ($C=3$–9) with the average value of 5/6 ($C=5$) for common polymers. The figure is based on data from references 2–4

in contrast to the relationship between T_{cmax} and T_m as seen in *Figure 4*. However, most of the experimental data in both figures lie in the range of $C=3$–9. In addition, the ratio of T_0/T_g could be expressed as $T_0/T_g=(C-2)/(C-1)$ and its mean value could be calculated as 3/4, because the mean value of C is 5. This value is also in accord with the reported values[14,15].

ΔE may be compared with the activation energy for viscous flow or self-diffusion of molecules which could be a measure of chain mobility. ΔH_m could be thought of as a measure of intermolecular forces. $\bar{\sigma}$ may affect the degree of crystallizability of polymers. These three parameters in C could be expressed by cohesive energy, chain stiffness and geometry. And T_m is affected by intermolecular forces, chain stiffness and geometry. T_g is also related to cohesive energy, chain stiffness and geometry. Thus, the ratios of T_g/T_m and T_{cmax}/T_m will be expressed adequately as a function of C.

CONCLUSIONS

Relationships between T_m, T_{cmax} and T_g were formulated as $T_{cmax}/T_m=C/(C+1)$ and $T_g/T_m=(C-1)/(C+1)$ on the basis of an iso-volume state model and a crystallization theory. C is a function of the activation energy of migration, the surface energy and the heat of fusion. In general C varies from 3 to 9 and the mean value is about 5. That is, the ratio of T_g/T_m changes from 1/2 to 4/5 and the mean value is 2/3. The ratio of T_{cmax}/T_m changes from 3/4 to 9/10 and the mean value is 5/6. Thus estimated variations in the ratios correspond well to the fact that the experimental data of T_g/T_m are more widely distributed in nature than those of T_{cmax}/T_m.

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