Universal relation for polymer crystallization rates from the melt

Valery P. Privalko
Institute of Macromolecular Chemistry, Academy of Sciences of the Ukrainian SSR, 252160 Kiev, USSR
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Analysis of spherulitic growth rate data for a number of linear polymers has shown that the temperature at maximum growth rate, T^*, is related to the glass transition temperature, T_g, through the empirical equation, $T^* = 1.26\,T_g$. The universal master curve for the temperature dependence of the growth rate of crystals from the melt in reduced Gandica–Magill coordinates, $\ln(G/G^*) = f(T - T_\infty)/(T_m - T_\infty)$, is possible only on the condition that the following empirical equation holds: $0.26 = T_\infty/T_g - T_\infty/T_m$. Finally, limits of variation of the 'conformational' contribution to the excess entropy, and of the free volume fraction at T^* were evaluated for some polymers.

INTRODUCTION

The temperature dependence of polymer crystallization rates from the melt, G, generally obeys the following bi-exponential equation:

$$G = G_0\exp(-\Delta F/kT)\exp(-\Delta E/kT) \qquad (1)$$

where the first exponential term accounts for the probability of formation of a critical size crystallization nucleus, the second refers to the probability of a transport across the melt–crystal interface, ΔF and ΔE are the values of energetic barriers for the corresponding processes, k is Boltzmann's constant, T is temperature and G_0 is the pre-exponential term. Equation (1) predicts the increase of G from a zero value at $T = T_m$ to a maximum value G^* at some intermediate temperature T^*, and a subsequent gradual decrease to zero at $T = T_g$(here T_m and T_g are polymer melting and glass transition temperatures, respectively), which is in good agreement with experimental data (see plots of spherulitic crystallization rate vs. temperature for a number of polymers in *Figure 1*, which were constructed from data presented in papers[1–6]). In the literature one can find many attempts to relate T^* to temperatures of other thermal transitions. As an example, we may refer to an empirical relation[1,7–9]:

$$T^* = (0.82 - 0.85)T_m \qquad (2)$$

which was found to be in satisfactory agreement with the majority of available experimental data. A more general approach was proposed in a recent paper by Gandica and Magill[10]. Starting from the premise that all crystallizable polymers are in the 'corresponding states' at their T^* temperatures, these authors obtained the 'universal' master curve of temperature dependence on spherulitic growth rates for a limited number of polymeric and low molecular weight liquids in reduced coordinates:

$$\ln(G/G^*) = f(T - T_\infty)/(T_m - T_\infty) \qquad (3)$$

where $T_\infty = T_g - 50\text{K}$[10] is the temperature corresponding to the disappearance of a liquid free volume or excess entropy. It was also observed[10] that the numerical value of the dimensionless ratio:

$$(T^* - T_\infty)/(T_m - T_\infty) = X \qquad (4)$$

equals 0.63 ± 0.01 and 0.84 ± 0.01 for polymeric and 'monomeric' liquids, respectively. However, when data for more polymers are treated according to equation (3), it can be shown (*Figure 2*) that they cannot be reduced to a single universal curve[11]. Moreover, the data points on the plot, $\log(T^* - T_\infty)$ vs. $\log(T_m - T_\infty)$, constructed from the data listed in *Table 1* (*Figure 3*), exhibit rather a large scatter around the 'universal' value, X = constant = 0.63 for poly-

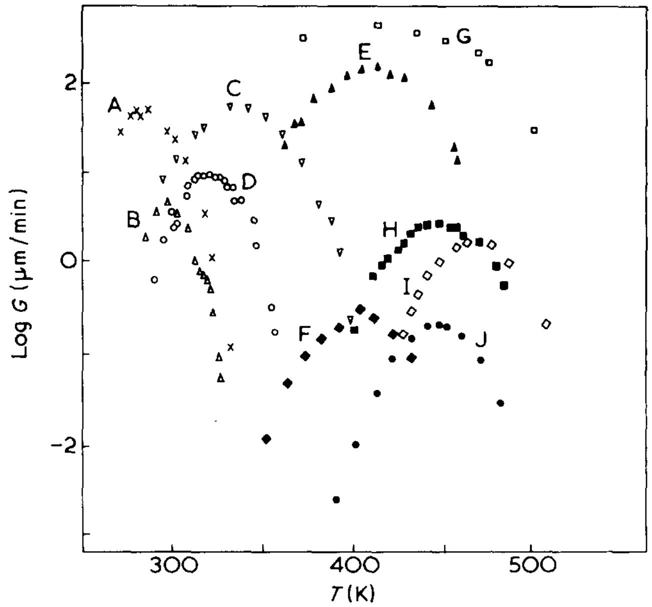

Figure 1 Temperature dependence of spherulitic growth rates from the melt. Samples nos: A, 10; B, 11; C, 1; D, 22; E, 5; F, 14; G, 6; H, 4; I, 2; J, 7

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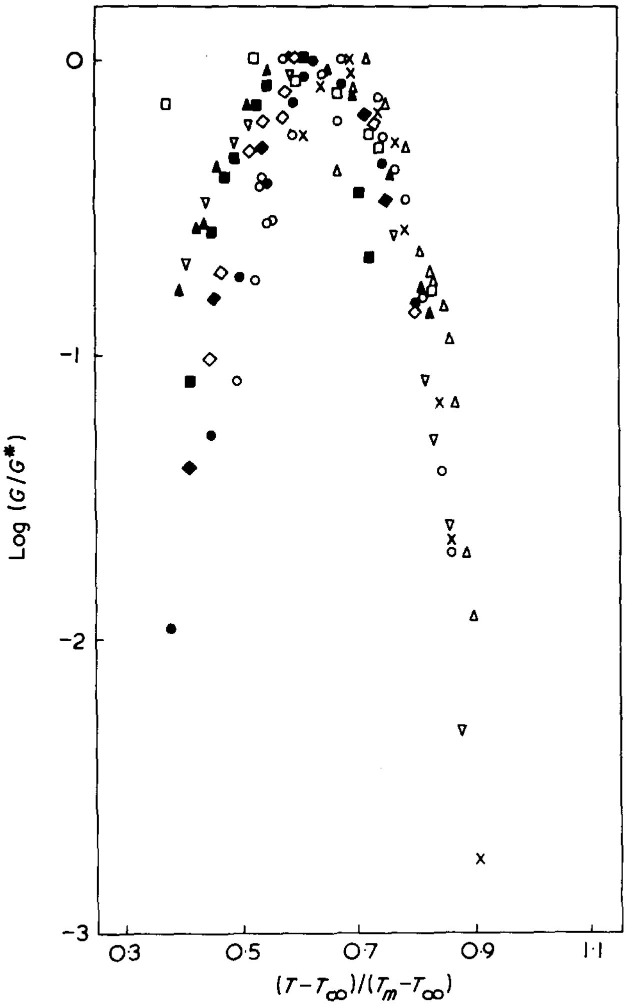

Figure 2 Treatment of the data in *Figure 1* in the reduced coordinates of equation (3). Samples: X, 10; △, 11; ▽, 1; ○, 22; ▲, 5; ◆, 14; □, 6; ■, 4; ◇, 2; ●, 7

mers (broken line in *Figure 3*). It was therefore considered useful to elucidate the origin of this failure and to propose an alternative approach to define the universal curve of temperature dependence of polymer crystallization rates from the melt.

DERIVATION AND ANALYSIS OF A NEW CORRELATION

Starting from the observation that the numerical values of the parameter X, as defined by equation (4), scatter in the same interval (i.e. 0.51 to 0.79) as the ratio T_g/T_m for the majority of polymers studied so far[9] and taking into consideration that the ratio X contains only those parameters which are related either to T_m (see equation 2 for T^*), or to T_g (as mentioned above, $T_g = T_\infty + 50\text{K}$ is assumed to apply), it may be suggested that $X = T_g/T_m$. Therefore, rewriting equation (4) as:

$$T^* = XT_m + (1 - X)T_\infty$$

and substituting $X = T_g/T_m$, we obtain:

$$T^* = T_g(1 + Y) \tag{5}$$

with

$$Y = T_\infty/T_g - T_\infty/T_m \tag{6}$$

In *Figure 4* log T^* is plotted against log T_g using the data from *Table 1*. It can be seen that the dependence of T^* on T_g in the above plot is adequately accounted for by equation (4) with $Y = 0.26$ (full line in *Figure 4*) at a standard deviation $\delta = 1.69 \times 10^{-2}$ [11]. To check the validity of our starting assumption, $X = T_g/T_m$, we have also studied equation

Table 1 Transition temperatures for polymers

No.	Polymer	T_m(K)	T_g(K)	T^*(K)	T_2‡ (K)
1	Poly(tetramethyl-*p*-silphenyl siloxane), $M_v = 2.5 \times 10^4$ (ref 10)	423	260	338	(180)
2	Poly(tetrachloro-bis-phenol adipate), $M_n = 1.9 \times 10^4$ (ref 4)	556	373	468	(300)
3	Polyacrylonitrile[b] (ref 15)	590	377	435	(255)
4	Poly(ethylene terephthalate), $M_n = 3.54 \times 10^4$ (ref 5)	557	342	448	228[c]
5	Nylon-6, $M_n = 2.5 \times 10^4$ (ref 2)	500	325	411	255[d]
6	Nylon-6,6, $M_n = 1.7 \times 10^4$ (ref 2)	545	325	414	(210)
7	Polystyrene, $M_v = 2.2 \times 10^6$ (ref 3)	515	364	450	281 (ref 37) (325)
8	Poly(butene-1)[e] (ref 8)	401	249	332	200[f]
9	Poly(pentene-1)[e] (ref 8)	368	233	300	185[g]
10	Poly(propylene oxide), $M_n = 10^4$ (ref 10)	348	201	280	162[h]
11	Poly(ethylene adipate), $M_n = 10^4$ (ref 1)	343 (ref 38)	230	298	175 (ref 40)
12	Poly(tetramethylene oxide), $M_n = 3.7 \times 10^3$	330 (ref 38)	187	–	135 (ref 41)
13	Natural rubber[e] (ref 8)	303	201	249	164 (ref 42)
14	Selenium (ref 6)	492	305	403	(215)
15	Polyurethane from hexa(methylene diisocyanate) (HMDI) and di(ethylene glycol) (ref 43)	411	275	335	238
16	Polyurethane from HMDI and tetra(ethylene glycol) (ref 43)	368	253	–	208
17	Polyurethane from HMDI and hexa(ethylene glycol) (ref 43)	343	240	306	194
18	Poly(ethylene oxide) (ref 44)	348	220	–	180
19	Polydioxolane (ref 45)	347	209	–	138[i]
20	Polydioxepane (ref 46)	296	189	–	147[j]
21	Polyoxacyclobutane (ref 47)	305	195	–	155
22	Poly(ethylene succinate), $M_w = 6 \times 10^3$ (ref 2)	381	250[k]	320	(190)
23	Polypentamer (ref 48)	293	173	–	110[l]

[a] Numbers in brackets refer to 'theoretical' values derived from equation (6); [b] growth rate data for single crystals; [c,d,f–j, l] values calculated from calorimetric data in ref 49, 50, 53, 51, 52, 45, 46, 48; [e] bulk crystallization rate data: [k] estimated by van Krevelen's procedure[9]

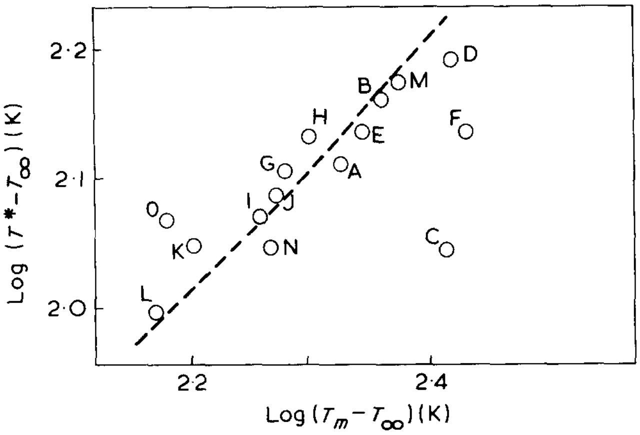

Figure 3 Dependence of log $(T^* - T_\infty)$ on log $(T_m - T_\infty)$ for the standard definition, $T_\infty = T_g - 50$K. (— — —), is drawn according to equation (4). Samples: A, 1; B, 2; C, 3; D, 4; E, 5; F, 6; G, 7; H, 8; I, 9; J, 10; K, 11; L, 13; M, 14; N, 15; O, 17

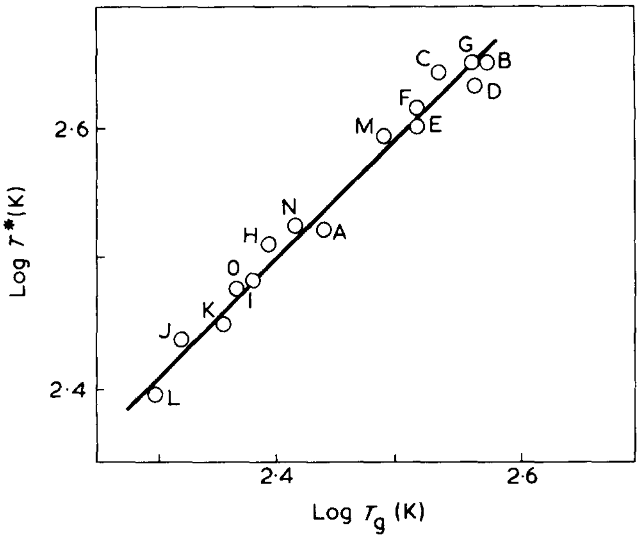

Figure 4 Dependence of log T^* on log T_g. A–N as in *Figure 3*

(6). It is appropriate here to recall that the usual definition, $T_\infty = T_g - 50\text{K}^{10}$, is very approximate, and this often calls for a more general expression, $T_\infty = T_g - C$ (where C is an adjustable parameter) to describe the temperature dependence of various transport properties of liquids[12,13], including crystallization kinetics from the melt[14–16]. Therefore, in the subsequent analysis we used the parameter T_2 from Gibbs–DiMarzio theory of the glass transition instead of T_∞[17,18], which can be accurately determined from the data of precise calorimetric measurements, and may thus be regarded as an inherent physical characteristic of a polymer.

Numerical values of T_2 in *Table 1* were either borrowed from original calorimetric works, or calculated from pertinent calorimetric data by a standard extrapolation of curves describing the temperature dependence of a liquid excess entropy ΔS_e to $\Delta S_e = 0$. As can be seen from the plot of T_2/T_g vs. T_2/T_m (*Figure 5*), there exists a rather satisfactory agreement (standard deviation $\delta = 2.6 \times 10^{-2}$) of the experimental data with equation (6) at $Y = 0.26$. This is an empirical proof of our hypothesis, $X = T_g/T_m$.

The above results suggested the possibility of construction of a single master curve for the temperature dependence of the spherulitic growth rate data for all polymers in the reduced coordinates, $\ln(G/G^*)$ vs. T/T_g. However, as is evident from *Figure 6*, notwithstanding the slight reduction of the data scatter in the temperature range below T^*, such an approach has no fundamental advantages as compared to that of Gandica and Magill (*Figure 2*), at least in the range $T > T^*$. Evidently, the reason should be sought in the different values of energetic parameters of a nucleation process, as well as those of transport acts for different polymers. To check this idea, we have calculated G theoretically using equation (1) at the following numerical values of pertinent parameters: $\Delta F/k = ZT_m/(T_m - T)$; $\Delta E/kT = 4120/(T - T_g + C)$ (ref 7) and $G_0 = 10^5$ cm/sec; $T_m = 400$K; $Z = 250$K (these figures approximately correspond to crystallization of polyethylene), as well as $Z = 50$K and $T_g = 200$, 250 and 300K. Besides, ΔE was calculated for two cases: (a) 'ideal' (i.e. $C = 50$K), and (b) 'realistic'. (Here C is not the arbitrary parameter, but obeys our equation 6 involving $T_2 = T_\infty$, T_g and T_m at $Y = 0.26$. For the chosen values of T_g = 200, 250 and 300K, this condition is satisfied at $C = 100$, 70 and 0K, respectively.)

The results of our calculations are shown in *Figure 7*, from which it is seen that the shape of the curves obtained, as well as the numerical values of T^* strongly depend on the interrelation between various parameters entering equation (1). To check theoretically equations (2), (4) and (5), we have constructed (*Figure 8*) plots of G/G^* against dimensionless ratios, $(T - T_2)/(T_m - T_2)$, T/T_g and T/T_m. As seen from *Figure 8a* for case (a), the variation of T_g/T_m leads to the splitting of curves in the region $T < T^*$, but relatively little affects X, while smaller values of Z bring about the shift of X from 0.65 to 0.82. The main contribution to Z is made by the energetic parameters of nucleation, σ and σ_e, corresponding to the free surface energies of lateral and basal (i.e. fold-containing) faces on a 'critical' nucleus. Recalling the non-existence of a 'polymeric' contribution to σ_e in the case of low molecular weight liquids, one may draw the conclusion that the observed shift of X from 0.65 to 0.82 with the decrease of the nucleation energetics parameter, Z, should be regarded as a qualitative criterion of transition to non-polymeric liquids, essentially in agreement with Magill's data[10]. However, for the more realistic case (b) we observe the shift of X from 0.6 to about 0.77 following the increase of the ratio, T_g/T_m, at constant Z and, as a

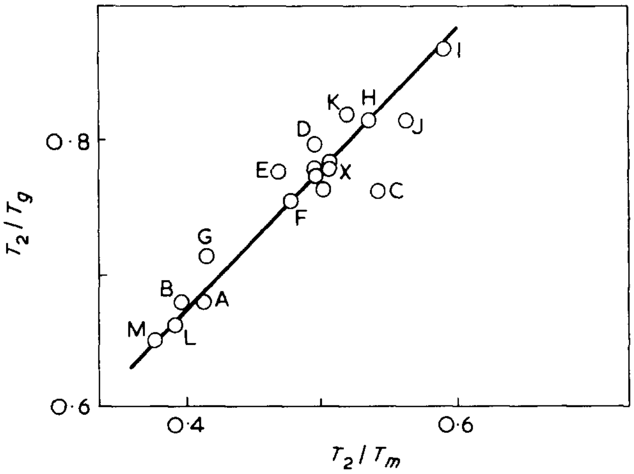

Figure 5 Dependence of T_2/T_g on T_2/T_m. Samples: A, 3; B, 4; C, 7; D, 8; E, 10; F, 11; G, 12; H, 13; I, 15; J, 16; K, 17; L, 19; M, 24

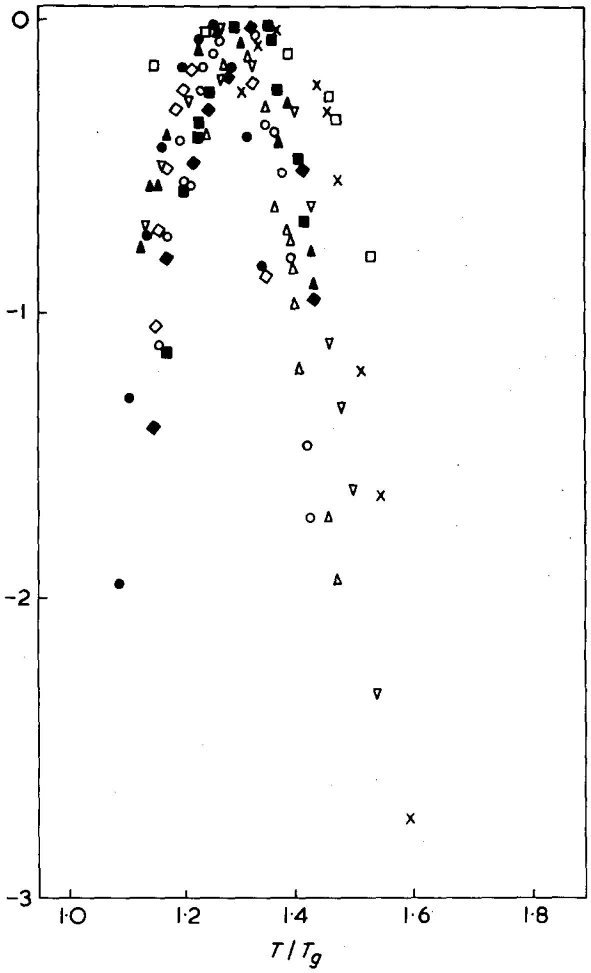

Figure 6 Treatment of the data in *Figure 1* in the reduced coordinates, G/G^* vs. T/T_g

consequence, a very large discrepancy between the curves for reduced crystallization rates. Taking into consideration the fact that for the majority of polymers studied so far, the numerical value of Z changes relatively little[19,20], one is forced to conclude that the scatter of experimental data treated according to the original Gandica–Magill scheme[10] is real. It is seen from *Figure 8b* that in case (a) the parabolic curves shift to higher values of the reducing parameter, T/T_g, and their splitting becomes more pronounced as T_g/T_m increases and Z decreases. On the other hand, in case (b) the curves (and, correspondingly, values of the ratio, T^*/T_g) become closer, the theoretical values, T^*/T_g ($\simeq$ 1.22–1.3), in the range $T_g/T_m > 0.62$ being in the same interval as experimental ones (*Figure 4*).

Finally, we note from *Figure 8c* that the ratio T^*/T_m shifts to higher values with an increase in T_g/T_m or decrease in Z, transition from case (a) to case (b) being accompanied not by convergence of the tops of parabolas but by their further divergence. In the range $T_g/T_m > 0.62$ the calculated values of T^*/T_m lie in the interval 0.74 to 0.81, i.e. they roughly conform to the empirical rule[2].

Thus, our analysis seems to show that neither dependence of those considered above, permits us to obtain the universal curve of the reduced crystallization rate as a function of reduced temperature for all polymers, although theoretically the Magill–Gandica approach is the most promising. One could therefore expect that their equation (3) will form the basis for a universal correlation, on the condition that in place of the rather poor definition, $T_\infty = T_g - 50$K [case (a)] one uses the more realistic approximation $T_\infty = T_2$ [case (b)] satisfying our equation (6) when $Y = 0.26$. The corresponding plot is shown in *Figure 9*, where we have used the values of T_2 calculated from calorimetric data, or 'theoretical' values of T_∞ conforming to the above condition. One can immediately see that this approach is superior to the one originally proposed by Gandica and Magill (compare scatter of data in *Figures 2* and *9*).

Physical meaning of the parameter T*

In a previous paragraph we obtained equation (5) which in conjunction with Y = 0.26 virtually coincides with the definition[21] of a 'universal' reference point, T_s, for liquid shear viscosities. This result is in harmony with our earlier suggestions[22,23] on the close connection between T_s and T^*. Recently, Utracki[24] came to the same conclusion. It follows that the temperature, T^*, as defined by equation (5), might be a fundamental reference point for all transport processes in polymeric liquids, whether we deal with segmental transport across the melt–crystal interface or with the viscous melt flow. It was considered therefore worth exploring the possibility of theoretically estimating the excess entropy and/or free volume fraction of polymer melts at T^* since it is these characteristics which are known to control the temperature dependence of transport processes[18,25,26]. For this purpose we made use of the equations below which were first proposed by Miller[26]:

$$(T - T_\infty)/B = T\,(\Delta S_T)_{\mathrm{conf}}/C$$

$$(T - T_\infty)/B = f_T/b$$

In the above equations B, b and C are the material constants, $(\Delta S_T)_{\mathrm{conf}}$ is the conformational part of the liquid excess entropy, and f_T is the free volume fraction at T. It follows from these equations, that:

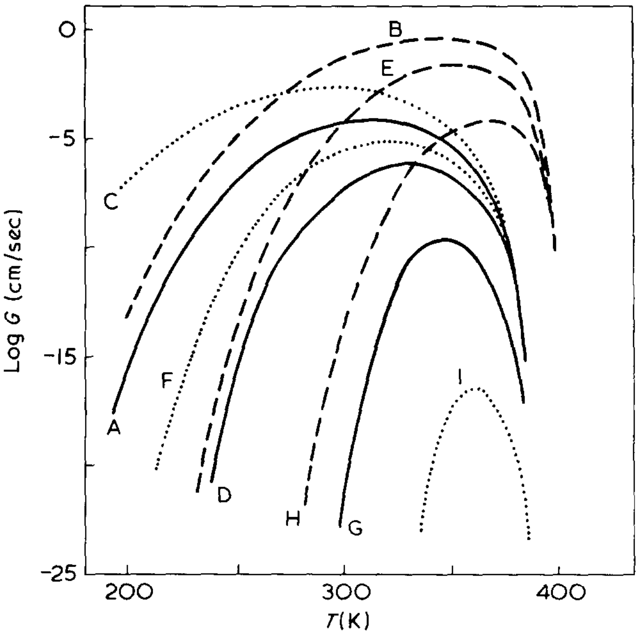

Figure 7 Theoretical dependence of spherulitic crystallization rate on temperature calculated by equation (1) with the following input parameters: $G_0 = 10^5$ cm/sec; T_m = 400K, Z = 250K (A, B, C, D, E, F); Z = 50K (A, D, G); T_g = 200K (A, B, C); 250K (D, E, F); 300K (G, H, I); T_∞ = 100K (C), 150K (A, B); 180K (F); 200K (D, E); 250K (G, H) and 300K (I)

$$\text{Constant} = (T - T_\infty)/T(\Delta S_T)_{\text{conf}} =$$

$$(T^* - T_\infty)/T^*(\Delta S^*)_{\text{conf}} = (T_m - T_\infty)/T_m(\Delta S_m)_{\text{conf}} = \ldots \quad (7)$$

$$\text{Constant} = (T - T_\infty)/f_T = (T^* - T_\infty)/f^* =$$

$$(T_g - T_\infty)/f_g = (T_m - T_\infty)/f_m = \ldots \quad (8)$$

The indices, g, $*$ and m in equations (7) and (8) refer to corresponding quantities measured at T_g, T^* and T_m. Equating, as before, $T_\infty = T_2$, one obtains from equation (7):

$$(T^* - T_2)/(T_m - T_2) = T^*(\Delta S^*)_{\text{conf}}/T_m(\Delta S_m)_{\text{conf}} \quad (9)$$

Recalling now that the left-hand side of this equation is T_g/T_m (see the preceeding paragraph), and using equation (5), we find after some rearrangements:

$$(\Delta S^*)_{\text{conf}} = (\Delta S_m)_{\text{conf}}/(1 + Y) \approx 0.8(\Delta S_m)_{\text{conf}} \quad (10)$$

Thus, we may now define the parameter T^* as a temperature at which the conformational contribution to the excess entropy of a liquid polymer is approximately 80% of the corresponding value at T_m. We also note in passing that substitution of equation (10) into the right-hand side of equation (9) makes it clear that the ratio, T^*/T_m, in general, cannot be considered as a universal constant for polymers.

Similarly, we obtain from equation (7):

$$(\Delta S_g)_{\text{conf}}/(\Delta S_m)_{\text{conf}} = 1 - Y/(1 - T_2/T_m) \quad (11)$$

which in conjunction with $T_2/T_m = 0.4$ to 0.6 (see *Figure 5*) and $Y = 0.26$ yields:

$$(\Delta S_g)_{\text{conf}}/(\Delta S_m)_{\text{conf}} = 0.36 \text{ to } 0.57$$

Gutzov[28] has found that $\Delta S_g/\Delta S_m = 0.33$ using the assumptions that T_g/T_m = constant = 0.667 and $T_2/T_m = 0.5$, while the experimental values of this ratio, $\Delta S_g/\Delta S_m$, for some polymers lie in the range 0.11 to 0.80[27].

Finally, it follows from equation (8) that:

$$(T^* - T_2)/(T_g - T_2) = f^*/f_g \quad (12)$$

which yields in conjunction with equation (5):

$$f^* = f_g[1 + Y(1 - T_2/T_g)] \quad (13)$$

Since the ratio T_2/T_g was found to vary in the range, 0.65 to 0.87 (*Figure 5*), equation (13) gives:

$$f^* = (1.72 \text{ to } 3.0)f_g$$

It is worth noting that comparison of equation (13) with an alternative definition of f^*, namely:

$$f^* = f_g + \Delta\alpha(T^* - T_g) = f_g + \Delta\alpha Y T_g \quad (14)$$

leads to:

$$T_g = f_g Z_g \quad (15)$$

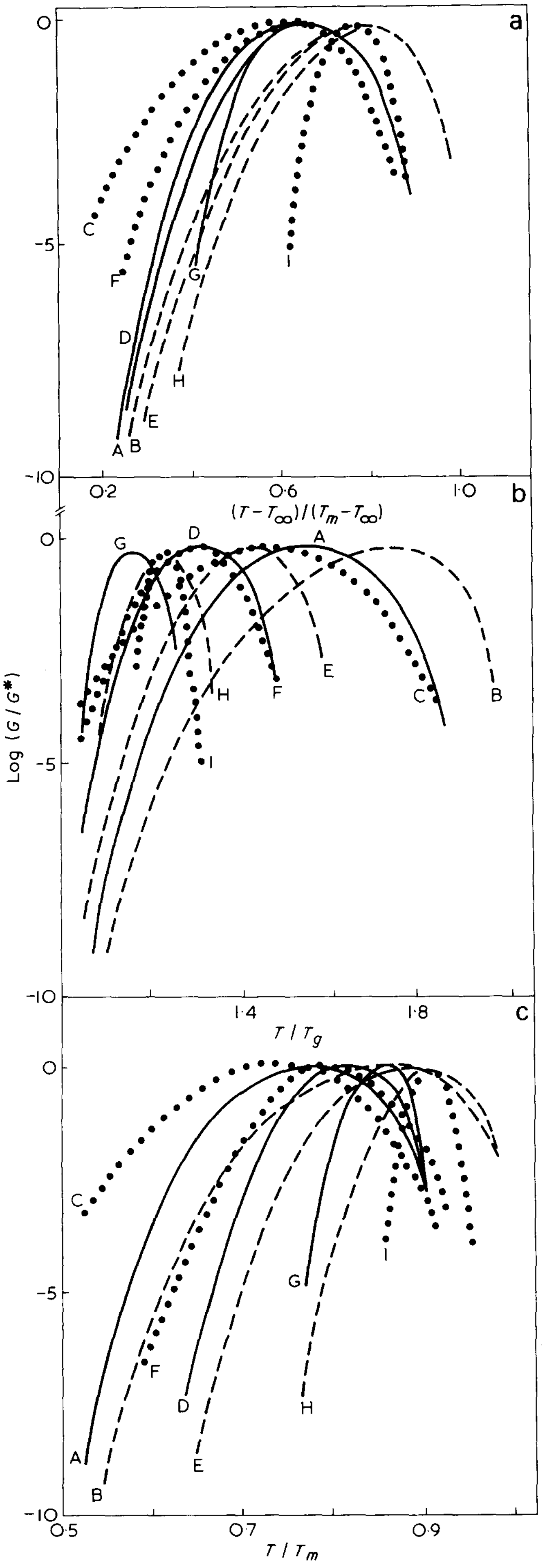

Figure 8 Dependence of the reduced spherulitic growth rate, (G/G^*), on the following ratios: (a), $(T - T_\infty)/(T_m - T_\infty)$; (b), T/T_g; and (c) T/T_m. A–I definitions as in *Figure 7*

Table 2 Values of melt specific volume, v^*, and molecular packing coefficient, $(K_a)^*$ for some polymers at T^*

Polymer	Thermal expansion coefficient of the melt $dv/dT \times 10^4$, (cm^3/g K)	Melt specific volume at temperatures 298K	T^*	V_0 (cm^3/mol)	$(K_a)^*$
Poly(ethylene terephthalate)	7.4	0.753	0.863	102.4	0.618
Nylon-6	5.6	0.927	1.004	139.2	0.617
Polystyrene	4.3	0.945	1.012	66.0	0.610
Poly(butene-1)	8.8	1.165	1.196	41.4	0.619
Poly(pentene-1)	9.2	1.174	1.193	51.6	0.621
Poly(propylene oxide)	7.0	1.000	1.010	35.2	0.612
Poly(ethylene adipate)	7.5	0.827	0.831	95.5	0.669
Natural rubber	6.0	1.096	1.080	49.3	0.672

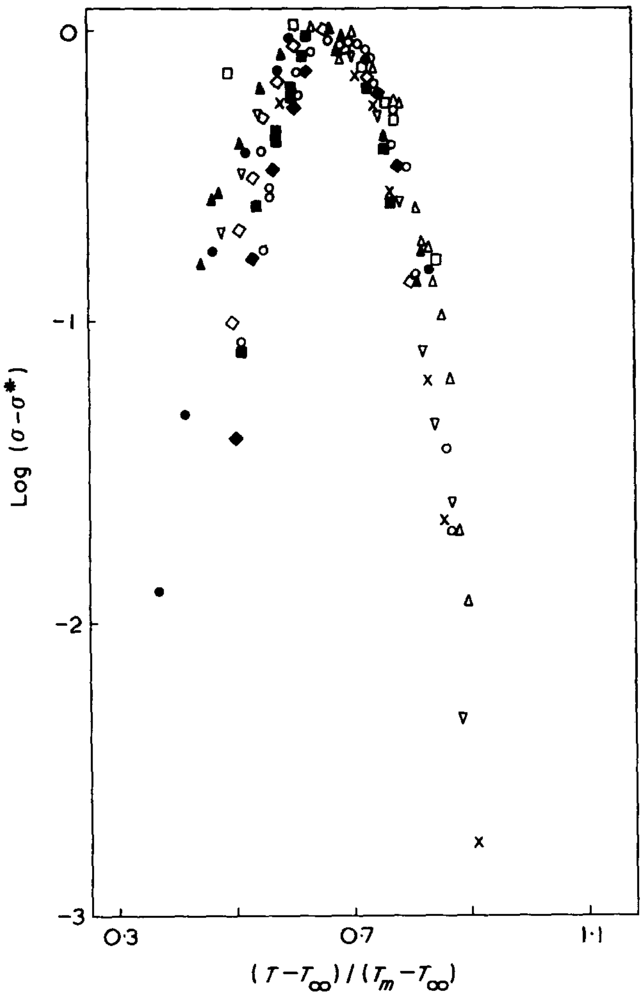

Figure 9 Treatment of the data in Figure 1 reduced coordinates of equation (3) at the values of $T_\infty = T_2$ given in Table 1

where the parameter $Z_g = (1 - T_2/T_g)^{-1}$ represents a minimum number of main chain bonds forming the regions of 'cooperative segmental rearrangements' in the Adam–Gibbs' theory[18,26]; $\Delta\alpha$ is the difference of coefficients of volume thermal expansion above and below T_g. Since the 'viscosity' free volume fraction has an apparently constant value, $f_g = 0.025$, for the majority of linear polymers[29], it follows from equation (15) that the product, $\Delta\alpha T_g$, which in the Simha–Boyer model has the meaning of a 'geometrical' free volume fraction at T_g[30,31], can in principle be constant only on the condition that the ratio T_2/T_g is constant, which is contrary to observations (Figure 5). A similar conclusion was derived earlier[32] on different grounds.

We will also consider one more definition of a 'geometrical' free volume fraction, that is[32]:

$$f'_T = 1 - (K_a)_T \tag{16}$$

where $(K_a)_T = V_0/V_T$ is the molecular packing coefficient of an amorphous polymer, V_0 is an intrinsic (van der Waals) volume of a chain repeating unit and V_T is the polymer molar volume. In Table 2 we have presented the values of $(K_a)^*$ and $(V_a)^*$ at corresponding T^* values for some polymers. It can be seen that for the majority of polymers listed in Table 2 [with the exception of poly(ethylene adipate) and natural rubber] the values of $(K_a)^*$ are very close to a seemingly constant value of about 0.615. Therefore, from equation (16) $f'^* = 0.385$. By definition:

$$(K_a)^* = (K_a)_g/[1 + \alpha(T^* - T_g)] \tag{17}$$

where α is the thermal expansion coefficient of a liquid polymer. Taking into account that $(K_a)_g \approx$ constant ≈ 0.68[32], and substituting equation (5) into (17), we obtain $\alpha T_g = 0.405$ for the case, $(K_a)^* = 0.615$, whereas the Simha–Boyer result is $\alpha T_g = 0.17$[30,31], which requires $(K_a)^* = 0.65$. We shall not pursue the question of limits of variation of $(K_a)^*$ for polymers further in view of scarcity of pertinent experimental data.

CONCLUSIONS

Our analysis of experimental data on the temperature dependence of the spherulitic growth rates for molten polymers has shown that it is possible in principle to obtain the 'universal' master curve in the reduced coordinates of equation (3), provided that the parameter T_∞ is defined by an empirical equation (6) involving T_g and T_m. The position of the temperature of maximum growth rate, T^*, on the temperature scale between T_g and T_m for polymers with $T_g/T_m < 0.62$, is adequately accounted for by equation (2) while in the case $T_g/T_m > 0.62$ better agreement is found for our equation (5)†. It can be shown that this result may be regarded as an empirical criterion of the probability of spontaneous crystallization of a liquid polymer during its slow cooling below T_m, expressed as an inequality, 0.8 $T_m >$

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† Our equation (5) is thus applicable in a broader interval than equation (2) since more than 70% of polymers studied so far possess the ratio T_g/T_m above 0.6 (ref 9).

$1.26\ T_g$ (i.e. $T_g < 0.667\ T_m$), while in the opposite case crystallization would be initiated only by quenching the polymer below T_g and subsequent heating. This conclusion stems from the experimentally observable change of liquid structure during cooling through T_m, which takes place both in low molecular weight[12,13], as well as in polymeric[33] liquids. If one assumes that in the supercooled liquids 'anticrystalline' clusters are formed[34], then it is easy to imagine the situation when molecular rearrangement in the cluster, necessary for the formation of crystallization nucleus, becomes impossible due to the drastic viscosity increase in the melting interval, as is typical for liquids with high T_g/T_m ratios (cf. the corresponding drop of G^* in *Figure 7*). Therefore, the liquid loses its capability of spontaneous crystallization during slow cooling below T_m. However, if we quench the liquid to exclude the possibility of structural rearrangements (i.e. the formation of 'anticrystalline' molecular clusters) at T_m, then on subsequent heating of the glassy sample above T_g we should expect the spontaneous formation of crystalline nuclei in the supercooled liquid state. On the other hand in those liquids having low ratios of T_g/T_m the viscosity in the vicinity of T_m is low (i.e. G^* is relatively high), and thus forms the favourable kinetic conditions for structural rearrangements in anticrystalline clusters and the formation of thermodynamically stable crystallization embryos. These arguments permit us to understand the reason for the ability of poly(2,4-methylphenylene ether) to undergo spontaneous crystallization from the melt when the ratio T_g/T_m decreases to 0.6 due to plasticizers[35], as well as the inability of 1,3,5-tri-α-naphthylbenzene to crystallize spontaneously[36] during slow cooling from the melt.

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