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Maximum crystal growth rate and its corresponding state

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SUMMARY

For the temperature dependence of linear crystal growth rate, the activation energy for the molecular transport could be expressed in terms of the equation of either WLF or Arrhenius. On the basis of the Arrhenius expression, the corresponding state of the crystal growth rate was formulated theoretically as

$$\ln(G/G_{max})/\ln(G_{max}/G_o) = (T_{cmax} - T)^2/T(T_m - T).$$

INTRODUCTION

According to a classical crystallization theory [1,2] for the temperature dependence of linear crystal growth rate (G) from melt, G is generally described by the following exponential equation.

$$G = G_o \exp(-\Delta E/RT - \Delta F^*/RT) \qquad \ldots (1)$$

where ΔE is the activation energy for migration through a nucleus-melt interface, ΔF^* is the free energy of formation of a critical nucleus size, T is a crystallization temperature and G_o and R are constants. This equation has been applied frequently to data of spherulitic growth rate for polymeric materials. In equation (1), the terms of ΔE and ΔF^* have opposing temperature dependence thereby bring about a maximum in the growth rate (G_{max}) at a temperature T_{cmax}. On the basis of G_{max} for many crystalline materials such as polymers and organic compounds, an universal master curve in G has been proposed empirically by Magill et al. [3,4] as expressed by a logarithm of G/G_{max} versus a reduced parameter $(T-T_o)/(T_m-T_o)$.

$$\ln(G/G_{max}) = f\{(T - T_o)/(T_m - T_o)\} \qquad \ldots(2)$$

where T_o is a hypothetical temperature at which the macro-Brownian motion of polymer molecules ceases and generally lies about 50K below T_g. However, in an extensive study on such universal curve for many polymers, the data can not be reduced to a single universal curve [5]. This universal master curve comes from totally empirical background. So, a purpose of the present paper is to find a theoretical background on the corresponding state in the crystal growth rate.

TEST OF WLF AND ARRHENIUS EXPRESSIONS

In a polymer crystallization from melt, ΔF^* in equation (1) is commonly expressed as $\Delta F^* = KT_m/(T_m-T)$ [2], where T_m is the thermodynamic equilibrium melting temperature. And K is the nucleation parameter expressed as $K = nb_0\sigma_e\sigma_u/\Delta H_m$ where n is a parameter of a mode of nucleation such as regime I and regime II, 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 and ΔH_m is the heat of fusion. An application to the polymer crystallization leads to that the transport term of ΔE is considerably important in the lower temperature ranges. The transport term can be expressed in terms of the equation of either Arrhenius type ($\Delta E/RT$) or WLF type ($C_1C_2/R(T-T_g+C_2)$) where C_1 and C_2 are adjustable parameters.

In analyzing the crystallization data in bulk polymers, the WLF expression has been used much familiar than the Arrhenius-type, since it has been believed that the former expression fits the data better than the later one. Meanwhile, Mandelkern et al. [6] have proposed that ΔE could be sufficiently expressed by the Arrhenius-type in the polymer crystallization and also stated that the validity of applying the WLF equation to the linear growth rate is merely a repetitive assertion not involving any direct proof of substantiation. For an example, Mandelkern et al. reported that the value of ΔE was 20.2 kcal/mol for PS. On the other hand, Suzuki and Kovacs [7]

Table 1. Values of the parameters characterizing the best fit to the data for various polymers by WLF and Arrhenius expressions.

Sample			Arrhenius		WLF		Ref.
Polymer	M_w ($\times 10^4$)	T_m/T_g (K)	ΔE (kcal/mol)	<R>	C_1/C_2 *	<R>	
i-PS	220.0	515/373	20.2 56.7	0.006 0.9836	40/38	0.9985	7
PET	2.74	550/340	39.1	0.9979	60/57	0.9987	18
PTMPS	3.75	433/247	15.1	0.9984	40/43	0.9996	19
PESu	0.596	377/239	20.1	0.9812	85/18	0.9850	22
PPO	1.03	348/212	10.6	0.9975	90/9	0.9982	23
N-6	2.74	505/303	18.8	0.9979	49/43	0.9992	25

* C_1:(cal/mol/deg), C_2:(deg), i-PS:isotactic poly(styrene), PET:poly (ethylene terephthalate), PTMPS:poly(tetramethyl-p-silphenylene siloxane), PESu:poly(ethylene succinate), PPO:poly(propylene oxide), N-6:Nylon-6.

and Hoffman et al. [8] have claimed that the Arrhenius-type expression yielded a farinferior fit to the data of i-PS when 20.2 kcal/mol of ΔE was used (Hoffman et al. used, however, 21 kcal/mol in their calculation). However, Hoffman et al. reported that both WLF and Arrhenius expressions could fit the data for many polymers with the high correlation coefficient, only except for i-PS. Here the question is raised as to why the i-PS data can not be fitted by the Arrhenius. It is worth to re-examine the transport term expressed by WLF or Arrhenius in order to obtain an acceptable fit to the data for i-PS and other common polymers. In the expression of Arrhenius, ΔE must be treated as an adjustable parameter to get the best fit to the data by a linear least squares procedure. A correlation coefficient <R> is strongly depended on a choice of ΔE value and a set of crystallization temperature range. For an example, Mandelkern et al. used the i-PS data at temperature ranges in the vicinity of T_{cmax} and above T_{cmax} (here, the data set is defined as A), while Hoffman et al. used the data with much wider temperature ranges especially at the lower temperature regions (here, the data set is defined as B). It is true that the Arrhenius yields a good fit to the data set A, but an inferior fit to the data set B when 20.2 or 21 kcal/mol is used. However, the data set B can be fitted with reasonable high correlation coefficient when 56.7 kcal/mol of ΔE is used as seen in table 1 listed with the other several polymers which are crystallized in the wide temperature ranges encompassed T_{cmax}. It is clear in table 1 that both expressions of WLF and Arrhenius can fit the data with the sufficiently high correlation coefficient. The values of <R> for the WLF-type (two adjustable parameters) are slightly

Table 2. Values of the temperature and the growth rate at the maximum crystallization rate for various polymers.

Sample	No.	M_w ($\times 10^4$)	T_{cmax} (K)	$\ln G_{max}$ (nm/s)	Ref.	Sample	No.	M_w ($\times 10^4$)	T_{cmax} (K)	$\ln G_{max}$ (nm/s)	Ref.
i-PS	a	6.0	457	1.50	15	PTMPS	o	3.75	345	6.58	19
	b	19.0	448	2.30	16		p	5.60	342	6.30	19
	c	33.0	455	1.49	17		q	43.10	345	5.96	19
	d	125.0	455	1.62	15		r	140.00	343	5.76	20
	e	138.0	451	0.93	16	PESU	s	0.15	330	6.49	21
	f	220.0	453	1.69	7		t	0.205	326	6.18	21
PET	g	1.90	451	4.94	18		u	0.27	327	5.96	21
	h	2.74	452	4.43	18		v	0.596	329	5.07	22
	i	3.91	448	3.33	18	PPO	w	1.03	285	6.88	23
PTMPS	j	0.87	342	7.45	19	N-6	x	2.47	417	7.78	24
	k	1.00	344	7.23	19		y	2.74	418	8.02	25
	l	1.58	345	6.97	19	Se*	z	---	406	1.60	26
	m	2.50	344	6.74	19						
	n	2.70	344	6.68	19						

*; Values of T_m and T_g for Se (Selenium) are 492K and 305K, respectively.

higher than those for the Arrhenius-type (a single adjustable parameter). In principal, the usage of two adjustable parameters in the data analysis yields the better fit than that of a single parameter. The discrepancy between them could be thought within an acceptable error. So, the simple expression of Arrhenius type is preferred to use in the present paper.

THEORETICAL ASPECT OF G_{max} AND ITS CORRESPONDING STATE

Maximum growth rate (G_{max}) is observed by equating to zero the derivative of equation (1) with respect to the temperature. The relation so found is [9],

$$G_{max} = G_o \exp\{-KT_m/R(T_m - T_{cmax})^2\} \quad ...(3)$$

$$= G_o \exp\{-\Delta E/R(2T_{cmax} - T_m)\} \quad ...(4)$$

$$T_{cmax}/T_m = C/(C + 1) \quad ...(5)$$

where T_{cmax} is the temperature at which crystal growth rate is maximum and $C = (1+\Delta E/K)^{1/2}$. The ratio of T_{cmax}/T_m increases with an increase in the ratio of $\Delta E/K$, however, a large variation in $\Delta E/K$ in its high value regions causes a little change in T_{cmax}/T_m [9]. The ratio of T_g/T_m could be also expressed with C [10]: $T_g/T_m = (C-1)/(C+1)$. The two ratios expressed by the function of C can sufficiently reveal the empirical prior-rules in most polymers such as $T_{cmax}/T_m = 0.8\sim0.9$ and $T_g/T_m = 2/3$. In general, C varies 3 to 9 and the mean value is roughly about 5 [9], so that the ratio of T_{cmax}/T_m changes from 3/4 to 9/10 and the mean value is 5/6 and the T_g/T_m changes from 1/2 to 4/5 and the mean value is 2/3.

Rearrangements in equation (1) with equations (3)-(4) yield

$$\ln(G/G_{max}) = \ln(G_{max}/G_o)(T_{cmax} - T)^2/T(T_m - T) \quad ...(6)$$

In the crystallization data obtained over a wide range of temperature through T_{cmax}, a data set of G_{max}, T_{cmax} and T_m can be easily determined by experimentally. Therefore, the plot of $\ln(G/G_{max})$ vs. the reduced temperature of $(T_{cmax}-T)^2/T(T_m-T)$ predicts the linear relation with the slope of $\ln(G_{max}/G_o)$. Such plots are shown in figures 1 and 2 for several polymers with various molecular weights as listed in table 2. Each polymer shows a fairly good linear relation and this indicates that the slope of $\ln(G_{max}/G_o)$ shows almost no molecular weight dependence, while G_{max} shows the molecular weight dependence. Thus obtained slopes were treated to get the best fit to the reduced parameter as expected in equation (4) by a linear least squares procedure. The relationship so found is shown in figure 3 and can be expressed as,

$$\ln(G_o/G_{max}) = 227(T_g - 170)/R(2T_{cmax} - T_m) \quad ...(7)$$

$$\Delta E = 227(T_g - 170) \quad ...(8)$$

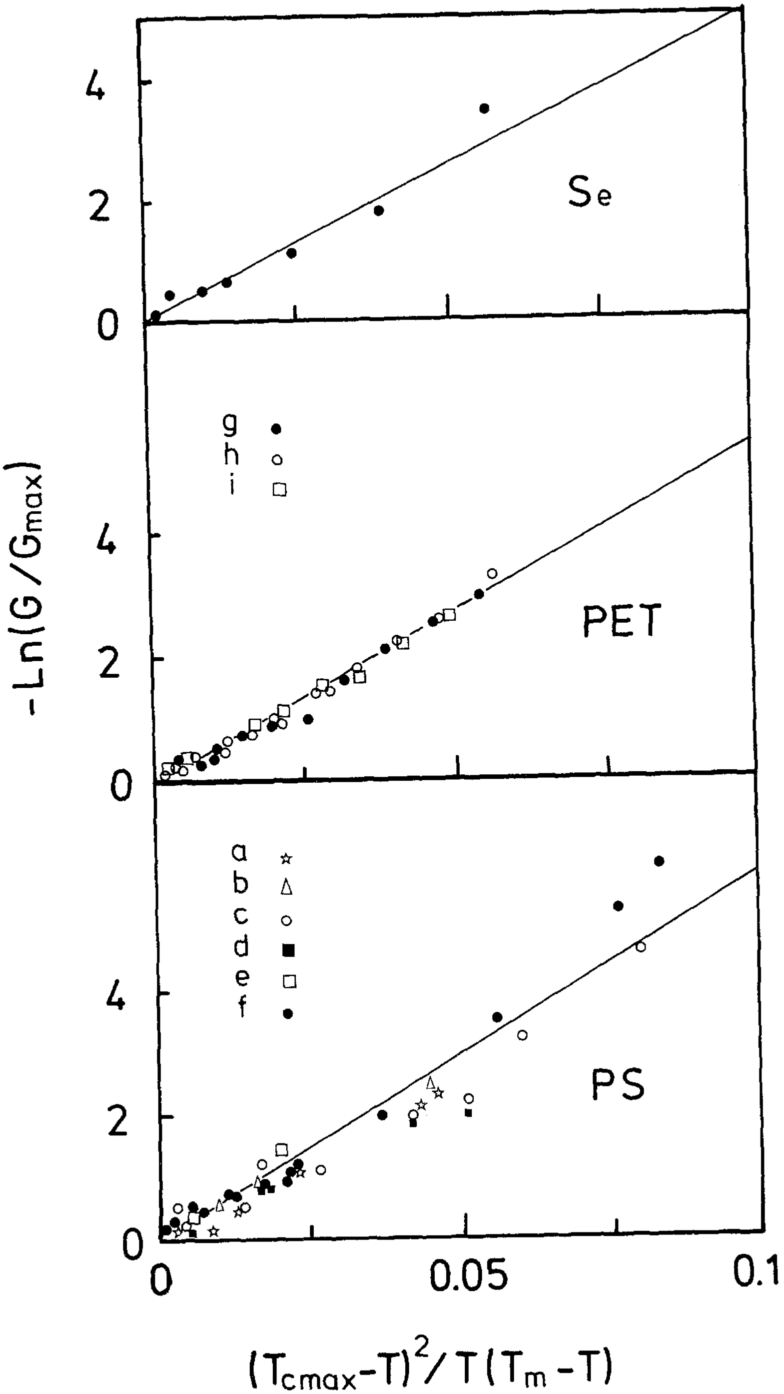

Figure 1. Plots of logarithm of (G/G_{max}) versus the reduced temperature for i-PS, PET and Se.

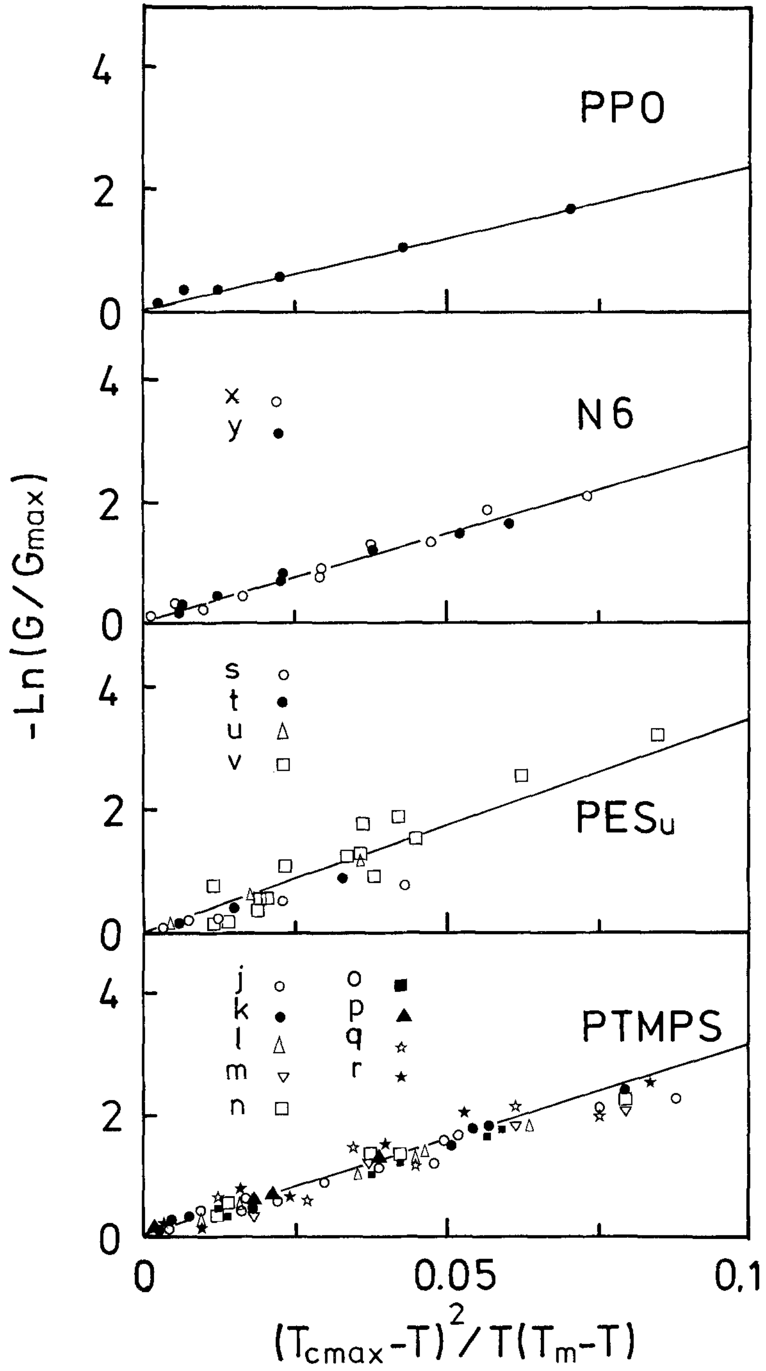

Figure 2. Plots of logarithm of (G/G_{max}) versus the reduced temperature for PTMPS, PESu, N6 and PPO.

It is interesting to note that the activation energy for migration ΔE depends strongly on the glass transition temperature of polymers. Similar relationship has been pointed out by Mandelkern et al. [6] on the basis of their crystallization data. Here, ΔE can be compared with the activation energy for viscous flow or the self-diffusion of polymer chain which may be related to the cohesion energy. And the molar cohesion energy can be closely related with the glass transition temperature [11].

According to the various experimental data between T_m, T_{cmax} and T_g, the expression of $2T_{cmax} = T_m+T_g$ has been found by van Krevelen [12]. That is, the maximum crystal growth rate will occur at the middle of T_m and T_g. This interesting empirical relation could be predicted by an iso-volume state model [10]. By employing this relation, equation (4) can be approximated as $\ln(G_o/G_{max}) = \Delta E/RT_g$. Here, the Arrhenius expression can be identical with the WLF expression when C_2 puts to T_g. This gives that $C_1 = \Delta E/T_g$. Also, C_1 can be expressed as a function of the free volume fraction at T_g. Therefore, G_o and ΔE can be closely associated with the free volume fraction [13]. In addition, it may be thought that G_o depends on the type of nucleation regime [8] and the entropy contribution to crystallization [14]. In general, G_o is commonly treated simply as a scaling constant. On the other hand, C_1 will not be expected to be constant for all polymers. In fact, the slope of $\ln(G_{max}/G_o)$ shows different for each polymer as seen in figures 1 and 2. This means that the data in the crystal growth rate can not be reduced to a single universal relation without consideration of G_o. It is difficult, however, to expect the value of G_o from theoretical grounds. Detailed studies on G_o must be required for further discussion.

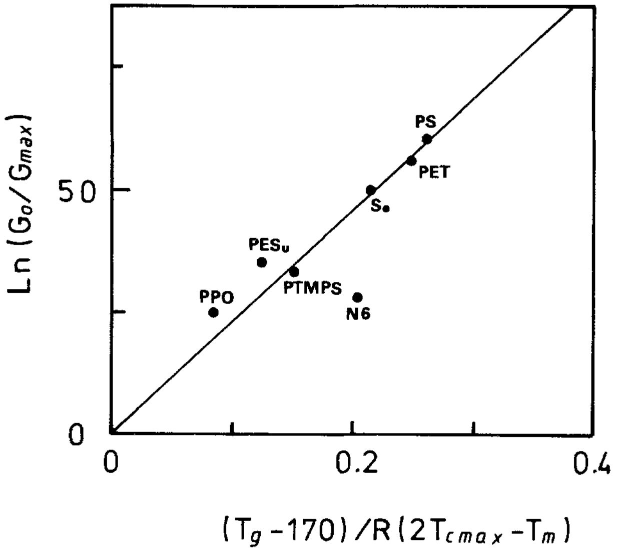

Figure 3. Relationship between the logarithm of (G_o/G_{max}) and the reduced parameter of $(T_g-170)/R(2T_{cmax}-T_m)$.

CONCLUSION

For the temperature dependence of linear crystal growth rate, the activation energy for molecular transport could be expressed either by WLF or Arrhenius type. On the basis of the Arrhenius expression, the corresponding state of the crystal growth rate was formulated theoretically as $\ln(G/G_{max}) = \ln(G_{max}/G_o)(T_{cmax}-T)^2/T(T_m-T)$. Plots of $\ln(G/G_{max})$ versus the reduced parameter $(T_{cmax}-T)^2/T(T_m-T)$ showed a good linear relationship for various polymers. The magnitude of the activation energy expressed by Arrhenius type is found to be dependent on the glass transition temperature of polymers.

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