ELSEVIER

Polymer 43 (2002) 1423–1427

polymer

www.elsevier.com/locate/polymer

Master curve of crystal growth rate and its corresponding state in polymeric materials

Susumu Umemoto, Norimasa Okui*

Department of Organic and Polymeric Materials, International Research Center of Macromolecular Science, Tokyo Institute of Technology, Ookayama, Meguroku, Tokyo, Japan

Received 26 April 2001; received in revised form 21 September 2001; accepted 16 October 2001

Abstract

The temperature dependence of linear crystal growth rate (G) for various polymers shows a bell shape with the maximum growth rate ($G_{\max}$). The $G_{\max}$ shows remarkable molecular weight dependence. The $G_{\max}$ was formulated on the basis of a crystallization theory, both for Arrhenius and WLF expressions in the molecular transport term. The plots of the reduced growth rate ($G/G_{\max}$) against the reduced temperature (T/T_{cmax}) for a given polymer showed a single master curve without molecular weight dependence. The ratio of $G_0/G_{\max}$ gave a constant value for each polymer, indicating a material constant. On the basis of $G_{\max}$ for many polymers, a universal master curve was observed when the ratio of $\ln(G/G_{\max})/\ln(G_0/G_{\max})$ was plotted against the reduced temperature (T/T_{cmax}). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer crystallization; Maximum crystal growth rate; Master curve

1. Introduction

According to a crystallization theory for a temperature dependence of linear crystal growth rate (G) from the melt, G is generally described by a following exponential equation [1–3].

$$G = G_0 \exp\left[-\frac{\Delta E}{RT} - \frac{\Delta F}{RT}\right] \tag{1}$$

where G_0 is a constant almost independent of temperature, 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 R is a gas constant. This equation has been applied frequently to data of spherulitic growth rate for polymeric materials. In Eq. (1), the terms of ΔE and ΔF have opposing temperature dependence thereby bring about a maximum growth rate ($G_{\max}$) at a temperature T_{cmax}. Fig. 1 shows spherultic growth rate data for a wide variety of polymers in a wide range of crystallization temperature in the referenced literature [4–9]. Data plots show a bell shape temperature dependence of crystal growth rate, giving the maximum crystal growth rate. On the basis of $G_{\max}$ for many crystalline materials, an universal master curve of temperature dependence of crystal growth rate has been proposed empirically by Magill et al. [10,11] as expressed by the ratio of the logarithm of the growth rate (G) at any temperature (T) to the value of $G_{\max}$ versus a reduced temperature $(T - T_0)/(T_m^0 - T_0)$,

$$\ln\left(\frac{G}{G_{\max}}\right) = f\left(\frac{T - T_0}{T_m^0 - T_0}\right) \tag{2}$$

where T_m^0 is the thermodynamic equilibrium melting temperature and T_0 is a hypothetical temperature at which the macro-Brownian motion of polymer molecules ceases. However, in an extensive study on such universal curve for many polymers, whole crystal growth data cannot be reduced to a single universal curve [12]. This universal master curve comes from a phenomenological basis. The present paper was studied on the corresponding state in the crystal growth rate on the basis of a theoretical background.

2. Best fitting growth data by WLF and Arrhenius expressions

In a polymer crystallization from the melt, ΔF in Eq. (1) is commonly expressed as $\Delta F = KT_m^0/(T_m^0 - T)$, where K is the nucleation parameter expressed as $K = nb_0\sigma_e\sigma_s/\Delta H_m$, where n is a parameter of a mode of nucleation, b_0 is the

---

* Corresponding author. Tel./fax: +81-03-5734-2469.
E-mail address: nokui@o.cc.titech.ac.jp (N. Okui).

0032-3861/02/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00707-8

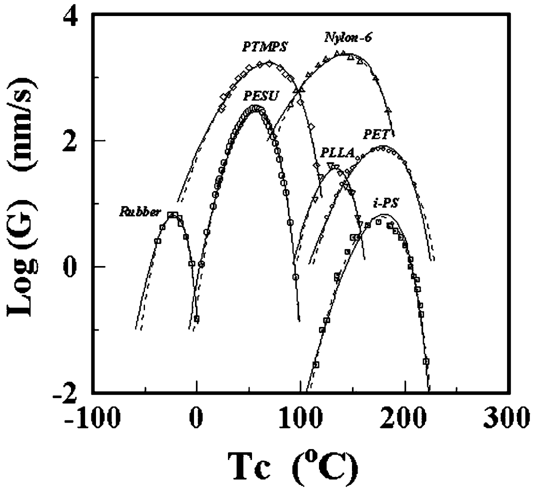

Fig. 1. Temperature dependence of crystal growth rate from the melt for a variety of polymers; rubber [4], Nylon6 [4], PTMPS [5], PET [6], i-PS [7], PLLA [8], PESU [9]. Solid and broken lines are best fitting by Arrhenius and WLF expressions, respectively.

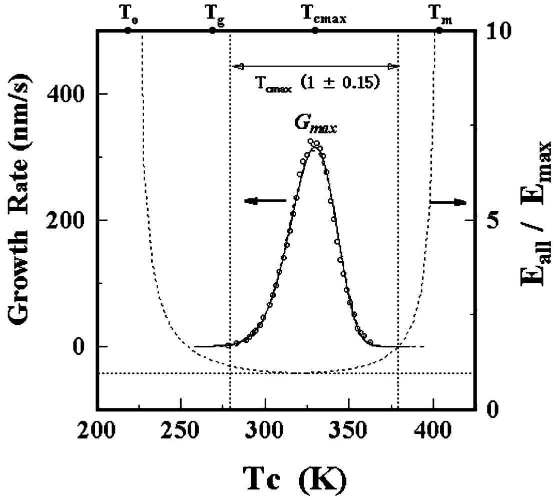

Fig. 2. Temperature dependence of linear crystal growth rate and overall activation energy (E_{all}) for molecular transport and nucleation terms for PESU. E_{max} is the activation energy at T_{cmax}. Solid and broken lines in linear crystal growth rate are best fitting by Arrhenius and WLF expressions, respectively.

thickness of the depositing growth layer and σ_e and σ_s are the end and the lateral surface energies, respectively, and ΔH_m is the heat of fusion [3]. 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 ($\Delta E_{ARH}/RT$) or WLF type ($\Delta E_{WLF}/R(T - T_0)$). 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. The transport term of ΔE is considerably important in the lower temperature ranges, therefore the molecular transport term is often employed by WLF expression. The transport term expressed by WLF increases significantly when crystallization temperature reaches near T_0. However, the transport term could be sufficiently expressed by the Arrhenius-type in the polymer crystallization [13–15].

It is worth to recheck which transport term equation is better describing the temperature dependence of the linear crystal growth rate. We employ a conventional activation energy expressed as $E_D/(T - T_0)$ for the molecular transport term and $E_K/(T_m^0 - T)$ for the nucleation term. Thus the overall activation energy of the crystal growth process is given by the following equation [16]

$$E_{all} = \frac{E_D}{T - T_0} + \frac{E_K}{T_m^0 - T} \tag{3}$$

Fig. 2 shows the temperature dependence of E_{all} and the linear crystal growth rate for PESU. The growth rate shows a typical bell shape curve. The observed bell shape curve locates in the temperature range of T_{cmax} (1 ± 0.15), whereas the growth rate in the external temperature regions of the curve is extremely slow. No crystal growth data in the vicinity of T_g has been reported in polymeric materials. However, the crystal growth rate is comparable to/or slower than that of the rate of molecular transport via reptation process in the vicinity of T_g [15]. It is interesting to note that some organic [17] and inorganic [18] materials can crystallize even below T_g. The overall activation energy increases significantly when the crystallization temperature reaches near to T_0 and T_m^0. However, the temperature dependence of E_{all} becomes very small in the vicinity of T_{cmax}. This indicates that Arrhenius law can be used sufficiently for the temperature dependence of molecular transport term. In other words, the activation energy for the molecular transport is expressed either by WLF or Arrhenius-type in a wide crystallization temperature range encompassed through T_{cmax}. Fig. 2 shows that either Arrhenius or WLF expression in the molecular transport term fits very well the linear crystal growth rate of PESU with a wide temperature range.

3. Theoretical aspect of G_{max} and master curve for crystal growth rate

Maximum growth rate (G_{max}) can be observed by equating to zero the derivative of Eq. (1) with respect to the temperature. The relations so found for the Arrhenius expression have been reported in the previous work [19] and those for WLF expressions are formulated in this work as follows. For Arrhenius expression in the molecular transport term

$$G_{max} = G_0 \exp\left[-\frac{\Delta E_{ARH}}{R(2T_{cmax} - T_m^0)}\right] \tag{4}$$

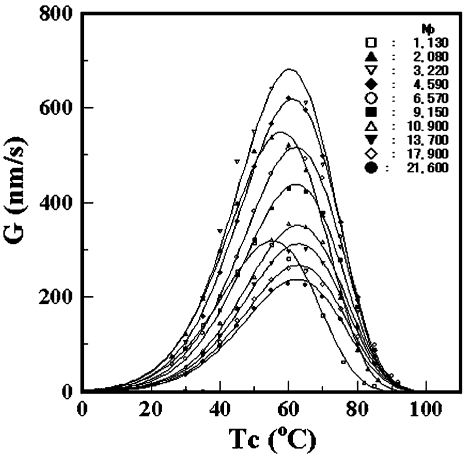

Fig. 3. Temperature dependence of linear crystal growth rate for poly(ethylene succinate) with various molecular weights [9]. Indicated molecular weights in the figure are the peak molecular weight measured by GPC.

$$\ln\left(\frac{G}{G_{\max}}\right)=\left[\ln\left(\frac{G_{\max}}{G_0}\right)\right]\left[\frac{(1-X)^2}{X(A-X)}\right] \tag{5}$$

For WLF expression in the molecular transport term,

$$G_{\max}=G_0\exp\left[-\left(\frac{\Delta E_{\mathrm{WLF}}}{R(2T_{\mathrm{cmax}}-T_{\mathrm{m}}^0)}\right)\left(1+\frac{T_0\left(T_{\mathrm{m}}^0-T_0\right)}{(T_{\mathrm{cmax}}-T_0)^2}\right)\right] \tag{6}$$

$$\ln\left(\frac{G}{G_{\max}}\right)=\left[\ln\left(\frac{G_{\max}}{G_0}\right)\right]\left[\frac{(1-X)^2}{X(A-X)}\right]\times\left[\frac{X(1-2B+AB)-B(A-1)^2}{(X-B)(1-2B+AB)}\right] \tag{7}$$

where X is the reduced crystallization temperature of T/T_{cmax} and A and B are the ratios of $T_{\mathrm{m}}^0/T_{\mathrm{cmax}}$ and T_0/T_{cmax}, respectively.

In polymer crystallization data obtained over a wide range of temperature through a maximum crystal growth rate, data sets of $G_{\max}$, T_{cmax} and T_{m}^0 for many polymers are available in the referenced literature. $G_{\max}$, T_{cmax}, and T_{m}^0 show remarkable molecular weight dependence. For example, Fig. 3 shows the temperature dependence of the linear crystal growth rate for poly(ethylene succinate) (PESU) with various molecular weights [9]. Each molecular weight fraction shows bell shape crystal growth rate behavior. The $G_{\max}$ increases with the molecular weight up to 3200 and then decreases. The details in the molecular weight dependence of $G_{\max}$ for PESU will be reported in a separate paper. T_{cmax} increases with molecular weight similar to the molecular weight dependence of T_{m}^0. The ratio of $T_{\mathrm{cmax}}/T_{\mathrm{m}}^0$ is almost independent of the molecular weight, yielding the constant value of 0.83. In fact, values of $T_{\mathrm{cmax}}/T_{\mathrm{m}}^0$ lie between 0.8 and 0.9 for most polymers [12,19,20], which are discussed in detail in Section 4.

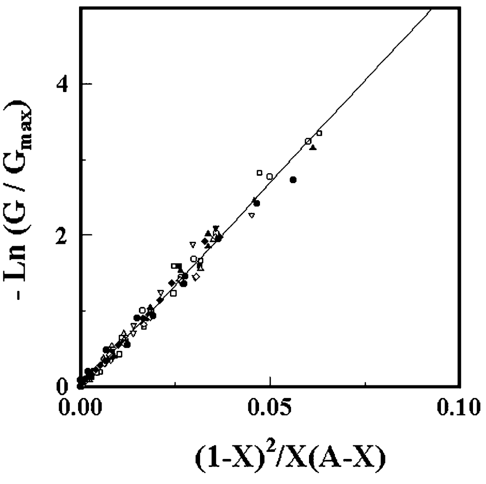

Fig. 4. Plots of the ratio of logarithm of the growth rate (G) at any temperature (T) to the value of $G_{\max}$ versus a reduced temperature $[(1-X)^2/X(A-X)]$ based on Arrhenius expression of Eq. (5). Symbols in the figure are the same in those in Fig. 3. $X=T/T_{\mathrm{cmax}}$, $A=T_{\mathrm{m}}^0/T_{\mathrm{cmax}}$.

When the crystal growth data are plotted according to Eq. (5) (Arrhenius expression), the reduced growth rate ($G/G_{\max}$) shows a linear relationship with the reduced temperature of the second term in the right hand side of Eq. (5) $(1-X)^2/X(A-X)$ as shown in Fig. 4, indicating no molecular weight dependence in growth rate. The linear relation is true for other various polymers [13], such as poly(ethylene terephthalate) (PET), isotacitc polystyrene (i-PS), nylon-6 (N-6), poly(tetramethyl *p*-silphenylene siloxane) (PTMPS), poly(ethylene succinate) (PESU), poly(L-lactide) and rubber as listed in Fig. 1.

WLF expression also shows the linear relationship plotting $\ln(G/G_{\max})$ against the reduced temperature of $[(1-X)^2/X(A-X)][(X(1-2B+AB)-B(A-1)^2)/(X-B)(1-2B+AB)]$ in the right hand side of Eq. (7) as shown in Fig. 5, indicating also no molecular weight dependence. Here, T_0 was assumed to be 0.5 T_{m}^0 [21], which is discussed in detail in Section 4. The linear relation based on WLF expression was also true for other various polymers as listed in Fig. 1. These linear relationships indicate that ratios of $G_{\max}/G_0$ (the slope in Figs. 4 and 5) are independent of molecular weight. In other words, the molecular weight dependence of G_0 is the same in that of $G_{\max}$.

Fig. 6 shows the plots of the reduced crystal growth rate ($G/G_{\max}$) against the reduced crystallization temperature of (T/T_{cmax}) for PESU. Master curve of crystal growth rate is observed showing no molecular weight dependence of the crystal growth rate. The master curve can be fitted either by Eq. (5) (Arrhenius; solid line) or Eq. (7) (WLF; dotted line). The master curve was also true for other polymers as listed in Fig. 1. These polymers were drawn in the master curve also. However, each polymer gave a different value to the ratio of $G_{\max}/G_0$ indicating a material constant. The value of $G_{\max}/G_0$ was dependent on characteristics of polymer molecules, such as molecular flexibility and crystallizability

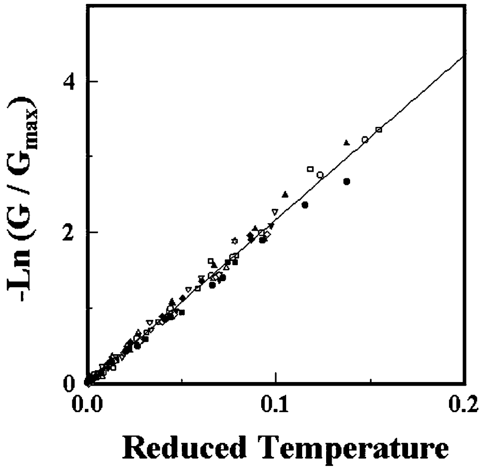

Fig. 5. Plots of the ratio of logarithm of the growth rate (G) at any temperature (T) to the value of $G_{\max}$ versus a reduced temperature $[(1-X)^2/X(A-X)][(X(1-2B+AB)-B(A-1)^2)/(X-B)(1-2B+AB)]$ based on WLF expression of Eq. (7). Symbols in the figure are the same in those in Fig. 3. $X = T/T_{\mathrm{cmax}}$, $A = T_{\mathrm{m}}^{0}/T_{\mathrm{cmax}}$, $B = T_0/T_{\mathrm{cmax}}$.

based on a chemical structure. Therefore, the reduced growth rate ($G/G_{\max}$) in each polymer should be normalized by the value of $G_{\max}/G_0$. All experimental crystal growth data (total numbers of data points are over 400) are drawn in to a single master curve as seen in Fig. 7.

4. Relationship between T_{m}^{0}, T_{cmax}, T_{g} and T_0

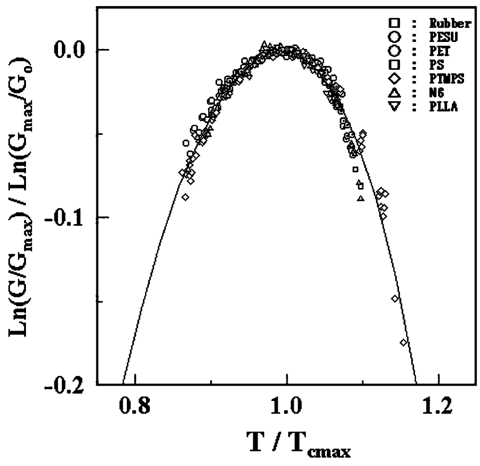

Fig. 7. Universal curve for crystal growth rate for various polymers. □: rubber [4], △: N6 [4], ◇: PTMPS [5], ○: PET [6], □: i-PS [7,23], ▽: PLLA [8,22], ○: PESU [9].

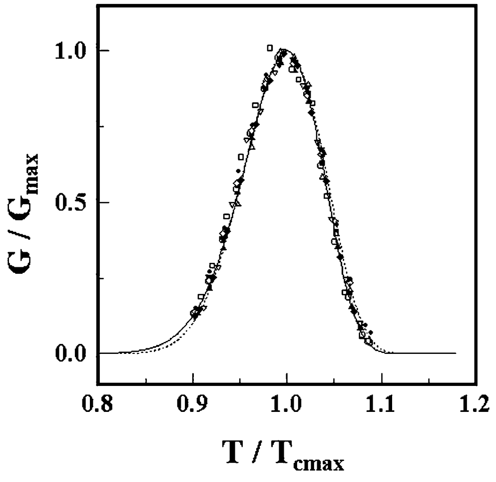

Fig. 6. Master curve of crystal growth rate for poly(ethylene succinate). Symbols in the figure are the same in those in Fig. 3. Solid and dotted lines are calculated from Eq. (5) (Arrhenius) and Eq. (7) (WLF), respectively.

There are many characteristic temperatures, such as T_{m}^{0}, T_{cmax}, T_{g} and T_0. It has been well known that a ratio of $T_{\mathrm{cmax}}/T_{\mathrm{m}}^{0}$ is nearly constant for a wide variety of materials [12,20] including metals, inorganic substances, organic compounds and polymers. Constancy of the ratio of $T_{\mathrm{g}}/T_{\mathrm{m}}^{0}$ is also widely known as Boyer–Beaman rule [24]. Boyer classified polymers into two groups as a symmetrical polymer and an un-symmetrical polymer. However, in an extensive study on more than 130 polymers [25], the average value of $T_{\mathrm{g}}/T_{\mathrm{m}}^{0}$ is about 2/3 for all polymers, indicating no discrimination between symmetrical and un-symmetrical polymers. According to WLF relationship, $T_0 = T_{\mathrm{g}} - f_{\mathrm{g}}/\Delta\alpha$, where f_{g} is a free volume at T_{g} and $\Delta\alpha$ is the difference of the thermal expansivity between a glass and a super-cooled liquid [26]. This equation is rewritten as follows,

$$T_0/T_{\mathrm{g}} = 1 - f_{\mathrm{g}}/\Delta\alpha T_{\mathrm{g}}, \tag{8}$$

The mean values of $\Delta\alpha T_{\mathrm{g}}$ and f_{g} are approximated to be 0.1 and 0.025 [27], respectively. Thus the ratio of T_0/T_{g} yields to be 3/4, which coincides with the ratio reported by Gibbs–DiMarizio theory [28].

The ratio of $T_{\mathrm{cmax}}/T_{\mathrm{m}}^{0}$ can be formulated from Eq. (1). For Arrhenius expression in the molecular transport term, which is formulated previously [19,20],

$$\frac{T_{\mathrm{cmax}}}{T_{\mathrm{m}}^{0}} = \frac{C_{\mathrm{ARH}}}{1 + C_{\mathrm{ARH}}} \tag{9}$$

$$C_{\mathrm{ARH}} = \sqrt{1 + \left(\frac{\Delta E_{\mathrm{ARH}}}{K_{\mathrm{ARH}}}\right)} \tag{10}$$

For WLF expression in the molecular transport term, which is formulated in the present work,

$$\frac{T_{\mathrm{cmax}}}{T_{\mathrm{m}}^{0}} = \frac{C_{\mathrm{WLF}}}{1 + C_{\mathrm{WLF}}} \tag{11}$$

$$C_{\mathrm{WLF}} = \sqrt{1 + \left(\frac{\Delta E_{\mathrm{WLF}}}{DK_{\mathrm{ARH}}}\right)} \tag{12}$$

$$D = \left(\frac{T_0}{T_{\mathrm{cmax}}} - 1\right)^2 \tag{13}$$

Fig. 8 shows the ratio of $T_{\mathrm{cmax}}/T_{\mathrm{m}}^{0}$ vs. C (either C_{ARH} or C_{WLF}) according to Eqs. (9) or (11). $T_{\mathrm{cmax}}/T_{\mathrm{m}}^{0}$ increases with an

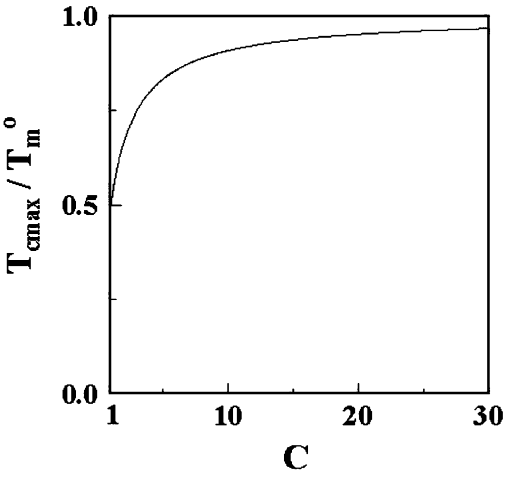

Fig. 8. Ratio of maximum crystallization temperature (T_{cmax}) to melting temperature as a function of a parameter C expressed in terms of the equation of either WLF or Arrhenius for molecular transport term.

increase in C value and its value saturates to 1. In general, the mean value of C lies in about 5 [19], yielding that T_{cmax}/T_m^0 is about 5/6. Based on these empirical rules, the ratio of T_0/T_{cmax} gives a constant value of 0.6 and T_0/T_m^0 yields to 0.5 [21]. On the basis of the mean value of C, $\Delta E_{ARH}/K_{ARH}$ gives 24 for Arrhenius expression and $\Delta E_{WLF}/K_{WLF}$ gives 3.8 for WLF expression. In fact, these ratio for $\Delta E_{ARH}/K_{ARH}$ and $\Delta E_{WLF}/K_{WLF}$ are calculated by the best fitting to data and thus calculated values showed a constant [9,13]. Therefore, these constant ratios with no molecular weight dependence give rise to the master curve of crystal growth rate in polymeric materials.

5. Conclusion

The maximum growth rate is formulated from a crystallization theory based on the molecular transport term expressed by Arrhenius and WLF expressions. Based on the formulated maximum growth rate, a universal master curve of temperature dependence of crystal growth rate is proposed theoretically as expressed by the ratio of the logarithm of the growth rate (G) at any temperature to the value of the maximum growth rate G_{max} versus a reduced temperature T/T_{cmax}. The molecular weight dependence of G_0 is the same in that of G_{max}. The ratio of G_0/G_{max} gives a constant value for each polymer. The plots of the reduced growth rate (G/G_{max}) normalized by the ratio of (G_{max}/G_0) against the reduced temperature (T/T_{cmax}) show a universal master curve for many polymers. The ratio of T_{cmax}/T_m^0 is also formulated by WLF expression, yielding the similar formulation as the result by Arrhenius.

Acknowledgements

This work was supported by grant-in-aid for Science Research on Priority Areas, 'Mechanism of Polymer Crystallization' (No. 12127202) from the ministry of education, culture, sports, science and technology, Japan.

References

[1] Turnbull DJ. Appl Phys 1950;21:1022.
[2] Takayanagi M, Yamashita T. J Polym Sci 1956;22:552.
[3] Hoffman JD, Weeks JJ. J Chem Phys 1962;37:1723.
[4] Burnett BB, McDevit WF. J Appl Phys 1957;28:1101.
[5] Magill JH. J Appl Phys 1964;35:3249.
[6] van Antwerpen F, van Krevelen DW. J Polym Sci B, Polym Phys 1972;10:2423.
[7] Suzuki T, Kovacs AJ. Polym J 1970;1:82.
[8] Vasanthakumari R, Pennings AJ. Polymer 1983;24:175.
[9] Kobayashi N, Umemoto S, Kikutani T, Okui N. Polym Prepr Jpn 2000;49:2656.
[10] Gandica A, Magill JH. Polymer 1972;13:595.
[11] Magill JH, Li HM, Gandica A. J Cryst Growth 1973;19:361.
[12] Privalko XP. Polymer 1978;19:1019.
[13] Okui N. Polym Bull 1990;23:111.
[14] Mandelkern L, Jain NL, Kim H. J Polym Sci 1968;A2,6:165.
[15] Okui N. In: Dosiere M, editor. Crystallization of polymers, Nato ASI Series, vol. 405. Dordrecht: Kluwer Academic Publishers, 1993. p. 593–8.
[16] Vrbanovici E, Scheider HA, Cantow HJ. J Polym Sci B, Polym Phys 1997;35:359.
[17] Hikima T, Adachi Y, Hanaya M, Oguri M. Phys Rev 1995;52:3900.
[18] Abe Y, Arahori T, Naruse A. J Am Ceram Soc 1976;59:487.
[19] Okui N. Polym J 1987;19:1309.
[20] Okui N. J Mater Sci 1990;25:1623.
[21] Okui N. Polymer 1990;31:92.
[22] Miyata T, Masuko T. Polymer 1998;39:5515.
[23] Lemstra PJ, Postma J, Challa G. Polymer 1974;15:757.
[24] Boyer RF. J Appl Phys 1954;25:825.
[25] Lee WA, Knight GJ. Br Polym J 1970;2:73.
[26] Simha R, Boyer RF. J Chem Phys 1962;37:1003.
[27] van Krevelen DW. Properties of polymers. Amsterdam: Elsevier, 1990. p. 92.
[28] Gibbs JH, DiMarzio EA. J Chem Phys 1958;28:373.