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Thermochimica Acta 267 (1995) 259–268

thermochimica
acta

Activation energy for crystallization of low molecular weight poly(ethylene oxide) and low molecular weight poly(ethylene oxide)/poly(methyl methacrylate) blends determined by DSC and polarized optical microscopy[1]

Shinya Imai, Shinji Shimono, Yousuke Fukushima, Kazuyuki Umezaki,
Motoyuki Okada, Masato Takahashi*, Hideomi Matsuda

*Department of Fine Materials Engineering, Faculty of Textile Science and Technology,
Shinshu University, 3-1 5-1, Tokida, Ueda, Nagano 386, Japan*

Received 12 December 1994; accepted 3 April 1995

Abstract

The crystallization process of poly(ethylene oxide) (PEO) and PEO/poly(methyl methacrylate) (PMMA) blends in the low molecular weight region of PEO was studied by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The half-time of the crystallization $t_{1/2}$, the time at which crystallinity $X(t) = 1/2$, was inversely proportional to the linear growth rate G of spherulite, i.e. $t_{1/2}^{-1} \propto G$. The value of E characterizes the temperature dependence of the activation energy for the formation of a secondary nucleus on the growing side surface of the crystal lamella and was evaluated from the $t_{1/2}$ measured by DSC. The value of E of PEO was not affected by blending PMMA. However, the slightly increasing tendency of E was observed for PEO and PEO/PMMA blends with increasing molecular weight of PEO, M_{PEO}. This tendency may correspond to the crossover of E from low molecular weight material to polymer.

Keywords: Crystallization; DSC; Polarized optical microscopy; Poly(ethylene oxide); Poly(ethylene oxide)/poly(methyl methacrylate) blends

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1. Introduction

The heat of crystallization $\Delta H(t)$ measured by differential scanning calorimetry (DSC) in the crystallization process of polymer yields the evolution of crystallinity, $X(t)$, as a function of time by the relation [1]:

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* Corresponding author.

[1] Presented at the 30th Anniversary Conference of the Japan Society of Calorimetry and Thermal Analysis, Osaka, Japan, 31 October–2 November 1994.

SSDI 0040-6031 (95) 02484-0

$$X(t) = \frac{\int_0^t (\mathrm{d}\Delta H(t)/\mathrm{d}t)\,\mathrm{d}t}{\int_0^\infty (\mathrm{d}\Delta H(t)/\mathrm{d}t)\,\mathrm{d}t} \tag{1}$$

$X(t)$ thus obtained is usually analyzed according to the Avrami equation

$$X(t) = 1 - \exp(-kt^n) \tag{2}$$

in order to evaluate the rate constant k and the Avrami exponent n [2].

On the other hand, the crystallization process of a polymer is often studied by polarized optical microscopy (POM) to evaluate the crystallization rate, e.g. the linear growth rate G of spherulite, the lateral growth rate V of single crystal lamella, etc. [3–7].

The rate constant k obtained by DSC is related to the growth rate G obtained by POM by the relation

$$\mathrm{k} \propto G^d \tag{3}$$

where d represents the dimensionality of the crystal formed in the system and has the value 1, 2 or 3 depending on the crystallization mechanism [2]. Most studies on the crystallization of polymers are based on experimental results obtained by just one of these two procedures, i.e. DSC or POM. Although the rate constant k is thus related directly to the crystallization rate G, the validity of Eq. (3) has not yet been proved experimentally by comparing DSC and POM measurements.

In this study, isothermal crystallization of poly(ethylene oxide) (PEO) and PEO/poly(methyl methacrylate) (PMMA) blends in a low molecular weight region of PEO was measured by DSC and POM. PEO/PMMA blend is the compatible polymer blend with a negative value of the interaction parameter χ [8,9]. Therefore, we can investigate the crystallization process of polymer blend without the influence of the liquid–liquid phase separation. The aims of this study are (1) the experimental verification of the relation of Eq. (3); (2) the exploration of the PEO molecular weight dependence of the crystallization of PEO and PEO/PMMA blends and (3) the examination of the effect of blended PMMA on the crystallization of PEO.

2. Experimental

PEOs were products of Wako Pure Chemical Ind. Ltd. with nominal average molecular weights $M_{\mathrm{PEO}} = 4 \times 10^3$ and 5×10^4 and of Scientific Polymer Products, Inc. with nominal weight average molecular weight $M_{\mathrm{PEO}} = 6.8 \times 10^3$. PMMA was the product of Scientific Polymer Products, Inc. The weight average molecular weight $M\mathrm{w}_{\mathrm{PMMA}}$ and the index of the molecular weight distribution $(M\mathrm{w}/M\mathrm{n})_{\mathrm{PMMA}}$ were determined as 1.7×10^3 and 1.7, respectively, by gel permeation chromatography (GPC) using polystyrenes as the standards.

Sample films were obtained by casting from chloroform solutions. Namely, homogeneous solutions with a concentration of about 5 wt% were cast on a teflon sheet at 35°C.

Table 1

Equilibrium melting temperature $T_m{}^0$ for various PEOs and PEO/PMMA blends

M_{PEO}	$T_m{}^0$/K	
	PEO	PEO/PMMA
4×10^3	333.9	331.8
6.8×10^3	343.4	338.4
5×10^4	346.5	341.2

The film thus obtained was kept under a vacuum at room temperature for 24 h, then heated to 80°C and dried further for 10 h under a vacuum. The blends contained 20 wt% of PMMA.

DSC measurements were carried out using a Seiko DSC200 instrument. About 10 mg of specimen were sealed in an Al pan. The isothermal crystallization process was induced by melting the specimen at about 90°C, annealing for 40–50 min, quenching to the crystallization temperature T_c at 20°C min^{-1}, and then recording the DSC curve. The DSC melting curve of the crystallized specimen was measured at a heating rate of 10°C min^{-1} after cooling the specimen to −5°C at 10°C min^{-1} and holding the specimen for 5 min in order to stabilize the base line. The melting temperature T_m was evaluated as the peak temperature of the DSC melting curve. According to the method proposed by Hoffman and Weeks, the equilibrium melting temperature $T_m{}^0$ was determined by extrapolating linearly the plot of T_m against T_c to the $T_m = T_c$ line (Hoffman–Weeks plot) [10]. Hoffman–Weeks plots of these systems measured here were previously reported [11]. The values of $T_m{}^0$ are listed in Table 1.

POM measurements were carried out using an Olympus BHS-751-P. After being melted at 80°C and annealed for 30 min, the specimen was quenched to the crystallization temperature T_c by inserting the specimen into an originally designed hot stage, which was installed on the sample stage of the POM and controlled at T_c. The isothermal crystallization process thus initiated was measured by a CCD camera mounted on the POM. The POM image taken by the CCD camera was transferred to a computer digital image analysis system (PIAS Co. LA525), and the time dependent growth of the radius of spherulite was measured.

3. Results and discussion

Fig. 1 shows the Avrami plots of PEO ($M_{PEO} = 5 \times 10^4$) at the crystallization temperature $T_c = 320$, 325 and 327 K. The Avrami exponent n takes 1.9–2.3 for PEO ($M_{PEO} = 5 \times 10^4$) and 2.1–2.3 for PEO ($M_{PEO} = 5 \times 10^4$)/PMMA blend. The maximum, minimum and average values of n for PEOs and PEO/PMMA blends are listed in Table 2. As easily understood from Table 2, the value of n was not affected by blending PMMA and was independent of the molecular weight of PEO M_{PEO}. Theoretically, the Avrami exponent n depends on the morphology of the crystal and the nucleation mecha-

Table 2

Maximum, minimum and average values of Avrami exponent *n* for various PEOs and PEO/PMMA blends

M_{PEO}	n_{max}		n_{min}		$n_{average}$	
	PEO	PEO/ PMMA	PEO	PEO/ PMMA	PEO	PEO/ PMMA
4×10^3	2.2	2.4	1.7	1.9	1.9	2.3
6.8×10^3	2.4	2.2	1.8	1.6	2.1	2.0
5×10^4	2.3	2.3	1.9	2.1	2.1	2.2

nism, i.e. homogenous nucleation or inhomogenous nucleation [2]. The value of n observed here shows that the morphology of the crystal and the nucleation mechanism are not affected by blending PMMA. In POM measurements, the growth of spherulite was observed with the progress of time. Time evolution of the radius of spherulite r is shown in Fig. 2. Spherulite radius r increases linearly with time t. Linear growth rate G was evaluated from the slope of the straight lines. For the growth of a three-dimensional spherical crystal, the Avrami exponent n takes 4 or 3 for homogeneous or inhomogenous nucleation, respectively [2]. The results of Figs. 1 and 2 show that the PEO and PEO/PMMA blends crystallize spherically by inhomogenous nucleation. Actually, the crystallization took place by inhomogenous nucleation as seen from Fig. 3. Here, $X'(t)$ is the apparent crystallinity defined as the fraction of the region occupied by the crystal domain in the field of POM. N is the number of nuclei formed in the field of POM. Fig. 3 shows that the number of nuclei was already saturated in the very early stage of crystallization. Similar values of the Avrami exponent n were obtained for other polymers forming spherulites by inhomogenous nucleation [6,7,12]. The reason why the exponent n observed here took a fractal value, which is smaller than the theoretically predicted value $n = 3$, is not explained at the present stage. However, since the spherulite of polymer is not perfectly spherical, but a three-dimensional spherical assembly of two-dimensional lamellar crystals, a slightly smaller value of n may be observed. Since the values of n are equal to the dimensionality d of the crystal for the crystallization induced by inhomogenous nucleation, the following relation is derived from Eqs. (2) and (3):

$$G \propto t_{1/2}^{-1} \tag{4}$$

between the half-time $t_{1/2}$, the time at which the crystallinity $X(t) = 1/2$, and the linear growth rate G. The half-time $t_{1/2}$ and the linear growth rate G evaluated from Figs. 1 and 2 are plotted against crystallization temperature T_c in a double-logarithmic scale in Fig. 4. G and $t_{1/2}^{-1}$ can be superposed by shifting the data along the ordinate, and hence, Eq. (4) is experimentally verified. Therefore, for inhomogenous nucleation, DSC and POM measurements yield essentially the same information about the crystallization rate. It is generally difficult to obtain the reproducible value of G in POM measurements because of the difficulties such as temperature control and others, as shown in Fig. 4. On the other hand, $t_{1/2}$ can be precisely determined by DSC. Therefore, although it is difficult to de-

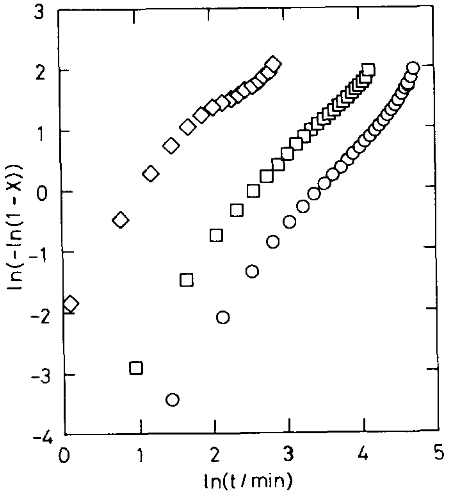

Fig. 1. Avrami plots for PEO ($M_{PEO} = 5 \times 10^4$) at crystallization temperature $T_c = 320$ (○), 325 (□) and 327 K (◇).

termine the absolute value of *G* from DSC compared with POM measurements, the relative value is obtained precisely. Therefore, DSC measurements can be a strong means to determine the relative value of *G*, e.g. in determination of the temperature dependence of *G*. Such a case is shown below.

A number of studies on the crystallization process of polymer show that *G* follows

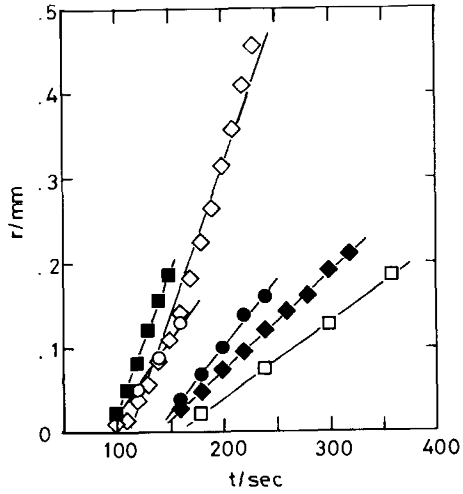

Fig. 2. Time evolutions of radii of spherulite *r* for PEO ($M_{PEO} = 5 \times 10^4$) at $T_c = 320.5$ (■), 321.2 (◇), 323.2 (●), 323.4 (◆), 323.5 (○) and 324.6 K (□).

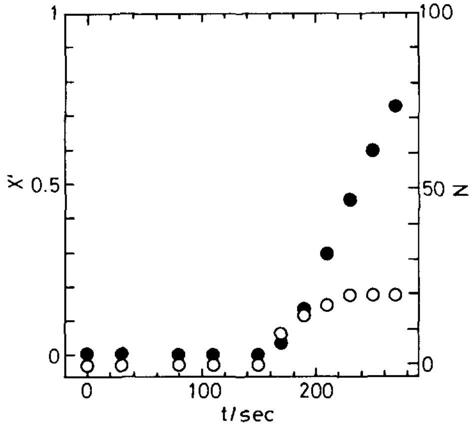

Fig. 3. Time evolutions of apparent crystallinity X' (●) and the number of nucleus N (O) for PEO ($M_{\mathrm{PEO}} = 5 \times 10^4$) at $T_c = 326.0$ K.

$$G = G_0\eta(T_c)\exp(-E/\Delta T_m) \tag{5}$$

where G_0 is a constant [3,4] and $\eta(T_c)$ the viscosity term which represents the temperature dependence of the mobility of segments of crystalline polymer [13–15]. The WLF equation, which is used in polymer rheology as the function representing the temperature dependence of the shift factor, is usually used as $\eta(T_c)$ [16]. However, since the temperature dependence of $\eta(T_c)$ is very small compared with the temperature dependence of the

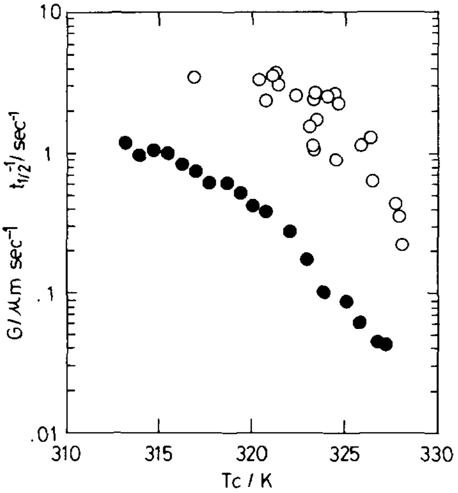

Fig. 4. Plots of log G (O) and log $t_{1/2}^{-1}$ (●) for PEO ($M_{\mathrm{PEO}} = 5 \times 10^4$) versus T_c.

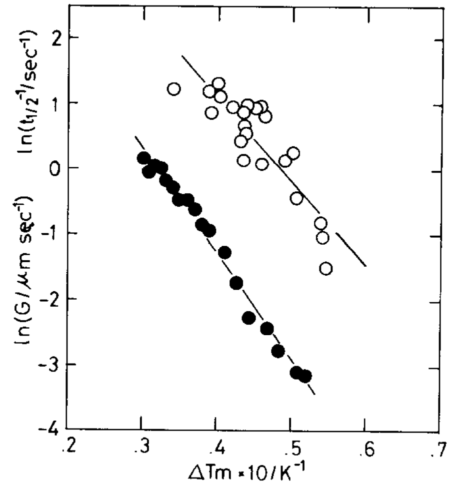

Fig. 5. Arrhenius plots of G (○) and $t_{1/2}^{-1}$ (●) for PEO ($M_{\mathrm{PEO}} = 5 \times 10^4$).

exponential term in the usual temperature region ($\Delta T_m = | T_m^0 - T_c| \sim 10$ K) as measured here, $\eta(T_c)$ can be regarded as a constant. The T_c-dependence of $\eta(T_c)$ is necessary in consideration of crystallization over a wide range of crystallization temperature T_c, i.e. crystallization from both melt (melt crystallization) and glassy state (cold crystallization). E is regarded as a constant representing the temperature dependence of G. Eq. (5) differs from the usual Arrhenius type equation

$$G = G_0 \exp(-E_a/T_c) \tag{6}$$

In Eq. (5), the temperature variable ΔT_m representing the temperature difference of T_c from T_m^0 is used in the exponential term instead of the crystallization temperature T_c. The activation energy E_a for the formation of a secondary nucleus on the growing side surface of the crystal is inversely proportional to ΔT_m ($E_a = k/\Delta T_m$, k a constant). The variation of ΔT_m^{-1} is much larger than that of T_c^{-1} in the temperature region usually observed in the melt crystallization. Therefore, k/T_c (= E in Eq. (5)) is usually regarded as constant, and hence the temperature dependence of G is represented by Eq. (5). Exactly, E in Eq. (5) is the constant characterizing the temperature dependence of the activation energy ($\propto E/\Delta T_m$) for the formation of a secondary nucleus on the growing side surface of crystal. Thus, the temperature dependence of G is mainly determined by the exponential term in Eq. (5). Fig. 5 shows Arrhenius plots of ln $t_{1/2}^{-1}$ and ln G versus ΔT_m^{-1}. As reasonably expected from Fig. 4, the values of the slopes of ln $t_{1/2}^{-1}$ and ln G are the same within experimental error, and yield $E = 160$ and 129 for ln $t_{1/2}^{-1}$ and ln G, respectively. It should be noted that an enormous number of data points are needed to obtain good results in POM measurements, but a relatively small number of data can yield good results in DSC measurements. When the temperature dependence of G is required rather than the

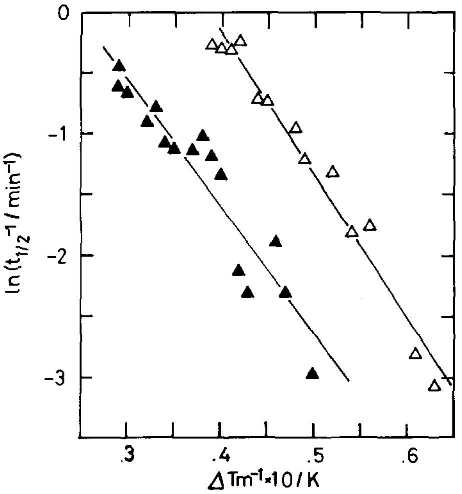

Fig. 6. Arrhenius plots of $t_{1/2}^{-1}$ for PEO ($M_{PEO} = 4 \times 10^3$) (△) and PEO (4×10^3)/PMMA (▲).

absolute value of G, DSC measurements yield better results rather than POM measurements.

In order to verify Eq. (4), we examine below whether the results obtained by DSC and POM measurements for PEOs and PEO/PMMA blends with different molecular weight of PEO yield consistent results. Fig. 6 shows the Arrhenius plots of $t_{1/2}^{-1}$ obtained by DSC for PEO ($M_{PEO} = 4 \times 10^3$) and PEO ($M_{PEO} = 4 \times 10^3$)/PMMA blend. Fig. 7 shows the Arrhenius plots of G obtained by POM for the same samples. In POM measurements,

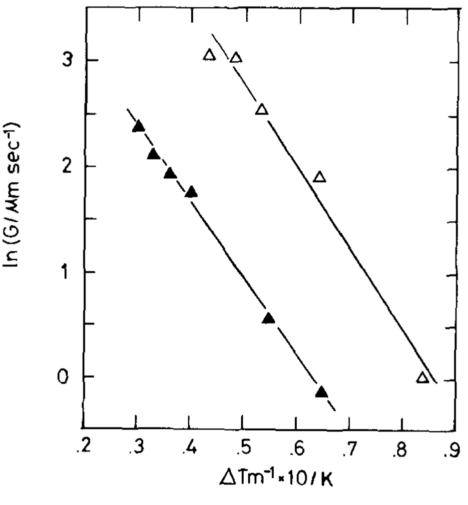

Fig. 7. Arrhenius plots of G for PEO ($M_{PEO} = 4 \times 10^3$) (△) and PEO (4×10^3)/PMMA (▲).

Table 3

Values of E obtained by DSC and POM for various PEOs and PEO/PMMA blends

M_{PEO}	E_{DSC}/K		E_{POM}/K	
	PEO	PEO/PMMA	PEO	PEO/PMMA
4×10^3	117	104	76	71
6.8×10^3	112	112	110	104
5×10^4	160	163	129	163

data points show some scatter because of the relatively low accuracy. Therefore, E also shows some scatter taking the value around the DSC value. However, E approached the DSC value by repeating the measurements. The slopes of the plots for PEO and PEO/PMMA blend in Figs. 6 and 7 show that the value of E characterizing the temperature dependence of the activation energy for formation of a secondary nucleus is not affected by blending PMMA. The values of E are listed in Table 3. The values of E for PEO ($M_{PEO} = 4 \times 10^3$) and PEO ($M_{PEO} = 4 \times 10^3$)/PMMA blend determined by POM are slightly smaller than those determined by DSC. In POM measurements of these systems, the crystallization rate was 1–2 orders of magnitude faster than that of other systems. Therefore, in the low temperature region, crystallization took place in the cooling process before reaching the isothermal state. This fact makes the measured value of G smaller than the true value. Smaller values of E for PEO ($M_{PEO} = 4 \times 10^3$) and PEO ($M_{PEO} = 4 \times 10^3$)/PMMA blend were thus obtained in the low temperature region. The disagreement between E values determined by DSC and POM seems to be due to the underestimation of G in POM measurements in the low temperature region. Therefore, the disagreement of E was not responsible for the invalidity of Eq. (4) but the limitation of measurements by POM. E values listed in Table 3 may show an increasing tendency with increasing molecular weight of PEO. Generally, the activation energy of polymers is much higher than that of low molecular weight materials. The difference in activation energy between polymers and low molecular weight materials can be easily understood by their difference in crystallization behavior. That is, polymer can crystallize only in the large ΔT_m region, while low molecular weight materials can easily crystallize even in the small ΔT_m region. The variation of the activation energy E in Table 3 may correspond to the crossover of E from low molecular weight material to polymer.

4. Conclusion

The following conclusion was obtained from the measurements of isothermal crystallization of PEO and PEO/PMMA blends in low molecular weight region of PEO. (1) Eq. (4) holds in the crystallization process of polymer induced by inhomogenous nucleation. (2) Therefore, the temperature dependence of the activation energy for the formation of a secondary nucleus can be evaluated from the $t_{1/2}$ value measured by DSC. (3) The value of E characterizing the temperature dependence of the activation energy is not affected by blending PMMA. (4) The increasing tendency of E with molecular weight of PEO may correspond to the crossover of E from low molecular weight material to polymer.

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