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The activation energy of Poly (D, L-lactide) in relation to the enthalpy relaxation induced by the cooling rate experiment

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ABSTRACT
Enthalpy relaxation experiments were conducted for racemic poly(D, L-lactide) with different cooling rates (q) using differential scanning calorimetry to examine the relationship between the rate and limiting fictive temperature (T_f'), which is used as an index of the departure from the equilibrium state. The collected heat flow curve was converted to heat capacity data with reference to a heat capacity of standard indium sample. The T_f' value for a given cooling rate was calculated using the "equal area" method, and the apparent activation energy was evaluated from the slope of a plot of $\ln(q)$ vs. $(T_f')^{-1}$. The value calculated in this study was discussed with reference to the activation energy reported for poly(D, L-lactide) in the existing literature and compared with other polymers of various types.
Keywords **-** activation energy, enthalpy relaxation, fictive temperature, glass transition, polylactide

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I. INTRODUCTION

1. Introduction

Polymer glasses are mostly disordered materials, that display short-range ordering over only few molecular dimensions. Although they do not have an ordered structure like crystals, they mechanically behave like solid materials. Practical plastics, for example, often regarded as having disordered structures, are of significant interest because of their inherently non-equilibrium properties. Even materials that are not polymers can form glasses when they are cooled from the melt at a cooling rate sufficient to avoid crystallization. In addition, they exhibit very different chemical nature and physical properties, and the cooling rate applied to achieve a glass is nature-specific. Independently of its nature, when the glass-forming material is cooled sufficiently fast, its viscosity increases and reaches an order of 100 GPa·s at a temperature that defines the well-known glass transition temperature (T_g). The significant factors affecting glass formation are time and temperature. Consequently, the thermodynamic properties (volume, enthalpy, and entropy, etc.) of the resultant glass go out of equilibrium.

In the past century, numerous concepts have been used to characterize the time-temperature dependency of the glass transition. In 1931, Tool et al. introduced the concept of limiting fictive temperature (T_f), which characterizes the transition of the glassy state to the liquid state to represent the index of the departure from the equilibrium state [1]. Due to the non-equilibrium state of a glass, its thermodynamic properties slowly evolve towards equilibrium below T_g. Accordingly, T_f is the temperature at which the thermodynamic property variation related to structural relaxation would be at equilibrium. The variable used to characterize the slow evolution is the relaxation time (τ). Nonlinearity was proposed by Narayanaswamy in the evolution by allowing τ to be an explicit function of T_f and real temperature [2].

$$\tau = A\exp\left(\frac{x\Delta h^*}{RT}+\frac{(1-x)\Delta h^*}{RT_f}\right) (1).$$

A, Δh^*, R are pre-exponential factor, the activation energy, and the ideal gas constant. The variable x ($0< x < 1$) is a parameter that partitions the temperature dependence and structural dependence of τ. Successful analyses for structural relaxation in many polymer species have been reported using phenomenological models that incorporate eq.(1) [3–8]. In particular, in the enthalpy relaxation study using the differential scanning calorimetry (DSC) technique, the calculation for τ using eq.(1) is frequently conducted to capture basic relaxation features. In

determining the value of Δh^*, the method often seen is the cooling rate dependence.

$$\frac{d(\ln(q))}{d(1/T_f)} = -\frac{\Delta h^*}{R} \quad (2)$$

Note that the cooling rate (q) is used as $q > 0$. Eq.(2) expresses a method using an Arrhenius type relationship between q and T_f [9,10] .

Although this method is extensively utilized, it is an empirical treatment to apply the cooling rate data to Arrhenius-type temperature dependence. Different approaches have been presented to estimate the activation energy, including other similar energy constants [11]. The activation energy is closely related to the configurational energy barrier, which is described to originate from bond rotations in the skeletal chain. In addition, Δh^* reflects the cooperative nature of the relaxation process and is highly dependent on the structure and morphology of the polymer. Accordingly, an investigation into Δh^* estimation would have significance from the viewpoint of plastic processing.

We examined the cooling rate method in this study for the purpose of extending examples of the measurements to contribute to increase reliability of the method of eq.(2). The sample used was poly(D, L-lactide) (PDLLA) because of its ease of availability and relatively higher responsiveness to cooling rate experiments. The significance of presenting fundamental physical properties was also taken into consideration, since a great deal of interest has been expressed as a biodegradable and biocompatible material [12,13]. With respect to Δh^* value of PDLLA, previous study has already reported the data obtained from q and T_f, in which PDLLA of slightly lower molecular weight was used [14]. Moreover, several studies have reported the thermal relaxation of PDLLA, for example, the relationship between T_g and molecular weight examined using fast-scan calorimetry, and the transition behavior examined from the viewpoint of mobile and rigid amorphous fractions [15–17]. The results obtained in this study were discussed with reference to these previous reports, which would contribute to the fundamental data within the plastic engineering.

II. Experimental

Racemic PDLLA copolymer pellets were purchased from Sigma-Aldrich(USA), product no. 531162. The nominal number average (M_n) and weight average (M_w) molecular weights were 75,000 and 120,000 , respectively. DSC scans up to 180°C showed no peaks resulting from crystallization and melting, which suggests that the PDLLA pellets used in this study did not show any property of a crystalline state. Metal indium was provided by Epolead Service Inc. (Japan) as a standard substance. DSC examinations were conducted with a Seiko DSC 200 (SII Seiko Instrument Inc. Japan) equipped with a module chamber of refrigerant using aluminum open sample pans of 5ϕ. The weight of the PDLLA sample was 17.50 mg.

The temperature programs employed for the cooling rate experiment were as follows: starting from a temperature of 110°C, well above T_g (the former history is erased), PDLLA sample was cooled to approximately 5°C at a constant rate of q (°C/min), then the heating scan was performed after an isothermal hold of 20 min, at a rate of 5°C/min between 5°C and 95°C to collect the heat flow (HF) curve. The HF curve of PDLLA was converted to the heat capacity data ($c_p(T)$) with reference to the HF values of 47.3 mg of indium using the following temperature program: starting from a temperature of 5°C with a hold time of 20 min, and then heating scan was performed at a rate of 5°C/min between 5°C and 85°C. Likewise, a heating scan of an empty pan was conducted; that is, two empty pans were placed at both the reference and sample holders.

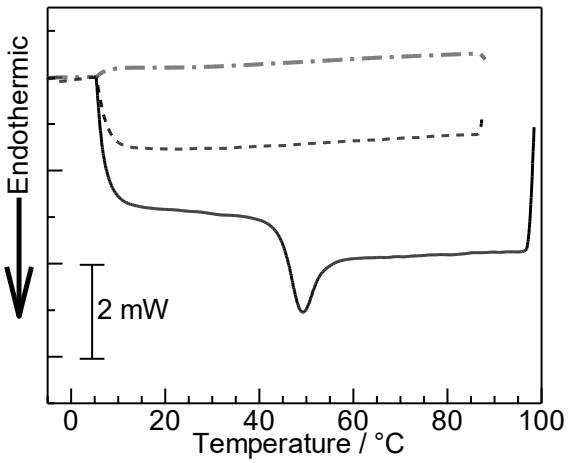


Figure 1.
Heat flow curves of an empty pan (grey dashed line), standard indium (black dotted line), and PDLLA (black solid line) acquired by heating scans at 5°C/min.

III. Results and Discussion

Figure 1 shows the HF curves of the empty pan, indium, and PDLLA cooled with q = 1°C/min, collected by heating scans. An isothermal hold of 20 min was applied prior to the heating scan to stabilize the baseline approximately 5°C, allowing the three curves to be aligned by shifting along the Y-axis. At the beginning of the scan, the HF of the empty pan slightly increased, followed by a flat stable line, whereas the curves of indium and PDLLA showed

large decreases. A typical stepwise curve, usually called the T_g-shoulder, accompanied by an overshoot appeared in the HF of PDLLA in the broad temperature range of approximately 40 – 55°C. T_g= 43.5°C was determined by the onset definition in the T_g-shoulder. The stable baselines before and after the transition zone enabled the calculation of $c_p(T)$ by defining Y_{ref} and Y_{samp} as the differences in the HF between indium and empty pan, and between PDLLA and empty pan at the respective temperatures. It was obtained using eq.(3).

$$c_{p,samp} = \frac{Y_{samp} \times m_{ref}}{Y_{ref} \times m_{samp}} \times c_{p,ref} \qquad (3)$$

$c_{p,samp}$ and $c_{p,ref}$ are the heat capacities of PDLLA and indium, respectively, m_{samp} and m_{ref} are their weights. The following cubic function was applied with respect to $c_{p,ref}$.

$$c_{p,ref} = pT^3 + qT^2 + rT + s \qquad (4)$$

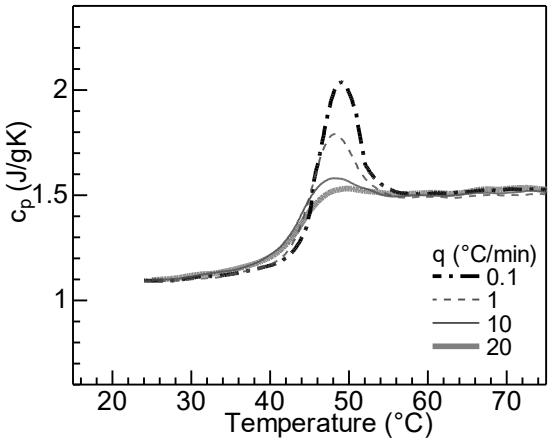


Figure 2.
$c_p(T)$ curves of PDLLA cooled at the rates indicated in the figure.

The coefficients derived with reference to the literature value were [18] , $p = 7.5\times10^{-9}$, $q = -1.7\times10^{-6}$, $r = 2.7\times10^{-4}$, and $s = 2.3\times10^{-1}$. The HF curves of PDLLA with q = 0.1, 1, 10, and 20°C were collected and converted to $c_p(T)$ curves (see Figure 2), indicating typical relaxation behavior in the vicinity of T_g caused by the cooling rate experiments. The observed relaxation indicates that, the glassy states during the isothermal hold at 5°C reached with different cooling rates were in different enthalpies. The difference in enthalpy can be assessed using the limiting value of the fictive temperature (T_f') determinable with the method of "equal area" expressed by eq.(5).

$$\int_{T_f'}^{T>T_g} (c_{pl} - c_{pg})dT = \int_{T<T_g}^{T>T_g} (c_p - c_{pg})dT \qquad (5)$$

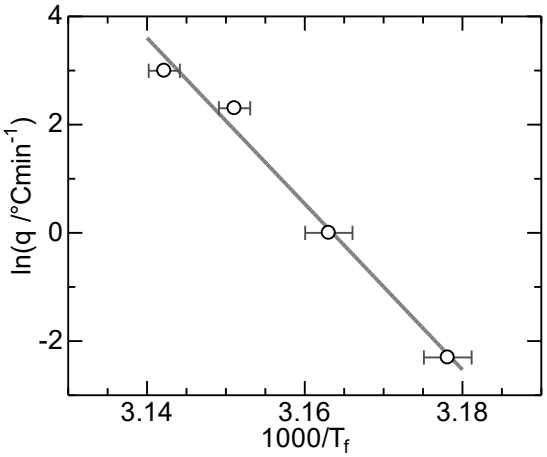


Figure 3. Plot of log(cooling rate) vs. the reciprocal fictive temperature for the $c_p(T)$ curves shown in Figure 2. The straight line represents the least-squares fit to the data.

c_{pg} and c_{pl} represent the values of the glassy and liquid heat capacities, respectively. They were expressed by the following linear equations with coefficients determined using data fitting:

$c_{pg} = a\times T + b$; $a = 3.21\times10^{-3}$, $b = 1.012$.

$c_{pl} = a\times T + b$; $a = -1.19\times10^{-3}$, $b = 1.570$.

On the basis of the calculation results of T_f', a plot of $\ln(q)$ vs. $(1000/T_f)$ was constructed assuming that T_f' = T_f (see Figure 3). The plot result clearly shows the linear relation between $\ln(q)$ and T_f^{-1}, that is, the Arrhenius type dependence was observed between them. The value of Δh^* was calculated from the slope of the plot, and listed in Table 1 together with the values reported in the literatures for various polymers.

Table 1. Literature values of the activation energy (Δh^*) of various polymers.

Polymer	Δh^* (kJ/mol)	Ref.
PDLLA	1274	This work.
PDLLA	1123	[14]
Polystyrene (D.P.=7)	293	[19]
Polyvinyl acetate	462	[20]
4PM[(a)]	700	[21]
Thiol-Ene network[(b)]	353	[22]

(a) poly((3-methyl-4'-pentyloxy) azobenzene) hexyl-methacrylate) .

(b) polymer network of (trimethylolpropane tri(3-mercapto-propionate)- co –(allyl pentaerythritol))

In Table 1, polystyrene with a low molecular weight (degree of polymerization (D.P) is 7), polyvinyl acetate as a representative of conventional polymer, 4PM as an example of side-chain type polymer, and Thiol-Ene copolymer as an example of

network polymer, their Δh^* values were listed for comparison [14,19–22]. The value obtained in this study was the highest among those listed in Table 1. This value was slightly larger than that reported in the literature, which might be attributable to the difference in the molecular weight (M_w value of PDLLA reported in the literature is M_w = 46000) [14]. The fact that Δh^* of PDLLA is higher than the values of other polymers shown in Table 1 may indicate that the rigidity of polymer chain can be one of the factors that have increased the energy value, as the higher rigidity inevitably requires a higher configurational activation threshold. The incorporation of the D unit into the PLLA chains changes the chain conformation, particularly at the D-L junctions, as well as chain rigidity, which is also a factor to increase Δh^*. In conclusion, an Arrhenius type relationship was obtained in this study between $\ln(q)$ and T_f^{-1} from the cooling rate experiments on PDLLA. The value of the activation energy determined was comparable to that reported in the existing literature.

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