



## Enthalpy Relaxation Rate of Poly(ethylene terephthalate) During Isothermal Crystallization†

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Isothermal crystallization behaviour of poly(ethylene terephthalate) (PET) from its melt were studied from the viewpoint of enthalpy relaxation rate ( $r_h$ ). The ratios of  $r_h$  and relative crystallization rate ( $r_c$ ) are constant and their trends are the same during the whole crystallization. There is one relative degree of crystallinity ( $X_c$ ) and time critical point ( $t_c$ ) at which the trend of  $r_h$  increasing ended and it began decreasing. The values of degree of crystallinity, time critical point and enthalpy relaxation rates at 0 and  $X_c$  were figured out directly from the curve of enthalpy relaxation rate. It is provided new angle to insight crystallization process of polymeric melt.

**Keywords:** Isothermal crystallization, Enthalpy relaxation rate, Poly(ethylene terephthalate).

### INTRODUCTION

Crystallization behaviours of polymeric melt, including those of isothermal and non-isothermal, are still interesting to polymer scientists<sup>1-6</sup>. Much attention has been paid to explain the crystallization mechanism. It is well known that it is beneficial to grasp and uncover more details when crystallization mechanisms are investigated. Among a variety of experimental techniques used to investigate the crystallization behaviours under isothermal and non-isothermal conditions, differential scanning calorimetry (DSC) technique is the most common one. The isothermal crystallization data are usually analyzed using the Avrami theory of phase transformation (eqn. 1). Where,  $X(t)$  is the fractional relative crystallization at time  $t$ ,  $Z$  the rate constant and  $n$  the Avrami exponent.

$$1 - X(t) = \exp(-Zt^n) \quad (1)$$

$$X(t) = \frac{\Delta H_t}{\Delta H_\infty} = \int_0^t \left( \frac{dH}{dt} \right) dt / \int_0^\infty \left( \frac{dH}{dt} \right) dt \quad (2)$$

In this paper, one new function of enthalpy relaxation rate ( $r_h$ ) was defined and studied. More information related to isothermal crystallization was provided. In this paper, poly(ethylene terephthalate) was selected as sample study.

### EXPERIMENTAL

Poly(ethylene terephthalate) was synthesized according to our previously described method<sup>7</sup>. It had an intrinsic viscosity of 0.671 measured with Ubbelohde viscometer.

The characterization of crystallization behaviours was carried out with a DSC-7 Perkin Elmer instrument under a nitrogen atmosphere. The heat flow and temperatures of the DSC were calibrated with standard materials, indium and zinc. The weight of the specimen was 4.2 mg. The specimen was heated to 520 K and kept at this temperature for 5 min in order to eliminate the heating history. After rapidly cooling to a selected crystallization temperature ( $T_c$ ) at the rate of the 130 K/min, all samples were kept at  $T_c$  to the end of their exothermic crystallization peak. In this paper, crystallization temperature  $T_c$  of 475, 477, 479, 481 and 483 K were selected. All collected DSC dates were processed by software of "Microcal Origin 6.0".

### RESULTS AND DISCUSSION

Data of  $dH/dt$  used in eqn. 2 were collected by DSC directly. In this paper, one new function, the enthalpy relaxation rate ( $r_h$ ) was defined by eqn. 3. There is a negative sign in eqn. 3 is based on the fact that enthalpy kept decreasing during the crystallization and the values of  $r_h$  are smaller than 0.

$$r_h = -\frac{dH}{dt} \quad (3)$$

The eqn. 2 was differentiation and eqn. 4 yielded.

$$\frac{dX(t)}{dt} = \frac{1}{\Delta H_\infty} \left( \frac{dH}{dt} \right) = \frac{-1}{\Gamma} \left( \frac{dH}{dt} \right) = \frac{1}{\Gamma} \left( -\frac{d(H)}{dt} \right) = \frac{r_h}{\Gamma} \quad (4)$$

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where,  $\Gamma$  is equal to  $-\Delta H_{\infty}$  and larger than 0.  $\Gamma$  is a constant for the whole crystallization process and is not time-independent. The  $r_c$  in eqn. 4 is the change of relative degree of crystallinity in unit time and is named  $r_c$ , namely,  $r_c = dX/(dt)$ . So eqn. 5 is produced.

$$r_c = \frac{dX}{(dt)} = \frac{r_h}{\Gamma} \quad (5)$$

From eqn. 5, the ratio of  $r_h$  and  $r_c$  is the constant  $\Gamma$  and trends of  $r_h$  and  $r_c$  are the same during the whole isothermal crystallization because the value of  $\Gamma$  is larger than 0.

Fig. 1 shows DSC thermograms for various crystallization temperatures. The time at which isothermal crystallization began was taken as the point where the melt was equilibrated at the isothermal crystallization temperature. This point is illustrated with primary heat flow data in the inset of Fig. 1. The dates of heat flow in Fig. 1 were transmitted into  $-dH/dt$  ( $r_h$ ) and plotted with time  $t$ . The curves of  $r_h$  versus  $t$  were presented in Fig. 2, which described enthalpy relaxation rate ( $r_h$ ) was time-dependant.

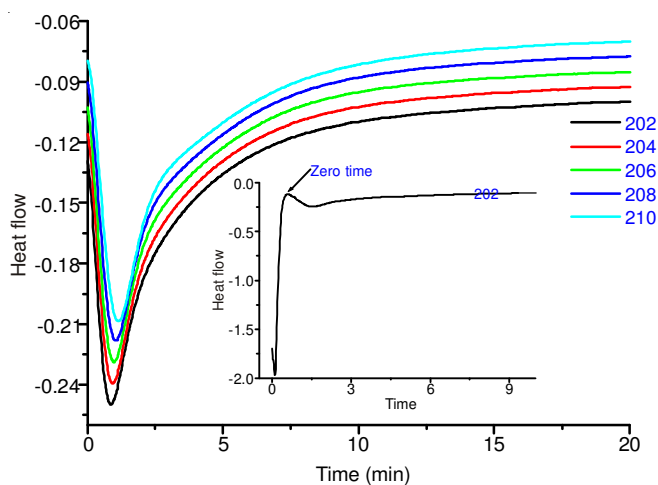


Fig. 1. DSC thermograms for various crystallization temperatures

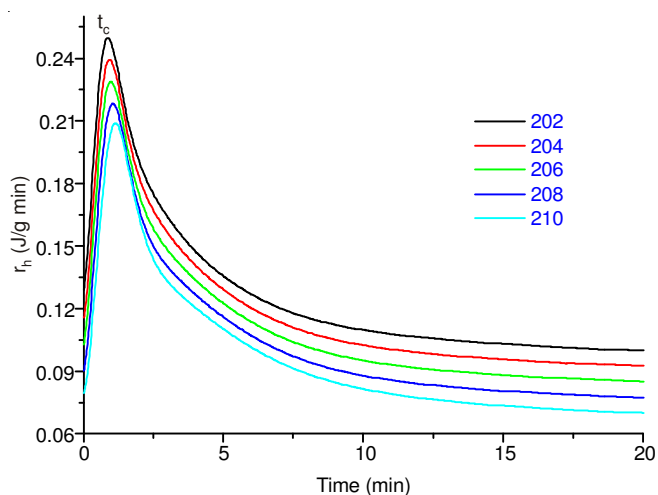


Fig. 2. Curves of  $r_h$  versus  $t$  for various crystallization temperatures

Fig. 2 showed that there is a maximum enthalpy relaxation rate ( $r_h$ ) in each enthalpy relaxation rate curve, which indicates there is one the maximum crystallization rate ( $r_c$ ) during the

crystallization process from eqn. 5. The time point at which the maximum enthalpy relaxation or crystallization rate appeared is a critical point in the  $r_h$  and were labeled as  $t_c$ . From Fig. 2, for all curves, the trends of  $r_h$  are opposite before and after time point  $t_c$ . Based on eqn. 5, trend of  $r_c$  are same with that of  $r_h$ . So trends of  $r_c$  are opposite before and after time point  $t_c$ . The different trends of  $r_h$  and  $r_c$  before and after time point  $t_c$  suggested that different controlling mechanisms for enthalpy relaxation and crystallization before and after time point  $t_c$ .

The values of  $r_h$  for different enthalpy relaxation temperatures (crystallization temperatures) at zero time point and  $t_c$  were obtained from the  $r_h$  curves in Fig. 2 and are named  $r_{h,0}$  and  $r_{h,max}$ . The values of  $r_{h,0}$  and  $r_{h,max}$  are listed in Table-1.

Crystallization temp. (K)	475	477	479	481	483
$r_{h,0}$ (J/g min)	0.130	0.116	0.103	0.0906	0.0797
$r_{h,max}$ (J/g min)	0.250	0.239	0.229	0.218	0.209
$t_c$ (min)	0.88	0.93	0.99	1.05	1.13
$X_c$ (%)	20.5	19.9	19.6	19.5	19.2

When lower crystallization temperatures were used, both  $r_{h,0}$  and  $r_{h,max}$  were larger (Table-1). For example, the values of  $r_{h,0}$  (J/g min.) were 0.072 and 0.130 for 485 and 475 (K), respectively. The  $r_{h,0}$  (J/g min) at 485 K was only 55 % for that for 475 K. The crystallization temperature affected  $r_{h,0}$  (J/g min) significantly. When the poly(ethylene terephthalate) melt was cooled to  $T_c$ , excessive enthalpy was stored in the investigated system and can be regarded as a kind of thermal load. The release of thermal load was time-dependant and involved one kind of relaxation process. When the poly(ethylene terephthalate) melt was cooled to a lower  $T_c$  temperature, the thermal load became bigger and the enthalpy relaxation was driven by a larger driving-force. So,  $r_{h,0}$  and  $r_{h,max}$  were faster at the lower temperature than those at the higher temperature.

It can also be seen from Table-1, for all crystallization temperatures,  $r_{h,max}$  (J/g min) was faster than  $r_{h,0}$ . For example, when crystallization was carried out at 479 K,  $r_{h,max}$  (J/g min) was 0.229 and  $r_{h,0}$  (J/g min) was 0.103. The ratios of  $r_{h,max}/r_{h,0}$  were 1.9, 2.0, 2.2, 2.4 and 2.6 for crystallization temperature of 475, 477, 479, 481 and 483 K, respectively. The difference between the enthalpy relaxation rates  $r_h$  at zero time-point and  $t_c$  was significant and can be interpreted by crystallization mechanism.

As mentioned above, the trends of  $r_c$  before and after time point  $t_c$  were opposite. It indicated different crystallization controlling mechanism before and after time point  $t_c$ . So based on difference of crystallization controlling mechanism during the isothermal crystallization, the crystallization process can be divided into two stages and named stage I and stage II. Although, many reports have suggested a two-stage crystallization theory, but none of these reports clearly give out the critical time point which primary crystallization transmitted into secondary one and no pick out the critical time point is crystallization-dependant. In this paper, the critical time point  $t_c$  between stage I and stage II for different crystallization temperature can be obtained directly from curves in Fig. 2

and were also listed in Table-1. From Table-1, when isothermal crystallization is higher temperature, longer time will be needed to reach  $r_{h,max}$ .

### Conclusions

Based on above study, the following conclusions can be concluded:

- The ratios and trends of enthalpy relaxation rate ( $r_h$ ) and crystallization rate ( $r_c$ ) ( $dX/dt$ ) were constant and simultaneous during the whole isothermal crystallization process from the poly(ethylene terephthalate) melt for special selected crystallization temperature.

- There excited critical value of time ( $t_c$ ) and relative degree of crystallinity ( $X_c$ ) during the isothermal crystallization process. The trends of  $r_h$  (and  $r_c$ ) were opposite before and after  $t_c$ . Based on the difference of trends before and after critical value of time and relative degree of crystallinity, the process was divided into two stages. The viewpoints of chain-entanglement and disentanglement were used to explain the results.

- In general, trends of enthalpy relaxation rate were provided one new angle to investigate the process of phase evolution or crystallization and could uncover more details and information related.

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