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SOLID-STATE CRYSTALLIZATION AND THERMAL RELAXATION IN NYLON 1010

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Quenched nylon 1010 was taken as a sample. Through demonstration that the exothermic peak in the DSC curve is a cold-crystallization peak, the effects of isothermal-crystallization periods and isochronal-crystallization temperatures on the cold-crystallization peak were studied. The effects of annealing temperatures and periods on the thermal relaxation peak were studied. It turned out that the rate of solid-state crystallization is higher in a short period of isothermal crystallization than that in a long period, which possibly results from new hydrogen-bond formation. The solid-state crystallization proceeds easily at higher temperature; the optimum crystallization temperature is 315 K. The temperature range between 277 K and 284 K is a sensitive one as concerns thermal relaxation, the most sensitive point being 281 K.

Introduction

Nylon 1010 is a particular engineering plastic in China. Since few studies had been made on its thermal behaviour, we earlier used DSC to investigate its multiple melting behaviour and its structural reorganization during heating [1, 2]. The present reports on a study of the solid-state crystallization and the thermal relaxation in the glass state, as nothing has been published on this topic to the best of our knowledge. Some phenomena were discovered, which were interpreted theoretically.

Experimental

Nylon 1010 with a molecular weight of ca. 20.000 (original sample) was supplied by Nanlin Chemical Factory. 5 mg samples were weighed in a

Perkin–Elmer AD–2Z autobalance, and were heated to 30 deg beyond the melting point inside the sample holder of a Perkin–Elmer DSC–2C apparatus, kept at this temperature for 5 minutes, allowing it to melt completely, and quenched in liquid nitrogen immediately. The quenched samples were then made. After being subjected to different heat treatments inside the sample holder protected by nitrogen, the quenched samples were scanned at a heating rate of 20 deg/min. The temperature and enthalpy were calibrated with indium, and the experimental results were obtained with a 3600 Data Station.

Results and discussion

I. Studies on solid-state crystallization

Characteristics of the exothermic peak

As shown in Fig. 1, when the original sample was scanned, the melting peak and the glass transition were observed as in curve *a*; when the quenched sample was scanned, the melting peak and an exothermic peak following a thermal relaxation peak were observed as in curve *b*. In order to assess the nature of the exothermic peak, two methods were adopted. First, as shown in Fig. 2, the quenched sample was scanned to the temperature (332 K) at the end of the exothermic peak, followed by quenching in liquid

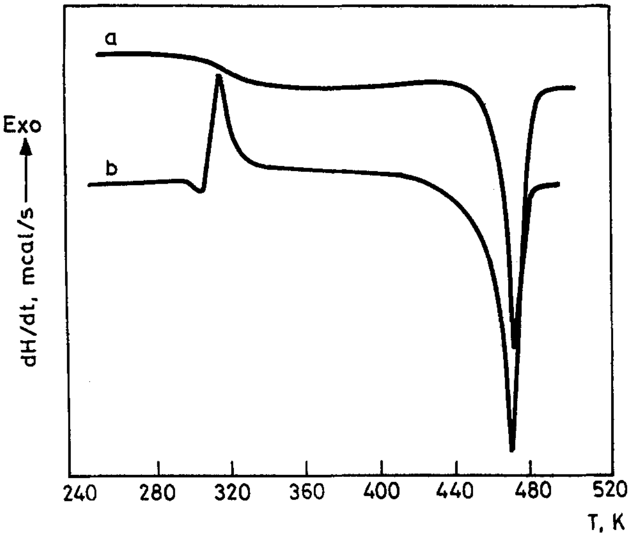

Fig. 1 DSC curves of original sample (a) and quenched sample (b)

nitrogen (curve *a*). On rescanning at 20 deg/min, the exothermic peak disappeared (curve *b*). This phenomenon indicated that the amorphous region in the quenched sample completed cold-crystallization upon being heated to 332 K. Therefore, the exothermic peak is judged to be a cold-crystallization peak. Secondly, the original samples were melted completely and cooled

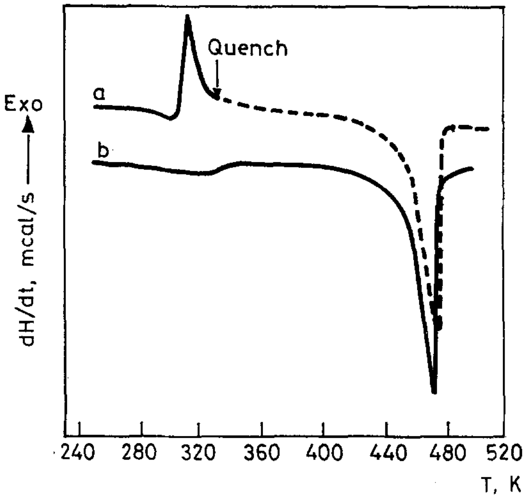

Fig. 2 Effect of partial scanning on exothermic peak; (a) quenched into liquid nitrogen after partial scanning. (b) reheating scanning

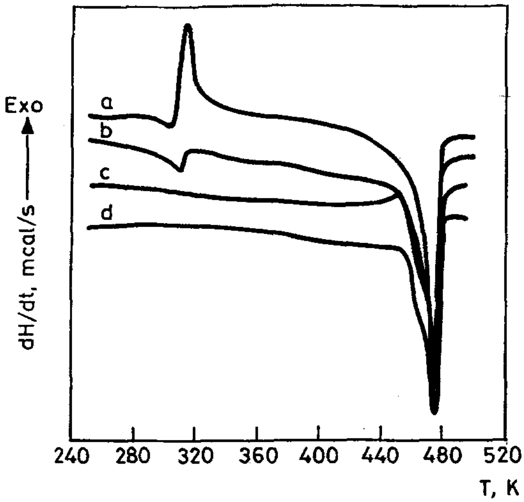

Fig. 3 Effect of cooling rate on exothermic peak; (a) quenched to liquid nitrogen from the melt, (b) cooled in air, (c) cooled at 320 deg/min, (d) cooled at 80 deg/min

from the melt at different cooling rates, i.e. quenched in liquid nitrogen; cooled in air; and cooled to 232 K at cooling rates of 320 deg/min and 80 deg/min, followed by scanning at 20 deg/min. As shown in Fig. 3, the exothermic peak became smaller as the cooling rate decreased; when the cooling rate was decreased to 320 deg/min or 80 deg/min, the exothermic peak disappeared (curves *c* and *d*). This phenomenon indicated that the quenched sample contained a larger amount of amorphous region, which crystallized during heating scanning, displaying a larger exothermic peak. When the sample was cooled in air, the content of amorphous region decreased and the exothermic peak became smaller; when the sample was cooled at 320 deg/min or 80 deg/min, the content of amorphous region decreased further, and only a little crystallization heat was produced during heating scanning; this was concealed in the baseline, and therefore no exothermic peak was observed. The results again led to the conclusion that the exothermic peak is a cold-crystallization peak. It can therefore be employed to demonstrate the content of amorphous region in the sample [3, 4].

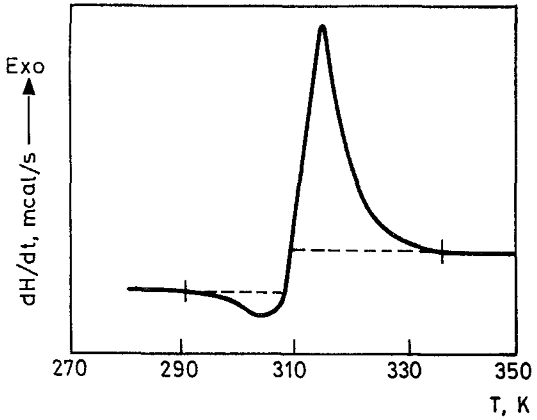

Fig. 4 Method of evaluation of peak area

Since the thermal-relaxation peak appeared accompanied by the cold-crystallization peak, it was difficult to determine the areas of the two peaks by connecting the initial and the return baseline of the peaks as recommended by ICTA. As shown in Fig. 4, the Witlels method [5] was employed to decide the peak area: the initial baseline of the thermal-relaxation peak was extended to determine its peak area, and the return baseline of the cold-crystallization peak was prolonged to determine its peak area.

Effects of isothermal and isochronal crystallization on cold-crystallization peak

The quenched samples were isothermally crystallized for different periods (t) at 299 K, which was lower than the initial temperature of the cold-crystallization peak, and finally scanned at 20 deg/min. As shown in Fig. 5, when the period for isothermal crystallization was prolonged, the area of the cold-crystallization peak became smaller, and the peak temperature of the cold-crystallization peak (T_c) shifted to higher temperature. Its peak temperatures and enthalpies are listed in Table I. The results indicated that the quenched sample underwent crystallization in the isothermal process. The difference between the cold-crystallization enthalpy of the quenched sample (ΔH_{qc}) and the cold-crystallization enthalpy resulting from different annealing periods (ΔH_{tc}) was taken as due to the crystallization in the isothermal process, as demonstrated by the hatched area in Fig. 6 [3]. (ΔH_{qc}–ΔH_{tc}) was plotted as a function of log t, as shown in Fig. 7.

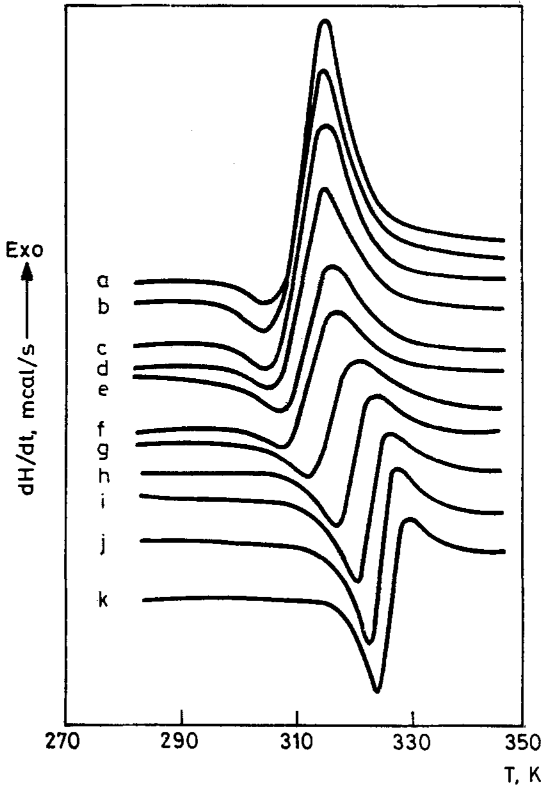

Fig. 5 Cold crystallization curves through different isothermal crystallization periods

Table 1 Enthalpies and peak temperatures of crystallization through different isothermal crystallization period

Isothermal crystallization periods, sec		Cold crystallization	
		ΔH_C, cal/g	Tc, K
(a)	unisothermal	3.65	315.00
(b)	60	3.39	315.42
(c)	120	3.09	315.63
(d)	360	2.43	316.00
(e)	600	1.81	316.44
(f)	900	1.15	317.43
(g)	2700	0.95	321.00
(h)	14400	0.48	324.46
(i)	39600	0.46	327.23
(j)	135000	0.44	328.19
(k)	172800	0.33	330.23

It was found that the rate of solid-state crystallization was higher when the period for isothermal crystallization was limited to within 900 seconds, and was lower beyond 900 seconds. It is worth mentioning that there was an induction period in the T_C *vs.* log t curve, which happened within 900 seconds; T_C rose rapidly after the induction period (Fig. 8). This phenomenon might be explained as follows: According to the record [6, 7], the ordinary polyamides contain a small quantity of free amide groups (less than 1%) [7]. It is probable that the free amide groups in the amorphous chains were rearranged and formed new hydrogen-bonds during the heat treatment at the glass-transition temperature [6]. Thus, the above experimental results seemed to relate to the new hydrogen-bonds formed in the isothermal

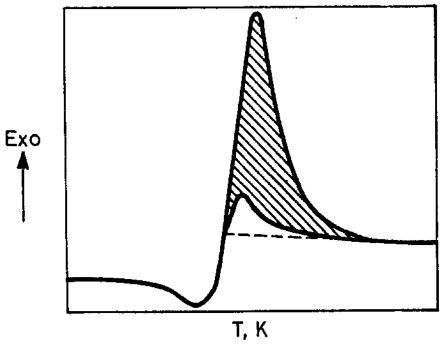

Fig. 6 Schematic figure of amount of crystallization in isothermal process

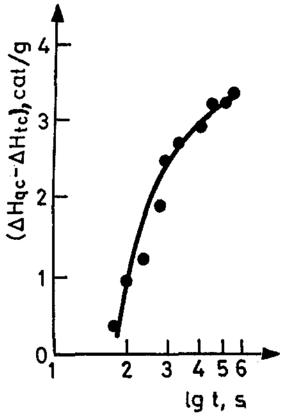

Fig. 7 Rate curve of isothermal crystallization

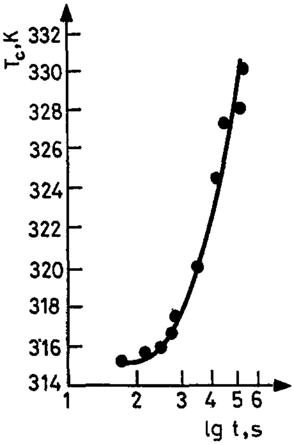

Fig. 8 Relation curve between T_c and lg$t$

process. When the period for isothermal crystallization was shorter, fewer new hydrogen-bonds formed, which meant that there was less resistance to the movement of the molecular chains and allowed the quenched sample to crystallize more easily in the isothermal process, so that the rate of solid-state crystallization was higher. For the same reason, the uncrystallized amorphous region in the isothermal process crystallized easily during heating scanning; thus, T_c was lower, and the induction period emerged. When the period for isothermal crystallization was longer, more new hydrogen-bonds formed, which resulted in an increased resistance to the movement of the molecular chains. Thus, the rate of solid-state crystallization was lower, and the uncrystallized amorphous region in the isothermal process could crystallize only at higher temperature during heating scanning. T_c went up quickly beyond the range of the induction period.

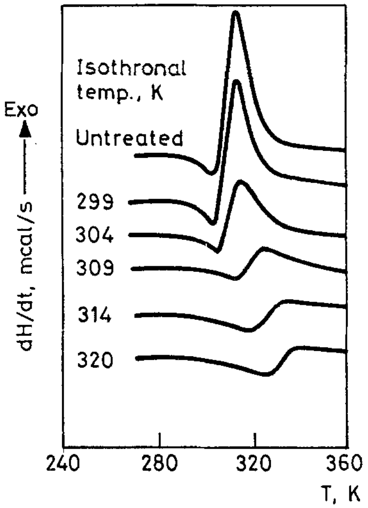

Fig. 9 Curves of cold crystallization through isochronal crystallization at different temperatures

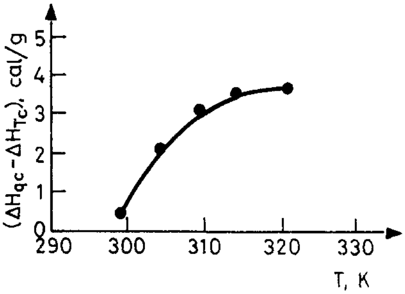

Fig. 10 Rate curve of isochronal crystallization at different temperatures

The quenched sample was subjected to isochronal crystallization for 2 minutes at 299 K, 304 K, 309 K and 314 K, then finally scanned at 20 deg/min. As shown in Fig. 9, as the temperature of isochronal crystallization increased, the peak temperature of cold-crystallization increased and the area of the cold-crystallization peak decreased. The difference between the cold-crystallization enthalpy (of the quenched sample (ΔH_{qc}) and the cold-crystallization enthalpy) resulting from the different isochronal temperatures (ΔH_{Tc}) was taken as due to the crystallization at the isochronal temperature (T). (ΔH_{qc}–ΔH_{Tc}) was plotted as a function of T, as shown in Fig. 10. With regard to the same period of crystallization , Fig. 10

can be considered to be the curve for which the rate of solid-state crystallization was plotted as a function of crystallization temperature. It can be seen that the rate of solid-state crystallization increased as the crystallization temperatures elevated. Beyond 315 K, it did not increase. This indicated that the solid-state crystallization proceeds easily at higher temperature, and that the optimum crystallization temperature is 315 K. As shown in Fig. 11, T_c shifted to higher temperature as the crystallization temperature was increased, which seems to indicate that the uncrystallized amorphous region in the isochronal process could be crystallized only at higher temperature during heating scanning. The origin of this phenomenon demands further study.

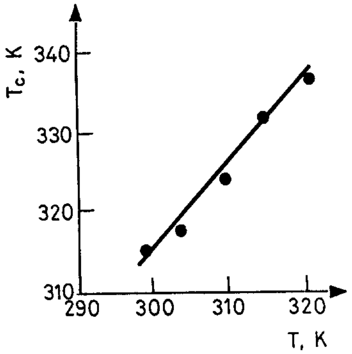

Fig. 11 Relation curve between T_c and T

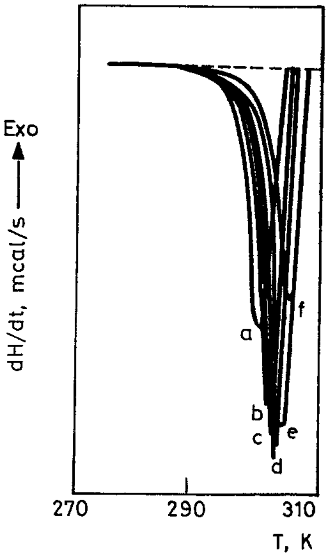

Fig. 12 Thermal relaxation peaks through annealing at different temperatures

II. Studies on thermal relaxation in the glass state

Effects of annealing temperature on thermal-relaxation peak

As shown in Fig. 1.*b*, the quenched sample exhibited a thermal-relaxation peak in the glass state. With a view to investigation of the effects of the annealing temperature on this peak, the quenched sample were annealed for 12 hours at 274 K, 277 K, 279 K, 281 K, 284 K and 289 K, which were lower than its peak temperature, and were then scanned at a heating rate of 20 deg/min. As shown in Fig. 12, the thermal-relaxation peak varied with the

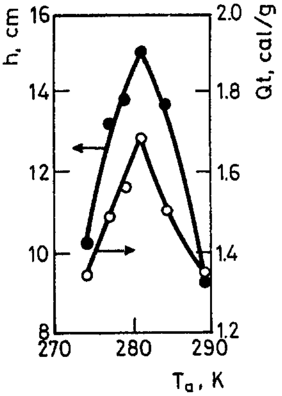

Fig. 13 Relation curves between annealing temperature and peak height/endothermic amount

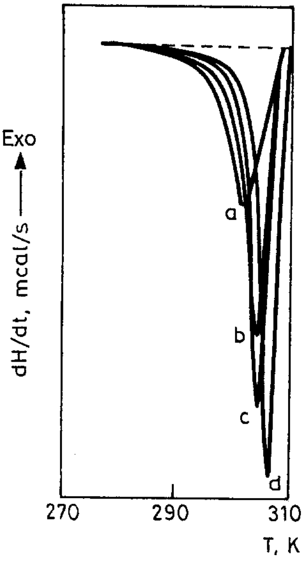

Fig. 14 Thermal relaxation peaks through different annealing periods at 281 K; (a) 1; (b) 6; (c) 12; (d) 22 hr

annealing temperature. The peak height (h) and the endothermic amount (Q_t) were plotted against the annealing temperature (T_a) as shown in Fig. 13. It was found that the peak height and the endothermic amount increased as the annealing temperature was elevated. These values reached their maxima at 281 K, and then decreased as the annealing temperature was continuously raised. It seems that the temperature range between 277 K and 284 K is the range of sensitivity as concerns thermal relaxation.

Effects of annealing period on thermal-relaxation peak

The quenched samples were annealed at 274 K, 281 K and 294 K for different periods and scanned at 20 deg/min. As shown in Fig. 14, the thermal-relaxation peak increased as the annealing period was extended. The endothermic amount (Q_t) was plotted against the annealing period (t), as

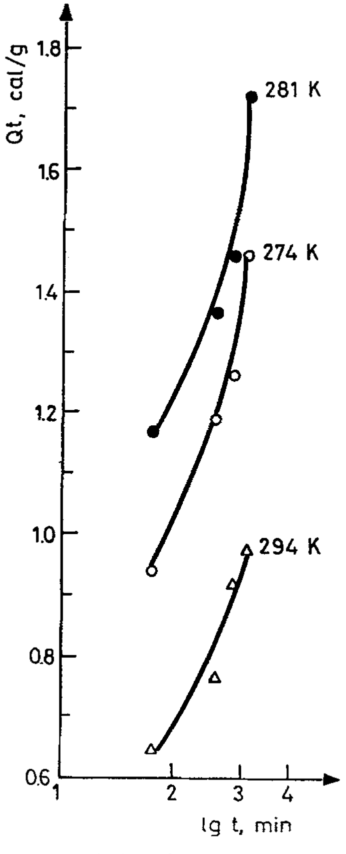

Fig. 15 Relation curves between endothermic amount and annealing periods at different annealing temperatures

shown in Fig. 15. The quenched sample was similar in the thermal-relaxation process at the above annealing temperatures, but different in endothermic amount. All the endotherm maxima appeared at 281 K within the same annealing period. The endothermic amount gradually approached its equlibrium value as the annealing period was extended. It emerged that the structure in the glass state tended to stabilize.

Conclusions

1. The exothermic peak in the DSC curve of the quenched sample is considered to be a cold-crystallization peak.
2. The rate of solid-state crystallization is higher in a shorter crystallization period, and an induction period appeared in the T_c *vs.* log t curve, while the rate was lower in a longer period, and T_c rose rapidly.
3. The solid-state crystallization proceeds easily at higher temperature, and the optimum crystallization temperature is 315 K.
4. The temperature range between 277 K and 284 K is a sensitive one as concerns thermal relaxation; 281 K is the most sensitive point.

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Zusammenfassung — Als Proben wurden abgeschrecktes Nylon 1010 verwendet. Anhand der Demonstrierung, daß es sich bei dem endothermen Peak der DSC Kurve um den Peak einer kalten Kristallisation handelt, wurde der Einfluß von isothermen Kristallisationsperioden und isochroner Kristallisationstemperaturen auf den Peak der kalten Kristallisation untersucht. Der Einfluß des oberen Kühlpunktes und der Kühlperioden auf den Peak der thermischen Relaxation wurde untersucht. Es stellte sich heraus, daß die Geschwindigkeit der Feststoffkristallisation bei einer kürzeren isothermen Kristallisationsperiode höher liegt, als bei einer längeren Periode, was möglicherweise von der Bildung neuen Wasserstoffbrückenbindungen herrührt. Bei höheren Temperaturen verläuft die Feststoffkristallisation einfacher, die optimale Kristallisationstemperatur beträgt 315 K. Der Temperaturbereich 277 – 284 K ist wegen der thermischen Relaxation empfindlicher, der empfindlichste Punkt liegt bei 281 K.