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THERMAL PROPERTIES AND MORPHOLOGY OF CRYSTAL IN NYLON 1010 FORMED ISOTHERMALLY AT MELTING PEAK TEMPERATURE

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Thermal properties and morphology of crystal in NYLON 1010 formed isothermally at melting peak temperature were studied by using DSC, TEM and ED. It turns out that the crystal on the time scale of the DSC experiment is stable, which is not transformed from the crystal with low melting point. Its electron diffraction pattern shows symmetrical and clear electron diffraction spots of single crystal and is proved to be the electron diffraction pattern of single crystal by means of index with parameters of unit cell of Nylon 1010.

Keywords: DSC, electron diffraction, nylon 1010, morphology of crystal, transmission electron microscope

Introduction

Nylon 1010 is a particular engineering plastic in China. We earlier investigated its multiple melting behaviour and structural reorganization during heating by using DSC [1, 2]. This paper is to study the thermal properties and morphology of crystal in Nylon 1010 formed isothermally at melting peak temperature by means of DSC, TEM (Transmission Electron Microscope) and ED (Electron Diffraction).

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Experimental

The preparation of quenched sample for DSC

The original sample with molecular weight 20000 was produced by Jinlin United Chemical Engineering Factory in China. Each original sample of approximately 10 mg was weighed on an AD–2Z autobalance and heated to 503 K in Perkin–Elmer DSC–2C in pure nitrogen, then quenched in liquid nitrogen.

The preparation of TEM sample

Take a few drops of the 0.1% Nylon 1010 in phenol/tetrachloroethane to deposit on a microscope slide and run evenly. After the solvent evaporated, a film was formed, which was subsequently melted completely to erase thermal history and quenched immediately in liquid nitrogen. The so-prepared film was transparent. Put it into a solution of 2% HF in water, allow it to float and be rinsed in distilled water, then pick it up on a microscope slide. When it got dry, the film was examined by PLM (Polarizing Light Microscope). It was found out that the film of PLM was amorphous. The amorphous film was moved to the copper grids and placed in a sample cell of DSC. Subsequently, it was heated to 474 K and crystallized isothermally for different periods followed by cooling to room temperature.

The crystallized sample was carried out electron diffraction at 100 KV by using JEOL JEM–100 CX Electron Microscope. The electron diffraction parameter L_λ was measured by the diffraction ring of gold.

Results and discussion

In order to study thermal properties of the sample crystallized isothermally at melting peak temperature (474 K), various scanning methods were adopted.

Continuous scanning and rescanning after cooling circulation

The quenched sample was crystallized isothermally at 474 K for different periods following scanning. An endothermic peak (Peak I) appeared, in which both peak temperature and peak area increased as crystallization period prolonged (Fig. 1). If the quenched sample was crystallized isothermally at 474 K for different periods, underwent slower and rapid cooling circulation, and rescanned subsequently, a high temperature (Peak II) and a low temperature

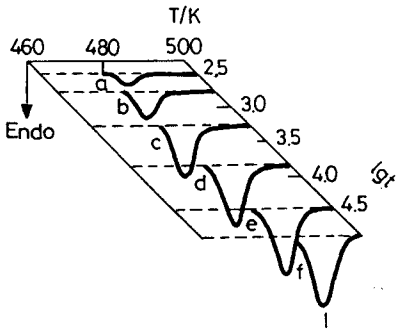

Fig. 1 DSC curves of continuous scanning a, 5; b, 9; c 30; d, 120; e 480; f, 1440 min

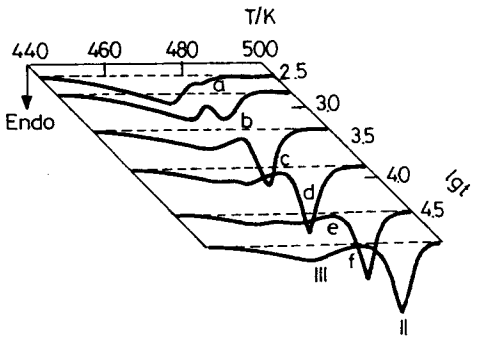

Fig. 2 DSC curves of rescanning after undergoing slower cooling circulation a, 5; b, 9; c 30; d, 120; e 480; f, 1440 min

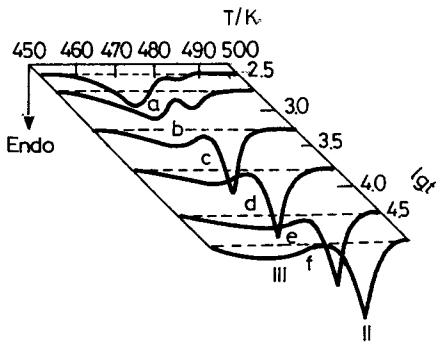

Fig. 3 DSC curves of rescanning after undergoing rapid cooling circulation a, 5; b, 9; c 30; d, 120; e 480; f, 1440 min

(Peak III) endothermic peaks were observed on two groups of DSC curves (Figs 2, 3). The peak temperature and area of Peak II also increased with crystallization period prolonged. The peak temperatures and peak areas of both peaks I and II were taken as a function of isothermal crystallization periods, almost all data fell on the curve. Therefore, Peaks I and II were attributed to the fusion of the crystals formed at melting peak temperature.

Partial scanning

The quenched sample was crystallized isothermally at 474 K for 1440 minutes, and cooled to room temperature followed by rescanning, Peaks II and III appeared (Fig. 4a). The same sample was scanned to a temperature just beyond that of Peak III as shown in Fig. 4b taken out and quenched in liquid nitrogen. Upon rescanning, a high and a low melting peaks still appeared (Fig. 4c), of which both peak temperature and peak area were identical with that of Peaks II and III. It was indicated that the crystals symbolized by Peak III can not be transformed to the crystals symbolized by Peak II through structural reorganization during heat.

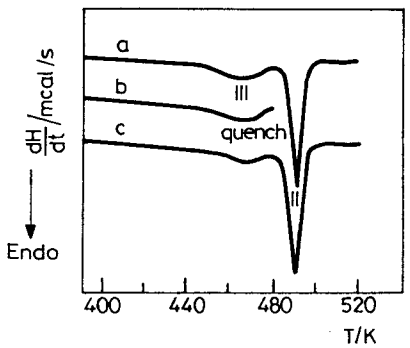

Fig. 4 Nature of Peaks II and III judged by partial scanning

Changing heating rate

The same crystallized sample used in the partial scanning was scanned at various heating rates, as shown in Fig. 5. The relative positions of both Peaks II and III were not influenced by changing heating rate. It was indicated that Peaks II and III may be attributed to the fusion of different crystal in morphology [3].

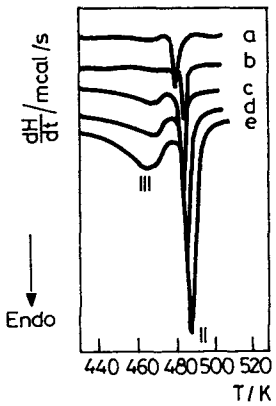

Fig. 5 Nature of Peaks II and III judged by changing heating rate a 1.25; b 2.5; c 5; d 10; e 20 deg·min^{-1}

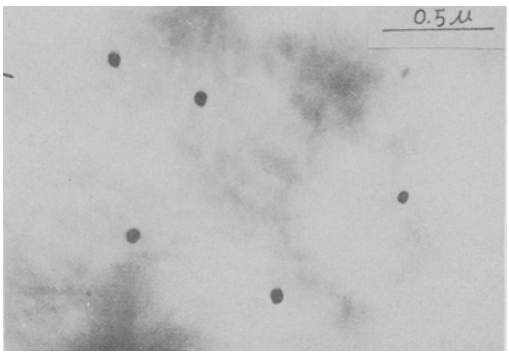

Fig. 6 Crystal formed through isothermal crystallization for 5 min

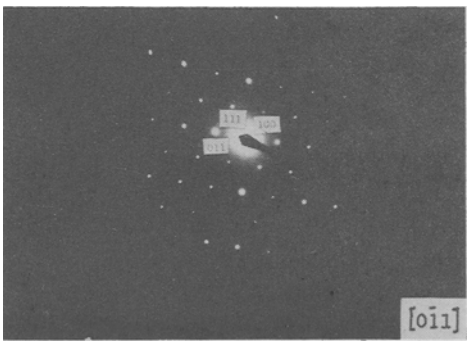

Fig. 7 Electron diffraction pattern of single crystal

Table 1 The examined values and calculated values of spacing and that of angle between refractions

hkl	Spacing		θ 100 – *hkl*	
	d_{cal}	d_{ex}	Cal.	Ex.
100	4.363	4.41		
011	4.152	4.18	115.65	115.5
111	3.991	4.03	60.07	60.0
211	2.407	2.44	31.51	31.5
311	1.607	1.62	20.41	20.4
411	1.189	1.19	14.96	15.0
511	0.940	0.94	11.77	11.8
–111	2.513	2.52	146.93	147.0
–211	1.658	1.67	158.90	159.0
–311	1.218	1.22	164.67	164.7
122	2.300	2.33	87.27	87.3
322	1.547	1.56	42.18	42.1
–122	1.622	1.62	135.23	135.2
–322	1.004	1.00	154.15	154.2

In order to elucidate the reason why the thermal properties appeared, the morphology of crystal formed isothermally at melting peak temperature was studied by using TEM and ED.

When the quenched sample was crystallized isothermally at 474 K for 5 minutes, the crystals with 500 Å in dimension were examined (Fig. 6). The amount and dimension of the crystals increased with crystallization period prolonged. When the period prolonged to 1440 minutes, the crystals increased to 1000 Å in dimension. When the crystals were examined by using ED, their electron diffraction pattern showed symmetrical and clear electron diffraction spots (Fig. 7). By means of index with parameters of unit cell in Nylon 1010 (a = 4.94 Å, b = 5.4 Å, c = 27.8 Å, α = 49, β = 77, γ = 63.5) [4], both the examined value and calculated value of spacing and that of angle between refractions were identical (Table 1). Therefore, the electron diffraction pattern was proved to be that of single crystal in Nylon 1010.

Conclusion

1. The crystal in Nylon 1010, formed by isothermal crystallization at melting peak temperature are different to that formed by slow cooling from the melt in

thermal properties. The former on the time-scale of the DSC experiment is stable and remains its melting characteristics, while the latter can be transformed to the crystals with high melting point through structural reorganization [1].

2. The electron diffraction pattern of the crystals in Nylon 1010 formed by isothermal crystallization at melting peak temperature shows symmetrical and clear electron diffraction spots of single crystals, which proved to be the electron diffraction pattern of single crystal by means of index with the parameters of unit cell in Nylon 1010.

References

1 Fu Shuren et al., Thermal Analysis, Proc. 7th ICTA, Ed. by B. Miller, Vol.2, 1982, p. 1063.
2 Fu Shuren et al., J. Thermal Anal., 36 (1990) 999.
3 D. P. Pope et al., J. Polym. Sci. Phys. Ed., 14 (1976) 811.
4 Mo Zhishen et al., Acta Polymerica Sinica (China), 6 (1990) 655.

Zusammenfassung — Mittels DSC, TEM und ED wurden die thermischen Eigenschaften und die Kristallmorphologie in NYLON 1010 untersucht, welches isotherm bei der Schmelzpeaktemperatur gebildet wurde. Es zeigt sich, daß sich der Kristall in der Zeitskala des DSC-Experimentes stabil erweist, welcher nicht aus dem Kristall mit niedrigem Schmelzpunkt umgewandelt wird. Die Elektronenbeugungsbilder zeigen eine symmetrische und klare Elektronenbeugung von Einkristallen und erweisen sich als Elektronenbeugungsbild eines Einkristalles mit Hilfe von Indizes mit den Parametern der Elementarzelle von Nylon 1010.