

CRYSTALLIZATION BEHAVIOR OF A THERMOTROPIC LIQUID CRYSTAL COPOLYESTER*

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ABSTRACT

A thermotropic liquid crystal copolyester resin based on *p*-hydroxybenzoic acid, 2,6-naphthoic acid, hydroxyquinone and PET was synthesized by melt condensation and studied. The results based on DSC and X-ray diffraction indicated that there were a rapid and a slow crystallization processes for the copolyester at certain conditions. A critical temperature was suggested, below which the slow crystallization could hardly happen. Above the critical temperature the extent of the slow crystallization process depended not only on annealing temperature but also on the annealing time. A fine crystal structure with high melting point and narrow diffraction peak was formed under favorable conditions.

INTRODUCTION

Thermotropic liquid crystal copolyesters (LCP) are of high strength, high modulus and good formability. Nowadays LCP are gaining more and more scientific and commercial importance.

The mechanical properties and processability of LCP strongly depend on their thermal history. Recently there are many reports about the studies of thermal properties of LCP, especially for Vectra made by Celanese^[1-3]. Kamal and his coworkers^[2] reported that there were two crystallization processes with different rates for LCP composed of 70 mol% *p*-hydroxybenzoic acid (HBA) and 30 mol% 2,6-hydroxynaphthoic acid (HNA). But they did not discuss the relations between the two crystallization processes.

In our labs we have synthesized a kind of LCP which was a quaternary random copolyester composed of *p*-hydroxybenzoic acid (HBA), 2,6-naphthoic acid (TNA), hydroxyquinone (HQ) and PET. Compared with Vectra, the copolyester synthesized by us was more complex and more irregular in its molecular structure. So it would be very interesting to see how the structure changes would influence the crystallization processes. Furthermore, it is significant to understand the relation between the two crystallization processes.

EXPERIMENTAL

Synthesis of LCP

HBA and HQ were acetylated, recrystallized and dried. A reactor was charged

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with powders of acetylated HBA, HQ, TNA and chips of PET ($[\eta] = 0.5 - 0.6$ dl/g) in mol ratio of 57.5 : 20 : 20 : 2.5. With nitrogen being fed to the reactor, the temperature was raised and distilled acetic acid was collected to estimate the degree of the reaction. A copolyester with high molecular weight was obtained by reducing pressure at high temperature for certain time.

The nematic texture of the obtained melted LCP was proved by using polarized microscopy equipped with hot stage. The characteristic threaded texture of typical nematics can be seen clearly in Fig. 1. The specific optical property of liquid crystal was also checked for our samples by the method of stir-opalescence, in which the sample was melted and sheared between a pair of slides and turbidity was found^[4].

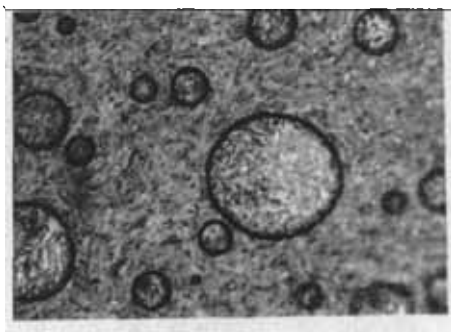


Fig. 1 Nematic texture of the prepared LCP

Sample preparation

In order to keep the conformity of sample preparation, all samples had been pretreated in DSC. There were four groups of samples prepared for DSC measurements:

- Melts were cooled from 370 °C to 30 °C at different speeds from 0.31 to 160 °C/min.
- Melts were quenched to 50 °C at 160 °C/min and then annealed for two hours at temperatures from 160 to 310 °C.
- Melts were cooled from 350 °C to 275 °C and then annealed for different times from 10 to 1360 minutes.
- Melts were cooled from 350 °C to 210 °C and then annealed for different times from 0.5 to 5 hours.

Two groups of samples were prepared for WAXD measurements:

- The same as c), but the annealing temperature was 290 °C.
- Melts were quenched in liquid nitrogen.

Instrumentation

A Perkin-Elmer DSC-2 equipped with TADS was used to carry out calorimetric measurements. Samples were purged with nitrogen and the heating speed was 20 °C/min. All DSC curves shown in this paper came from heating scanning.

X-ray diffraction data were obtained by using a Rigaku Rotaflex D/max-ra X-ray diffractometer with $\text{CuK}\alpha$ radiation and Ni filter at voltage of 40KV and current of 100mA.

RESULTS AND DISCUSSION

The DSC curves for samples which had been cooled from melts at different cooling rates from $0.31\text{ }^{\circ}\text{C}/\text{min}$ to $160\text{ }^{\circ}\text{C}/\text{min}$ were shown in Fig. 2. It is obvious that each sample exhibited a rather broad endothermic peak, even though the fastest cooling rate was about 500 times the slowest one in their thermal history. The endothermic peaks began at about $200\text{ }^{\circ}\text{C}$ and ended at about $310\text{ }^{\circ}\text{C}$. Results from WAXD indicated that there was crystal diffraction pattern even for samples quenched in liquid nitrogen. Therefore the endothermic peaks came from melting of the crystals formed in a rather rapid crystallization process and with less order and wide crystal size distribution. It is different from Vectra in that no other crystallization process could be observed in our system even the melts had been cooled at $0.31\text{ }^{\circ}\text{C}/\text{min}$. In contrast, a slow crystallization process was reported for Vectra if cooling rate was lower than $3.2\text{ }^{\circ}\text{C}/\text{min}$. It seems that our copolyester is more difficult than Vectra to form crystals with higher order because the chain regularity of our LCP was deteriorated by small amount of PET contained in the copolymer chains.

The effect of annealing temperature in a period of two hours can be seen in Fig. 3. When the annealing temperature was raised to about $200\text{ }^{\circ}\text{C}$, a narrow peak began to emerge which was overlapped with original broad peak. With the increase of annealing temperature the peak became narrower and peak position moved towards higher temperature. It can be explained as the effect of slow crystallization and improving of crystals during annealing. In fact the nature of slow crystallization is a recrystallization process. First, part of crystals formed in fast crystallization begin to melt and then more perfect crystals are formed in the process of recrystallization or so-called slow crystallization because of its low speed. From Fig. 3 we can also find that there were no characteristics mentioned above for samples if the annealing temperature was higher than $310\text{ }^{\circ}\text{C}$. The reason is that at that temperature all crystals formed during rapid crystallization have already been melted completely, therefore there are no crystal nuclei for slow crystallization going on.

Fig. 4 shows the DSC curves of samples which had been annealed at $275\text{ }^{\circ}\text{C}$ for different intervals. The general characteristics of rapid crystallization process was kept unchanged if the annealing time was shorter than 100 minutes, but when time was longer than 200 minutes, a sharper melting peak appeared at higher temperature. It is the mark of the existence of crystals formed in slow crystallization, which proceeded more fully with the increase of annealing time. But such effect of annealing time strongly depends on annealing temperature. As we can see from Fig. 5 that at $210\text{ }^{\circ}\text{C}$ no apparent changes could be observed with the increase of annealing time.

It should be mentioned that the broad peaks corresponded to melting of crystals formed in rapid crystallization occurred in all DSC curves. It means rapid crystallization always happens no matter what the annealing temperature and/or annealing time are.

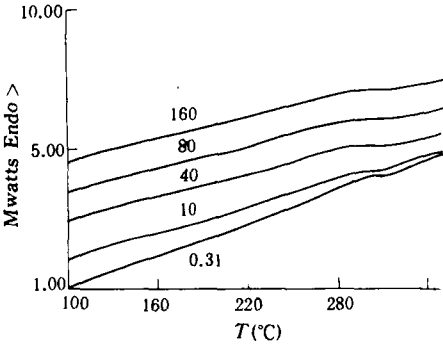


Fig. 2 Melting of crystals formed in fast crystallization. The samples had been cooled at speeds shown on each curve (°C/min)

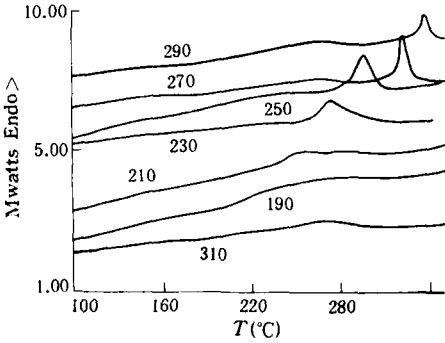


Fig.3 Melting of crystals formed in slow crystallization. Samples had been annealed for two hours at the temperatures(°C) shown on each curve

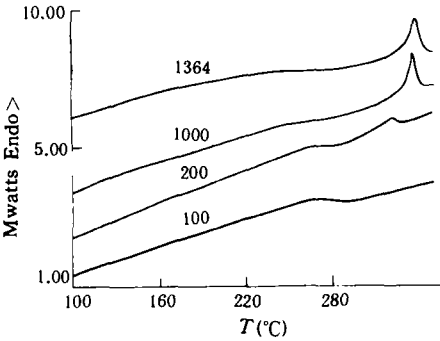


Fig. 4 The effect of annealing time (min.)for the samples which were annealed at 275 °C

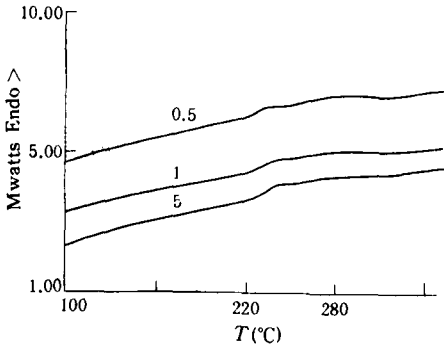


Fig. 5 DSC curves of the samples annealed at 210 °C with different annealing intervals (have on the curve)

The X-ray patterns were obtained for samples treated by annealing or quenching in liquid nitrogen. Both exhibited eight diffraction circles with the following diffraction angles and interplanar distances.

Table 1 X-ray results of the sample

Peak code	Diffraction angle (2θ)	Interplanar distance (Å)
1	8.62	10.30
2	13.64	6.51
3	17.74	5.01
4	19.65	4.53
5	25.34	3.50
6	27.46	3.25
7	29.66	3.02
8	35.42	2.53

The characteristic reflections for pure PET at 5.10, 3.83 and 3.43Å were not found in our samples, neither for pure poly (p - hydroxybenzoic acid) at 4.48,4.24 and 3.73Å [5] or 3.95Å for HNA homopolymer[6]. So it is reasonable to consider our sample as a random copolymer. The X- ray patterns proved that there must be a very fast crystallization process, otherwise there would not be possible for samples quenched in nitrogen to have diffraction characteristics of crystals. Some

crystals parameters were calculated by peak resolution method. There were three peaks which could be observed on the X-ray step scan diffraction curves, while the positions of other peaks had to be determined according to X-ray patterns. There were two presumptions in resolution of multiple peaks:

1. Taking the shape of X-ray scatter curve of an amorphous model sample of LCP as the basis for calculation^[7].
2. The apex of amorphous curve is equal to the value of the lowest point between $2\theta = 25 - 27^\circ$ on X-ray diffraction curve.

In order to study structure changes during annealing treatment, the sample was tested at room temperature and 250°C respectively and then cooled to and measured at room temperature again. The results are shown in Table 2.

Table 2 WAXD results

Parameters	Sample 1 ^{a)}			Sample 2 ^{b)}		
Position of peaks (2θ) $^\circ$	8.4 [#]	19.8 [#]	27.3 [#]	8.4 [#]	19.8 [#]	27.1 [#]
	8.4 [*]	19.3 [*]	26.5 [*]			
	8.4 ^{**}	19.8 ^{**}	27.3 ^{**}			
Width of peaks (2θ) $^\circ$	0.68 [#]	1.30 [#]	1.60 [#]	0.68 [#]	1.54 [#]	3.0 [#]
	0.58 [*]	1.12 [*]	0.90 [*]			
	0.58 ^{**}	1.29 ^{**}	1.54 ^{**}			
Crystallinity (%)		58 [#]			55 [#]	
		59 ^{**}				

a: the sample which had been annealed at 290°C for two hours.

b: the sample which had been quenched in liquid nitrogen.

#: data from initial measurements at room temperature.

*: data from the measurements at 250°C .

**: data from the measurements at room temperature again after measuring at 250°C .

From Table 2, it can be seen that the main differences between annealed and quenched samples are the width of the diffraction peaks. For annealed samples the peaks are much narrower, it means their crystals are bigger and have higher degree of ordering. As we discussed above, quenched samples can be considered as a product which have been experienced with rapid crystallization and samples annealed at 290°C have been experienced with both rapid and slow crystallization. Through the slow crystallization the smaller and poorer crystals formed in rapid crystallization transfer to larger and more perfect crystals. Therefore, there is no significant change in crystallinity, which further proves the crystals formed in slow crystallization came from the melted crystals formed in rapid crystallization. 250°C is in the melting range of the crystals formed in rapid crystallization (see Fig. 2), but lower than the melting point of the crystals formed in slow crystallization (see Fig. 3). So at 250°C part of crystals formed in rapid crystallization have been melted, therefore the average crystal size increases, which causes the width of diffraction peaks become narrower. When cooled from 250°C to room temperature, samples once again experience a fast crystallization, therefore X-ray data appear rather reversible.

CONCLUSION

HBA/TNA/HQ/PET thermotropic liquid crystal copolyester has a rapid crystallization process and a slow one. The former's speed is so high that it always takes place no matter how fast the melt has been cooled. The latter one can only be observed for samples annealed above a certain temperature which is referred here to as critical temperature T_{cr} . Increasing annealing time has no effect on promoting slow crystallization if $T_{anne.} < T_{cr}$. But if $T_{anne.} > T_{cr}$, the slow crystallization proceeds more favorably and crystals formed become more and more perfect as annealing time increases. The crystals formed during slow crystallization are built on crystals which have been formed in rapid crystallization, but have not been melted. So T_{cr} is near the lower edge of the melting range of crystals formed in rapid crystallization.

Keywords:

Thermotropic liquid crystal copolyester; LCP; crystallization.

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