

Thermal transition behaviors in a liquid crystalline polyesterimide

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Received 30 September 2004; received in revised form 3 February 2005; accepted 1 March 2005

Available online 25 May 2005

Abstract

The crystallization and melting behaviors of the polyesterimide, derived from *N,N'*-hexane-1,6-diylbis(trimellitimides), 4,4'-dihydroxybenzophenone and *p*-hydroxybenzoic acid, were investigated by using polarized light microscopy (PLM), differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). The nematic texture of the polyesterimide was observed on raising temperature to 265 °C, and the nematic phase was found to convert to isotropic melt beginning from about 300 °C, the ordered nematic micro-domains still surviving after 320 °C. Isothermal crystallization of the samples was performed at 180 °C after heating samples at various temperatures in the range of 265–360 °C, and a completed crystallization peak can appear on DSC curves up to the heating temperature of 360 °C in the presence of the nematic phase and the ordered nematic micro-domains. Non-isothermal crystallization of the samples at different cooling rate was carried out, and the melting of the resulting crystals exhibits double endotherms. It is indicated that a fast crystallization in the nematic phase forms relatively more ordered crystals, which melt at higher temperature, and a slow crystallization in the isotropic phase or in the biphasic melt produces poor crystals, which melt at lower temperature. The crystallized polyesterimide was annealed, which has a minor effect on the high-melting peak but leads to a continual shifting of the low-melting peak to higher temperature with increasing annealing temperature or annealing time. WAXD patterns indicated that the structural transform was not found during annealing process.

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Keywords: Polyesterimide; Liquid crystalline crystal; Crystallization

1. Introduction

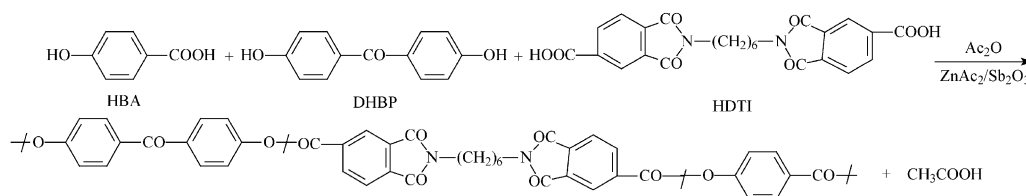
Polyimides have attracted much attention due to their high thermal stability and good mechanical and electrical properties [1]. However, the difficulty in processing caused by poor flow properties and infusibility has restricted their wide application. The synthesis of polyesterimides was motivated to resolve such problems [2], and the flexible ester linkage was assumed to lower melting temperature and improve the flow at the expense somewhat of thermal stability. Many polyesterimides have been synthesized which exhibit liquid crystalline properties [3]. In particular, an important contribution to the synthesis of thermotropic liquid crystalline polyesterimides was made by Kricheldorf

and co-workers [4–10], and also by Lenz et al. [11–13] and Chung et al. [14,15].

Study of crystallization and melting in liquid crystalline polymers is a very interesting subject and enormous effort has been made to understand the thermal transition nature [16–23]. Two crystallization processes in liquid crystalline polymers have been identified: the fast process, which occurs first in nematic phase and is practically independent of the crystallization temperature and time; and the slow process, which takes place later to transform the remaining part of the sample into ordered structure, and is affected by crystallization conditions.

Semi-rigid liquid crystalline polymers with flexible spacers in main chain have been extensively studied because of their accessible transition temperature and improved solubility. Crystallization and melting behaviors of several polyesters containing flexible spacers were investigated by Carpaneto and his co-workers [24,25]. The melting profiles of the crystallized samples reveal two melting endotherms at temperatures T_{m1} and T_{m2} , which could not be interpreted as usual in the case of conventional polymers. They

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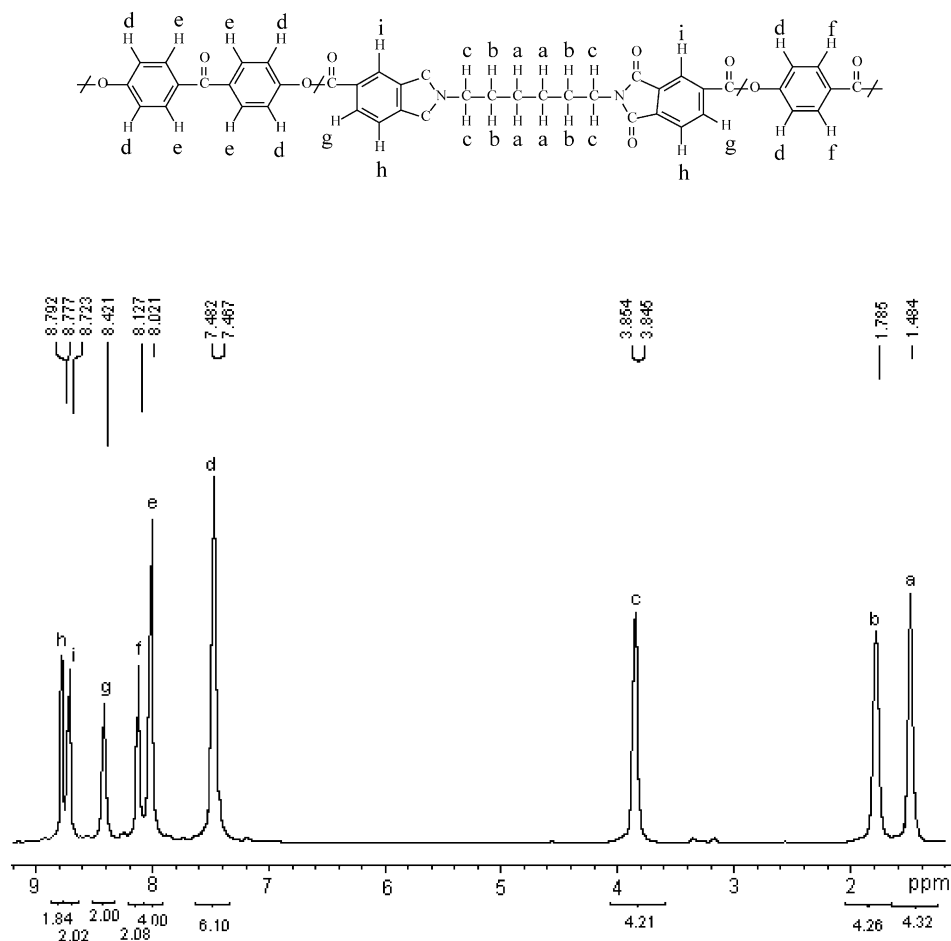


Scheme 1. Polymerization reaction route.

proposed a new model of crystallization, taking into account that a certain registry of neighbouring chains persists in the nematic state above melting temperature T_m and becomes more and more poor with increasing the temperature and time beyond T_m ; this persistent registry or ordered nematic phase can be regarded as potential nuclei for crystallization. The melting of the resulting crystals should be responsible for the high-temperature endotherm, while the low-temperature endotherm corresponds to the melting of crystals arising from the ordering of the remaining nematic phase.

In addition, it is well known that macroscopic properties of semicrystalline polymers are governed by their microscopic morphology, which in turn depends on their crystallization conditions and on their thermal history. Therefore, the study of crystallization and melting behaviors of

conventional polymers has been a very interesting and important topic in the past several decades. More recently, a number of investigations can be found for elucidating the crystallization and melting mechanism of polymers [26–35], resulting a deeper understanding. While multiple melting behavior is very common to many conventional semicrystalline polymers, the origin of the multiple melting is still not very clear. A variety of explanations for this phenomenon have been suggested: (i) the presence of more than one crystallographic forms (polymorphism) [36–39], (ii) the dual lamellar population model due to the primary and secondary crystallization [40–44], and (iii) the melting-recrystallization-remelting model [45–51]. In some cases, it was observed that the multiple melting behavior originates from the combined mechanism among them [38,39]. These

Fig. 1. ^1H NMR spectrum of the polyesterimide in CF_3COOD .

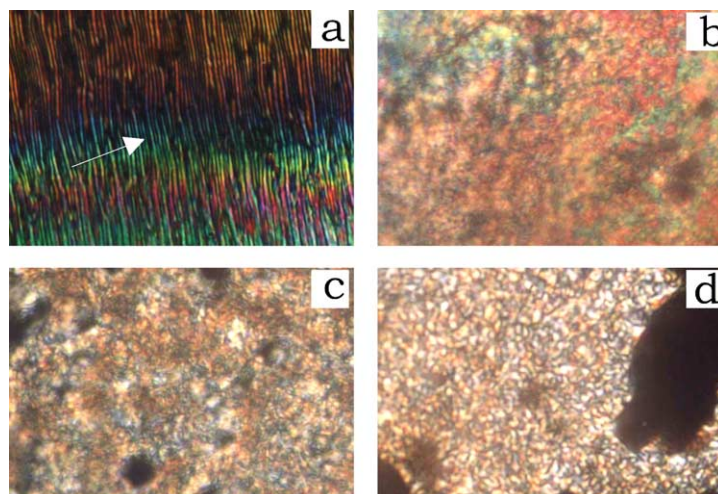


Fig. 2. PLM photographs of polyesterimide at different temperatures ($\times 500$): (a) room temperature after the melt was sheared (shear direction indicated by arrow), (b) 265 °C, (c) 290 °C, and (d) 320 °C.

investigations and discussions would be helpful to understand the crystallization and melting behaviors of liquid crystalline polymers.

In our previous paper [52], we have reported on the synthesis of a polyesterimide with good thermotropic liquid crystalline properties, derived from *N,N'*-hexane-1,6-diylbis(trimellitimides), 4,4'-dihydroxybenzophenone and *p*-hydroxybenzoic acid, by polycondensation reaction in a mixed solvent of benzenesulfonyl chloride, *N,N'*-dimethylformamide and pyridine. In the present investigation, the same polyesterimide is synthesized by direct melt transesterification, and the crystallization and melting behaviors of the polyesterimide were studied, aiming at the elucidation of transition mechanism.

2. Experimental part

2.1. Materials and polyesterimide preparation

4,4'-Dihydroxybenzophenone (DHBP) was synthesized from phenol and *p*-hydroxybenzoic acid (HBA) according to the method of Stanley [53]. *N,N'*-hexane-1,6-diylbis(trimellitimides) (HDTI) was synthesized from trimellitic anhydride and 1,6-hexane diamine according to the method detailed by Kricheldorf and Pakull [5]. All other materials were supplied by Guangzhou Medicine Company (Guangzhou, China) as chemical-grade reagents and were used without further purification.

Scheme 1 shows the polycondensation reaction route of the polyesterimide, monomer structures and the chemical repeat unit of the polymer. A reaction vessel equipped with a stirrer, an inlet and an outlet for nitrogen, thermometer and reflux condenser was charged with 207 g (1.5 mol) of HBA, 321 g (1.5 mol) of DHBP, 669 g (1.5 mol) of HDTI, 500 g (4.9 mol) of acetic anhydride, 0.6 g zinc acetate and 0.6 g antimony trioxide. Following sufficient purge of the reaction

vessel with nitrogen gas, the temperature was raised to 150 °C over 15 min under the nitrogen gas flow, and refluxed for 2 h at the same temperature. Thereafter, the temperature of the reactants was raised to 300 °C over about 3 h while distilling off acetic acids by-product and unreacted acetic anhydride. To bring the conversion to completion, the pressure was then reduced in several stages to about 30 Pa over a time of 1.5 h. The resulting polymer had an inherent viscosity of 0.70 dl g⁻¹ measured in phenol/1,1,2,2-tetrachloroethane (60/40 by weight) at 30 °C.

The ¹H NMR spectrum of the polyesterimide, determined in deuterated trifluoroacetic acid (CF₃COOD), is shown in Fig. 1. The integrated ratios of different protons and their chemical shifts are fully in conformity with the structure of the polyesterimide.

2.2. Instrumentation and measurements

The texture of liquid crystalline phase was examined by using a Leitz Orthoplan polarized light microscope (PLM) equipped with a hot stage. The sample was first sandwiched between two glass covers at 300 °C on a hot plate, and then quenched to room temperature. The evolution of liquid crystalline texture was observed at different pre-fixed temperatures.

The investigation of melting behavior of the samples was carried out with a Du Pont DSC-910 differential scanning calorimeter (DSC) under nitrogen at a heating rate of 20 °C/min. Isothermal crystallization of the samples was conducted in nitrogen atmosphere with a Perkin–Elmer DSC-7 differential scanning calorimeter: the samples were heated to various temperatures for 5 min, and then cooled to selected temperatures at a cooling rate of 200 °C/min to perform isothermal crystallization. Non-isothermal crystallization was also performed using a Perkin–Elmer DSC-7 differential scanning calorimeter at different cooling rates from the nematic phase of the samples heated above melting

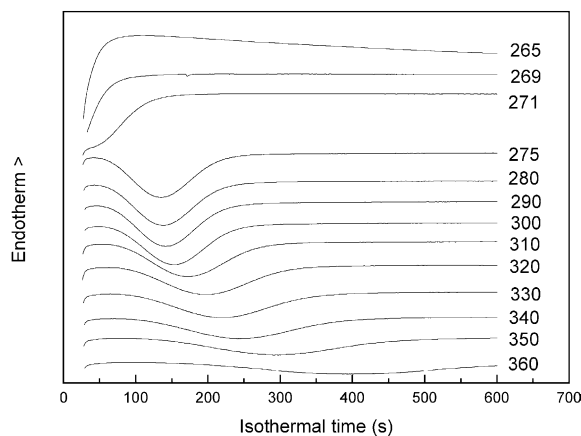


Fig. 3. DSC curves of isothermal crystallization of polyesterimide at 180 °C, the sample was heated at different temperatures (labeled on each curve, °C) before crystallization.

point previously. Both temperature and heat flow scales were calibrated with standard materials.

Wide angle X-ray diffraction (WAXD) was performed using a Bruker D8 advanced X-ray analytical systems (Nickel-filtered Cu K α radiation with wavelength of $\lambda = 0.154$ nm) in reflection mode. The scanning 2θ angle region was between 2 and 35°.

3. Results and discussion

3.1. Texture

After the polyesterimide was melted and sheared at about 300 °C and quenched to room temperature, a typical nematic banded texture with bands perpendicular to the direction of shear is clearly observed under the PLM as shown in Fig. 2(a). The polyesterimide is not found to exhibit nematic texture until the temperature is raised to

approximately 265 °C (Fig. 2(b)), in other words, it changes from the solid state into liquid crystalline state at this temperature. This is in good agreement with DSC observation, as discussed later. On reaching 290–300 °C, the melt is still in liquid crystalline state, although birefringence is partially extinct due to the occurrence of nematic-isotropic phase transition. Starting from 320 °C, extinction is gradually extended to the main area of sample, i.e. a major part of the nematic phase has converted to isotropic phase, and finally, birefringence disappears totally at about 360 °C.

3.2. Isothermal crystallization

The samples were heated for 5 min at a chosen temperature within the temperature range of 265–360 °C, and then cooled as rapidly as possible to 180 °C for isothermal crystallization. Fig. 3 shows the DSC traces of isothermal crystallization of the samples at 180 °C. The temperature, at which the sample was heated for 5 min before crystallization, is labeled on each curve and thereafter, defined as ‘heating temperature’. The DSC curves in Fig. 3 can be seen to have a close correlation with the heating temperature. The isothermal crystallization exotherm does not appear until the heating temperature 269 °C; but the isothermal crystallization occurs beginning from the heating temperature 271 °C, and a complete crystallization peak can be observed starting from the heating temperature 275 °C. Surprisingly, a weak crystallization peak can still be observed even if the heating temperature is as high as 360 °C.

Fig. 4 shows that the half-time of crystallization ($t_{1/2}$) increases with increasing heating temperature, indicating the reduction of crystallization rate with increasing heating temperature. The enthalpy change (ΔH_c) during crystallization is also shown in Fig. 4 as a function of the heating temperature. The value of ΔH_c is slightly increased below

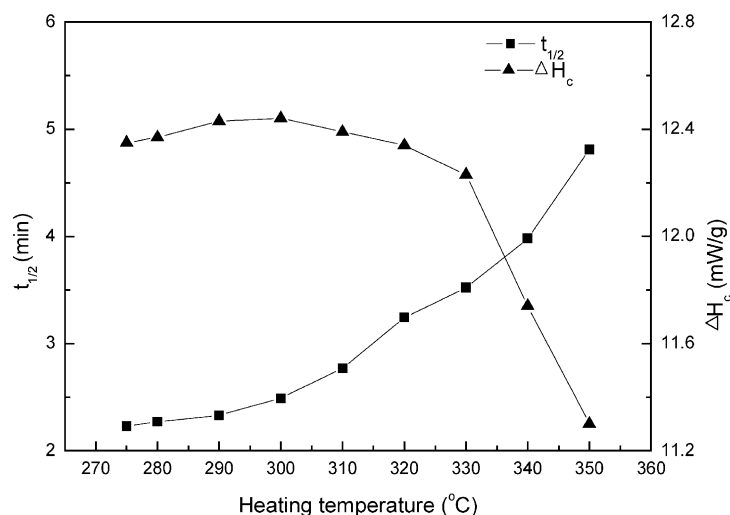


Fig. 4. Half-time of crystallization ($t_{1/2}$) and crystallization enthalpy as a function of the heating temperature.

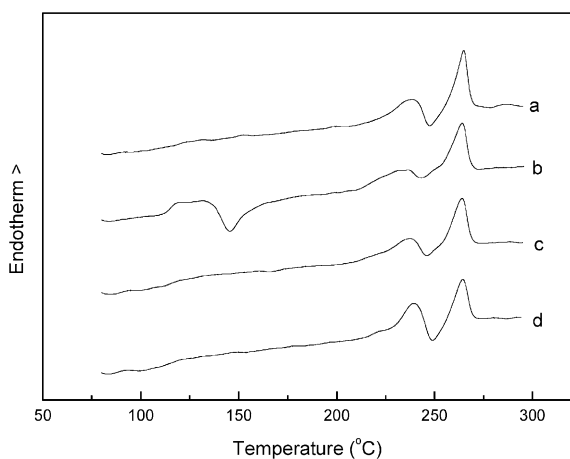


Fig. 5. DSC heating curves of polyesterimide with different thermal histories: (a) as-synthesized sample, (b) sample quenched with liquid N_2 , (c) sample cooled at $10^\circ\text{C}/\text{min}$, and (d) sample cooled at $3^\circ\text{C}/\text{min}$.

300°C , but thereafter is reduced with increasing heating temperature and markedly decreased starting from 330°C .

The crystallized polyesterimide melts at about 262°C (see below, melting behavior), undergoing a crystal–nematic phase transition, but the nematic–isotropic phase transition was not found on the DSC heating profiles. Fig. 2 indicates that the polyesterimide has a wide temperature range of stability of the nematic phase, which gradually converts to isotropic phase with increasing temperature so that completion of the nematic–isotropic transition could occur at very high temperature. By careful observation with PLM, the nematic–isotropic melt transition was found to start at about 290°C ; when the sample was kept at this temperature for 20 min, the texture of liquid crystalline crystals disappeared. Therefore, the condensed state of polyesterimide should change with increasing heating temperature before crystallization (Fig. 3). Nematic melt could exist above the melting temperature and below the heating temperature 290°C , while a biphasic melt might be attained above 290°C , i.e. regions of local nematic phase existing within isotropic melt. When the heating temperature further increases to around 330°C , the persistent registry of neighbouring chains or small ordered nematic domains [24] might survive in the isotropic melt. The small ordered nematic would become poorer with increasing heating temperature, and finally, disappear when the equilibrium state is achieved.

As is commonly recognized, the crystallization occurs with different rates at different places within sample for rigid liquid crystalline polymers. Crystallization occurs in two steps: the first is a fast process in the nematic phase and takes place independently of the crystallization conditions; the second has a slow crystallization rate to transform the remaining part of nematic melt into an ordered structure and is similar to the crystallization of conventional polymers, depending on crystallization conditions. For semi-rigid liquid crystalline polymers with flexible spacers in the main

chain, another crystallization model was proposed: fast crystallization takes place first in nematic phase, followed by a slow crystallization in isotropic melt [38,39]. The first model refers to the crystallization in nematic melt; while the second model to the crystallization in biphasic melt, namely, coexistence of nematic and isotropic phase. In the nematic phase, chains are already extended, parallel and free of entanglements and a certain registry of neighbouring chains exists, and therefore, the crystallization can occur rapidly. The crystallization mechanism would be similar to conventional polymers: nucleation, followed by crystal growth.

Actually, Fig. 3 shows a rather rapid crystallization of the polyesterimide at 180°C in the presence of nematic phase or the coexistence of nematic and isotropic melt, completed crystallization exotherms appear within a few minutes at a wide range of the heating temperature. By close observation, a half crystallization peak has already appeared on the DSC trace at the heating temperature 271°C , indicating a very fast crystallization process which is finished in one minute. Evidently, the fast crystallization process in liquid crystalline phase would make a major contribution to the crystallization peak. We can imagine many locally ordered nematic domains of various sizes are present in the nematic melt just beyond melting point, some being as large as a nucleus for crystallization, some as small as an aggregate on a scale of a few chains with one or two aromatic rings along chain, i.e. the registry of neighbouring chain. With increasing heating temperature, locally ordered nematic domains are destroyed first in the nematic melt; then, the nematic phase begins to convert to isotropic above 300°C , and finally, only a small part of nematic phase with some registry of neighbouring chains survives above 330°C , leading to longer half-time of crystallization ($t_{1/2}$) and flatter crystallization peaks. Beyond 360°C , the nematic phase and the ordered nematic micro-domains would finally disappear, and the equilibrium state, that of homogeneous isotropic phase, would be attained; and thus, the crystallization could not be completed within the time scale of DSC scanning due to a slow homogeneous nucleation rate. On the other hand, the crystallization heat changes correspondingly. With increasing heating temperature, locally ordered nematic domains melt and the physically crosslinked nematic network disintegrates; the increasing molecular motion is able to make a better matching between chains, causing a slight increase in crystallinity up to 300°C . And thereafter, the crystallinity reduces due to the decrease in the crystallization rate with further increase of the heating temperature.

3.3. Melting behavior

3.3.1. Melting of samples crystallized from the melt by cooling at different cooling rates

The polyesterimide was melted at 300°C and cooled at different cooling rates, and then the resulting samples were

analyzed with DSC at a heating rate of 20 °C/min. Fig. 5 shows their DSC heating traces, including the as-synthesized sample as a control. Curve a stands for the heating trace of the as-synthesized sample, curves b, c and d represent the heating traces of the samples obtained by quenching to liquid nitrogen temperature, and by cooling at cooling rates of 10 and 3 °C/min, respectively. All DSC heating traces reveal two endotherms at temperatures T_{m1} and T_{m2} : the high-temperature peak (P_2 , at T_{m2}) remains almost unchanged, but the low-temperature peak (P_1 , at T_{m1}) depends upon the cooling rate.

Fig. 5(b) shows a relatively large high-temperature melting peak with $\Delta H_{m2}=10.1$ J/g and a small low-temperature melting peak with $\Delta H_{m1}=3.9$ J/g, indicating the crystallization related to the former is a very fast process despite the sample being quenched with liquid nitrogen. A well-defined exothermic peak ($\Delta H_c=8.5$ J/g) above the glass transition temperature can be observed, but the exothermic enthalpy is obviously less than the sum of ΔH_{m1} and ΔH_{m2} , and therefore, the crystallization does occur during quenching. Other samples also exhibit a high-temperature melting peak almost with the same size and at the same temperature as the quenched sample, and thus these melting peaks must have the same origin. The higher melting peak is usually assumed to be related to the melting of crystals formed by fast crystallization process [16,18], while the lower melting peak to the melting of crystals formed by slow crystallization process in the nematic phase [24] and in the isotropic melt [54,55]. Since the nematic phase has partially converted to isotropic melt on melting polyesterimide at 300 °C, both crystallization processes in the nematic and isotropic should have some contribution to the lower melting peak.

In the early stage of crystallization, the initial organized regions in the nematic phase first transforms to crystalline phase with a minimal rearrangement, or even no rearrangement at all during quenching from the nematic melt. The resulting primary crystals may be thicker and more ordered and thus melt at higher temperature although the crystallization process is fast. The later-forming secondary crystals grow slowly in the remaining nematic melt or in an amorphous melt of restricted mobility due to the entanglement effects caused by the primary crystals. The secondary crystals may be thinner, less ordered and melt at lower temperature.

Curves a and d in Fig. 5 clearly show a small exotherm after endotherm P_1 , while curves b and c exhibit a small shoulder on the endotherm P_2 . These could be considered, respectively, to be recrystallization after melting of the secondary crystals and melting of the resulting crystals from recrystallization. The assumption which attributes multiple melting endotherms to the presence of two different distributions of lamellar thickness and recrystallization on heating has been confirmed by temperature modulated DSC (MTDSC) [30,33,34]. MTDSC signal reveals the melting of crystals present originally in the sample as endotherms, and

also detects the recrystallization as an exotherm in the reversing component of the heat flow during heating. A recent study [56] on the melting behavior of poly (ethylene terephthalate) (PET) observed only one single broad melting peak at very high heating rate, which prevents the occurrence of recrystallization. The results give clear evidence for the validity of a melting-recrystallization-remelting process at low heating rate; however, they do not provide evidence for the formation of different populations of lamellar thicknesses in the samples crystallized isothermally. Recrystallization is a fast process due to a high density of nucleation sites at the edges of the survived lamellae [29], a continuous melting-recrystallization process leads to more stable crystals, melting at higher temperature as shoulder (Fig. 5); but the P_2 should come from the melting of crystals formed originally in the samples by a fast crystallization process (Fig. 5).

3.3.2. Influence of annealing on melting behavior

As discussed above, the ‘primary crystals’ were formed through a fast crystallization process; especially, the chains were immediately frozen into solid materials during quenching from the nematic melt. As a result, the packing of the ‘primary crystals’ is far from perfect, and chain conformations do not change very much from their nematic melts. As to the ‘secondary crystals’, the crystal packing is even much poorer. Therefore, a substantial annealing effect is expected for the crystals formed from liquid crystalline polymers.

The polyesterimide was melted at 300 °C and then quenched to room temperature to obtain an initial sample, which was used for annealing and as a control. Fig. 6 shows the DSC heating traces of the polyesterimide annealed at different annealing temperatures T_a for 120 min. It can be seen that the samples exhibit two endothermic transitions below $T_a=230$ °C, and only one melting peak is present above this temperature. With increasing T_a , the high-temperature peak slightly shifts to higher temperature,

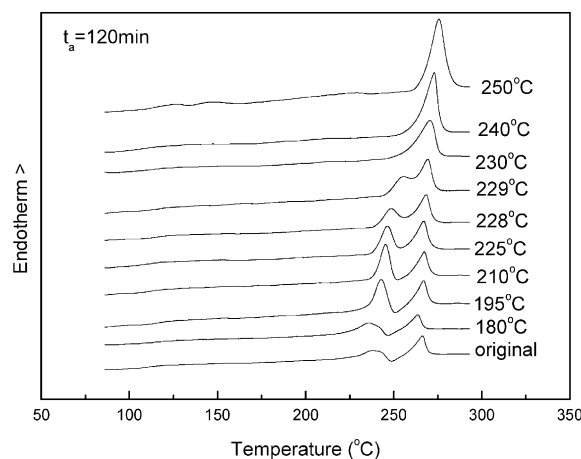


Fig. 6. DSC heating curves of the polyesterimide samples annealed at various temperatures for 120 min.

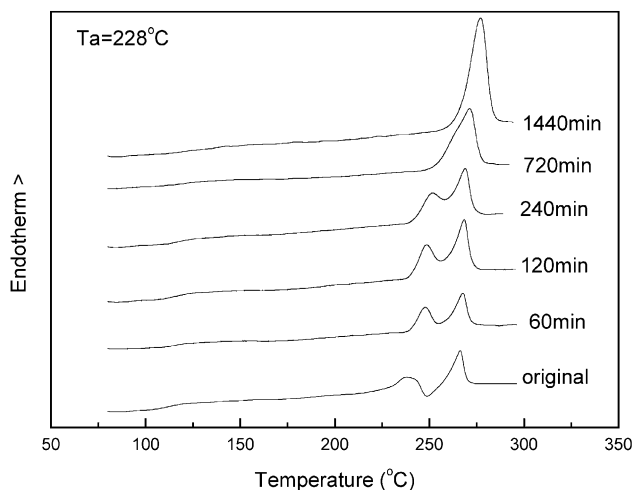


Fig. 7. DSC heating curves of polyesterimide annealed at 228 °C for various annealing times.

while the low-temperature endotherm considerably shifts to higher temperature. In the meantime, the low-temperature peak can be seen to enhance with increasing annealing temperature to $T_a=225$ °C, then partially and in the end totally merges into high-temperature peak. Beyond 230 °C, the high-temperature peak (P_2) continually shifts to higher temperature with increasing T_a , accompanied by an evident increase in transition enthalpy.

Fig. 7 shows a set of DSC heating traces related to the polyesterimide annealed at 228 °C for various periods of time. Similarly, dual transition peak is clearly observed below 720 min. With increasing annealing time, the low-temperature melting peak shifts to higher temperature, while the high-temperature melting peak slightly moves to higher temperature. Eventually, the two melting peaks combine into one endothermic peak beginning from 720 min, and both temperature and enthalpy of the melting peak rise further with the increase of annealing time.

During annealing, molecular motion of the chains takes place if the annealing temperature is high enough. The molecular motion includes: translational motion along chain direction, rotational motion around chain axis and rotational motion of a part of one chain with respect to other, enabling chains to find better matching between aromatic rings for a dense packing of crystals, as indicated by the raising of both low and high melting temperatures in Figs. 6 and 7. It is very interesting to note that the primary crystals formed in fast crystallization process are more stable than the secondary crystals crystallized in slow process. However, it is not unexpected that the freezing of chains occurs in initially more ordered region in nematic melt, and thus more ordered structure of crystals was obtained. Comparing Figs. 6 and 7, it can also be found that increasing annealing temperature is a little more effective for reorganizing crystals than increasing annealing time.

Structural transform of crystals [18,20,40] was observed during annealing: the hexagonal packing formed in fast

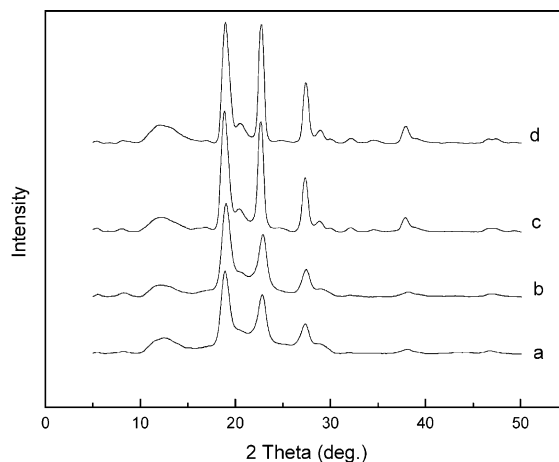


Fig. 8. WAXD profiles of samples annealed at various temperatures and for different times (a) sample after annealing at 195 °C for 120 min, (b) sample after annealing at 195 °C for 1440 min, (c) sample after annealing at 240 °C for 120 min, and (d) sample after annealing at 240 °C for 1440 min.

crystallization process due to aggregation of rigid chains converts to orthorhombic packing. However, the structural transform is not found in the annealing of the polyesterimide in this study. Fig. 8 shows the WAXD patterns for several samples. The reflection spectra are similar except for the diffraction intensity, although their DSC traces exhibit substantial difference.

Annealing at a higher temperature, post-polymerization may occur [57,58], leading to a high molar mass; in the meantime, sequence ordering within crystals could also be possible due to sufficient chain mobility, via transesterification between neighbouring chains [59,60]. Both factors could also increase the melting temperature and crystallinity.

Acknowledgements

The financial supports of this study were provided by grants from Major Research Projects of Chinese National Nature Science Foundation (90103037) and Chinese National Nature Science Foundation (20474013), and by PhD funds of the State Education Department of China. We are grateful to Dr Robert R. Luise (Hytem Consultants Inc., USA) for his useful suggestions and discussions during this research.

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