

Influence of the Monomer Feeding Sequence on the Structure and Properties of Thermotropic Liquid-Crystalline Poly(ester imide)s

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ABSTRACT: A series of poly(ester imide)s mainly derived from *N,N'*-hexane-1,6-diylbistrimellitimidates, 4,4'-dihydroxybenzophenone, and *p*-hydroxybenzoic acid were synthesized by a direct polycondensation method in benzenesulfonyl chloride, *N,N'*-dimethylformamide, and pyridine with different monomer feeding sequences. The molecular structures and properties of the resultant poly(ester imide)s were characterized with NMR, IR spectrometry, polarized light microscopy, wide-angle X-ray diffraction, differential scanning calorimetry, and thermogravimetric analysis. The results showed that the monomer feeding sequences had a

great effect on the sequential structure of the molecular chains of the copolymers and consequently on their liquid-crystalline (LC) properties, fiber-forming capability, and other properties. Thus, it is probable that one could obtain an LC poly(ester imide) with given properties by controlling the monomer feeding sequence during the polycondensation process. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3001–3008, 2008

Key words: gelation; liquid-crystalline polymers (LCP); polyimides; synthesis

INTRODUCTION

Like the properties of other commodity polymeric materials, the excellent properties of a liquid-crystalline polymer (LCP) are mainly determined by its molecular structure, including the chemical composition, chain sequence structure, molecular weight, and molecular weight distribution. To obtain thermotropic LCPs with appropriate processing temperatures, most are prepared by copolymerization with two or more monomers. During the copolymerization process, some monomers can not only copolymerize with other monomers but also self-polymerize. In addition, in the competitive reactions, the differ-

ence in the relative reactivities of the functional groups in the monomers is usually involved under certain conditions. Even if synthesized with the same types of monomers, the obtained polymers will show different properties by a random polymerization, an alternate polymerization, or a block polymerization. Consequently, polymers with different sequential structure distributions of the comonomers will have different properties.¹

A large amount of work has been done to prepare thermotropic liquid-crystalline (LC) poly(ester imide)s by Kricheldorf's and Lenz's groups since 1987.^{2–11} Yet, to the best of our knowledge, nearly all the reported poly(ester imide)s with higher molecular weights have been synthesized by the melt transesterification approach at high temperatures under reduced pressure.¹² It is well recognized, however, that the molecular structure as well as the chain sequence of the polymers can be hardly controlled during the melt transesterification copolymerization. To overcome this problem, there is the possibility of controlling the monomer sequences in copolycondensation by a new solution direct polycondensation for the synthesis of copolyesters with tosyl chloride in pyridine (Py) by *N,N'*-dimethylformamide (DMF)-catalyzed alcoholysis, as reported by Higashi and coworkers.^{13–15} For example, the copolyesters derived from *m*-phthalic acid (IPA), terephthalic acid, 2,2-bis(4-hydroxyphenyl) propane (BPA), and *p*-hydroxybenzoic acid (PHB), prepared by the usual

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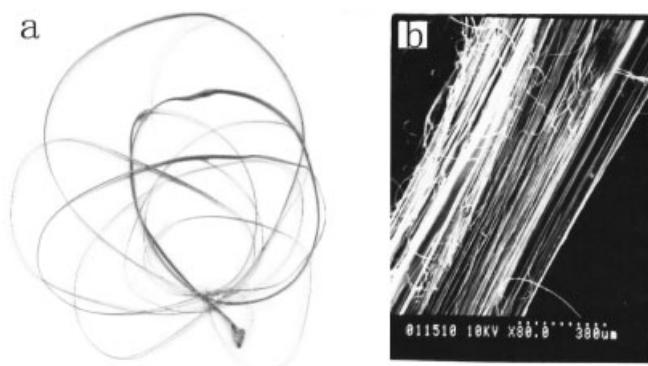


Figure 1 (a) Picture of the fiber forming from polymer BB and (b) SEM photograph of the fiber after tearing.

random copolymerization, are not LCs until the PHB content is greater than 70 mol % in the composition, but thermotropic LC copolyesters with about 40 mol % PHB can be obtained by the stepwise addition of BPA and PHB through two- and three-stage reactions using tosyl chloride/DMF/Py as a condensing agent. It has been suggested that the reason is that the latter polymerization method could easily produce mesogenic segments of more than three PHB units in the copolycondensation.¹⁶

Recently, we reported a series of thermotropic LC poly(ester imide)s synthesized according to the Higashi copolymerization approach.¹⁷ We here describe the influence of the monomer feeding sequence on the structure and properties of the thermotropic LC poly(ester imide)s

EXPERIMENTAL

Materials

4,4'-Dihydroxybenzophenone (DHBP) was synthesized from phenol and PHB according to Stanley.¹⁸ *N,N'*-Hexane-1,6-diylbistrimellitimidates (IA6s) and *N,N'*-butane-1,4-diylbistrimellitimidates (IA4s) were synthesized from trimellitic anhydride and corresponding diamines according to Kricheldorf and Pakull.³ All the other materials, such as benzenesulfonyl chloride, DMF, Py, IPA, 4,4'-dihydroxydiphenylsulfone (BPS), BPA, 4,4'-biphenol (BP), and hydroquinone (HQ), were obtained as chemical-

grade reagents from a commercial source (Guangzhou Medicine Co., Guangzhou, China) and used without further purification.

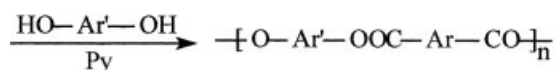
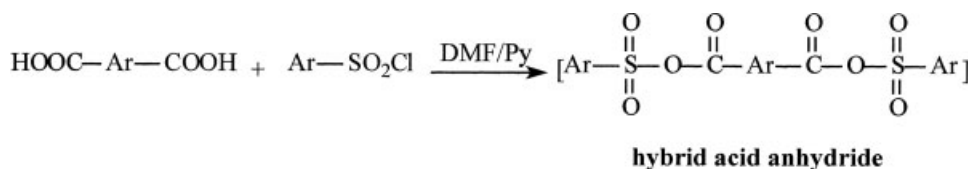
Polycondensation

Benzenesulfonyl chloride (3.32 mL), 1.55 mL of DMF, and 10 mL of Py were inserted with a pipette into a 250-mL, round-bottom flask with an electromagnetic stirrer. The mixture was kept at room temperature for 30 min; 5 mmol of IA6 was then weighed and added to the flask under stirring. After the resultant mixture became solidified, the flask was placed into an oil bath preheated to 80°C and maintained there for 10 min. Then, the Py (10 mL) solution of DHBP (5 mmol) and PHB (10 mmol) were gradually dropwise added to the mixture over about 10 min. The temperature was then raised to 120°C at 10°C/min as the final polymerization temperature and maintained there for 2 h. After dilution with 20 mL of DMF, the precipitate was filtered and washed with alcohol. The collected polymers were dried in a far-IR oven for 24 h.

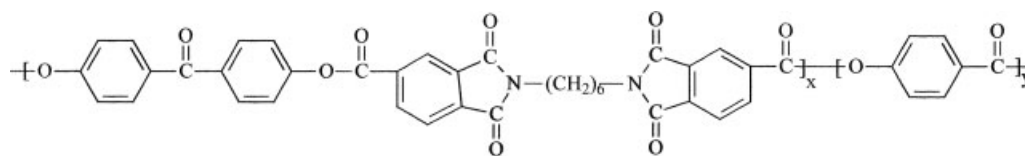
The polymer obtained previously through the feeding of the mixture of DHBP and PHB (PHB/IA6 = 2 : 1) was labeled polymer AA. A similar procedure was followed in the synthesis of polymers BB and CC; only the feeding sequence of PHB and DHBP was changed. For polymer BB, PHB was added first, and after 30 min, DHBP was added. For polymer CC, the monomer feeding sequence was just reversed; that is, DHBP was followed by PHB.

Characterization

The IR spectra were recorded with KBr pellets on a Nicolet (Madison, WI) 210 spectroscope. The ¹H-NMR spectra were obtained with a Varian (Palo Alto, CA) Inova-500 in deuterated trifluoroacetic acid (CF₃COOD). The LC texture of the resultant polymers was observed under a Leitz Orthoplan optical microscope (Leica Microsystems GmbH, Wetzlar, Germany) equipped with crossed polarizers. The samples were sheared in the melt state and quenched to room temperature. Wide-angle X-ray diffraction (WAXD) curves were recorded with a



Scheme 1 Model reaction of the polycondensation (Ar and Ar' = aromatic ring).



Scheme 2 Chemical structure of polymer CC synthesized by the PHB-first method.

Rigaku (Tokyo, Japan) XD-3A diffractometer using Ni-filtered Cu K α radiation ($\lambda = 0.154$ nm). Differential scanning calorimetry (DSC) measurements were conducted with a TA Instruments (New Castle, DE) MDSC 2910 under a nitrogen purge. The scanning rate was 10°C/min.

RESULTS AND DISCUSSION

Forming fibers

When the molten poly(ester imide)s were drawn, it was found that the ease of forming fibers from the polymers was different: AA \sim BB $>$ CC. The fibers drawn from polymers AA and BB exhibited good strength and toughness, but those from CC were very brittle. It is suggested that the differences in the monomer addition sequence resulted in differences in the molecular weights or sequential structures of the polymers and furthermore in the capacity variance of the fibers formed from them.

Figure 1(a) shows a fiber formed from molten polymer BB, and Figure 1(b) is an SEM photograph of the fiber after it was torn. In Figure 1(b), the orientated microfibrillar structure can be observed clearly, indicating good orientation of the polymer chains or segments in the drawing direction. It is well known that the high strength of LC fibers originates from their high orientation of molecular chains. Therefore, this kind of poly(ester imide) has potential applications in spinning high-strength LC fibers.

Solubility

The solubility of the poly(ester imide)s was observed through the dissolution of 0.1 g of polymers AA, BB, and CC in 10 mL of phenol/1,1,2,2-tetrachloroethane (60/40 w/w) or trifluoroacetic acid. This indicated that polymers AA and BB could be dissolved completely in the solvents, and polymer AA was dissolved more quickly than polymer BB. However, polymer CC was insoluble in both solvents.

According to the polymerization mechanism (illustrated in Scheme 1), when DHBP is first added to activated IA6, most DHBP will polymerize with IA6 because the molar ratio of DHBP to IA6 is 1 : 1, and when PHB is fed after the addition of DHBP, it can carry out only self-polymerization. Therefore, the resulting products will include a large amount of self-polymerized PHB products or block polymers with long PHB segments. According to this explanation, the chemical structure of polymer CC is illustrated in Scheme 2.

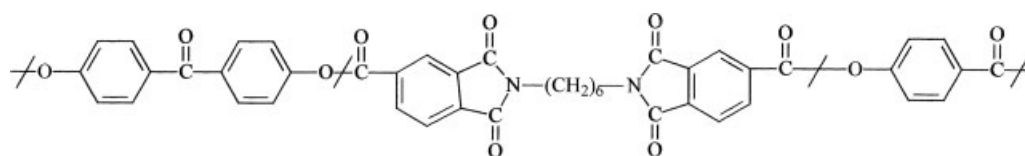
It is well known that when the number of PHB homopolymerization is greater than 3, the solubility of the resulting product remarkably decreases. Thus, the result of the solubility experiment agrees with the molecular structure of poly(ester imide) CC.

In the case of the DHBP-mixed-with-PHB feeding method, according to the chemical structure of the monomer, the reactivities of the phenolic groups between DHBP and PHB are quite similar. Therefore, the chances of the reaction of DHBP with IA6 or PHB and the self-condensation of PHB are approximately equivalent. Thus, it is imaginable that resulting polymer AA must be a random polymer. The chemical structure is shown in Scheme 3.

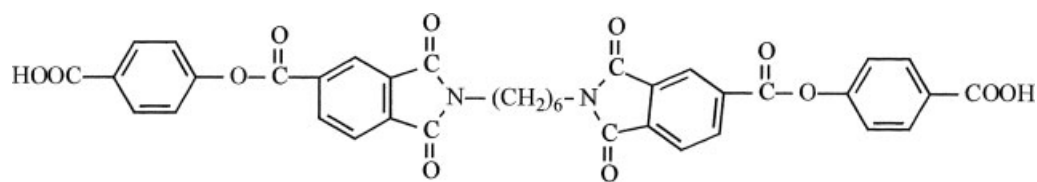
Concerning the synthesis of poly(ester imide) BB, the feeding monomer method is that PHB is fed first. When PHB is added to activated IA6, for the PHB/IA6 molar ratio of 2 : 1, according to the condensation mechanism, PHB and IA6 form a new diacid, PHB-IA6-PHB, as shown in Scheme 4.

After the new diacid has been activated, it is polymerized with DHBP, and a polymer is formed whose chemical structure is shown in Scheme 5.

According to the previous discussion on the chemical structures of poly(ester imide)s AA and BB, the probability of forming long PHB block segments through the self-polycondensation of PHB is low, and this is the main reason that the solubility of AA and BB is better than that of CC.



Scheme 3 Chemical structure of polymer AA synthesized by the DHBP-mixed-with-PHB feeding method.



Scheme 4 Chemical structure of the new diacid of PHB-IA6-PHB.

¹H-NMR and IR investigations

¹H-NMR spectra of polymers AA and BB, determined in trifluoroacetic acid (CF₃COOD), are shown in Figure 2. Polymer CC could not be dissolved in this solvent, and so its ¹H-NMR spectrum is not available. The integrated ratios of the different protons are fully consistent with the structures of the two copolymers according to the molar compositions of the comonomers (see Scheme 6).

Figure 2 shows that the ¹H-NMR spectra of AA and BB are almost the same in the number of peaks, chemical shifts, and coupling splits of each peak. This result implies that the molecular chain sequential structures of the two poly(ester imide)s could not be well differentiated by the ¹H-NMR spectra. However, the results indicate that the distribution of the monomers was random or homogeneous and that there did not exist segments with enrichment of one monomer, such as PHB. This agrees with the molecular structures of poly(ester imide)s AA and BB discussed previously.

The structures of the poly(ester imide)s were further characterized with IR spectra (Fig. 3). The IR spectra of the three polymers are very similar to one another. However, there exists a fine distinction between CC and AA (BB) at about 874 cm⁻¹, which can be attributed to the vibration absorption of the para-substitution of the benzene ring (Fig. 3). This distinction could have originated from the differences in the molecular chain structures obtained with the different feeding sequences. However, in the IR spectra, there is no obvious difference between polymer AA and polymer BB, and this is consistent with the results obtained by ¹H-NMR.

Texture

Under a hot-stage polarizing optical microscope, the copolymers showed evident birefringence with a threaded texture in the molten state, which is characteristic of a nematic LCP.¹⁹ After melt shearing

and quenching to room temperature, polymer CC could not form a banded texture; in contrast, polymers AA and BB could form the banded texture easily after shearing of the samples in the molten state (Fig. 4). This was probably due to the chain structural difference that originated from the feeding monomer sequence.

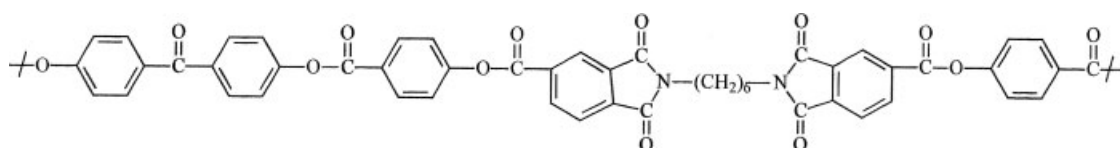
WAXD investigation

Figure 5 shows the WAXD patterns of the as-synthesized powdery samples. All the samples showed notable crystallinity, as indicated by several strong diffraction peaks in the range of 2θ = 15–30°. However, for polymer CC, several weak diffraction peaks can also be observed at lower and higher angles, probably indicating the formation of higher ordered structures, as suggested by other researchers.²⁰ In other words, the molecular chain of polymer CC was more regular than those of polymers AA and BB, and this resulted in the formation of a higher ordered structure.

DSC measurements

All the as-synthesized polymers were subjected to DSC measurements. Figure 6 records the DSC curves during heating processes at 10°C/min after different cooling conditions. Curve 1 represents the as-synthesized polymer; curves 2, 3, and 4 represent the polymers after cooling from 300 to 50°C at 200, 10, and 3°C/min, respectively, followed by subsequent heating at 10°C/min. The glass-transition temperature of polymers AA and BB can be clearly observed in curves 2, 3, and 4; however, under the same cooling and heating conditions, the glass-transition temperature of polymer CC could not be observed clearly.

The values of the two melting peaks (T_{m1} and T_{m2}) for each sample in different DSC runs are summarized in Table I. The values of T_{m1} and T_{m2} for CC were the highest for the three polymers; and the values for BB were obviously lower than those for AA.



Scheme 5 Chemical structure of poly(ester imide) BB synthesized by PHB-first-then-DHBP method.

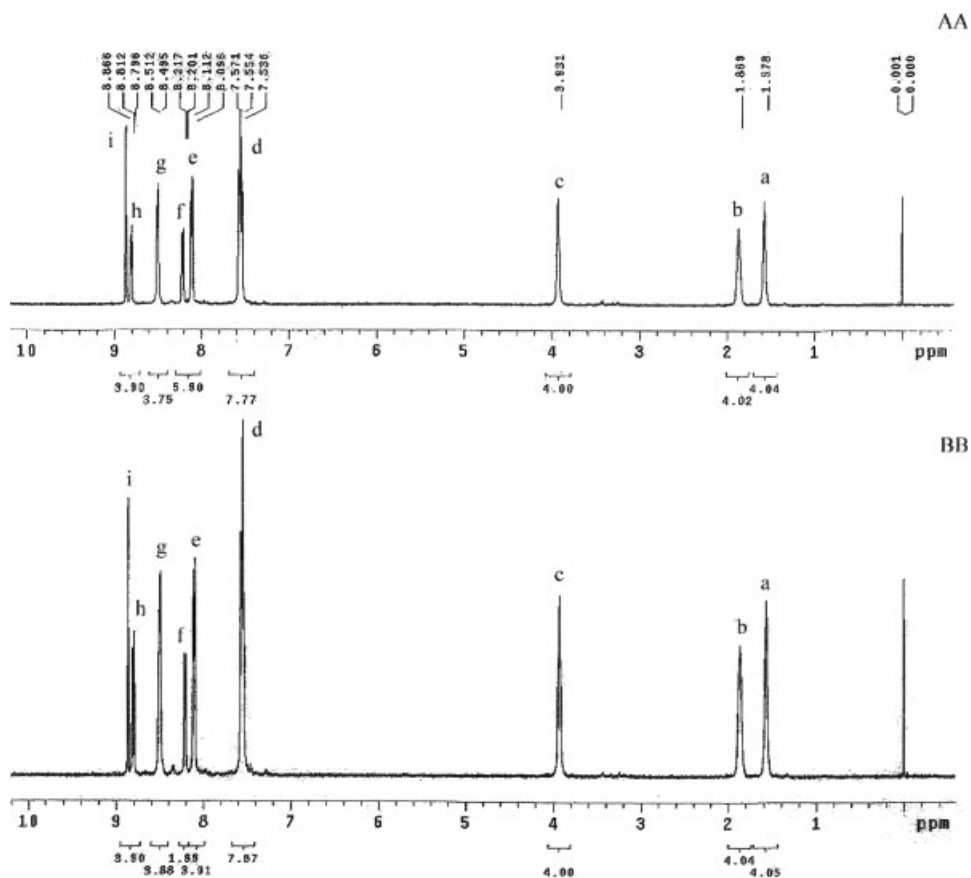
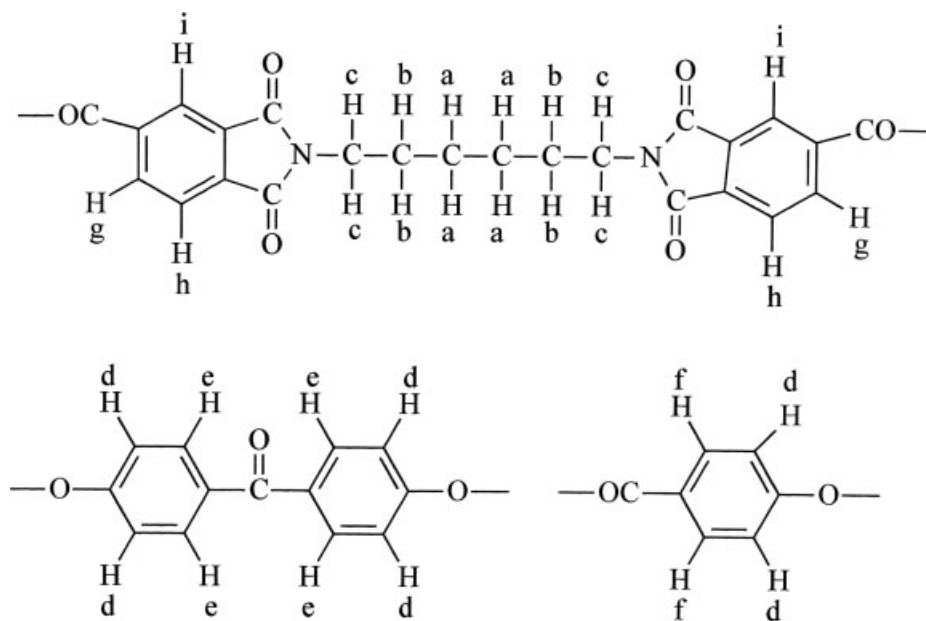


Figure 2 ¹H-NMR spectra of polymers AA and BB (in CF₃COOD).

In other words, the melting temperature of the poly(ester imide) was evidently lowered by the method of feeding PHB first versus the method of feeding a mixture of PHB and DHBP. We have investigated other copolymers with different como-

nomer compositions with different feeding monomer methods and obtained similar results. The results are summarized in Table II. Therefore, to synthesize a copolymer with a lower melting temperature, employing the PHB-first method is suitable.



Scheme 6 Corresponding protons from Figure 2.

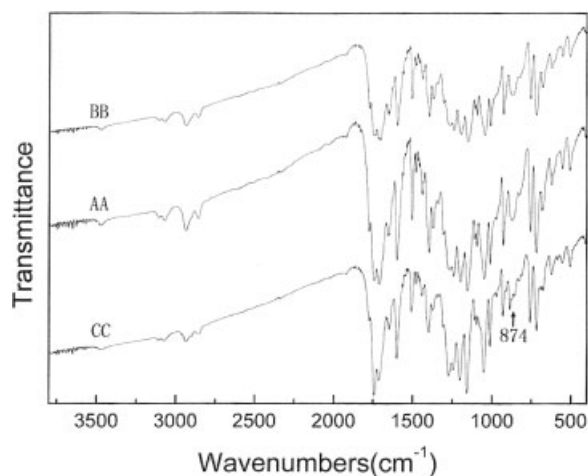


Figure 3 IR spectra of the as-synthesized polymers AA, BB, and CC.

Gelation phenomenon and the solutions

When the PHB and biphenol monomer mixed feeding method was used, a gelation phenomenon was not observed during the polymerization process. However, when PHB was added before the addition of biphenols, gelation was observed at a certain temperature, especially when the biphenols were bisphenol A (BPA) and bisphenol S (BPS). When this phenomenon happened, the reaction mixture became very viscous, and the gelation occurred during the addition of the biphenols. The occurrence of gelation resulted in stirring difficulty, and the biphenol monomers added later could not well participate in the reaction; this caused the molecular weight of the resultant product to be very low.

The same observation was also reported by Higashi et al.²¹ in the synthesis of a poly(ester amide) derived from IPA, terephthalic acid, BPA, and 4,4'-diaminodiphenyl ether.²¹ However, in the literature,

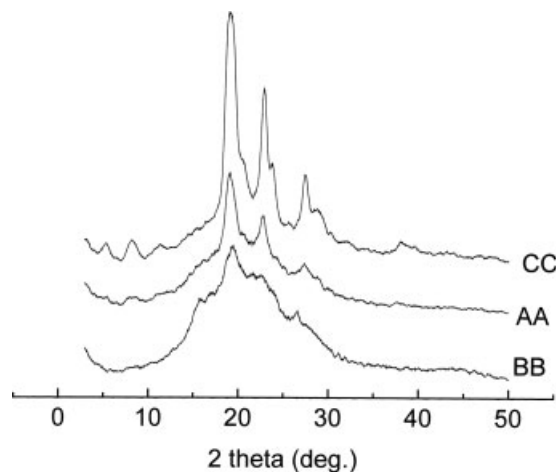


Figure 5 WAXD patterns of the as-synthesized polymers.

they did not provide an explanation for the gelation generation or a solution to avoid gelation.

With the PHB-first polycondensation method, several sets of monomer compositions and temperatures for generating gelation are summarized in Table III. A comparison of these data illustrates that it was easier to cause gelation in the reaction system containing BPA or BPS as the biphenol monomers. Meanwhile, BP, HQ, and DHBP were not easy to gel unless the reaction temperature was very high. From these results, we concluded that if biphenol or diacid monomers improve the solubility of an oligomer in a reaction medium, gelation will easily occur. In fact, increasing the reaction temperature could also improve the solubility of the oligomer. Thus, at a higher reaction temperature, gelation will also occur. As a result, the reason that gelation occurs is illustrated with diagrammatic sketches in Figure 7. In general, the molecular chain of an LCP is a rigid or semirigid rod structure. This structure has a preference for stretching. Such a condition will weaken

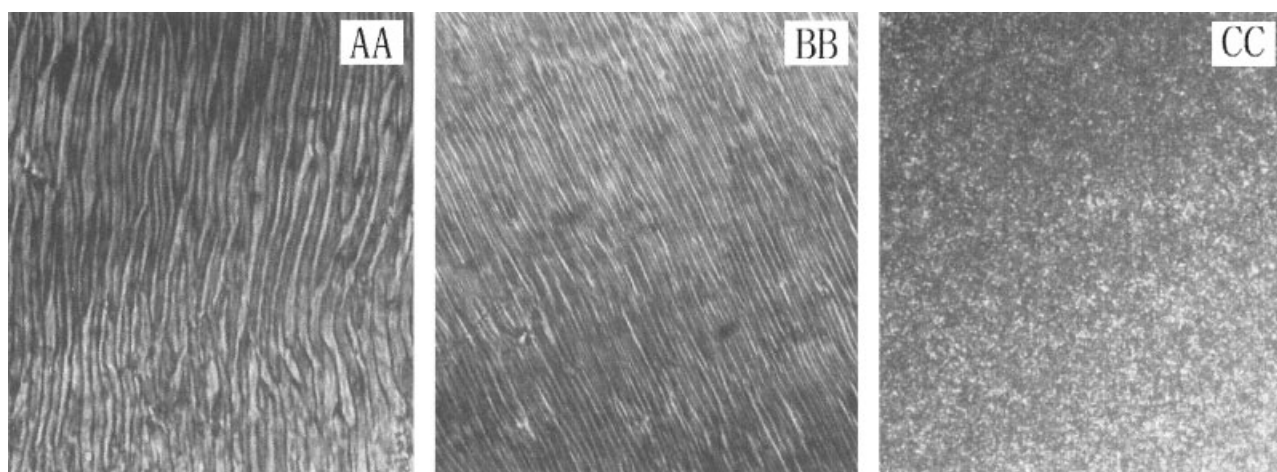


Figure 4 Feeding sequence effects on the texture under polarized light microscopy (after melt shearing and quenching to room temperature; 500 \times).

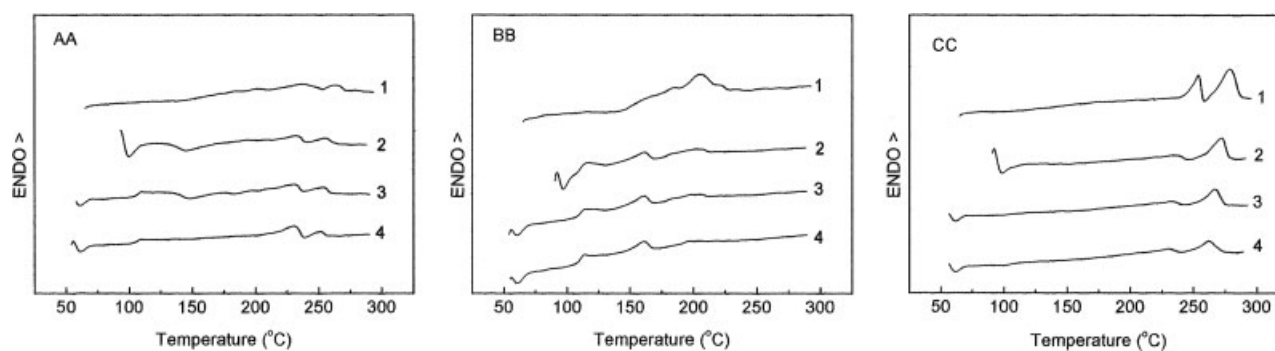


Figure 6 DSC heating curves of the polymers after they were cooled from 300°C at different cooling rates: (1) as-synthesized polymer and the polymer after cooling at (2) 200, (3) 10, and (4) 3°C/min.

molecular interactions (e.g., a kinked monomer, a bulky substituent group, or an increasing reaction temperature); the oligomer will be well dissolved in the reaction medium, and the molecular chains will be stretched. This will result in a high viscosity for the reaction system. Polymerization will proceed to some extent, and the viscosity of the reaction system will become too high for stirring; finally, a gel is formed [as shown in Fig. 7(a)].

On the contrary, the molecular chains of the oligomer will shrink. With the progress of the polymerization, the product will be precipitated from the reaction medium, and a granular product will be obtained [as shown in Fig. 7(b)].

TABLE I
Relationship Between the Melting Transition Temperature and Heating Run

Melting peak	Run	AA	BB	CC
T_{m1} (°C)	1	237.8	—	253.6
	2	233.1	160.8	236.3
	3	231.9	161.1	232.8
	4	230.0	161.1	230.8
T_{m2} (°C)	1	264.3	205.5	278.6
	2	254.4	202.5	271.8
	3	253.0	202.3	267.1
	4	250.9	201.9	262.0

TABLE II
Transition Temperatures of the Other Polymers

Sample	Feeding method	T_{m1} (°C)	T_{m2} (°C)
PIPDBi50 ^a	Mixed	—	233.4
	PHB first	—	211.4
PIPDBs75 ^b	Mixed	193.6	237.5
	PHB first	171.9	194.9
PIPDH50 ^c	Mixed	—	224.2
	PHB first	—	214.1

^a Monomer composition (molar ratio): PHB/IA6/DHBP/BP = 2 : 1 : 0.5 : 0.5.

^b Monomer composition (molar ratio): PHB/IA6/DHBP/BPS = 2 : 1 : 0.75 : 0.25.

^c Monomer composition (molar ratio): PHB/IA6/DHBP/HQ = 2 : 1 : 0.5 : 0.5.

On the basis of this understanding, the experiments were carried out at different reaction temperatures: 60°C for the monomer compositions with a gelation temperature of 80° and 80°C for the monomer compositions with a gelation temperature above 80°C. Because of the control of the reaction temperature, the obtained granular products possessed high molecular weights.

As mentioned previously, if the PHB and biphenol mixed feeding method is employed, granular products will also be obtained. It is possible that during the mixed feeding process, the self-polymerization of PHB will occur to a certain extent. These PHB segments, having rather low solubility, may become seed crystals, and this will result in the gradual precipitation of the polymers by crystallization from the reaction medium.

CONCLUSIONS

With the same monomers, a series of poly(ester imide)s with different molecular chain structures were synthesized through the control of the monomer feeding sequence. The monomer feeding sequences led to different polymer structures that showed different fiber-forming and LC natures. The poly(ester imide)s synthesized by PHB-first feeding or

TABLE III
Monomer Compositions and Gelation-Generating Temperatures

Diacid	Biphenols	Ratio of biphenols	Gelation temperature (°C)
IA6	BPA/DHBP	25 : 75	80
	BPS/DHBP	25 : 75	80
	BPA	—	80
	DHBP	—	140
	HQ	—	No gelation
IA6/IA4	BP	—	No gelation
	DHBP	—	140
IA6/IPA	DHBP	—	130
IPA	BPA/DHBP	25 : 75	80

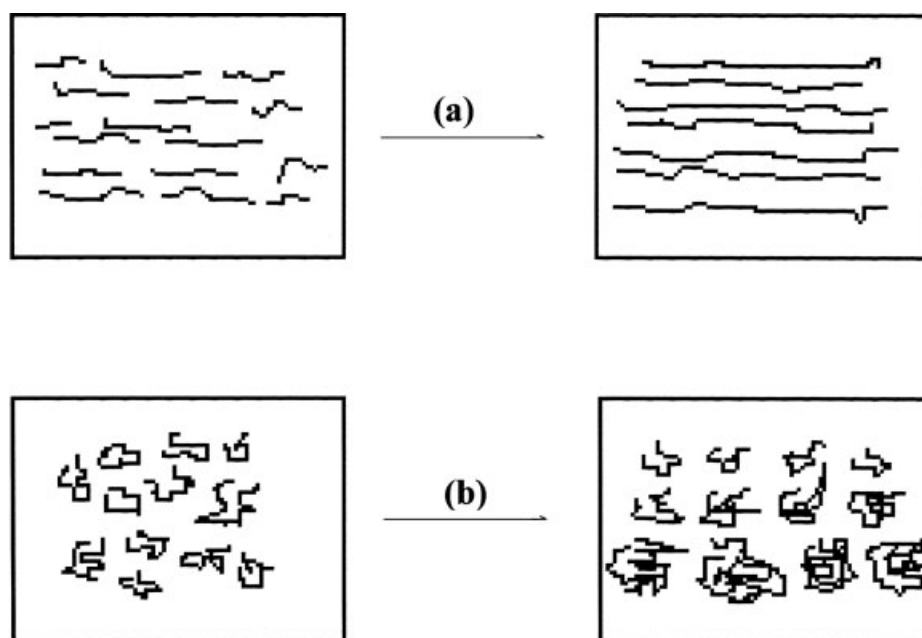


Figure 7 Illustration of (a) gelation and (b) precipitation.

PHB and biphenol mixed feeding possessed good solubility and fiber-forming properties. The melting points of the poly(ester imide)s synthesized by PHB feeding first were lower than those of the poly(ester imide)s synthesized with the other feeding methods. By PHB-first feeding, gelation occurred at a certain polymerization temperature in the copolymerization process. The reason for gelation was well explained by a model, and according to the model, the gelation problem was solved by the choice of the appropriate biphenol, a reduction of the polymerization temperature, or the adoption of the PHB and biphenol mixed feeding method. This work therefore suggests that poly(ester imide)s with given properties can be obtained through the control of the monomer feeding sequence.

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