

Novel Polyimides with Liquid Crystalline Side-chain for Film Materials*

Haojun Fan Meili Xie Yi Gu**

Department of Polymer Material Science & Engineering of Sichuan University, Chengdu .610065

Abstract : Two type of polyimides(PI) with liquid crystalline(LC) side-chain were synthesized in this paper by means of modification of macromolecular, and its properties were characterized by FTIR, TGA and polarized optical microscopy. The results show that these PI with LC side-chain have good processability , higher thermal stability and exhibit liquid crystalline behavior in a broad temperature ranges.

Key words: polyimide LC side-chain LC behavior film materials

Polyimide(PI) with reactive side-group or functional side-chain have shown wide application for second order non-linear optical(NLO)^[1-2], electro-optical^[3], photosensitive polyimide(PSPI)^[4] and high-temperature gas-liquid separating membranes. But unfortunately , the introduction of side-chain to the backbone of polyimide can cause the decrease of polymer' s heat-resistance ^[5]. In order to overcome this shortcoming , a molecular-self-assemble technology can be applied to enhance the functionalized PI with side-chain thermal stability . For example, the combination of the PI backbone with a in-situ self-reinforce Liquid crystalline (LC) moiety could be expected to result in high-performance with excellent thermal and mechanical properties for functional PI materials.

Recently, we have synthesized aromatic dinitro and diamine compounds bearing reactive side-group. By means of the conversion of the side-group to the functional LC side-chain, new novel polyimides or copolyimides from these diamines and 4,4' -oxydiphthalic anhydride(ODPA) can be obtained. The polymer solution was cast to film and a suitable dipole voltage and temperature were applied, new novel LC side-chain in-situ self-reinforce PI film materials can be achieved. The polymers' structure and thermodynamic properties and liquid crystalline behaviors were characterized by FTIR, TGA and polarized optical microscopy respectively. It was found that these PIs with LC side-chain have good processibility. The introduction of LC side-chain does not decrease the PI' s thermal stability , on the contrary, due to the in-situ self-reinforce of LC side-chain , these functionalized PIs exhibit higher tensile-strength and higher thermal stability .

1. Experiments

1.1 Materials and instruments

All raw materials are CP or AR grade , and purified for further experiments.

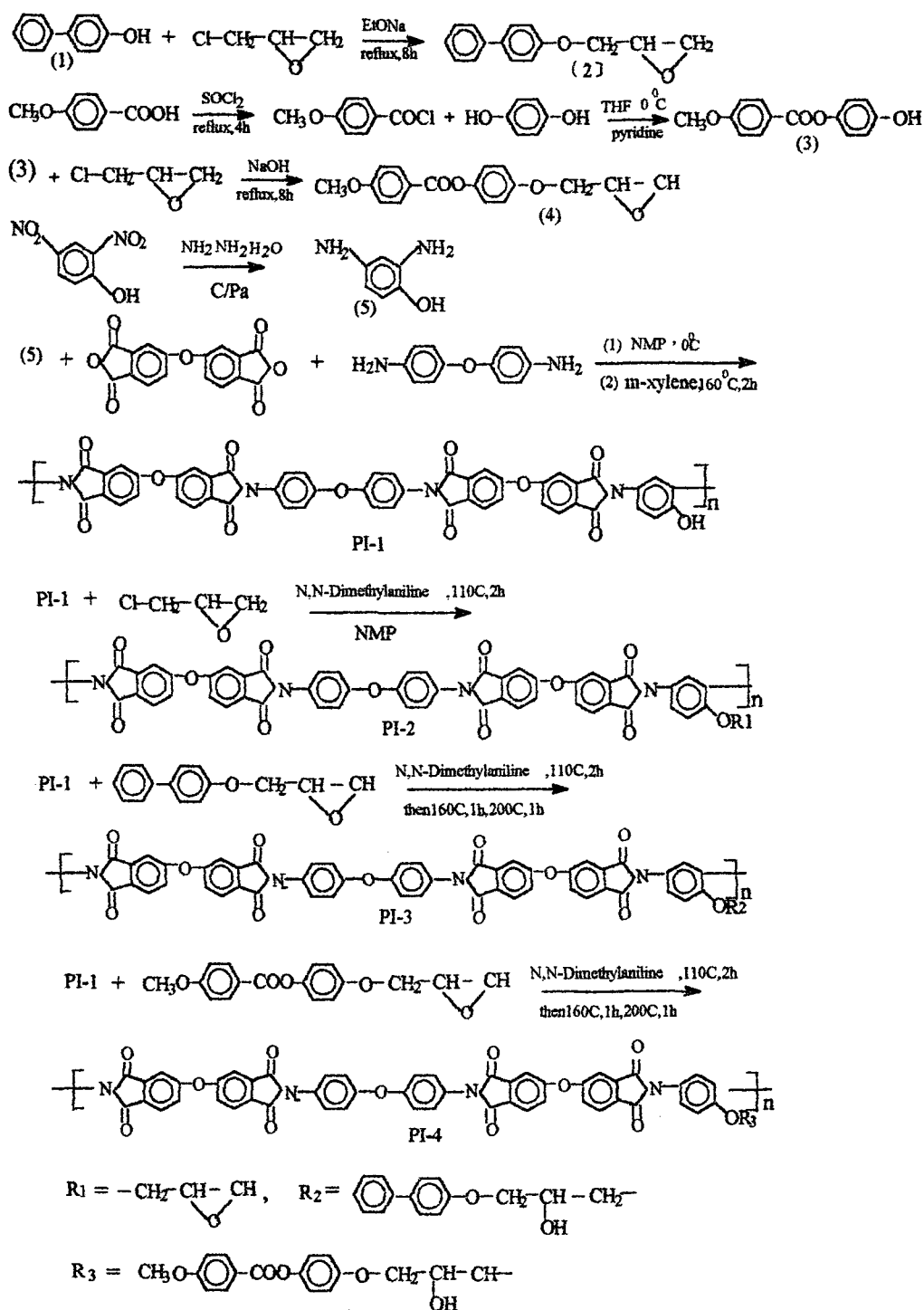
Melt point was measured by X4 melt microscope(the third photics instrument factory, Beijing , Chian) ; Infrared(IR) spectra were obtained on Nicolet 560; Themogravimetry (TGA) was measured on LCT-1 Differential Thermal Analyzer(Beijing Photic Instrument Factory) at a heating rate of 10°C/min under N₂ ; The liquid crystalline behaviors were studied on polarized optical microscopy (XTP-7, 60X); the tensile-strength were characterized by XLL-50, 25mm/min.

1.2 Typical synthesis of monomers and polymers

*This subject was supported by NNSFC(29874021)

**To whom correspondence should be addressed

Typical synthesis of monomers and polymers were described as scheme 1
 scheme 1 synthesis of monomers and polyimides



Synthesis of compound 2: 4-hydroxybiphenyl was dissolved in epichlorohydrin, the equivalent sodium hydroxide and equivalent water were added, the mixture was stirred at 80 °C for 4h, then raising the temperature to 100-110°C for 8h, after removing the solvent under vacuum condition at 25°C, the mixture was precipitated from water, the solid was washed by 1% sodium hydroxide and water to yield compound 2. m.p= 86~87°C; IR(KBr): 912cm⁻¹, epoxy group; 1607, 1485cm⁻¹, aromatic C-H; 1243, 1084cm⁻¹, -O-

Synthesis of compound 3: A suspension of p-methoxybenzoic acid in sulfoxid chloride under nitrogen atmosphere, then the mixture was heated to refluxing temperature, 4h later, cooling the mixture to room temperature and removing the excessive sulfoxid chloride under vacuum, then added some dried THF to dissolve the product so as to be added to 1,4-p-diphenyl solution (in THF) dropwisely. The reaction was carried out on an ice water bath and some pyridine were introduced as a catalyst. After the addition was completed (about 2h), the mixture was stirred at room temperature for 5h, the solvent was removed under vacuum and then precipitated from water, the crude product was dried and re-crystallized by toluene to yield white needle crystalline. m.p=118~118.5°C; IR(KBr): 1778cm⁻¹, -COO-; 1510, 1608cm⁻¹, aromatic C-H; 3426cm⁻¹, -OH.

Synthesis of compound 4: compound 3 was used as a raw material, compound 4 can be prepared as the same route as compound 2. Compound 4 is a white powder, m.p =96~98 °C, IR(KBr): 914cm⁻¹, epoxy group; 1776cm⁻¹, -COO-; 1243, 1082cm⁻¹, -O-

Synthesis of compound 5: 2,4-dinitrophenol and active palladium-carbon were dissolved in alcohol and was placed in three-necked round bottom flask, equipped with a stirring, pressure equalizing addition funnel under nitrogen atmosphere, the hydrazine hydrate was added dropwisely via the addition funnel for a period of 2.5h and the reaction was carried out at refluxing temperature for 5~6h, then the mixture was filtered warmly and a clear yellowish solution was concentrated by rotatory evaporator, a yellow needle was crystallized out at -18 °C. m.p=170~171 °C; IR(KBr): 3499cm⁻¹, 3349cm⁻¹, -NH₂; 3268cm⁻¹, -OH; 1259cm⁻¹, C-O.

Typical synthesis of PI

Synthesis of PI-1: After compound 5 and 4,4'-diamino-diphenylether (mole ratio 1:4) were dissolved in NMP at 0°C in an ice-water bath, the dianhydride monomer (ODPA) was added with magnetic stirring, the reaction was carried out in 10h, a polyamic acid was obtained. Then m-xylene was added to the polyamic acid solution and the solution was heated at 160°C for 2h to imidize the polymer, during this step, the water released by the ring-closure reaction was separated as a m-xylene azeotrope. After the reaction was completed, the resulting polyimide was precipitated into methanol and washed with methanol for two times, removing methanol by vacuum and PI-1 was obtained. IR(KBr): 1778, 1718cm⁻¹, imido -C=O; 3435cm⁻¹, -OH, 1607, 1500cm⁻¹, aromatic C-H.

Synthesis of PI-2: The epichlorohydrin with a few drops of N,N-dimethylaniline was added to the polyamic acid solution (prepared as PI-1) and the solution was warmed at 110°C for 1h, then the product was precipitated into methanol and washed with methanol for several times. PI-2 was prepared after removing methanol under vacuum condition. IR(KBr): 912cm⁻¹, epoxy group; 1778, 1718cm⁻¹, imido -C=O; 1707, 1500cm⁻¹, aromatic C-H.

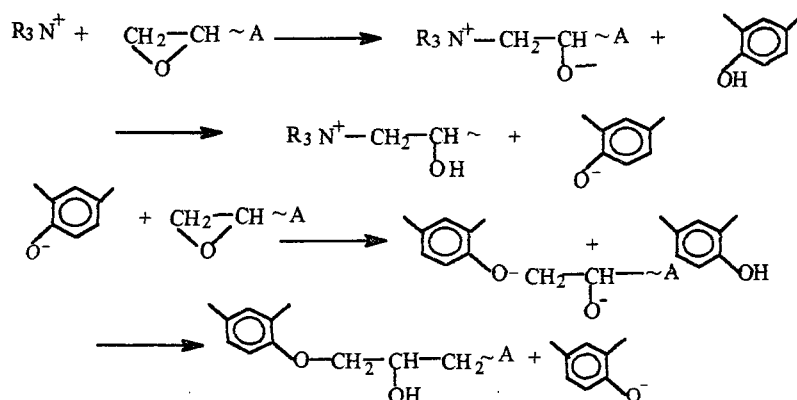
Synthesis of PI-3 and PI-4: PI-1 was dissolved in NMP with stirring, after the addition of compound 2 or compound 4 (compound 5:compound 2(or4)=1:1, mole ratio) and a few drops N,N-dimethylaniline, the solution was cast to form optical-quality films either by spin-casting or casting on glass substrates, the imidization process was carried out at 110 °C for 2h, 160°C for 1h and 200°C for 2h, The resulting PIs were called PI-3 and PI-4 respectively. Similarly, PI-2 reacted with compound 1 or compound 3 to prepare PI-3 and PI-4. IR(KBr) PI-3: 1776, 1716cm⁻¹, imido -C=O; 1608, 1501cm⁻¹ aromatic C-H; 3481cm⁻¹, -OH; 912cm⁻¹, no absorption. PI-4: 1774, 1721cm⁻¹, imide -C=O; 3456cm⁻¹, -OH; 1776cm⁻¹ ester bonds -COO-; 912cm⁻¹, no absorption.

2. Results and discussion

2.1 Reaction between hydroxy group and epoxy group

The pendent hydroxyl group of PF's backbone can react with D-COCl^[6] and epoxy group^[4], though the reaction mechanism of hydroxyl group of alcohol and phenol react with epoxy group displayed many similarities, the reaction rate of phenol is faster than that of alcohol because of the stronger acid nature of phenol. As a rule, this ring-opening reaction of epoxy group could not occur up to 200°C without catalyst, and it take place at 100°C in presence of the quaternary ammonium^[7]. The reaction mechanism of the epoxy groups catalyzed by the quaternary ammonium is described as scheme 2.

scheme 2 mechanism of reaction between hydroxyl group and epoxy group



Changes spectra of the epoxy group absorption in IR can indicate whether a ring-opening reaction take place. The absorbance at 912 cm⁻¹ characteristic to the cyclic ether Structure decreased (or disappeared) indicating quaternary ammonium-catalyzed ring-opening occur.

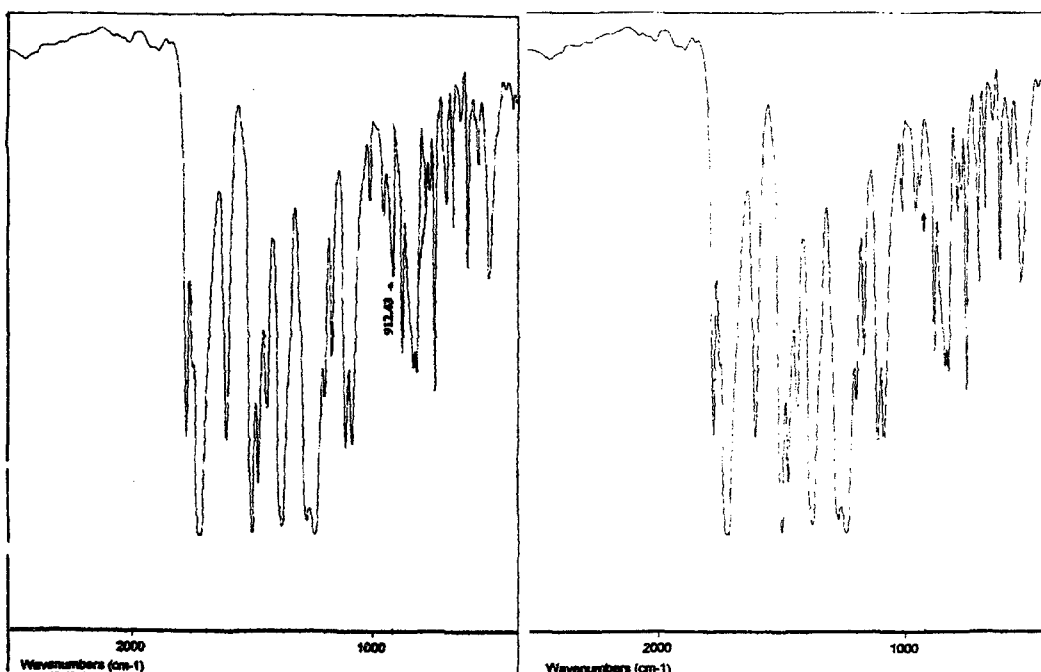


fig. 1 IR spectra of PI-3 after reaction at 80°C for 2h(a. left) and 110°C for 2h(b. right).

Figure 1 shows a decrease in the epoxy group concentration versus time during ring-opening

reaction for the same sample with different reaction condition(80°C, 2h,a; then 110°C 2h,b). During the reaction, the epoxy group reacted with -OH slowly in the first stage (at 80°C), followed by a faster rate at 110°C. The of epoxy group absorptions at 912 cm⁻¹, shown by the decrease ,are used to trace the reaction .H.sungyu' s research [4]showed that the ring-opening reaction occurs only at a temperature exceeding 200°C,or no changes are observed upon heating a film to 200°C in the absence of acid catalyst.

2.2 Solubility, thermal stability and molecular weight of PIs with LC side-chain

The introduction of side-chain or side-group to the backbone of PIs can cause a decrease of the regularity of polymers^[5]. As a result, these PIs with LC side-chains are soluble in many non-proton solvents, such as DMF, DMAC, NMP, and DMSO etc. Because the introduction of side-chain is achieved by means of macromolecules' reaction route , the stereo- retard has little effect on the formation of poly(amic acid), so high molecular weight (characterized by [η]) can be obtained, Theoretically, the introduction of side chain will make the polymer' s thermal stability lower, but the TGA data indicate that PI with LC side-chain decomposed at 320°C (PI-3) and 314°C(PI-4) by 5% weight loss, exhibited good thermal stability , the reason can be suggested as the combination of PI backbone with a in-situ self-reinforce LC moiety^[8]. Studies for tensile-strength draw the similar conclusion. The properties of PI are listed in table 1.

table 1 comparison of properties of polyimides

	solubility				[η],25°C	Td(°C)	Td(°C)	tensile- strength
	NMP	DMSC	DMAC	DMF	(g/dL)	(5% weight loss)	(10% weight loss)	(MPa)
PI-3	s	s	s	s*	1.08**	320	533	94.8
PI-4	s	s	s	s*	1.08**	314	529	79.2

*under 60°C, **poly(amic acid), Td: Temperature of decomposition (N₂)

2.3 liquid crystalline behaviors of monomers and polymers

Liquid crystalline behaviors of monomers (compound 2 and compound 4) and polymers(PI-3, PI-4) were studied by polarized optical microscopy, the results show that compound 2, 3 and PI-3,4 all exhibit thermotropic LC in a wide temperature range. Their phase transition temperature and isotropization temperature were listed in table 2. figure 2 shows typical texture structure of PI-3 and PI-4.

table 2 observed results of compound s and polymers

sample	LC phase (°C)	Ti(°C)
Compound 2	140~180	220
compound 3	80~175	210
PI-3	85~185	266
PI-4	90~175	254

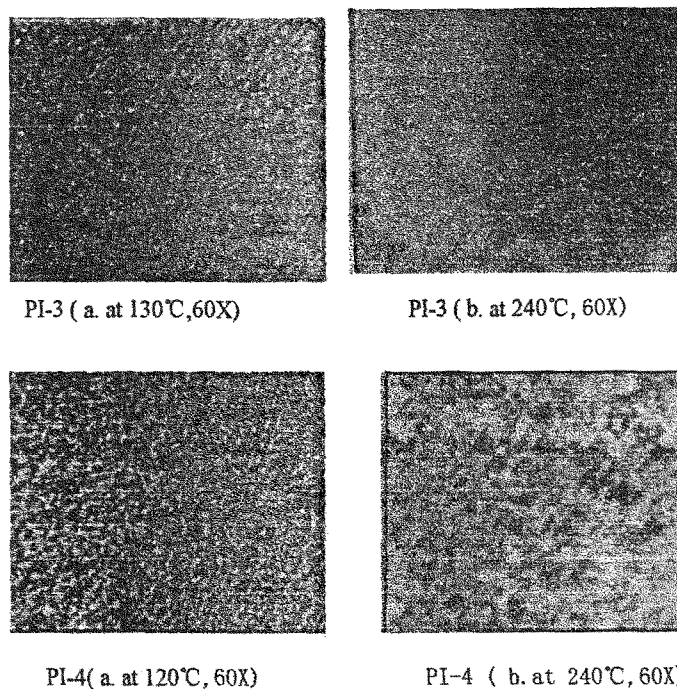


fig. 2 are typical texture structure of PI-3 and PI-4.

With the increase of temperature, double refractive and fluid properties appeared for PI-3 and PI-4. PI-3 exhibits schlieren texture at 130°C (fig 2. a) and a cloudy shadow texture following with the temperature increase. The isotropization temperature of PI-3 is about 264°C. The granular texture of PI-4 presented in figure 2.b was observed clearly at 120°C with a magnification of 60X, this indicates that PI-4 is a thermotropic nematic polymer^[9-10]. Raised to 240°C, its texture show a snow-flower shape, and the clear point temperature is 254°C.

3. Conclusion

- (1) In presence of quaternary ammonium at 110°C for 2h, new type of PIs with LC side-chain can be achieved by the conversion of reactive group (-OH, epoxy group) on the backbone of PI.
- (2) The introduction of LC side-chain decrease the regularity of PI, those functionalized PIs can dissolved in many non-proton solvents, so they exhibit good processability.
- (3) The combination of PI backbone with a in-situ self-reinforce LC side-chain make a contribution to higher tensile-strength and higher thermal stability.
- (4) Texture structures under polarized optical microscopy indicate that PI-3 and PI-4 are the thermotropic nematic polymers and show LC behaviors in a wide temperature range.

Reference

- (1) Eun-Ha Kim, In Kyu moon. *Polymer* (40), 6157-6167(1999)
- (2) Tsutsumi N, Morishima M, Sakai W *Macromolecules* 31(22), 7764-7769(1998)
- (3) John, T. Kenney et al. *Polymer Preprints*. 2(2), 1012(1998)
- (4) H. Sungyu, T. Yamashita, K. Horie. *Macromolecules*, 29, 1144(1996)
- (5) Dong Yu, Ali Gharavi. *Polymer preprints* 37(2), 374(1996)
- (6) T. Omote, H. Mockizuki, K. Koseki, T. Yamoka. *Macromolecules*, 23, 4796(1990)
- (7) chen Ping et al. *Epoxy resin*. Chemical Industry Press. Beijing, 46-47(1993)
- (8) zhao yu. *New Chemical Material*. (4), (5), 20(1996)
- (9) Krichel HR et al. *J. polym. Sci. Polym. Chem. Ed*, 987, 25:489
- (10) Ni rushang et al. *Polymer material science & engineering*(4) 117-110(1994)