*A nevol side-chain liquid crystalline polyimide for film materials

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ABSTRACT A novel side-chain crystalline polyimide (SLCPI) was prepared via co-polycondensation from 3,5-diamino-benzenic-4'-biphenyl ester、 4,4'-diamino-diphenyl ether. The energy-minimized structure and crystallinity of SLCPI were investigated by molecular modeling 、DSC、WAXD and polarized optical microscopy respectively. The results indicated that this polyimide with side-chain mesogenic unit exhibited nemactic (NI) phase and the mechanical properties can be greatly improved due to the in-situ self-reinforced of side-chain mesogenic unit. Furthermore, this polyimide with high thermal stability exhibited good solubility resulting from co-condensation and the introduction of side-chain mesogenic unit .

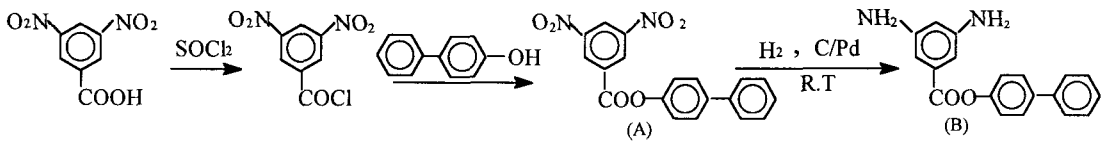
Key words side-chain crystalline polyimide ; molecular modeling ; nematic texture ; in-situ self-reinforced ; film materials ; properties

Polyimide containing mesogenic units on its backbone[1] or polyimide with in-situ self-reinforced side-chain mosogenic units[2] was designed to prepare high tensile strength 、 high modulus and high dimensional stability film materials[3~6]. On this basis, recently, we have synthesized a novel semi-rigid main-chain SLCPI with diphenyl mesogenic units from 3,5-diamino-benzenic-4'-biphenyl ester, 4,4'-diamino-dipheyl ether and dianhydride monomer (ODPA). The Computer Molecular Dynamic Simulation 、 WAXD、 DSC and Polarized Optical Macroscopy were employed to investigate its structure and liquid behaviors and the results indicate that this SLCPI exhibits nematic NI phase. Due to the in-situ self-reinforced of mesogenic units, the improvement of tensile strength and modulus of PI films can reach 270% and 300% respectively; the coefficient of thermal expansion (CTE) of films decrease 40%. DSC and TGA study indicate that the phase transition temperature of SLCPI is above 240~270℃ and the 5%weight loss temperature is above 520℃. Moreover, the co-poly-condensation and the incorporation of mesogenic units decrease the regularity and symmetry of main-chain, as a result, the SLCPI possesses good film processability.

1. Experiments

1.1 Synthesis and Instrumemts

3,5-diamino-benzenic-4'-biphenyl ester and its side-chain liquid crystalline polyimides (SLCPI) were prepared as described as figure 1.



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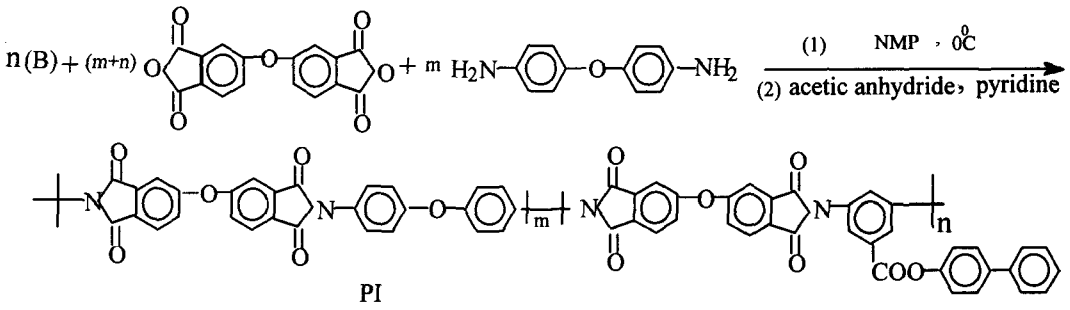


Fig 1 the reaction schems of diamine and SLCPI

The tensile strength and modulus were characterized by Instron 4302 (England); Themogravimetry (TGA) was measured on 2100 Differential Thermal Analyzer (Dupont Company) at a heating rate of 10℃/min under N_2; The liquid crystalline behaviors were studied on polarized optical microscopy (XTP-7, 60X, Jiangnan Photic Instrument Factory, China), 20mm / min. Wide-Angle X-ray Scattering (WAXS) patterns were obtained from a Japan D/MAX-IIIA diffractometer, in which the high-intensity monochromatic Cu K α radiation. Scattering rate : 0.05^0/min; Scattering range :5~45^0. DSC was studied on PE-7C (PE Company) or MDSC (TA Company) at rate 10℃/min, N_2. The CTE was measured on Rheometric Scientific TM DMTA IV (TMA model) at 5 deg/min in air.

The Computer Molecular Dynamic Simulation: By means of Cerius2 soft ware (Version 4.0) supplied by Molecular Simulation INC), the molecular mechanics and the energy-minimized configuration analogy of SLCPI were performed using PCFF force field.

2 Results and discussions

2.1 The phase texture and characterization of SLCPI

Previous works have shown that the polymer with side-chain mesogenic units have not all exhibited side-chain crystallinity and that success depends on many factors such as the rigidity of main-chain, the structure of mesongic units and the connecting model between the two components [7]. Although many methods such as the analysis of DSC, WAXD and palorized optical macroscopy are employed to probe the detailed phase texture, the prediction of inter-reaction between main-chain and mesoginc units is still not possible, therefore, the computer molecular simulation has been recently used to investigate the energy-minimized configuration of SLCP and to reveal the essence reaction between main-chains and mesogenic units [8].

Figure 2 (3 structure units) is the energy-minimized configuration of SLCPI with the diphenyl mesogenic units attached directly on the backbone of polyimide, the molecular length of mesogenic units is 11.856Å, the dihedral angle of the two aromatic rings of diphenyl is 50^0, the dihedral angle between the $^-COO^-$ and benzene ring of main-chain is 3.3^0. Obviously, the main-chains of SLCPI with rigid biphenyl mesogenic units attached directly on its backbone have to adopt to flat configuration (at the expense of conformation entropy) which is main-chain vertical index vectorguantity of mesongenic units so as to yield to rigid mesongenic units, as a result, the SLCPI exhibited nematic NI phase [9].

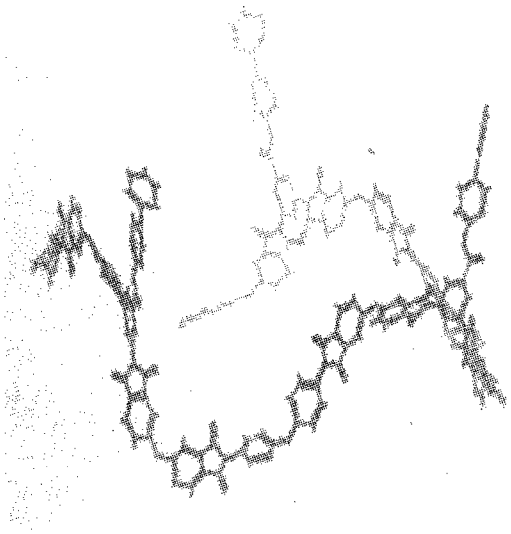
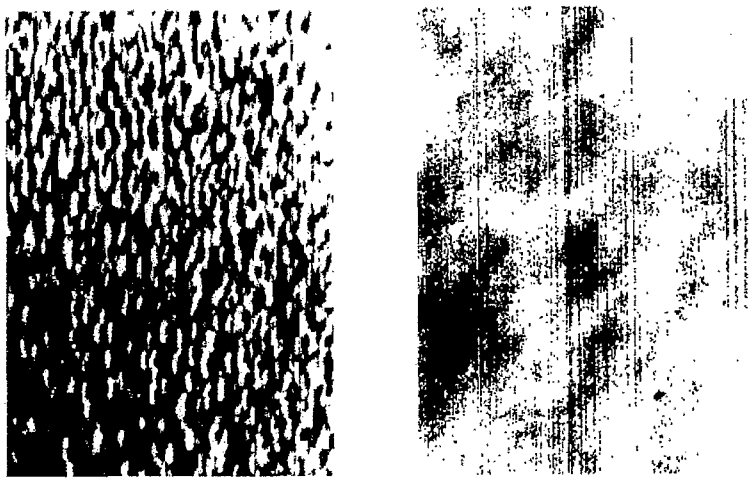


Fig 2 the energy-minimized configuration of SLCPI (3 structure units)

Under poralized optical microscopy, a double refraction appeared for all SLCPI samples. Figure 3(a) is the typical texture of SLCPI at 250℃, the banded texture is consistent with nematic phase characters, when the temperature excesses isotropic point (270 ℃), the double refraction disappeared (figure 3-b). Generally, the banded texture is a marked nematic texture of rigid-main-chain SLCPI or mesogenic –jacked SLCPI [10].



(a) 250℃ (b) 270℃

Fig 3 the banded texture of SLCPI (a): melt state and (b): isotropic state
(3,5-diamino-benzonic-biphenyl ester: 4,4'-diamino-diphenyl ether =3:7, mole ratio)

Figure 4 is the WAXD profiles of SLCPI samples with different mesogenic units levels. Some weak diffraction peaks occurred in low-angle region were suggested to be the intrinsic properties of polyimide rather than to be a symbol of the polymer tending to form layer structure, because the polyimide with no any mesogenic units shows the samilar pattern in this area. A predominant peak in 2 θ=20^0 for all SLCP samples keep good consistent with nematic phase.

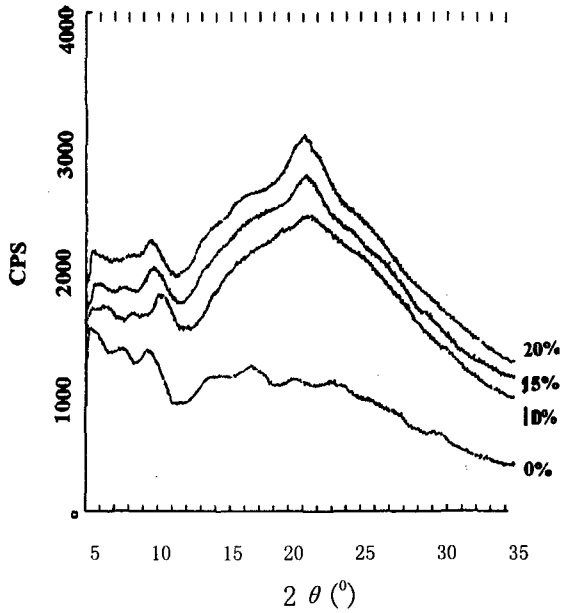


Fig.4-27 WAXD film patterns of PIs
(Content of 3,5-diamino-Benzonic-4' -diphenyl ester, from top to bottom: 25%, 20%, 10%, 0% (mole ratio)

2.2 The mechanical properties and solubility of SLCPI

The introduction of mesogenic units was expected to result in in-situ self-reinforced so as to improve the mechanical properties and dimensional stability of SLCPI. The data from table 2 show that these properties were greatly enhanced (the improvement of tensile strength and modulus are 270% and 300% respectively; the coefficient of thermal expansion decrease 40%) with the improvement of side-chain mesogenic units. Unfortunately, the mechanical properties tend to decrease caused by the low reactivity of 3,5-diamino-benzonic-4'-diphenyleste and huge stero-retard of mesogenic units when the content of 3,5-diamino-benzonic-4'-diphenylester excesses 20% (mole ratio), so the optimum mechanical properties and dimensional stability of SLCPI occurred at the 20% mole ratio of 3,5-diamino-benzonic-4'-diphenyl ester / all diamines.

Tab. 1 properties of side-chain liquid crystalline polyimide

Mole ratio[a]	$[\eta]^b$	Tensile strength	Modulus	CTE[c]	Solubility[d]		
	(dl/g)	(MPa)	(GPa)	(PPm/K)	NMP	DMAc	DMSO
0	1.12	78.4	1.738	64	S*	S*	S*
10	1.08	98.2	2.418	/	S	S*	S
15	1.04	139.2	2.732	/	S	S	S
20	0.98	235.2	5.360	41	S	S	S
25	0.82	148.3	2.987	/	S	S	S

a. 3,5-Dimino benzonic-4'-diphenyl ester/ all Dimines (mole ratio); b. the viscosity of the poly(amic acid)s ; c. /: not measured; d. S*: 60℃,dissolved; S: dissolved at room Temperature;

Another interesting result is that the co-polycondensation and the incorporation of mesogenic units improved the solubility of polyimides. All SLCPI samples can dissolve in common solvent such

as NMP, DMAc and DMSO at ambient condition.

2.3 Thermal stability of side-chain liquid crystalline polyimides

The phase transition temperature and thermal stability of SLCPI were traced by DSC and TGA measurement respectively and described in table 2.

Tab.2 the phase transition temperature and thermal stability of SLCPI

Mole ratio (%)	5% weight loss (N_2) temperature from TGA (℃)	Phase transition temperature from DSC (℃)
15	539	g 246 N 267 I
20	553	g 245 N 262 I
25	523	g 241 N 260 I

*3,5-diamino-benzonic-4'-diphenyl ester / all diamines. g: glassy state; N: nematic phase; I: isotropic temperature

The results from table 1 and table 2 imply that The phase transition temperature and thermal stability of SLCPI relate to the molecular weight of poly(amic acid)s. Once the introduction of mesogenic units cause the molecular weight of poly(amic acid)s decrease, the phase transition temperature and 5% weight loss temperature tend to decrease. In any way, the 5% weight loss temperature of SLCPI is above 520℃, the glass transition temperature and isotropic temperature of SLCPI are above 240 ℃and 260℃, high thermal stability combined with high tensile strength、high modulus and high dimensional stability provide a wide application prospect in micro-electro industry for SLCPI film materials.

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