

## Recent R&D Progress in Polyimide Fibers( CIAC)

Lianxun Gao(高连勋) , Senbiao Huang(黄森彪) , Xuepeng Qiu , Mengxian Ding(丁孟贤)  
Changchun Institute of Applied Chemistry, Chinese Academy of Sciences  
(中国科学院长春应用化学研究所) Changchun 130022, China

### Introduction:

High performance polymeric fibers with high strength and modulus, excellent chemical and heat resistance have been widely applied to many aspects of national economy. The significant developments were achieved since 1960s, and high performance fibers have become an absolutely necessary part of modern technology. Some high performance fibers such as carbon fiber[1-4], poly(p-phenylene terephthalamide) (Kevlar TM or TwaronTM) [5-10], poly(p-phenylene benzobisthiazole) (PBT) [11,12 ], poly(p-phenylene benzobisoxazole) (PBO) [13-17], poly(p-phenylene benzobisimidazol) (PBI) [18,19], PIPD (M5) [20-22] and UHMWPE fiber[23-25] have been successfully developed one after another. In view of high properties of polyimides, It will be an essential tendency to polyimides being used for high performance fibrous materials.

The polyimide fiber spinning procedure is divided into one-step process or two-step process on basis of the spinning solution is polyimide or poly(amic acid) (including partial imidization), respectively .

PI fibers underwent about three stages in their history. The first stage , the R&D polyimide fibers were focused on the two-step process at 1960s-1970s. The chief works were promoted by R&D personnels in US and Japan[26-27], the representative works were carried out in du Pont [28-32]. the characterization of this stage is that the tensile strength and modulus of PI fibers are low, and the preparation scale was limited to laboratory. In second stage, the emphasis of developing PI fibers were turned into one-step process in 1980s-1990s. The high strength and modulus PI fibers were successfully obtained. The typical representative works were done by researchers[33-35] in Arkon University , US and professor Masao Horio and coworkers[36] in Kyoto University, Japan. In spite of the great achievements were acquired with one-step process, the endeavor didn't cease with two-step process because the selection of structure of PI was not limited by the solubility of polyimides. In third stage, the main tendency was converted back into the two-step process again at 1990s until now. One typical representative was that P84 PI fibers were successfully developed on a scale of industrialization by Lenzing AG Inc. ( Now Inspec Fibers) in Austria[37]. The most great achievement was obtained by Russian researchers in the end of 20 century[38-39]. They incorporated PRM moiety into the mainchain of copolyimides, the fibers thus prepared had tensile strength of 5-6 GPa, and modulus of 250-280 GPa.

In this presentation we would like to introduce our work on polyimide fibers.

## 2. Experimental section

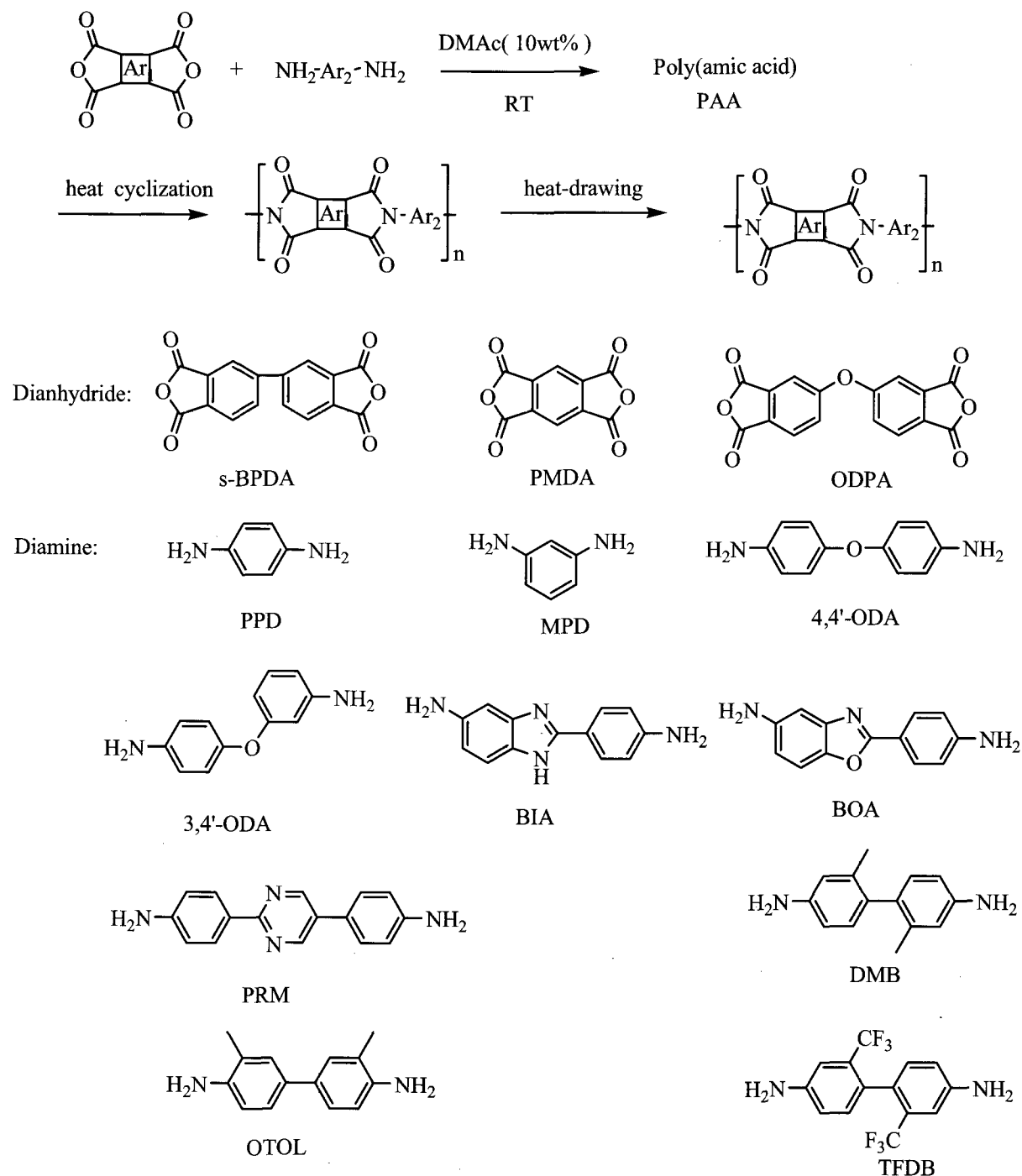
### 2.1 Characterization

The fiber imidization extent was checked with ATR- FT-IR, Glass transition temperatures ( $T_g$ ) were determined with DMAT at a heating rate of  $10^\circ\text{C min}^{-1}$  in an atmosphere. Inherent viscosities ( $\eta_{inh}$ ) were obtained on 0.5g/dL poly (amic acid) solutions in DMAc at  $30^\circ\text{C}$ . Thermogravimetric analysis(TGA) were performance on a PerkinElmer. Fiber samples at a heating rate of  $10^\circ\text{C min}^{-1}$  in a nitrogen atmosphere. The morphology of fibers were obtained with scanning electron microscope(SEM) .The structure features of fibers were exhibited with SAXS, and the orientation of fibers were carried out in WAXD. The diameters of fibers were determined with gold-image optic microscope. Tensile properties

such as the tensile strength, tensile modulus and elongation of fibers at break were measured with Donghua XQ-1 tensile apparatus.

## 2.2. Synthesis of Poly(amic acid) spinning solutions

The poly(amic acid) spinning solutions were prepared via usual procedure with solid content of 10-15 wt% and inherent viscosity of 1.80-3.0 dL/g. the route of preparing PI fibers was shown in scheme1.



Scheme1: the route of preparing polyimide fibers with PAA solution

## 2.3. Preparation of polyimide fibers

The PAA solutions were filtered and degassed prior to use. The PAA fibers were spun by dry-jet wet spinning. The PAA dopes were extruded through a spinneret (34 holes with measuring 0.12mm in diameter) into a air gap, then into a coagulation bath. The solidify filament entered into the second and the third washing bath, and then clustered at the fourth spool. The fibers were dried, and then heating imidized and drawn at a heating furnace over 400°C.

### 3.Results and Discussion

Several kinds of PI fibers were prepared, and the structure and properties of PI fibers were investigated.

#### 3.1 PMDA-ODA system

A wholly continous production line in thousand-ton scale is establishing by HiPolyKing Co. in jilin city. The thermal and mechanical properties of the modified PMDA/ODA PI fiber are summarized in Table1.

**Table1. Thermal and mechanical properties of modified PMDA/ODA PI fiber**

	Tenacity (GPa)	Modulus (Gpa)	Elongation (%)	HD (°C)	T <sub>5</sub> (°C)	
	PPD:ODA	Tenacity (GPa)	Modulus (GPa)	Elongation (%)	HD (°C)	T <sub>5</sub> (°C)
B1	95:5	1.10	80	2.88	560	540
B2	90:10	1.85	90	2.85	560	530
B3	85:15	2.25	100	4.00	550	517
B4	80:20	1.25	65	4.53	570	535
A	0.84	7.0	10.14	565	490	

#### 3.2 BPDA-PPD-ODA system

The PI fibers based on BPDA, PPD and ODA were prepared in CIAC. The thermal and mechanical properties of the PI fiber were summarized in Table2.

**Table2. The thermal and mechanical properties of BPDA/PPD-ODA PI fibers**

The typical FT-IR curve of PI fibers was shown in Figure3.2.a

The typical TGA curve of PI fibers in N<sub>2</sub> was shown in Figure3.2.b

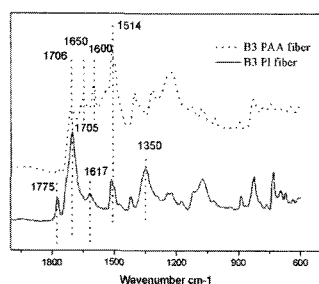


Figure3.2.a

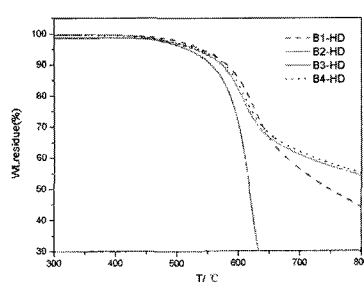


Figure3.2.b

The glass transition temperature (T<sub>g</sub>) values and viscoelasticity of heat- imidized fibers and heat-drawn fibers, measured by DMA and shown in Figure3.2.c.

The x-ray diffractometer scans were implemented with parallel (meridional direction) and perpendicular (equatorial direction) to fiber axis ,and shown in Figure3.2.d and Figure3.2.e, respectively.(In all Figures : HI: heat-imidized fiber, HD: heat-drawn fiber)

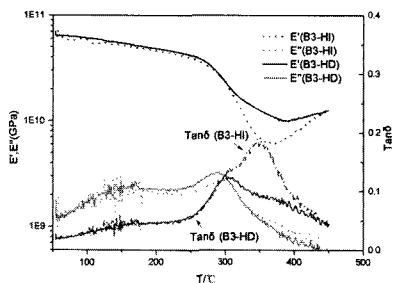


Figure3.2.c

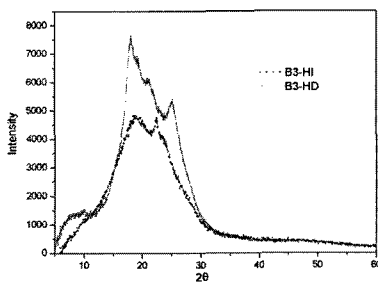


Figure3.2.d

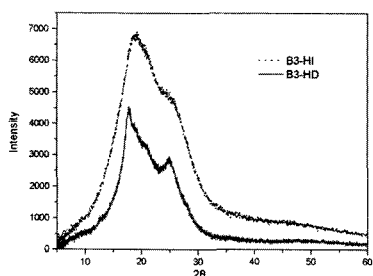


Figure3.2.e

### 3.3. BPDA-PPD-BIA system

The properties data of the PI fibers based on BPDA, PPD and BIA were shown in Table 3.

	PPD:BIA	Tenacity (GPa)	Modulus (GPa)	Elongation (%)	HD (°C)	T <sub>5</sub> (°C)
C1	95:5	0.95	95	3.02	570	537
C2	90:10	1.85	125	2.30	535	569
C3	85:15	2.40	130	3.10	520	552
C4	80:20	1.40	115	2.13	510	562

**Table 3. The properties data of BPDA/PPD-BIA PI fibers**

The typical FT-IR curve of PI fibers was shown in Figure3.3.a

The typical TGA curve of PI fibers in N<sub>2</sub> was shown in Figure3.3.b.

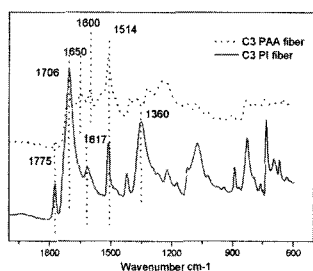


Figure3.3.a

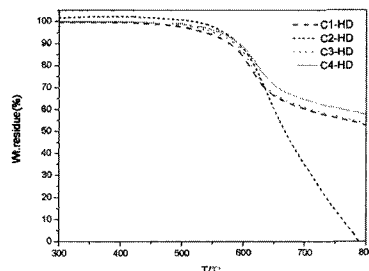


Figure3.3.b

The glass transition temperature (T<sub>g</sub>) values and viscoelasticity of heat-imidized fibers and heat-drawn fibers, measured by DMA and shown in Figure3.3.c.

WAXD with meridional direction and equatorial direction were shown in Figure3.3.d and Figure3.3.e, respectively.

SEM micrograph exhibited a slight extent of skin-core structure for the PI fiber, attributing to the coagulation process of PAA fiber. AS shown in Figure3.3.f, the fiber was well coagulated in fiber formation process due to no big microvoids in fiber. Besides, there are no microfibrils in the fiber can be confirmed.

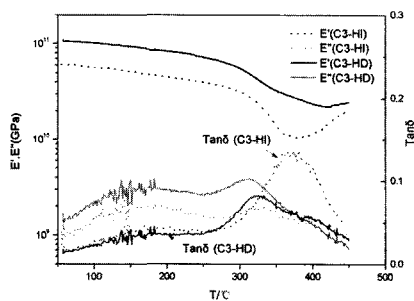


Figure3.3.c

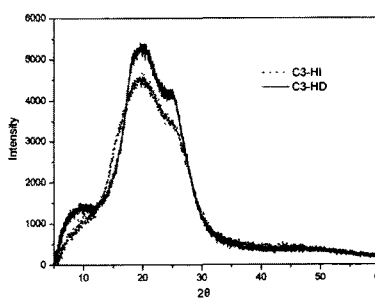


Figure3.3.d

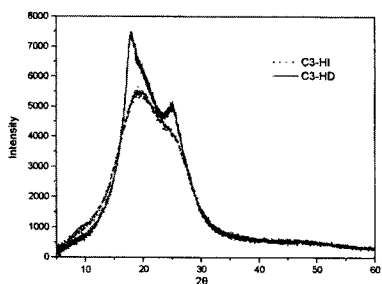


Figure3.3.e

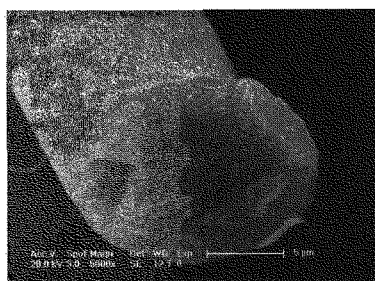


Figure3.3.f

### 3.4. BPDA-PPD-BOA system

The characteristic properties of the PI fibers based on BPDA, PPD and BOA were listed in Table 4.

**Table4: The characteristic properties of BPDA/PPD-BOA PI fibers**

	PPD:BOA	Tenacity (GPa)	Modulus (GPa)	Elongation (%)	HD (°C)	T <sub>5</sub> (°C)
D1	95:5	0.85	102	1.42	540	578
D2	90:10	0.65	75	1.99	510	537
D3	85:15	0.98	90	2.06	490	526
D4	80:20	1.00	110	1.85	500	507
D5	75:25	0.52	90	1.71	480	481

The typical FT-IR curve of PI fibers was shown in Figure3.4.a.

The typical TGA curve of PI fibers in N<sub>2</sub> was shown in Figure3.4.b.

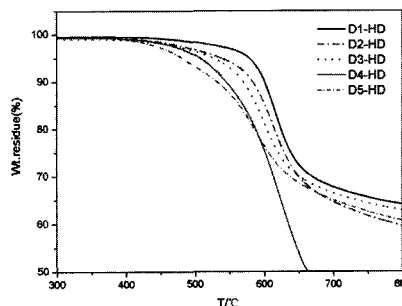
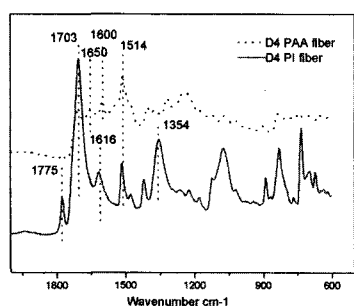


Figure3.4.a

Figure3.4.b

The glass transition temperature ( $T_g$ ) values and viscoelasticity of heat- imidized fibers and heat-drawn fibers, measured by DMA and shown in Figure3.4.c.

WAXD with meridional direction was shown in Figure3.4.d.

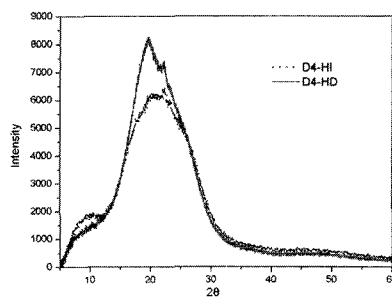
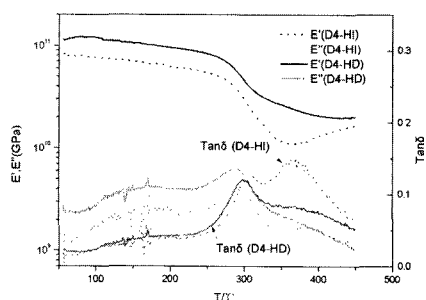


Figure3.4.c

Figure3.4.d

### 3.5. BPDA-PPD-PRM system

The properties of the PI fibers based on BPDA, PPD and PRM were summarized in Table 5

**Table5: The properties of BPDA/PPD-PRM PI fibers**

	PPD:PRM	Tenacity (GPa)	Modulus (GPa)	Elongation (%)	HD (°C)	$T_5$ (°C)
E1	90:10	0.74	90	1.55	570	506
E2	80:20	1.60	115	2.94	570	500
E3	70:30	2.30	110	2.78	575	512
E4	60:40	1.30	95	2.35	570	491
E5	50:50	1.51	90	2.62	not	445
E6	30:70	3.70	120	3.33	not	520

The typical TGA curve of PI fibers in  $N_2$  was shown in Figure Figure3.5.a.

The glass transition temperature ( $T_g$ ) values and viscoelasticity of heat- imidized fibers and heat-drawn fibers, measured by DMA and shown in Figure3.5.b.

WAXD with meridional direction and equatorial direction was shown in Figure3.5.c.

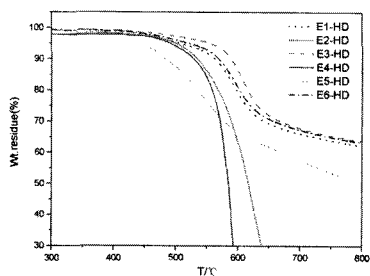


Figure3.5.a

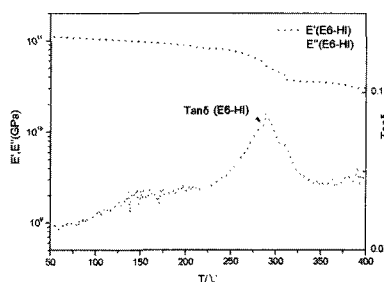


Figure3.5.b

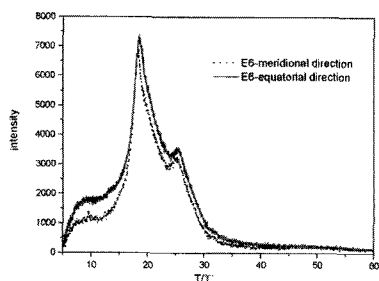


Figure3.5.c

### 3.6. BPDA(PMDA)-PPD- DMB system

The characterization of the PI fibers based on BPDA, PMDA, PPD and DMB were shown in Table 6

**Table6: The characterization of BPDA(PMDA)/PPD- DMB PI fibers**

	Monomer ratio	Tenacity (GPa)	Modulus (GPa)	Elongation (%)	HD (°C)	T <sub>5</sub> (°C)
F1	100:0	0.85	85	1.92	560	557
F2	90:10	1.33	120	2.07	550	533
F3	80:20	1.25	102	2.38	530	514
F4	70:30	1.18	85	2.70	530	522
F5	60:40	1.12	75	2.90	530	517
F6	65:35	0.71	62	2.21	480	483
F7	70:30	0.80	61	2.58	490	511
F8	75:25	1.10	69	2.67	490	491

F1-F5: Dianhydride: BPDA, Diamine: PPD:DMB=100:0,90:10,80:20,70:30,60:40

F6-F8: Dianhydride: BPDA :PMDA=65:35,70:30,75:25

The typical FT-IR curve of PI fibers was shown in Figure3.6.a.

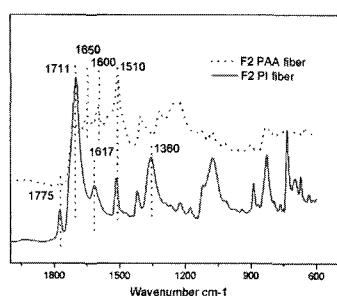


Figure3.6.b

The typical TGA curve of PI fibers in N<sub>2</sub> was shown in Figure3.6.b.

The glass transition temperature (T<sub>g</sub>) values and viscoelasticity of heat- imidized fibers and heat-drawn fibers, measured by DMA and shown in Figure3.6.c.

WAXD with meridional direction was shown in Figure 3.6.d.

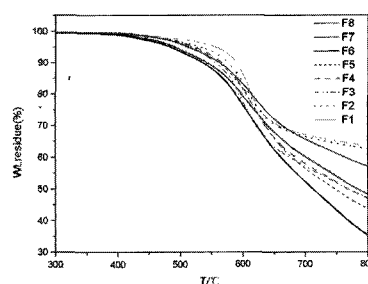


Figure3.6.a

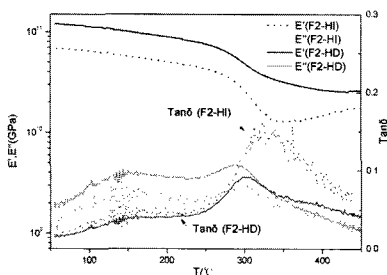


Figure3.6.c

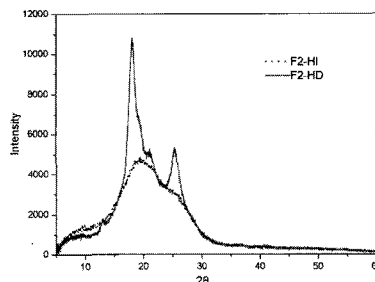


Figure3.6.d

### 3.7. BPDA-PPD-OTOL system

The properties of the PI fibers based on BPDA, PPD and OTOL were summarized in Table7

**Table7: Summary of the properties of BPDA/PPD-OTOL PI fibers**

	PPD:OTOL	Tenacity (GPa)	Modulus (GPa)	Elongation (%)	HD (°C)	T <sub>5</sub> (°C)
G1	90:10	1.30	100	2.47	545	525
G2	80:20	1.30	95	1.98	540	551
G3	70:30	1.50	115	2.07	545	538
G4	60:40	1.15	75	2.40	535	537

The typical FT-IR curve of PI fibers was shown in Figure3.7.a.

The typical TGA curve of PI fibers in N<sub>2</sub> was shown in Figure3.7.b.

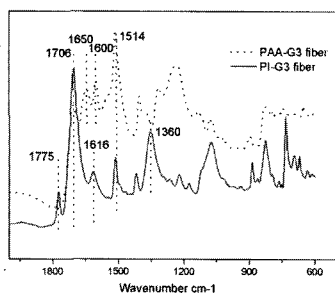


Figure3.7.a

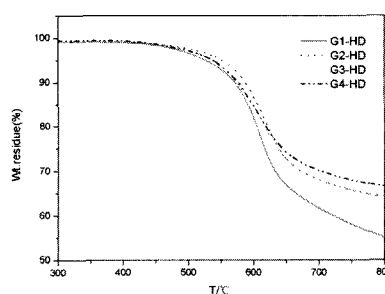


Figure3.7.b

The glass transition temperature (T<sub>g</sub>) values and viscoelasticity of heat-imidized fibers and heat-drawn fibers, measured by DMA and shown in Figure3.7.c.

WAXD with meridional direction was shown in Figure3.7.d.

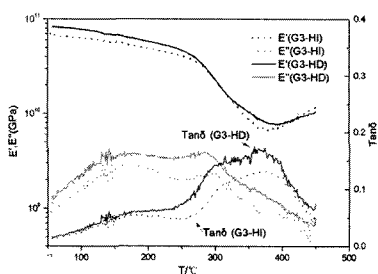


Figure3.7.c

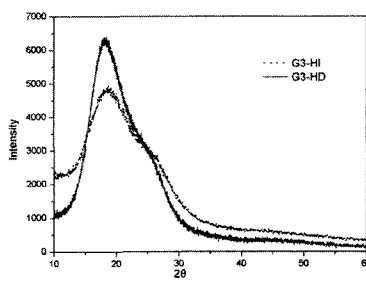


Figure3.7.d

### 3.8. BPDA-PPD-TFDB system



The properties data of the PI fibers based on BPDA, PPD and TFDB were listed in Table 8.

**Table8: The thermal and mechanical properties of BPDA/PPD-TFDB PI fibers**

	PPD:DFB	Tenacity (GPa)	Modulus (GPa)	Elongation (%)	HD (°C)	T <sub>5</sub> (°C)
H1	90:10	1.6	100	2.52	520	550
H2	80:20	1.5	100	2.77	520	546
H3	70:30	1.1	80	2.33	500	540
H4	60:40	1.0	65	3.00	490	539

The typical FT-IR curve of PI fibers was shown in Figure3.8.a.

The typical TGA curve of PI fibers in N<sub>2</sub> was shown in Figure3.8.b.

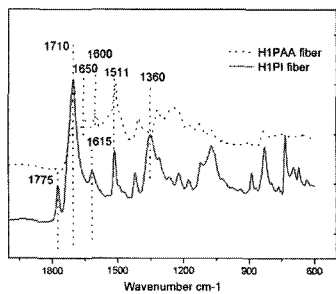


Figure3.8.a

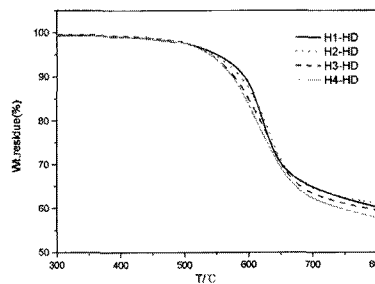


Figure3.8.b

The glass transition temperature (T<sub>g</sub>) values and viscoelasticity of heat-imidized fibers and heat-drawn fibers, measured by DMA and shown in Figure3.8.c

WAXD with meridional direction and equatorial direction were shown in Figure3.8.d and Figure3.8.e

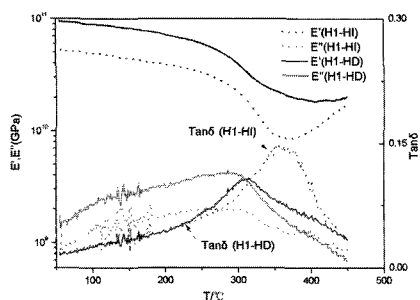


Figure3.8.c

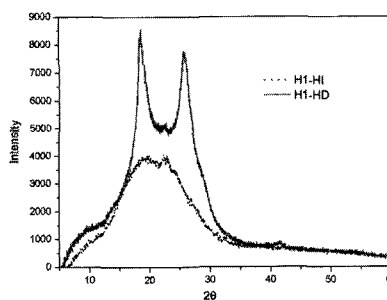


Figure3.8.d

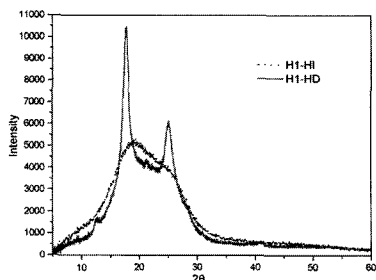


Figure3.8.e

### 3.9. BPDA-PPD-MPD system

The properties data of the PI fibers based on BPDA, PPD and MPD were listed in Table 9.

**Table9: The properties of BPDA/PPD-MPD PI fibers**

	PPD:MPD	Tenacity (GPa)	Modulus (GPa)	Elongation (%)	HD (°C)	T <sub>5</sub> (°C)
I1	95:5	0.70	80	2.12	550	521
I2	90:10	1.03	95	1.99	550	527
I3	85:15	0.9	90	1.82	550	539
I4	80:20	1.10	95	2.20	550	529
I5	75:25	1.20	80	3.11	520	514

The typical FT-IR curve of PI fibers was shown in Figure3.9.a.

The typical TGA curve of PI fibers in N<sub>2</sub> was shown in Figure. 3.9.b

WAXD with meridional direction was shown in Figure and Figure3.9.c.

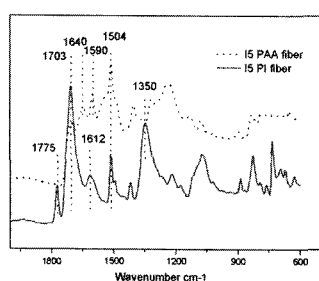


Figure3.9.a

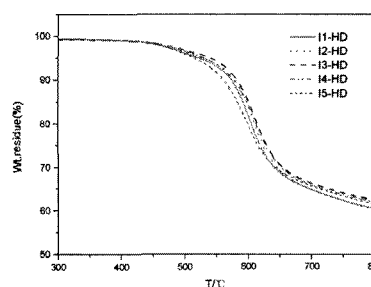


Figure3.9.b

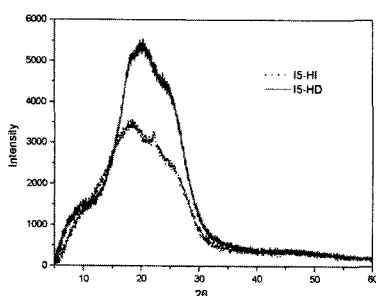


Figure3.9.c

### 3.10. BPDA-PPD-3,4'-ODA system

The PI fibers incorporating 3,4'-ODA show very poor mechanical properties. The possible cause is that the asymmetric structure and the flexible ether bond in polymer chains commonly lead to the result. The detailed researches aren't done.

TO our surprise, the BPDA-ODPA-PPD also show very poor mechanical properties. The cause for this is not known.

· Besides, Modifying PI fibers can obtain better mechanical properties.

### 3.11. Other system

A series of new type high tensile strength and modulus PI fibers are being developed, the better mechanical properties can be expected.

### 4. The plan for PI fibers in the future.

There are also many problems for PI fibers to be solved, and the relationship of structure and properties is also unclear. Among all factors of influencing the fiber performance, we must assure which are of vital importance, and furthermore improve the performance properties of fibers through controlling the factors.

It is very difficult to develop high mechanical properties of PI fibers with two-step process, especially in tensile strength. There also have many works to be done. As for us, our efforts will focus on three levels at a later time.

1): We make our further efforts to improve the production flow and process conditions for the wholly continuous production line in thousand-ton scale, continuing to propel the industrialization of heat-resistance PI fibers.

2): We continue to enhance the mechanical properties of high tensile strength and modulus PI fibers, and meanwhile reducing the cost of PI fibers through further clarifying which are vital importance to enhance fiber properties in order to prepare for the large scale production of high mechanical properties PI fibers.

3): We do our best to develop the ultrahigh performance PI fibers at an acceptance cost to industrial production. The ultrahigh performance is that the tensile strength is above 6Gpa, the modulus is above 280Gpa. It is possible to successfully develop the ultrahigh performance PI fibers through taking new ideas and methods, as well as new equipments and process flow.

#### References:

1. Donnet J B, Qin R Y (1993) Carbon 31: 7
2. Chand S (2000) J Mater Sci 35:1303
3. Yu MJ, Wang CG, Bai YJ, Wang YX, Wang QF, Liu HZ (2006) Polym Bull 57: 525
4. Yu MJ, Wang CG, Bai YJ, Wang YX, Xu Y (2006) Polym Bull 57: 753
5. LYNN PENN, J Appl Polym Sci, Vol. 23, 59-73 (1979)
6. Kwolek SL. US Pat. 3671542; US Pat. 3,819,587 1972.
7. Northolt MB, Aartsen JJV. J Polym Sci: Polym Symp 1977;58:283-296.
8. Barton R. Macromol Sci Phys 1986;B24:119.
9. Hindeleh AM, Abdo SM. Polym Commun 1989;30:184.
10. Lee KD, Barton R, Schultz JM. J Polym Sci: Part B: Polym Phys 1995;33:1.
11. Shawn Jenkins,† Karl I. Jacob,† Malcolm B. Polk,† Satish Kumar,\*,† T. D. Dang,‡ and F. E. Arnold‡ Macromolecules 2000, 33, 8731-8738
12. Yachin Cohen\* Yasuo Saruyama, Edwin L. Thomas Macromolecules 1991,24, 1161-1167
13. TOORU KITAGAWA, HIROKI MURASE, KAZUYUKI YABUKI J Polym Sci: Part B: Polym Phys 1998;36:39-48.
14. D. C. Martin and E. L. Thomas, Macromolecules, 24, 2450 (1991).
15. S. Kumar, S. Warner, D. T. Grubb, and W. W. Adams, Polymer, 35, 5408 (1994).
16. M. E. Hunsaker, G. E. Price, and S. J. Bai, Polymer, 33, 2128 (1992).
17. S. J. Bai and G. E. Price, Polymer, 33, 2136 (1992).
18. Y.-H. Tanga, M.-H. Tsai,\*, C.C. Wub, S.J. Baib Polymer 45 (2004) 459-465
19. Junwen Lv, Kai Yu Wang, Tai-Shung Chung\* J Membr Sci 310 (2008) 557-566
20. Leal AA, Deitzel JM, Gillespie JW. J Compos Mater 2009;43:661.
21. Sirichaisit J, Young RJ. Polymer 1999;40:3421.

22. Lammers ME, Klop A, Northolt MG, Sikkema DJ. *Polymer* 1998;39:5999.
23. Jothi, D. *Synth Fibres* 2000, 29(1), 5.
24. Smith, P.; Lemstra, P. J.; Booij, H. C. *J Polym Phys Ed* 1981, 19,877.
25. Zhou, H.; Huang, X. C. *Hi-Tech Fiber Appl* 1998, 23(5), 28.
- 26.Hara S, Yamada T,Yoshida T,US Pat,1974,3,829,399
- 27.Yokoyama T, Miradera Y, Shito N, Suzuki H, Wakashima Y. US Pat. 1977,4,64,389
- 28.W.M.Edwards,U.S.Pat.3,179,614(1965) to E.I. du Pont de Nemours and Co
- 29.A.L.Eendrey, U.S.Pat.3,179,630(1965) to E.I. du Pont de Nemours and Co
- 30.A.L.Eendrey, U.S.Pat.3,179,631(1965) to E.I. du Pont de Nemours and Co
- 31.A.L.Eendrey, U.S.Pat.3,179,632(1965) to E.I. du Pont de Nemours and Co
32. A.L.Eendrey, U.S.Pat.3,179,633(1965) to E.I. du Pont de Nemours and Co
33. Mark Eashoo, Zongquan Wu, Anqiu Zhang, Dexing Shen, Cecilia Be, Frank W. Harris, Stephen Z. D. Cheng\* *Macromol. Chem. Phys.* 195,2207-2225 (1994)
34. M. Eashoo, D.-X. Shen, Z.-Q. Wu, C. J. Lee, F. W. Harris, *Polymer* 33, 3209 (1993)
- 35.Harris F W, Stephen Z. D. Cheng.US Pat.1995,5378420
- 36.Takaho kaneda, Toshio Katsura, Masao Horio\* *J Appl Polym Sci* 32,3133-3149(1986)
- 37.Jr Farrissey WJ, Onde KB.Ger.1975,2,442,203; *chem.Abatr*,1975,83:116726
- 38.Mihailov.GM,Korzawin LN, *J.Pract.Chem.(RUSS.)*,1998,71(12)
- 39.Mihailov GM, Lebejeva, *J.Pract.Chem.(RUSS.)*,2000,73(3):472

(continuing from p110)

- [26] Saxena A, Sadhana R, Rao VL, Ravindran PV, Ninan KN. *J Appl Polym Sci* 2005,7:1987-94.
- [27] Sivaramakrishnan KV, Marvel CS. *J Polym Sci Polym Chem Ed* 1974,12:651-62.
- [28] (a) Shimizu MA, Higashi Shimbashi KK, Kakimoto MA, Imai Y. *J Polym Sci Polym Chem* 1987,25:2385-93; (b) Matsuo S, Murakami T, Takasawa R. *J Polym Sci Part A Polym Chem* 1993,31:3439-46; (c) Takekoshi T, Wirth JG, Heath DR, Kochanowski JE, Manello JS, Webber MJ. *J Polym Sci Polym Chem Ed* 1980,18:3069-80.
- [29] Haddad I, Hurley S, Marvel CS. *J Polym Sci Polym Chem Ed* 1973,11:2793-811.
- [30] Bengelsdorf IS. *J Am Chem Soc* 1958,80:803-8.
- [31] Keller TM · Price TR. *Journal of Macromolecular Science Part A* 1982,6:931-7.
- [32] Keller TM. *Chem Mater* 1994,6:302-5.
- [33] (a) Keller TM. *J Polym Sci Part A Polym Chem* 1988,26:199-3212; (b) Laskoski M, Dominguez DD, Keller TM. *J Polym Sci Part A Polym Chem* 2005,43:4136-43.
- [34] Boyle MD, Adkins JD, Snow AW, Cozzens RF, Brady RF. *Journal of Applied Polymer Science* 1995,57:77-85.
- [35] Jian XG, Cheng L. *J Polym Sci Part A Polym Chem* 1999,37:1565-7.