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Past, Present and Future of High Performance Polyimide Fibers

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Outline

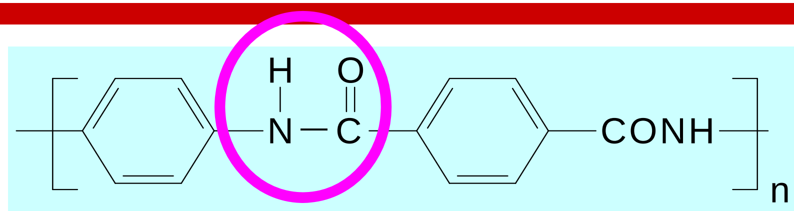
- High performance Fibers
- History of PI Fibers
- Preparation, Structure & Properties
- Applications
- Acknowledgement

Organic High Perform. Fibers

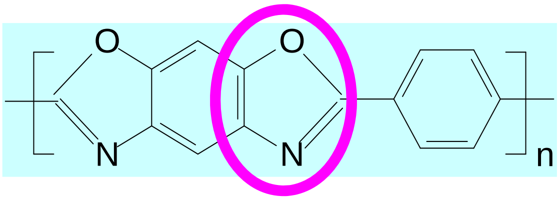
- 1960's, aromatic polyamide lyotropic liquid crystal phenomenon was found; and 1970's, aramid fibers were developed, Kevlar & Twaron.
- 1970's, heterocyclic aromatic polymers were synthesized, including PBO, PBI, PBZT. 1990's, PBO fibers were prepared in large scale by Toyabo.
- 1970's, DSM published its patent on gel-spinning of polyethylene; 1990's, Dyneema was developed.
- 1990's, Akzo Nobel developed a new polymer (PIPD) and M5 fiber, and the fibers were manufactured by Magellan Systems International.

Chemical structures of the polymers

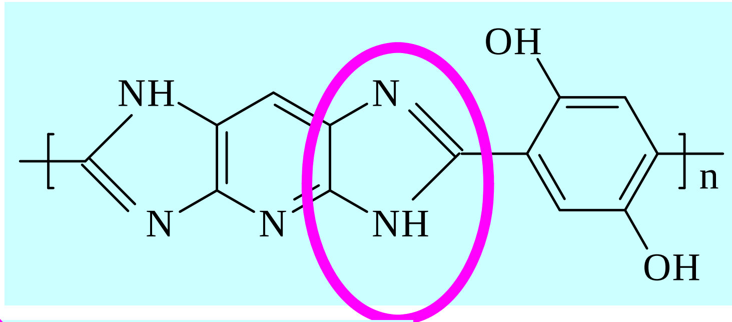
Kevlar



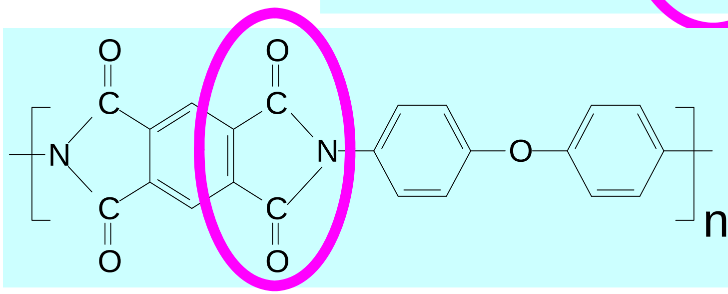
PBO



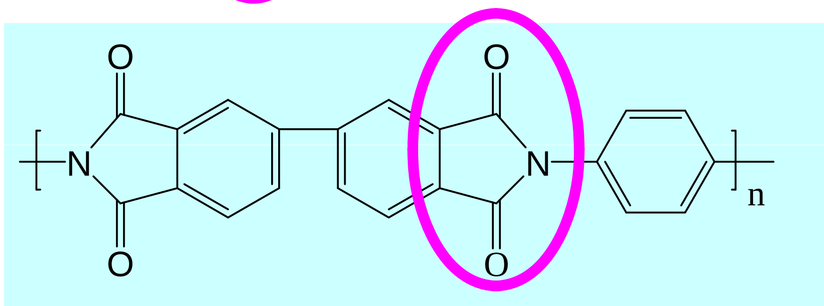
PIPD (M5)



Polyimide (Kapton)



Polyimide (Upilex)



Mechanical properties of some fibers

Fibers	Density g/cm^3	Tensile GPa	Modulus GPa	Elongation %	LOI
CF T700	1.80	4.9	230	2.1	—
Kevlar 49	1.45	2.9	124	2.8	29
Armos	1.44	4.5-5.5	145	2.8-4.0	42
Rusar	1.43	5.0	140	3	42
PBO	1.59	4.8-5.8	211-280	2.5	68
PI fiber (biphenyl)	**1.44**	**3.1**	**128**	**2**	**40**
PI fiber (pyrimidine)	**1.45**	**5.2**	**280**	**2**	**35**

History of polyimide fibers

- **1965** Dupont: PMDA+ODA/DMF, wet-spinning into water, σ= 1.1g/d，M=44g/d，E=6.5%
- **1967** Dupont: PMDA+PDA/DMAc, in water or water/DMAc, σ= 6.9 g/d, M=72 g/d，E=13%
- **1987** Dupont: PMDA+ODA/PDA, σ= 15.6g/d, M=570g/d, E=3.3%

Why did NOT Dupont further develop PI fibers?

- Nomex is enough for market?
- Kevlar has good properties?
- More cost for PI fibers?
- More ……

Edward W M. US Patent, 1965, 3179614

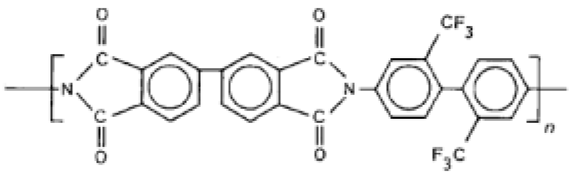
Irwin R S, etc., US patent, 1968, 3415782; US patent, 1987, 4640972

Irwin R S, etc., J. Polym. Sci. Part C, 1967, 19, 41

High strength PI fibers

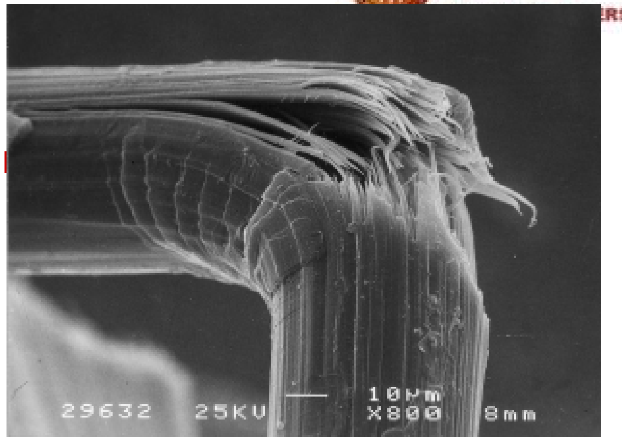
- **1983–1986,** UBE Japan, BPDA+ODA/*p*-chlorophenol, Dry-jet wet-spinning, then drawn at 300–500°C.
  σ = 3.0 GPa, M = 110 GPa

- **1990's,** Akron USA, BPDA +PFMB/*m*-cresol, Dry-jet wet-spinning into H_2O/methol, then drawn at ~380°C.
  σ = 3.2 GPa, M > 130 Gpa



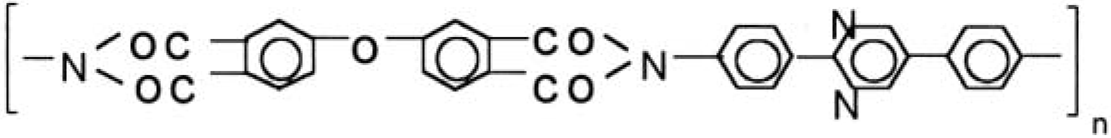
Makino H. etc, US Patent, 1983, 4370290
Kaneda T. etc, J. Appl. Polym. Sci., 1986, 32, 3133 & 3151
Cheng SZD, etc., Polymer, 1991, 32,1803

- **1990's later, Russia, Heterocyclic diamine introduced into main chains of PI.**
- **σ = 5.8 GPa, M = 280 GPa !!!**
- **No products in large scale**



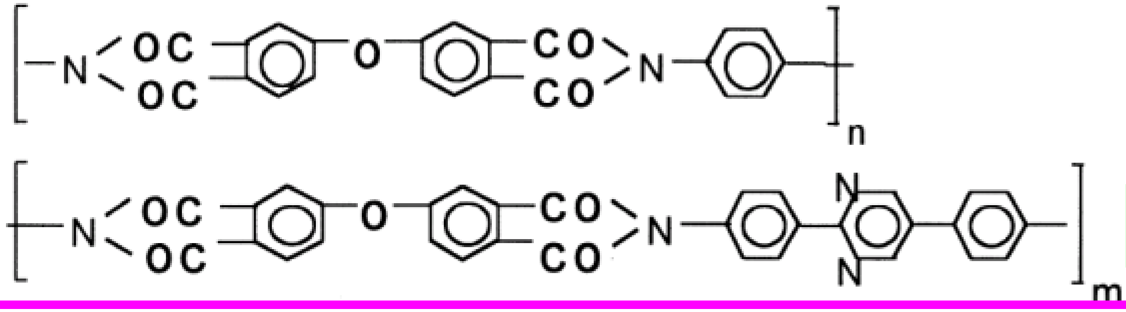
DPhO-PPh

σ=1.0 GPa, M=91 GPa



DPhO-2,5PRM

σ=1.5 GPa, M=118 GPa



DPhO-PPh/2,5PRM

σ=3.0 GPa, M=130 GPa

Sukhanova TE, Baklaginaa YuG, et al. *Polymer* 1999, 40, 6265.

PI fibers in China

- 1960s–1970s, PI fiber developed by China
  - As an anti-radiation fiber
- 2000 -, PI fiber re-developed by means of wet-spinning and dry-spinning by CIAC, Donghua Univ., Sichuan Univ.
  - High strength & modulus
  - Anti-radiation fiber
- PI (PMDA-ODA) fibers have been produced in large scale with 1000 t/a in Jilin and Jiangsu, by wet-spinning and dry-spinning technology.
  - Tensile, 3–5 cN/dtex; fineness: 1–3 dtex,

Preparation of PIF: two-step method

Dianhydride＋Diamide

↓ **Synth. Sol.**

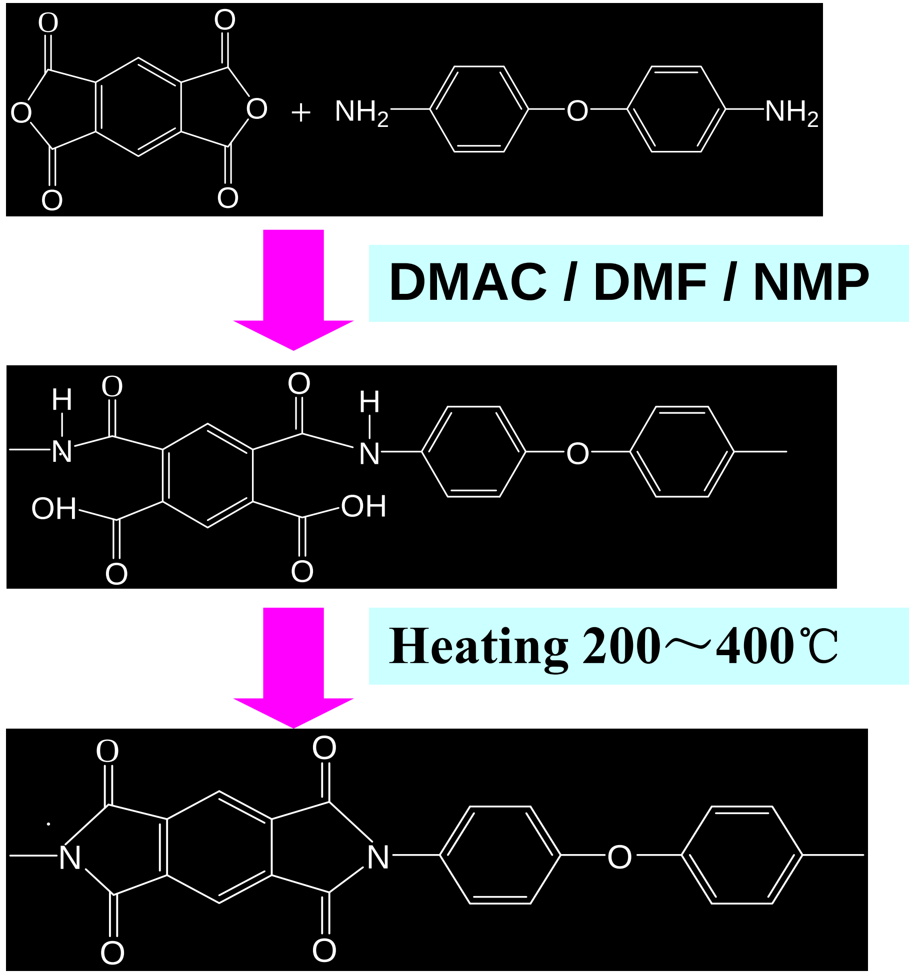
Polyamic acid solution
PAA, the precursor

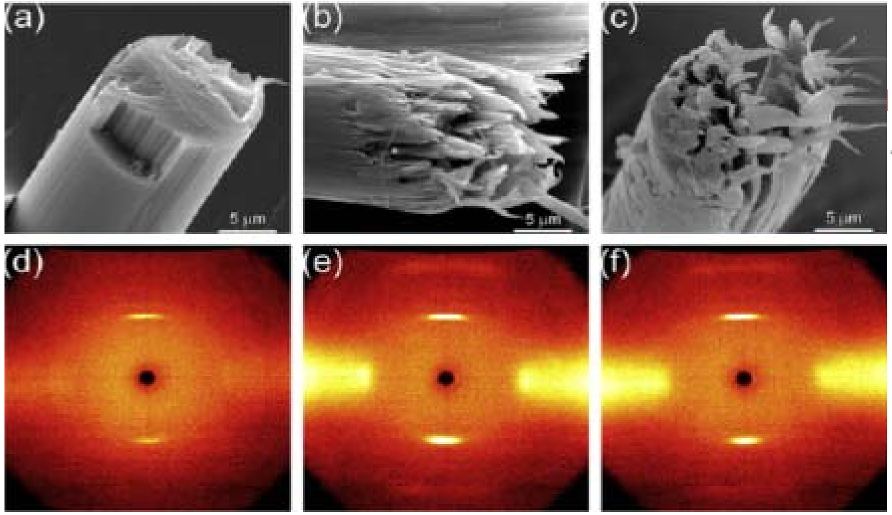
↓ **Spinning**

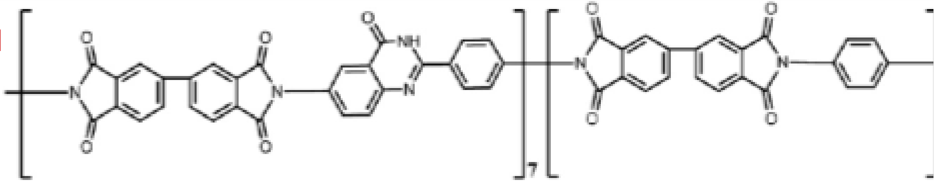
PAA (precusor) fiber

↓ Imidization, Drawing

High perform. PI fiber

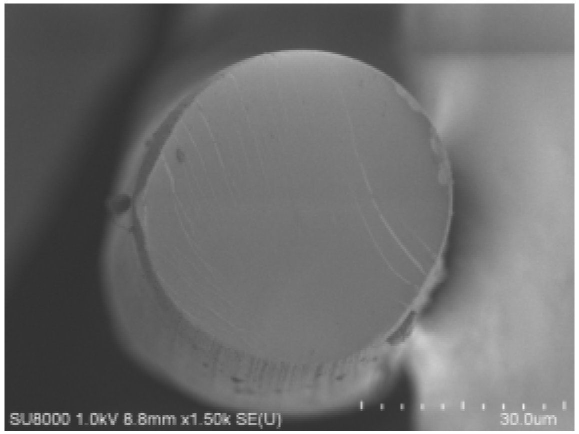


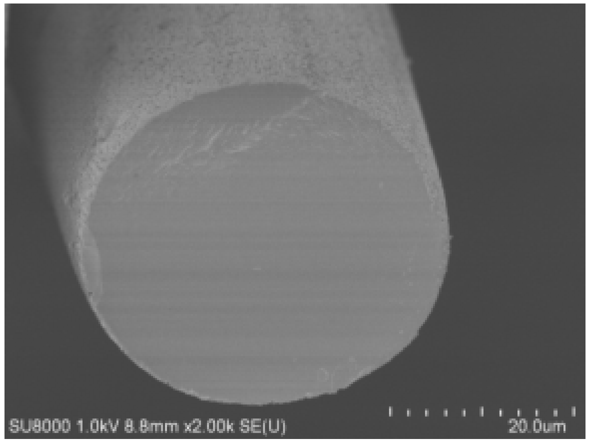


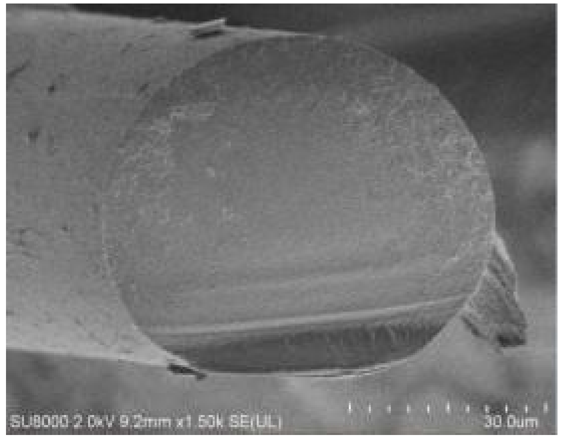


BPDA-AAQ/PDA

T：2.80 GPa
M：115 GPa





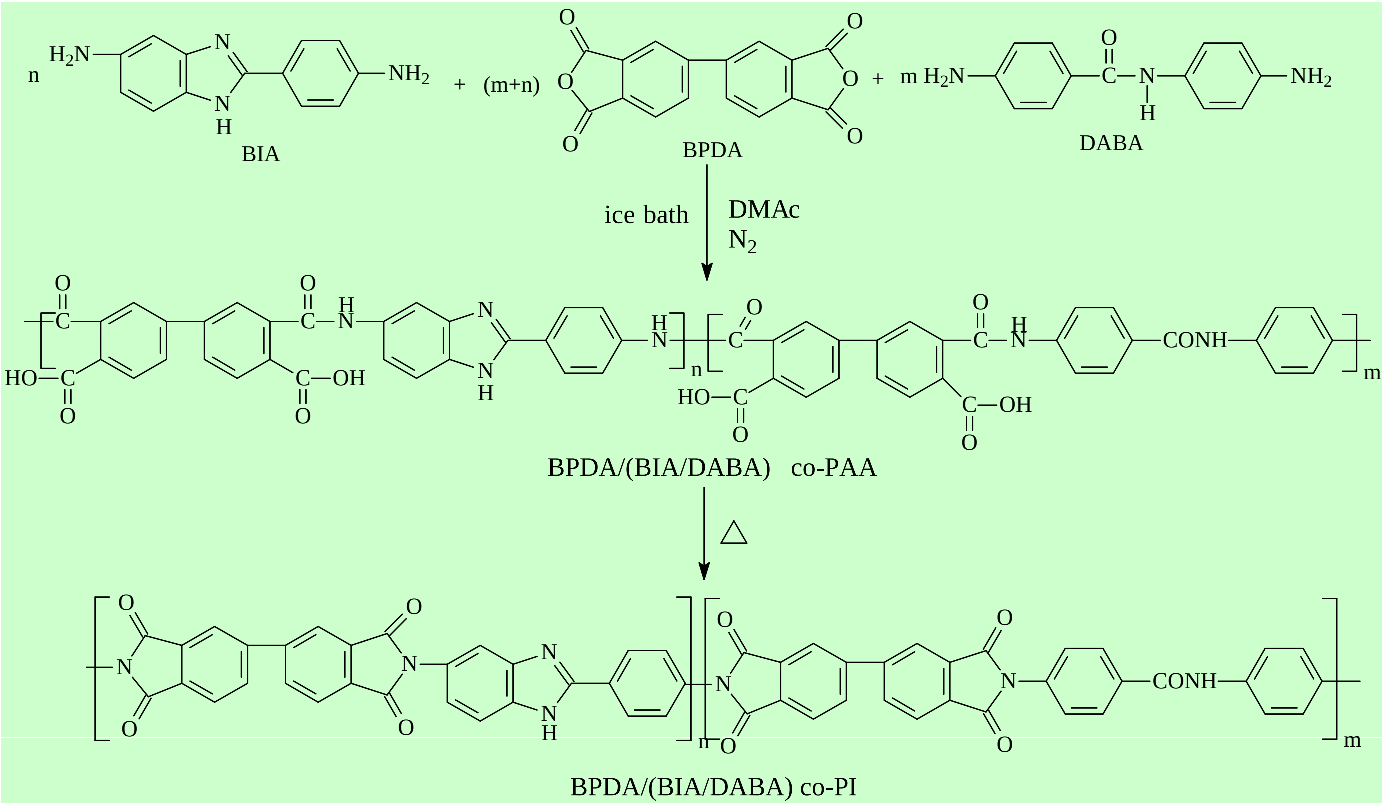


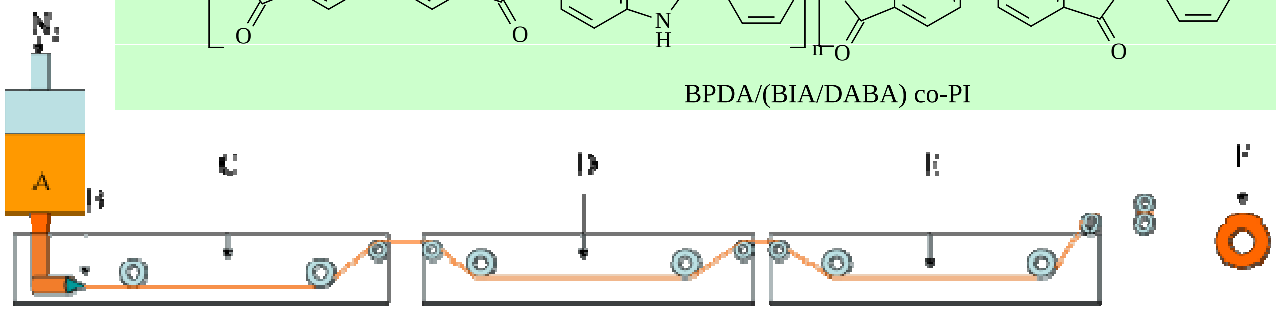
BPDA/BIA
T：2.24 GPa
M：102 GPa

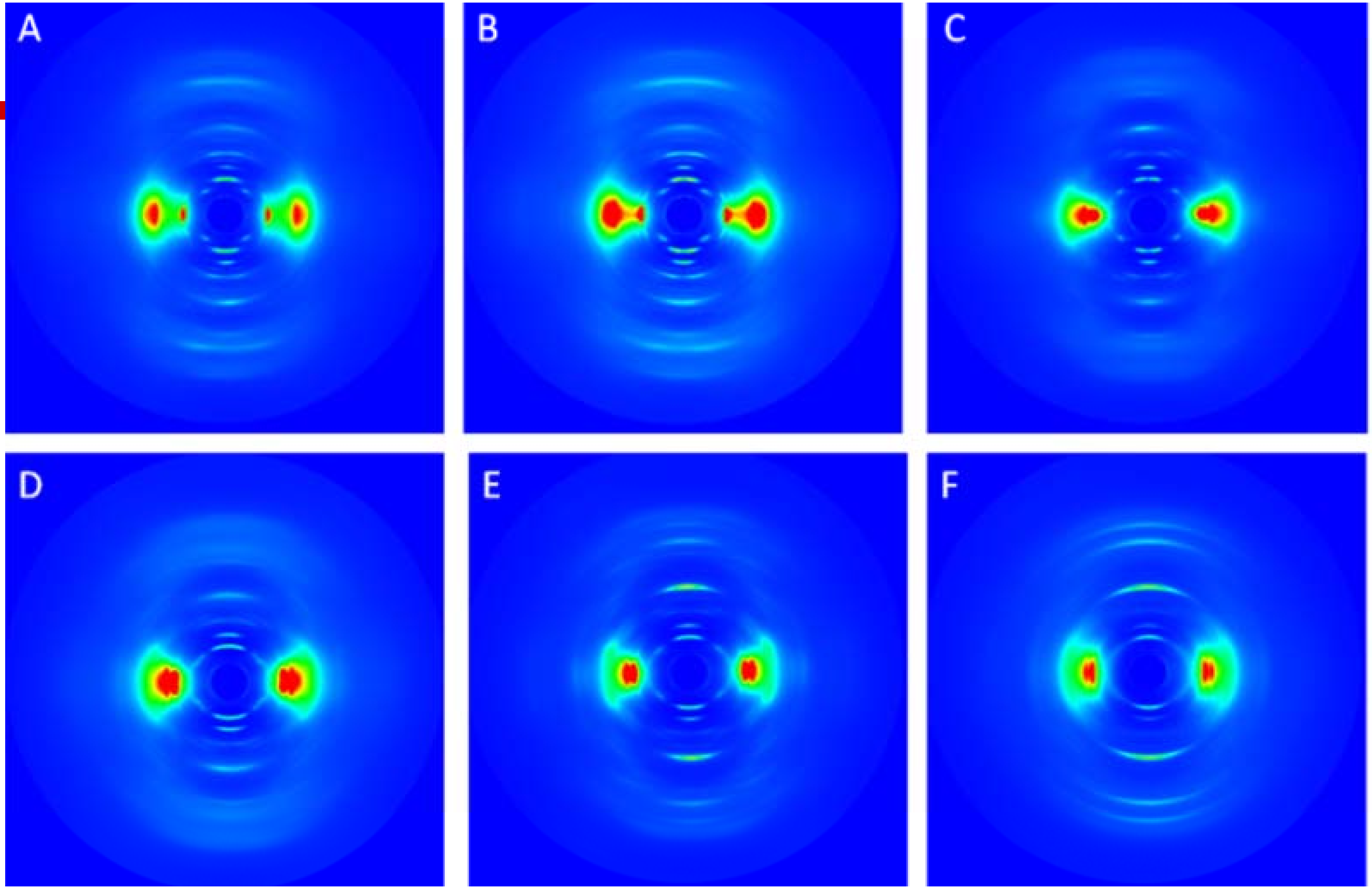
BPDA/BIA/ODA
T：2.0 GPa
M：100GPa

BPDA/BIA/DABA
T：2.3 GPa
M：140GPa

Copolyimides: BPDA-BIA-DABA

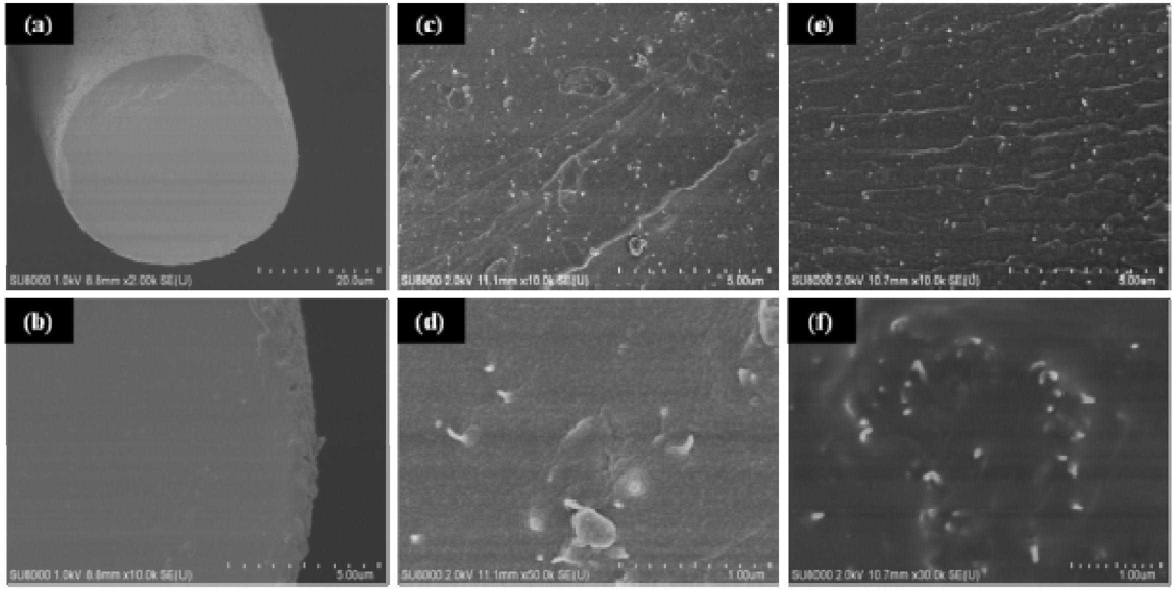


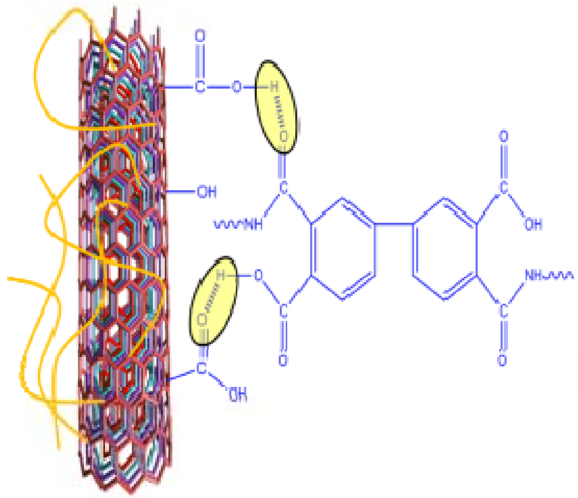


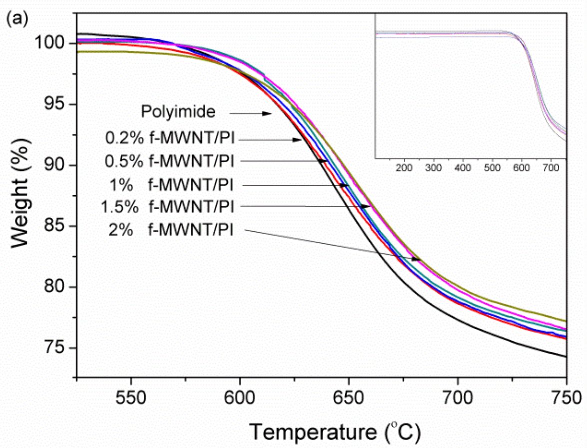


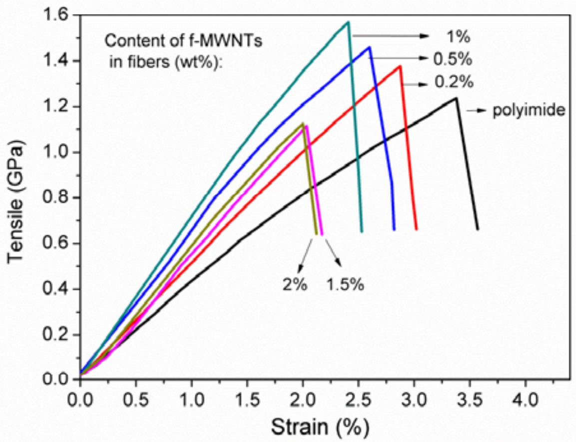
WAXD patterns of the PI fibers with various diamine molar ratios (BIA/DABA): (A) 10/0, (B)9/1, (C) 7/3, (D) 5/5, (E) 3/7 and (F) 0/10.

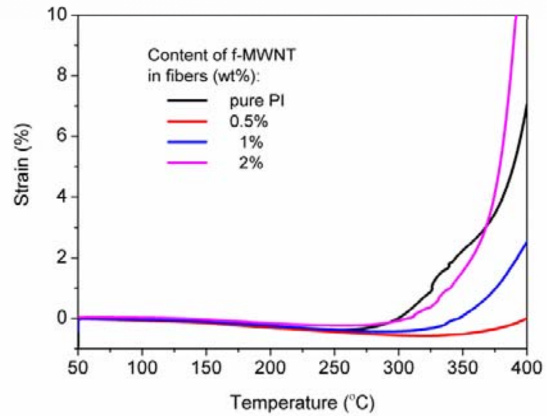
Modification to improving properties











Yin, Zhang*, et al. *Composites: Part B,* 2014, 58, 430

Dry-spinning and simulation

Dianhydride & diamine

↓ Synthesis

PAA solution

↓ Spinning@200°C

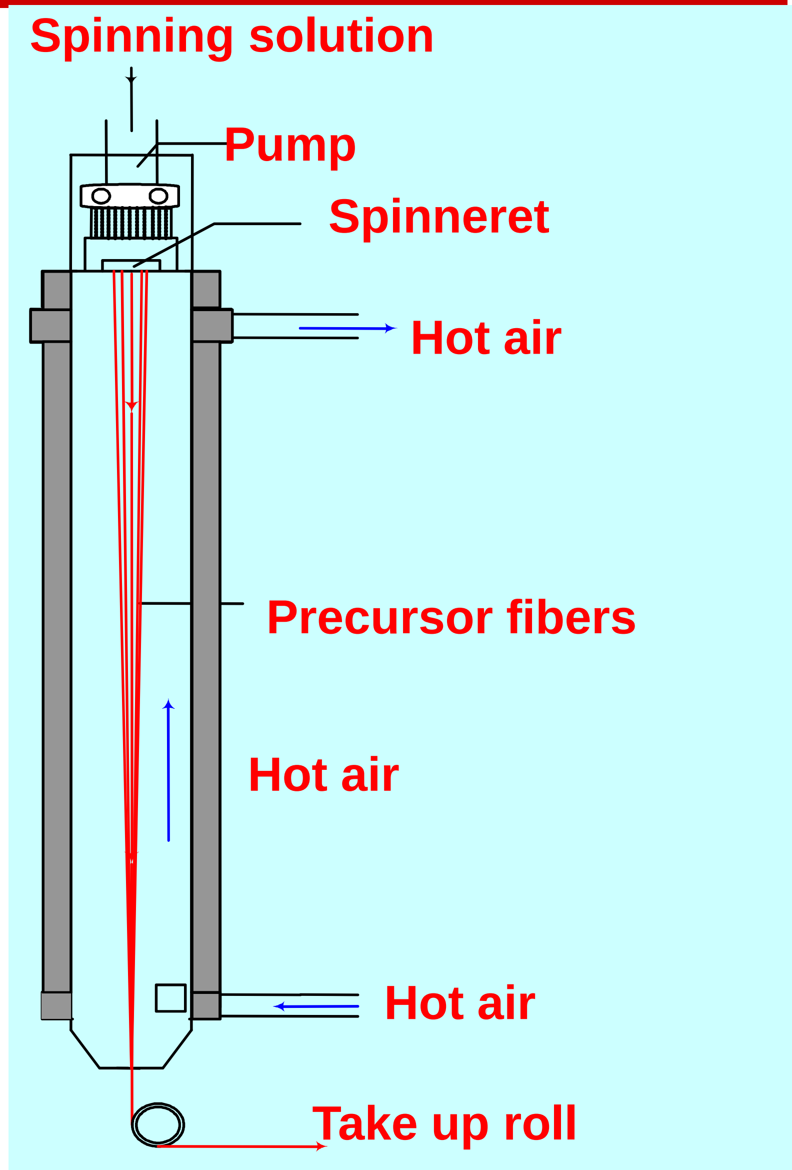
PAA fibers

↓ Cyclization 350°C

Polyimide fibers

↓ Drawing @ 400°C

PIF products



Simulation of dry spinning process.

Models modified to fit formation of PAA/DMAc system.

Continuity equation

$$w_S = w_{S,0} + 4(w_S{}^0 - w_{S,0})\mu_1^{-2}\exp(-\frac{\mu_1^2 D_{PS} z}{VR^2})$$

Momentum equation

$$\frac{dF}{dz} = \rho AV\frac{dV}{dz} + \pi RC_f\rho_a(V - V_{za})^2 - \rho gA$$

Energy equation

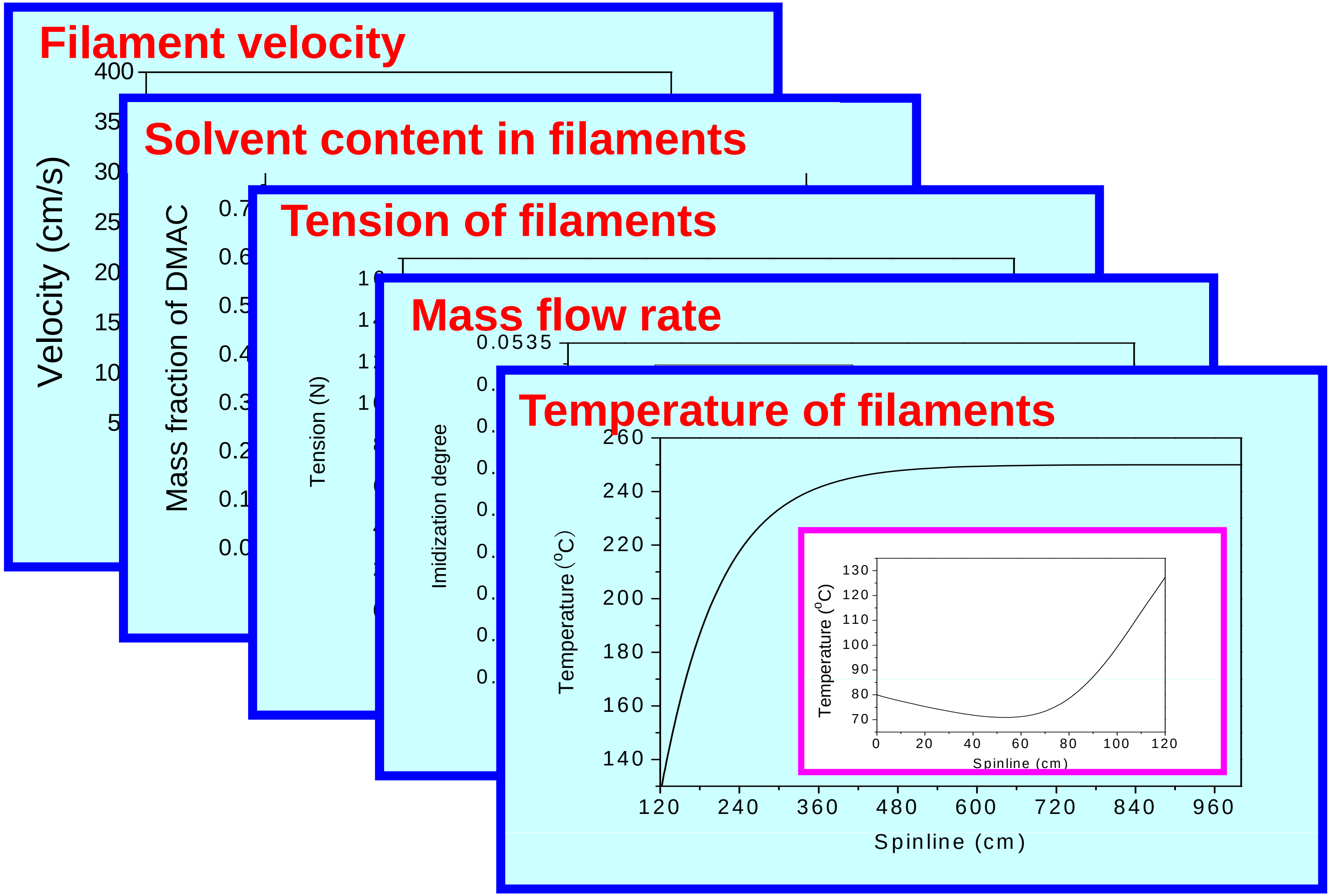
$$\rho C_p V_z\frac{dT}{dz} = \frac{2}{R}[h(T_a - T) - \Delta H_v k_y M_s(y_s - y_0)]$$

Viscoelastic constitutive equation

Modified White-Metzer model

$$F(1-2\lambda\dot{\varepsilon})(1+2\lambda\dot{\varepsilon}) = 3\eta_0 A\dot{\varepsilon} \qquad \dot{\varepsilon} = \frac{dV}{dz}$$

Changes of parameters along the spinline are simulated.



Products

Preparation: One-step method

Dianhydride＋Diamide

Synth. Sol.

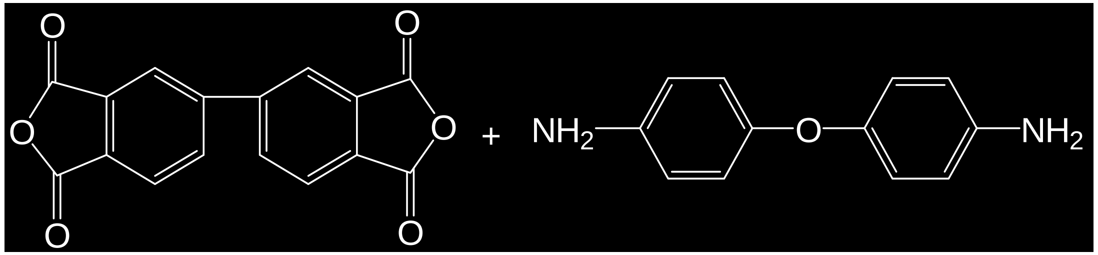
Polyimide Solution

spinning

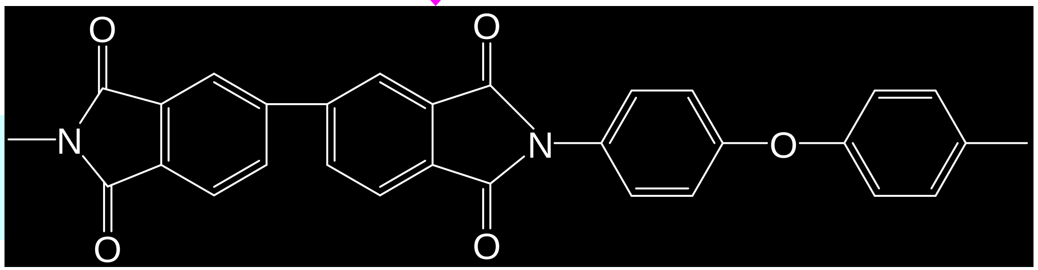
Polyimide fiber

Drawing & post-treatment

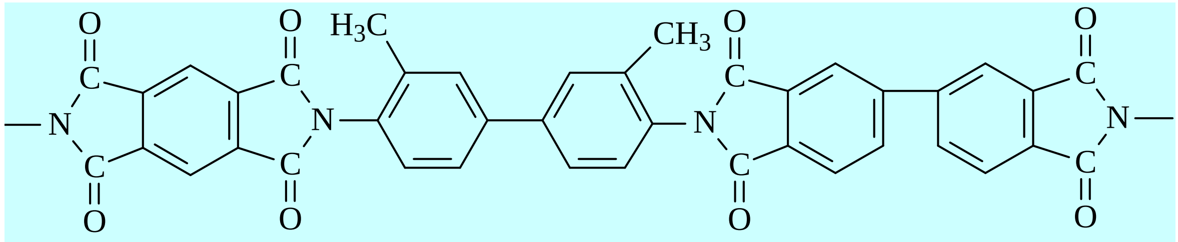
High perform. PI fiber

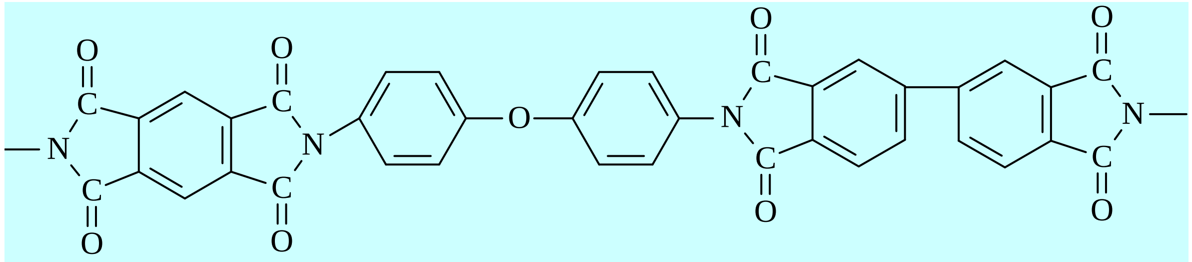


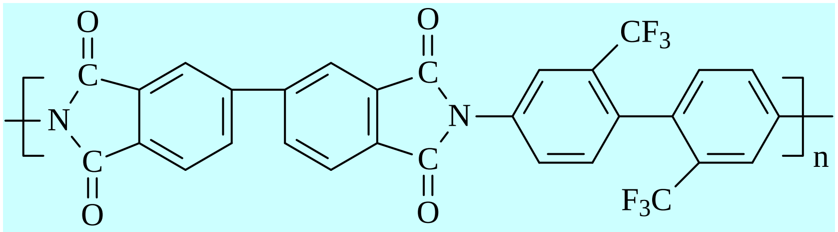
p-chlorophenol,
m-cresol, PPA, etc.

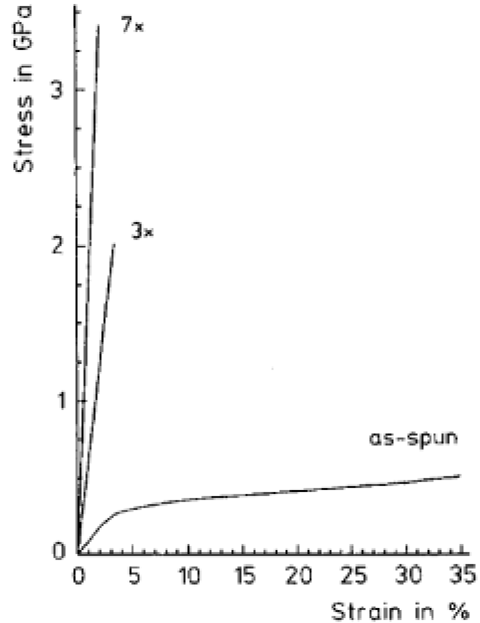


Synthesis of soluble polyimides







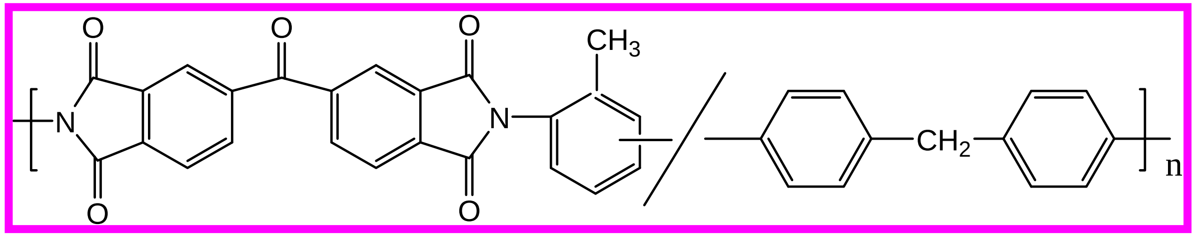


***m*-cresol**
***p*-chlorophenol**

Horio M, et al. J. Appl. Polym. Sci, 1986, 32, 3133 & 3151.
Cheng ZDS, et al. Polymer 1991, 32, 1804 & 1003, 34, 3209;
& Macromol. Chem. Phys. 1994, 195, 2207.

P84: soluble PI (BTDA-MDI-TDI)

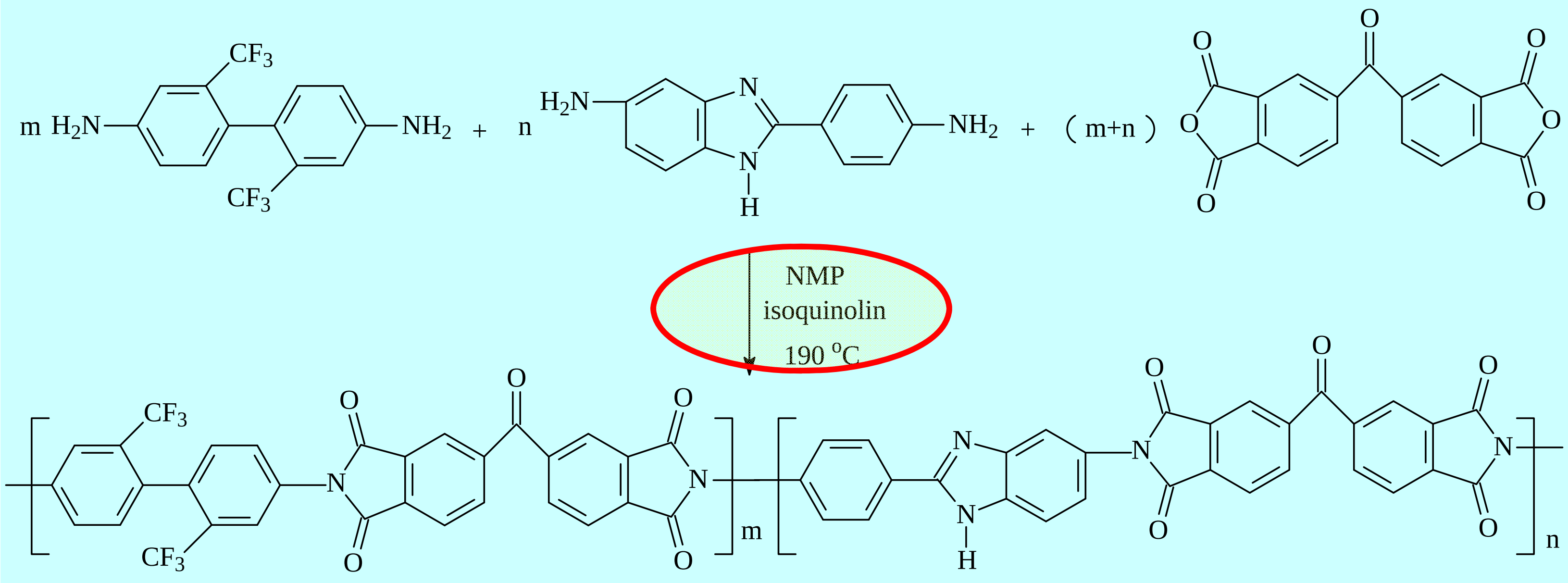
- P84 developed by Lenzing in 1980's, Evonic & Degussa now, is **the first commercial PI fiber**.
- Prepared by wet-spinning methods.
- Fabricated into heat-resistant filter bags. Glass fiber is usually blended with P84 to reduce the price.
- Mechanical properties: 2.2 dtex sample, σ =3.8 cN/dtex, LOI~38，Tg~315℃，260－280°C



BTDA-MDI-TDI

From http://www.p84.com/

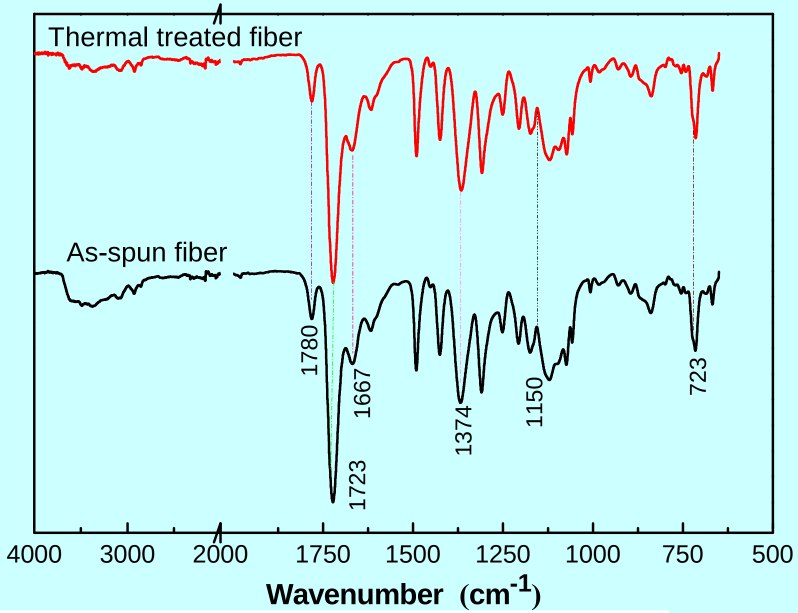
Soluble PI and fibers



Code m/n	NMP	DMAC	DMF	DMSO	THF	$CHCl_3$	m-cresol	Toluene	CCl_4
PI-85/15	++	++	+	+	-	+	+	-	-
PI-75/25	++	++	+	+	-	+-	+	-	-
PI-50/50	++	++	+	+	+-	+-	+	-	-
PI-40/60	++	++	+	+-	+-	+-	+-	-	-

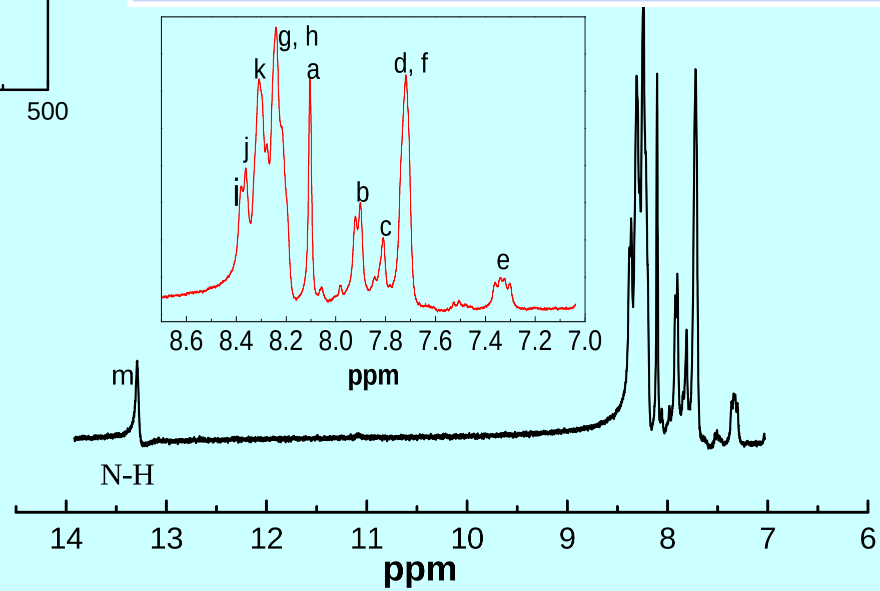
++: soluble at room temperature; +: soluble on heating; +-: partly soluble on heating; -: insoluble.

FTIR & NMR confirm the polyimide structures



ATR-FTIR spectra of PI-50/50

1H NMR of PI-50/50



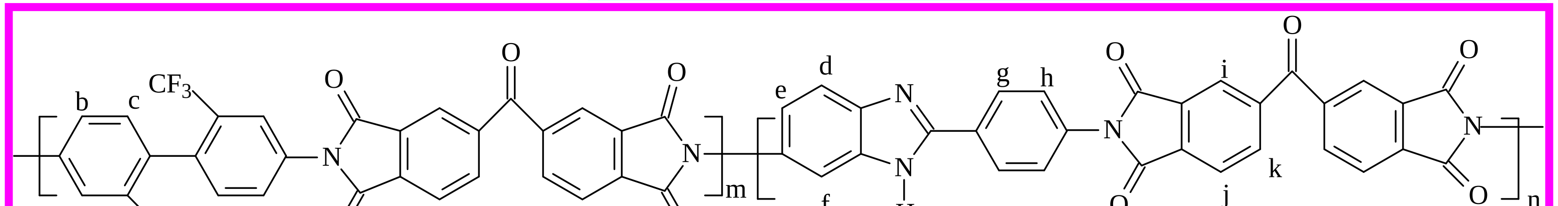
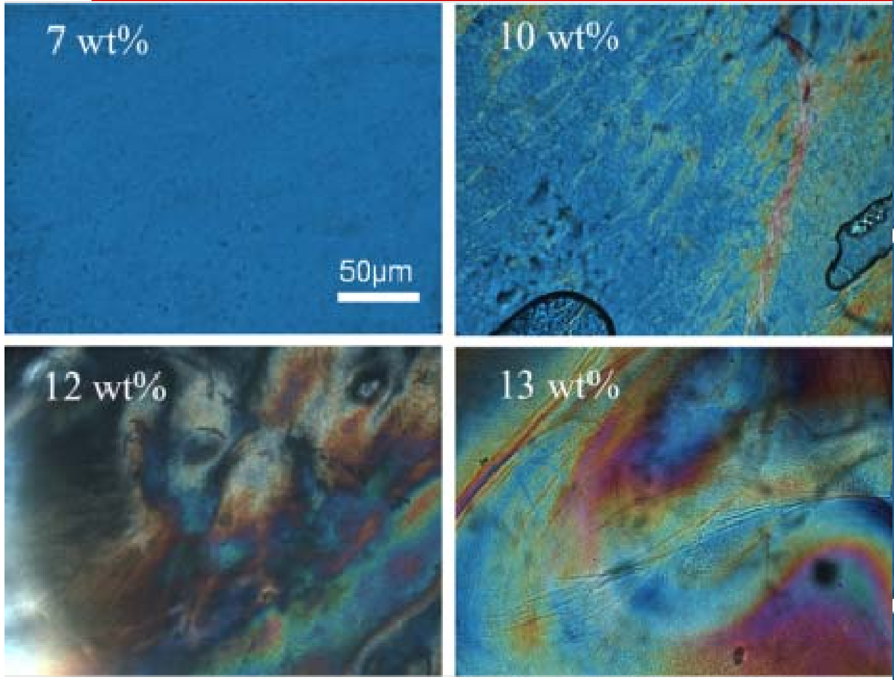
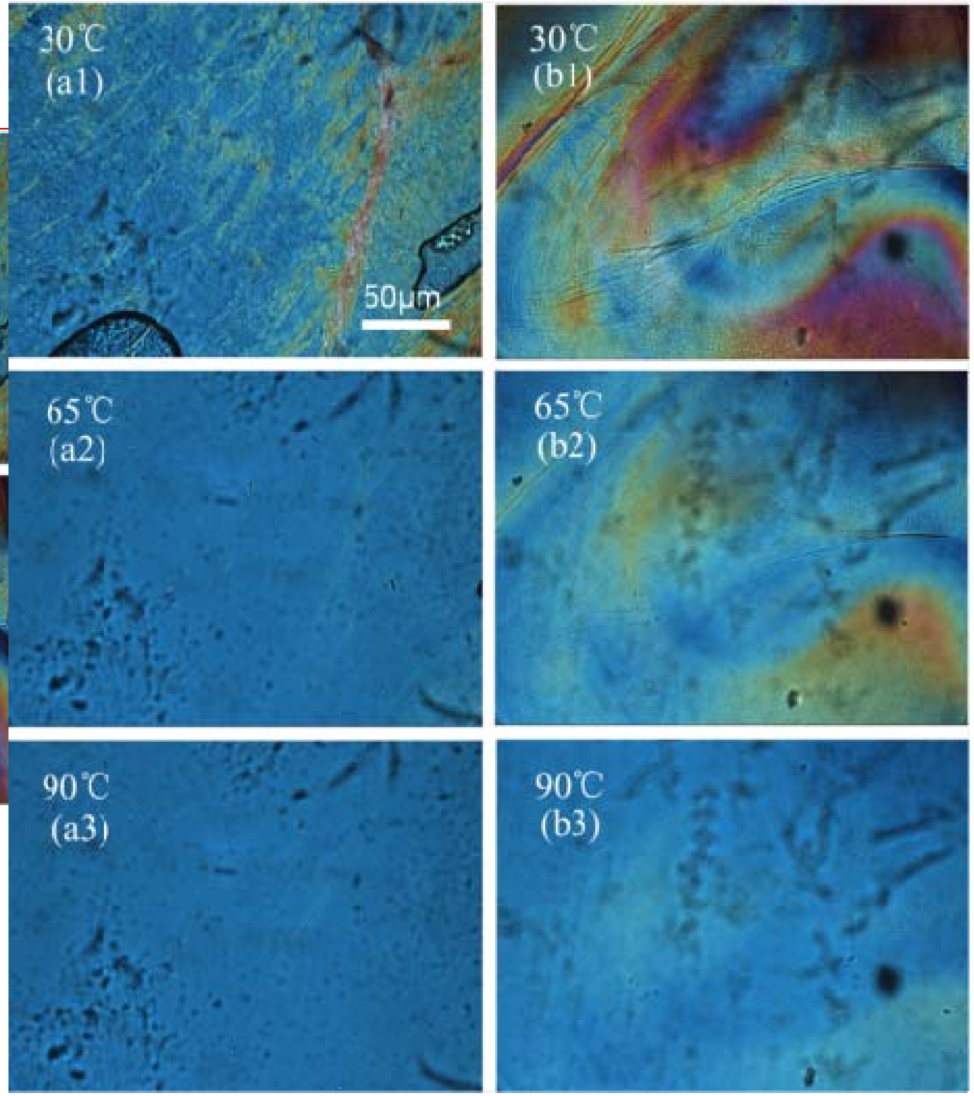


Fig. 2. ^{1}H NMR spectra of co-PI-3 fiber.

PI/NMP exhibits anisotropic phase

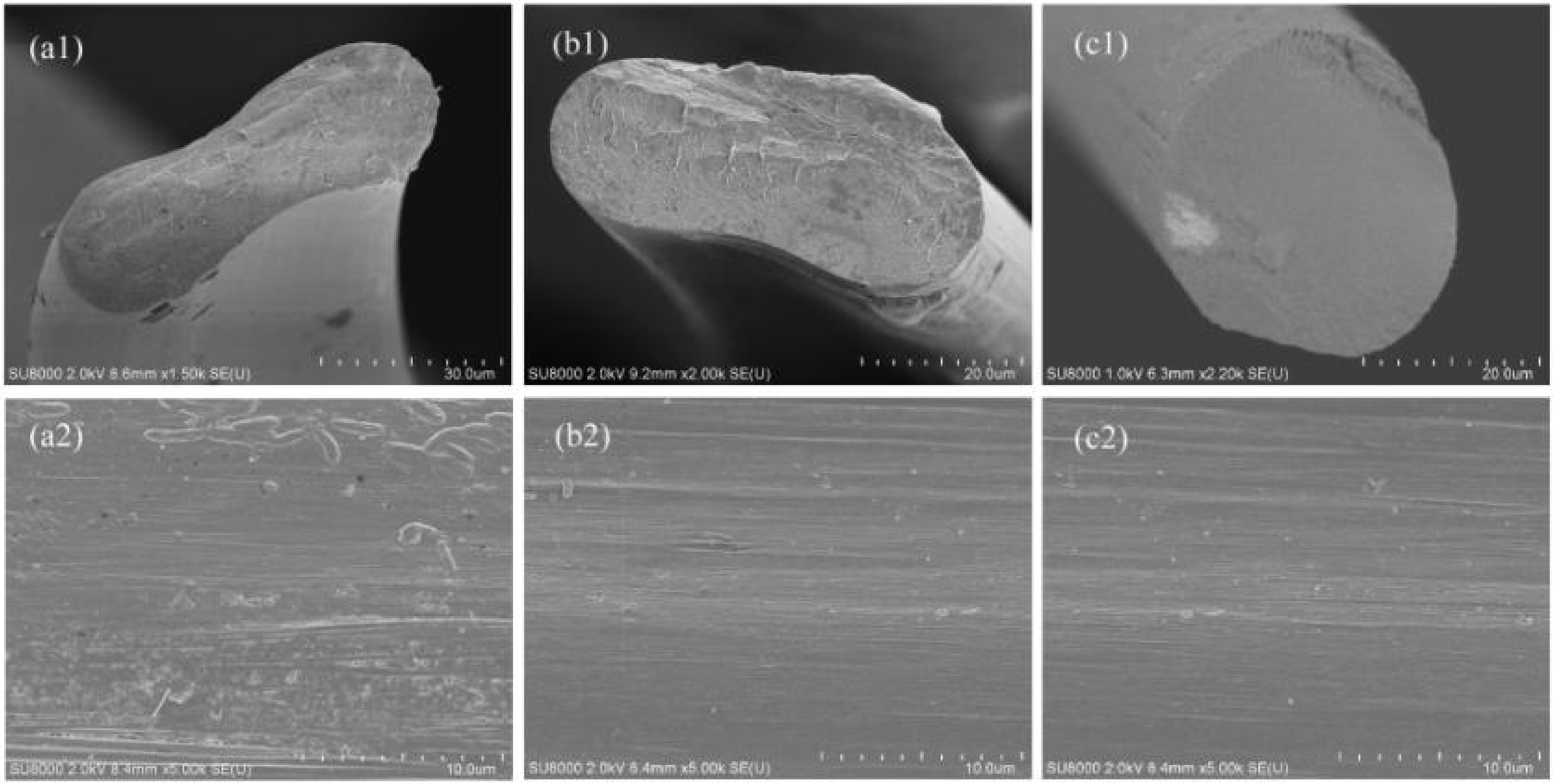


POM of the PI/NMP systems with various content (25 C).

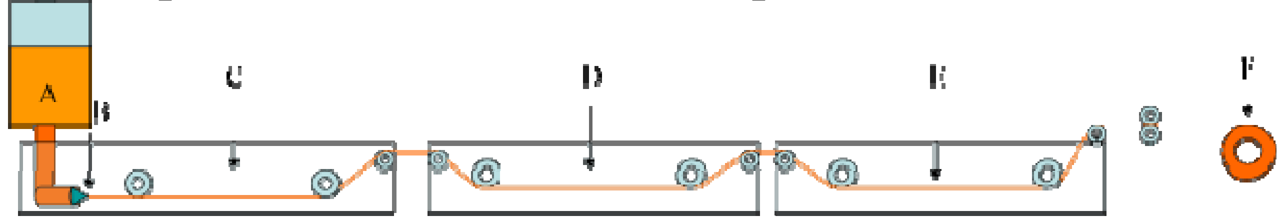


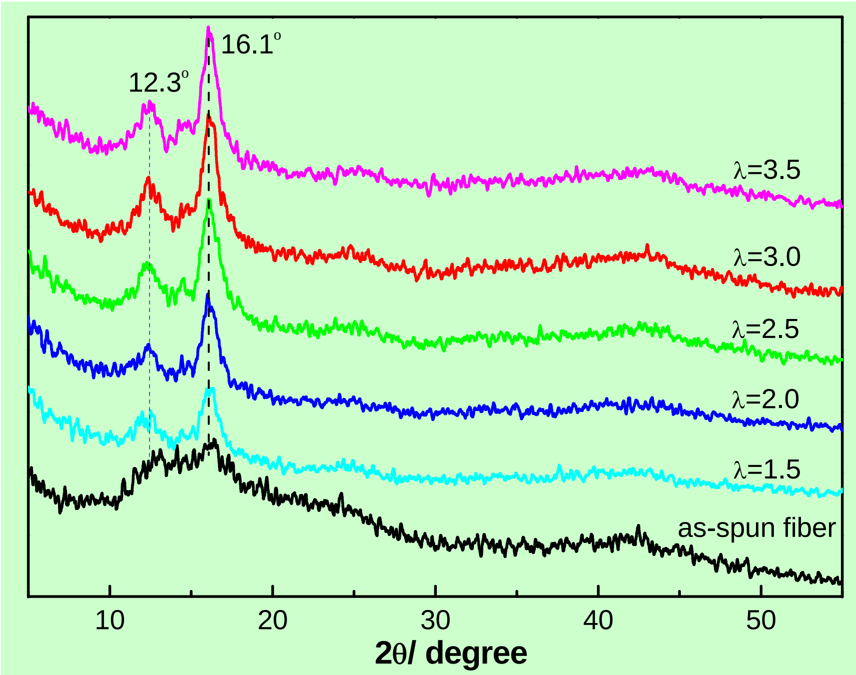
POM of PI/NMP solutions at various temperature (a,10 wt%; b, 13 wt%).

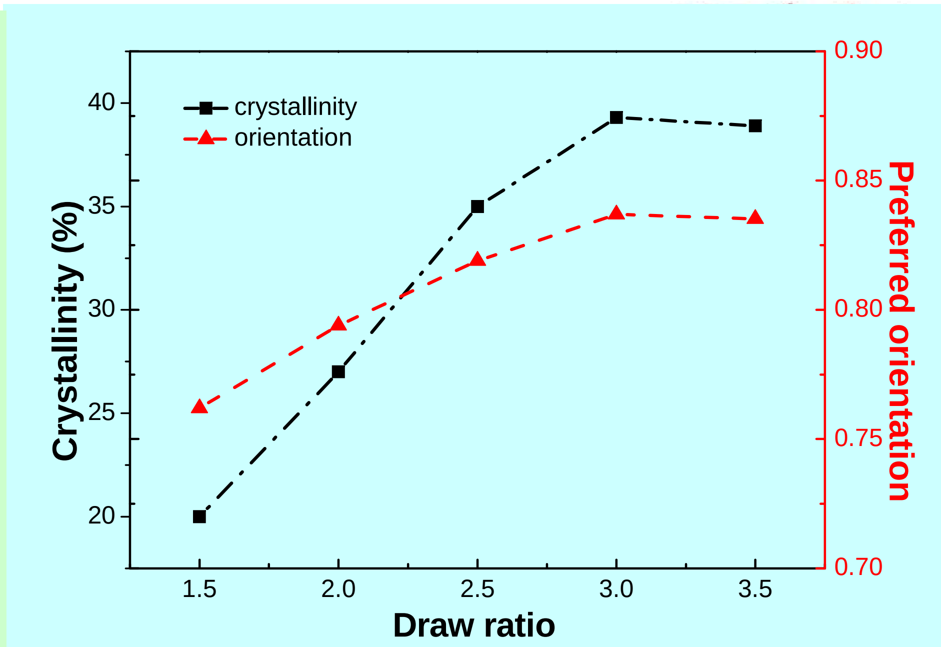
Dong, Zhang*, et al. J Polym Sci B: 2014, 52, 450

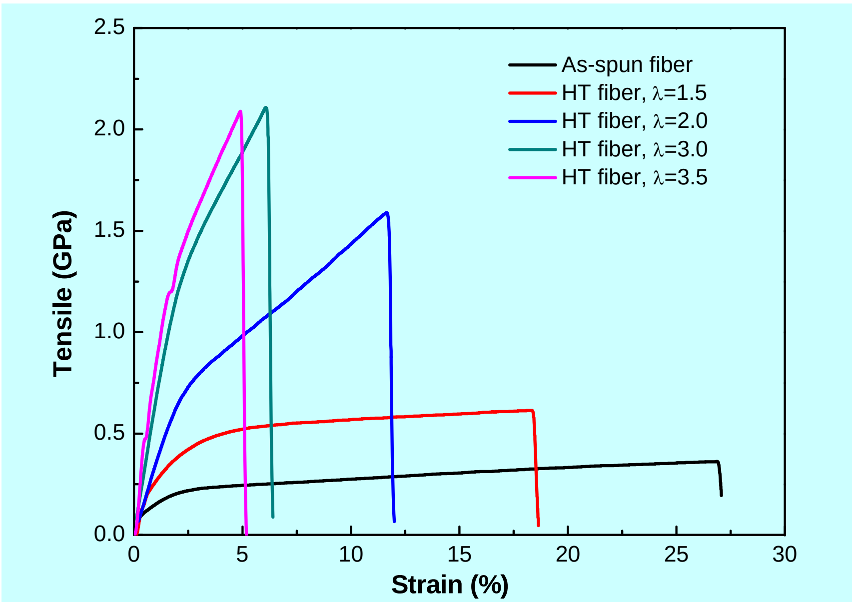


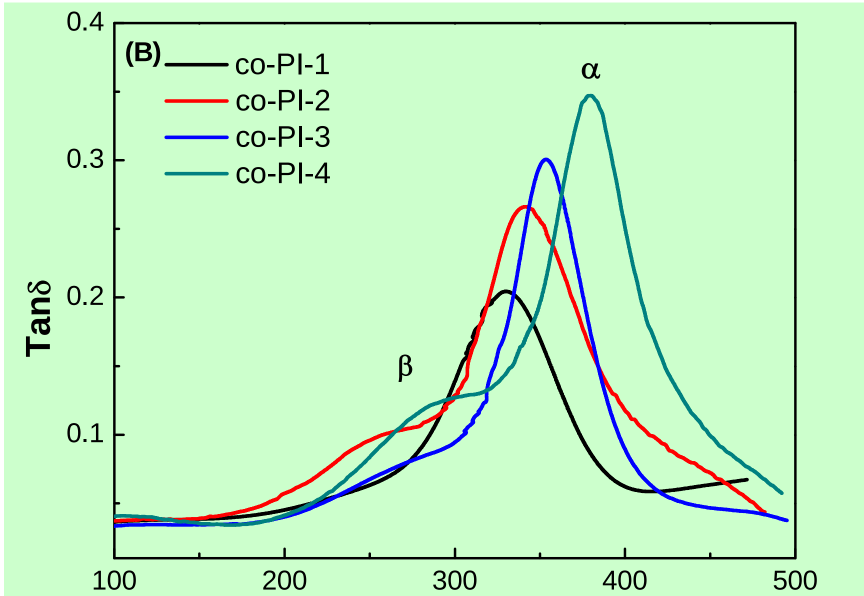
Morphology of co-PI fibers produced from coagulation bath of H_2O (a), H_2O/NMP=95/5 (v/v) (b), and H_2O/NMP=90/10 (c)







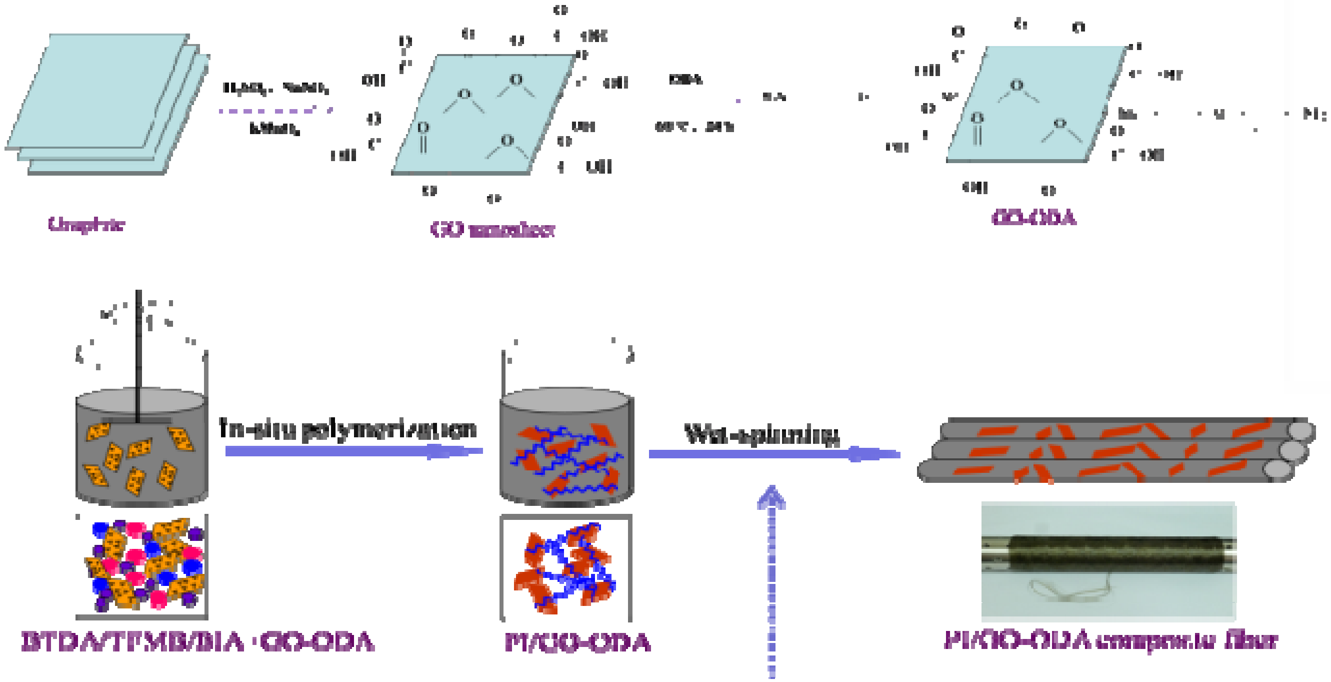


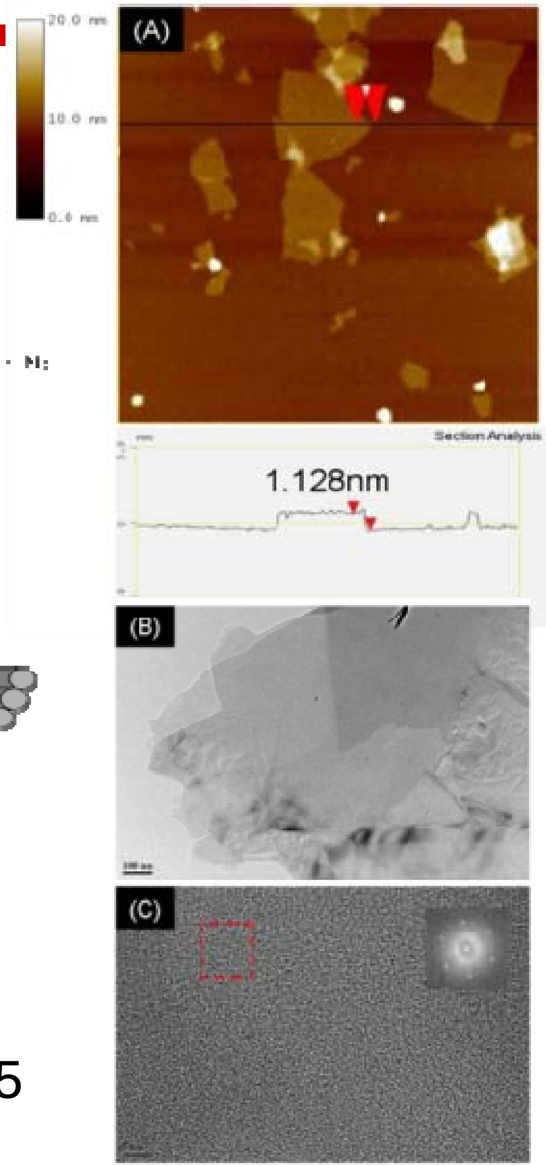


Dong, Zhang*, et al. J Mater Sci, 2013, 48, 7594

PI/Graphene composite fibers

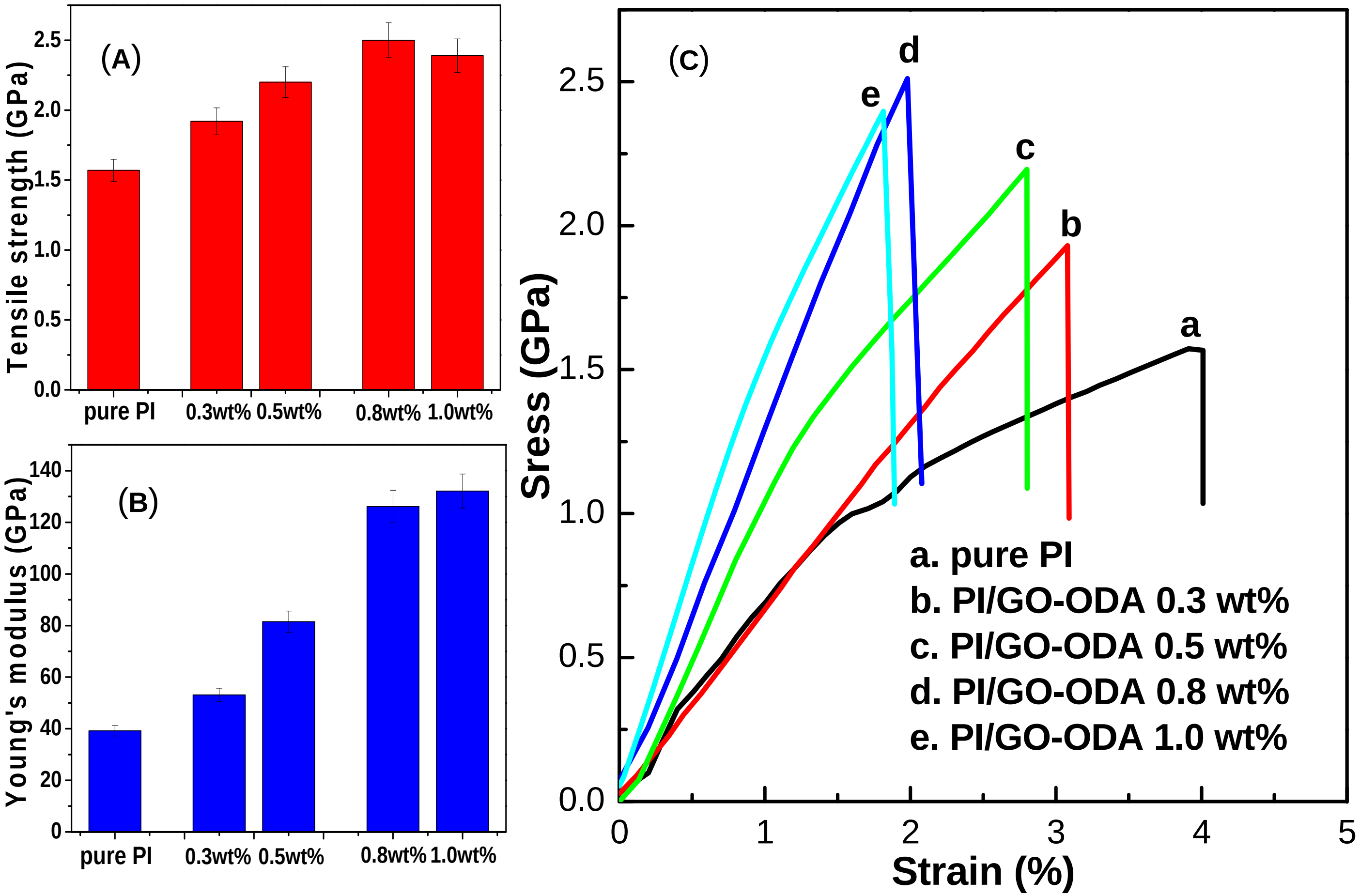
Modification to improving modulus





Dong, Zhang*, et al. Polymer, 2013, 54, 6415

PI/Graphene composite fibers



Thermal stability

Dynamical and thermal properties

Content of GO-ODA	T_g (°C) in DMA	T_{5d} (°C) in TGA	T_{max} (°C) in TGA
Pure PI	356	585	638
0.3 wt%	360	593	650
0.5 wt%	369	602	651
0.8 wt%	374	604	653
1.0 wt%	378	606	654

Properties of PI fibers

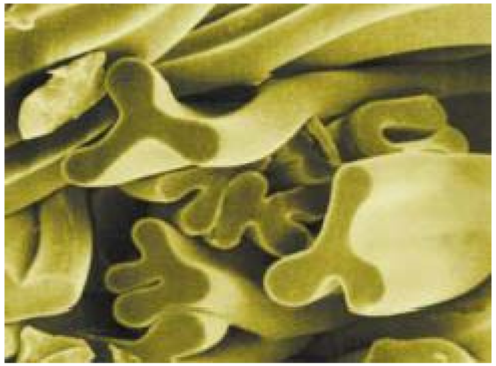
Mechanical | Stability | Radiation-Resistant

Properties	Kevlar 49	BPDA-ODA PI fiber
Tensile, GPa	2.9	3.0
Modulus, GPa	120	128
Limited Oxygen Index, %	29	50
Stability in air @300°C	Remain 60% for 15 h	Remain 90% for 15 h
Stability in vapor@200°C	Remain 35% for 8 h	Remain 65% for 8 h
Stab. in 40%H_2SO_4@85C	Remain 60% for 40 h	Remain 95% for 200 h
Stab. in 10%NaOH@85C	Remain 50% for 50 h	Remain 60% for 1 h
UV Xe@80-100 °C	Remain 30% for 8 h	Remain 90% for 24 h

Applications of heat-resistant PIF

- PI fibers have high thermal stability, anti-corrosion of chemicals, and environmental stability.
- They are extensively used in filter at high temperature and protection, such as filter bags to reduce dust pollution.
- P84 developed by Lenzing in 1980's, Evonic & Degussa now, the only commercial PI fibers, is fabricated into heat-resistant filter bags
- High price ($60/kg) limits applications in large scale.



Applications of high-strength polyimide fibers in structure materials

- Aviation & aerospace
- Defense & safety
- Bulletproof equipment
- Speed vehicles
- Sport equipment
- Ocean Development

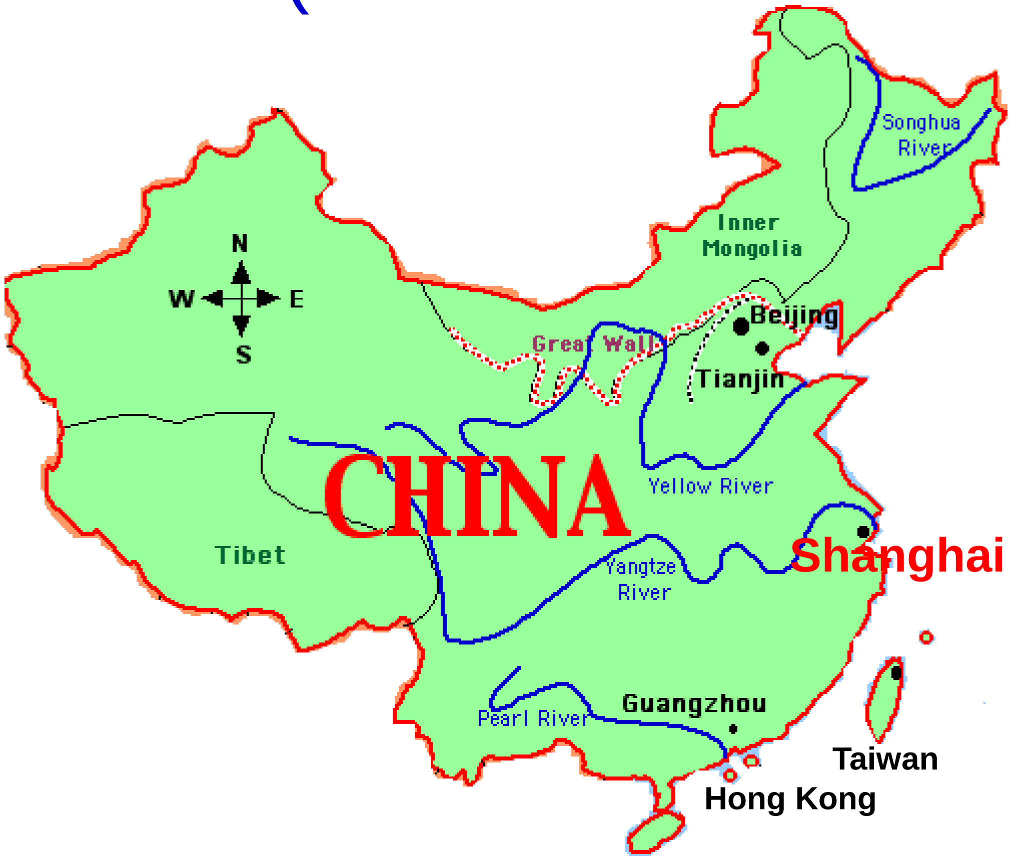
東華大學
DONGHUA UNIVERSITY

Acknowledgement

- National Science Foundation of China (NSFC 51233001, 51173024)
- High-tech Development Plan (863 Plan) – High-Performance Fibers

Donghua University

(Former China Textile University)



- Staff: ~ 3,000
- Undergraduate ~20,000
- Graduate: ~ 6,000

College of Mater. Sci. & Eng.

- State Key Lab of Modif. Chem. Fibers & Polym Mater.
- Ministry Key Lab of High Perform. Fibers & Products
- Engineering Research Center of Adv. Glass Tech.
- Innovation Center for Adv. Fibers & Tech. (111 Plan)

- Depart. Polymer Science and Engineering
- Depart. Inorganic Materials and Engineering
- Depart. Composite Materials and Technology

- Staff 130; Profs. 40
- undergraduates 250/a
- Master 180/a
- Ph.D. candidates 45/a

Thank You