Preparation of A Novel Polyimide Fibers Containing Phosphorus Through Dry-wet Spinning

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Abstract

The monomer containing phosphorous was synthesized by a four step reaction with a total yield about 40% and a novel polyimide fiber containing phosphorous was prepared by a dry-jet wet-spinning process. The diamine was characterized by FT-IR, NMR and elemental analysis to certify the high purity production synthesized. The polyimide fiber was measured by SEM, DSC and mechanical property.

Keywords: Polyimide; Fibers; Phosphorus; Dry-wet spinning

1.Introduction

Polyimide (PI) is one of performance polymer since the mid-twentieth century, because the existence of the aromatic or heterocyclic ring in main chain which retain excellent properties[1]. In 1960s, DuPont developed the first commercial PI product, from then on this material have attracted many researchers and been growing rapidly. PI itself have owned a variety of performances, excellent mechanical properties, temperature resistance, good dimensional stability, lower dielectric properties and resistance to radiation capability, which was widely used in the aerospace. Materials are required more performances in complex environment of the outer space. Traditional PI resin have been a barely satisfactory on atomic oxygen (AO) exposure in outer space. As early as 1983, P-containing PIs were synthesized and showed high thermal stability, good adhesive property, excellent tensile strength[2]. As reported by NASA, USA a series of inherently AO-resistant PIs, typically the ones containing phenylphosphine oxide (PPO) moiety were developed[3]. Many literatures have reported PIs containing PPO which mainly focus on PI films and PI resin, however, PI fibers containing PPO have not been reported.

In the present work, a novel polyimide fiber was synthesized by self-synthesis diamine, commercial diamine and aromatic dianhydride polymerization. Diamine containing PPO of small molecular weight was synthesized by a four step reaction, aiming at the maximum in phosphorous content of polyimide fiber.

2. Experimental

2.1. Materials

Methyl iodide, triphenylphosphonine, sodium hydroxide, magnesium sulfate and sodium dicarbonate were purchased from Darui Finechemical Co., Ltd. Shanghai and toluene, ethanol absolute, dichloromethane, concentrated sulfuric acid, fuming nitric acid, hydrazine were purchased by Tianjin Fuyu Finechemical Co., Ltd and used as received. and 4,4′-Oxydianiline (4,4′-ODA, >99%) and 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (s-BPDA) were purchased from Shanghai Research Institute of Synthetic Resins and dried in vacuum at 160 °C overnight prior to use. N,N′-dimethyacetamide (DMAc, analytic pure, ≥99.5%) was purchased from Tianjin fine chemical co., china and used as received. Other solvents were purified by distillation prior to use. The commercially available reagents were used without further purification.

2.2. Monomer synthesis

Bis(3-aminophenyl) methyl phosphine oxide was synthesized a modified literature method[4].

2.2.1. Synthesis of methyl triphenyl phosphonium iodide (MTI)

CH_3I (7.5 mol, 1064 g) was added slowly to a chilled solution of 7.5 mol of Ph_3P (1967.18 g) in 6 L toluene solvent, which was reacted in a 10 L round bottom three neck flask with an ice bath system. The mixture solution was stirred for more than 6 hours and filtered, then the residue was washed with fresh toluene and dried in a force air oven, white powder (Ph_3PCH_3) was obtained with 98% yield.

FT-IR (KBr): 2920, 2869 cm^{-1}($-CH_3$). ^1H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.92 (dq, J=8.8, 3.2 Hz, 3H), 7.88–7.73 (m, 12H), 3.24 (d, J=14.5 Hz, 3H). ^{31}P NMR (162 MHz, DMSO-d_6) δ (ppm) 22.30. ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 134.71, 133.19, 133.08, 130.05, 129.93, 120.18, 119.31, 7.75, 7.20. Anal. calcd for $C_{19}H_{18}IP$: C, 56.46 %; H, 4.49 %; P, 7.66 %. Found: C, 56.89 %, H, 4.485 %; P 5.07%.

2.2.2. Synthesis of methyl biphenyl phosphine oxide (MDPO)

Sodium hydroxide (64.29 mol, 2571.43 g) was added into 10 L round bottom three neck flask equipped with a mechanical stirrer, a reflux condenser, an oil bath and a nitrogen inlet. Then, water (6250 ml) was added. The mixture was stirred and heated to reflux about 100 °C for more than 6 hours which produced a cloudy suspension in the mixture solution, until all the formed benzene had distilled. The reaction was monitored by TLC (dichloromethane: methanol= 9:1). The mixture was cooled, extracted with dichloromethane and the combined organic extracts were dried with magnesium sulfate, filtered, and the solvent was evaporated and further dried in a vacuum oven for 24 hours. The product was obtained as a white solid with 80% yield, m. p. 114-116 °C.

FT-IR (KBr): 1172 cm^{-1} (P=O). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ (ppm) 7.83–7.73 (m, 4H), 7.58–7.44 (m, 6H), 2.04 (d, J=13.4 Hz, 3H).^{31}P NMR (162 MHz, DMSO-d$_6$) δ (ppm) 27.27. ^{13}C NMR (101 MHz, DMSO-d$_6$) δ (ppm) 135.62, 134.64, 131.39, 130.19, 130.10, 128.58, 128.46, 16.25, 15.52. Anal. calcd for $C_{13}H_{13}OP$: C, 72.21%; H, 6.06 %; P 14.33 %. Found: C, 72.35 %; H, 5.93 %; P 13.61 %.

2.2.3. Synthesis of bis(3-nitrophenyl) methyl phosphine oxide (BNMPO)

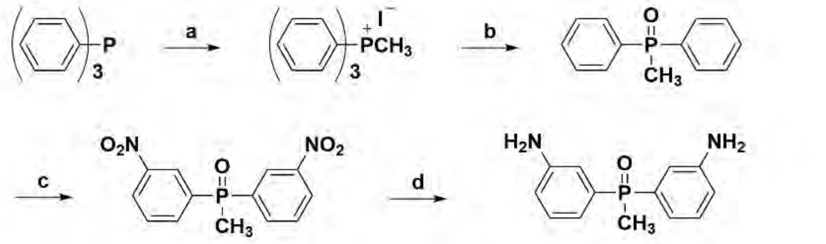
Methyl biphenyl phosphine oxide (2 mol, 432.44 g) was charged into a 10 L round bottom three neck flask equipped with a dripping funnel, a mechanical stirrer and an ice bath. The concentrated sulfuric acid (2000 ml) was added to the flask carefully, then stirring the mixture until the starting material dissolved. The solution was cooled to 0-5 °C and the mixture of concentrated sulfuric acid (2000 ml) and fuming nitric acid (4000 ml) was added dropwise from the funnel into the react solution. The solution was stirred for 4 hours at 0-5 °C and 24 hours at room temperature respectively. The reaction was monitored by TLC (dichloromethane: methanol= 9:1) and then precipitated into ice water, extracted with dichloromethane and washed with aqueous sodium dicarbonate solution until the neutral pH and then dried the dichloromethane organic layer with magnesium sulfate. The solvent was removed and recrystallized with absolute glycol ether and obtained white solid with 70% yield, m. p. 245-248 °C.

FT-IR (KBr): 1530、1351 cm^{-1} (-NO$_2$). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ (ppm) 8.72-8.52 (m, 2H), 8.40 (dd, J=8.2, 2.3 Hz, 2H), 8.29 (dd, J=11.0, 7.6 Hz, 2H), 7.84 (td, J=7.9, 2.8 Hz, 2H), 2.32 (d, J = 14.1 Hz, 3H). ^{31}P NMR (162 MHz, DMSO-d$_6$) δ (ppm) 26.62. ^{13}C NMR (101 MHz, DMSO-d$_6$) δ (ppm) 147.92, 147.79, 136.99, 136.67, 136.57, 136.01, 130.75, 130.63, 126.62, 125.01, 124.90, 15.59, 14.86. Anal. Calcd for $C_{13}H_{11}N_2O_5P$: C 50.99 %; H 3.62 %; N 9.15 %; P 10.12 %. Found: C 51.15 %; H 3.71 %; N 9.16 %; P 9.87 %.

2.2.4. Synthesis of bis(3-aminophenyl) methyl phosphine oxide (BAMPO)

bis(3-nitrophenyl) methyl phosphine oxide (1.385 mol, 424 g) and ethanol (3000 ml) were charged into a 5 L round bottom three neck flask fitted with an addition funnel, a mechanical stirrer, a reflux condenser, a nitrogen inlet and an oil bath. Before heating the solution the 10% Pd/C was added into the mixture. Hydrazine (8.308 mol, 415.9 g) was dropped with the addition funnel into the solution carefully and the black mixture was refluxed simultaneously at 90 °C. The reaction was monitored by TLC. Finally, the black mixture was filtered through diatomite using Buchner funnel to afford ethanol solution. The solvent was removed, recrystallized by absolutely ethanol and 70% yield, m. p. 155-156 °C.

FT-IR (KBr): 3367、3220 cm^{-1} (N-H). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ (ppm) 7.12 (td, J=7.8, 3.7 Hz, 1H), 6.96-6.87 (m, 1H), 6.80 (dd, J=11.4, 7.4 Hz, 1H), 6.73-6.65 (m, 1H), 5.35 (s, 2H), 1.82 (d, J=13.1 Hz, 1H). ^{31}P NMR (162 MHz, DMSO-d$_6$) δ (ppm) 28.17. ^{13}C NMR (101 MHz, DMSO-d$_6$) δ (ppm) 148.79, 148.65, 136.16, 135.18, 129.10, 128.97, 117.10, 117.00, 116.46, 115.19, 115.08, 16.37, 15.65. Anal. Calcd for $C_{13}H_{15}N_2OP$: C, 63.41 %; H, 6.14 %; N, 11.38 %; P, 12.58 %. Found: C, 63.61 %; H, 6.18 %; N, 11.48 % P, 12.61%.



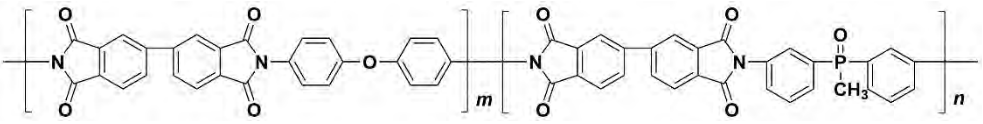
Reagents: a: MeI, Toluene (99%); b: aq. NaOH (30%); c: HNO_3/H_2SO_4; d: Ethanol, Pd/C

Scheme 1. Synthesis of bis(3-aminophenyl) methyl phosphine oxide (BAMPO).

2.3. Polyamide acid preparation

The polyamide acids were prepared with dissolving diamine in DMAc and nitrogen passing through the solution, stirred at room temperature until the diamine dissolved to form a solution or slurry. At the same time, adding a stoichiometric quantity of the dianhydride to adjust the solid content of the reaction to be 15 wt% by adding DMAc. The reaction mixture was stirred at relatively cool temperature about 12 °C for 2 days until the maximum viscosity of the solution obtained. Furthermore, the solution was heated at 50 °C by stirring until the viscosity satisfying acceptable ranges. The viscosities of the polyamide acids are presented in **Table 1**.

Table 1. The relationship of chemical structure and properties.

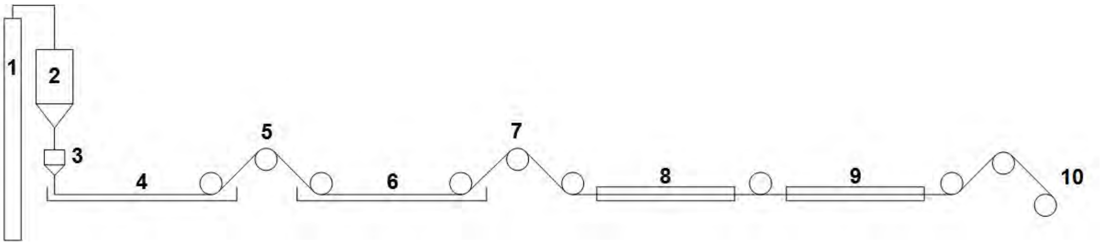


Polymer no./ m:n	Draft / Draw ratio	η_{inh} (dl/g) PAA	Fiber color	mechanical properties Strength (cN/dtex)	Modulus (cN/dtex)	Strain (%)
10:0 (Polyimide)	3.06/ 1.6	1.71	Bright yellow	5.72	64.69	15.41
	3.80 /1.6			6.14	65.55	14.62
8:2 (co-polyimide)	3.06 /1.6	1.68	Yellow	4.64	47.00	22.70
	3.80 /1.6			5.24	51.21	19.55

In this study, a co-polyamide acid was prepared as follow. The co-polyamied acid solution was prepared by upsetting the specific proportion of the diamines which consisted of BAMPO and 4,4′-ODA as described above. BPDA was selected to synthesize the co-polyamide acids solution. The chemical structure of the solution can be the combination of the portion of BPDA/ODA and the one of BPDA/BAMPO as shown in **Scheme 3**.

2.4. Preparation of polyimide fibers

The polyamide acids solution was filtered and degassed in a vacuum atmosphere overnight for the slurry homogeneity. Polyamide acid fibers were conducted on a spinning machine which was homemade designed as demonstrated in **Scheme 2**. The dopes were spun into a coagulation bath by a dry-jet wet-spinning process through an air gap of 10 mm-20 mm. The coagulation usually was consisted of water, alcohol, DMAc and NMP, or some of them. The as-spun fibers entered into the washing bath which was assembled by water and DMAc or NMP. The next progress was drying, drawing process. Finally, the fibers conducted on two tubes as shown in **Scheme 2**.



Scheme 2. Process of spinning polyamide fibers. 1. Air compressor; 2. Polyamide acids solution; 3. Spinning spinneret; 4. Coagulation bath; 5 and 7. Rollers; 6. Washing bath; 8. Drying-tube; 9. Heating-tube with 340 °C; 10. Winder.

2.5. Measurements

Fourier transform infrared (FT-IR) spectra was obtained with VERTEX 70 spectrometer and was used to determine the presence of specific groups in the monomers and polymers. Nuclear magnetic resonance (^{1}H, ^{13}C and ^{31}P NMR) spectra was recorded on BRUKER AV-400 spectrometer and used to measure the monomer and polymer structures. Inherent viscosity was measured using a Canon-Ubbelohde viscometer at 30 °C. Glass transition temperatures and cure exotherms were performed by differential scanning calorimetry operating at TA Q100. Scans were run at a heating rate of 5 °C min^{-1} and reported records were obtained at heating process stages. Thermogravimetric analysis were recorded on Perkin-Elmer TGA7 system at heating rate of 10 °C min^{-1} from room temperature to 1000 °C in nitrogen. The tensile properties were performed on XQ-1 single filament apparatus with the length of 20 mm at drawing rate of 20 mm min^{-1}. Each sample was tested ten times and taking the averages as the final result. The surface morphology of the fibers were characterized by XL30 ESEM FEG SEM.

3. Results and discussion

3.1. Monomer synthesis

The novel diamine containing phosphorous (BAMPO) was synthesized via a four step reaction with a total yield of about 40% as shown in **Scheme 1**. The starting material was conveniently available triphenlyphosphine. Salt compound of starting material was obtained with adding CH_3I and then MTI was formed. Selective decomposition of MTI with base, yielded MDPO. Nitration of MDPO formed with a mixture of fuming nitric acid and concentrated sulfuric acid, yielded BNMPO which was reduced catalytically by hydrazine and Pd/C to obtain the final product BAMPO with the melting point of 155-156 °C accordance with the literature[4]. The diamine BAMPO was obtained and verified by elemental analysis, FT-IR, NMR and TLC.

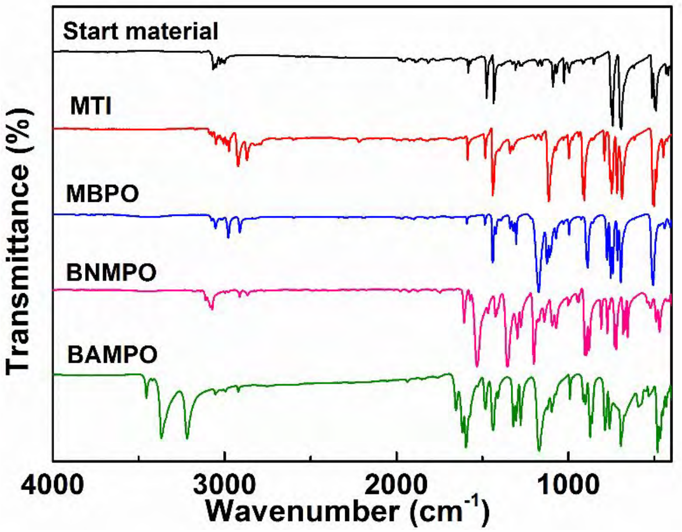


Figure 1. FT-IR spectra of monomers

Figure 1 compares the FT-IR spectra of four monomers which was used to synthesis the final product diamine containing phosphine. The characteristic absorptions at 3367 and 3220 cm^{-1} due to the N-H stretching of a primary amino group is clearly observed in the spectrum of BAMPO, however, these absorptions on the other spectrums are not existed. The characteristic absorptions of $-CH_3$ at 2920 and 2869 cm^{-1} appear in the spectrums of MTI, MBPO, BNMPO and BAMPO proving the presence of methyl group. The characteristic bands of C=O at about 1180 cm^{-1} in the spectrum of MBPO emerge attributing to MTI converted to MBPO. The characteristic absorption of $-NO_2$ at 1530 cm^{-1} in spectrum of BNMPO appear and at the same time, the one disappears in the spectrum of BAMPO.

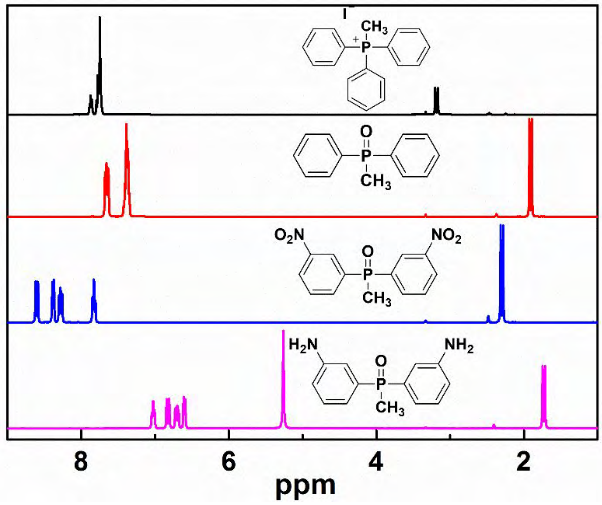


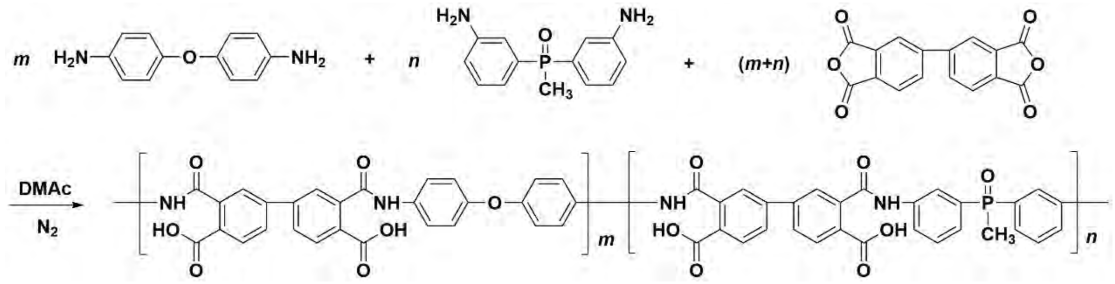
Figure 2. ^{1}H NMR spectrum of monomers

The ^{1}H NMR spectra of monomers which used to synthesize BAMPO with assignments of all peaks is presented in **Figure 2**. As shown in **Figure 2**, the protons are attributed to different hydrogen atoms in the monomer chemical structures. Further analysis was done by element analysis for monomers.

3.2. Preparation of polymer solution and polyimide fibers

3.2.1. Preparation of polyamide acid solution

As shown in **Scheme 3**, solutions of polyamide acids were prepared in a homemade apparatus (**Figure 4** (d)) at about 12 °C, the colors of the solutions were changed deeply with the increase of the proportion of BAMPO in the stoichiometry of the mixture diamines. Meanwhile, the viscosity of the solutions became decrease which of the reason probably was the meta-structure of BAMPO tending to the molecular chain into the ring as a result of the viscosity of solutions declined. So as to formed fibers using the solution of polyamide acid, moderate viscosity was needed. Storage of solution in relevant low temperature and efficient filtration of them were to prevent the decomposition of polyamide acid slurry.



Scheme 3. Preparation of polyamide acid solution.

Figure 3 compares the FT-IR spectra of polyimide and co-polyimide fiber in spite of similarity in both of them, however, the characteristic absorption of P-C bond at 1466 cm^{-1} in the spectra of co-polyimide fiber is appeared, which prove that the polyimide fiber containing phosphorous was synthesized.

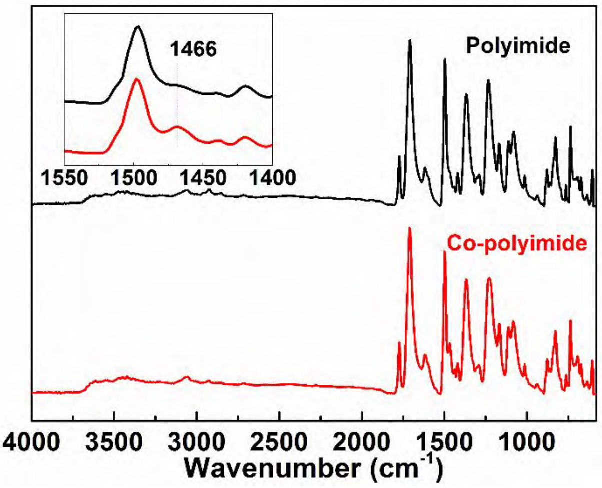


Figure 3. FT-IR spectrum of polyimide and co-polyimide

3.2.2. Polyamide acid and polyimide fibers

The polyamide acid fibers also called as-spun fibers were generated through a dry-jet wet-spinning process in the coagulation bath consist of water and DMAc from a spinneret with 50 holes. The air gap of 20 mm could greatly increase the draft ratio more than a wet-spinning process. Fibers structures were formed passing through the coagulation and the counterdiffusion of solvent and nonsolvent and then phase separation of the solution were took place immediately. In the spinning experiment, it found that the concentration of coagulation bath was the main one of the factors affecting the as-spun fiber structure as shown in **Figure 4** (a). Heating in the tube for drying and for imidization of polyamide acid fibers, the as-spun fibers converted into polyimide fibers as described in **Figure 4** (b, c). With the introduction of the BAMPO into the polymer, we see the color of the fibers darken.

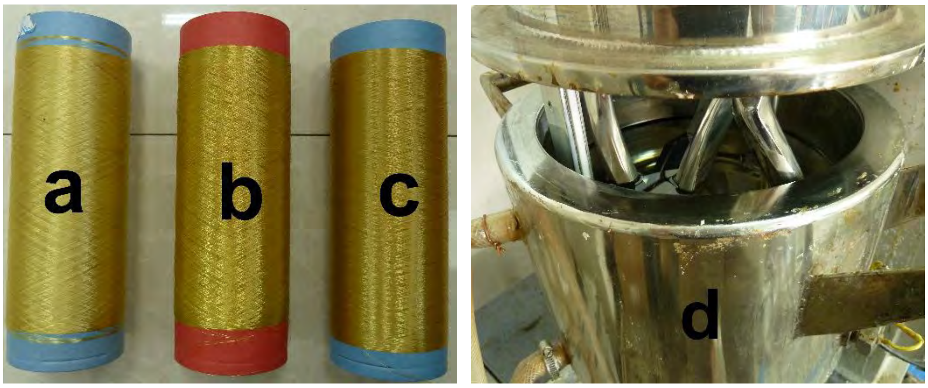


Figure 4. Polyamide acid (a), polyimide (b, c) fibers and aggregation apparatus (d).

3.3. Mechanical properties

The linear density of a single fiber was measured using the average single weight of a bundle of fibers in ten thousand meters for the calculation of Young's modulus and tensile strength. A typical load-strain curve is shown in **Figure 5**. Exhibiting growth of load nonlinear to fracture and having an apparent yield. The data of mechanical properties are listed in **Table 1**. Results indicated that the strain of co-polyimide fiber is much larger than that of polyimide fiber in the same condition. Conversely, the strength and modulus of co-polyimide fiber is less than that. The reason can be considered that meta-substituted diamine decreased the arrangement of polymer chain while increased the extension of polymer chain.

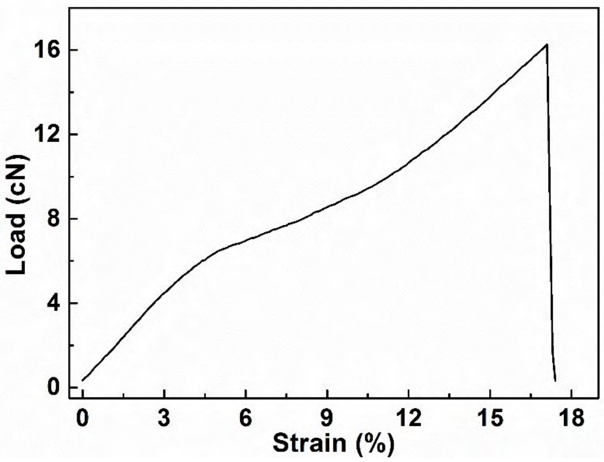


Figure 5. Typical load versus strain curve of polyimide fiber.

3.4. Thermal properties

Figure 6 shows the DSC curves of polyimide and co-polyimide fibers, indicating that co-polyimide fiber had higher glass transition temperature than corresponding polyimide fiber. The phenomenon could attribute to the structure of PPO which had a greater barrier for rotation of P-Ar bond.

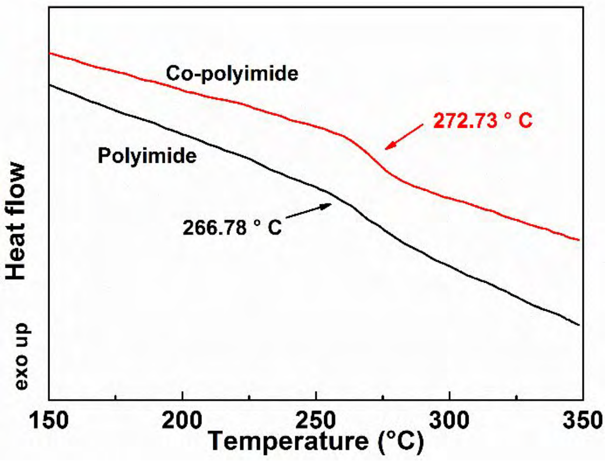


Figure 6. DSC curve of polyimide and co-polyimide fibers.

3.5. Morphology properties

Figure 7 shows micrograph of the surface and cross section of polyimide fiber. The image reveal the surface of fiber smoothly and no defects appear. Moreover, the margin line of cross section of the fiber was regular circle, even if it was broken in liquid nitrogen. Furthermore, it is found that there are many little dots in the cross section, considering to be the crystallization of polymer.

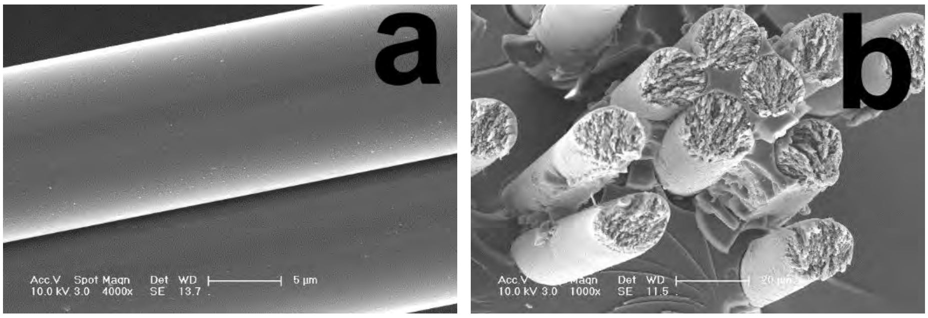


Figure 7. SEM images of surface (a) and cross section (b) of polyimide fiber.

4. Conclusion

A meta-substituted diamine and polyimide fiber containing phosphorous were synthesized by a four step reaction and dry-jet wet-spinning process, respectively. High purity of diamine was required by the viscosity of spinning fiber. The introduction of phosphine into the polyimide fiber caused the strain changing larger, strength and modulus smaller.

References

[1] Zhang, Y., *et al.*, *Sci Adv Mater* (2014) **6** (1), 44
[2] Varma, I. K., and Rao, B. S., *Journal of Applied Polymer Science* (1983) **28** (9), 2805
[3] Li, Z., *et al.*, *Prog Org Coat* (2012) **75** (1-2), 49
[4] Tan, B., *et al.*, *Polymers for Advanced Technologies* (1998) **9** (1), 84