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Synthesis and Characterization of Novel Polyamide Containing Ferrocene and Thio-Ether Units

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Two kinds of new aromatic diamine monomer containing thio-amide unit, bis[4-(p-aminothiophenyl)benzoyl]diamine (ATPBA), were synthesized by two steps, which was reacted with 1,1′-Ferrocenedicarbonyl Chloride (FCDC) to prepare a new polyamide containing ferrocene and thio-ether unit. The polymers were characterized by FT-IR spectrum, ^{1}H-NMR spectrum, X-ray diffraction, element analyzer, DSC, TGA, SEM, AFM and dissolvability experiment and so on. The intrinsic viscosity of FC-PASAA was 0.42–0.58 dl/g obtained with optimum synthesis conditions. The polymers were found to have excellent thermal performance with glass transition temperature (T_g) of 229.9–276.8°C, initial degradation temperature (T_d) of 389.2–391.5°C. They could afford flexible and strong films with tensile strength 66.0–83.9MPa. They showed improved solubility in polar aprotic solvents. They were used to preparing separation membrane successfully.

Keywords: Ferrocene, polyamide, heat-resistant, solubility, membrane

1 Introduction

Metal containing polymers had emerged as an important category of polymeric materials. The impetus for the development of these materials was based on the premise that polymers containing metals were expected to possess properties significantly different from those of conventional organic polymers (1). They could be used in a variety of applications including resins for ion and electron exchange, radiation-resistant polymers, catalysts, organic semiconductors, photoconductors and ferromagnets (2–9). Ferrocene-containing polymers possess better properties including air-, heat-, and photo-chemical stability (10–12). These interesting features had made them suitable for wide applications. Aromatic polyamides were a class of high-performance polymers that had outstanding thermal stability and mechanical properties. However, aromatic polyamides had generally poor processability caused by high processing temperature or poor solubility (13–15). To enhance their processability, the structure modification of polyamides was necessary. One of the main aspects in this field was incorporation of flexible or unsymmetrical structure (16–17). While thio-ether was a flexible structure, it not only improved the polymer's solubility but also did not decrease the material's thermal performance (18).

Here we describe the synthesis of two kinds of novel diamine containing amide group and thio-ether unit. Polycondensation reactions of this diamine with 1,1′-Ferrocenedicarbonyl Chloride (FCDC) in the presence Me_3SiCl (TMSCl) as catalyst resulted thio-ether, amide units and ferrocene-containing polyamides. The obtained polyamides were fully characterized and their physical properties were studied.

2 Experimental

2.1 Materials

Commercially available 4,4′-diaminobenosulfone (DABS) (AR, JiangSu YangZhong Synthesis chemical industry Company), m-phenylenediamine (m-PDA) (AR, SiChuan ChengDu ChangLian chemical reagent Company), 4-flurobenzoyl chloride (p-FBC) (AR, JiangSu JinTan LanLing Chemical Industry Ltd. Company), 4-aminobenzenthiol(AR, Zhe Jiang Shou Er Fu Chemical Industry Group Co., Ltd.), sodium hydroxide (NaOH) (AR,

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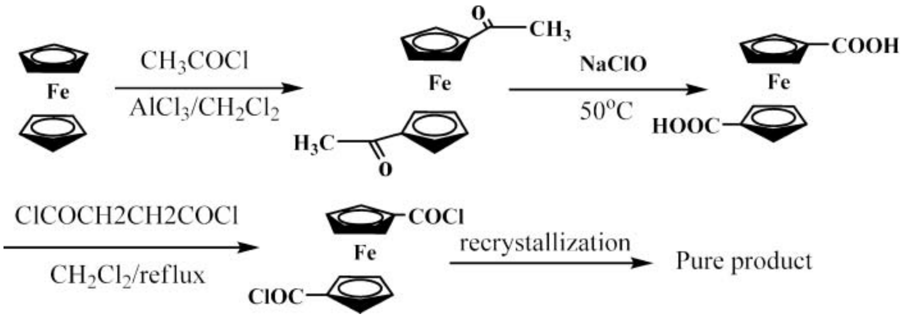


Scheme 1. Synthesis route of 1,1′-Ferrocenedicarbonyl Chloride (FCDC).

SiChuan ChengDu ChangLian chemical reagent Company), N-methyl-2- pyrrolidone (NMP) (JiangSu NanJing JinLong Chemical Industry Company), Me_3SiCl (TMSCl) (AR, Aladdin-reagent Company), all of them were used without further purification. Tetrahydrofuran (THF) (AR, SiChuan ChengDu ChangLian Chemical Reagent Company) was purified by reduced pressure distillation. Other reagents and solvents were obtained commercially.

2.2 Monomer Synthesis

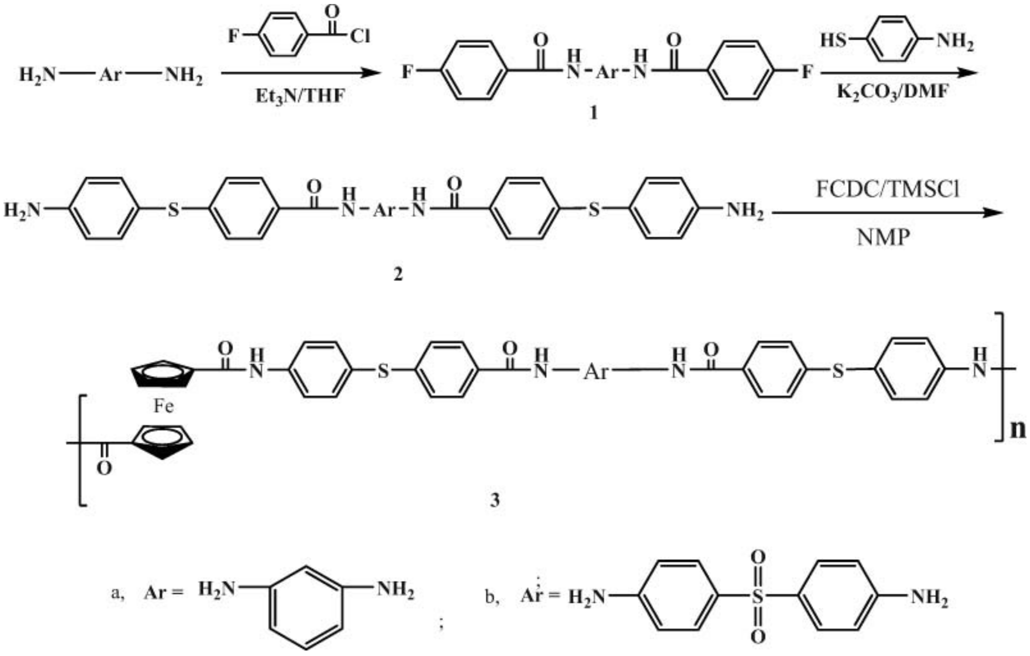
2.2.1. *1,1′-Ferrocenedicarbonyl chloride (FCDC) (shown as Scheme 1)*

1,1′-Ferrocenedicarbonyl acid was prepared according to the reported procedure (19–21), FCDC was prepared based on the following method: A mixture of 5.48 g (0.02 mol) 1,1′-Ferrocenedicarbonyl acid, 120 ml of dry CH_2Cl_2, 9 ml of freshly distilled oxalyl chloride and 5 drops of pyridine were added and stirred in a round-bottom flask at room temperature under N_2atmosphere in the dark for 0.5 h and then refluxed for 10 h. The mixture was distilled to dryness under reduced pressure. The residue was extracted repeatedly at 70°C with dry petroleum ether (b.p. 60–90°C). Then, the solvent was evaporated under reduced pressure and the product was dried under vacuum at 40°C.

Yield: 5.36 g, 86.2%. m.p.: 98–100°C.

2.2.2. *1,3-bis(4-diflurobenzoyl) diaminobenzene (1a) (shown as Scheme 2) (22–24)*

1a was prepared as Scheme 2 with the following procedure: to a 250 ml round bottom three-necked flask was added 10.8 g (0.1 mol) of m-phenylenediamine, 20.2 g (0.2 mol) of Et_3N, and 300 ml of THF. The mixture was stirred under nitrogen until the solids dissolved, then cooled in an ice bath, 31.7 g (0.2 mol) of p-FBC was added dropwise. The mixture was stirred for 1 h in ice bath, 24 h at room temperature. Then, the reaction solution was poured into water.



Scheme 2. Synthesis route of FC-PASAA (**3a**-**3b**).

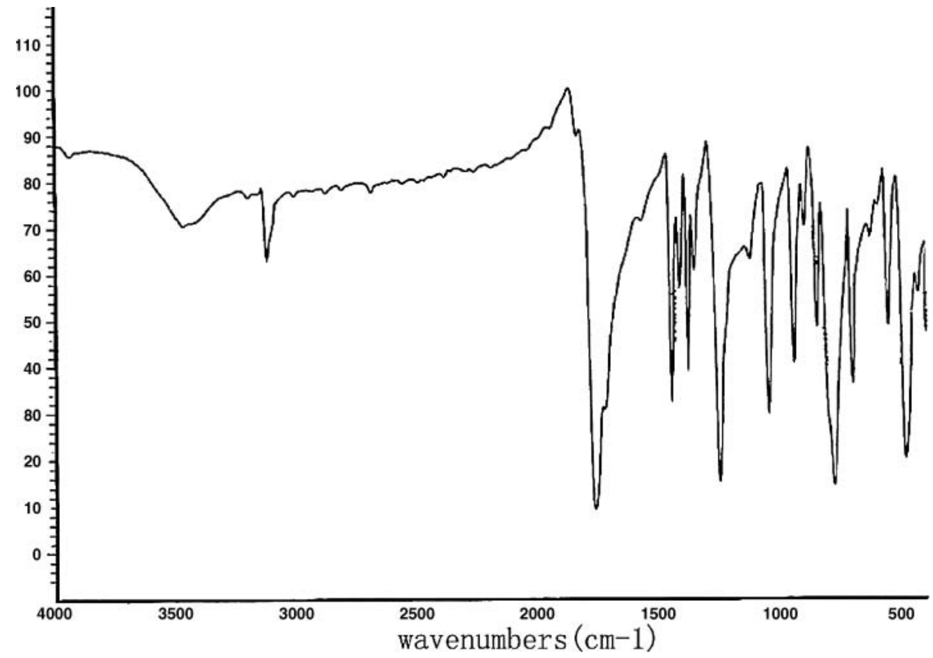


Figure 1. FT-IR spectrum of FCDC.

The resulting solid was filtered, washed with hot water and methanol, dried, recrystallized from the mixture of DMF and water (3:1). That afforded **1a** as white sheet crystal.

Yield: 29g, 82.3%. m.p.: 265–267°C.

2.2.3. *4,4′-bis (4-diflurobenzoyl) diaminophenyl sulfone (***1b***)*

1b was prepared as **1a**. The crude product of **1b** was recrystallized from pyridine. That afforded **1b** as white needle crystal.

Yield: 40.6g, 82.5%. m.p.: >300°C.

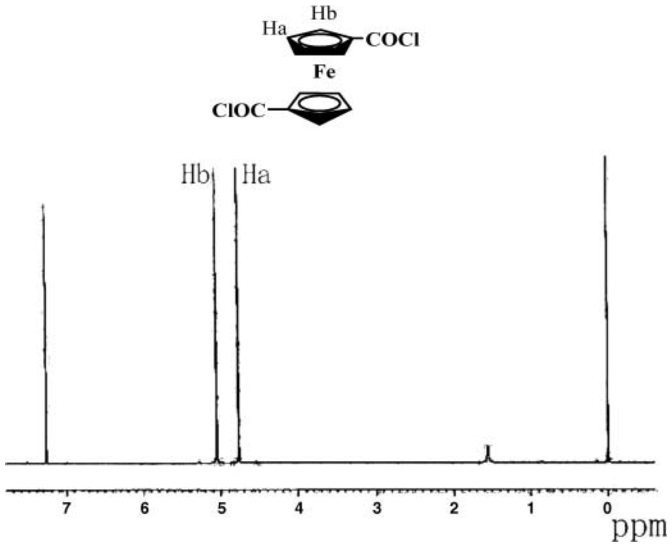


Figure 2. ^{1}H-NMR spectrum of FCDC.

2.2.4. 4 *bis[4-(p-aminothiophenyl)benzoyl]diamine (ATPBA)*

Then **1** was converted to ATPBA **2** through nucleophilic etherification: **1** reacted with 4-aminobenzenethiol in DMF at 155°C for 4 h as shown in Scheme 2. The reaction solution was then poured into water. The resulting solid was filtered, washed with water and methanol, then recrystallized from the mixture of water and DMF (1:1). That afforded **2a**-**2b** as yellow sheet crystal.

2a Yield: 83.4%. m.p.: 157–159°C, m/z(M$^-$): 561.35.

2b Yield: 78.6%. m.p.: 262–264°C, m/z(M$^-$): 701.26.

2.3 Polymer Synthesis

2.3.1. *Synthesis of FC-PASAA (shown as Scheme 2.)*

A typical polymerization was prepared as shown in Scheme **2**. In a 100 ml three-necked flask equipped with mechanical stirrer and thermometer, 2.81 g (0.005 mol) Bis[4-(p-aminothiophenyl)benzoyl] meta-phenylene diamine (**2a**) and 0.33 g (0.003 mol) Me_3SiCl (TMSCl) was dissolved in 60 ml NMP. After **2a** was dissolved completely, 1.56 g (0.005) FCDC was added. The mixture was stirred at 0°C for 2 h, then at room temperature for about 8 h to afford a viscous Tuscan-red solution. It was then poured into water to obtain a fibrous precipitate, washed with ethanol and water, and dried in a vacuum oven. Then the fibrous precipitate was pulverized into powder, washed with ethanol and water, dried in a vacuum oven at 120°C for 12 h to give FC-m-PPSAA (**3a**) 3.85 g (yield: 96%). FC-PPSSAA (**3b**) (4.61g, yield: 98%) was prepared with a similar procedure.

Table 1. Elemental analysis results of *1a-1b*

Compound	*C(%)*	*H(%)*	*N(%)*
1a	68.22 (68.18)	4.09(4.01)	7.99 (7.95)
1b	63.42 (63.4)	3.74 (3.68)	5.66 (5.69)

The data in brackets were those calculated.

2.4 Characterizations

2.4.1. *Intrinsic viscosity and gel permeation chromatography (GPC)*

Intrinsic viscosity of FC-PASAA was obtained in NMP at 30 ± 0.1°C with 0.500 g of polymer dissolved in 100 ml NMP, using a Cannon-Ubbelodhe viscometer. The resulting values were obtained by a one-point method (or Solomon–Ciuta equation) as follows: (25)

$$\eta_{int} = \frac{\sqrt{2\left(\eta_{sp} - \ln \eta_r\right)}}{C}$$

Where $\eta_r = \eta/\eta_0$, $\eta_{sp} = \eta/\eta_0 - 1$.

Number-average molecular weights (Mn's) and weight-average molecular weight (Mw's) were obtained via GPC performed with a set of a Water 1515 performance liquid chromatography pump, a Waters 2414 differential refractometer (Waters Co., Milford, MA), and a combination of Styragel HT-3 and HT-4 (Waters Co., Milford, MA), the effective molecular weight ranges of which were 100–10000, 500–30000 and 5000–800000, respectively. N,N-dimethyl formamide (DMF) was used as an eluent at a flow rate of 1.0 ml/min at 35°C. Polystyrene standards were used for calibration.

2.4.2. *Elemental analysis*

The monomers (**2a-2b**) and FC-PASAA were determined by elemental analyzer (EURO EA-3000)

2.4.3. *Characterization of chain structure*

The samples of the mixture of FC-PASAA and KBr were prepared. FT-IR spectroscopic measurements were determined by NEXUS670 FT-IR instrument. Nuclear magnetic resonance (^{1}H-NMR) instrument for the determination of the samples structure were provided with a BRUKER-400 NMR Spectrometer. The samples were dissolved in deuterated dimethyl sulfoxide.

2.4.4. *Characterization of aggregation structure*

The samples (subsequently dried at 120°C in vacuum oven for 12 h, then annealed at 240–280°C for 4 h.) were characterized by X-ray diffraction (XRD) (Philips X'pert Pro MPD).

2.4.5. *Thermal properties test*

Differential scanning calorimetry (DSC) was performed with NETZSCH DSC 200 PC thermal analysis equipment, fitted with a cooler system using liquid nitrogen. It was operated at a gas rate of 10 ml/min under nitrogen atmosphere. The heating rate of DSC measurement was 10°C/min. Thermogravimetric analysis (TGA) measurement was conducted using TGA Q500 V6.4 Build 193 thermal analysis equipment with a heating rate of 10°C/min under nitrogen atmosphere.

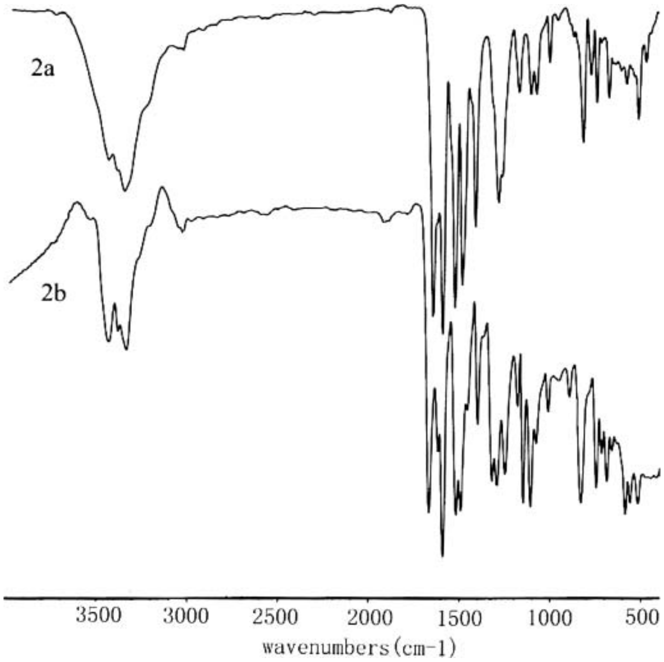


Figure 3. FT-IR spectrum of **2a**-**2b**.

2.4.6. *Characterization of the membrane micro-structure*

The samples were characterized by SEM (JSM-5900) and atomic force microscopy (AFM-SPA-400 SPM UNIT). Membranes were prepared by casting a different concentration solution on microscopy slide glass. Samples were emerged into de-ionized water, then the separation membrane formed after a while. The roughness (Ra), the root-mean-square roughness (RMS) and the water-flux (F) of the separation membrane were obtained by the following method respectively (26):

$$Ra = \frac{1}{S_0}\int_{Y_B}^{Y_T}\int_{X_L}^{X_R}\sqrt{\{F(X, Y) - Z_0\}^2}dXdY$$

$$RMS = \sqrt{\frac{1}{S_0}\int_{Y_B}^{Y_T}\int_{X_L}^{X_R}\{F(X, Y) - Z_0\}^2\, dXdY}.$$

$$F = \frac{Q}{At}$$

Where Q: penetrant volume (L), A: effective area of membrane (m^2), t: penetrant time (h)

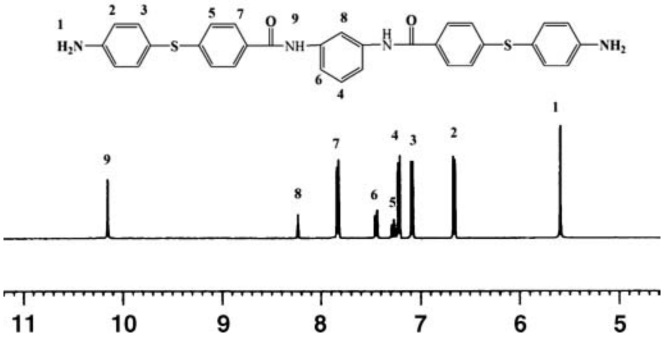


Figure 4. ^{1}H-NMR spectrum of monomers **2a**.

2.4.7. *Tensile properties*

An Instron Corporation 4302 was used to study the stress-strain behavior of FC-PASAA film samples (films were prepared by casting NMP solution on microscopy slide glass. Samples were subsequently dried at 100°C, 120°C, 140°C, 180°C for 10 h in an oven, then dried for 4 h at 210°C), and the tensile strength was detected according to GB/T 13022-1991.

2.4.8. *The electrical properties of FC-PASAA*

The electrical insulation and dielectric strength of FC-PASAA (**3a** and **3b**) were detected by resistivity detector equipment ZC36 and high-voltage detector YDQ10/100.

2.4.9. *Solubility*

The solubility of polymers in various solvents such as: N,N-dimethyl formamide (DMF), N, N-dimethyl acetamide (DMAC), dimethyl sulfoxide (DMSO), NMP and normal solvents were determined at room temperature and the temperature of solvent boiling point.

3 Results and Discussion

3.1 Monomers

3.1.1. *Synthesis of FCDC*

The whole procedure must be anhydrous or the yield would be very low.

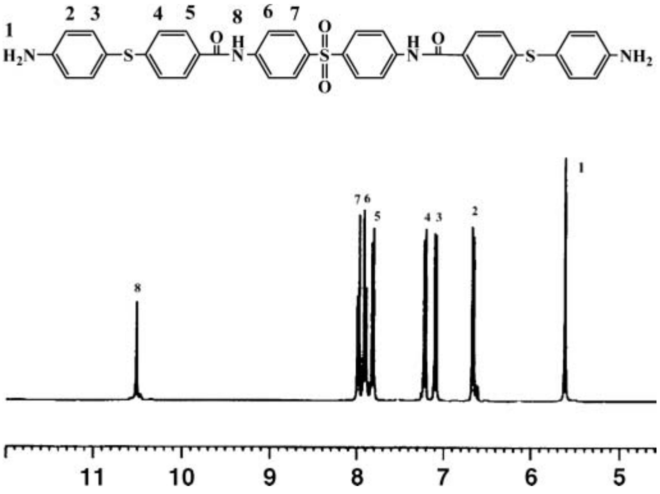


Figure 5. ^{1}H-NMR spectrum of monomers **2b**.

3.1.2. *The chain structure of FCDC*

Figure 1 showed the FT-IR spectrum of **FCDC**. The absorption of 3111cm^{-1} was the C-H stretching vibration absorption of benzene. The absorption of 1757cm^{-1}, suggested the formation of -COCl-. We observed the benzene rings absorption: 1604 cm^{-1}, 1506 cm^{-1} and 1489 cm^{-1} was also present. Figure 2 was the ^{1}H-NMR spectrum of **FCDC**. Two groups of peaks were appeared in the ^{1}H-NMR spectrum of **FCDC**, in Figure 2. The ratio of corresponding integral curves was about 1:1. Combining the results of FT-IR, these two groups of peaks were ascribed to the construction units of Ha, and Hb. The chemical shifts (δ) of **FCDC** were 4.761–4.771 and 5.046–5.056.

3.1.3. *Synthesis of 1a-1b*

1a-1b was prepared by the reaction of DABS/m-PDA, Et$_3$N and 4-flurobenzoyl chloride at 0–5°C in THF. 4-Flurobenzoyl chloride was kept a little excessive.

3.1.4. *Elemental analysis of monomers*

Table 1 showed that the experimental results were similar with the calculated results. It suggested the monomers were synthesized as Scheme 2.

Table 2. Chemical shifts (δ) of **2a**-**2b**

2a	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9
Chemical shifts δ(ppm)	5.592	6.649–6.670	7.075–7.096	7.207–7.235	7.251–7.271	7.433–7.457	7.820–7.841	8.232	10.152
2b	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	
Chemical shifts δ(ppm)	5.617	6.651–6.672	7.084–7.105	7.203–7.224	7.809–7.830	7.895–7.917	7.973–7.995	10.514	

Table 3. Intrinsic viscosity (η_{int}) and molecular weights of FC-PASAA (**3a-3b**)

Sample	η_{int} *(dL/g)*	*Mn (g/mol)*	*Mw (g/mol)*	*PDI (Mw/Mn)*
3a	0.42	5.1×10^4	8.86×10^4	1.74
3b	0.58	6.7×10^4	1.02×10^5	1.52

3.1.5. *Synthesis of 2a-2b and analysis of their chain structure*

2a-2b was synthesized through nucleophilic etherification: **1** reacted with 4-aminobenzenethiol in DMF at 155°C under the N_2 atmosphere for 4 h. Figure 3 showed the FT-IR spectrum of **2a-2b**. **2a**: the absorption of 3429 cm^{-1} and 3352 cm^{-1} was the -NH_2 stretching vibration absorption, 3390 cm^{-1} was the N-H stretching vibration absorption. The absorption of 1649 cm^{-1}, 1528 cm^{-1} suggested the formation of -CO-NH-. We observed the benzene rings absorption:1595 $cm^{-1}$and 1489 cm^{-1}, the -S- absorption of 1083 cm^{-1} and the absorption of benzene meta-substitute: 784 cm^{-1} was also present. **2b**: the absorption of 3435 cm^{-1} and 3337 cm^{-1} was the -NH_2 stretching vibration absorption, 3392 cm^{-1} was the N-H stretching vibration absorption. The absorption of 1667cm^{-1}, 1526 cm^{-1} suggested the formation of -CO-NH-. We observed the benzene rings absorption:1590 $cm^{-1}$and 1492 cm^{-1}, the sulfone group absorption: 1302 cm^{-1}, 1151cm^{-1} and the -S- absorption of 1076 cm^{-1}. Figure 4 was the ^{1}H-NMR spectrum of **2a**. Nine groups of peaks were appeared in the ^{1}H-NMR spectrum of **2a** in Figure 4. The ratio of corresponding integral curves was about 4:4:4:4:1:2:4:1:2. Combining the results of FT-IR, these nine groups of peaks were ascribed to the construction units of H_1, H_2, H_3, H_4, H_5, H_6, H_7, H_8, H_9. The chemical shifts (δ) of **2a** were listed in Table 2. **2b**: Eight groups of peaks appeared in the ^{1}H-NMR spectrum of **2b** in Figure 5. The ratio of corresponding integral curves was 2:2:2:2:2:2:2:1. Combining the results of FT-IR, these eight groups of peaks were ascribed to the construction units of H_1, H_2, H_3, H_4, H_5, H_6, H_7, H_8. The chemical shifts (δ) of **2b** were listed in Table 2.

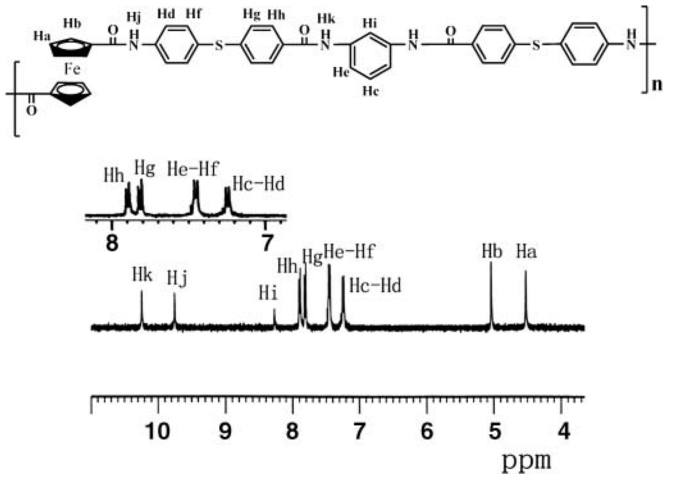


Figure 7. ^{1}H-NMR spectrum of FC-m-PPSAA (**3a**).

3.2 Polymers

3.2.1. *Synthesis of FC-PASAA (3a-3b)*

Polycondensation reaction of the diamine with FCDC was carried out in the presence of TMSCl as catalyst in NMP. Silylation of the diamine was an efficient method for activation of diamine to obtain high molecular weight polymers. The reaction could be activated by adding TMSCl to the diamine solution according to the literature (27–30). As shown in Scheme 3, due to the strong affinity of Si for oxygen, the carbonyl oxygen of the acid chloride is attracted to the Si atom in the amine derivatives, which in turn facilitates

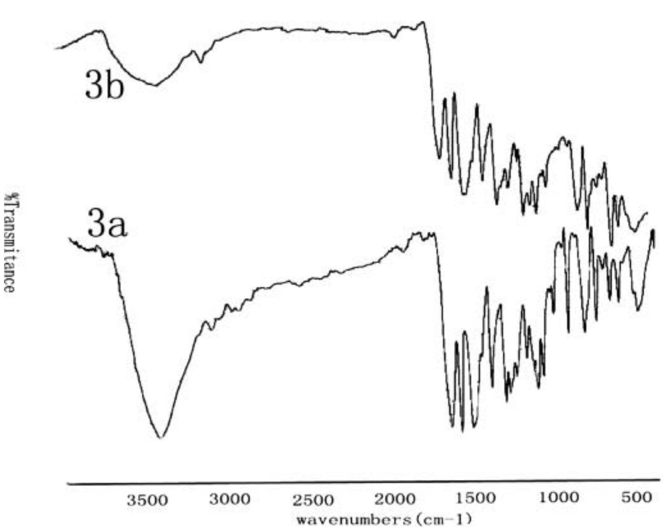


Figure 6. FT-IR spectrum of FC-PASAA (**3a-3b**).

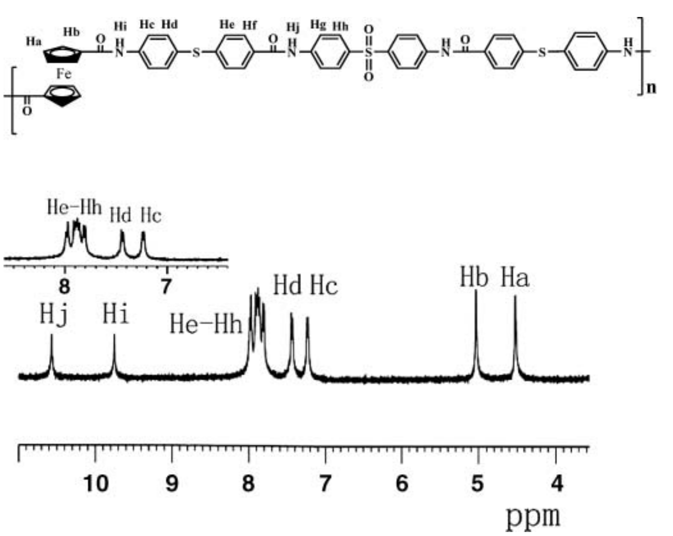


Figure 8. ^{1}H-NMR spectrum of FC- PPSSAA (**3b**).

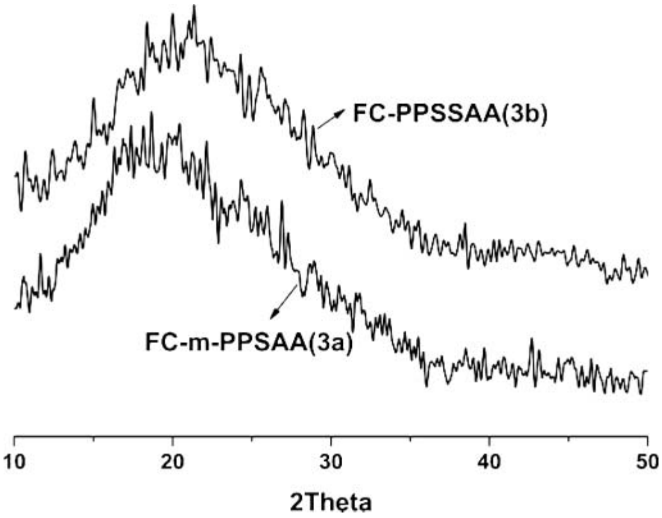


Figure 9. XRD spectra of FC-PASAA annealed (**3a-3b**).

the nucleophilic attack of the N atom of the N-silylated amine on the carbonyl carbon. Then, the elimination of chloride ion from the tetrahedral intermediate is enhanced by the presence of the β–silicon throngh the σ–π effect, affording rapidly the amide product along with TMSCl. (as shown in Scheme 3) Another important aspect of using TMSCl was that it could avoid the subsidiary reaction of the small amount of water.

3.2.2. *The intrinsic viscosity (*η_{int}*) and molecular weights of FC-PASAA*

The molecular weight of FC-PASAA was determined by η_{int} and GPC as shown in Table 3. The η_{int}'s of **3a-3b** were measured in the range 0.42–0.58 dL/g. **3a** and **3b** showed Mn values in the range 5.1–6.7 × 10^4, and Mw values in the range 8.86–10.2 × 10^4, respectively. The polydispersity indices (PDIs, PDI=Mw/Mn) of **3a-3b** ranged from 1.52–1.74.

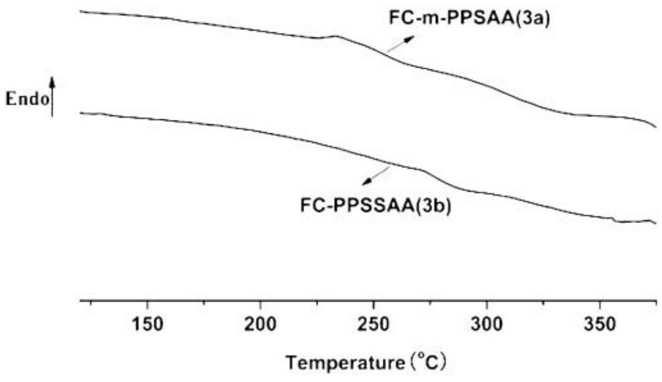


Figure 10. DSC analysis of FC-PASAA (**3a-3b**) at heating rate of 10°C/min.

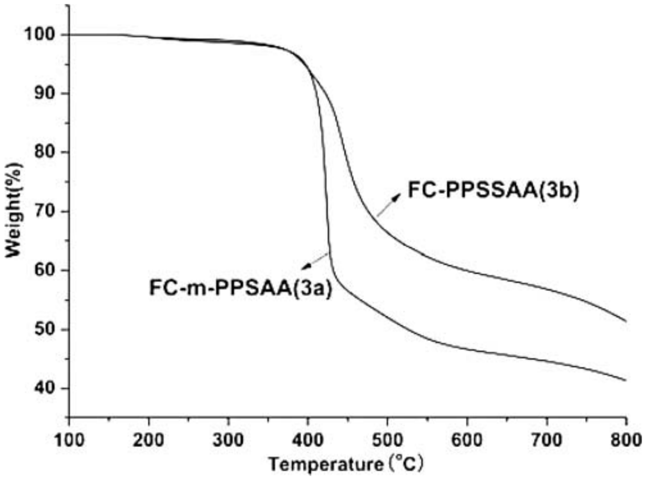


Figure 11. TGA weight loss behavior of FC-PASAA (**3a-3b**) at heating rate of 10°C/min in N_2.

3.2.3. *Elemental Analysis of FC–PASAA*

Table 4 showed the experimental results were similar with the calculated results. It suggested that FC-PASAA was successfully synthesized as Scheme 2.

3.2.4. *The chain structure of FC-PASAA*

Figure 6 showed the FT-IR spectrum of FC-PASAA (**3a-3b**). Comparing with monomer (**2a-2b**), the strong absorption of the amide bond near 3370 cm^{-1} could be identified in the spectrum of **3a** and **3b** in Figure 6. It suggested the polymers were prepared as prospective synthesis route.

Figure 7 showed the ^{1}H-NMR spectrum of FC-m-PPSAA **3a**. Eleven groups of peaks appeared in the ^{1}H-NMR spectrum of **3a**. The ratio of corresponding integral curves was about 4:4:2:4:2:4:4:1:2:2. Combining the results of FT-IR, these eleven groups of peaks were ascribed to the construction units of Ha, Hb, Hc, Hd, He, Hf, Hg, Hh, Hi, Hj and Hk. The chemical shifts (δ) of **3a** were listed in Table 5. **3b**: Ten groups of peaks appeared in the ^{1}H-NMR spectrum of **3b** in Figure 8. The ratio of corresponding integral curves was 2:2:2:2:2:2: 2:2:1:1, Combining the results of FT-IR, these ten groups of peaks were ascribed to the construction units of Ha, Hb, Hc, Hd, He, Hf, Hg, Hh, Hi and Hj. The chemical shifts (δ) of **3b** were listed in Table 6.

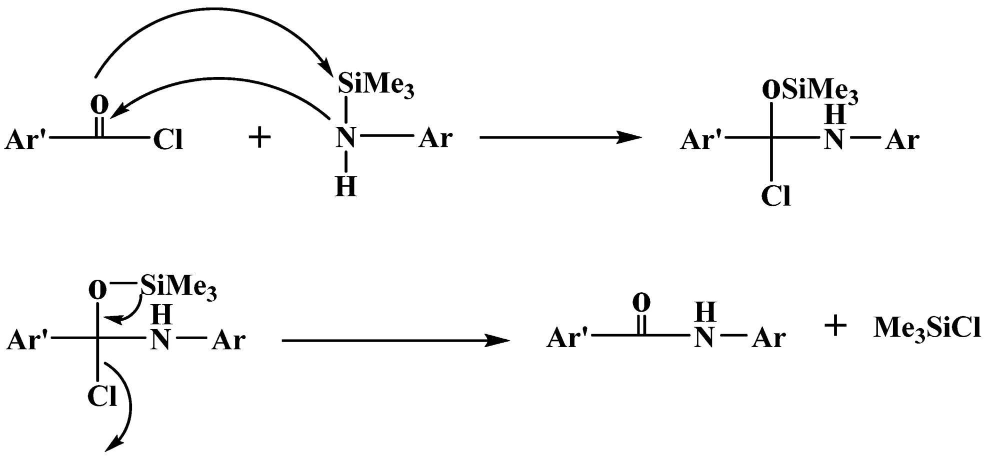
3.2.5. *The aggregative structure of FC-PASAA*

X-ray diffraction of FC-PASAA (**3a-3b**) annealed was listed in Figure 9. As manifested in Figure 9. the polymer

Table 4. Elemental analysis results of FC-PASAA (**3a-3b**)

Compound	*C(%)*	*H (%)*	*N(%)*
3a	66.43 (66.50)	4.59 (4.61)	6.68 (6.74)
3b	64.32 (64.32)	4.30 (4.36)	5.69 (5.77)

The data in brackets were those calculated.



Scheme 3. Mechanism of polymer formation by silylation.

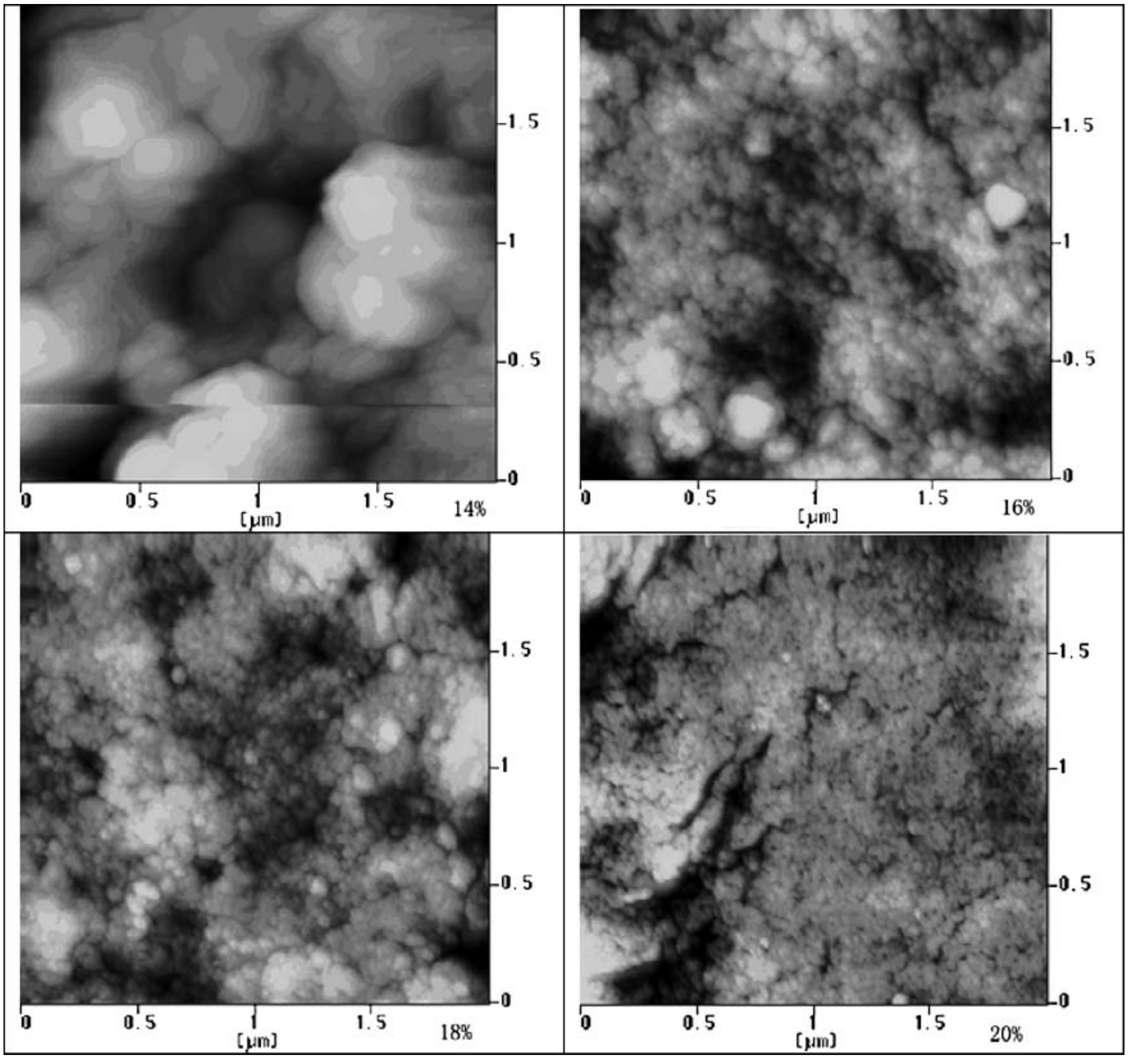


Figure 12. The atomic force microscopy of the membranes (**3b**) prepared from different concentration.

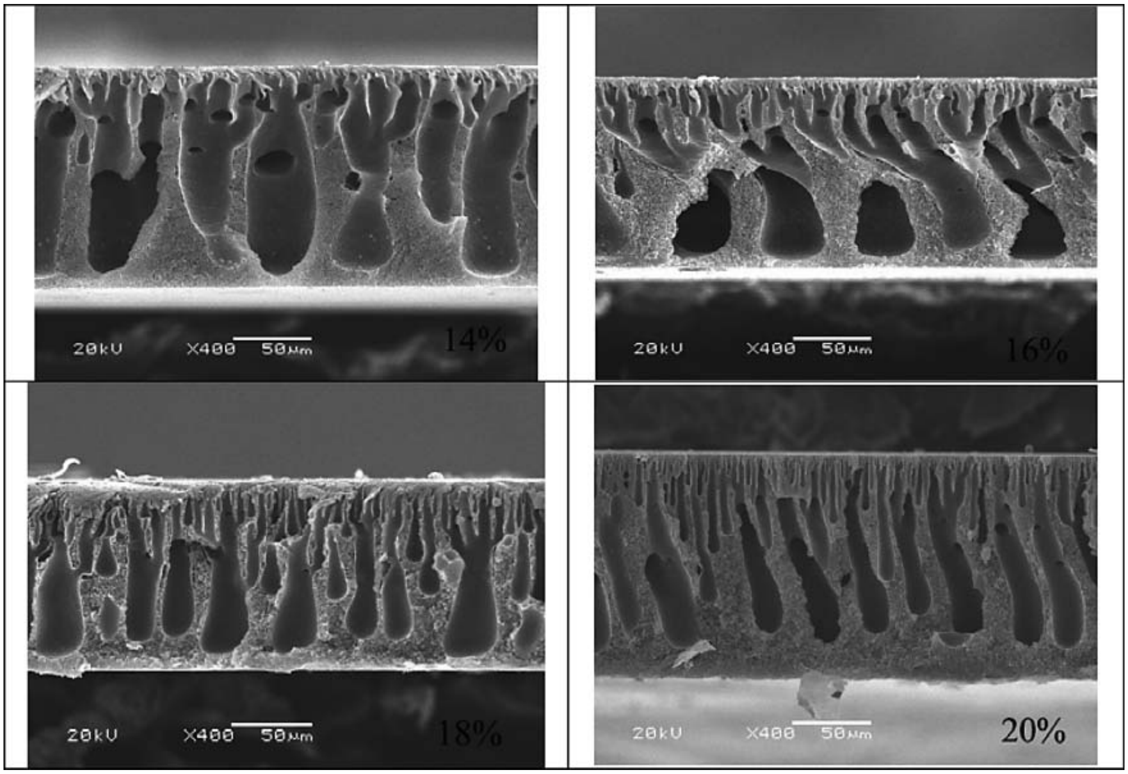


Figure 13. The scan electronic microscopy of the membranes (**3b**) prepared from different concentration.

of **3a** and **3b** was amorphous, the most reason was the existence of strong polarity sulfone group and the asymmetry of the molecular chain. The molecular chain locomotion was limited by the sulfone group so it could not arrange in order.

3.2.6. *The thermal properties of FC-PASAA*

The thermal properties of FC-PASAA were examined by DSC and TG analysis. The results were displayed in Figures 10 and 11. As shown in Figure 10, the T_g values of **3a** and **3b** were 229.9°C, 276.8°C (listed in Table 6), respectively. We had not found melting endothermic peak in the curves of **3a** and **3b.** It revealed that **3a** and **3b** was amorphous. That agreed with the results of X-ray diffraction. As manifested in Figure 11 the initial degradation temperature (T_d) of **3a** and **3b** in nitrogen were 389.2°C, 391.5°C, respectively. **3a** and **3b** left more than 50% and 40% char yield respectively at 800°C (in Table 7). The TGA data indicated that these two kinds of polymer had better thermal stability.

3.2.7. *Characterization of the membrane micro-structure*

The membrane-surface micro-structure of **3b** was detected with AFM. As shown in Figure 12, it could be found that the surface of the membrane (**3b**) became more and more compact with increasing the mass concentration, which might be due to the various speed of phase inversion during

Table 5. Chemical shifts (δ) of FC-m-PPSAA (**3a**)

3a	H_a	H_b	H_c- H_d		H_e- H_f
Chemical shifts δ(ppm)	4.516	5.032	7.227–7.248		7.432–7.453
3a	H_g	H_h	H_i	H_j	H_k
Chemical shifts δ(ppm)	7.799–7.821	7.879–7.900	8.270	9.747	10.237

Table 6. Chemical shifts (δ) of FC- PPSSAA (**3b**)

3b	H_a	H_b	H_c	H_d	H_e
Chemical shifts δ(ppm)	4.516	5.028	7.221–7.241	7.424–7.445	7.795–7.816
3b	H_f	H_g	H_h	H_i	H_j
Chemical shifts δ(ppm)	7.853–7.874	7.889–7.910	7.968–7.989	9.745	10.562

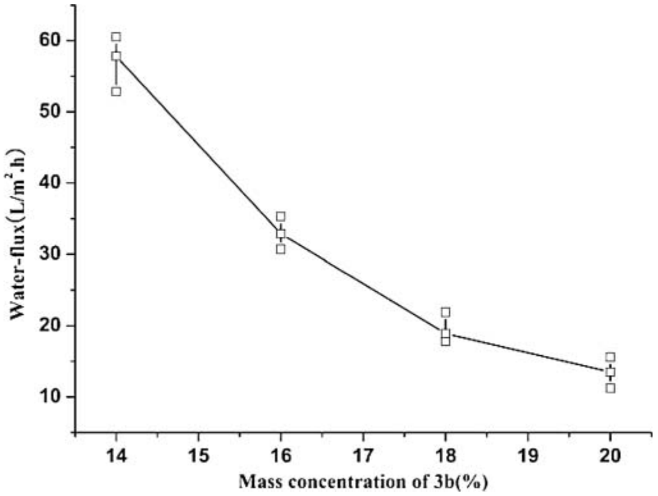


Figure 14. The Water-flux of the membranes (**3b)** prepared from different concentration.

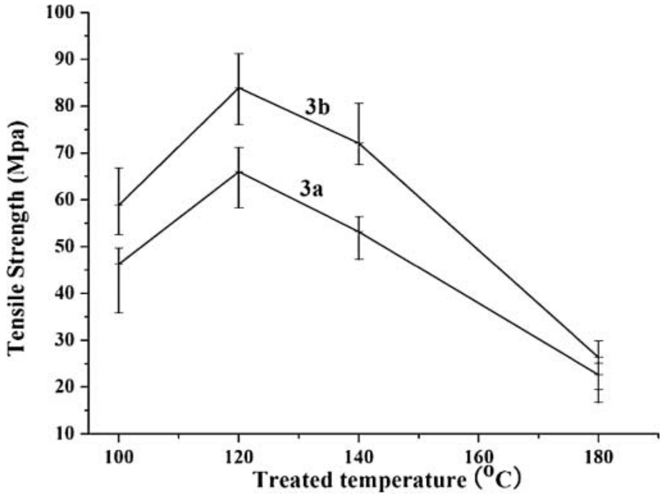


Figure 15. The tensile strength of FC-PASAA (**3a-3b**).

Table 7. Thermal Properties of FC-PASAA (**3a-3b**)

*P*olymer	T_g(°C)	T_d(°C)	*C*har Yield(%)
3a	229.9	389.2	51.4
3b	276.8	391.5	41.3

Table 8. Water-flux of FC-PPSSAA (**3b**)

*M*ass *c*oncentration(%)	*1*4	*1*6	*1*8	*2*0
Ra (nm)	67.78	24.06	22.83	4.99
RMS(nm)	79.17	29.88	28.48	6.87

Table 9. Electrical Properties of FC-PASAA

*P*olymer	Dielectric *s*trength(kv/mm)	Volume resistivity *(*Ω·cm)
3a	93.7	9.2*10^{11}
3b	106.2	2.6*10^{12}

preparation membranes (31–34). As shown in Table 8, the roughness (Ra) and root-mean-square roughness of membranes (**3b**) (RMS) decreased from 67.78–4.989 nm and 79.17–6.867 nm, respectively. The fracture surface of membranes (**3b**) was detected by SEM. The results were displayed in Figure 13. As shown in Figure 13, they exhibited a characteristic morphology of asymmetric membrane consisting of a dense top layer and a porous sub-layer. As the concentration of casting-solution increased, the pores appearing at sub-layer became smaller and smaller. At the same time the water-flux decreased from 57.8–13.5 L/m^2 □h as show in Figure 14.

3.2.8. *Tensile properties*

The average tensile strength of FC-PASAA (**3a-3b**) casting-film treated at different temperature (dried at 100°C, 120°C, 140°C, 180°C for 10 h in oven, then dried for 4 h at 210°C) were given in Figure 15. As shown in Figure 15, the tensile strength of **3a** and **3b** presented a tendency of first increasing and then decreasing with the treated temperature from 100°C to 180°C. The best treated temperature was 120°C–140°C, with the optimum condition the average tensile strength of the films **3a** and **3b** was 66.0MPa and 83.9MPa, respectively. We ascribed this phenomenon to the procedure of casting-film. The lower treated temperature the more quantity of solvent in the films. On the other hand, it caused the solvent volatilized quickly under higher treated temperature and it maybe resulted in forming flaw on the film's surface. So it was not good to treat the film under lower or higher temperature.

3.2.9. *The Electrical properties of FC-PASAA*

The electrical insulativity and dielectric strength of FC-PASAA (**3a** and **3b**) were detected by resistivity detector equipment ZC36 and high-voltage detector YDQ10/100. Their volume resistivity (ρ_v) were 9.2*10^{11}Ω·cm and 2.6*10^{12}Ω·cm; their dielectric strength were 93.7kv/mm and 106.2 kv/mm respectively as shown in Table 9. It suggested their electrical conductivity was better than other aromactic polyamide which had not ferrocene unit. Also, we studied that FC-PASAA had higher dielectric strength from Table 9.

3.2.10. *Solubility experiment*

Table 10 showed that FC-PASAA (**3a-3b**) had better solubility in polar aprotic solvents. They were soluble in NMP, DMF, DMAC, DMSO and concentrated sulfuric acid etc. at room temperature and showed no tendency to precipitate. So they could be processed by more methods, such as electro-spinning, solution casting and so on. But they cannot dissolve in HCl, formic acid, toluene and 1, 4-dioxane etc. Comparing to polyamide, FC-PASAA showed a better corrosion resistance.

Table 10. Solubility behavior of FC-PASAA

	Polymer			*Polymer*	
Solvent	*3*a	*3*b	*Solvent*	*3*a	*3*b
Concentrated sulfuric acid	++	++	Chloroform	+-	+−
formic acid	−	−	DMSO	++	++
NMP	++	++	1, 4-Dioxane	−	−
DMF	++	++	Toluene	−	−
HCl	+−	+−	DMAC	++	++
acetone	−	−	phenol+tetrachloroethane	++	++

* + +: soluble at room temperature; +: soluble on heating; +−: slightly soluble; −: insoluble with heating.

4 Conclusions

In this paper, higher molecular weight FC-PASAA (**3a-3b**) was prepared successfully by polycondensation reaction. FC-PASAA was a kind of thermo-stable resin with higher glass transition temperature and initial degradation temperature. **3a** and **3b** were both amorphous. They had better solubility in polar aprotic solvents. Their solution was stable. They were used to preparing separation membrane successfully. All of the membranes exhibited a characteristic morphology of asymmetric membrane consisting of a dense top layer and a porous sub-layer. As the concentration of casting-solution increased, the water-flux and the pores appearing at sub-layer became smaller and smaller, the top layer became more and more compact.

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