Int. J. Electrochem. Sci., 9 **(2014)** 8120 - 8130

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Synthesis and Electrochemical Characterization of Polycyclotriphosphazene Derivative Doped SPEEK Proton Exchange Membrane

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Received: 18 September 2014 / *Accepted:* 17 October 2014 / *Published:* 28 October 2014

A novel polycyclotriphosphazene derivative (Poly(hexa-amino-benzenesulfonic acid)cyclotriphosphazene, PCPPD) was synthesized using one-step method by hexachlorocyclotriphosphazene and sulfanilic acid. The structure was characterized by FTIR and NMR. Then the membranes of sulfonated poly(etheretherketone) with 65% sulfonation degree were prepared by doping of it. The morphology shows that the PCPPD could be dispersed evenly in the membranes. Comparing to SPEEK membranes, all the properties increased with the PCPPD content increasing. The proton conductivity reached 9.85×10^{-3} S/cm with 10 wt.% PCPPD blended. The methanol permeability coefficient got 3.92×10^{-7} $cm^2\cdot s^{-1}$ which is 3 time as pure SPEEK membrane.

Keywords: polyphosphazene dericative, SPEEK, properties

1. INTRODUCTION

Nowdays, the growing attentions have been paid to sulfonated poly (etheretherketone) (SPEEK) membrane due to its good chemical stability and mechanical properties [1-3]. However, the conductivity of pure SPEEK proton exchange membrane would be decreased at high temperature and low humidity. In our previous works, a series of SPEEK composite membranes by doping of rare earth and ionic liquid had been prepared [4-5]. The characteristic peaks of Y_2O_3 were disappeared but a typical amorphous diffraction peak appeared in the X-ray diffraction patterns, which proved the coordination between yttrium cation of Y_2O_3 and oxygen anion of sulfonic groups, resulting in the change of the original crystal form. However, the neutralization occurred between Y_2O_3 and sulfonic groups in composite membrane, which decreased their proton conductivities. Ionic liquids, particularly its unique excellent physical and chemical properties, are being extensively studied for a variety of applications. The high molecular polymer doped with ionic liquids would have good proton conduction at higher temperature and anhydrous condition. In conclusion, the properties of the membranes were all improved to a certain extent.

In this paper, the composite membranes based on SPEEK would be prepared by doping with a novel polycyclotriphosphazene derivative (PCPPD) and their properties were investigated.

2. EXPERIMENTAL SECTION

2.1 The materials

Hexachlorocyclotriphosphazene (HCCP) was recrystallized from dry hexane followed by sublimation (60 °C, 0.05 mmHg) twice before use (mp=112.5-113 °C). Phenol, tetrahydrofuran (THF), dimethylacetamide, sulfanilic acid were obtained from Sinopharm Chemical reagent Co., Ltd (Shanghai China). All chemicals and solvents were provided commercially by Sinopharm Chemical Regents Co. Ltd (China) and used without further purification unless otherwise noted. All glassware was dried in an oven under vacuum before use.

Poly (etheretherketone) (PEEK) was obtained from Chemistry Department of Jilin University (Jilin, China), in the form of particle, and SPEEK was prepared as reported in the literature 4. After SPEEK with DS of 65% was triturated, it was dissolved in dimethylacetamide to make 10 wt. % solution.

2.2 The synthesis of PCPPD

Hexachlorocyclotriphosphazene (3.48g, 0.01mol), sulfanilic acid (10.39g, 0.06mol) and triethylamine (20 mL) were dissolved in 500 mL THF in a three-neck flask equipped with a refluxing condenser under stirring and nitrogen atmosphere for 24 h. After reaction, cooling filtered, washed with acetone and water several times repeatedly and dried under vacuum to obtain the objective products.

2.3 The preparation of Membranes

Composite membranes were obtained by casting their viscous solution onto a glass plate and thickness of the dried composite membranes was about 100 μm. 5 wt.% and 10 wt.% content of PCPPD composite membranes were prepared, which singed as D05, D10, respectively.

2.4 The characterization and testing

Fourier Transform Infrared (FTIR) spectra of the membrane specimens were recorded with an AVATAR370 infrared spectrometer (ThermoNicolet Instrument Co., USA). The NMR spectra were recorded on a Varian DRX 400 NMR spectrometer with the operating frequency at 400 MHz using $CDCl_3$ or DMSO as a solvent, using TMS as inner reference and H_3PO_4 (85%) as external reference. The thermal stability of membranes was evaluated by recording thermo-gravimetric (TG) traces in nitrogen atmosphere (Q500, TA Company, USA). Heating rate was $10°C \cdot min^{-1}$, temperature ranged from 50 °C to 400 °C and specimen weight of 5±2 mg in the membrane form was used for recording TG traces.

The proton conductivity of membrane specimens in the traverse direction was measured in a measurement cell using AC Electrochemical Impedance Spectroscopy (EIS), which was composed of a Solartron Instruments 1287 electrochemical interface and a Solartron Instruments 1255B frequency response analyzer (Farnborough, UK), both of which were interfaced via GPIB to a computer. The EIS recorded over a frequency range of $1\text{-}10^6$ Hz. The amplitude of the sinusoidal modulation voltage was 10mV. The temperature ranged from 30ºC to 90ºC and the RH was 50% and 100%, respectively. Before the test, all membrane specimens were soaked in $1mol \cdot L^{-1}$ hydrochloric acid solution for 4h, and then rinsed for several times with deionized water. The resistance of the membranes was measured and the proton conductivity was calculated as described in detail in reference [6-8].

Methanol permeability coefficient of membrane specimen was determined by a home-made diaphragm diffusion cell, which was amply described in reference 6. The membranes were immersed in de-ionized water at room temperature for 24 h before testing, and both thickness and area of wet membrane specimens were measured. Thereafter, membrane specimens were placed in diffusion cell for the measurement of methanol permeability. 70 ml 5 mol/L methanol solution was placed in one side of the diffusion cell and de-ionized water of the same volume was placed in the other side. The methanol permeability coefficient was calculated by the second of law of Fick's diffusion as showed below (Equation 1) [9].

$$S_d = \frac{V_{wet} - V_{dry}}{V_{dry}} \times 100\% \qquad (1)$$

The water uptake (S_w) of the membrane specimens was calculated by measuring the weight difference between the dry and hydrous membrane specimens $^{6\text{-}8}$. The dried membrane specimens at 90 °C for 24 h were weighted ($mass_{dry}$) and then immersed in deionized water for 24 h. Then the membranes were wiped with blotting paper to remove the surface water and quickly weighted ($mass_{wet}$) again. The S_w was calculated using equation $S_w=(m_{wet}-m_{dry})/m_{dry}\times 100\%$, where m_{dry} was the mass of dry membrane, m_{wet} was the mass of membrane after immersion in deionized water.

3. RESULTS AND DISCUSSION

The polycyclotriphosphazene derivative was synthesized using one-step method by hexachlorocyclotriphosphazene and sulfanilic acid. The reaction route is shown in figure 1.

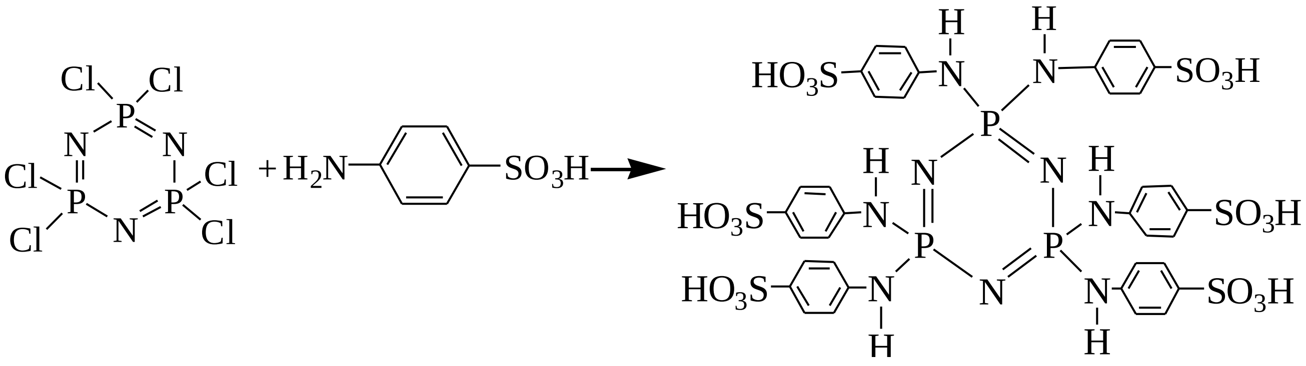

Figure 1. Synthesis of PCPPD

The chemical structure of PCPPD was confirmed by FT-IR as shown in figure 2. From the curve, we can see that a characteristic absorption peak due to the N=P group at 1256 cm^{-1}, P-N stretching vibration appeared at 870 cm^{-1}, which are proved the existence of phosphazene cycle. The characteristic absorption peak due to the P-Cl groups at 550 and 650 cm^{-1} disappears which indicated that Cl has been completely replaced by aminobenzene sulfonic. The sulfonic acid groups were corresponding to characteristic absorption peaks as 1250, 1092, 1020 and 710 cm^{-1}. 3370 cm^{-1} is due to the stretching vibration absorption peak of N-H.

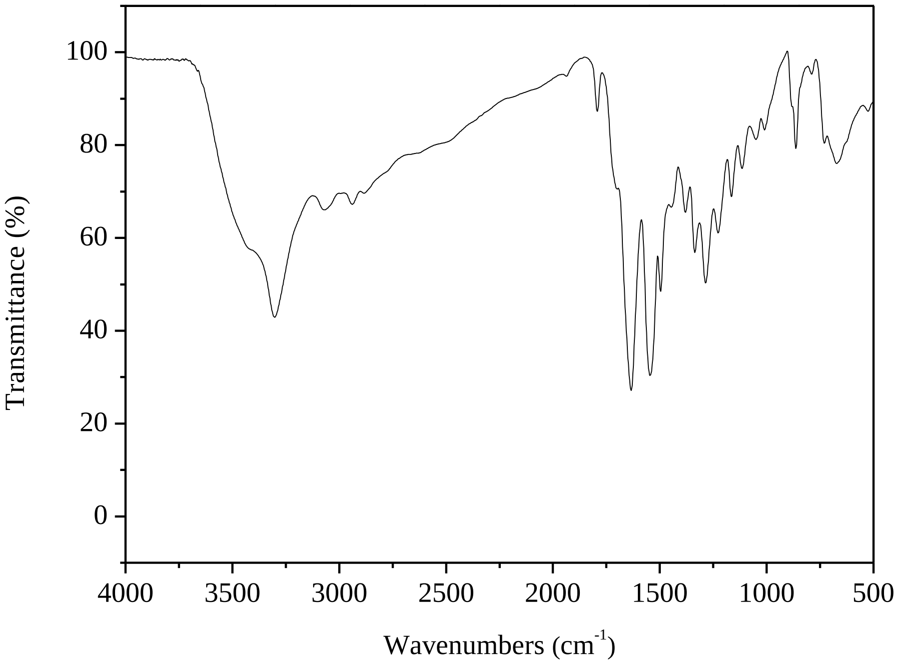

Figure 2. FT-IR spectrum of PCPPD

The P^{31} and H^{1} NMR spectra are shown in figure 3 and 4. There only existed one kind chemical atmosphere at 7.8 ppm corresponded to –P-NH-. In contrast to HCCP, there was no chemical shift at 19.8 ppm which proved chlorine atoms were completely substituted by sulfonic acid.

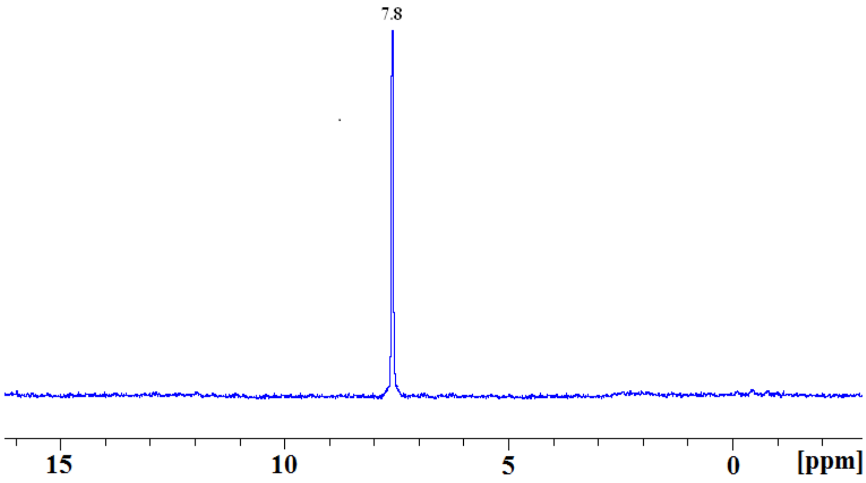

Figure 3. ^{31}P NMR spectrum of PCPPD

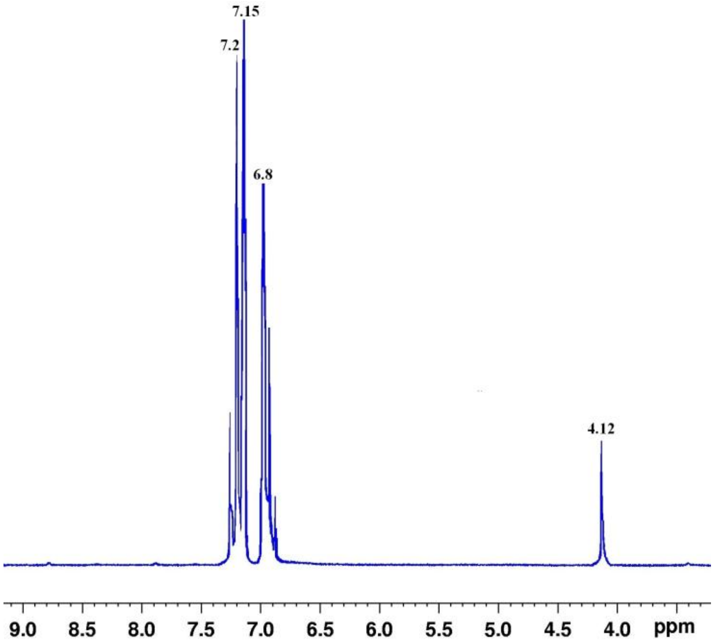

Figure 4. ^{1}H NMR spectrum of PCPPD

The proton conductivity of the membranes is shown in figure 5. As the temperature rising, the proton conductivity of the pure SPEEK membrane increased. However, D05 and D10 membranes exhibited a tendency to increase more than it in the earlier stage and final stabilizing. The proton conductivity of the membranes increased with the doping content of PCPPD.

Figure 5 illustrated that the proton conductivity increases with the increases of using temperature. However the proton conductivity tends to smooth and the overall increases is not obvious at high temperature. The reasons could be due to the water-resistant swelling properties of the membranes. Excessive water-swelling caused its mechanical performance down. When the sulfonic acid groups reached a certain number, the hydrophilic regional became stability and the proton transition changed smoothly.

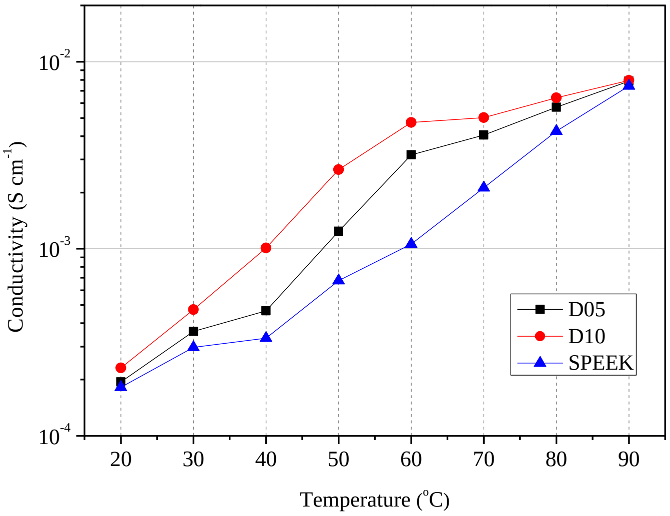

Figure 5. Proton conductivity of polycyclotriphosphazene derivative doped SPEEK membranes vs temperature

Methanol resistance for PEM needs high performance requirements in the direct methanol fuel cell. Comparing to Nafion membrane, one big advantage of SPEEK proton exchange membrane is more excellent resistance alcohol performance.

Using GC9800 gas chromatograph testing and combined with the standard curves in figure 6, the relationships between methanol concentration down ionized water side and versus time of the membrane samples obtained at 30 °C are obtained as shown in figure 7.

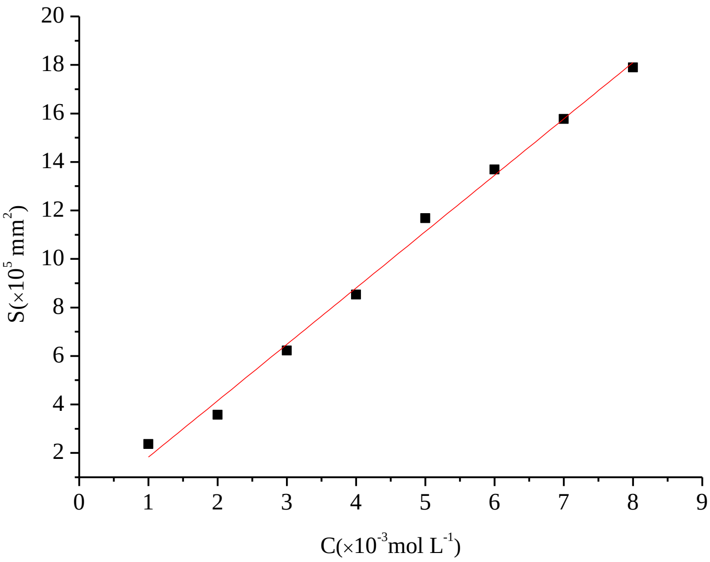

Figure 6. The curve of peak area versus methanol concentration

Diffusion methanol concentration of the membrane samples increased over time, S is the slope of the change rate of the methanol concentration in the deionized water side with time, and proportional to methanol permeability coefficient of the samples.

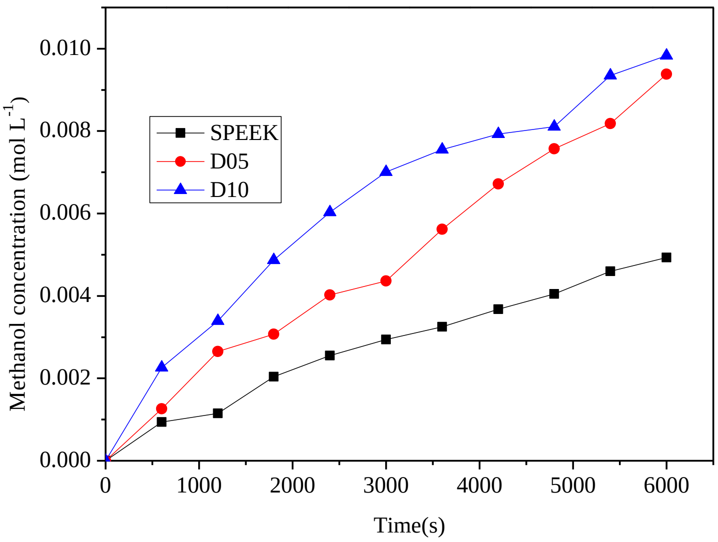

Figure 7. Methanol concentration of polycyclotriphosphazene derivative doped SPEEK membranes vs time

As shown in figure 7, the methanol proliferation concentration of membrane samples increases over time, the methanol permeability concentration curve slope of D05 and D10 membranes were slightly higher than the pure SPEEK membrane. For the D05 membrane, pre-change trend of methanol osmotic concentration was similar to pure SPEEK membrane but tended to increase at the late slope of the curve. For the D10 membrane, pre-change trend of methanol osmotic concentration was more than pure SPEEK but tended to similar to pure SPEEK membrane at the late slope of the curve. According to curve of deionized methanol concentration at water side versus time to get the slope S, calculated the methanol permeability coefficient P values as shown in Table 1. Compared with the table, methanol permeability coefficients of the D05 and D10 membrane were greater than the pure SPEEK membrane, but far less than the Nafion membrane.

Table 1. Methanol permeability coefficient of SPEEK membranes

CODE	Thickness （cm）	Area （ cm^2）	Water Volume （ml）	Straight Slope （$\times 10^{-6}$mol·L^{-1}·s^{-1}）	Methanol permeability coefficient （$\times 10^{-7}$ cm^2·s^{-1}）
SPEEK	0.0101	0.345	30	0.746	1.30
D05	0.0114	0.345	30	1.451	2.87
D10	0.0110	0.345	30	1.687	3.92

According to table 1, the methanol permeability coefficient of pure SPEEK membrane (DS 64.5%) is 1.30×10^{-7} $cm^2\cdot s^{-1}$. After doping by polycyclotriphosphazene derivative, the membrane permeability coefficients were higher than the pure SPEEK. The methanol permeability coefficient of the samples increased with the increase of doping amounts, D05 membrane reached 2.87×10^{-7} $cm^2\cdot s^{-1}$, D10 membrane reached 3.92×10^{-7} $cm^2\cdot s^{-1}$, which both are three times to pure SPEEK membrane but less than the Nafion membrane.

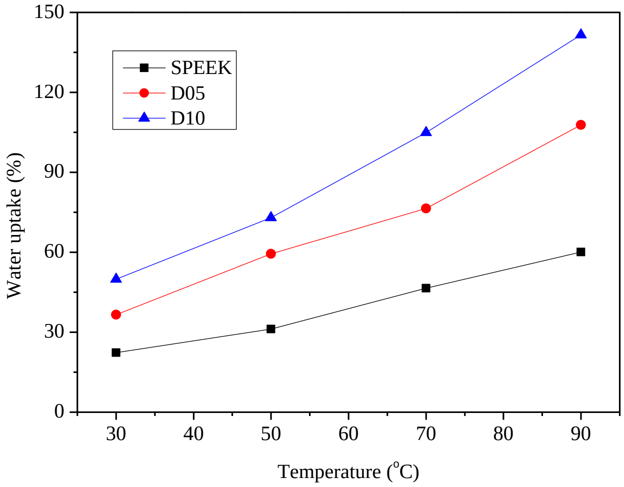

Figure 8. Water uptake of polycyclotriphosphazene derivative doped SPEEK membranes vs temperature

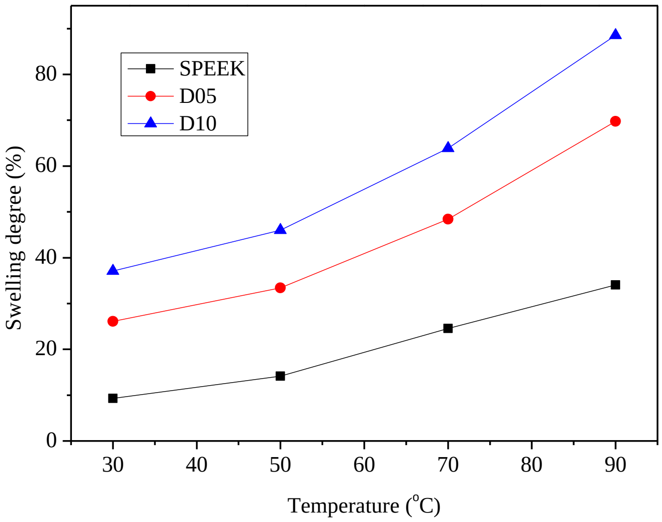

Figure 9. Swelling degree of polycyclotriphosphazene derivative doped SPEEK membranes vs temperature

For the polycyclotriphosphazene derivative doping, the large amount of hydrophilic groups, amino acid, which were clustered structure, after absorption water molecules, formed water micro-phase surrounding itself. The structure not only helped to methanol diffused but also conducive to proton transfer, leading to the decrease of the alcohol resistance performance [10].

The test and the results of absorption and swelling of pure SPEEK and doping polycyclotriphosphazene membrane samples are shown in figure 8 and 9. As shown in figures, the water absorption and swelling of the membrane samples were increased over temperature, and the higher the temperature, the rising trend is more obvious. Water absorption and swelling increased over the doping content. Water absorption of pure SPEEK membrane reached 60.1% at 90 °C and swelling was 34.1%. Water absorption of D05 membrane reached 107.8% and the swelling was 69.8%. Water absorption of D10 reached 141.5% and swelling was 88.5%. The water-swelling properties of doping membranes were less than pure SPEEK which indicated that the microstructure of the doping membrane were not dense due to the water absorption and swelling too high.

Water absorption and swelling of the doping membranes increased significantly and two times of pure SPEEK membrane at 90 °C. High water absorption and swelling reduced the dimensional stability of the membrane, decreased mechanical properties, or even not be used. Combining with the performance of the proton conductive, the proton conductivity decreased with higher water absorption and swelling of the membrane at high temperatures. Water absorption and swelling depends on the degree of density and content of sulfonic acid groups in the membrane. The more sulfonic acid groups, the greater loose and value of microstructure and water absorption, resulting in larger swelling of the membrane and the structural stability is reduced. The proton exchange membrane fully hydrated has higher proton conductivity according to the transfer characteristics of a proton exchange membrane. The water absorption rate increases in favor of improving the proton conductivity. But when the excessive water absorption and swelling, it will cause swelling and poor dimensional stability to be cannot even use. Compared with proton conductivity, the proton conductivity of the D05 and D10 begin to drop when the temperature is higher than 70 °C. It also proves that the mechanical properties of the membrane began to decline, excessive swelling of the membrane, or even unusable.

The thermal properties of the membranes were analyzed by thermal gravimetric analysis and TG curves are shown in figure 10. From the curves, its shows that pure SPEEK has significant weight loss processes. The first process of a thermal weight loss occurs at room temperature to 150 °C which due to a small amount of water evaporation or volatile solvent remaining in the molding process. The second thermogravimetric process took place at 250-400 °C which due to the thermal decomposition of the sulfonic acid groups. The third thermogravimetric process was 450-550 °C corresponding to the heat degradation of the polymer main chain [11-12]. Poly(hexa-amino-benzenesulfonic acid)cyclotriphosphazene existed a little amount weightlessness in the range of room temperature to 150 °C which due to the adsorption of small molecules of water or residual solvent. 150-400 °C was the major thermal decomposition process. The main reason could be the thermal decomposition of sulfonic acid groups. Polyphosphazene rings took placed ring-opening reaction in the thermal generation process to from a P-O-P crosslinked structure or produced a more stable solid residue [13-14]. All the above cases due to the decomposition rate slowed upon 400 °C and significantly higher rate of solid residual (62.8%) at 700 °C.

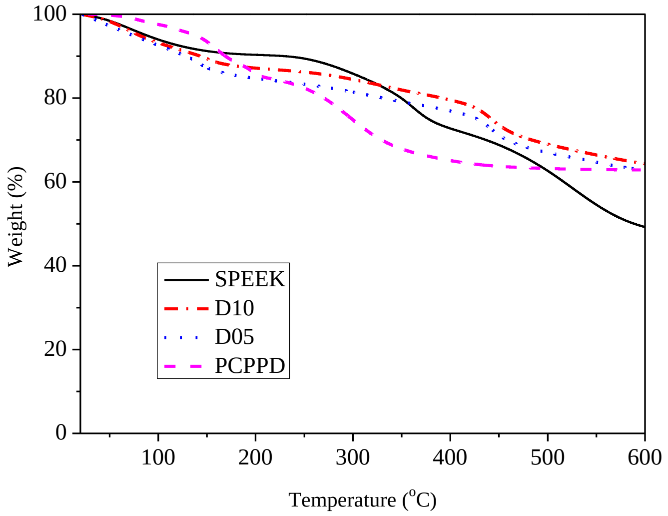

Figure 10. TG curve of polycyclotriphosphazene derivative doped SPEEK membranes

4. CONCLUSIONS

Poly(hexa-amino-benzenesulfonic acid)cyclotriphosphazene can improve the performance of proton conductivity by doping SPEEK, but the effect is not obvious. The proton conductivity exhibits a tendency to increase over temperature. But the proton conductivity tends to smooth at high temperature. With the increase of doping content, the proton conductivity of the membranes raised, but the proton conductive of the samples do not reach 10^{-2} S· cm^{-1}.

Methanol diffusion concentrations of the doping membranes increased over time. The methanol permeability coefficients of doping membranes were higher than pure SPEEK. D05 membrane reached 2.87×10^{-7} $cm^2\cdot s^{-1}$, D10 membrane reached 3.92×10^{-7} $cm^2\cdot s^{-1}$, which both are three times to pure SPEEK membrane but less than the Nafion membrane.

The water absorption and swelling of the membrane samples were increased over temperature and the higher the temperature, the rising trend is more obvious. Water absorption and swelling increased over the doping content. Water absorption of pure SPEEK membrane reached 60.1% at 90 °C and swelling was 34.1%. Water absorption of D05 membrane reached 107.8% and the swelling was 69.8%. Water absorption of D10 reached 141.5% and swelling was 88.5%. The water-swelling properties of doping membranes were less than pure SPEEK which indicated that the microstructure of the doping membrane were not dense due to the water absorption and swelling too high.

Poly(hexa-amino-benzenesulfonic acid)cyclotriphosphazene can improve the thermal stability of the membrane. D10 membrane has the best thermal stability. The doping membrane samples had excellent thermal stability and achieved the usage requirements of proton exchange membrane.

ACKNOWLEDGEMENTS

We are thankful to the Project Supported by Zhejiang Provincial Natural Science Foundation of China (Grant No. LQ14E030004) for the support to this research.

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