

Synthesis and characterization of sulphonated polymer derived from 6FDA-ODA polyimide

Jian-Li Wang¹ (✉), Myong-Hoon Lee², Jun Yang²

¹Zhejiang Key Laboratory of Green Chemistry Synthesis Technology, College of Chemical Engineering and Materials, Zhejiang University of Technology, 310014, Hangzhou, China
wangjl@zjut.edu.cn

²Department of Polymer Science and Technology, Chonbuk National University, 664-1, Dukjin, Chonju, Chonbuk 561-756, Korea

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Summary

6FDA-ODA polyimide was sulfonated with concentrated sulfuric acid at room temperature in order to convert the polymer into proton-conducting polymer. The sulfonation process was supervised with UV-vis. The results indicated that the reaction carried out quickly and was agreement with the analysis of resulted polymer. The sulfonation degree can be controlled by reaction time. The structure of the resulted polyelectrolytes were analyzed and confirmed by NMR, FT-IR. There are two weight-loss steps at 300 and 500 °C in TG curves, which correspond to the presence of two degradation processes for –SO₃H and polymer backbone. It indicated that the sulfonated polyimide had good thermo stability. The solubility of sulfonated polymer are also discussed.

Introduction

Sulfonated polymer is a sort of widely used polymer. For many years sulfonated polymer (SP) are investigated intensively because of their current and potential applications in many areas. For instance, sulfonated polystyrene (SPS) is usually made into spheric cation exchange resins or hetero-phase ion exchange membranes. Sulphonated polymers are also considered to be much more resistance to membrane fouling induced during the separation processes [1]. Sulfonated polysulfone and the blends of polysulfone and sulphonated polyetherether ketone (SPEEK) membranes were shown to be anti-fouling [2]. Recently, some works were contributed to developing novel polyelectrolyte based on sulfur modified polymer as proton exchange membrane (PEM) for proton exchange membrane fuel cell (PEMFC) or direct methanol fuel cell (DMFC). Generally, the sulfonation of the polymer is usually carried out as follows:

The polymer is converted to a sulfonated form by either (1) direct sulfonation of sulfuric acid functions; (2) radiation grafting of sulfonated monomers onto the polymer backbone; (3) chemical grafting of sulfonated monomers onto the polymer backbone; The polymer is built from monomeric units which bare sulfonic acid group.

The synthesis and characterization of sulfonated poly (aryl ether sulfone) (PAES) was reported by Nolte et al [3], and Lufrano et al [4]. Wang [5] et al. estimated sulfonated PAES random copolymers for proton exchange membrane. The preparation methods and the main characteristics of the sulfonated poly(ether-etherketone) (PEEK) was reported by Linkous et al [6], Schmeller et al [7], Bailey et al [8], Kobayashi et al [9], and Bauer et al [10]. Steck and Stone [11] studied the sulfonated polyphenylquinoxalines. P. Staiti [12] et al. prepared sulfonated polybenzimidazole (PBI) by sulfuric treatment directly on the pre-formed PBI membranes. Bae JM et al [13]. developed sulfonated polymer from poly(4-phenoxybenzoyl-1,4-phenylene) (PPBP), PBI-PS (propanesultone) and PBI-BS (butanesultone). The first sulfonated polyimides (SPIs) were based on 4,4'-diamino-biphenyl 2,2'-disulphonic acid (BDSA), 4,4'-oxydianiline (ODA) and oxy-diphthalic dianhydride (ODPA) which are commercially available. These polymers called phthalic polyimides were soluble in m-cresol but were not stable enough in fuel cell conditions. Mercier et al [14]. developed an alternative sulfonated polyimide based on 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) instead of ODPA. In their papers, a series of sulfonated polyimides (SPI), which were designed for high temperature proton exchange membrane, were obtained by the polycondensation of the sulfonated aromatic dianhydrides [15]. Aromatic ether diamines having different amino-substituted positions and/or bulky groups in their structure were synthesized. Almost all reported sulfonated polyimides were prepared through polycondensation with sulfonated monomer. By far, there is little knowledge about the preparation and characterization of sulfonated polyimide derived directly from polyimide backbone. The present work focuses on the direct sulfonation of PI backbone with concentrated sulfuric acid as reagent. This paper deals with the influence of the sulfonation condition of 6FDA-ODA polyimide on (1) the control of sulfonation degree (DS), (2) the confirmation and characterization of SPI with FT-IR, UV-Vis.

Experimental

Materials

N-methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF) were dried by refluxing over CaH_2 and distilled before use. 4,4'-Hexafluoroisopropylidene)diphthalic anhydride (6FDA, Aldrich) was without purification, 4,4'-Diaminodiphenylether (ODA, TCI) was sublimated at 22°C under reduced pressure. Sulfuric acid (SA) of 95% and N,N-Dimethyl formamide (DMF) (Duksan pure chemical Co. Ltd.) was used as received.

Preparation of 6FDA-ODA polyimide

The preparation of 6FDA-ODA polyimide was described in our early work [16]. ODA was dissolved in purified NMP in a flask, and then equivalent 6FDA was added. The mixture was stirred under nitrogen at room temperature for 24 hours. After that, acetic anhydride with pyridine was added to the reaction solution. The mixture was stirred for another 24 hours at room temperature and the resulted polymer was precipitated by pouring it into water. The yellow precipitate was collected by filtration and purified further by reprecipitation. 6FDA-ODA polyimide was identified by NMR and FT-IR spectroscopy.

Sulfonation of 6FDA-ODA polyimide

Polyimide powder (5.0g) was dissolved in sulfuric acid (100ml) in a glass reactor equipped with a stirring. In experiments, the 6FDA-ODA polyimide powder can be dissolved in the fresh concentrated sulfuric acid rapidly and the solutions showed bright yellow color at room temperature. After a determined reaction time the reaction solution was diluted and poured into a large amount of cold water under strong stirring. The pale yellow precipitate was collected by filtration and was washed with deionized water until the value of the washing-water was neutral. The polymer were dried for 24hours at 40 °C and was reprecipitated by dissolving in DMF. Sulfonated polymer was dried at 40°C for 48hours in a vacuum oven. **Figure 1** shows schematically the structures of 6FDA-ODA polyimide and sulfonated polyimide.

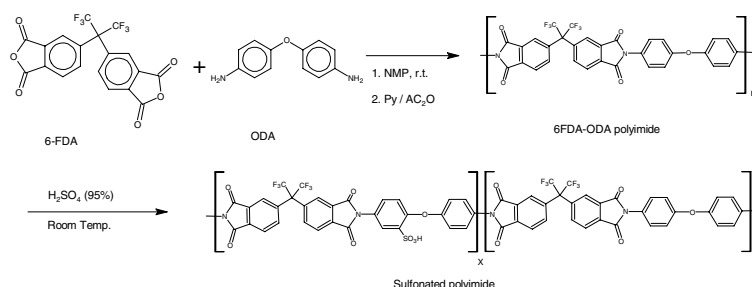


Figure 1. Scheme of chemical structure of 6FDA-ODA polyimide and sulfonated polyimide

¹HNMR spectrophotometry

The ¹HNMR spectra were recorded on a JEOL model 400 (400MHZ) instrument in DMSO-d₆ using tetramethylsilane (TMS) as internal standard.

UV-Vis spectrophotometry

A dynamic spectra of the PI-Sulfuric Acid (SA) sulfonation reaction were recorded with a Shimadzu model UV-2100s at room temperature. UV-Vis spectra of PI-sulfuric acid dilute solution were recorded continuously with an interval time. The first testing was carried out in 25 minutes later to ensure getting the uniform solution.

FT-IR spectrophotometry

The IR spectra were recorded on a JASCO FT/IR-300E at room temperature. The SPI powder samples were made into slice with KBr.

Thermo analysis

Thermogravimetry was performed in the range of temperature from 50 to 800°C under nitrogen by using TGA 2050 (TA instruments) at a heating rate 10°C/min. All the samples were put into the furnace of the machine for 30 minutes to remove the moisture before testing.

Results and discussion

PI-sulfuric acid dilute solution

In order to find out effect of sulfonation time on the sulfonation speed at the room temperature, a continuous UV test was carried out. For this purpose, PI-SA dilute solution was put into quartz cell for testing at static state. There are three main peaks (230nm, 275nm and 310nm) from 200 to 400nm in the UV spectra (see **Figure 2**). It is clear that the intensity of the peak (230nm) decreases rapidly within 4 hours and then changes little. It seems that the peak positions (230nm) transfer to short wave number. These changes are contributed to the introduction of $-\text{SO}_3$ into the benzyl. At the same time, the strengths of the other two peaks (275nm, 310nm) increase apparently during the starting two hours and then change little.

The phenomenon indicated that, with the reaction time, the sulfonation degree increases first rapidly, then more slowly (see **Figure 2**). However, the reaction rate pattern (without leveling-off for long-time reactions) is not reminiscent of that of a reaction, which approaches an equilibrium. We speculate that the change in the reaction rate is due to a change in the reaction mechanism: the sulfonic groups, once fixed on the aromatic rings, deplete the aromatic rings of their electrons by attractive and resonance effects, and reduce the rate of subsequent electrophilic substitutions on the rings. A similar result was reported that the sulfonation reaction of polyethersulfone Cardo was controlled by dynamic factors in the literature [17].

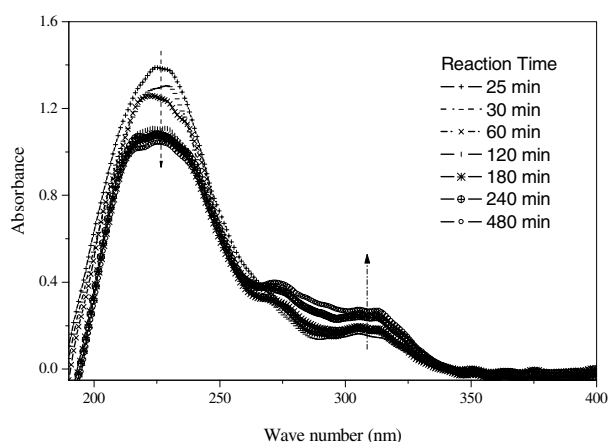


Figure 2. Influence of the reaction time on the UV-Vis spectra of the reaction medium. Sulfonation conditions: room temperature; polymer/acid ratio is about 10^{-6} (w/v)

Characterization of polyimide and sulfonated PI by ^1H NMR, FT-IR and TGA

As shown in **Figure 1**, there are five kinds of proton in 6FDA PI, corresponding to H_a , H_b , H_c , H_d and H_e . The ^1H NMR spectrum of 6FDA-ODA polyimide as precursor of sulphonated polymer is shown in **Figure 3**. The integration area ratio of each proton agrees with the structure well [18]. In the sulfonation reaction, the sulfonic acid group is usually restricted to the activated position ortho to the aromatic ether bond, as

indicated in structure in **Figure 3**. From the represented partially sulfonated molecular structure, there are another five sorts of proton appeared and named $H_{a'}$, $H_{b'}$, $H_{a''}$, $H_{b''}$, H_f . As it shown in **Figure 4**, $H_{a'}$ and $H_{b''}$ have the same chemical shifts as H_a and H_b , respectively, in NMR spectra.

Compared with the original PI, a series of spectrums of SPI prepared with different reaction time are illustrated in **Figure 4**. With the sulfonation degree (reaction time), the integral areas of peak H_a and H_b decreased and finally disappeared. The possible reason is as follows: The substitution of $-SO_3H$ for proton decreased the amount of H_b directly; The chemical shift of H_f moved to lower field nearly to H_e , which was caused by the strong electronic acceptor influence of $-SO_3H$; The substituted $-SO_3$ influence on the chemical shift of the H_a and cause shift to lower field 8.0 (-0.4ppm to the chemical shift of H_a), which is almost the position of H_e . The overlapping of the two kinds of protons induced the apparent increase of the peak-e, which can be used for the calculation of sulfonation degree. $H_{a'}$, $H_{a''}$, $H_{b'}$ and $H_{b''}$ moved to little higher field, which is contributed to the introduction of $-SO_3H$ and its baffling effect on the motion of O-O-O structure. It's the explanation of the new peak appearing. The $^1\text{HNMR}$ signal for the $-SO_3H$ group is less easy to record directly because this proton is labile.

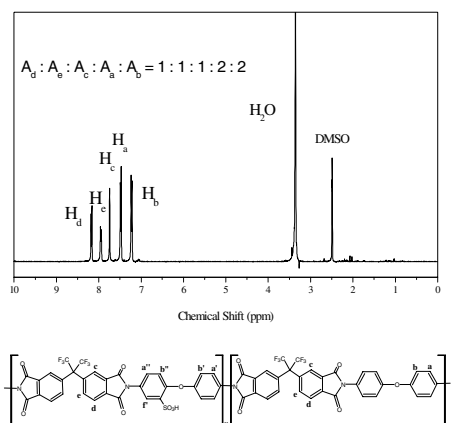


Figure 3. $^1\text{H-NMR}$ spectra of 6FDA-ODA polyimide in DMSO-d_6

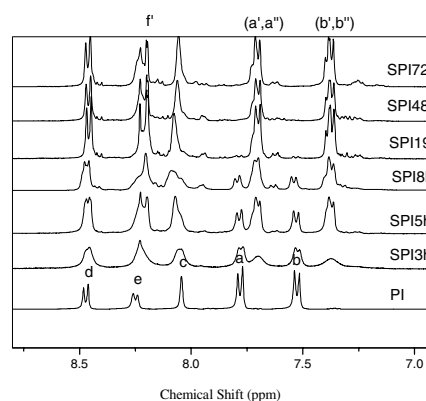


Figure 4. $^1\text{H-NMR}$ spectra of polyimide and sulfonated polyimides in DMSO-d_6

Based on above explanation, we developed a simple equation (1) to evaluated the degree of sulphonation (DS) of these sulfonated polymers.

$$SD\% = 2 \times \left(\frac{A_e - A_d}{A_d} \right) \times 100\% \quad (1)$$

Where A is the integration area of proton, the subscript presents different proton. Here the area of H_d is selected as an inner standard, because it is influenced by the $-SO_3H$ little.

The sulfonation degree evaluated from $^1\text{HNMR}$ spectra showed in **Figure 5**. The sulfonation of 6FDA-ODA PI at room temperature in concentrated sulfuric acid places

a limit of one sulfonic group per repeat unit as S-PEEK [19]. These data fits the results from UV supervision of PI-sulfuric acid solution well.

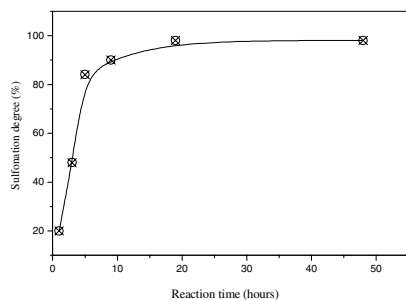


Figure 5. Effect of reaction time on the sulfonation degree of SPI

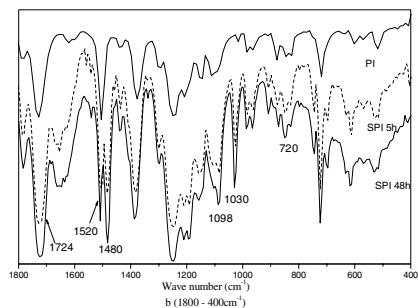


Figure 6. FT-IR spectras of 6 FDA-ODA polyimide and sulfonated polyimides

FT-IR was used to analyze characteristic bands corresponding to the sulfonate groups in the different polymer, e.g. sulfonated poly(arylene ether ketone)s [20-22], polystyrene [23], polyester [24], and poly(phenylene sulfide) [25]. There are wide and large water peak of the IR spectras of all sulfonated polymer indicate that the polymer is very easy to absorb water. The water peaks were inevitable and its intensity increased with reaction time (**Figure 6**). Successful introduction of the sulfonated groups was confirmed by FT-IR spectra, where strong characteristic peaks at 1030 and 1098 cm^{-1} assigned to symmetric and asymmetric stretchings of the sulfonate groups were observed for all sulfonated polymers. The intensity of absorption bands at 730 cm^{-1} attributed a para substituted benzene ring and the vibration increased with sulfonation level. The spectrum of polyimide (in **Figure 6**) shows strong peaks at 1724 cm^{-1} and 1520 cm^{-1} , which are corresponding to the imide linkages and ODA symmetric benzene stretching [18]. The intensity of ODA symmetric benzene stretching (1520 cm^{-1}) of the sulphonated polymer (eg. SPI5h) decreased. While another peak at 1480 cm^{-1} , which is ODA symmetric benzene (sulphonated) stretching appeared and increased with the reaction time.

Thermo stabilities of the control and sulfonated polyimide were investigated by TGA. All the sulfonated samples were pre-heated at 150 $^{\circ}\text{C}$ for 30 min in TGA furnace to remove moisture. The dynamic TGA tests were run from 50 to 800 $^{\circ}\text{C}$, at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere. The thermo stabilities of sulfonated polyimide are compared in **Figure 7**. SPI-100 show the first weight loss of about 14% between 350 to 400 $^{\circ}\text{C}$, which induced the loss of $-\text{SO}_3\text{H}$ group. The second thermal weight loss at 480 $^{\circ}\text{C}$ was corresponded to the decomposition of the polymer main chain. The theoretical weight percent of $-\text{SO}_3\text{H}$ group in SPI-100 is 13.7%, assuming that the elimination of sulfonation acid group (1 mol per repeat unit), which is in close agreement to the first weight loss step in the TGA curve for SPI-100 (D.S 100% evaluated from ^1H NMR). It indicates that the desulfonation of sulfuric group. Similar observations were made for sulfonated polysulfones [26], and sulfonated polyether ether ketone [27].

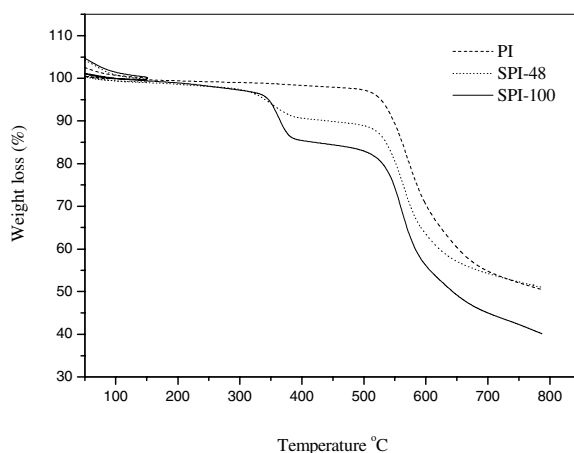


Figure 7. Dynamic thermogravimetry curves for PI and SPI heated in nitrogen at a rate of 10°C per minute

Solubility

Solubilities of 6FDA-ODA polyimide and SPI with D.S 20, 48, 82 and 100% were tested and the results are listed in **Table 1**. The SPIs were soluble in DMAc and in aprotic polar solvents such as DMSO, DMF and NMP, and they were partially soluble in THF. The polymers were not soluble in hydrocarbon solvents such as hexane, ethyl acetate, and toluene or in an alcoholic solvent such as methanol. It shows that the solubilities of polymers are different before and after sulfonation. 6FDA-ODA polyimide is soluble in selected polar aprotic solvents and partially in chlorinated solvents such as chloroform. Moreover, SPI with higher DS can not dissolve in the methanol, which was desirable for direct methanol fuel cell membrane materials.

Table 1. Results of the solubility of SPI in various solvents (48hrs)

Sample	THF	DMAc	NMP	DMF	DMSO	CH ₃ Cl	Ethyl-acetate	n-Hexane	MeOH
6FDA-PI	●	●	●	●	●	●	⊗	⊗	⊗
SPI-20	●	●	●	●	●	▲	⊗	⊗	⊗
SPI-48	●	●	●	●	●	▲	⊗	⊗	⊗
SPI-82	◐	●	●	●	●	⊗	⊗	⊗	⊗
SPI-100	◐	●	●	●	●	⊗	⊗	⊗	⊗

● = Soluble; ◐ = Partially soluble; ⊗ = Insoluble; ▲ = Swollen

Casting film

Serial resulted Sulfonated 6FDA-ODA polyimides (SPI) were dissolved in DMAc by stirring at room temperature. In succession, the solution was cast into an about 200µm deep PTFE model and dried at in a 40°C oven. After above proceeding, the model was

dried further at 120°C for a desired time. As the model cooling down to room temperature, SPI film can be peeled off from the model. It's found that the film fabricated from higher degree SPI was more brittle. It implied the degradation of polyimide backbone. However, the film fabricated from SPI sulfonated less than several hours possessed a good shape.

Conclusion

This research involved the synthesis and characterization of sulfonated polyimide. 6FDA-ODA polyimide were prepared by chemical imidization and sulfonated. The results indicate that 6FDA-ODA polyimide is easily dissolved and sulfonated with concentrated sulfuric acid as reagent. The sulfonation degree of the polymer can be calculated from ¹HNMR spectra and be confirmed by FT-IR and TGA analysis. The sulfonated polymer demonstrated a two-step degradation. Their acid-form with no significant weight loss until ~300°C in TGA at 10 °C/min. The second weight loss, typically at 480°C, was due to the decomposition of the polymer backbone. The TGA results show that SPI has good thermo stability if it is used in a high temperature proton membrane fuel cell system. The first-loss temperatures are considerably above the proposed operation temperature (120 - 150°C) of proton exchange membrane fuel cells. However, recently it's reported [28] that the presence of the hexafluoroisopropylidene groups in the polymer chain induced more easily degradation of molecular. Moreover, it needs a high molecular weight of polymer to cast a useful film. Consequently, the molecular degradation in the sulphonation process and the film mechanic properties will be explored.

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