

Sulfonated Dendrimers for the Application of Fuel Cell Membranes

1. Synthesis and Characterization of Sulfonated Dendrimers

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Abstract: 1,3,5-Substituted polyphenylene type dendrimers were synthesized. The dendrimer was heated in conc. H₂SO₄ at 120°C. The reaction mixture was precipitated to ether after simple filtration to get *para*-sulfonated dendrimer as the chief product. To give mechanical properties to the sulfonated dendrimer, it was partially cross-linked with phenyl ether in the medium of P₂O₅ and CH₃SO₃H.

Keywords: sulfonation, dendrimer, cross-linking, oligomerization, P₂O₅ and CH₃SO₃H

1. Introduction

Dendrimers are the compounds that same units are repeated with exact same sequences. They can be used additives, adhesives, coating materials and membranes. Also, its usage can be extended if there are some functional groups. We developed a simple synthetic method of the dendrimers which have sulfonic acids as a functional group. Sulfonated compounds, which have proton conductivity, have been studied for fuel cell membranes. The sulfonated dendrimers do not have sufficient mechanical properties. However, if they can be cross-linked or blended with high mechanical property polymers, the dendrimers can be a part of a fuel cell membrane.

Dendrimers were synthesized using the methods described earlier[1]. The dendrimers were sulfonated under mild reaction conditions with relatively high yield. We modified direct sulfonation method[2] and obtained *para*-sulfonated dendrimers as the chief product. The sulfonated dendrimers were oligomerized by the reaction with phenyl ether using a dehydrating

agent[3]. The results of the study are presented below.

2. Experimental

2.1. Materials and Methods

All Glassware, syringes, needles were oven-dried overnight before use. All reagents were purchased from commercial sources. ¹H-NMR (200 MHz) and ¹³C-NMR (50 MHz) spectra were recorded on a Varian Gemini 200 spectrometer 20°C in DMSO-*d*₆ with tetramethylsilane (TMS) internal standard. TGA was performed on a TA Instruments Thermal Analyst 2100, TGA 2950. TGA was tested under nitrogen atmosphere.

2.2. Synthesis of Dendrimers

3,5-Dibromophenyltrimethylsilane (**1**): 1,3,5-Tribromobenzene (10.0 g, 31.8 mmol) was dispersed in 100 mL dried ethyl ether under N₂. It was placed in dry ice/methanol bath. BuLi (20 mL (1.6 M in hexanes), 31.8 mmol) was added drop-wise over 5 min. The reaction mixture was stirred for 15 min at -78°C under N₂. Chlorotrimethylsilane (8.1 mL, 63.5 mmol) was added to the mixture. The flask was gradually warmed to room temperature, and left overnight. Water (100 mL)

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was added to the flask and organic layer was collected using a separatory funnel. The organic layer was washed with water twice and brine once and dried with anhydrous MgSO_4 . It was concentrated to get a white powder. This was recrystallized from ethanol/water mixture to get 7.3 g (75% yield). $^1\text{H-NMR}$ (CDCl_3) δ 7.79 (t, 1H, $J_4=1.8$ Hz), 7.72 (t, 1H, $J_4=1.8$ Hz), 0.37 (s, 9H).

3,5-Diphenyl-1-(trimethylsilyl)benzene (2): Phenylboronic acid (3.71 g, 28.9 mmol) in EtOH and 17 mL of Na_2CO_3 (2 M) were placed in a 250 mL round bottom three neck flask and deoxygenated with stream of N_2 for 25 min. 3,5-Dibromophenyltrimethylsilane (4.0 g, 13.1 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.7 g) were placed in deoxygenated toluene (50 mL). Two dispersions were mixed and refluxed under N_2 for 8 h. After cooling to room temperature, the dispersion was poured to a mixture of ether (100 mL) and water (100 mL), and stirred for 30 min. The organic layer was collected and washed with NaOH solution (1 M) and water and brine. It was dried with anhydrous MgSO_4 and concentrated. The crude sample was dissolved in very small quantity of methylene chloride and the solution was passed through a silica gel using n-hexanes as eluent. The hexane was evaporated to get a white powder. It was recrystallized from aqueous methanol to get 3.55 g (90%). $^1\text{H-NMR}$ (CDCl_3) δ 7.79 (t, 1H, $J_4=1.8$ Hz), 7.77-7.64 (m, 6H), 7.57-7.35 (s, 6H).

3,5-Diphenylphenylboronic acid (3): 3,5-Diphenyl-1-(trimethylsilyl)benzene (3.1 g, 10.3 mmol) was dissolved in 20 mL of methylene chloride under N_2 . It was placed in dry ice/ methanol bath. Methylene chloride of BBr_3 (1.5 mL of BBr_3 / 20 mL of methylene chloride) was added drop-wise to the solution over 15 min under N_2 . It was stirred at the temperature for 1 h and warmed up to room temperature over 2 h and heated at 45 C for 16 h. The solution was then cooled to -78°C again. 15 mL of 5 M KOH solution was added drop-wise to the solution over 10 min under N_2 . The solution was warmed up to room temperature. 100 mL of water was added to the reaction mixture and aqueous layer was collected. It was

poured into a mixture of ether (300 mL) and 15% HCl (300 mL). The organic layer was collected and washed with water and brine, and dried over anhydrous MgSO_4 and concentrated to obtain 2.6 g of a white powder (92%). $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ 8.30 (s, 2H), 8.11 (d, 2H, $J_4=1.7$ Hz), 7.95 (t, 1H, $J_4=1.7$ Hz), 7.80 (dd, 4H, $J_3=8.2$ Hz, $J_4=1.5$ Hz), 7.60-7.37 (m, 6H).

3,5-Dibromoacetophenone (4): 1,3,5-Tribromobenzene (15.0 g, 47.5 mmol) was dispersed in 150 mL dried ethyl ether under N_2 . It was placed in dry ice/ methanol bath. BuLi (30 mL (1.6 M in hexanes), 47.5 mmol) was added drop-wise over 10 min. The reaction mixture was stirred for 30 min at -78°C under N_2 . Then, dry DMAc (5 mL, 53.4 mmol) was added drop-wise for 5 min to the mixture. It was gradually warmed to room temperature, and left overnight. It was quenched with 10% HCl (150 mL). The organic layer was collected and washed with water twice and brine once, and dried over anhydrous MgSO_4 . The solvent was evaporated to get a yellow powder. It was recrystallized with ethanol and water to get 8.9 g (67% yield). $^1\text{H-NMR}$ (CDCl_3) δ 8.01 (t, 1H, $J_4=1.8$ Hz), 7.86 (t, 1H, $J_4=1.8$ Hz).

1,3,5-Tris(3,5-dibromophenyl)benzene (6-Br) (5): 3,5-Dibromoacetophenone (3.5 g, 0.0126 mmol), conc. H_2SO_4 (0.23 g) and $\text{K}_2\text{S}_2\text{O}_7$ (4.09 g) were placed in a 100 mL round bottom flask. It was heated at 180°C for 17 h. After cooling to room temperature, 70 mL of ethanol was added and the suspension was refluxed for 2 h. After cooling to room temperature, the ethanol was decanted; 70 mL of water was added and the suspension was refluxed for 2 h. The crude product was isolated by filtration and washed with water and ethanol several times. It was dispersed in 25 mL of chloroform and filtered to get a gray product. $^1\text{H-NMR}$ (CDCl_3) δ 7.74 (s, 9H), 7.66 (s, 2H).

Generation 2 dendrimer: 3,5-Diphenylphenylboronic acid (1.73 g, 6.3 mmol) was dissolved in 20 mL of THF and 20 mL of ethanol and the solution was degassed. It was mixed with 1,3,5-tribromobenzene (0.5 g, 1.6 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.2 g), 30 mL of degassed

toluene and 3 mL of degassed Na_2CO_3 solution (2 M). The mixture was refluxed for 30 h under N_2 . After cooling to room temperature, 70 mL of CH_2Cl_2 and 70 mL of H_2O was added and organic layer was collected and washed with water and brine, and dried over MgSO_4 . It was concentrated to get dark brown gummy material. It dissolved in very small quantity of methylene chloride and the solution was passed through a silica gel using the mixture of CH_2Cl_2 and n-hexanes (1:3 ratio) as eluent. The eluent was evaporated to get a white powder that was recrystallized from CH_2Cl_2 and methanol to get 0.5 g of G2 dendrimer (41% yield).

Generation 3 dendrimer: 3,5-Diphenylphenylboronic acid (5.0 g, 18.2 mmol) was dissolved in 50 mL of THF and 50 mL of ethanol and the solution was degassed. It was mixed with 6-Br (1.25 g, 1.6 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.6 g), 70 mL of degassed toluene and 4 mL of degassed Na_2CO_3 solution (2 M). The mixture was refluxed for 2 days under N_2 . After cooling to room temperature, 500 mL of CH_2Cl_2 and 500 mL of H_2O was added and the organic layer was collected and washed with water and brine, and dried over MgSO_4 . It was concentrated to black gummy material. It dissolved in very small quantity of methylene chloride and the solution was passed through a silica gel using the mixture of CH_2Cl_2 and n-hexanes (1:2 ratio) as eluent. The eluent was evaporated to get a white powder. It was recrystallized from CH_2Cl_2 and methanol to get 1.97 g of G3 dendrimer (65% yield). $^1\text{H-NMR}$ (CDCl_3) δ 8.11 (s, 3H), 8.06 (s, 6 H), 8.04 (s, 3H), 7.91 (s, 12H), 7.83 (s, 6H), 7.70 (d, 24H, $J=7.4$ Hz), 7.53-7.26 (m, 36H).

2.2. Synthesis of Sulfonated Dendrimers

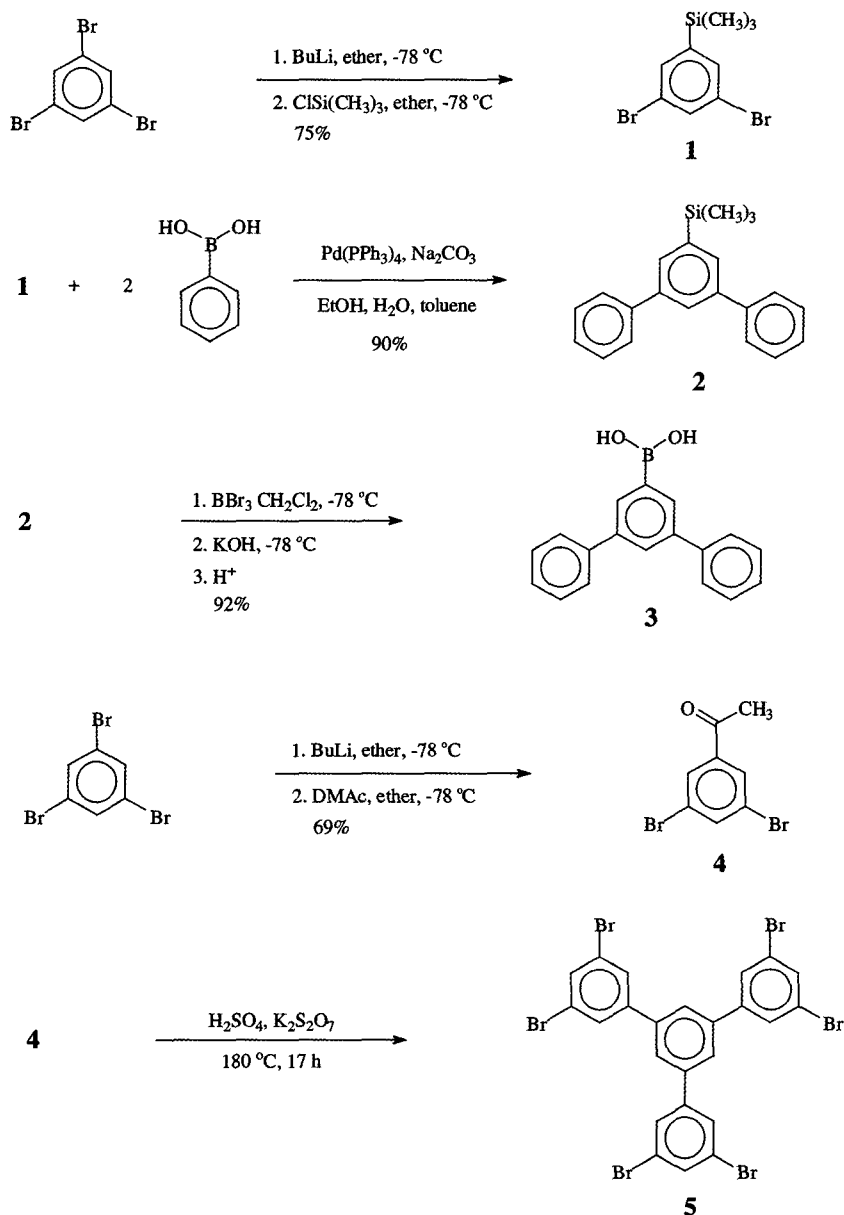
$\text{G1}(\text{SO}_3\text{H})_3$: 1,3,5-Triphenylbenzene (1.0 g, 3.3 mmol) was dispersed in 16 mL of conc. H_2SO_4 and heated at 115°C for 1 h. After cooling to room temperature, it was poured to ethyl ether to get a white precipitate. It was collected by filtration to get 1.6 g (89% yield). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$) δ 7.95 (s, 3H), 7.88 (d, 6H, $J=8.4$ Hz), 7.74 (d, 6H, $J=8.4$ Hz). $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$) δ 147.3, 141.1, 140.2, 126.7, 126.2, 124.6.

$\text{G3}(\text{SO}_3\text{H})_{12}$: G3 dendrimer (0.3 g, 0.18 g) was dispersed in 16 mL of conc. H_2SO_4 . It was heated at 115°C for 1 h. After cooling to room temperature, precipitate was filtered; according to $^1\text{H-NMR}$ analysis, it was partially sulfonated dendrimer (0.22 g) and it was sulfonated further repeating the above procedure. The H_2SO_4 solution was poured into ether to get a white precipitate. It was collected by filtration to get 0.16 g. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$) δ 8.38 (s, 3H) 8.26 (s, 9H), 8.10 (s, 12H), 7.94 (s, 6H), 7.89 (d, 24H, $J=8.1$ Hz), 7.71 (d, 24, $J=8.1$ Hz). $\text{G2}(\text{SO}_3\text{H})_6$ was synthesized using the same method as for $\text{G3}(\text{SO}_3\text{H})_{12}$.

2.3. Synthesis of Oligomer and Cross-linked Sulfonated Dendrimer

Oligomer from $\text{G1}(\text{SO}_3\text{H})_3$ and phenyl ether: P_2O_5 (1.5 g) and $\text{CH}_3\text{SO}_3\text{H}$ (10 mL) was mixed and stirred overnight under N_2 to get homogeneous solution. $\text{G1}(\text{SO}_3\text{H})_3$ (0.4 g, 0.73 mmol) was dispersed in the solution. The reaction mixture was heated at 125°C under N_2 , and phenyl ether (0.11 g, 0.64 mmol) was added. The solution became transparent in 20 min and a precipitate started forming in the solution in 3 h. The heating was continued for 20 h. After cooling to room temperature, the precipitate was removed by filtration. The filtrate was poured into ice water to get a grey powder. It was dried under vacuum at 60°C to get 0.16 g. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$) δ 8.30-7.92 (m, 48H), 7.88 (d, 12H, $J=8.0$ Hz), 7.73 (d, 12H, $J=8.0$ Hz), 7.32 (d, 12H, $J=6.0$ Hz).

Cross-linked dendrimer from $\text{G}_3(\text{SO}_3\text{H})_{12}$ and phenyl ether: P_2O_5 (0.75 g) and $\text{CH}_3\text{SO}_3\text{H}$ (5 mL) was mixed and stirred overnight under N_2 to get a homogeneous solution. $\text{G}_3(\text{SO}_3\text{H})_{12}$ (0.23 g, 0.087 mmol) was dispersed in the solution. The reaction mixture was heated at 125°C under N_2 for 15 min, and phenyl ether (0.016 g, 0.094 mmol) was added. The dispersion was heated for 20 h at 125°C . A small amount of liquid was taken out of the reaction mixture and poured into water. Everything was soluble. Another portion of phenyl ether (0.016 g, 0.094 mmol) was added. After 2 h stirring at 125°C , a small amount



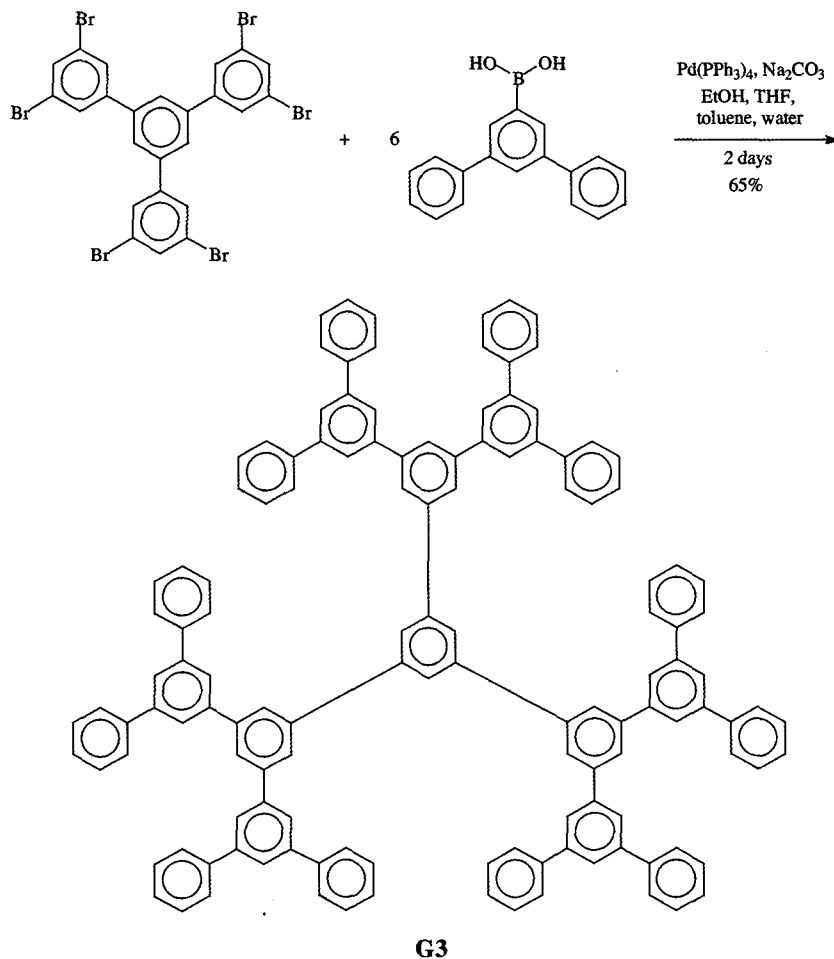
Scheme 1. Synthesis of generation 3 dendrimer, part1.

was taken out of the reaction mixture, and poured into water. Some precipitate was seen. After another 1 h stirring, the reaction was stopped because some material had precipitated. After cooling to room temperature, the precipitate was filtered and washed with water and MeOH to get a gray powder (0.19 g) which was not soluble in organic solvents. The filtrate was poured into water and the precipitate that formed was filtered to obtain 0.09 g of a white powder which was also

insoluble in organic solvents.

3. Results and Discussion

Generation 2 and 3 dendrimers were synthesized using the modified methods described earlier[1]. Schemes 1 and 2 show the synthetic procedures for the Generation 3 dendrimer. The MALDI-TOF of the Generation 3 dendrimer is shown in the Figure 1. The Generation 3



Scheme 2. Synthesis of generation 3 dendrimer, part2.

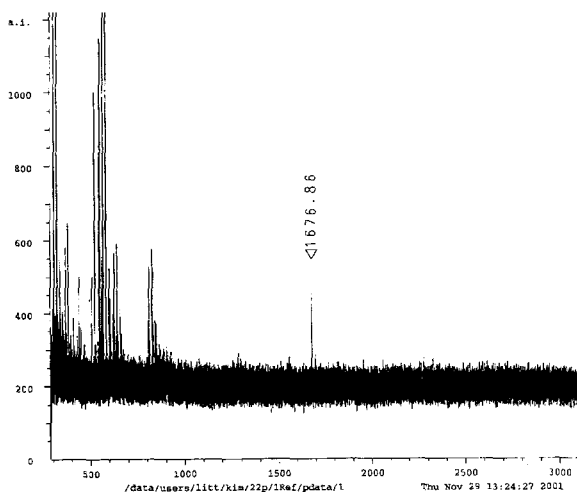
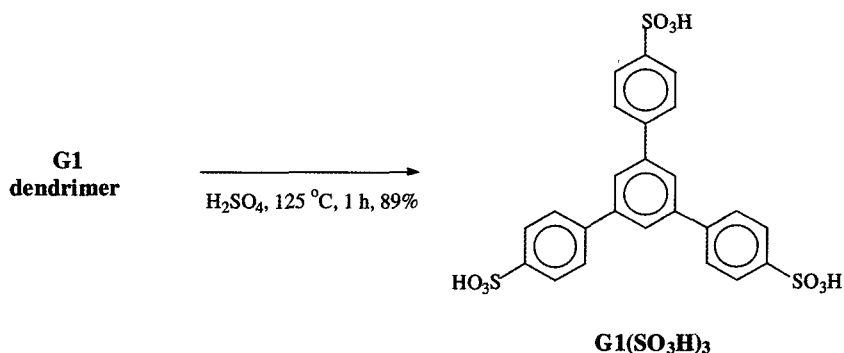
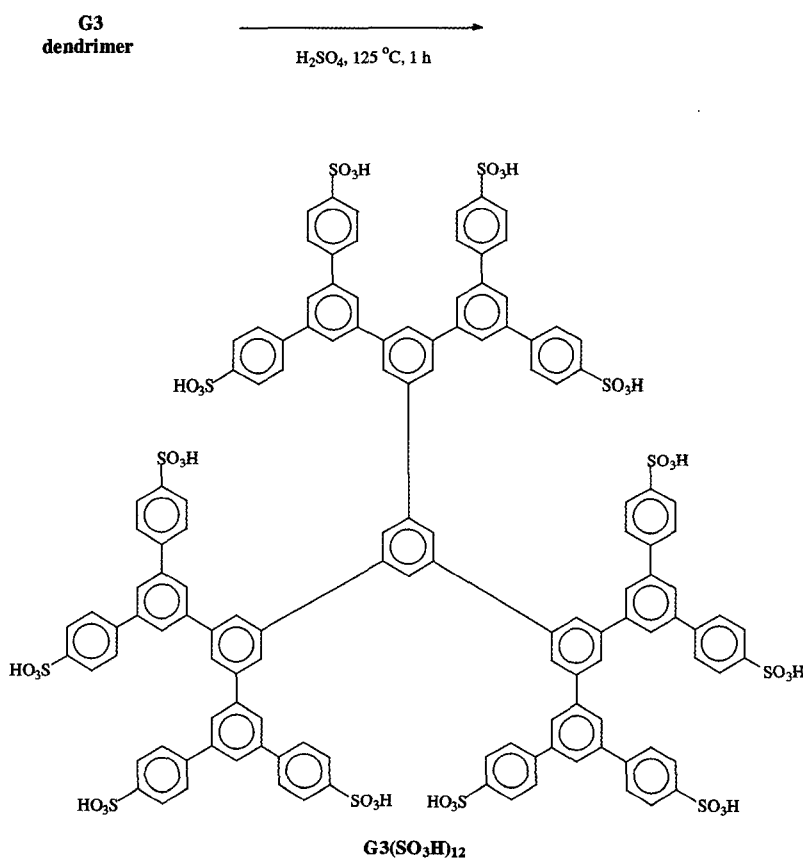


Fig. 1. MALDI-TOF of Generation 3 Dendrimer.

dendrimer has a molecular mass of 1676.17. The isolated peak at 1676.86 is thus due to the protonated dendrimer.

Sulfonated dendrimers were synthesized by a simple and relatively mild method (Schemes 3 & 4). 1,3,5-Triphenylbenzene was sulfonated in the conc. H_2SO_4 with high yield. The $^1\text{H-NMR}$ spectrum is shown in Figure 2. $\text{G3}(\text{SO}_3\text{H})_{12}$ was synthesized using the same method as for $\text{G1}(\text{SO}_3\text{H})_3$ and the $^1\text{H-NMR}$ spectrum is shown in Figure 3. Assignments of peaks for the compound are given in the figures.

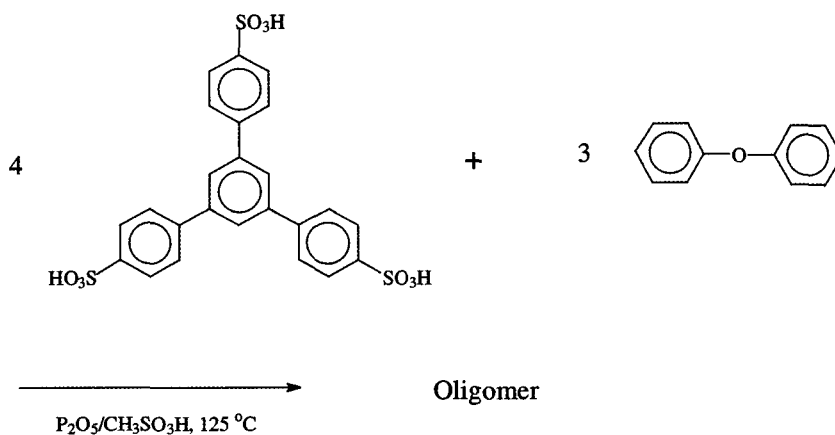
The thermal properties of $\text{G1}(\text{SO}_3\text{H})_3$ and $\text{G3}(\text{SO}_3\text{H})_{12}$ were tested using TGA (rate: $20^\circ\text{C}/\text{min}$). The spectra are shown in Figures 4 and 5, respectively. In Figure 4, the first 15% of weight loss, up to 150°C , corresponds to the loss of about 2 waters per acid group in

Scheme 3. Synthesis of G1(SO₃H)₃.Scheme 4. Synthesis of G3(SO₃H)₁₂.

the sulfonated G1 dendrimer. The second weight loss of 15%, between 150 and 250°C, might be due to the loss of SO₂ in sulfonic acid groups in the dendrimer [1]. The G3(SO₃H)₁₂ also loses about 15% of its weight up to 150°C, which corresponds to a loss of two waters per acid group. There is a further small weight loss, about 3%, below 220°C. The weight decreases contin-

uously above that temperature, indicating the loss of SO₂ in sulfonic acid groups in the dendrimer. The residue for sulfonated G1 dendrimer at 800°C is only 30%. However, sulfonated G3 dendrimer has a residue of 53%, showing that it cross-links extensively. That is usual for such poly-aromatic compounds.

G1(SO₃H)₃ was oligomerized with phenyl ether in



Scheme 5. Synthesis of oligomer from of $\text{G1(SO}_3\text{H)}_3$ and phenyl ether.

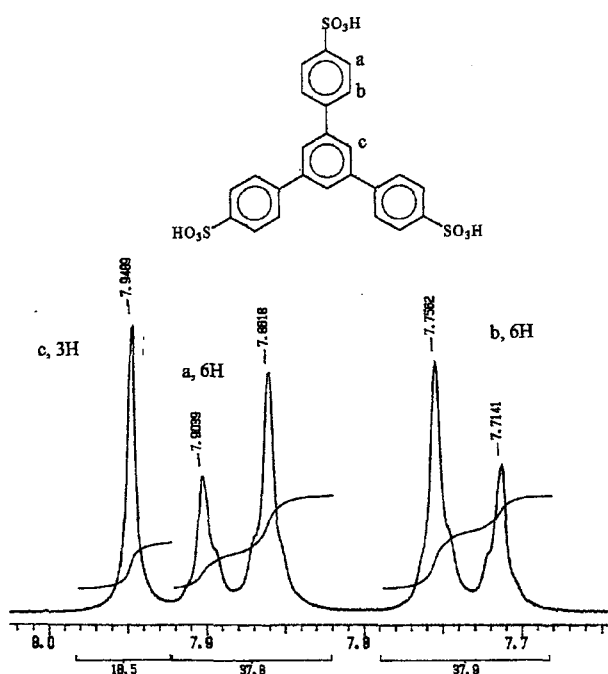


Fig. 2. $^1\text{H-NMR}$ Spectrum of $\text{G1(SO}_3\text{H)}_3$.

the presence of P_2O_5 and $\text{CH}_3\text{SO}_3\text{H}$ [3]. The $^1\text{H-NMR}$ spectrum is shown in Figure 6 and peak assignments are given in the figure. According to the spectrum, all the phenyl ether has reacted with about half of the phenyl sulfonic acids. With same reaction method, $\text{G3(SO}_3\text{H)}_{12}$ was oligomerized. However, there was very fast cross-linking reaction to control the reaction and isolate a soluble product in organic solvent.

Even the preparation of the sulfonated dendrimer membrane, the dendrimers synthesized containing sul-

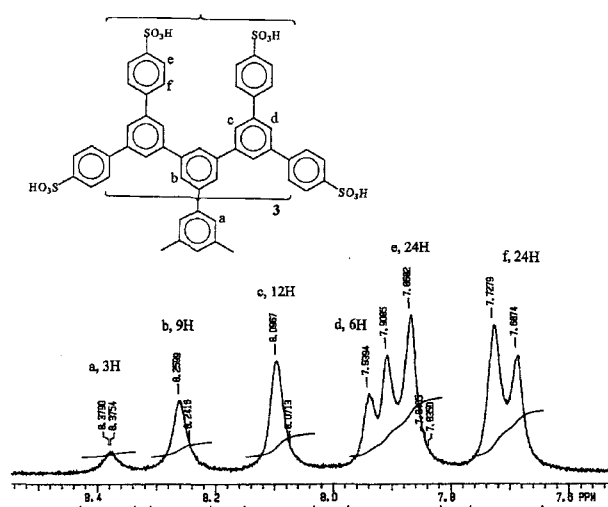


Fig. 3. $^1\text{H-NMR}$ Spectrum of $\text{G3(SO}_3\text{H)}_{12}$.

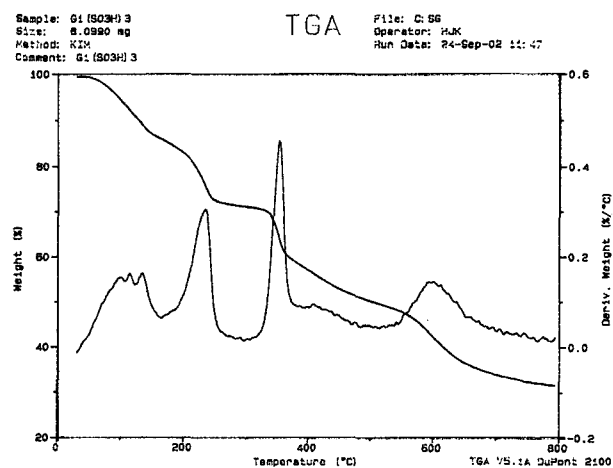


Fig. 4. TGA of $\text{G1(SO}_3\text{H)}_3$.

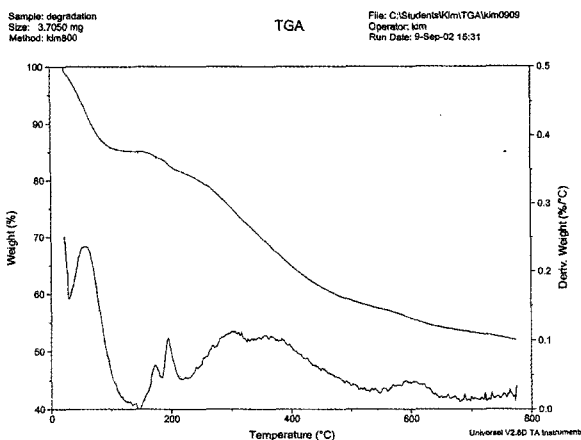


Fig. 5. TGA of G3(SO₃H)₁₂.

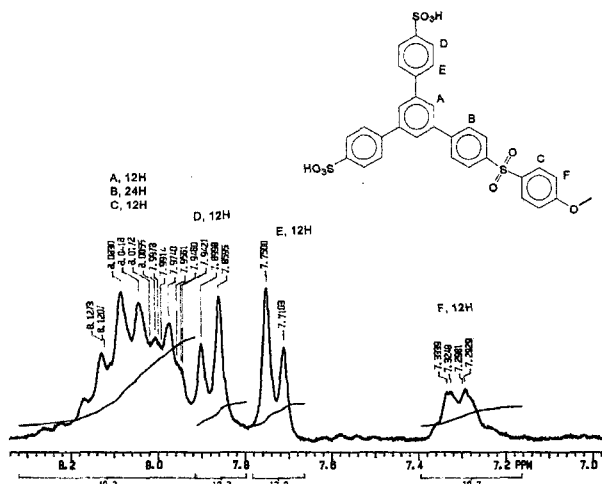


Fig. 6. ¹H-NMR spectrum of Oligomer from G1(SO₃H)₃ and Phenyl Ether.

fonic acid group could be a promising materials for the application of electrolyte membrane of the fuel cell.

4. Conclusions

1,3,5-Substituted polyphenylene type dendrimers were synthesized. The dendrimer was heated in conc. H₂SO₄ at 120°C to get *para*-sulfonated dendrimer as the chief product. In the medium of P₂O₅ and CH₃SO₃H, the sulfonated dendrimer was oligomerized or cross-linked. In case of sulfonated G3 dendrimer, there was very fast cross-linking reaction to control the reaction and isolate a soluble product in organic solvent.

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