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Synthesis of Cation Exchange Membrane from Polypropylene Fabric using Simultaneous Radiation Grafting

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Abstract— **In this work, cation exchange membrane is developed using simultaneous radiation induced grafting technique. Grafting of styrene monomer has been done on polyethylene coated polypropylene fabric (PPF) using different absorbed doses upto maximum of 10 kGy. The sulphonation of styrene grafted PPF has been done by refluxing it in sulphuric acid. Fourier transform infrared spectroscopy (FTIR) has confirmed the grafting of styrene on PPF and the intensity of the phenyl groups is dependent on the amount of absorbed dose. X-ray diffraction (XRD) analysis revealed a decrease in crystallinity of grafted PPF and its sulphonated form. Thermal analysis (TGA) showed marked decrease in the thermal stability of sulphonated PPF as compared to styrene grafted PPF. Scanning electron microscopy (SEM) showed an increase in the thickness of fiber after grafting and sulphonation. In addition, the smooth surface of the fabric is changed into rough surface in sulphonated PPF. The PPF has shown 205.4 % grafting of styrene at 10 kGy and its sulphonated form have an ion exchange capacity value of 3.66 meq/g.**

Index Terms: Gamma radiation; Grafting; Sulphonation; Ion exchange membrane; Polypropylene.

I. INTRODUCTION

Ion exchange membranes are widely used in industrial processes such as: water purification, ion exchange processes and fuel cell applications. With the advancement of technologies and availability of new materials, the focus of interest is to fabricate a cost-effective ion exchange membrane. Radiation induced grafting has been found to be one of the rapid and advanced technique which has been successfully used for fabricating such type of membranes [1]. In water purification applications, it is used for desalination of sea and brackish water, ultrapurification of water and removal of pollutants from waste water [2]. In chemical industry, major application areas are water electrolysis, solvent mixtures separation and recovery of precious metals and gas separation membrane [3-6].

Various types of ion exchange membranes have been developed and classified on the basis of their homogeneity and heterogeneity. Polymer based Ion exchange membranes are usually hydrophilic in nature having ionic groups attached to the backbone of polymer chain. Its characteristics are mostly defined on the basis of base polymer, functional group attached and its method of fabrication. Graft polymerization is one of significant method for the fabrication of functional membranes in which the desired monomers are attached covalently to main chain forming a graft polymer [7] .

Grafting can be initiated by different methods such as: plasma, chemical, thermo-mechanical and with ionizing radiations. In comparison, radiation induced grafting (RIG) is more versatile method for modification of polymeric material from surface to bulk while other processes are limited to surface modification only. The radiation either from gamma source or from electron beam interact with the polymer, produces radicals and ions which initiates the grafting of monomers upto a few millimeters of irradiated substrate [8]. It can be done by simultaneuous irradiation or preirradation methods depending upon the chemical nature of monomers and base polymer. In simultaneous irradiation, both the monomer and base polymer are irradiated at the same time under the ionizing source. In preirradiation method, base polymer is first irradiated and the generated radicals are reacted with the monomer afterwards [9, 10].

In radiation induced graft polymerization, ion exchange membranes are produced by grafting a monomer on base polymer and its modification gave a desired ion exchange charateristics to membrane. The monomers that can be grafted for the purpose are divided into two categories: (i) polar monomers, (ii) non-polar monomers. Polar monomers have futher three categories bearing monomers based on carboxylic acid, sulfonic acid and phosphonic acid. Non-polar monomers are categorized as styrenic and alkyl acrylate monomers [11]. Hegazy et al. reported the fabrication of cation exchange membrane by grafting acrylic acid onto low-density polyethylene film for reverse osmosis process. A single-step method for preparation of sulfonic acid proton exchange membranes (PVDF-g-PSSA) by grafting of sodium styrene sulfonate (SSS) onto irradiated poly(vinylidene fluoride)

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(PVDF) was reported by Nasef [11]. Seko et al. has studied the grafting of 2-hydroxyethyl methacrylate phosphoric acid on polyethylene-coated polypropylene nonwoven fabric [6]. El-Salmawi has used the simultaneous grafting method to graft acrylic acid and stryene onto polypropylene film [12].

In this work, commerically available PPF is converted into styrene grafted cation exchange membrane using simultaneous RIG technique. Both the styrene grafted PPF and its sulphonated form are characterized by different techniques such as: FTIR, TGA, XRD and SEM.

II. EXPERIMENTAL

A. Materials

PPF was obtained from Takasaki Advanced Radiation Research Institute (TARI) and it was manufactured by (Kurashiki MFG Co., Osaka, Japan). Styrene monomer (monomer, > 99 %) and sulphuric acid having purity 98 % were purchased from Sigma Aldrich. All other chemicals like sodium hydroxide, tetrahydrofuran (THF) and ethanol were of analytical reagent grade.

B. Grafting of Styrene on PPF

Simultaneous radiation induced grafting method was used for grafting of PPF in inert atmosphere. PPF was first washed with ethanol and dried in vacuum oven at 60 ^oC. The PPF was placed in glass reactor and purged with nitrogen gas. The mixture of styrene and methanol (styrene : methanol, 4 : 7) was added in each bottle. The samples were purged again with nitrogen gas to make the inert atmosphere in each bottle and sealed subsequently. These bottles were irradiated by gamma rays at Nuclear Institute of Food and Agriculture, Peshawar and three different doses: 5 kGy, 7.5 kGy, 10 kGy at a constant dose rate of 5.40 kGy/h. The grafted samples were washed with ethanol and THF to remove unreacted styrene and homopolymer respectively and dried under vacuum at 60^{o}C till constant weight.

The percentage degree of grafted samples was calculated by following equation:

$$\text{Grafting (\%)} = (W_g - W_o)/W_o \times 100 \qquad (1)$$

Where 'W_o' is the initial weight of ungrafted PPF and 'W_g' is the weight after grafting.

C. Sulphonation of Grafted PPF

Sulphonation of grafted PPF fabric was carried out by refluxing it for two hours in a glass reactor containing sulphuric acid. The change in color of PPF from white to brown determines the sulphonation process (Fig. 1). Ion exchange capacity (IEC) of the sulphonated PPF was measured by using titration method. Dried sulphonated PPF was first equilibrated in 3M NaCl solution for 24 h. The solution was then titrated with NaOH (0.05M) solution using phenolphthalein as an indicator. The IEC was calculated by using the following formula:

$$\text{IECexp} = 0.05 \times V_{NaOH}/W_{dry} \quad \text{(meq/g)} \qquad (2)$$

Where V_{NaOH} was the volume of NaOH solution consumed during titration. W_{dry} is the dry weight of the sulphonated PPF. The different forms of PPF were assigned following identification codes. 'G' denoted the grafted PPF defined the dose (5.0 kGy, 7.5 kGy, and 10.0 kGy). 'S' represented the sulphonated PPF. The overall process involved during the fabrication of cation exchange membrane is shown in Fig. 1.

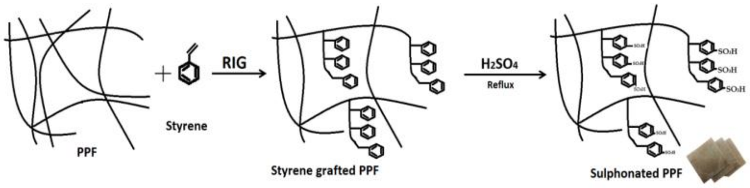

Fig. 1. Chemical Processes involved during the fabrication of cation exchange membrane

Structural analysis was performed with Fourier transform infrared spectroscopy. The spectrum of each sample was collected using Nicolet-6700 FTIR spectrometer (Thermo Electron Corp, Waltham, Massachusetts, USA) in attenuated total reflectance mode. Spectra were collected at a constant spectral resolution of 6 cm^{-1} in the range of 4000-500 cm^{-1} by taking an average of 100 scans. Thermal decomposition behaviour of membranes was studied by using METTLER-TOLEDO TGA/DSC1 thermogravimetric analyzer (Schwerzen-bach, Switzerland). The analysis were performed by heating the samples (~ 10mg) from 30^{o}C to 1000^{o}C at heating rate of 10^{o}C/min in nitrogen environment. X-ray diffraction pattern of PPF and its ion exchange form was obtained by using X-ray diffractometer (Model X' TRA48 Thermo ARL) operating at 45 kV and 40 mA. For all samples, radial scans were recorded in reflection scanning mode from 5^o to 70^o at a scanning rate of 11^o/min at room temperature. Scanning Electron Microscopy (Tescon Mira 3) was used for the morphological studies. The samples were first gold-coated before placement in SEM chamber for analysis.

III. RESULTS AND DISCUSSION

A. Effect of Absorbed dose on Grafting and Sulphonation

Irradiation of polymeric materials under inert atmosphere generated active species (free radicals and ions) on polymer backbone. These active species are responsible for crosslinking, chain scission or grafting of polymer. In simultaneous grafting mechanism, the active species present on the polymer backbone and monomer introduced a grafting link on a polymer chain. Generally, the grafting percentage is increased with the increase in absorbed dose. The simultaneous irradiation of PPF/styrene system gave different grafting percentage at various doses and highest grafting value of 205.4 % is obtained at 10 kGy (see Table 1). The grafted samples were treated with sulphuric acid to get sulphonated products. The ion exchange capacity of sulphonated PPF was determined and presented in Table 1. The ion exchange capacity of PPF grafted at 10 kGy was found to be highest i.e. 3.66 meq/g, because of greater number of grafted styrene groups.

TABLE 1
RADIATION GRAFTING OF STYRENE ON PPF AND THE ION EXCHANGE CAPACITY OF ITS SULPHONATED FORM AT DIFFERENT DOSES

Sample	Dose (kGy)	Grafting (%)	Ion Exchange Capacity (meq/g)
G-5	5	28.6	1.82
G-7.5	7.5	153.6	3.42
G-10	10	205.4	3.66

B. *Structural Analysis*

FTIR spectra of PPF, styrene-g- PPF and its sulphonated product are shown in Fig. 2 (A). This figure shows the structural changes of PPF during grafting of PPF at different doses. In PPF spectrum, peaks at 2913 cm^{-1} and 2847 cm^{-1} correspond to C-H stretching vibration and peaks at 1461 cm^{-1}, 1374 cm^{-1}, 729 cm^{-1} and 717 cm^{-1} are the C-H bending [13].

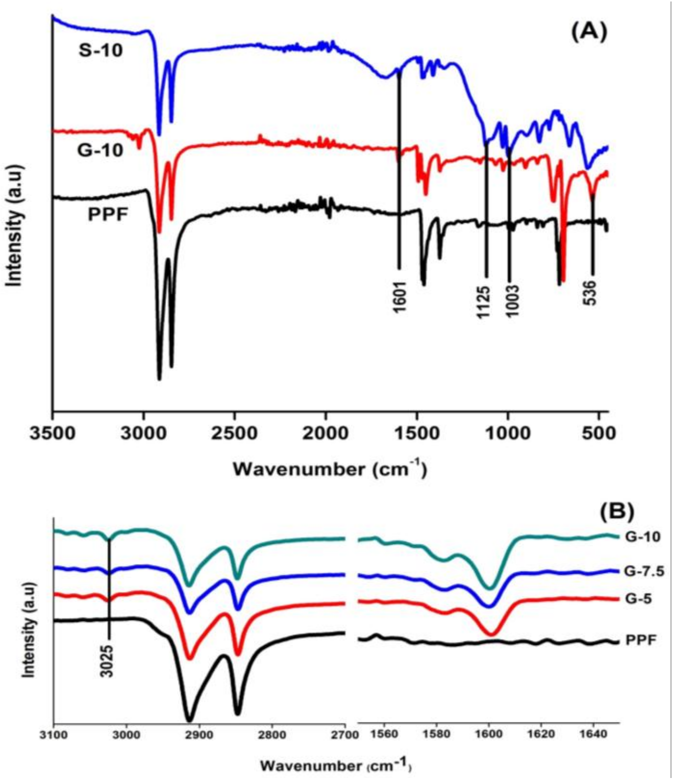

Fig. 2. FTIR spectra of PPF, grafted and sulphonated PPF (A) and comparison of G at different doses (B)

After styrene grafting additional peaks correspond to styrene are observed (G-10). The stretching peaks of aromatic C-H are observed at 3080 cm-1, 3059 cm-1 and 3025 cm-1. Similarly, the stretching vibrations of aromatic C=C bond is present at 1601 cm-1 and 1491 cm-1. Additional peaks are also observed at 696 cm^{-1} and 536 cm^{-1} after grafting that are the out of plane bending of C-H bond as shown in Fig. 2 (A). [13-17]. Sulphonation of styrene also affected the chemical structure and additional peaks belong to new bonds are observed. The peak at 1125 cm^{-1} is attributed to the stretching of C-S bond and the symmetric stretching peak of -SO^{3-} group is observed at 1033 cm^{-1}. The in plane bending of para-substituted phenyl ring is observed at 1003 cm^{-1} that also confirm the sulphonation of PPF [18].

Figure 2B shows the comparison of grafting (%) with absorbed dose on PPF sample. The spectra of styrene grafted PPF obtained at different doses clearly indicates the increase in peaks at 3025 cm^{-1}, 1601 cm^{-1} and 536 cm^{-1} with dose.

C. *Thermogravimetric Analysis*

Thermal stability of PPF, grafted and sulphonated PPF is performed by using thermogravimetric analysis and the thermograms are shown in Fig. 3. It can be seen from the figure that PPF has single step degradation curve. The onset of PPF degradation is started around 257 ^{o}C and its inflection temperature is 386 ^{o}C. The degradation profile of PPF-g-St (G) follows the same trend like PPF. That shows the grafting of styrene has a little effect on the thermal stability of PPF. The styrene grafted PPF followed similar degradation pattern of PPF and the total mass loss of 95.7% is observed at 800 ^{o}C [19, 20].

Fig. 4 shows the degradation profile of sulphonated PPF samples prepared after sulphonation of PPF-g-St obtained at different doses. It is observed from this figure that the onset temperature of degradation is decreased as the amount of sulphonic groups is increased in PPF and the initial mass loss (%) is increased after sulphonation with increase in its amount. The initial mass loss in ‘S’ is due to the removal of water molecules and it reached its maximum value of 55% in S-10. This behavior shows that the hydrophilic sulphonic group imparts hygroscopic nature in that is attached with the sulphonic group via hydrogen bonding. The removal of sulphonic group is started around 286 ^{o}C and continued with the degradation of grafted styrene at 386 ^{o}C. It is difficult to differentiate between de-sulphonation and decomposition of PPF because the mass loss is almost continuous from 220 ^{o}C to 580 ^{o}C. It may be due to the fact that sulphonation enhances the degradation process [21].

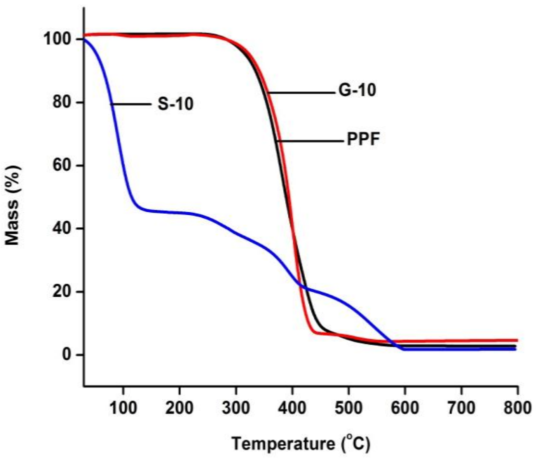

Fig. 3. TGA of PPF grafted at 10 kGy absorbed dose and its corresponding sulphonated form

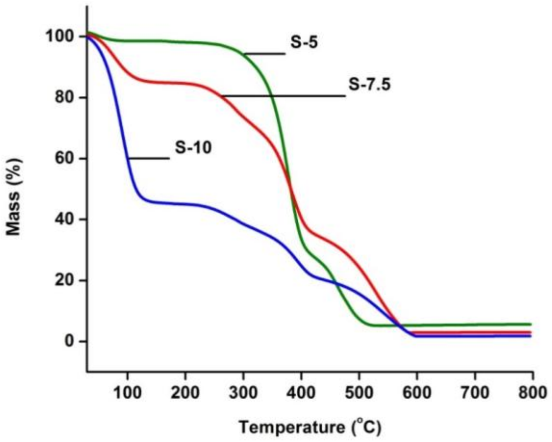

Fig. 4. Effect of sulphonation on the thermal stability of sulphonated PPF obtained at different doses

D. *XRD Analysis*

The effect of styrene grafting and sulphonation on the crystal structure of PPF is shown in Fig. 5 (A). XRD analysis of PPF shows the reflection pattern belong to both polyethylene and polypropylene. The main reflection belongs to polyethylene are present at 19^{o}, 24^{o} whereas the reflection of polypropylene are observed at 22^{o}, 26^{o}, 28^{o}, 31^{o}. Upon grafting of styrene, the crystallinity nature of PPF is affected and decrease in the crystallinity is observed with increase in grafting as shown in figure. Table 2 shows the crystallinity of PPF, styrene grafted PPF and its sulphonated form. It is observed from this table that crystallinity of PPF is 82 % and it decreased to 49.1 % in G-10. It is observed that increase in absorbed dose has introduced more styrene group on PPF which reduces the packing density of the molecular chains. The sulphonation of G-10 further lower the crystallinity from 49.1 % to 31.9 %.

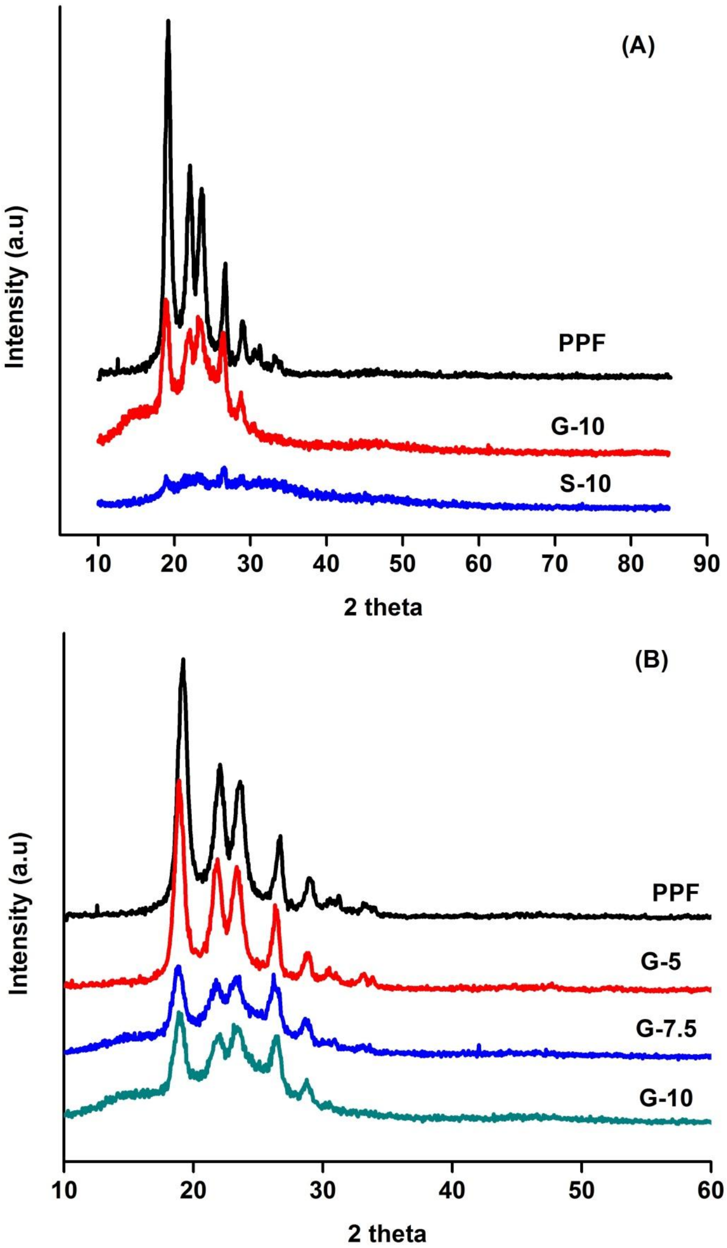

Fig. 5. XRD analysis of grafted and sulphonated PPF (A) and the effect of grafting on crystal structure of grafted PPF

TABLE 1
PERCENTAGE CRYSTALLINITY OF PPF, PPF-G-STYRENE AND SULPHONATED PPF

Samples	F	G-5	G-7.5	G-10	S-5	S-7.5	S-10
Crystallinity (%)	82	79.4	59.4	49.1	77.3	55.9	31.9

E. *Field Emission Scanning Electron Microscopy*

The presence of styrene grafting and sulphonation can be predicted by the change in morphology PPF. The morphological images of PPF and its grafted form at different magnifications are shown in Fig. 6. An increase in the thickness of fibers is seen indicating the grafting of styene monomer on PPF. This increase is due to grafting of styrene as polystyrene on base polymer. The comparison of sulphonated form with its corresponding grafting form reveals that the sulphonation of styrene grafted PPF further increased the size of the fiber and made its surface rough. Table 3 shows the elemental analysis of sulphonated PPF grafted at different doses. At lower dose the sulphonic groups are present in lower amount whereas the weight percentage is increased upto 12% at 10 kGy absorbed dose. It is due to the fact that increase in the grafting of styrene monomer allows more sulphonic groups to get attached.

TABLE 2
ELEMENTAL COMPOSITION OF SULPHONATED PPF

SAMPLE	ELEMENTAL COMPOSITION		
	CARBON (%)	OXYGEN (%)	SULPHUR (%)
S-5	79.14	14.29	6.56
S-7.5	75.24	13.62	11.14
S-10	70.56	17.08	12.35

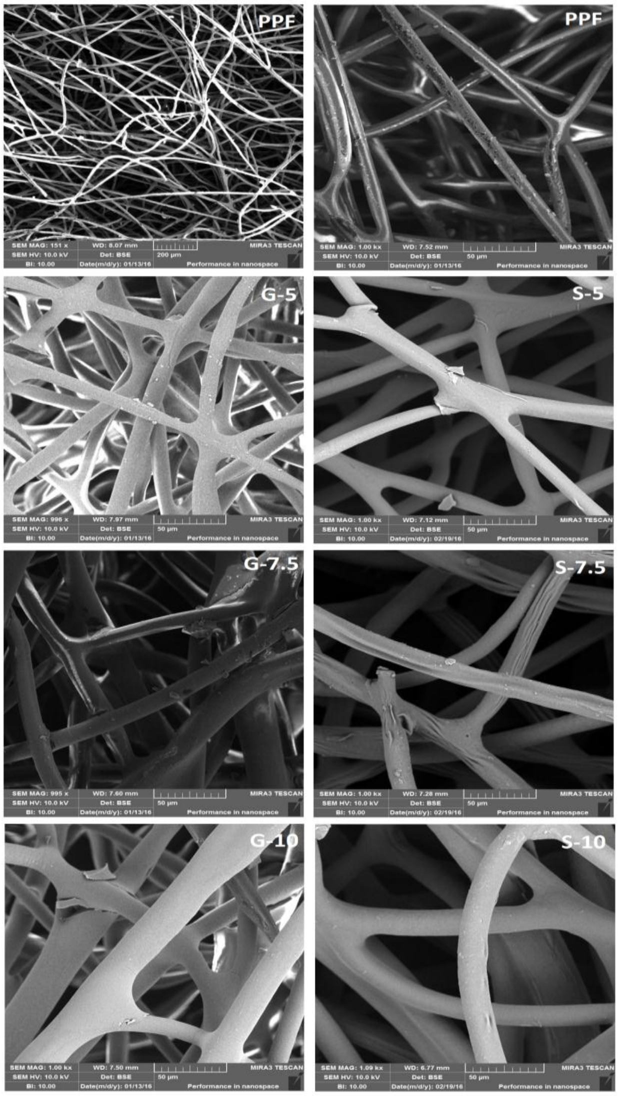

Fig. 6 FESEM images of PPF, PPF grafted with styrene at different absorbed dose and its sulphonated form.

IV. CONCLUSIONS

Cation exchange membrane was successfully prepared by using simultaneous RIG technique. These membranes were analyzed by various characterization techniques. FTIR spectroscopy confirmed the grafting of styrene on PPF and its conversion to sulphonated form. The degree of grafting was enhanced by the absorbed dose. Styrene grafted PPF obtained at 10 kGy showed maximum grafting of 205.4 % showed an ion exchange capacity of 3.66 meqg^{-1}. TGA result shows the presence of large amount of adsorbed water in sulphonated PPF which confirms the presence of sulphonic groups in PPF. Change in crystallinity and morphology during grafting and sulphonation also supported these results.

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