

Proton Exchange Membranes by Grafting of Styrene–Acrylic Acid onto FEP by Preirradiation Technique. II. Physicochemical Properties of the Membrane and Its Sulfonated Derivatives

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Received 8 April 2003; accepted 27 October 2003

ABSTRACT: Poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP)-g-styrene–acrylic acid and its sulfonated derivative membranes were prepared by graft copolymerization of styrene–acrylic acid onto FEP by using preirradiation of γ -ray technique followed by sulfonation. The physicochemical properties such as ion exchange capacity, water uptake, ionic resistance of the grafted membranes, and their sulfonated derivatives were studied as a function of degree

of grafting. These membranes on sulfonation gave acid base, indicating property. The membranes gave yellow color in acidic medium and purple color in alkali medium. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2318–2325, 2004

Key words: FEP; styrene–acrylic acid; radiation grafting; sulfonation; indicator property

INTRODUCTION

Radiation grafting is a convenient route to the synthesis of ion exchange membranes. By varying the reaction parameters, the grafting can be controlled to get the desired property.¹ Synthesis of proton exchange membranes by radiation grafting of various vinyl monomers onto fluorinated polymers has been widely studied.^{2–14} Fluoropolymers are preferred because of their excellent mechanical as well as chemical stability. Use of fluorinated ethylene propylene copolymer (FEP) as base polymer is advantageous because of its high irradiation resistance compared to Teflon.¹⁵ Grafting of different monomers onto FEP has been carried out by a number of research groups.^{5–6,8–12,14,16,17}

Our attempt has been to synthesize membrane having more than one type of ion exchange group so as to get better performance. In our previous study, we carried out grafting of styrene–acrylic acid comonomer pairs onto FEP by preirradiation technique and studied the effect of various reaction parameters on the degree of grafting.¹⁸ It was observed that stringent monomer purification and oxygen-free environment resulted in graft copolymerization following classical free-radical polymerization kinetics. It was also reported that on sulfonation these grafted membranes behave similar to acid base indicator. The present work deals with sulfonation and physicochemical

properties of the grafted membranes and their sulfonated derivatives as a function of degree of grafting.

EXPERIMENTAL

Materials

FEP films (75 μm) were received from DuPont (Wilmington, DE). Styrene (Fluka, Buchs, Switzerland) was freed from inhibitor by standard method and then vacuum distilled. Acrylic acid (Fluka) was purified by vacuum distillation. Benzene was freed of thiophene by washing with concentrated sulfuric acid as per the procedure given elsewhere.¹⁹ It was then distilled under vacuum and dried over sodium wire. Concentrated sulfuric acid (AR grade) was obtained from Qualigen (India).

Irradiation

FEP films were washed with acetone and dried at 50°C. These were irradiated by using γ -rays from a Co60 source with a dose rate of 10–9.5 kGy/h.

Method of grafting

The grafting was carried out as per the method reported in our earlier publication.¹⁸ The irradiated film was placed in a glass ampoule containing styrene and acrylic acid solution in benzene. The monomer concentration in benzene was in the range of 20–100% (in volume). The ratio of styrene to acrylic acid was maintained at 52 : 48 (mole ratio) for all the grafting reac-

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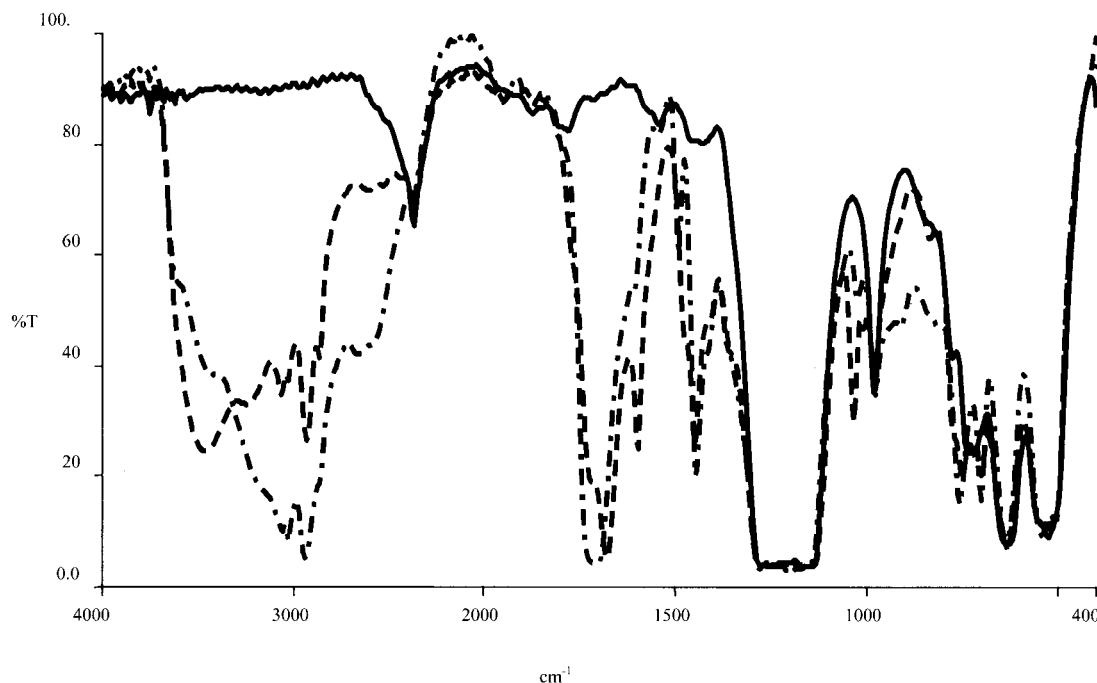


Figure 1 FTIR spectra of (—) FEP, (---) FEP-g-ST-AA, and (- - - -) FEP-g-STAA-SO₃H.

tions. Prior to sealing the ampoule, the content was freed from dissolved oxygen/air by repeated freezing and thawing under vacuum. Three freeze-thaw cycles were found adequate. Finally, the ampoules were sealed, brought to room temperature, and placed in an oil bath maintained at 70°C for polymerization. The degree of grafting was calculated by using the equation

$$\text{Degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100$$

where W_g is the weight of grafted film and W_0 is the weight of ungrafted film.

Sulfonation

The grafted membranes were taken in a hard glass tube and sulfonated in concentrated sulfuric acid at room temperature for different time intervals with constant stirring. The sulfonated membranes were then washed with distilled water until free from acid and stored in distilled water for further study.

Water uptake

The water uptake was measured by boiling the membrane in water for 4 h and left overnight to equilibrate. The membranes were removed from the water, blotted with absorbent paper to remove water adhering to the surface, and weighed. The membranes were then

dried in a vacuum oven at 80°C for 24 h and the dry weight was noted. The water uptake was calculated by

$$\text{Water uptake} = \frac{W_w - W_d}{W_d} \times 100$$

where W_w is the weight of wet membrane and W_d is the weight of dry membrane.

Ion exchange capacity (IEC)

The membrane samples in acid form were placed in 50 mL of 0.1N NaOH solution and left for 24 h at room temperature. The IEC was measured by back titrating the NaOH with 0.1N oxalic acid by using a phenolphthalein indicator. The ion exchange capacity was calculated as

$$\text{IEC (meq/g)} = \frac{(N_1 - N_2)XV}{W}$$

where N_1 and N_2 are normality of NaOH before and after exchange, V is volume of NaOH in milliliters, and W is the weight of dry membrane in grams.

IR spectroscopy

IR spectra of FEP and styrene-acetic acid-grafted FEP films were recorded by using a 1650 Perkin-Elmer FTIR.

TABLE I
Effect of Extent of Grafting on Polymer Composition

Degree of grafting (%)	IEC (meq/g)	Average composition of sty/ acrylic acid in graft chain	
		Calculated*	Experimental
7	0.404	49/51	44/56
11	0.693	49/51	41/59
24	1.195	49/51	46/54
30	1.55	49/51	49/51
46	1.733	49/51	51/49

* Based on Lewis–Mayo equation.

UV–vis measurements

Sulfonated membranes with different degrees of grafting were scanned by using a Varian Cary 500 scan UV–Vis spectrophotometer. The absorbance of these membranes was measured over the wavelength range of 350–700 nm.

Ionic resistance

A DC conductivity setup was employed to determine the ionic resistance of the membrane as per the method given elsewhere.²⁰ The resistance of the grafted membranes and sulfonated derivatives was measured by using 0.1 and 0.5M H₂SO₄ by applying DC pulse current and measuring the potential difference between the two Calomel reference electrodes. The conductivity setup consists of a membrane holder, in which membrane is fixed. The membrane separates the cell into two compartments. Two platinum electrodes are inserted into these compartments. The electrolyte was continuously flown through the compartment under gravity flow. The potential difference was measured in both modes by switching the polarity of

the electrodes at different current densities. All the potential difference-measured values are an average of steady-state values of forward and reverse flow. PAR model 173 potentiostat was used for applying current and an ADAM 4000 analog card was used for measuring potential difference. The membrane resistance was obtained by subtracting cell resistance measured in the absence of the membrane. All measurements were carried out at 25°C.

RESULTS AND DISCUSSION

Graft copolymers of FEP and styrene–acrylic acid having different degrees of grafting were prepared as per the procedure given in Experimental. As reported earlier,¹⁸ for all the grafting, the monomer feed composition of styrene and acrylic acid was constant [i.e., 52 : 48 (mole ratio)]. A few membranes with different degrees of grafting were sulfonated. The presence of the sulfonic acid group was confirmed by FTIR. The peak at 1040 cm⁻¹ represents the sulfonic acid group in the FTIR spectrum shown in Figure 1. The grafted membranes and their sulfonated derivatives were evaluated for the physiochemical properties such as ion exchange capacity, water uptake, ionic resistance, and indicator property (in the case of sulfonated derivatives).

Ion exchange capacity

Table I shows the variation of IEC with degree of grafting. As expected, IEC increases with the increase in the degree of grafting. A similar trend was obtained in the case of FEP-g-styrene–SO₃H.^{14,16}

The composition of the styrene–acrylic acid copolymer in the grafted membranes was calculated from the IEC values and represented in Table I and Figure 2. It

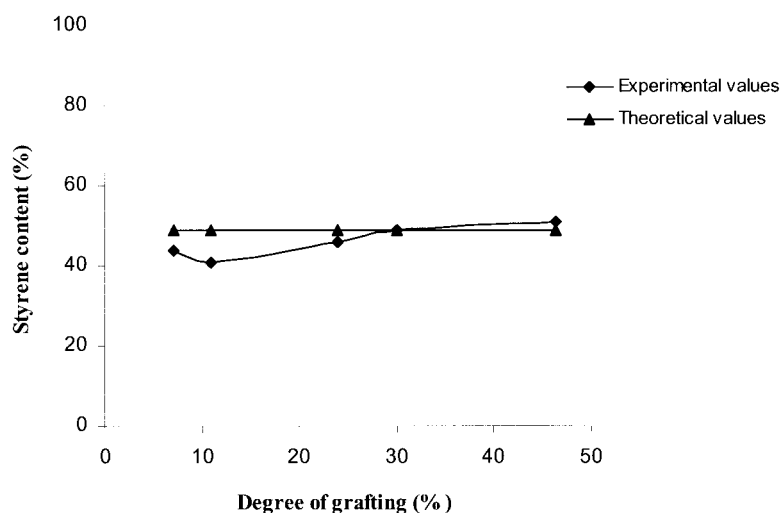


Figure 2 Variation of copolymer composition with degree of grafting.

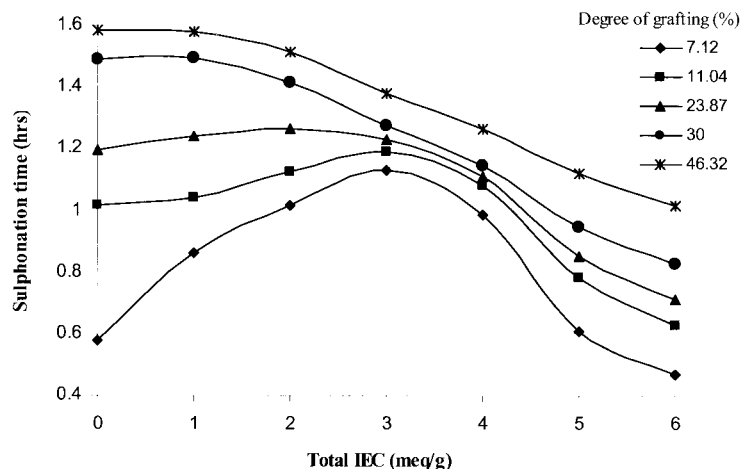


Figure 3 Variation of IEC with sulfonation time for membranes with different degree of grafting.

is seen from the table that the composition varies with degree of grafting. In our earlier study,¹⁸ we had assumed that monomer feed composition of 52 : 48 (styrene : acrylic acid) would give a 49 : 51 copolymer composition calculated by the Lewis–Mayo equation on the basis of the reported value of reactivity ratio from literature. It seems this assumption does not hold fully for grafted membrane. In fact, the grafted membrane is richer in acrylic acid than in styrene at a lower degree of grafting. However, as the degree of grafting increases, the fractions of the two monomers in the grafted membrane come closer to calculated values. During grafting of styrene in combination with various polar monomers onto low-density polyethylene (LDPE) and Teflon, Odian et al.^{21,22} observed that the grafted polymers are richer in polar monomer. They have attributed it to the polar effect of monomer, wherein during grafting preferential sorption of polar monomer occurs by the growing and relatively immobile chain. Similarly, in the present case, it appears

that acrylic acid being relatively polar solvates the grafting growing chain, resulting in richer acrylic acid grafted copolymer. As the grafting proceeds, the concentration of acrylic acid reduces. Conversely, the medium becomes richer with styrene, which, in turn, contributes to an increase in styrene fraction. Thus, at 30% grafting, the copolymer composition in the grafted polymer matches with the calculated value. Beyond this level of grafting, the styrene content increases in the grafted copolymer. This ambiguous observation was reflected in other properties of the membrane.

The IEC values for the sulfonated derivatives are given in Figure 3. It was observed in our earlier study²³ that during sulfonation of styrene-co-acrylic acid, the acrylic acid moiety undergoes cyclization, resulting in a condensed ring structure. This phenomenon takes place only when the maximum number of styrene and acrylic acid units are alternate to each other. From Fig. 3 it is seen that at a lower degree of

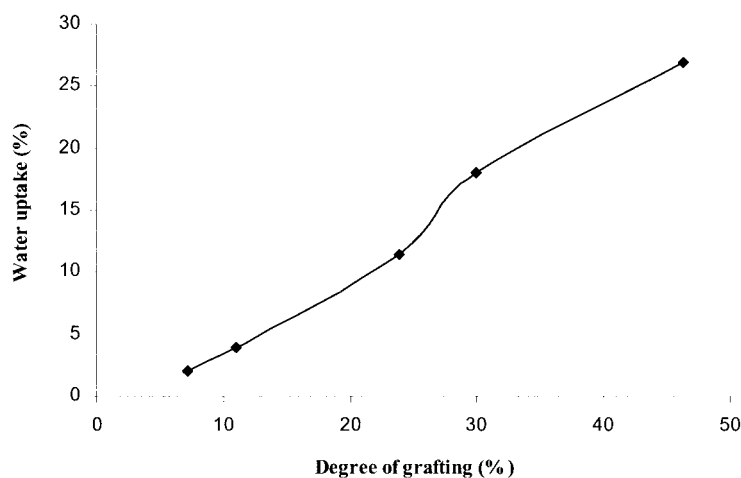


Figure 4 Variation of water uptake with degree of grafting.

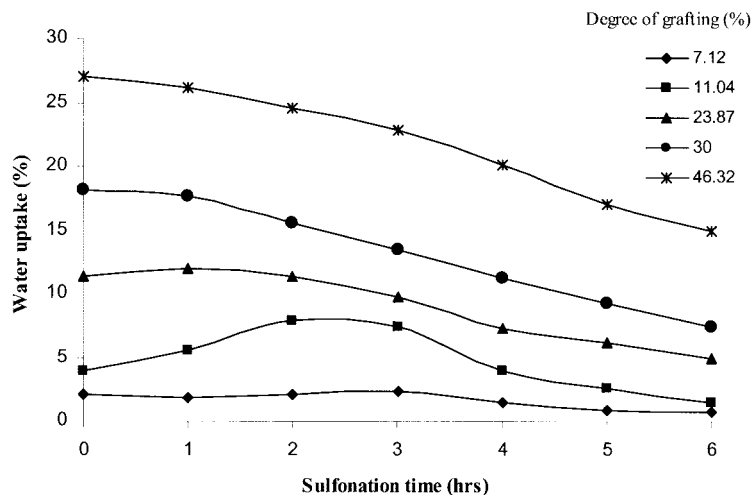
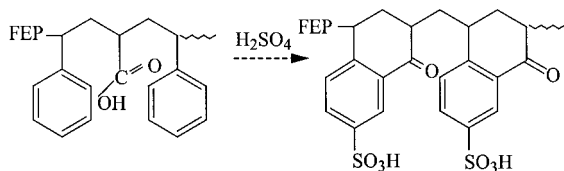


Figure 5 Variation of water uptake with sulfonation time for membranes with different degree of grafting.

grafting the IEC increases slowly, reaches a maximum value, and then decreases. This behavior can be explained on the basis of two factors: first, at a lower degree of grafting, the grafted chains are richer in acrylic acid and hence, a maximum number of styrene and acrylic acid units are not alternate to each other. As sulfonation proceeds, the benzene ring of styrene gets sulfonated, resulting in higher IEC. Second, as the time of sulfonation increases, acrylic acid undergoes the intramolecular cyclization involving styrene and acrylic acid placed alternate to each other, thereby reducing the IEC.²³

At a higher degree of grafting, the styrene and acrylic acid units are assumed to be almost alternate to each other (r_1 and r_2 values of styrene and acrylic acid are 0.15 and 0.25, respectively²⁴), and hence, on sulfonation, the IEC slowly decreases as the acrylic acid undergoes cyclization. This result further confirms the earlier observation about the composition of the copolymer at different levels of grafting in the grafted membrane. Also, the theoretically calculated IEC does not match with the experimental IEC, because of the cyclization of the acrylic acid during sulfonation of the benzene ring of styrene.



Water uptake

Figure 4 shows the variation of water uptake with the degree of grafting. Water uptake is directly related to the number of polar groups present in the membranes.

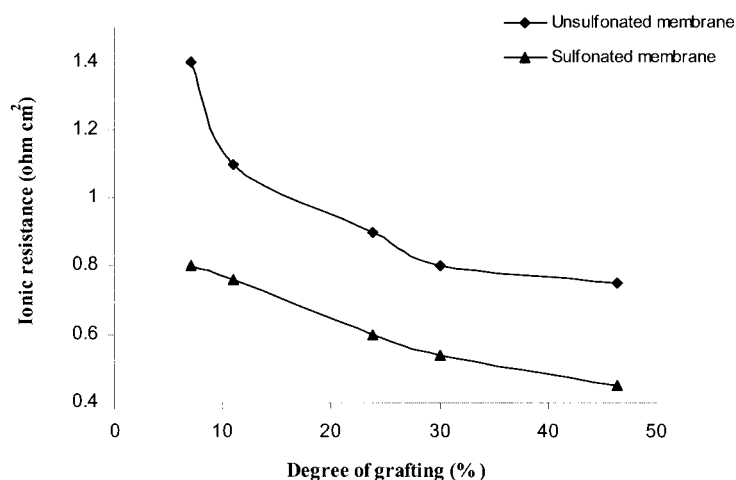


Figure 6 Variation of ionic resistance with degree of grafting.

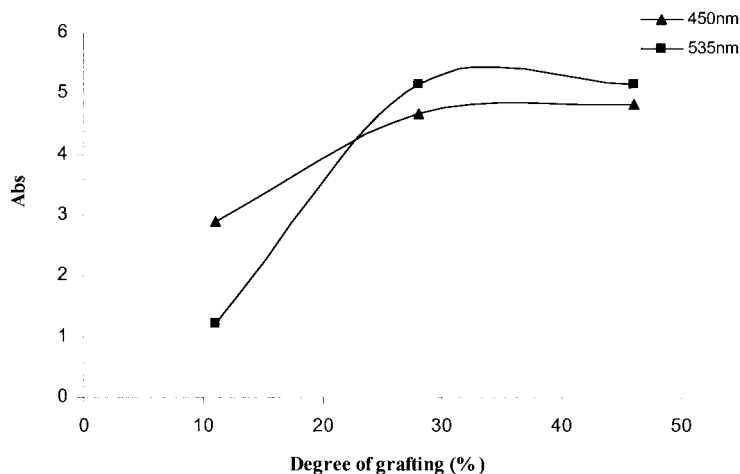


Figure 7 Variation of absorbance at 450 and 535 nm with sulfonation time.

As can be seen, the water uptake increases with the increase in degree of grafting, because a greater number of polar groups are present. Similar results were observed by Hegazy and coworkers²⁵ in the case of FEP-g-acrylic acid. Furthermore, with an increase in grafting, there is a decrease in the crystallinity of the polymeric matrix and hence the water molecules can reach the ionic sites at the middle of the film, thereby increasing water uptake.¹⁷

On sulfonation, the water uptake follows the same trend as that of IEC, as shown in Figure 5. The water uptake increases initially, reaches a maximum value, and then decreases for membranes with a lower degree of grafting. This can also be explained on the same lines as that for IEC. For a higher degree of grafting, the water uptake decreases as the time of sulfonation increases. This observation further confirms that there is a loss of —COOH as it undergoes intramolecular cyclization involving styrene and acrylic acid.

Ionic resistance

The ionic resistance of the grafted membranes as a function of degree of grafting is shown in Figure 6. The ionic resistance decreases with the increase in the degree of grafting. This decrease in resistance can be explained based on the fact that at a lower degree of grafting, the grafting is limited to the surface as the core of the polymeric matrix remains ungrafted, offering high resistance to the movement of H⁺ ions. As the grafting proceeds further through the membrane, it becomes homogenous and water uptake increases. As a result, the H⁺ mobility increases and there is a decrease in resistance. At a higher degree of grafting, the composition becomes homogeneous throughout the membrane and this facilitates the H⁺ mobility through the membrane.^{16,25} Yet the resistance of mem-

brane even with a higher degree of grafting is higher compared to NAFION because of weakly acidic characteristics of the —COOH group. On sulfonation, the ionic resistance decreases further because of the incorporation of the strong —SO₃H group, which increases the hydrophilicity of the membrane further and results in higher mobility of the H⁺ ions through the grafted membrane.

Indicator property

The sulfonated membranes show yellow color in acidic medium and purple color in alkaline medium. The mechanism of color change was explained elsewhere.²³ Styrene-acrylic acid copolymer during sulfonation undergoes an internal Friedel Crafts acylation followed by cyclic dehydration leading to a conjugated structure. Sulfonated membranes with

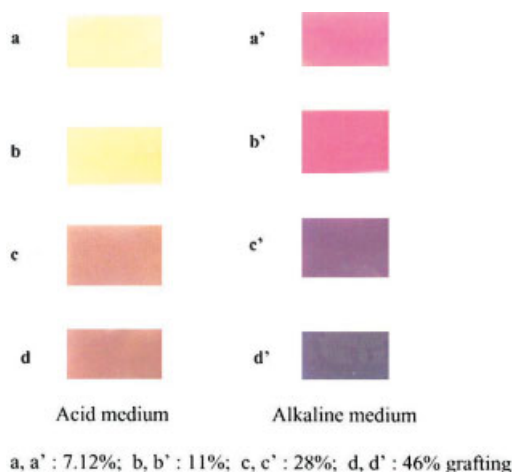


Figure 8 Variation of color change with degree of grafting (sulfonation time 4 h).

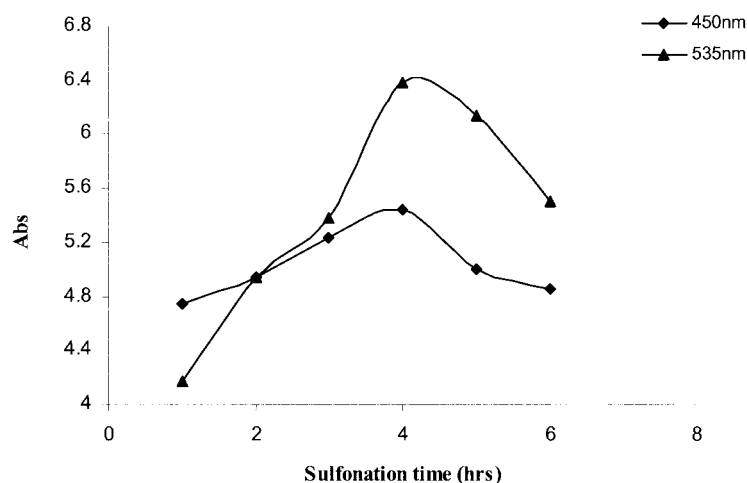
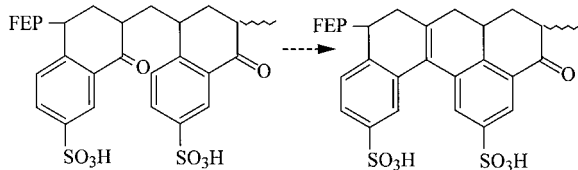


Figure 9 Variation of color change with degree of grafting FEP-g-STAA-SO₃H (sulfonation time 4 h) a, a', 7%; b, b', 11%; c, c', 28%; d, d', 46%.

different degrees of grafting were scanned in a UV-Vis spectrophotometer over the range 350–700 nm. The membrane in the acid form shows a broad peak at 450 nm, which in alkaline form shows a broad peak at 535 nm. The absorbance at 450 nm and of 28% grafted and sulfonated membrane in acid form versus sulfonation time is shown in Figure 7. It is seen that as the time of sulfonation increases the absorbance at 450 nm increases and reaches a maximum value at 4 h of sulfonation and then decreases on further sulfonation. A similar trend is observed when the absorbance of the membrane in alkaline medium is recorded at 535 nm (Fig. 7). This may be explained by assuming that at 4 h of sulfonation time there is maximum cyclization of the acrylic acid, resulting in an increase in color intensity. Beyond which, further intramolecular condensation takes place, resulting more of cyclic hydrocarbon structure, as depicted below.



Variation of color changes and their intensity with degree of grafting both in acid as well as in alkaline medium was presented in Figures 8 and 9, respectively. From Figure 9, it is seen that, as the degree of grafting increases, the absorbance for membrane in acid as well as alkaline medium at 450 and 535 nm, respectively, increases. This is because at a higher degree of grafting a larger number of styrene and acrylic acid units are alternate to each other and hence more cyclized structures are formed, which contribute to the increase in color intensity.

CONCLUSION

1. Composition of grafted chains of styrene-acrylic acid monomer pairs is different in overall graft copolymer graft at different levels of grafting. At the initial stage of grafting, grafted chain is richer in acrylic acid because of the polar effect. At a higher level of grafting, the composition matches with the calculated value.
2. Physicochemical properties such as IEC, water uptake, and ionic resistance are dependent on degree of grafting, composition of graft, and sulfonation level.
3. Intensity of color change for a sulfonated derivative of grafted membrane is dependent on sulfonation time. Beyond 4 h of sulfonation, the intensity decreases because of formation of cyclic hydrocarbon structure via intramolecular cyclization.

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