Proton Exchange Membranes by Grafting of Styrene–Acrylic Acid onto FEP by Preirradiation Technique. I. Effect of Synthesis Conditions

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ABSTRACT: Grafting of styrene–acrylic acid (sty–AA) polymer onto fluorinated ethylene propylene copolymer (FEP) was carried out by preirradiation of FEP with γ-rays. Effect of reaction conditions on the degree of grafting such as total radiation dose, monomer concentration, temperature, and time of grafting has been studied. From the study, it is seen that the degree of grafting is strongly dependent on the reaction conditions. The rate dependence of 0.53 ($\sim$0.5) and 1.03 ($\sim$1) have been obtained with respect to total dose and monomer concentration, respectively indicating that radiation induced grafting follows free radical polymerization. The activation energy for the grafting in the temperature range of 60–90°C is found to be 33 kJ/mol. The results indicate that the grafting takes place by the front mechanism where the grafting starts at surface and slowly proceeds inwards by diffusion of the monomer through the swollen grafted chains. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2572–2577, 2003

Key words: FEP; styrene–acrylic acid; radiation grafting; kinetics

INTRODUCTION

Radiation induced graft copolymerization is a novel method of modifying polymer structure. This method is very useful specially when it is required to modify fluorinated polymer as these polymers are not susceptible to chemical attack by common reagents and grafting by conventional method is not possible due to strong C—F bond energy. Considerable amount of work has been reported in literature on grafting of various monomers into fluorinated polymers.[1–7] One major area of work on polymer modification is being carried out by a few selective group of researchers[8–11] is development of ion-exchange membrane based on fluoro polymer for applications such as fuel cell, electro dialysis, etc. The most widely used cation-exchanging group in these types of membranes is $-SO_3H$ group due to its strong acidic characteristics. However, membranes having $-SO_3H$ group swell in water to a large extent due to its high hydrophilicity, whereas membranes having –COOH group are weakly acidic, less hydrophilic, and swell to a lesser extent in water. Due to low water content in these membranes, the transfer of water and solute is low. Few patent applications report that membranes having different ion exchange groups perform better than membranes having one type of ion-exchange group.[12]

In an earlier study,[13] it has been observed that sulfonated styrene–acrylic acid (sty–AA) copolymer beads, a polyelectrolyte, show acid–base indicator property in addition to its ion-exchange property. Since the resin is pH sensitive, it can be used as reusable pH sensor probe, ion-exchange cum indicator, reusable pH indicator. However, the resin is relatively brittle and cannot be cast into a film. A study has been undertaken to graft sty–AA into fluorinated ethylene propylene copolymer (FEP) by γ-radiation methods and subsequently sulfonate to get sulfonated FEP-g-sty–AA membrane. The present manuscript deals with study of reaction conditions on degree of grafting of sty–AA monomer pair into FEP.

EXPERIMENTAL

Materials

The base polymer FEP in the form of film thickness 75 μ was obtained from Dupont and used for grafting. Styrene obtained from Fluka was freed from inhibitor by standard method. The inhibitor free monomer was vacuum distilled at 30°C to get pure styrene. Acrylic acid (Fluka) was purified by distilling in presence of Cu turning under vacuum prior to use. Solvents such as benzene, methanol were of reagent grade. Benzene was freed from thiophene by shaking with concentrated sulfuric acid as per the procedure given elsewhere.[14] The thiophene free benzene was dried initially with calcium chloride and then placed over sodium wire.

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Irradiation

FEP films were cut into desired sizes (7 × 7 cm^2) and soxhleted with methanol. They were then dried and exposed to γ-rays of the Co^{60} isotope source with dose rate in the range of 10–9.40 kGy/h for the required time at ambient condition.

Method of grafting

The irradiated film was placed in a glass ampoule containing styrene and acrylic acid solution in benzene (dry and purified). The ratio of styrene to acrylic acid was maintained at 52:48 (mole ratio) for all the grafting reactions. The monomer concentration in benzene was in the range of 20–100% (in volume). Prior to sealing the ampoule, the content was freed from dissolved oxygen/air by freezing and thawing under vacuum until free from dissolved gas. Three freeze–thaw cycles were found adequate. Finally, the ampoules were sealed, brought to room temperature, and were placed in an oil bath maintained at a constant temperature for the desired period of time. Grafting was carried out at four different temperatures that is to say 60, 70, 80, and 90°C. After the reaction, the grafted film was taken out of the ampoule and placed in a thymbol. The thymbol was placed in a soxhlet apparatus to remove unreacted monomer, homopolymers, and ungrafted copolymer adhering to the film by extracting it for 24 h each with toluene and methanol.

The films were dried to constant weight in a vacuum oven at 40°C at least for 24 h. The degree of grafting was calculated using the equation given below:

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

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

Sulfonation

The sulfonation of the sty–AA grafted FEP films was carried out in concentrated sulfuric acid at room temperature for 2 h. The sulfonated membranes were washed with distilled water till acid free and stored in distilled water for further study.

IR spectroscopy

IR spectra of FEP and sty–AA grafted FEP films were recorded using 1650 Perkin Elmer FTIR.

RESULTS AND DISCUSSON

As was reported earlier[13] equimolar composition of styrene and acrylic acid in monomer feed gives approximately an equimolar composition in copolymer also within the limits of experimental error. In the case of graft copolymerization of FEP, this may not be totally true due to different diffusion rates of monomer across the polymer. However, it may be assumed here that a monomer feed composition of 52:48 (styrene:acrylic acid) could give a 49:51 copolymer composition calculated on the basis of reported values in literature.[15] This monomer feed composition has been used through out the entire course of this study. Another reason to work with this composition was to get maximum possible monomer alternation in the polymer chain for cyclization to achieve indicator property.[13]

The grafting of sty–AA into FEP by standard method as reported by many researchers was not uniform and the results were not reproducible. After several experimentations, it was found that purity of monomer and solvent played an important role in getting uniform grafting. In addition to uniformity, reproducible results could be achieved by adopting freeze-thawing technique to remove dissolved oxygen, which is known to inhibit polymerization.[16] For all graft copolymerization we strictly followed these conditions. As a result, high degree of grafting could be achieved with uniformity and reproducibility. It has been observed that the grafting is strongly influenced by reaction conditions.

Effect of total radiation dose

FEP films were irradiated for different total dose and grafting was carried out for different time period. The results are presented in Figure 1. It can be seen that irrespective of total dose, as the time of grafting increases the degree of grafting increases for all the systems upto a certain time period, beyond which the rate starts leveling off. Similar observations have been reported for other systems.[17,18] All the lines pass through origin showing no induction period during grafting. From the results it can also be seen that the degree of grafting increases with the increase in the total radiation dose, i.e., the time of exposure to γ-ray. This can be explained on the basis of the fact that at higher radiation doses, more number radicals/peroxides are formed, which contribute to increasing degree of grafting. Also it is seen that at higher doses, degree of grafting tends to level off earlier compared to lower doses. It appears that at higher doses, in addition to higher rate of grafting initially, radicals also undergo deactivation being in close proximity, thereby leaving behind few radicals for grafting at later stages.

Figure 2 presents a log–log plot of initial rate of grafting (derived from Fig. 1) versus total dose yield-

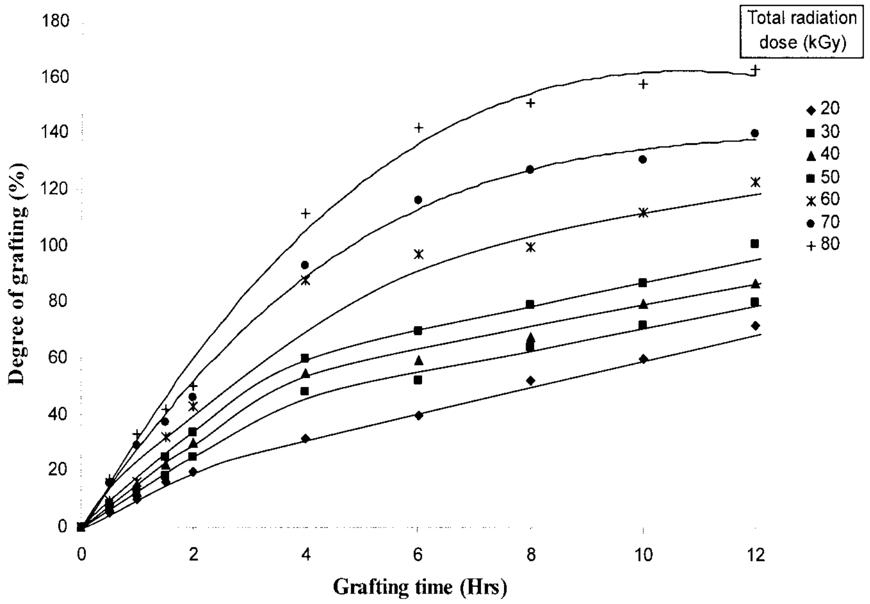


Figure 1 Variation of degree of grafting with grafting time at various preirradiation doses. Grafting conditions: monomer concentration, 60%; reaction temperature, 70°C; film thickness, 75 μm.

ing a slope of 0.53, closer to theoretical value of 0.5 for classical free radical polymerization. Heagazy et al.[18] have reported an order of dependence 0.58 for the grafting of acrylic acid into FEP. Similarly, Gupta et al.[17] for other system such as FEP-g-sty, by preirradiation method, have reported a higher order of dose dependence value (0.64)[17] and attributed that grafting was governed by "mechano-chemical grafting" process involving generation of new radicals due to rupture of strained grafted chain. It appears that this most possibly does not account for higher order of dose dependence. Monomer purity is also one of the reason for getting higher order. Because, on carrying out grafting without stringently purifying the monomer and extensive freeze–thawing, higher order of dose dependence was obtained in the present study also. However, upon purifying the monomer and adopting freeze–thawing technique the order of dose dependence of 0.53 on initial rate of grafting could be obtained. Initial rate of grafting of styrene into FEP by simultaneous method, as observed by Nasef et al.[20] has dose rate dependence of 0.5. Here purity does not affect as the radicals are constantly generated due to continuous exposure to radiation.

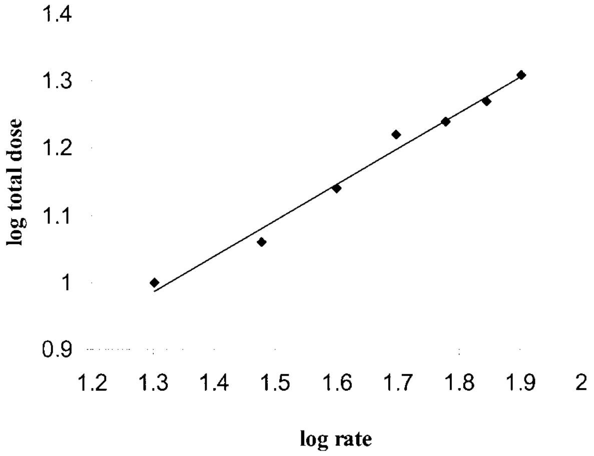


Figure 2 Log–log plot of the initial rate of grafting versus preirradiation dose.

The concept of front mechanism of grafting of vinyl monomers into fluoro polymers by radiation method has been well established by others.[1,17,19] In the present case also, the grafting front starts at the surface of the film initially and moves internally towards the middle of the film by successive diffusion of the monomer. The evidence of this phenomenon for this system will form a part of future communication.

Effect of monomer concentration

The effect of monomer concentration on degree of grafting is shown in Figure 3. From the graph it is seen that the degree of grafting increases with an increase in monomer concentration. This is quite understandable because of the fact that with an increase in monomer concentration more amount of monomer is available for grafting in the vicinity of the grafting sites resulting in higher degree of grafting. The grafting is known to occur by the front mechanism where the grafting starts at the surface and slowly proceeds inwards by the diffusion process. The grafted chains on the surface swell in the grafting medium thereby allowing the diffusion of the monomer into the core of the film.

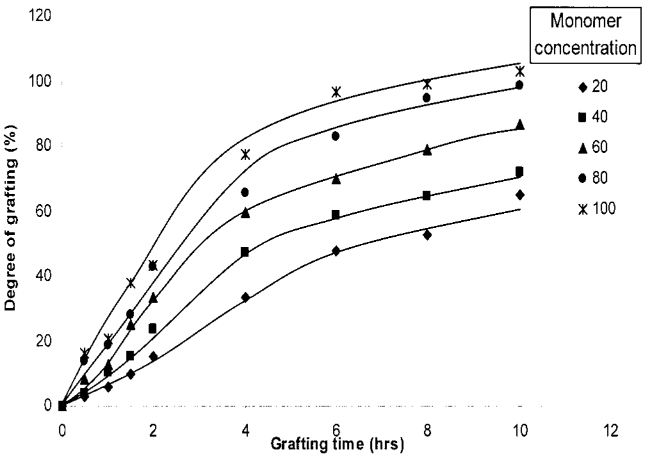


Figure 3 Variation of degree of grafting with grafting time at various monomer concentrations. Grafting conditions: preirradiation dose, 50 kGy; reaction temperature, 70°C; film thickness, 75 μm.

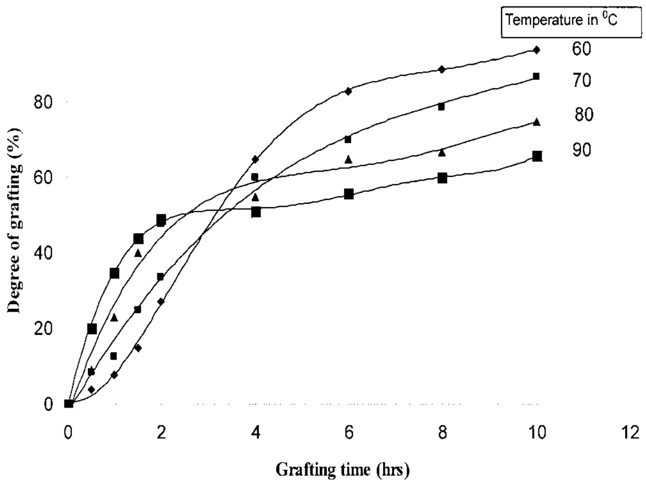


Figure 5 Variation of degree of grafting with grafting time at various temperatures. Grafting conditions: monomer concentration, 60%; preirradiation dose, 50 kGy; film thickness, 75 μm.

The rate of grafting of styrene/acrylic acid was calculated from initial slopes of Figures 3 and 4 the log–log plot of initial rate of grafting with respect to monomer concentration is presented. The dependence of initial rate of grafting and monomer concentration is found to be 1.03. This value is close to the theoretical value of 1 assuming free radical polymerization in the system. However, for other systems higher values are reported. Thus, grafting of styrene into FEP by preirradiation method[17] has given order of reaction 1.9 whereas grafting by simultaneous method[19] the order is 1.3. Similarly an order of 1.2 for grafting of acrylic acid onto poly(tetrafluoroethylene–ethylene) has been obtained by Hegazy et al.[18] Grafting of vinyl monomers into fluorinated polymer is a complex process and mainly controlled by monomer diffusion and swelling of grafted zone. Despite these facts, it is clear from our observation that use of inhibitor free monomer in oxygen free medium has resulted in a graft copolymer, which follows free radical polymerization kinetics.

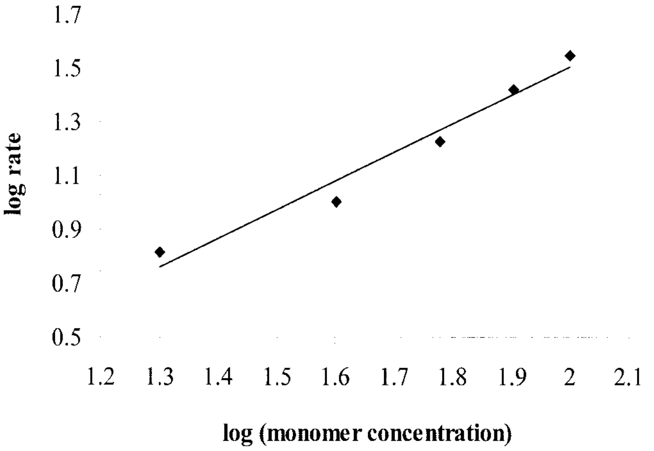


Figure 4 Log–log plot of the initial rate of grafting versus monomer concentration.

Effect of temperature

Grafting of styrene/acrylic acid into FEP was carried out at four different temperature that is to say 60, 70, 80, and 90°C. Figure 5 shows that with the increase in temperature initially the degree of grafting increases indicating the process has a positive temperature coefficient. Afterwards, the degree of grafting decreases with increase in temperature. The increase in initial rate of grafting can be explained on the basis that as the temperature increases the diffusibility of monomer increases thereby increasing the availability of monomer near the active reaction site for polymerization. Conversely, the lower degree of grafting beyond 3 h with increase in temperature is due to the fact that after a particular level of grafting, the chain initiation competes with decay of radicals due to combination. This process is augmented with increase in temperature as the mobility of chain increases resulting in termination by combination. Similar observations have been reported by others also.[17]

Figure 6 shows Arrhenius plot between initial rate of grafting and temperature. The energy of activation calculated from the slope using Arrhenius equation is 33 kJ/mol. This value is closer to the values reported in literature for other systems[17,21,22] but lower than the value for typical free radical polymerization involving generation of free radical by initiator decomposition. In preirradiation method of grafting in air, the FEP film is exposed to γ-rays, which leads to formation of radicals and hydroperoxides on the polymer chain.

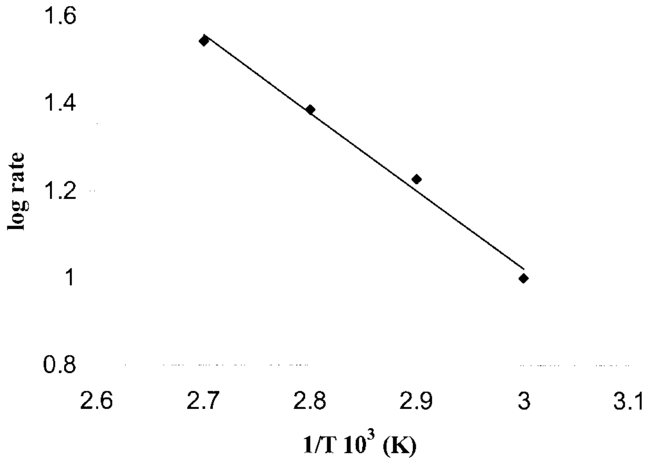


Figure 6 Arrhenius plot of rate of grafting versus [1/*T*].

The T_g of FEP being 54°C, these radicals remain trapped fairly for a longer period of time and they become the site of initiation during grafting and require no external energy for activation. Thus grafting of acrylic acid into FEP at 30°C has been observed by Gupta and Chapiro.[23]

According to this principle, graft copolymerization by radiation method does not require any decomposition of initiator. Energy of termination is difficult to envisage in such polymerization system as the growing radicals are mostly immobilized and hence the frequency of collision of the growing radicals will be very rare. Hence, the energy of activation involving no decomposition of radical and no chain termination for the present system should be about 21 kJ/mol.[24] A higher value of activation energy (33 kJ/mol) can be explained on the basis of either decomposition of few peroxide radicals formed during radiation exposure or diffusion of monomer pair to the site of free radical inside the membrane.

Characterization of FEP-g-sty–AA via IR spectroscopy

In comparison to IR spectrum of FEP, certain new bands appear in the case of grafted film (Fig. 7). Thus, bands at 3,028 and 2,933 cm^{-1} are due to C–H stretching whereas bands at 1,710 cm^{-1} is due to carboxylic C==O stretching.[25] Bands at 1,600 and 1,449 cm^{-1} are due to the stretching vibration of

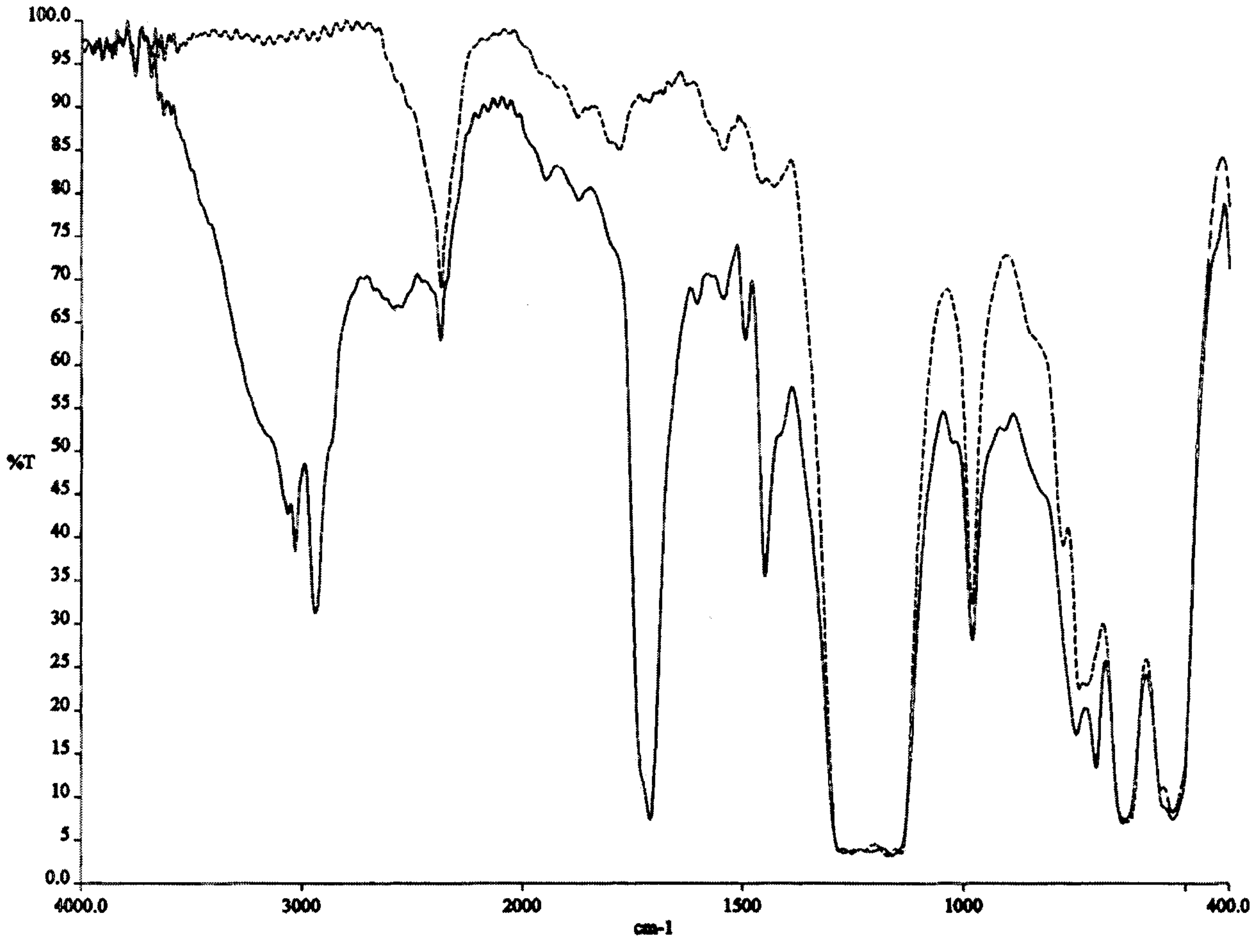
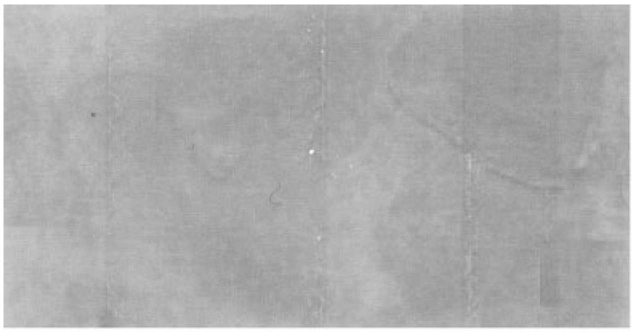
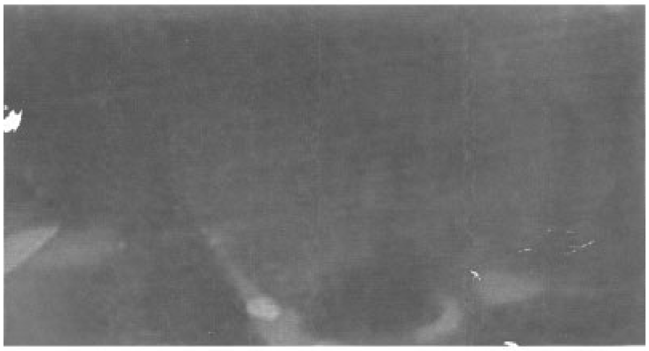


Figure 7 FTIR spectra of FEP (. . .. .) film and FEP-g-(styrene–acrylic acid (sty–AA)) (______).



Sulphonated FEP-g-STAA in acid medium



Sulphonated FEP-g-STAA in alkaline medium

Figure 8 Behavior of sulfonated FEP-g-sty–AA in acid and alkaline medium.

==C–H and C==C of the benzene ring. The observations clearly indicate that both styrene and acrylic acid are grafted into FEP.

Indicator property

A selected grafted film was sulfonated using sulfuric acid. The film is yellow in color on sulfonation and it changes to purple color in alkali (Fig. 8).) According to the mechanism of color change,[13] sty–AA copolymer during sulfonation undergoes an internal Friedel Crafts acylation followed by cyclic dehydration leading to a conjugated structure. This is possible only when styrene/acrylic acid are present alternate to each other. The result in Figure 8 indicates that a good degree of alternation of styrene/acrylic is present in the system and the indicator property of sulfonated sty–AA can be incorporated into FEP grafted film.

CONCLUSION

From the work carried out it may be concluded that the degree of grafting of styrene-co-acrylic acid onto FEP is strongly dependent on the reaction conditions. The degree of grafting increases with the increase in monomer concentration, total radiation dose, temperature, and time of the reaction. By varying the reaction conditions it is possible to synthesize graft copolymer with desirable properties to be used for various applications. Stringent purification and oxygen free environment can only provide uniform, homogenous, and reproducible grafted film.

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