Radiation-Induced Graft Copolymerization of α-Methyl Styrene and Butyl Acrylate Mixture into Polyetheretherketone Films

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ABSTRACT: Radiation-induced graft copolymerization of α-methyl styrene (AMS), butyl acrylate (BA) monomers, and their mixture was investigated on poly(etheretherketone) films. The graft polymerization was carried out using ethyl methyl ketone as the medium for the copolymerization and the maximum degree of grafting of 27% was achieved. It was observed that the grafting is significantly influenced by the reaction conditions, such as reaction time, preirradiation dose, monomer concentration, monomer ratio, and the reaction temperature. The degree of grafting increases as the monomer concentration increases up to 30%, beyond which a decrease in the grafting was observed. The degree of grafting showed a maximum at 40% BA content in the monomer mixture. The temperature dependence of the grafting process shows decreasing grafting with the increase in the reaction temperature. The presence of AMS and BA grafts in the film was confirmed by FTIR spectra. The relative change in the PBA/PAMS fraction with respect to the reaction temperature has been found in this study. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The increasing demand for environmental-friendly energy alternatives has driven the focus to the development of new energy sources as alternatives to fossil fuel.[1,2] The need for renewable fuels and the search for efficient and clean energy conversion technology have enhanced the fuel cell research in the past years. Fuel cells have received considerable attention because of their high efficiency, high power density, and pollution-free fuel utilization. In recent years, polymer electrolyte membrane fuel cells (PEMFC) are being considered as strong contender for the use in automotive, stationary, and portable power systems.[3] One of the areas currently being extensively explored is the development of membranes that would improve the durability, performance, and reliability of the PEMFC. The membrane is the central component, acting as electrolyte for proton transport as well as the barrier between hydrogen and oxygen. Nafion®, the commercial fluorinated membrane from DuPont, still dominates the market and is known for its high stability and high-proton conductivity. Alternatively, nonfluorinated materials are under investigation in many research groups worldwide, aiming to reduce the cost and to overcome technical obstacles of Nafion®.[4]

Enormous efforts have been made to develop proton exchange membranes by radiation-induced graft polymerization technique.[5,6] The magnetism of this approach arises from the flexibility of using any type of radiation, such as gamma rays and electron beam irrespective of the shape and size of the polymer matrix. The graft copolymerization offers a unique concept of combining desirable properties of two polymeric components along with the precise control by proper selection of the irradiation as well as reaction parameters. This process involves grafting of a functional polymer phase (grafts) into base polymer films (substrate) in which the functional polymer keeps its inherent characteristics intact.[7–9]

Fluorinated polymers, such as poly(tetrafluoroethylene-*co*-hexafuoropropylene) (FEP), polytetrafluoroethlene, and poly(ethylene-*co*-tetrafluoroethylene) (ETFE)[10–12] have been widely used as the base films for the preparation of fuel cell membranes and wide range of monomers such as styrene, α-methyl styrene (AMS), trifluorostyrene (TFS), and methacrylonitrile (MAN) have been grafted.[13–16] The grafting of styrene into FEP films and the sulphonation of the grafted films to produce membranes have been studied.[17] However, the partially fluorinated polymer films have advantages over perfluorinated ones in terms of the use of high radiation doses and dose rate during the membrane preparation. Relatively higher graft levels are achieved for the grafting of styrene over ETFE as compared to FEP.[3,18–20]

Poly(etheretherketone) (PEEK) is an aromatic, high performance, semicrystalline polymer with extremely good thermal stability, chemical resistance, and electrical as well as mechanical properties. This material has been investigated in the recent years to develop membranes for fuel cell application. One of the ways to produce membranes is by sulfonation to introduce sulphonic acid groups.[21–23] However, the graft polymerization of a monomer into PEEK films offers an interesting approach to develop proton exchange membranes with precise control over the material characteristics.[24–26] The grafting of styrene on PEEK followed by sulfonation leads to the membranes which exhibit swelling in aqueous medium and conductivity of more than 0.01 S/cm.[25] Alternatively, an ultra thin PEEK film was modified by thermal grafting of divinylbenzene followed by the radiation grafting of ethyl styrene sulfonate to develop a membrane for direct methanol fuel cells.[27]

Thermal stability of the membrane is the matter of concern for the membrane technologists, probably due to the tertiary hydrogen abstraction under fuel cell operation. The degradation of the ionic component affects the membrane performance, significantly. Efforts have been made to improve the membrane stability by using perfluorinated monomer, such as TFS followed by the sulfonation. However, the high costs of this monomer and difficult polymerization process have encouraged scientists to look for the alternative routes. This is where the incorporation of a crosslinker during the grafting or the use of α-substituted styrene monomers for the grafting has been recently investigated. The grafting of AMS by radical polymerization is the difficult process due to —CH$_3$ protective group at the α position; however, the ceiling temperature of the monomer is 60°C which leads to certain complications in the grafting process, hence it may lead to low graft yield and hence, low conductivity. It has been found that the addition of MAN to AMS leads to thermally stable and better performing membrane in fuel cell.[28]

Looking at the encouraging aspects of the cografting of AMS with MAN in increasing graft level and thermal stability, we have been working on the PEEK-based proton exchange membranes by radiation grafting of two monomers AMS and butyl acrylate (BA) under different reaction conditions. BA is expected to enhance the polymerization of AMS on one hand, while some flexibility may be achieved into the grafted films due to the presence of BA moieties along the PEEK backbone. The influences of various parameters on the degree of grafting have been investigated in this study.

EXPERIMENTAL

Materials
PEEK films (50 μm thickness) were obtained from AJEDIUM FILM, a division of Solvay solexis,. These films were cut into 2.5 × 2.5 cm^2 and wiped with ethanol to remove impurities from the film surface. The films were dried under vacuum at room temperature before their use for experiments.

AMS (Sigma Aldrich) and BA (Sigma Aldrich) were purified by vacuum distillation. Ethyl methyl ketone (Merck) was used as a solvent medium for grafting process.
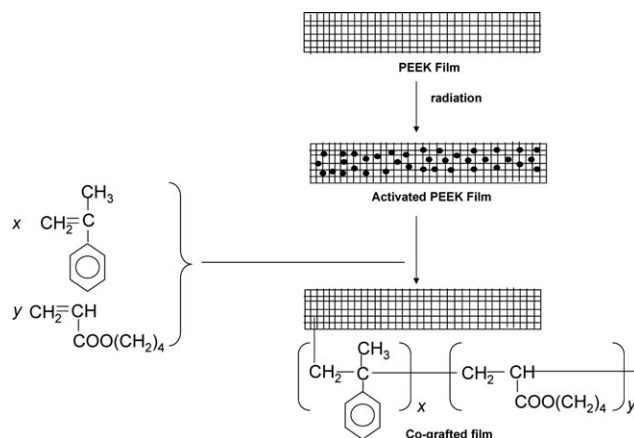

Figure 1. Schematic representation of the reaction scheme.

Irradiation
A Co-60 gamma radiation source (dose rate of 0.16 kGy/h), supplied by Bhabha Atomic Research Centre, India, was used for the irradiation of the samples. Irradiations were carried out in air under ambient conditions.

Membrane Preparation
Graft copolymerization of AMS, BA, and their mixtures on the PEEK film was carried out by preirradiation grafting. As per the method reported earlier,[29] films were exposed to gamma radiations for various doses in the range of 15–100 kGy. The irradiated samples were placed in a reaction tube containing aqueous monomer solution. The tube was deaerated by bubbling nitrogen for 15 min and was sealed. Subsequently, tube was placed in a thermostated water bath at required temperature for a desired period. After the reaction was over, samples were washed with toluene repeatedly at room temperature to extract homopolymer as well as unreacted monomer formed during the grafting reaction. The grafted sample was dried under vacuum to a constant weight. The degree of grafting was determined gravimetrically as per the following expression.[17]

$$\text{Degree of grafting} = (W_g - W_0)/W_0 \times 100 \qquad (1)$$

where, W_0 and W_g are the weight of the film before and after graft polymerization, respectively.

RESULTS AND DISCUSSION

The schematic representation of the grafting process is given in Figure 1. PEEK film is exposed to gamma radiation to generate hydroperoxides groups. The grafting of AMS-BA was carried out subsequently by varying several parameters and the presence of AMS and BA was confirmed with FTIR. The influence of various parameters on the degree of grafting is studied in following sections:

Influence of the Reaction Time
The variation of the degree of grafting with the reaction time is presented in Figure 2. The degree of grafting of pure AMS increases and tends to level off beyond 8 h, reaching saturation after 36 h while in case of pure BA, degree of grafting increases and tends to level off after 24 h. For the grafting of AMS-BA
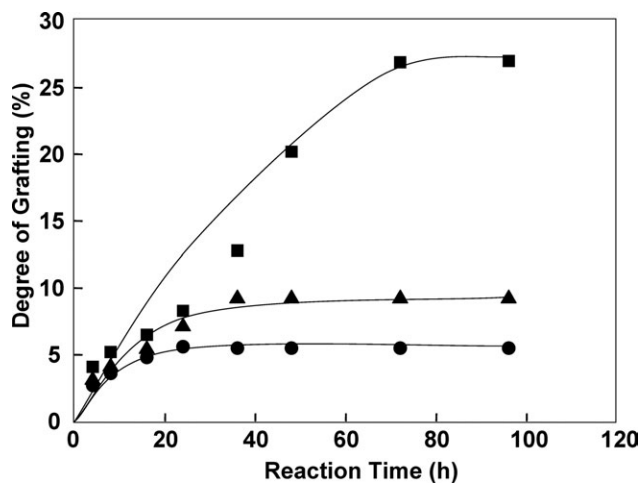
Figure 2. Variation of the degree of grafting with the reaction time. Pure AMS (●), Pure PBA (▲), AMS/BA (60 : 40) (■) Reaction conditions: dose, 100 kGy; monomer concentration, 30%; temperature, 50°C.

mixture, the saturation is achieved within 72 h. It may be stated that propagating chains are exhausted within 72 h and may be taken as the time for achieving equilibrium degree of grafting. AMS has a very little tendency for radical polymerization and hence leads to a small amount of grafting. On the other hand, BA undergoes radical polymerization and leads to the formation of graft copolymer along with homopolymerization to a level of 22% at 72 h. Interestingly, the monomer mixture offers much higher grafting as compared to the pure monomer. It seems that the monomers have tendency to copolymerize and produce high graft levels. The reactivity ratios of the two monomers BA and AMS are 0.118 and 0.298, respectively, and hence may be expected to copolymerize with a tendency to form alternate copolymer chain consisting of AMS and BA moieties in the grafted chain.[30]

FTIR Spectra

The FTIR spectra of virgin PEEK, irradiated PEEK, and AMS–BA grafted PEEK were recorded to characterize the structural changes at different stages of grafting process (Figure 3). No changes were observed in the virgin and irradiated PEEK which shows that the radiation is not affecting the inherent chemical structure of the polymer, at least apparently. The spectral difference between the irradiated and the grafted film was observed due to the presence of AMS-BA component. We observed a peak at 1731 cm^{-1} assigned to carbonyl group of BA in PEEK film. The absorption band at the 2873 and 2919 cm^{-1} associated with the symmetric and asymmetric vibration of $-CH_2$ groups, respectively, in AMS, was observed indicating the incorporation of graft in the polymer backbone. We tried to study the relative amount of the AMS and BA at specific graft levels. The optical density in the FTIR spectra of the films grafted with pure BA was used to prepare a calibration plot. The PBA content of the AMS-BA grafted films was obtained by measuring the optical density of $-CO$ group $[-CO_{1731}/-CH_{2\ 3045}]$ of the BA component. The PAMS content was estimated by subtracting the PBA content from the total graft add-on.
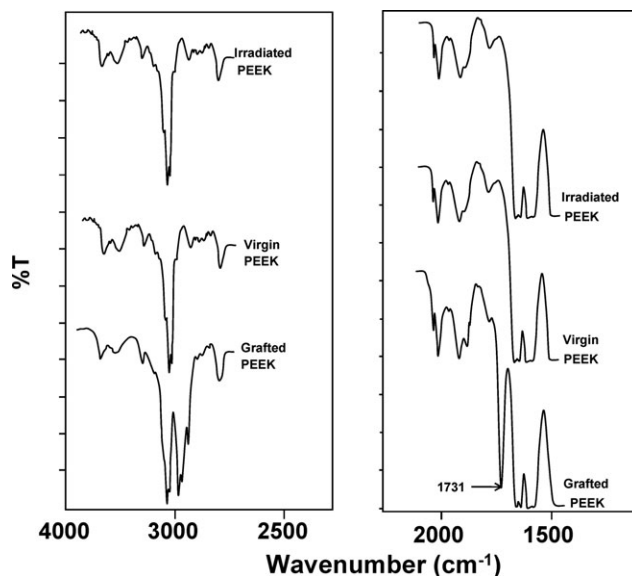

Figure 3. Comparative FTIR of (a) irradiated PEEK; (b) virgin PEEK; (c) grafted PEEK (degree of grafting, 24%).

A correlation of the variation of the PBA and PAMS fractions with the degree of grafting is presented in Figure 4. PBA content increases with respect to the degree of grafting and the reaction time while PAMS content shows an opposite trend. It seems that the grafting proceeds in such a way that it facilitates the diffusion of BA over AMS in the grafted matrix and leads to the enhancement of PBA in the grafted matrix. McManus et al.[31] have carried out the free radical polymerization of BA-AMS using identical monomer ratio and observed that the copolymer composition does not change with the conversion. In our system, the copolymer graft copolymerization indeed changes from 0.17 to 0.36 (weight fraction) with the graft variation from 4 to 27%. This seems to be the fall out of the relative diffusion of the two monomers within the grafted matrix. As soon as the initial grafting takes place, the surface turns from
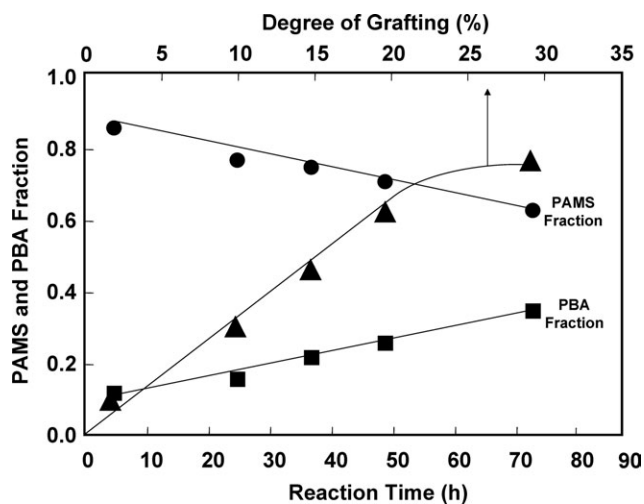

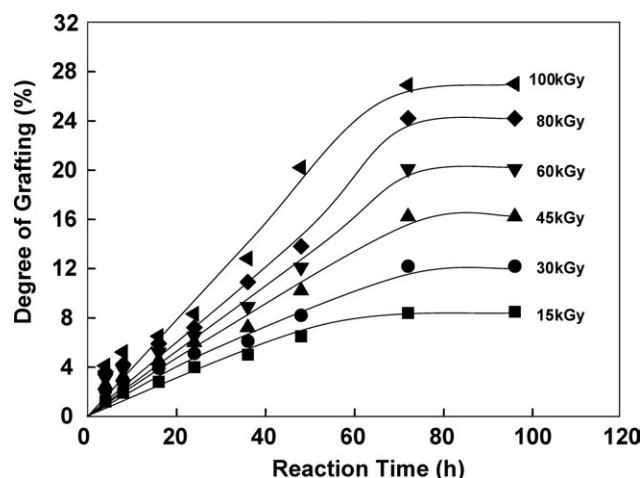**Figure 4.** Variation of (●) PAMS, (■) PBA, (▲) degree of grafting with reaction time.

Figure 5. Variation of the degree of grafting with the reaction time at different radiation doses. Monomer concentration, 30% AMS : BA (60 : 40), Temperature: 50°C.

virgin PEEK to the grafted one and regulates better diffusion of BA across this barrier.

Influence of Preirradiation Dose

The preirradiation dose has considerable influence on the degree of grafting. The variation of the degree of grafting as a function of the reaction time at various irradiation doses is presented in Figure 5. The increase in the degree of grafting with the dose is a consequence of the increasing number of active sites with increasing dose within the polymer matrix. The higher the number of radicals, the more initiating chains participates in the grafting process leading to the high graft level with increasing doses. The rate of grafting (R_g) was determined from the initial portions of the plots in Figure 5 and the log–log plot for the dependence of R_g over irradiation dose is presented in Figure 6. The dose rate dependence of 0.71 was found in the present grafting system. Our results show a bit of deviation from classical rate dependence, that is, 0.5. It seems that the primary radical termination dominates over the initiation process. May be, some of these radicals terminate by impurity and solvent molecules instead of propagating the chain.
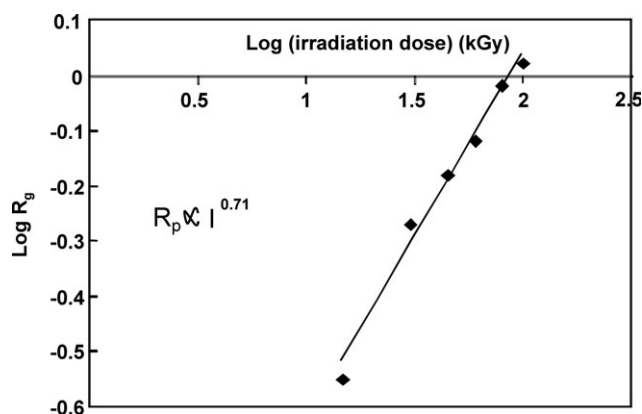

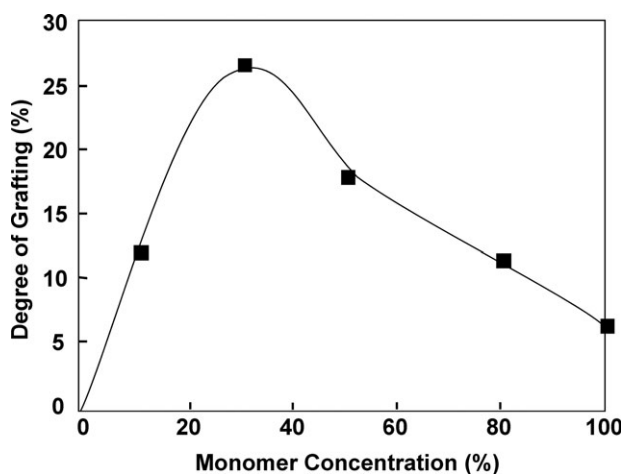**Figure 6.** Log–log plot of the rate of grafting versus irradiation dose.

Figure 7. Variation of the degree of grafting with monomer concentration of AMS: BA (60 : 40). Reaction conditions: dose, 100 kGy; temperature, 50°C; time, 72 h.

Influence of the Monomer Concentration

The effect of the monomer concentration on the degree of grafting is presented in Figure 7. The maximum degree of grafting is achieved at 30% monomer concentration with 60 : 40 AMS : BA ratio in monomer concentration. The increase in the degree of grafting with the increase in the monomer concentration may be attributed to the increase in monomer accessibility to the grafting sites. However, the decrease in the degree of grafting beyond 30% seems to be the outcome of the two cumulative factors: homopolymerization and the matrix swelling in the grafting medium. The homopolymerization does not take place during the grafting of the pure AMS. However, as soon as the BA is added to the AMS, homopolymerization is initiated. The homopolymer formation is still not evident till the BA content of 40%. As soon as the BA content increases further, the
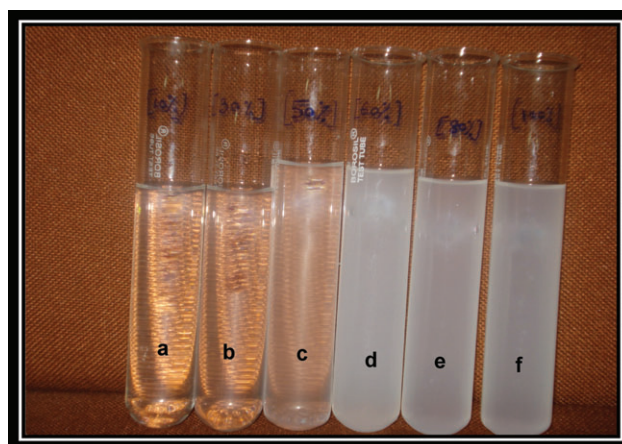

Figure 8. Photograph of the postgrafting reaction mixture at various monomer concentrations: (a) 10%, (b) 30%, (c) 50%, (d) 60%, (e) 80%, (f) 100%. Reaction conditions: Medium; ethyl methyl ketone AMS: BA (60 : 40) preirradiation dose, 100 kGy; temperature, 50°C; time, 72 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
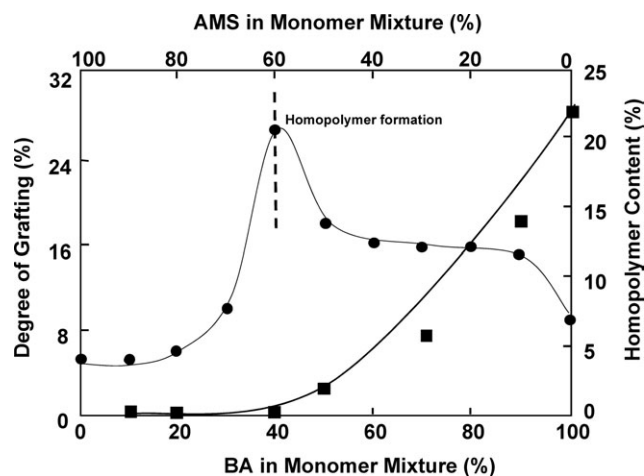
Figure 9. Variation of the degree of grafting with BA in total monomer. Reaction conditions: dose, 100 kGy; monomer concentration 30%; temperature, 50°C; time, 72 h.

Figure 11. Variation of PAMS and PBA fraction with % BA in monomer mixture. Reaction conditions: dose, 100 kGy; monomer concentration, 30%; temperature, 50°C.

homopolymerization proceeds, extensively. The homopolymerization is negligible at 40% BA content and thus increases, significantly in 100% BA. It is important to see that ethyl methyl ketone acts as a nonsolvent for the homopolymer and the homopolymer formed during the grafting process precipitates out leading to the opaque medium [Figure 8 (c–f)]. As a result, the medium viscosity remains intact which regulates the monomer diffusion to the grafting site. Despite of the proper monomer accessibility to the growing chains, the decrease in the grafting seems to be the outcome of the depleting monomer due to homopolymerization.

Influence of the Variation of Butyl Acrylate in Monomer Mixture

With the increasing content of BA in monomer mixture, the degree of grafting increases reaching maximum at 40% and then tends to decrease with the further increase of BA content in the monomer mixture (Figure 9). The homopolymer formation, on the other hand, starts at 40% BA content and reaches
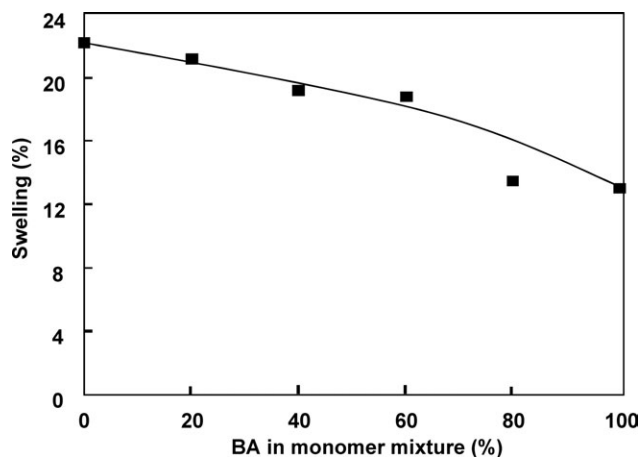
22% in pure BA. The swelling of PEEK matrix, however, decreases consistently with the increasing BA in the monomer mixture (Figure 10). However, in ethyl methyl ketone (EMK) as the solvent medium, PEEK film shows 20.1% swelling. This leads to significant decrease in the monomer diffusion to the polymer matrix and hence contributes to the decrease in the grafting which adds to the influence of homopolymerization in diminishing the grafting. The fraction of PBA within copolymers obtained at various BA content in BA/AMS mixture was obtained from FTIR. (Figure 11) Taking into consideration, the reactivity ratio of BA and AMS is 0.118 and 0.298, respectively, we can state that the results are in agreement with the reactivity ratios.

Influence of the Reaction Temperature

The variation of the graft level as a function of the reaction time in the temperature range of 50–80°C is presented in Figure 12. The initial rate of grafting and the equilibrium degree of

Figure 10. Variation of the swelling of irradiated PEEK with varying BA content in monomer mixture. Reaction conditions: dose, 100 kGy; monomer concentration 30%; time, 6 h.
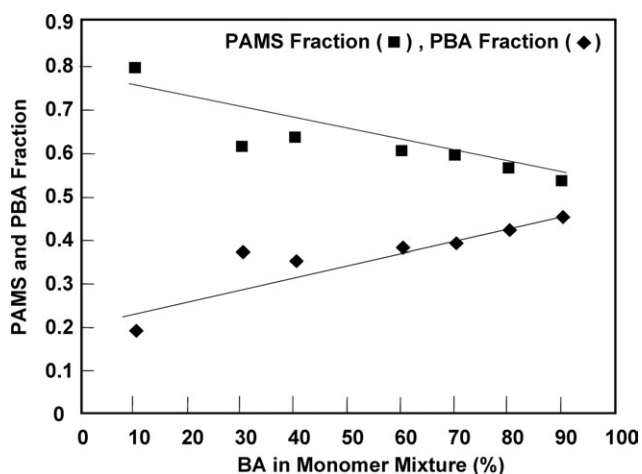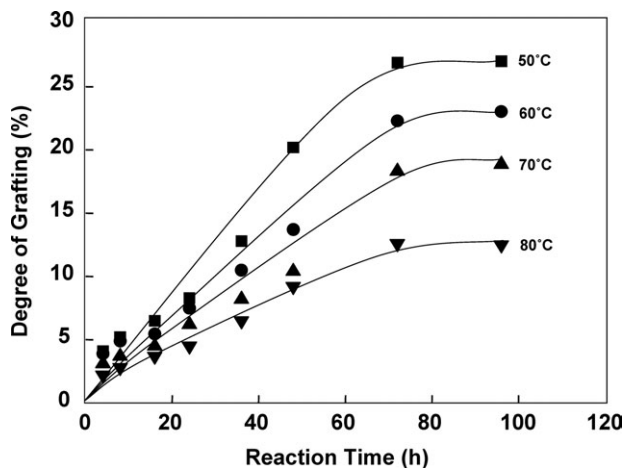

Figure 12. Variation of the degree of grafting with the reaction time at various reaction temperatures. Reaction conditions: AMS : BA (60 : 40) dose, 100 kGy; monomer concentration, 30%.
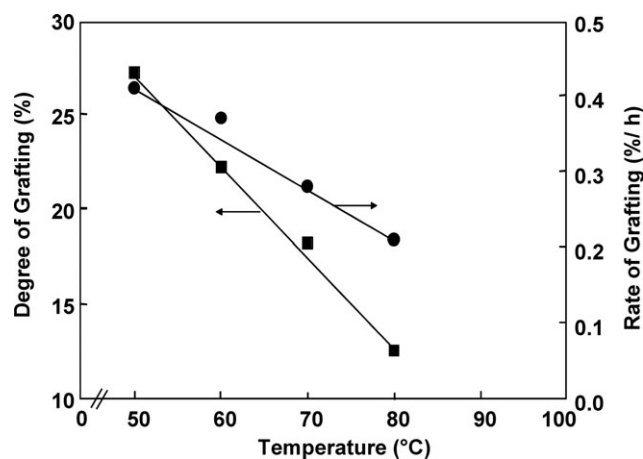
Figure 13. Variation of the degree of grafting and the rate of grafting with reaction temperature and rate of grafting (%/h). Reaction conditions: AMS : BA (60:40); dose, 100 kGy; monomer concentration, 30%.

grafting decrease at 72 h with the increase in the reaction temperature (Figure 13). These results are quite different than the observed behavior for styrene grafting with the reaction temperature. Termination of the two growing chains by mutual combination becomes dominant at higher temperatures. Grafting is the combination of two steps: addition of monomer to the primary radicals on the PEEK backbone as well as the monomer addition to the growing chains. The deactivation of primary radical may therefore take place by mutual recombination while it seems that both these steps are affected at the higher temper-
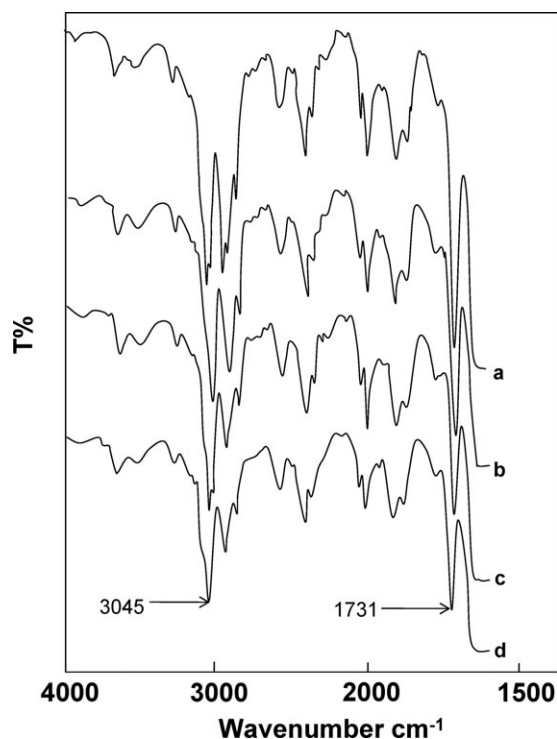

Figure 14. Comparative FTIR of grafted films with temperature (a) 50°C (DG = 27%); (b) 60°C (DG = 22.3%); (c) 70°C (DG = 18.3%); (d) 80°C (DG = 27%).
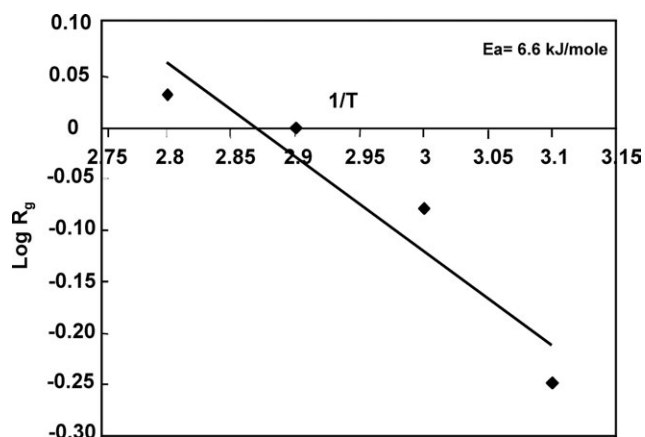

Figure 15. Arrhenius plot of the rate of grafting versus 1/T.

ature. The major factor contributing to the low grafting at higher temperature may be the low ceiling temperature of AMS ($-60°C$). It means the grafting at 60°C or beyond this temperature would be difficult to proceed. It is interesting to see that as the reaction temperature increases PAMS content tends to decrease. The FTIR peak at 3045 cm^{-1} decreases significantly when temperature increases from 50 to 80°C (Figure 14).

The Arrhenius plot of the initial rate of grafting versus 1/T from 50 to 80°C as presented in Figure 15 is linear. The activation energy obtained from the slope of the plot is 6.6 kJ/mol. This value is much lower than the one observed for the grafting of styrene on FEP films. However, the grafting of TFS on polyethylene has been found to be 6.6 kJ/mole. Our results are in agreement with the other investigations.[32]

CONCLUSION

The preirradiation grafting of AMS-BA mixture on PEEK films leads to the matrix with degree of grafting higher than that in the pure AMS and pure BA monomers. Both the irradiation and the grafting parameters play a key role in the graft management within the polymer backbone. The degree of grafting increases with the preirradiation dose which is due to the higher radical generation at higher doses. The increase in the monomer concentration leads to the increase in the degree of grafting up to 30% of the monomer concentration and then tends to level off. The addition of BA to AMS leads to the enhancement in the graft level, significantly. Interestingly, the grafting increased with BA content in monomer mixture only up to 40% and then showed a decreasing trend. This may be due to the higher degree of homopolymerization at higher BA content. The grafting was found to decrease as the reaction temperature increases from 50 to 80°C. At a higher temperature, monomer diffusivity within the matrix would increase and despite of that, the degree of grafting decreases. This is the outcome of enhanced deactivation of primary radicals and growing chains at higher temperature. It is observed that the film enrichment with BA is formed with the progress of the grafting process. It may be proposed that it is possible to design a proper graft copolymer matrix by suitable variation in the radiation and the grafting conditions. The interesting observation is that the reaction temperature

influences the relative composition of the PBA and PAMS within the grafted domain. PAMS decreases significantly when the temperature increases from 50 to 80°C. The characterization of these films is being investigated and is being communicated subsequently.

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