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Effect of reaction conditions on electron induced graft copolymerization of styrene onto poly(ethylene-*co*-tetrafluoroethylene) films: Kinetics study

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Abstract

Graft copolymerization of styrene onto electron preirradiated poly(ethylene-*co*-tetrafluoroethylene) (ETFE) films was investigated. Effects of reaction conditions: monomer concentration, irradiation dose, temperature, film thickness and storage time on the grafting yield (*Y%*) were studied. The initial rate of grafting was found to be heavily dependent on the monomer concentration and the irradiation dose and can be represented by the following equation: $dG_o/dt = k[M_o]^{2.0}[D]^{0.75}$. The overall activation energies for graft copolymerization were calculated to be 36.9 and 12.5 kJ/mol below and above 50 °C, respectively. The initial rate of grafting was found to decrease with the increase in the film thickness. The trapped radicals in the irradiated ETFE films were found to be highly effective in initiating grafting reaction up to 240 days when stored under −60 °C. Graft copolymerization in the present study essentially depends on the ability of the monomers to diffuse through the base film and the amount of the trapped radicals.

Keywords: Radiation-induced graft copolymerization; Styrene; ETFE films; Electron beam; Front mechanism

1. Introduction

Graft copolymerization with high energy radiation is an effective method for imparting new functional properties to existing polymers without altering their inherent properties. This technology has been of particular interest in the past 50 years for preparation of a variety of functional and ion exchange membranes for various applications in chemical, biochemical and biomedical industries. The attractiveness of this method lies in its versatility to combine virtually unlimited number of base polymers and monomers under controlled reaction conditions to achieve membrane compositions and properties for specific requirements [1].

In this method active sites are formed on the polymer backbone using high energy radiation (γ-radiation, electrons or swift heavy ions) and the irradiated polymer is allowed to react with monomer units, which then propagate to form side chain grafts when terminated. Two standard methods of radiation-induced graft copolymerization: (i) direct (simultaneous) irradiation and (ii) pre-irradiation have been developed over the past 50 years. In direct method, a polymer substrate is irradiated while immersed in the monomer solution. Alternatively, in preirradiation method the polymer is irradiated first in inert atmosphere or vacuum and subsequently brought to contact with the monomer solution under controlled conditions. If irradiation is conducted in air or O_2 either peroxy radicals or hydroperoxy groups are formed on the base polymer which, when heated in the presence of a monomer, decomposes and initiates grafting [2].

Radiation-induced graft copolymerization is often conducted in the liquid phase of pure monomer or its solution [3]. Obtaining desired grafting levels requires an optimization for the reaction parameters such as monomer concentration, irradiation dose, dose rate, temperature and type of solvent to vary the depth of penetration of the monomer into the polymer bulk to eventually allow control over the membrane composition to obtain tailored properties [4]. This requires an essential understanding for the kinetics of graft copolymerization reaction under various reaction conditions.

Radiation grafted membranes bearing sulfonic acid groups have been proposed as alternative polymer electrolyte candidates

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Nomenclature

dG_o/dt	initial rate of grafting (%/h)
D	irradiation dose (kGy)
k	apparent rate constant ($G\%/h\,mol^{-2}\,L^2\,kGy^{-0.75}$)
M_o	monomer concentration in bulk solution (mol/L)
T	reaction temperature (K)
W_o	weight of original ETFE film (g)
W_g	weight of grafted ETFE film (g)
$Y\%$	grafting yield (%)
$Y_f\ \%$	Final grafting yield (%)

for fuel cells [5]. Styrene has been widely used as a grafting monomer, because it shows favorable radical polymerization kinetics, and its aromatic ring can be easily sulfonated to introduce proton conducting sites [6,7]. Due to the chemical stability needed in fuel cells, fluorinated polymer films are commonly used because of their outstanding thermal, chemical and mechanical properties.

Among fluorinated polymers, poly(ethylene-*co*-tetrafluoroethylene) (ETFE) films is one of the excellent candidates for preparation of radiation grafted polystyrene sulfonic acid membranes because of their interesting properties such as high thermal and mechanical stabilities together with a superior resistance to radiation and fatigue [8]. Therefore, various research groups reported the use of ETFE films for preparation of fuel cell membranes by radiation-induced graft copolymerization styrene or its substituents and subsequent sulfonation [9–18]. Similar commercial radiation grafted membranes based on styrene and ETFE films are also available from Solvay S.A. (Paris, France). Nevertheless, reports on detailed kinetics of graft copolymerization of styrene/ETFE system under various grafting conditions can be barely found in literature. For example, Guilmeau et al. [19] reported a limited kinetics study in which effects of reaction temperature at two different film thicknesses were investigated for grafting of styrene onto ETFE films irradiated in air. Whereas the study by Brack et al. [12] focused on kinetics of the base film related properties such as type of thickness, orientation, irradiation method and atmosphere together with reaction temperature with most of the experiments conducted using air-irradiated films.

In this study a detailed account for the kinetics of graft copolymerization of styrene onto ETFE films irradiated in N_2 under various grafting conditions, i.e., monomer concentration, irradiation dose, temperature, film thickness and storage time is investigated. The formation of polystyrene grafts in ETFE films was verified by FTIR spectral analysis.

2. Experimental

2.1. Materials

ETFE films expressed by the molecular formula $(–CF_2CF_2CH_2CH_2–)_n$ with thickness of 125 μm and density of 1.7 g cm^{-3} were obtained from Goodfellow (UK) and used as polymer substrates in all experiments. Thinner films of 50 and 100 μm thicknesses were supplied by Asahi Chemicals (Singapore) and used to study the effect of thickness on the grafting yield. Pieces of ETFE film of surface area of 10 cm × 10 cm were used as standard samples. Styrene of purity more than 99% (Fluka, Switzerland) was used without further purification. Other solvents such as acetone, methanol and toluene were research grade and used as received.

Table 1
Parameters of EB accelerator and irradiation conditions of ETFE films

EB acceleration parameters	
Accelerating voltage	300 keV
Beam current	2.0 mA
Dose per pass	10 kGy
Irradiation conditions	
Dose range	20–100 kGy
Atmosphere	N_2
Temperature	Ambient

2.2. Irradiation of ETFE films

ETFE films were washed with acetone and dried in a vacuum oven at 70 °C for 1 h. The initial weights of the film samples were recorded. The ETFE films were irradiated by electron beam (EB) accelerator (Curetron, EBC-200-AA2, Nisshin High Voltage Kabushiki Kaisha, Japan) to doses ranging from 20 to 100 kGy at 10 kGy per pass under N_2 atmosphere. Details of parameters of EB accelerator and irradiation conditions are given in Table 1. After irradiation, the irradiated films were quickly sealed in evacuated thin polyethylene bags and kept in a low temperature freezer at −60 °C.

2.3. Graft polymerization

Graft copolymerization of styrene onto ETFE films was carried out using specially designed grafting system composes of cylindrical glass reactor connected to cold trap-type reaction tube through tri-way stopcock that allows N_2 bubbled monomer solution to be transferred to the reactor as schematized in Fig. 1. The irradiated ETFE film was placed in the glass reactor, which was tightly sealed then evacuated to remove air using a vacuum pump (10 mbar). In the mean time, a cold trap-type reaction tube containing a solution of the monomer solution (with a specified composition) was bubbled with purified N_2 gas for 10 min to remove air. The air free grafting solution was then transferred to the evacuated glass reactor containing ETFE film through a tri-way stopcock and the reactor side inlet was carefully sealed under N_2 atmosphere and eventually detached from the rest of the system. To allow the graft copolymerization reaction to be initiated, the glass reactor containing reaction mixture was placed in a thermostatic oil bath at specified temperature for a desired period of time.

After completion of the grafting reaction, the grafted films were removed and extracted in toluene-containing vessel placed

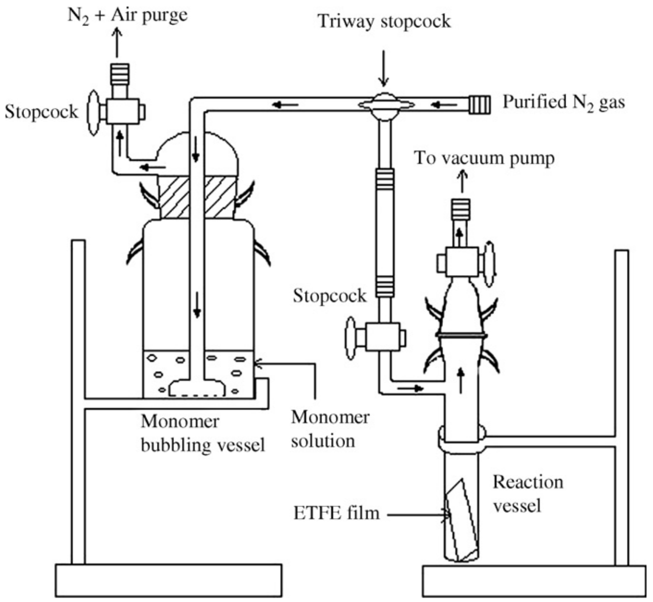

Fig. 1. Schematic diagram of the grafting system.

in ultrasonic machine for 1 day to remove the excess monomer and the homopolymer occluded in the surfaces of the films. The grafted films were dried under vacuum (10 mbar) at 70 °C until a constant weight was obtained. The grafted films were then weighed and the grafting yield (*Y%*) was calculated by considering the percent of weight increase according to Eq. (1).

$$Y\% = \frac{W_g - W_o}{W_o} \times 100 \tag{1}$$

where W_o and W_g are the weights of original and grafted ETFE films, respectively. To study the grafting behavior, various reaction parameters such as monomer concentration, irradiation dose, temperature, film thickness and storage time of irradiated films have been varied and their effects on *Y%* were investigated.

2.4. FTIR analysis

Fourier transform infrared (FTIR) measurements were carried out using a Nicolet (Magna-IR 560) spectrometer equipped with attenuated total reflection, ATR, (Thunder dome-HATR) having Ge spherical crystal. The spectra were measured in a transmittance mode in a wave number range of 4000–500 cm^{-1}.

3. Results and discussion

3.1. Effect of monomer concentration

Grafting yield-time courses at various monomer concentrations in bulk solution (1.74–8.70 mol/L) for graft copolymerization of styrene onto ETFE films is shown in Fig. 2. Obviously, *Y%* initially increases drastically with time at all monomer concentrations after 4 h beyond which, it tends to level off gently over a period of 48 h giving limiting value called final grafting yield (Y_f%). The Y_f% is found to increase with rise of the monomer concentration from 1.74 to 3.48 mol/L where it reaches its maximum value. Further increase in monomer concentration causes a sharp decease in Y_f%.

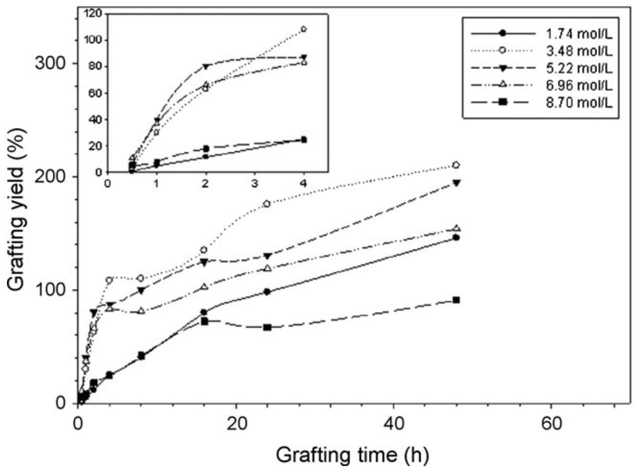

Fig. 2. Grafting yield-time courses at various monomer concentrations in bulk solution for graft copolymerization of styrene onto electron irradiated ETFE films. Grafting conditions are: irradiation dose, 100 kGy; temperature, 60 °C; film thickness, 125 μm; atmosphere, N_2.

The initial rates of grafting (dG_o/dt) obtained graphically from Fig. 2 are shown in Table 2. The dG_o/dt recorded the height value at 3.48 mol/L concentration whereas, the lowest value obtained at 8.70 mol/L. Moreover, the dG_o/dt at all monomer concentrations in the present system have greater values compared to those obtained for simultaneous grafting of styrene onto poly(tetrafluoroethylene) (PTFE) films [20]. This discrepancy is predominately due to the role of diluting solvent, i.e. methanol in present system and dichloromethane in the corresponding styrene/PTFE system. Compared to dilution with dichloromethane, which is a good solvent of polystyrene methanol, a non-solvent of polystyrene, prompts a Trommsdorff-type effect in which polymer chains mobility are hindered allowing more propagation of polystyrene growing chains and less termination by mutual combination [21]. This satisfactorily explains the presence of maxima in both initial rate of grafting and Y_f%.

The log–log plot of the initial rate of grafting versus the monomer concentration is presented in Fig. 3. The plot can be divided into two regions, i.e. A and B. In the region A, dG_o/dt shows a remarkable increase with the increase in the monomer concentration up to 3.48 mol/L beyond which it declines in the region B until achieving the lowest value at 8.70 mol/L, which corresponds to pure monomer concentration. The order of

Table 2
Initial rate of grafting vs. monomer concentration and apparent rate constant of graft copolymerization obtained at an irradiation dose of 100 kGy and 60 °C

M_o (mol/L)	dG_o/dt (%/h)	Apparent rate constant k_1 (G%/h mol^{-2} L^2 $\text{kGy}^{-0.75}$)$\times 10^{-3}$
1.74	6.91	72.20
3.48	28.83	75.30
5.22	21.13	24.50
6.96	19.22	12.50
8.70	5.49	2.30

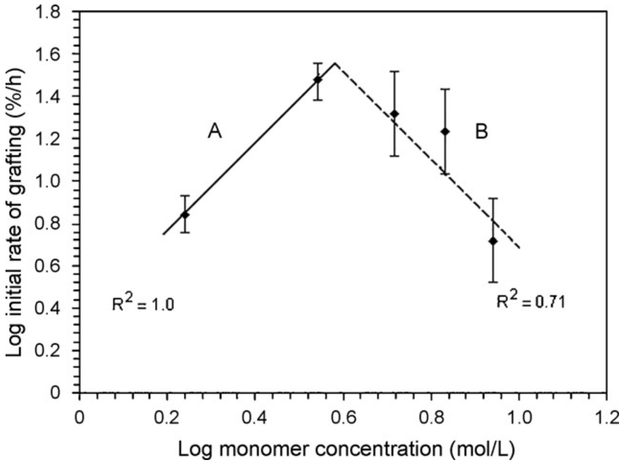

Fig. 3. Log–log plot for initial rate of grafting vs. monomer concentration. Grafting conditions are the same as in Fig. 2.

dependence of the initial rate of grafting on the initial monomer concentration in the bulk solution $[M_o]$ obtained from the slope equals 2.0 and can be expressed as:

$$\frac{dG_o}{dt}\alpha[M_o]^{2.0} \tag{2}$$

The high exponent of 2.0 of the monomer concentration is not consistent with the first order dependence of classical free radical polymerization. Similar deviations have been observed upon simultaneous grafting of styrene onto PTFE and poly(tetrafluoroethylene-*co*-hexafluoroproylene) (FEP) films [20,22]. Also, Gupta et al. [4] and Walsby et al. [23] reported an order of monomer concentration dependence of 1.9 and 1.2 for preirradiation grafting of styrene onto FEP and PVDF films, respectively. This behavior was ascribed to the increase in the viscosity of the grafting zone in a way that prompted termination by impurities and hindered the monomer diffusion. In a similar way, grafting of α,β,β-trifluorostyrene onto ETFE films showed a grafting rate of an order of dependence of 1.0 on the monomer concentration [9]. The reason of lowest initial rate of grafting recorded in region B at pure monomer concentration despite of styrene being a good solvent of polystyrene is unclear.

Based on these results, it can be conduced that the process of grafting of styrene onto ETFE is controlled to a great extent by diffusion, which suggests that grafting proceeds by a front mechanism. This means grafting starts at the surface of the film and proceeds internally toward the middle of the film by a continuous diffusion of the styrene through the already grafted layers, until an equilibrium swelling is reached at a certain monomer concentration. Similar grafting mechanism was reported for graft copolymerization of various monomers onto fluorinated polymers [24,25].

3.2. Effect of irradiation dose

Fig. 4 shows grafting yield-time courses at various electrons irradiation doses for graft copolymerization of styrene onto ETFE films. As can be seen, $Y\%$ initially increased drastically with time over a period of 4 h then slowed down as the reaction time prolonged to 8 h followed by a second increase at 8–24 h beyond which it leveled off. The $Y_f\%$ was also found to increase with the increase in the irradiation dose. In general, graft copolymerization with preirradiation method is well known to rely heavily on the amount and the efficiency of the trapped radicals generated in the base polymer and this explains the increase in the $Y_f\%$ with the rise in the dose under the influence of the increased amount of trapped radicals. Moreover, the increase takes place in $Y\%$ when propagation (chain transfer) is the dominant reaction and the slow down when termination reaction becomes more frequent.

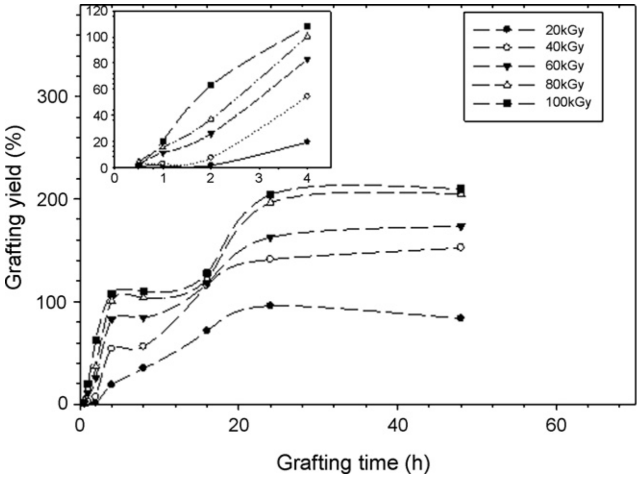

Fig. 4. Grafting yield-time courses at various preirradiation doses for graft copolymerization of styrene onto ETFE films. Grafting conditions are the same as in Fig. 2 except monomer concentration is kept at 3.48 mol/L.

Specifically, the second increase seen in Fig. 4 may be attributed the role of crystallinity in the irradiated films as ETFE crystallinity is reported to be a dose dependent [8]. Irradiation of semicrystalline polymer such as ETFE is well known to form radicals in both amorphous and crystalline regions with a polymer with high crystallinity is most likely to contain higher amount of trapped radicals than a polymer of low crystallinity. Assuming adequate supply of monomer, it is expected that grafting would be initiated by radicals in the amorphous region followed by propagation of growing chains that would continue dominating until consuming majority of radicals in the amorphous region causing a grafting slow down after 4 h. As the time prolonged with the monomer unable to diffuse in the crystallites, the trapped radicals in crystalline region would migrate to the lamella surface and participate in initiation and chain transfer causing further increase in $Y\%$ until termination reaction become more frequent above 24 h. Similar observation on the effect of crystallinity on $Y\%$ was reported for grafting of acrylic acid onto low density and high density polyethylene (PE) films [26].

The initial rate of grafting at various absorbed irradiation doses obtained graphically is presented in Table 3 and its corresponding log–log plot is in shown in Fig. 5. The dG_o/dt was found to increase linearly with the absorbed irradiation dose. The dependence of dG_o/dt on the irradiation dose (D) was obtained from the slope and found to be in the order of 0.75 and can be

Table 3
Initial rate of grafting vs. irradiation dose and apparent rate constant of graft copolymerization obtained at a monomer concentration of 3.48 mol/L and 60 °C

D (kGy)	dG_o/dt (%/h)	Apparent rate constant k_2 (G%/h mol^{-2} L^2 kGy$^{-0.75}$)$\times 10^{-3}$
20	5.44	47.50
40	15.65	81.20
60	23.33	89.40
80	27.78	85.80
100	30.41	79.40

expressed as follows:

$$\frac{dG_o}{dt}\alpha[D]^{0.75} \tag{3}$$

It can be obviously seen that the dose exponent of 0.75 is higher than the theoretical value of free radical polymerization which equals 0.5. Such high dependency on the absorbed dose reflects a possible mutual recombination of some of the trapped radicals caused by reduction in polymer chain mobility under the influence of crosslinking upon irradiation of ETFE [8,27]. This trend can be also explained by the 'mechano-chemical' grafting effect suggested by Bozzi and Chapiro [28] and Gupta et al. [29] to explain similar high dependency on the dose dependence of grafting of styrene onto PTFE and FEP, respectively. These authors proposed that in such grafting system the radicals are located far from each other at low doses and the polystyrene chains grow randomly and create discrete domains in PTFE or FEP. The grafted and the un-grafted domains have different swelling ability in the bulk monomer solution, thus it will introduce strains at the interface between different domains. As a result, polymeric chains are ruptured to create new radicals. Unlikely, grafting of styrene onto PVDF films was found to show a low dependence of initial rate of grafting of 0.43 on the irradiation dose. This behavior was ascribed to some recombinations of the trapped radicals caused by increasing chain mobility of PVDF irradiated and grafted above its glass transition temperature [23].

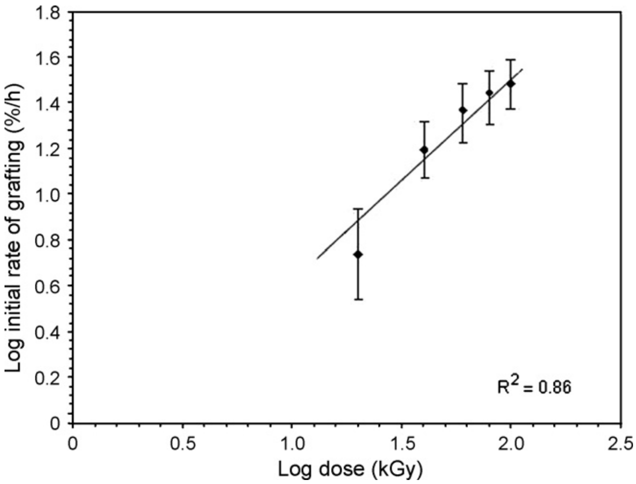

Fig. 5. Log–log plot of initial rate of grafting vs. irradiation dose. Grafting conditions are the same as in Fig. 4.

Based on Eqs. (2) and (3), the kinetic behavior for radiation graft copolymerization in the present system can be expressed in the form of the following grafting rate equation:

$$\frac{dG_o}{dt}\alpha[M_o]^{2.0}[D]^{0.75} \tag{4}$$

Eq. (4) can be written as:

$$\frac{dG_o}{dt} = k[M_o]^{2.0}[D]^{0.75} \tag{5}$$

where k is the apparent constant of the initial rate of graft copolymerization of styrene onto ETFE films. This equation can be used to calculate k_1 and k_2 as presented in Tables 2 and 3, respectively.

It can be suggested that grafting kinetics in the present system is mainly controlled by two parameters: (1) the amount of efficient trapped radicals and (2) the availability of the monomer molecules in the grafting sites.

3.3. *Effect of reaction temperature*

Fig. 6 shows grafting yield-time courses at various reaction temperatures. The initial rates of grafting were found to increase drastically at the first 8 h with temperature rise from 40 to 60 °C. The highest value of *Y%* is recorded at 60 °C which declines with further heating (65 °C). After 8 h, a slow down in *Y%* takes place at temperatures of 40, 55, 60 and 65 °C, whereas *Y%* at temperatures of 45 and 50 °C continue to increase and only starts to slow down at 24 h and above. The Y_f% is found to increase in sequence of 40 < 65 < 60 < 55 < 50 < 45 °C. The drastic increase in rates of grafting and *Y%* at the first 8 h can be attributed to the increase in the reactivity of the thermally decomposed trapped radicals with the rise in temperature, which is mostly accompanied by an enhancement in the monomer diffusion in the base polymer. Consequently, the initiation and propagation rates are enhanced. The decrease in rates of grafting and *Y%* at 65 °C is not only caused by mutual recombination of

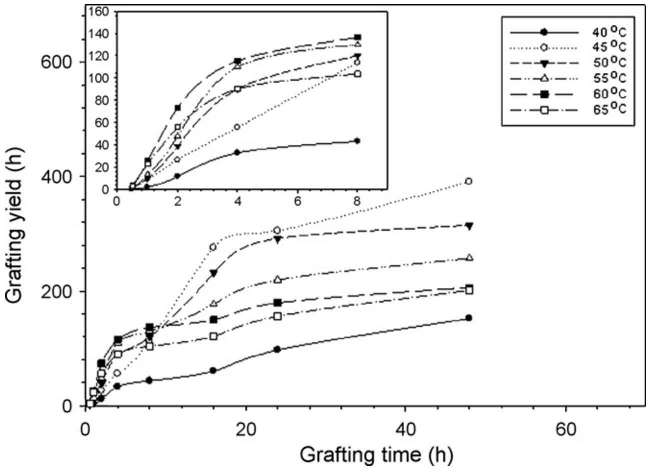

Fig. 6. Grafting yield-time courses at various reaction temperatures for graft copolymerization of styrene onto irradiated ETFE films. Grafting conditions are: dose 100 kGy; monomer concentrations, 3.48 mol/L. The rest of grafting conditions are as in Fig. 2.

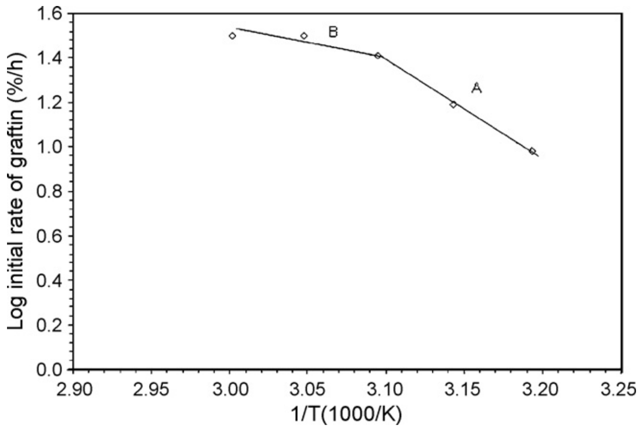

Fig. 7. Arrhenius plot of the initial rate of grafting vs. reciprocal of reaction temperature. Grafting conditions are as in Fig. 6.

trapped radicals taking place before reacting with the diffused monomer molecules but also by bimolecular termination of the graft growing chains enhanced at higher temperatures. The prolonged increase in $Y\%$ and the achievement of highest $Y_f\%$ at temperatures of 45 and 50 °C also reflects reaching highest rates of monomer diffusion, initiation and propagation that starts after 24 h. The considerable decrease in $Y_f\%$ above 50 °C indicates an increase in the rate of termination as discussed above. Similar behavior for grafting styrene onto preirradiated ETFE film under different conditions was reported by Guilmeau et al. [19] and Horsfall and Lovell [14] with maximum $Y\%$ achieved at 50 °C in both grafting system. Momose et al. [9] also reported a similar trend for grafting of α,β,β-trifluorostyrene onto ETFE film with a maximum $Y\%$ achieved at 50 °C.

Fig. 7 shows the Arrhenius plot of the initial rate of grafting for grafting of styrene onto ETFE films obtained graphically from Fig. 6 and plotted versus the reciprocal of temperature. Two regions A and B of linear dependency on the temperature could be observed with a break point located at 50 °C. The overall activation energies calculated from the slopes in regions A and B were found to be 36.9 and 12.5 kJ/mol below and above 50 °C, respectively. This behavior can be possibly attributed to presence of a glass transition temperature at around 50 °C in the base ETFE films taking into consideration the observation by Feng and Chang [30] who recorded a series of glass transitions in ETFE including one at the range of 40–60 °C. According to Ellinghorst et al. [25] the break in the Arrhenius plot is usually related to transition points in the base polymer film. This is because in semicrystalline polymers, the grafted monomer can easily reach the surface of the crystallites by diffusion through the amorphous surrounding. So, as the access of the monomer molecules to these radical sites is facilitated after passing the glass transition temperature, the overall activation energy for the graft reaction must decrease because the additive term in the overall activation energy corresponding to monomer diffusion in these crystalline–amorphous boundaries disappears [25].

Another possible explanation for the discontinuous behavior of activation energy can be reached by taking the glass transition of the grafted polystyrene into account. According to Brack et al. [12] the glass transition temperature of the grafted polystyrene domains in ETFE films, was suggested to be reduced from the range 80–85 °C to 45–70 °C by plasticizing effect of the styrene monomer on the polystyrene domain during the grafting. This is eventually led to the loss of reactive radical sites due to the termination reactions as the glass transitions temperature of styrene swollen polystyrene component in the grafted film approaches. Since, thermal properties including glass transition of ETFE films are expected to vary from one manufacturer to another, the latter explanation based on variation in the glass transition of grafted polystyrene is very likely to be favored over the former one for the present case. However, more research is needed to determine the glass transition temperature of the grafted films components to confirm such explanation.

A typical trend of breaking point in the activation energy at 50 °C was reported for preirradiation grafting of α,β,β-trifluorostyrene onto ETFE films under N_2. This behavior was attributed to the decomposition of trapped radicals instead of glass transition effect of ETFE film. Similar breaking points were also observed during grafting of acrylic acid onto PTFE [31] and PE [32] films at different temperatures. Some other grafting systems also behave in a similar manner despite the differences in the ranges of the corresponding reaction conditions [33,34].

Finally, the lower activation energy in region B is due to the increase in the ability of the monomer diffusion to the grafting zone whereas the rapid decay of the trapped radicals and the increase in chain mobility that cause bimolecular termination of the propagated grafts is accounted for the higher activation energy value in region A.

3.4. Effect of film thickness

Fig. 8 shows grafting yield-time courses for graft copolymerization of styrene onto irradiated ETFE films having various thicknesses. The $Y\%$ was found to increase rapidly in first 8 h and tends to gradually level off with further time increase. At the first hour $Y\%$ is found to decease as the film gets thicker reflecting an ideal behavior for such films. However, this trend was reversed as the time increased suggesting that the increase in the

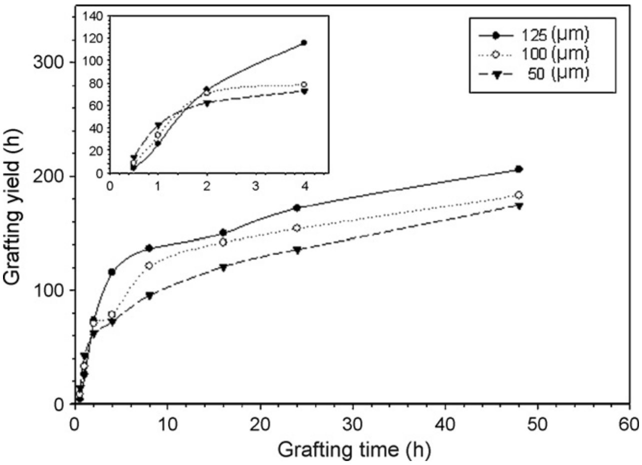

Fig. 8. Grafting yield-time courses at various film thicknesses. Grafting conditions are as in Fig. 2 except monomer concentration is kept at 3.48 mol/L.

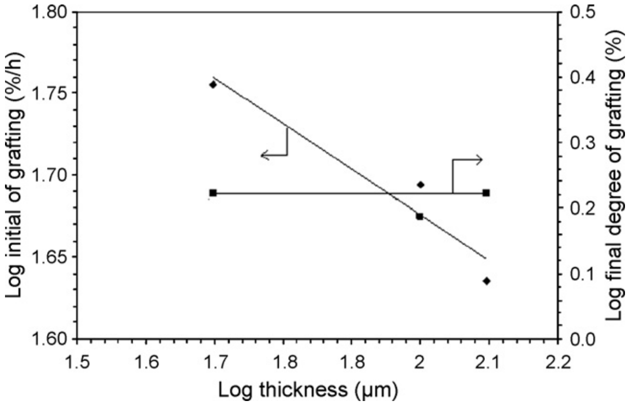

Fig. 9. Log–log plot of initial rate of grafting vs. thickness of films. Grafting conditions are as in Fig. 8.

film thickness extends the grafting through irradiated ETFE film in a way that made thicker films produce higher *Y%* compared to thinner ones at any subsequent grafting time. However, the thinner films also tends to achieve saturation grafting earlier than thicker ones and this is in a close agreement with the observation by Guilmeau et al. [19] who grafted styrene onto ETFE films of two distinct thicknesses (30 and 100 μm) and found that *Y%* of 100 μm film levels off slower than that of 30 μm thickness.

Fig. 9 shows log–log plot for the initial rate of grafting versus film thickness and the final grafting yield. The initial rate of grafting is shown to be decreasing with the increase in the film thickness with a negative order dependence on the film thickness of 0.3 but Y_f% remains almost constant. These results imply that grafting is this system is dependent not only on the concentration of trapped radicals but also on the monomer diffusion, i.e. grafting in the present system is a diffusion controlled process. The grafting initially begins at the surface of ETFE film and then the monomer diffuses through the grafted layers and reacts with the propagating polystyrene graft chains and the trapped radicals until the grafting fronts meet in bulk of the film and polystyrene distribution cover the whole thickness of the film [1,4]. The reaction continues until all chains are terminated and saturation grafting yield is reached.

The behavior of grafting of styrene onto ETFE in the present system in a good agreement with that obtained for grafting acrylic acid onto ETFE films [35] and styrene onto FEP films [29]. The similarity in monomer behavior in these three grafting systems is mainly due to the fact that neither styrene nor acrylic acid swells these fluorinated films. In contrast to this, Momose et al. [9] found that grafting of α,β,β-trifluorostyrene onto ETFE films resulted in grafting rates of similar values irrespective of the film thickness. They concluded that the initial grafting rate and the Y_f% were controlled by the radical concentration in the films and not by the monomer diffusion. In another study, Brack et al. [12] reported that the initial rate of grafting for copolymerization of styrene onto air irradiated ETFE films is not inversely proportional to the film thickness. These authors attributed such deviation from ideal film behavior to the extent of orientation in films: thinner films of greater extent of orientation inhibit monomer diffusion during grafting relative to thick counterparts. This deviation was alternatively explained on the basis of inhomogeneous radical distribution through the films depth that is transferred to polystyrene grafts and dissolution of polystyrene homopolymer in toluene during the extraction of the grafted films.

However, it important to mention that the effect of film thickness on grafting has been remaining subjective to contradictory results even in widely studied grafting systems such as graft copolymerization styrene and acrylic acid onto polyolefins and fluorinated polymers. Also, the grafting behavior of polymer films from various manufacturers may differ significantly, and in some cases, the grafting behavior of the same film material may differ in various regions due to inhomogenities arising during extrusion process [12].

3.5. *Effect of storage time*

Fig. 10 shows grafting yield-time courses at various storage time intervals. The irradiated films were stored under −60 °C for various time intervals in the range of 0–240 days. The *Y%* was found to increase rapidly at first 8 h beyond which it tends to level off. It can be obviously seen that the variation of storage time did not have a strong impact on *Y%* particularly in the early grafting hours which achieves grafting levels high enough to meet that required in radiation grafted fuel cell membranes.

Fig. 11 shows log–log plot of the initial rate of grafting versus the storage time. A very small slope of order of 0.04 is obtained reflecting the absence of any significant variation in *Y%* during investigated storage range of 0–240 days. These results suggests that there is no serious loss of radicals activity and the membranes can therefore be prepared from irradiated ETFE films that have been stored for at least 8 months under appropriate conditions. Moreover, preirradiation graft copolymerization method is superior for achieving desired *Y%* onto these films. These observations agree very well those reported by Horsfall and Lovell [14] for grafting of styrene onto air irradiated ETFE films stored up to 430 days under −18 °C.

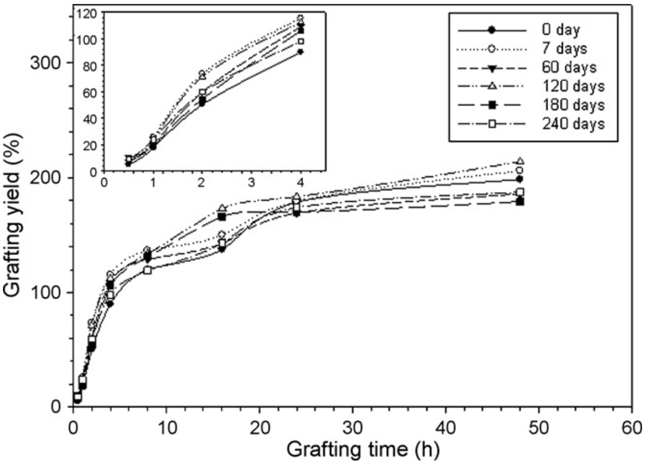

Fig. 10. Grafting yield-time courses at various intervals of storage time under −60 °C. Grafting conditions are as in Fig. 2 except monomer concentration is kept at 3.48 mol/L.

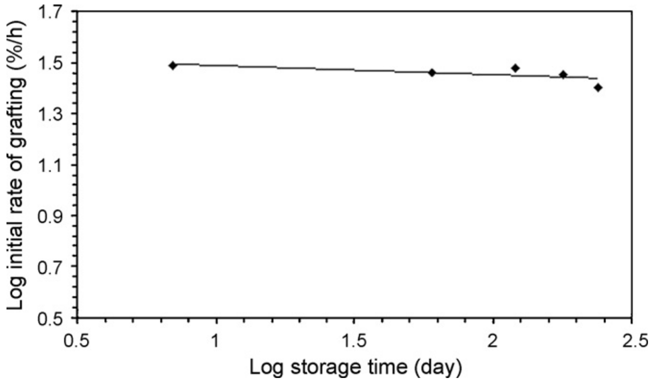

Fig. 11. Log–log plot of initial rate of grafting vs. film thickness. Grafting conditions are as in Fig. 10.

3.6. Evidence of grafting

Fig. 12 shows typical FTIR spectra of polystyrene grafted films having various grafting yields. The original ETFE film is used as a reference. The presence of polystyrene in the grafted films was confirmed by the additional peaks representing benzene ring features such as the stretching vibration of =C–H for benzene ring at 3010–3100 cm^{-1}, the skeletal C=C in-plane stretching vibrations in the range of 1500–1600 cm^{-1} and out-of-plane C–H deformation band at 700 cm^{-1} which is assigned for mono-substitution of the ring. These features confirm the formation of polystyrene in ETFE films.

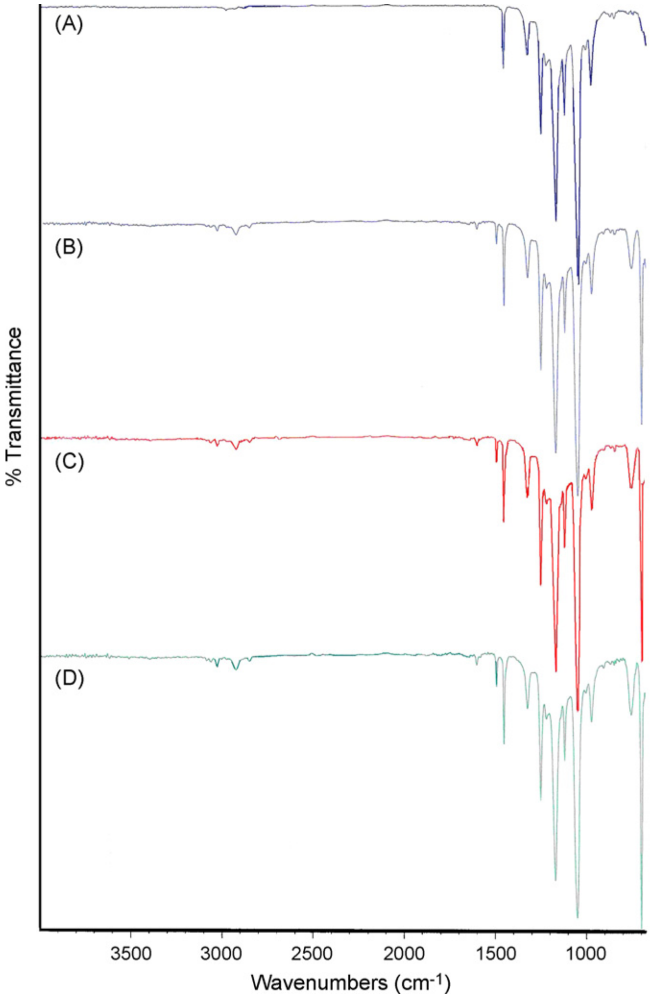

Fig. 12. FTIR spectra of (A) original ETFE film and polystyrene grafted ETFE films of various *Y*%: (B) 15%, (C) 32%, and (D) 60%.

4. Conclusions

The effects of monomer concentration, irradiation dose, temperature, film thickness and storage time on the grafting yield for graft copolymerization of styrene diluted with methanol onto ETFE films were kinetically investigated and the following conclusions can be drawn: (1) grafting yield and initial rate of grafting remarkably increase with the increase in the monomer concentration from 1.74 to 3.48 mol/L followed by a considerable decline suggesting the presence of Trommsdorff-type effect, (2) an order of 2.0 of dependence on the monomer concentration was obtained and that suggests grafting is a diffusion controlled process in this system, (3) higher irradiation doses produce higher grafting yields and speed up the initial grafting rates, (4) the initial rate of grafting increases with the temperature rise with maximum grafting yields achieved at 60 °C at first 8 h unlike the final degree of grafting which drops remarkably beyond this temperature, (5) the overall activation energies were found to respectively be 36.9 and 12.5 kJ/mol below and above 50 °C indicating the access of monomer molecules was facilitated by passing through glass transition temperature of ETFE films or polystyrene grafted component, (6) the initial rate of grafting is inversely proportional to the film thickness, (7) The storage of irradiated films under −60 °C up to 240 days does not cause major change in the grafting yield promoting this method for practical preparation of membranes. (8) Graft copolymerization in this system is mainly controlled not only by the amount of trapped radicals but also by the monomer diffusion into the base polymer.

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