

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: $dG_0/dt = k[M_0]^{2.0}[D]^{0.75}$. 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. © 2007 Elsevier B.V. All rights reserved.

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_0/dt	initial rate of grafting (%/h)
D	irradiation dose (kGy)
k	apparent rate constant (G%/h mol ⁻² L ² kGy ^{-0.75})
M_0	monomer concentration in bulk solution (mol/L)
T	reaction temperature (K)
W_0	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 N₂ 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 (–CF₂CF₂CH₂CH₂–)_n with thickness of 125 μm and den-

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

sity 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.

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 N₂ 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 N₂ 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 N₂ 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 N₂ 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

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