Synthesis of functional polymers by pre-radiation induced grafting of acrylaldehyde onto FEP film (Postprint)

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Abstract

FEP-g-acrylaldehyde graft copolymers were prepared by pre-irradiation-induced graft copolymerization of acrylaldehyde onto FEP (poly(tetrafluoroethylene-co-hexafluoropropylene)). The effects of grafting conditions including monomer concentration, irradiation dose, and solvent type were investigated. The formation of graft copolymers was confirmed by FTIR analysis. Structural investigation by X-ray diffraction (XRD) showed that the degree of crystallinity of these graft copolymers decreases with increasing grafting degree. Moreover, the acrylaldehyde content in the polymer and protein immobilization were investigated in correlation with the grafting degree.

Full Text

Preamble

Synthesis of Functional Polymers by Pre-radiation Induced Grafting of Acrylaldehyde onto FEP Film

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Abstract
FEP-g-acrylaldehyde graft copolymers were prepared by pre-radiation induced graft copolymerization of acrylaldehyde onto FEP (poly(tetrafluoroethylene-co-hexafluoropropylene)). The effects of grafting conditions such as monomer concentration, irradiation dose, and various solvents were investigated. The formation of graft copolymers was confirmed by FTIR analysis. Structural investiga-

tion by X-ray diffraction (XRD) revealed that the degree of crystallinity of such graft copolymers decreases with increasing grafting degree. Moreover, the acrylaldehyde content of the polymer and protein immobilization were investigated in correlation with the degree of grafting.

Keywords: Pre-radiation grafting, FEP, Acrylaldehyde, Immobilization, Protein

Introduction

Microarray technology has become a crucial tool for large-scale and high-throughput biology, enabling fast, easy, and parallel detection of thousands of addressable elements in a single experiment [1 3]. To attach proteins to a solid substrate, the surface must be modified to achieve maximum binding capacity [4]. The aldehyde group is a common functional group for the covalent binding of proteins to surfaces [5]. This covalent immobilization process offers several advantages: active sites are better accessible to analytes when positioned appropriately, and less variation in antibody affinities within each antibody population positively affects sensitivity [6,7].

Radiation-induced grafting of various monomers onto polymeric films provides a novel method to produce functional materials for modern technology, particularly in separation science, electrochemical devices (including fuel cells, batteries, and sensors), and biological and biomedical applications [8]. Additionally, acrylaldehyde has been grafted onto polyethylene and poly(methyl methacrylate) films using radiation energy [9,10] to create functional polymers containing hydrazone, oxime, and oxyacid groups [11]. However, to our knowledge, few detailed studies have investigated acrylaldehyde grafted onto FEP (poly(tetrafluoroethylene-co-hexafluoropropylene)) via radiation-induced graft copolymerization. We examined the influence of synthesis conditions, particularly radiation dose, on the degree of grafting. FTIR-ATR and X-ray diffraction measurements confirmed successful synthesis. Furthermore, the acrylaldehyde content of the polymer and protein immobilization were investigated in correlation with the degree of grafting.

2. Experimental

2.1 Materials

FEP film with a thickness of 100 m supplied by DuPont (USA) was used for grafting. Acrylaldehyde (from Sinopharm Chemical Reagent Co., Ltd., China) was distilled (bp 52°C, atmospheric pressure) prior to use and dissolved in solvents. All other chemicals were reagent grade and used as received.

2.2 Irradiation

FEP films were washed with methanol and dried under vacuum before irradiation. A 60Co gamma-ray source (10,000 Ci) was used for irradiation of FEP films. All irradiations were carried out under nitrogen atmosphere at ambient temperature.

2.3 Graft Copolymerization

Irradiated films were cut into pieces (2.5 cm × 4 cm) and immersed in acrylaldehyde solution placed in a glass ampoule. Several solvents (i.e., water, ethanol, methanol, diethyl ether, and dichloromethane) were used for the grafting reaction. The monomer solution was flushed with nitrogen for 30 min to remove air, and then the ampoule was sealed. Grafting was carried out by placing the ampoule in a water bath maintained at constant temperature for the desired period. After reaction, films were removed from the ampoule and extracted with ethanol to remove homopolymer adhering to the surface of grafted films. The films were dried under vacuum at 50°C until constant weight was obtained. The degree of grafting was gravimetrically determined as the percentage weight increase of the FEP film using the following equation:

$$\text{Degree of grafting} = \frac{w_g - w_0}{w_0} \times 100\%$$

where w_0 and w_g are the weights of original and grafted FEP films, respectively.

2.4 FTIR-ATR Measurements

FTIR-ATR measurements of original and grafted FEP films were carried out with an FTIR spectrometer at ambient conditions in transmittance mode. Film spectra were detected using an ATR accessory.

2.5 X-ray Diffraction Measurements

X-ray diffraction (XRD) measurements were performed using an X-ray diffractometer. Diffractograms were recorded over a 2 range of 5–50°.

2.6 Acrylaldehyde Content

The acrylaldehyde content of the membranes was determined by acid-base titration. Membrane samples (approximately 2.0 g) were immersed in 50 mL of 0.5 M NH2OH · HCl solution overnight at room temperature, followed by 1 h at 45°C with frequent stirring. The protons (H+) released into the solution were titrated with standardized 0.1 M NaOH solution until the color changed from yellow to green. The volume of standardized NaOH solution consumed was V_1. The same procedure was performed on 0.5 M NH2OH · HCl solution without membrane samples, and the volume of standardized NaOH solution consumed was V_0. The acrylaldehyde content of the membranes was determined using the following equation:

$$\text{Acrylaldehyde Content (\%)} = \frac{(V_1 - V_0) \times C}{m} \times 100\%$$

where V_1 and V_0 are the volumes of standardized NaOH solution consumed for titration of NH2OH · HCl solution with and without membrane samples, respectively, C is the concentration of standardized NaOH solution, and m is the weight of the membrane.

3. Results and Discussion

The grafting of acrylaldehyde onto pre-irradiated FEP films was studied to determine optimum conditions for preparing membranes with desired graft levels, as shown below. The grafting was found to be strongly influenced by reaction conditions such as radiation dose, monomer concentration, solvent, and reaction time.

3.1 Effect of Radiation Dose

The influence of radiation dose on the degree of grafting is presented in Fig. 1. For all doses, the degree of grafting increases with increasing irradiation dose. This behavior may be attributed to the fact that at higher radiation doses, the number of radicals generated in the system also increases, making more radicals available for the grafting reaction.

Fig. 1. Variation of the degree of grafting with time at various pre-irradiation doses. Grafting conditions: monomer concentration, 100%; reaction temperature, 55°C.

3.2 Effect of Monomer Concentration

The influence of monomer concentration on the degree of grafting is presented in Fig. 2. The degree of grafting increases with monomer concentration. Moreover, the degree of grafting increases as acrylaldehyde concentration rises from 20 to 100 vol%, though the increase is not substantial.

Fig. 2. Grafting degree of acrylaldehyde onto FEP versus monomer concentration. Grafting conditions: pre-irradiation dose, 30 kGy; reaction temperature, 55°C; reaction time, 16 h.

3.3 Effect of Diluent Type

Diluent is basically used in radiation-induced graft copolymerization processes to bring about swelling of the base polymer, thereby enhancing monomer accessibility to grafting sites. Therefore, the correct choice of diluent is crucial in radiation-induced grafting.

Fig. 3. Grafting degree of acrylaldehyde onto FEP versus reaction time in different diluents.

3.4 FTIR Measurements

Figure 4 [Figure 4: see original paper] shows FTIR spectra of original and grafted FEP films. Original FEP films are characterized by a narrow band at 1100–1200 cm^{-1}, representing the stretching vibration of C–F. The presence of acrylaldehyde in grafted FEP films is established by the C=O stretching vibration at 1710 cm^{-1} and the C–H aldehyde stretching vibrations at 2850 cm^{-1}. The spectra clearly indicate that bands arising from the aldehyde increase with increasing degree of grafting, demonstrating that acrylaldehyde is successfully grafted onto the FEP backbone.

Fig. 4. FTIR spectra of original FEP (A) and acrylaldehyde-grafted FEP membranes with various degrees of grafting: (B) 5.21%, (C) 10.52%, (D) 17.05%, (E) 28.65%.

3.5 X-ray Diffraction Measurements

Grafting of acrylaldehyde onto FEP brings about considerable changes in the crystallinity of the graft copolymer. Fig. 5 shows diffraction patterns of original and grafted FEP films. It was found that the crystallinity peak for both original and grafted films occurs at the same angle (2), indicating no change in crystal structure. However, the peak intensities of all grafted films are lower and decrease with increasing degree of grafting, meaning that crystallinity decreases with increasing degree of grafting. These results are similar to those obtained for grafting of styrene onto FEP and PFA. This behavior can be explained on the basis of dilution and partial destruction of inherent crystallinity during formation of graft copolymers.

Fig. 5. Diffraction patterns of original FEP (A) and acrylaldehyde-grafted FEP membranes with various degrees of grafting: (B) 5.21%, (C) 10.52%, (D) 17.05%, (E) 28.65%.

3.6 Acrylaldehyde Content

Fig. 6. Relationship between acrylaldehyde content of grafted membranes and degree of grafting.

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Note: Figure translations are in progress. See original paper for figures.