

Surface Modification of Acrylonitrile Copolymer Membranes by Grafting Acrylamide. III. Kinetics and Reaction Mechanism Initiating by $\text{Fe}^{2+}/\text{H}_2\text{O}_2$

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ABSTRACT: The kinetics and mechanism of grafting of acrylamide onto acrylonitrile copolymer membranes with $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ as the initiator in an aqueous medium were studied. The experimental results were found to be in good agreement with the proposed kinetic scheme. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1917–1921, 1998

Key words: acrylonitrile copolymer membranes; grafting copolymerization; acrylamide; $\text{Fe}^{2+}/\text{H}_2\text{O}_2$; kinetics

INTRODUCTION

Grafting of hydrophilic monomers onto the surface of porous membranes is an effective method for modifying their properties. Godjevargova and coworkers reported a series investigations on grafting dimethylaminoethyl methacrylate and similar monomers onto acrylonitrile (AN) copolymer (PAN) membranes and its application in biosensors.^{1–3}

In our previous studies, we reported ceric-initiated and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ -initiated grafting of acrylamide (AAM) onto PAN membranes.^{4,5} This is a report on the kinetics and mechanism of the grafting of AAM onto PAN membranes using an $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ initiating system.

EXPERIMENTAL

Materials

An AN copolymer containing $5.5 \pm 0.3\%$ methyl methacrylate (MMA) and $4.0 \pm 0.3\%$ sodium

methylpropylenesulfonate, with a molecular weight 60,000 (Jinshan Petrochemical Co., Shanghai, China) was used. PAN membranes were made in our laboratory as described earlier.⁵ AAM, ferrous ammonium sulfate (FAS), H_2O_2 , and other chemicals were used as received.

Synthesis

The grafting modification of PAN membranes was carried out in two stages: In the first stage, the membranes were hydrolyzed with an aqueous solution containing 1.5 mol/L NaOH at 50°C for 1 h. In the second stage, the membranes were impregnated in a 100-mL aqueous solution (pH 3) containing 5 wt % FAS for 1–1.5 h and added into a 200-mL aqueous solution (pH 5.0) containing 0.4225 mol/L AAM and 0.2545 mol/L H_2O_2 in a typical experiment. Then, the graft reaction was carried out in a three-neck 250-mL cylindrical flask under nitrogen at 60°C for 1–4 h.

To discover the optimal conditions for the grafting of AAM onto the PAN membrane using $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ as the initiator, copolymerization was carried out under various conditions as described earlier.⁵ The variables studies included the pH of the medium, reaction time and temperature, and

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concentration of AAm and H_2O_2 . The results of our previous study were used in the present work.

Determination of the Grafting Copolymerization Rate

The grafting copolymerization rate (R_g), defined as the reacted monomer amount in a definite time and a definite medium volume, can be calculated according to the following equation:

$$R_g = \frac{W - W_0}{mVt} \quad (\text{mol L}^{-1} \text{ s}^{-1})$$

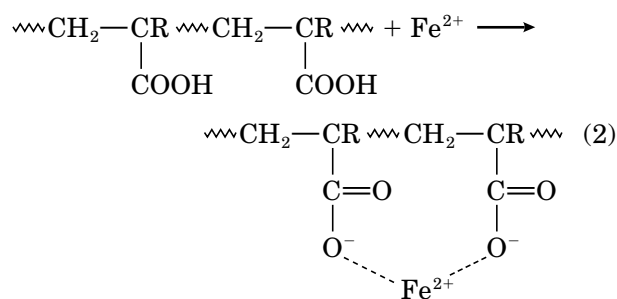
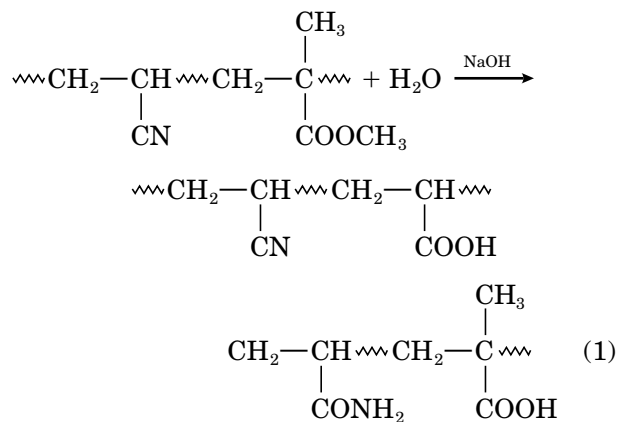
where W and W_0 are the membrane mass before and after grafting, respectively; m , the molecular weight of AAm; V , the volume of the medium; and t , the reaction time.

RESULTS AND DISCUSSION

Mechanism

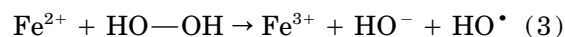
In regard to the mechanism of grafting of methyl methacrylate onto poly(ethylene terephthalate) (PET) using Fe^{2+}/H_2O_2 as the initiator, Hebeish and coworkers reported that Fe^{2+} first reacted with H_2O_2 to form a hydroxyl radical and the latter was transferred to the backbone of the PET macromolecule.⁶ Similarly, Shah et al. investigated the grafting of AN onto sodium alginate (SA).^{7,8} They have found that the hydroxyl radical formed from the reaction of Fe^{2+} and H_2O_2 attacked the SA macromolecules to produce macroradicals and then branches. In studying the modification of starch by grafting methacrylic acid, Vazquez et al. obtained similar results.⁹ From the above, we can conclude that the mechanism of grafting AAm onto PAN membranes is as follows:

When the PAN membrane is treated by a concentrated NaOH solution, $-CN$ as well as $-COOR$ groups of the PAN macromolecule on the surface of the membrane can be hydrolyzed into carboxyl groups. Then, Fe^{2+} would be absorbed on it while contacting the hydrolyzed membrane:

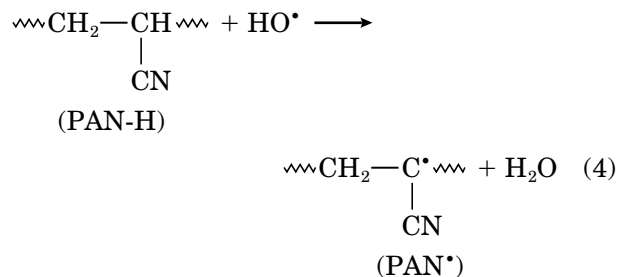


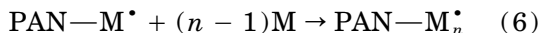
(R = H, CH_3)

When the membrane that absorbed Fe^{2+} was added into the aqueous medium containing H_2O_2 , the latter, a kind of low molecular weight molecule, diffused quickly onto its surface and reacted with Fe^{2+} to give $HO\cdot$:

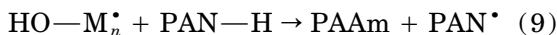
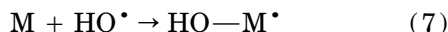


Hydroxyl radicals then abstracted hydrogen from the tertiary carbon in the PAN backbone to produce the PAN macroradical ($PAN\cdot$), which interacted with the monomer (M) to initiate grafting:

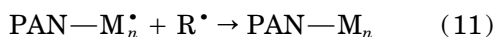
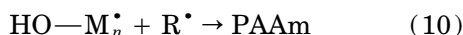




Since AAm is polymerized easily, HO^\bullet can also react with it to form a monomeric radical (M^\bullet) in the vicinity of the membrane and initiate homopolymerization to produce the homopolymer, PAAm. The homopolymeric radical can also transfer to PAN to form PAN^\bullet and then branch:



Macroradicals were terminated when they contacted each other or with ferric ions to produce the grafting copolymer ($\text{PAN}-\text{M}_n$):

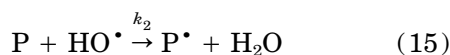


Kinetics

To analyze the kinetics of the grafting reaction, the above-proposed mechanism can be simplified, where I, $\text{P}-\text{H}$, P^\bullet , and $\text{P}-\text{M}^\bullet$ refer to H_2O_2 , $\text{PAN}-\text{H}$, PAN^\bullet , and $\text{PAN}-\text{M}^\bullet$ ($\text{PAN}-\text{M}_n^\bullet$), respectively. It was first assumed that no transfer reactions occurred and the contribution of the homopolymeric radicals to grafting was ignored:



$$R_1 = \frac{d[\text{HO}^\bullet]}{dt} = k_1[\text{Fe}^{2+}][\text{I}] \quad (14)$$



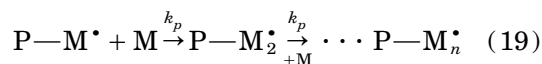
$$R_2 = -\frac{d[\text{HO}^\bullet]}{dt} = \frac{d[\text{P}^\bullet]}{dt} = k_2[\text{P}][\text{HO}^\bullet] \quad (16)$$



$$R_i = -\frac{d[\text{P}^\bullet]}{dt} = \frac{d[\text{PM}^\bullet]}{dt} = k_i[\text{P}^\bullet][\text{M}] \quad (18)$$

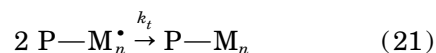
The activity of the macroradical was assumed to be the same. Grafting branches were assumed

to be very long and most of monomers were used in the propagation reaction:



$$R_g = -\frac{d[\text{M}]}{dt} = k_p[\text{PM}^\bullet][\text{M}] \quad (20)$$

The termination reaction was assumed to be taking place only between two macroradicals:



$$R_t = -\frac{d[\text{PM}^\bullet]}{dt} = 2k_t[\text{PM}^\bullet] \quad (22)$$

when the steady state was reached,

$$\begin{aligned} \frac{d[\text{HO}^\bullet]}{dt} &= -\frac{d[\text{HO}^\bullet]}{dt}; \quad \frac{d[\text{P}^\bullet]}{dt} \\ &= -\frac{d[\text{P}^\bullet]}{dt}; \quad \frac{d[\text{PM}^\bullet]}{dt} = -\frac{d[\text{PM}^\bullet]}{dt} \\ R_1 &= R_2; \quad R_2 = R_i; \quad R_i = R_t \end{aligned} \quad (23)$$

that is,

$$k_1[\text{Fe}^{2+}][\text{I}] = 2k_t[\text{PM}^\bullet] \quad (24)$$

Then, we can get the following equation from eqs. (24) and (20):

$$R_g = k_p \left(\frac{k_1}{2k_t} \right)^{1/2} [\text{Fe}^{2+}]^{1/2} [\text{I}]^{1/2} [\text{M}] \quad (25)$$

Influence of Reaction Parameters

Reaction Time

R_g decreased with increasing reaction time sharply before 1.5 h and slowly after then (Fig. 1).

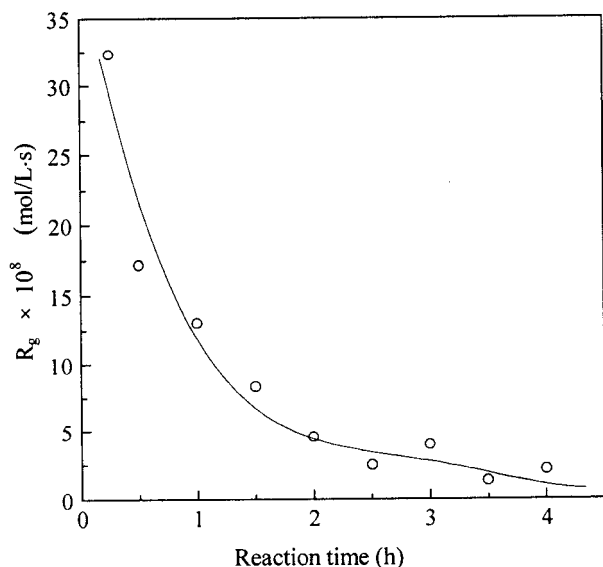


Figure 1 Effect of reaction time on graft polymerization rate: $T = 40^\circ\text{C}$; pH 5.0; $[\text{M}] = 0.4225$ mol/L; $[\text{I}] = 0.2545$ mol/L.

The amount of the copolymer on the membranes became greater and greater and the amounts of the monomer and H_2O_2 became smaller and smaller with the reaction proceeding. Both slowed down the grafting reaction and R_g decreased. After 1.5 h, the graft copolymerization reached the saturation state and R_g trended to a definite value.

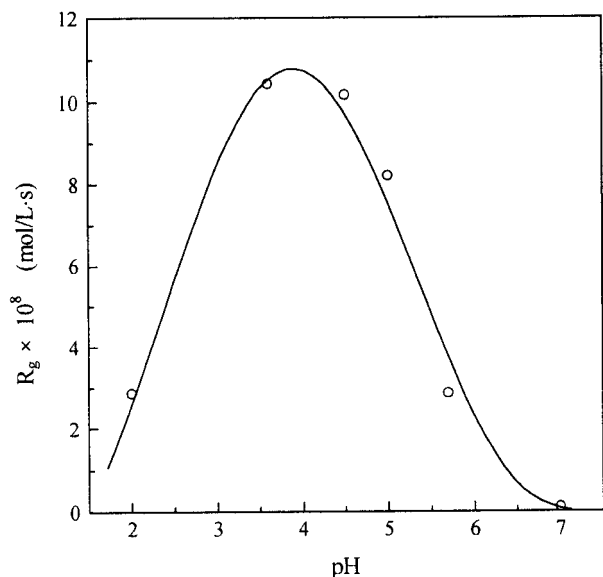


Figure 2 Effect of pH on graft polymerization rate: $T = 60^\circ\text{C}$; $t = 2$ h; $[\text{M}] = 0.4225$ mol/L; $[\text{I}] = 0.2545$ mol/L.

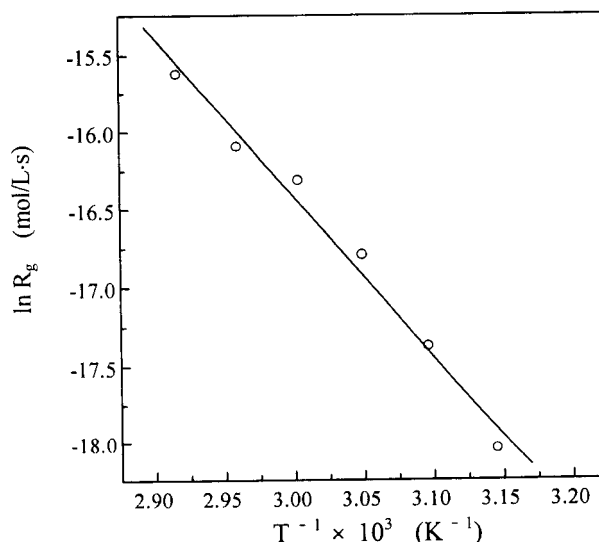


Figure 3 Effect of reaction temperature on graft polymerization rate: pH 5.0; $t = 2$ h; $[\text{M}] = 0.4225$ mol/L; $[\text{I}] = 0.2545$ mol/L.

Effect of pH of the Medium

The pH influenced R_g violently and reached a maximum when the pH was about 4.0 (Fig. 2). R_g was approximately zero with pH 7.0. The pH influences directly the reactive activity of Fe^{2+} and H_2O_2 . The larger the pH, the stronger the basicity and the more easily oxygen attacks Fe^{2+} . On the other hand, the decomposing rate of H_2O_2 increased with decreasing pH. Then, only when

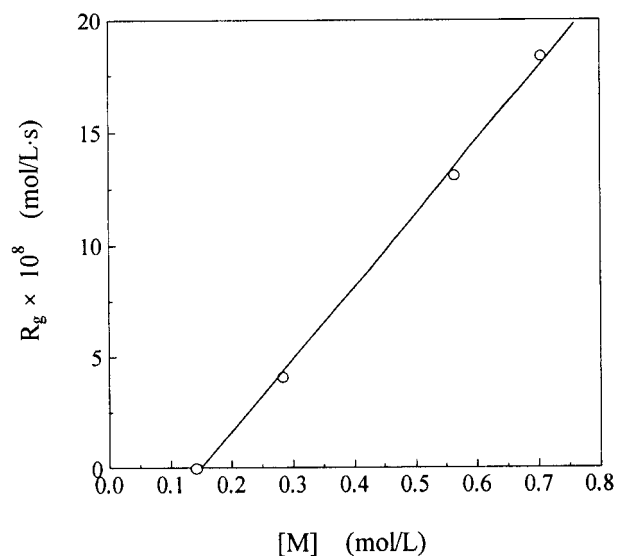


Figure 4 Effect of concentration of AAm on graft polymerization rate: pH 5.0; $T = 60^\circ\text{C}$; $[\text{I}] = 0.2545$ mol/L; $t = 1$ h.

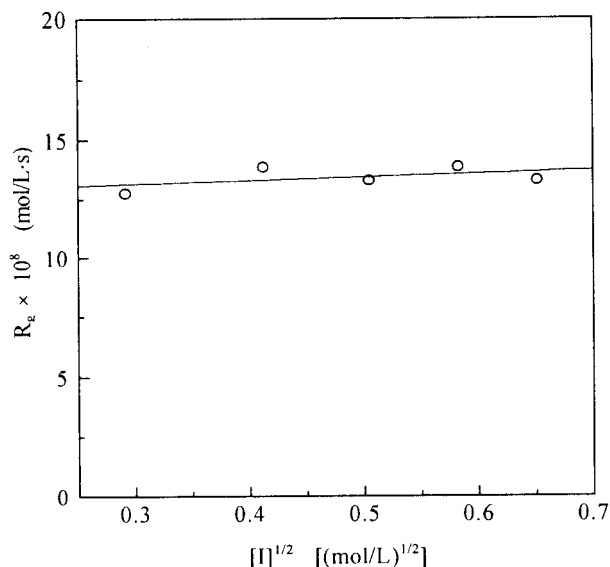


Figure 5 Effect of concentration of H_2O_2 on graft polymerization rate: pH 5.0; $T = 60^\circ\text{C}$; $[\text{M}] = 0.4225 \text{ mol/L}$; $t = 1 \text{ h}$.

the pH was in range 3.6–5.7 did the grafting reaction proceed normally and then R_g was high. When the pH was too low, that is, below 3.6, the Fe^{2+} ions adsorbed on the surface of the membrane can be deabsorbed into the medium. This led to homopolymerization in the medium and the extent of grafting was very low.

Reaction Temperature

Figure 3 shows a plot of the logarithm of R_g versus the reciprocal of the temperature scale (T). From the Arrhenius equation $\ln R = \ln k - [(E/R)(1/T)]$, we can get the active energy of the grafting reaction, that is, $E_g = 85.47 \text{ kJ/mol}$.

Concentration of AAm

Figure 4 indicates that R_g increased with increasing concentration of the AAm ($[\text{M}]$) linearly. It was found to coincide with eq. 25.

Concentration of H_2O_2

Figure 5 indicates that R_g increased with the square of the concentration of H_2O_2 ($[\text{I}]$) linearly, which agreed with eq. 25. Comparing Figures 4 and 5, we know that the former curve was more oblique than was that of the latter. The results show that it would be better to increase the concentration of AAm than that of H_2O_2 to increase R_g .

CONCLUSION

The mechanism and kinetics of the grafting of AAm onto PAN membranes with $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ as the initiator was proposed. The experimental results were in good agreement with the above. The graft copolymerization rate was also influenced by the reaction time and the pH of the medium.

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