

Compatibilization of Acrylic Polymer–Silk Fibroin Blend Fibers. I. Graft Copolymerization of Acrylonitrile onto Silk Fibroin

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ABSTRACT: To synthesize effective compatibilizers for the compatibilization of acrylic polymer–silk fibroin blend fibers, the homogeneous graft copolymerization of acrylonitrile onto silk fibroin, initiated by potassium persulfate–sodium bisulfite redox system in 60 wt % ZnCl₂ aqueous solution was investigated. The percentage graft, percentage efficiency, and molecular weight of the grafted polyacrylonitrile increase with the increase of the concentration of initiator, the concentration of acrylonitrile, and the temperature to optimum values, respectively, and then decrease. With the increase of reaction time, the percentage graft and percentage efficiency increase, whereas the molecular weight of the grafted polyacrylonitrile decreases. The influence of the reaction conditions on the molecular architecture of the graft copolymers is also discussed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1089–1097, 1998

Key words: silk fibroin; acrylonitrile; graft copolymerization; compatibilization

INTRODUCTION

We have a great deal of interest in acrylic polymer–silk fibroin (PAC–SF) blends.^{1–3} In a previous article,¹ it was reported that these two polymers can form useful blend fibers, whose moisture absorption increases with the increase of the SF content in the blends. However, in adding SF into PAC, the strength, elongation, and specific work of rupture of the resulting fibers decrease in comparison with that of the original pure PAC fiber. Morphological studies show that the blend fibers have a sheath–core structure, and the adhesion between the two polymers is very poor. It is believed that the poor mechanical properties of the blend fibers are due to the incompatibility of these two polymers, which can be alleviated by adding a graft copolymer (AN-g-SF) or a compatibilizer.

As a general rule, we believe that, to improve the mechanical properties of the blend fibers effectively, two requirements about the added AN-g-SF should be reached: (1) the number of grafts on SF should be as small as possible, and (2) the molecular weight of individual segment has to be equal or higher than those of corresponding homopolymers.⁴

Although numerous studies concerning grafting of vinyl monomers onto silk fibers can be found in the literature,^{5–12} it is surprisingly to note that, to our knowledge, there is only little information about the graft copolymerization of acrylonitrile (AN) onto SF.¹³ Furthermore, the main purpose of these studies concentrated on the improvement of some physical properties of SF, and the samples studied were usually mixtures of unreacted silk fibers, graft copolymers, and homopolymers formed in the grafting process. Except in a few reaction systems,^{14,15} no information can be obtained about the molecular weight and architecture of the grafted polymers, which are important parameters for an effective compatibilizer.

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Our interest here is to improve the mechanical properties of PAC–SF blend fibers by compatibilization. This article deals with the investigation of the graft copolymerization, which was initiated by the potassium persulfate–sodium bisulfite redox system¹⁶ in 60 wt % ZnCl₂ aqueous solution of AN onto SF. The influence of the reaction conditions on the percentage graft, percentage efficiency, and molecular weight of the grafted polyacrylonitrile (PAN), as well as the molecular architecture of the final products (AN-g-SF), is discussed. In the second article, the compatibilization effect of the synthesized compatibilizers on the morphological and mechanical properties of the blend fibers will be presented.

EXPERIMENTAL

Materials

All of the reagents were analytical grade. Potassium persulfate, sodium bisulfite, hydrochloric acid, acetone, and *N*-dimethylformamide (DMF) were used as supplied. ZnCl₂ and LiBr were dried at 120°C for 24 h and then stored under high vacuum. AN was washed with 5% aqueous sodium hydroxide and sodium chloride solutions, dried over anhydrous calcium chloride, and then fractionally distilled. The middle fraction of the monomer was collected and stored under refrigerated conditions. Triply distilled water was used in all cases for the copolymerization reactions.

Graft Copolymerization

Degummed SF from wasted silk fibers was dissolved in 60 wt % ZnCl₂ aqueous solution at room temperature under constant stirring for several hours. The solution was filtered, and the polymer concentration was made up to 3 wt %. The graft copolymerization reaction was conducted in a 250-mL, four-necked flask under a nitrogen atmosphere. The flask, containing 150 mL of 3 wt% SF solution and the required amount of AN (from 30 to 200% on the weight of SF) was immersed in a thermostated water bath and regulated to within ±0.5°C. Under gentle mixing, an appropriate amount of potassium persulfate, which was dissolved in a few milliliters of distilled water was added to the flask, after 3 min, the required amount of sodium bisulfite, which was also dissolved in a few milliliters of distilled water was added. In a separated study it was found that, if

more sodium bisulfite was used, the temperature of the reacting system would increase. On the other hand, if less sodium bisulfite was employed, the reaction would be relatively slow at room temperature. As mentioned previously, higher reaction temperature will decrease the molecular weight of the grafted PAN. Furthermore, the optimum range of sodium bisulfite is relatively small, (about one-third to one-half the weight of potassium persulfate). As a result, we chose 50% weight percentage of potassium persulfate throughout this work. Polymerization proceeded for a required time under constant stirring before it was stopped by the addition of 5 mL hydroquinone solution.

The reacted solution was then precipitated with large excess of acetone (10/1, v/v). The resulting precipitates (powders) were filtered, washed, dried, and treated with DMF at 80°C for 4 h to extract PAN homopolymer. Thereafter, the products were filtered and washed with DMF, acetone, water, and acetone, and dried at 105°C to constant weight. The dried samples were then immersed in 9.5 mol L⁻¹ LiBr aqueous solution at 80°C for 4 h under constant stirring to dissolve out the unreacted SF. Finally, the samples was filtered, washed, dried, and stored under vacuum before use.

Measurements

Percentage Graft and Percentage Efficiency

The percentage graft and percentage efficiency were calculated from the relations

$$\% \text{ Grafting} = [(W_3 - W_1) / (W_1 + W_4 - W_3)] \times 100 \quad (1)$$

$$\% \text{ Efficiency} = [(W_3 - W_1) / W_2] \times 100 \quad (2)$$

where W_1 and W_2 are the weights of the original SF and AN monomer added to the reaction system; and W_3 and W_4 are that of the products after extraction with DMF and after extraction with 9.5 mol L⁻¹ LiBr aqueous solution, respectively.

Molecular Weight of Grafted PAN

Two grams of the grafted samples were treated with 140 mL of 6 mol L⁻¹ hydrochloric acid at 60°C for 24 h. The undissolved residue was filtered out and dried, and was immersed in DMF at 20°C for 8 h under constant stirring. The undissolved residue was removed, and the solution was then

precipitated with distilled water, collected by centrifugation, rinsed with water and acetone, and dried at 105°C to constant weight. The resulting precipitates were believed to be the grafted PAN with a small piece of peptide fragment on one end of the PAN polymer.¹⁷ The molecular weight of the separated PAN was determined from its intrinsic viscosity in DMF at 25°C.¹⁸

Molecular Architecture of the Graft Copolymer

The molecular architecture of the graft copolymer was characterized by a parameter PAN/SF (mol mol⁻¹), which is calculated by the equation

$$\begin{aligned} \text{PAN/SF} &= MW_{\text{SF}} \times \text{PG}/MW_{\text{PAN}} \times 100 \\ &= 3.3 \text{ PG}/MW_{\text{PAN}} \quad (3) \end{aligned}$$

where MW_{SF} , PG, and MW_{PAN} are the molecular weight of SF (330 kD),¹⁴ percentage graft, and the average molecular weight of the grafted PAN segments.

Because the copolymerization process is very complicating, the graft copolymer is not well defined. Thus, this value (PAN/SF) is only a matter of "average." However, this parameter works well in providing the information of the molecular architecture of the graft copolymer, which is a very important parameter in choosing effective compatibilizers in the compatibilization process of PAC-SF blend fibers, as can be seen in the next section.

Fourier Transform Infrared (FTIR) Study

FTIR spectra were recorded on a MAGNA IR-550 (Nicolet) spectrometer by the method of transmission. The samples were examined in KBr discs. To obey the Beer-Lambert law, samples were made thin enough. All spectra presented here are expanded to full scale.

RESULTS AND DISCUSSION

Dissolving SF in ZnCl₂ Aqueous Solution

Several kinds of concentrated aqueous solutions of salts (such as LiBr,¹⁹ CaCl₂,²⁰ NaSCN,^{1,2} and ZnCl₂) have been used to dissolve SF. NaSCN and ZnCl₂ aqueous solutions are common solvents of SF and PAN. In a separated experiment, it was found that the molecular weight of the grafted PAN in ZnCl₂ aqueous solution was usually higher than that in NaSCN aqueous solution.

According to Freddi and colleagues,²¹ the molecular weight of SF was characterized by $[\eta]$ in aqueous solution at 20°C. It was found that the $[\eta]$ of SF that had been dissolved in ZnCl₂ aqueous solution is 0.54, whereas that did not undergo the procedure of ZnCl₂ aqueous solution treatment is 0.69. Furthermore, temperature has a very important influence on the $[\eta]$: if SF was dissolved in ZnCl₂ aqueous solution higher than 60°C, the final $[\eta]$ of SF decreases rapidly. It can thus be concluded that the molecular weight of SF is decreased by dissolving in ZnCl₂ aqueous solution. However, as suggested by Freddi and colleagues,²¹ such an extent of degradation may still be acceptable, because "such a value is normally attained during silk fiber processing on an industrial scale (after degumming, dyeing, etc.)."

It should be pointed out that the experimental evaluation of the molecular weight of SF meets, however, with several difficulties. As a matter of fact, literature values of the molecular weight of SF fall in the range of 10–400 kD.^{22–25} As it has been reported,²⁶ the large disagreement between the results reported in literature may be due to (1) SF does not give stable solutions in aqueous media, which is widely used for molecular weight determinations; and (2) several artifacts, which may influence the molecular weight, are involved in the procedures used for the preparation of SF samples. Furthermore, we believe that the different breeds of silkworms may also play a role. On the other hand, it is supposed that, although ZnCl₂ aqueous solution used in this study degrades SF slightly, it is still a high polymer. That is to say, although the exact molecular weight of SF may still be confusing, the uncertainty of the exact value may not influence the final results of this study (the trend of the influence of reaction conditions on the molecular weight of PAN and the architecture of the graft copolymers).

Separating the Grafted PAN from SF

After extracting with DMF and LiBr aqueous solution, the samples were believed to be the "pure" grafted copolymers. Figure 1 shows the FTIR spectra of PAN (A), AN-g-SF (B), and SF (C) in the range of 600–2500 cm⁻¹. It can be seen from Figure 1 that PAN (A) shows absorption at 2242, 1454, 1248, and 1073 cm⁻¹, which are attributed to the $\nu(\text{CN})$, $\delta(\text{CH}_2)$, $\gamma_w(\text{CH})$, and $\nu_+(0)$ resonances, respectively, in agreement with the previous study.² SF (C) shows the absorption bands at 1629 (amide I), 1530 (amide II), and 1265 cm⁻¹

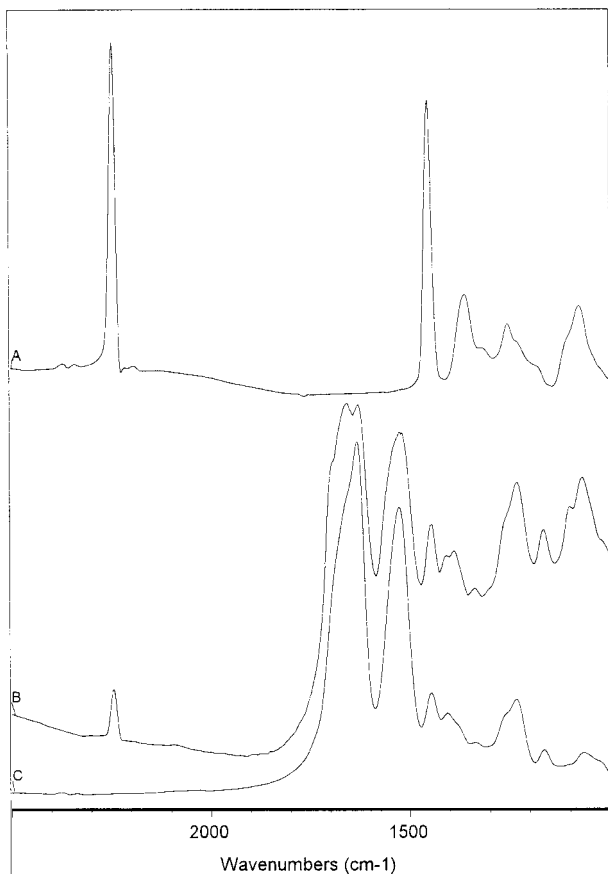


Figure 1 FTIR spectra in the range of 600–2500 cm^{-1} of: (A) PAN, (B) AN-g-SF (graft% is 30%), and (C) SF.

(amide III), assigned to silk II form.²⁷ AN-g-SF (B) shows the absorption bands typical of the two pure components, whose intensities are roughly related to the weight ratios of PAN and SF in the graft copolymer (the graft% of this sample is 30%).

Another thing worth noting about the FTIR spectrum of the graft copolymer is that the amide I and amide II bands of pure SF are at 1629 and 1530 cm^{-1} , respectively [see Fig. 2(B)], which are assigned to silk II form.²⁷ However, in the graft copolymer, besides the 1629 and 1530 cm^{-1} bands, three new bands, centered at 1684 (as a shoulder), 1658, and 1520 cm^{-1} , can also be detected. This phenomenon can be attributed to the conformation changes of SF induced by graft copolymerization, as well as the “dilution effect” of the grafted PAN on SF, in agreement with the previous study.²⁸

Several methods have been tried to separate the grafted polymers from SF: by treating the grafted polymers with NaOH aqueous solution,¹⁵

with 6 mol L^{-1} HCl at 115°C¹⁴ or 110°C,²⁸ or with 6 mol L^{-1} HCl at 60°C.¹⁷ As to AN-g-SF, however, our results show that: (1) alkaline treatment will heavily decrease the molecular weight of PAN homopolymer, in agreement with the published results³⁰; (2) acidic treatment with 6 mol L^{-1} HCl at 110 or 115°C also changes the molecular weight of PAN, and infrared spectra of the treated samples show several absorption bands in the range of 1600–1800 cm^{-1} , as shown in Figure 3(B), indicating the hydrolysis of the —CN group; and (3) treating the samples with 6 mol L^{-1} HCl at 60°C for 24 h is believed to be a suitable method to separate PAN from SF: the molecular weight of PAN is relatively unchanged, and only a negligible degree of hydrolysis of PAN can be detected in the infrared study, as shown in Figure 3(C).

Effect of Initiator Concentration

The effect of varying the concentration of potassium persulfate on the percentage graft yield, per-

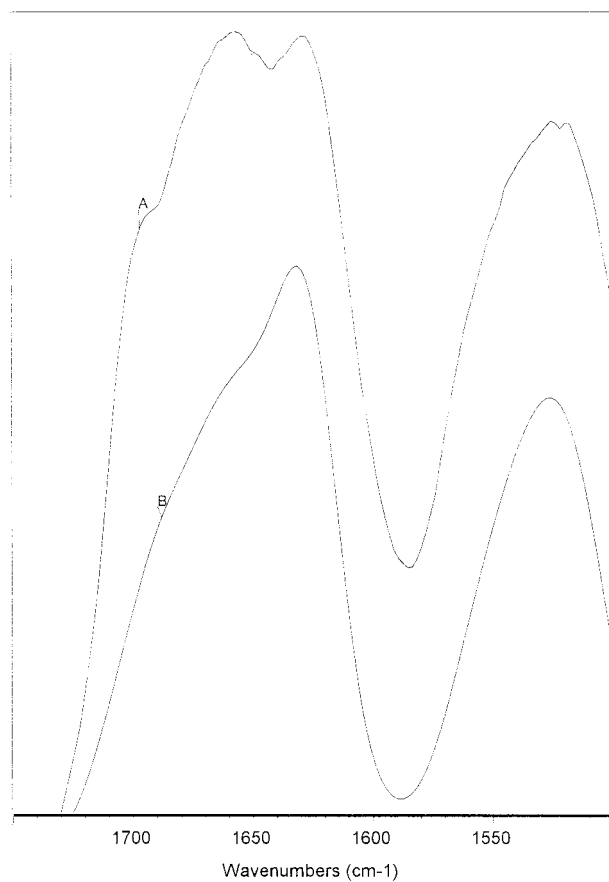


Figure 2 FTIR spectra in the range of 1500–1750 cm^{-1} of: (A) SF and (B) AN-g-SF (graft% is 30%).

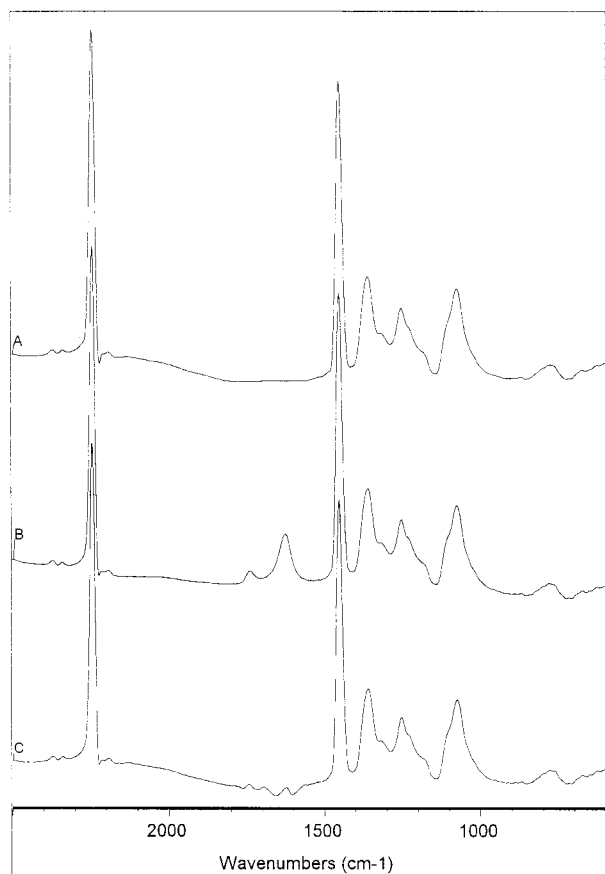


Figure 3 FTIR spectra in the range of 600–2500 cm^{-1} of: (A) PAN, (B) PAN treated with 6 mol L^{-1} HCl at 110°C for 4 h, and (C) PAN treated with 6 mol L^{-1} HCl at 60°C for 24 h.

centage efficiency, and the molecular weight of the grafted PAN is presented in Fig. 4. It can be seen clearly that the percentage graft, percentage efficiency, and the molecular weight of grafted PAN increase and then decrease after an optimum value of 0.3 g L^{-1} (i.e., $W_{in}/W_{AN} \times 100 = 1$, where W_{in} and W_{AN} are the weights of potassium persulfate and AN, respectively). As the concentration of potassium persulfate increases, a large number of silk macroradicals will be formed through the interaction of free radicals with the groups present in the silk main chain that initiate grafting, thereby increasing the graft yield and graft efficiency, as well as the molecular weight of the grafted PAN. However, when the concentration of potassium persulfate is higher than 0.3 g L^{-1} , further increase in initiator concentration will bring the following effects: (1) abundant free radicals, as well as homopolymer macroradicals are formed in the solution that might terminate

the growing chain; (2) the free radicals formed on the main chain of SF might be oxidized and thus terminating the reactive sites; and (3) the graft copolymerization and homopolymerization in such a system is of a matter of “competition,” which depends on the direct attack of free radicals to SF or to AN monomer. In a separate experiment, it was proved that the molecular weight of the grafting PAN branch was less than that of its homopolymers, which indicates that the activity of the SF macroradical is less than that of the AN radical present in homopolymerization, in agreement with the published results in similar systems.^{17,29} To sum up, a higher concentration of initiator will result in the production of more free radicals, more homopolymer macroradicals, as well as more homopolymer, thereby reducing the graft yield, graft efficiency, and the molecular weight of the grafted PAN.

Figure 4 also presents the influence of the po-

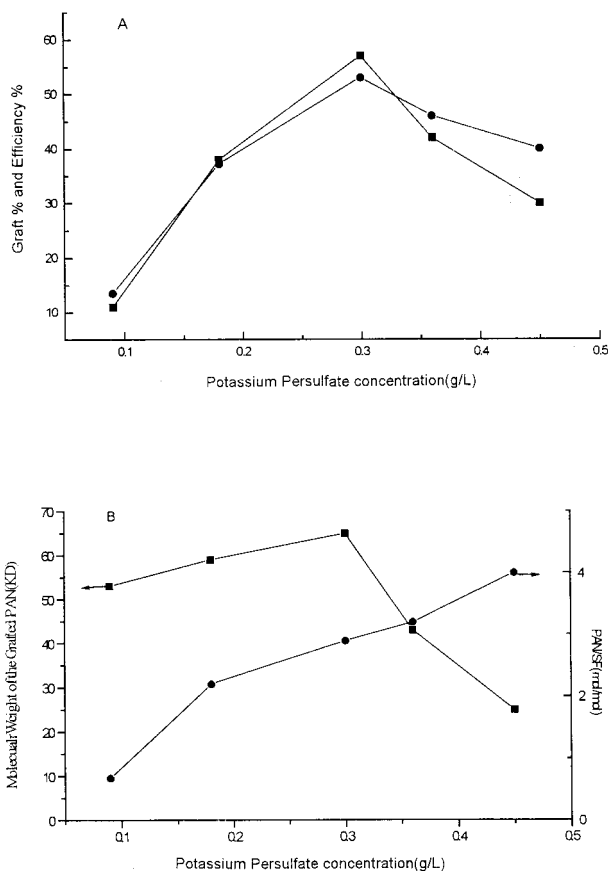


Figure 4 Effect of potassium persulfate concentration on (A) graft% (■) and efficiency (●), and (B) molecular weight of grafted PAN (■) and PAN/SF (mol mol^{-1}) (●). Reaction conditions: $W_{AN}/W_{SF} = 60/100$, 30°C, 60 min.

tassium persulfate concentration on the value of PAN/SF. It shows that, with the increase of the initiator concentration, the value of PAN/SF increases. This means that the number of PAN grafts on SF increases with the increase of initiator concentration, which might have a negative effect on the compatibilizing efficiency.

Effect of Monomer Concentration

The graft copolymerization of AN onto SF was investigated by varying the monomer concentration (the weight percentage AN was varied from 30 to 200% on that of SF, and W_{in}/W_{AN} was kept to be 1/100). A perusal of the result shows that the influence of the monomer concentration on the graft copolymerization can be divided into two stages: (1) when the weight percentage of AN on SF is <100%, the percentage graft yield, percentage efficiency and the molecular weight of the grafted PAN increase with the increase of AN weight percentage on SF up to 60%; and, thereafter, the molecular weight of the grafted PAN decreases with the further increase of monomer concentration, whereas the percentage graft and percentage efficiency are relatively unchanged; however, when the weight percentage of AN on SF is higher than 100%, the molecular weight of the grafted PAN increases with the increase of AN weight percentage, whereas the percentage graft and percentage efficiency are relatively constant, which are ~180% and 95%, respectively (see Fig. 5).

We believe that, in the first stage, the decreasing trend in the molecular weight of the grafted PAN may be ascribed to the possibility that at higher monomer concentration, the concentration of PAN macroradicals will increase. As it has been pointed out²⁹ in a similar system, the graft polymer radicals are mainly terminated by the interaction of active polymer radicals. So, the increasing PAN macroradicals will increase the opportunity of termination of the graft copolymer radicals, and thus the molecular weight of the grafted PAN decreases. On the other hand, when the weight percentage of AN on SF is higher than 60% (but lower than 100%), the AN concentration may have relatively little influence on the "competition" between graft copolymerization and homopolymerization, thus, the percentage graft and percentage efficiency are relatively unchanged.

In the second stage, because the copolymerization is homogeneous, increasing concentration of AN may increase the concentration of PAN, both

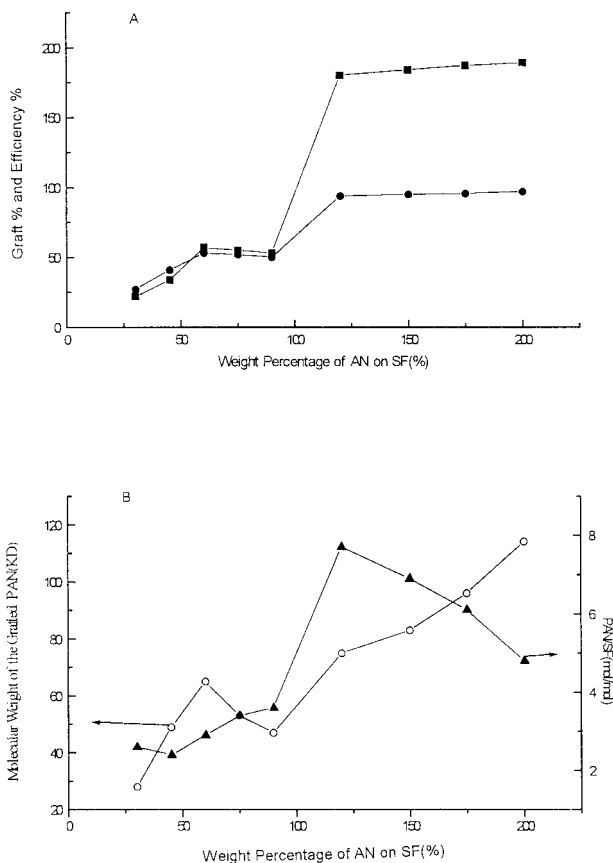


Figure 5 Effect of AN concentration on (A) graft% (■) and efficiency (●), and (B) molecular weight of grafted PAN (○) and PAN/SF (mol mol⁻¹) (▲). Reaction conditions: $W_{in}/W_{AN} = 1/100$, 30°C, 60 min.

grafted and ungrafted, and consequently, this will result in increased viscosity of the solution. This gel effect causes the hindrance in termination, particularly through the coupling of growing polymer chains. So, the molecular weight of the grafted PAN increases with the increase of AN weight percentage on SF. On the other hand, when the weight percentage of AN on SF is higher than 100%, an "equilibrium" of the "competition" between graft copolymerization and homopolymerization may be attained, and the percentage graft and percentage efficiency are thus relatively constant despite the increase of AN concentration. [The word "equilibrium" here may mean (1) the amount of AN consumed in the growing of the copolymer chains increase; and (2) the amount of the active sites per SF backbone decrease, as discussed herein, the final result is that the percentage efficiency and the percentage graft are relatively constant.]

The AN concentration influences the value of

PAN/SF in a quite different manner: this value increases with the increase of AN concentration up to 120% and then decreases with further increasing of the AN concentration. The mentioned increase trend may be the consequence of more free radicals present: with the increase of AN concentration, the concentration of the initiator also increases to maintain the value of W_{in}/W_{AN} to be 1/100; thus, the concentration of SF macroradicals will also increase. Thereby, more active sites are formed on SF, and the value of the grafted branches will thus increase.

When the AN weight percentage is higher than 120%, it was found that almost all of the added SF has been taken part in the graft copolymerization. (On extracting with 9.5 mol L^{-1} LiBr aqueous solution, the weight of the samples was relatively unchanged.) Thus, although the concentration of initiator increases by increasing the monomer concentration, the amount of the unreacted SF decreases, and thus the amount of the active sites per SF backbone decrease, which will lead to the decreasing trend of the grafted branches.

Effect of Temperature

The effect of temperature on graft copolymerization was investigated over the range of 10–70°C. The results are presented in Figure 6. It can be seen clearly that the percentage graft, percentage efficiency, and the molecular weight of the grafted PAN increase with the increase in temperature up to 30°C, and beyond this limit they decrease.

The initial increasing trend can be ascribed to a greater activation. As pointed out by Arai and Negishi^{29,31} in a similar system (methyl methacrylate grafting SF), the mobility of the grafted polymer chain end was controlled by the segmental mobility of the backbone polymer. Owing to the high stability of SF backbone chains, the mobility of graft copolymer radicals would be greatly restricted. As a consequence, increasing the temperature will thus increase the mobility of the graft copolymer radicals greatly. Furthermore, at higher temperature, the diffusion of the monomer to SF are also enhanced and, as a result, the initial increasing trend would be detected. However, when the temperature is higher than 30°C, the combination rates of radicals will increase and, as a result, the percentage graft, percentage efficiency, as well as the molecular weight of the grafted PAN decrease.

The influence of reaction temperature on the PAN/SF are rather complicated: peaks are pres-

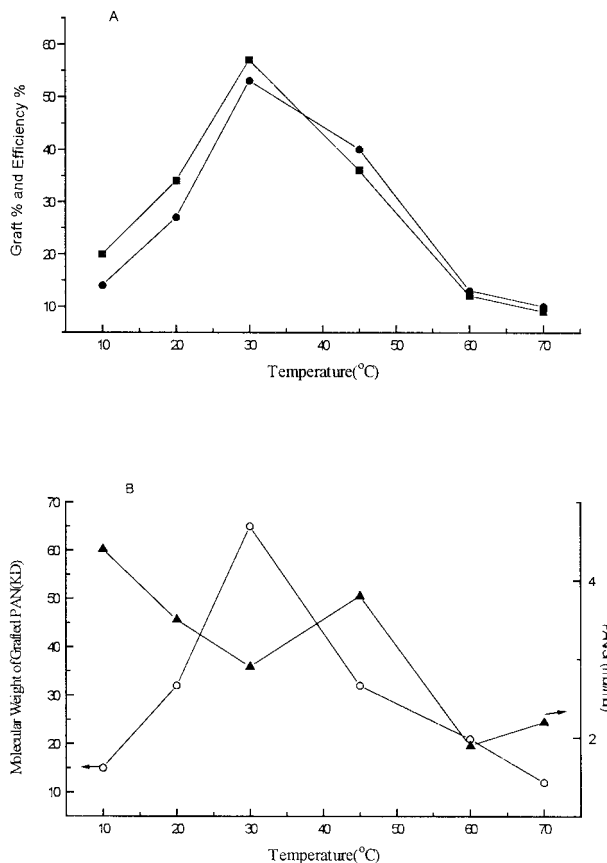


Figure 6 Effect of reaction temperature on (A) graft% (■) and efficiency (●), and (B) molecular weight of grafted PAN (○) and PAN/SF (mol mol^{-1}) (▲). Reaction conditions: $W_{AN}/W_{SF} = 60/100$, $W_{in}/W_{AN} = 1/100$, 30°C, 60 min.

ent on the temperature–PAN/SF curve, as shown in Figure 6(B). The increase in temperature will have several effects: (1) enhances the ease of free radical formation; (2) changes the balance of competition between graft copolymerization and homopolymerization—this will greatly influence the concentration of SF macroradicals; and (3) increase the diffusion rate of the monomer, etc. The final results must be the balance among these complicating effects.

Effect of Reaction Time

Figure 7 shows the influence of reaction time on the graft copolymerization. It can be seen that, with the increase of reaction time, the percentage graft and percentage efficiency increase up to 30 min and then become relatively constant with a further increase of reaction time. On the other hand, the molecular weight of the grafted PAN

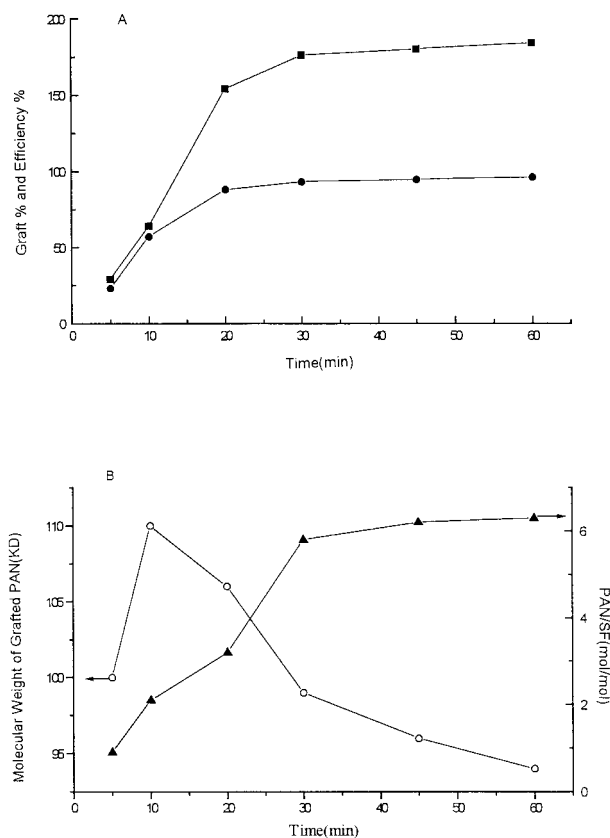


Figure 7 Effect of reaction time on (A) graft% (■) and efficiency (●), and (B) molecular weight of grafted PAN (○) and PAN/SF (mol mol^{-1}) (▲). Reaction conditions: $W_{AN}/W_{SF} = 175/100$, $W_{in}/W_{AN} = 1/100$, 30°C , 60 min.

increases up to 10 min and then decreases gradually with the increase of reaction time. Similar trend has been reported in the system of AN grafting on to SF in NaSCN aqueous solution.³² This phenomena may be explained as follows: with the increase of reaction time, the concentration of monomer decreases. As a result, the fraction of the low molecular weight-grafted PAN increases, and the decreasing trend in the average molecular weight can be detected.

On the other hand, with the increase of reaction time, the PAN/SF value increases gradually up to 30 min; thereafter, it becomes relatively constant. As the graft copolymerization is going on, more free radicals will attack the active site on SF, and the number of the grafted branches will thus increase. Not surprisingly, when most of the monomer, as well as the SF macroradicals, have been consumed (i.e., when the reaction time is longer than 30 min), the value of PAN/SF will remain unchanged.

It should be pointed out that, although we made no attempt to thoroughly study the reaction, we believe that the reaction can be controlled by regulating the conditions described herein, and other parameters (such as the concentration of sodium bisulfite, pH, reaction medium, etc.). Through these, we are able to optimize the reaction process.

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