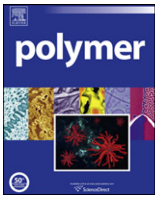
Polymer 50 (2009) 5675–5680

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Studies on graft copolymerization of chitosan with acrylonitrile by the redox system

Pengju Lv [a], Yuezhen Bin [a,*], Yongqiang Li [a], Ru Chen [a], Xuan Wang [b], Baoyan Zhao [b]

[a] *Department of Polymer Material Science, Dalian University of Technology, Dalian 116024, China*
[b] *Ningbo Key Lab of Advanced Textile Technology & Fashion CAD, Zhejiang Textile & Fashion College, Ningbo 315122, China*

ARTICLE INFO

Article history:
Received 28 July 2009
Received in revised form
2 October 2009
Accepted 2 October 2009
Available online 9 October 2009

Keywords:
Chitosan
Acrylonitrile
Graft copolymerization

ABSTRACT

Graft copolymers of chitosan with acrylonitrile (AN) were prepared by free radical polymerization using initiator pair of ammonium persulfate and sodium thiosulfate as redox system firstly. Graft copolymerization was confirmed by FTIR spectra, X-ray diffraction and ^{1}H NMR spectra measurements. The mechanism of graft copolymerization and factors affected graft reaction were explored in details, and the optimum reaction conditions were obtained at [AN] 0.9 mol/L, [CS] 13.3 g/L, [Initiator] 0.006 mol/L, $62 \pm 1\ ^{\circ}$C and 2 h. Then the solubility of chitosan-g-PAN was investigated by using several solvents. The concentrated nitric acid solution and NaSCN solution are good solvents for the graft product. It's confirmed that composites of graft copolymer and PAN had a good film-forming property, and it is suggested that the graft copolymer is promising for fabrication of acrylic fibers as a kind of functional additive.

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1. Introduction

Chitosan, a deacetylated product of chitin, is a high molecular weight heteropolysaccharide composed mainly of β-(1,4)-2-deoxy-2-amino-D-glucopyranose units and partially of β-(1,4)-2-deoxy-2-acetamido-D-glucopyranose [1]. Owning to its characteristics such as antimicrobial activity, biocompatibility, non-toxicity and biodegradability, chitosan can be applied in many fields, such as pharmaceutical and medical applications, environmental protection, textiles, wastewater treatment, biotechnology, cosmetics, food processing and agriculture [2–4]. However, chitosan can be only dissolved in a few dilute acid solutions, and this limits its applications. Therefore, a series of chemical modifications on chitosan have been conducted, such as nitration, phosphorylation and sulphation [5–7]. On the other hand, the graft copolymerization is expected to be one of the most promising approaches for molecular designs leading to novel types of hybrid materials, which can introduce desired properties and enlarge the application fields of chitosan [8].

On the other hand, polyacrylonitrile (PAN) is one of the most important fiber-forming polymers and has been widely applied in textiles because of its excellent physical and chemical properties. To endue PAN textiles with antibacterial functions from chitosan, the methods of blending PAN with chitosan or its derivatives such as carboxymethyl chitosan have been widely investigated [9]. However, this kinds of products are often accompanied with the problem of water stability, in which some of antibacterial reagent may be released during laundering. Therefore, graft copolymerize of PAN with chitosan is a novel and promising attempt due to the chemical binding between macromolecules.

Chitosan bears two types of reactive groups, the free amino group on deacetylated units and the hydroxyl group at the C3 and C6 on acetylated or deacetylated units [10], which will enable the easy occurrence of graft copolymerization on chitosan. Studies on the graft copolymerization of chitosan with various vinyl monomers have been conducted with different initiating systems and different mechanisms. There are mainly two kinds of initiating systems, i.e. chemical initiation and radiation initiation, to graft copolymerize different vinyl monomers such as vinyl acetate, acrylonitrile (AN), methacrylic acid (MA) and methylmethacrylate (MMA) [11,12], onto chitosan. There are reports about graft copolymerization of vinyl monomers onto polysaccharides using both high energy (e.g. β, γ, χ-ray) and low energy (e.g. photo, UV light) [13,14]. Although graft copolymerization with radiation initiation offers an economical and quick method, they are harder to handle under technical conditions [15]. Graft copolymer of carboxymethyl chitosan with methacrylic acid(MA) was prepared by using the ammonium persulfate as the initiator and its water solubility was greatly improved [16]. The reaction of chitosan-graft-polyacrylonitrile was carried out in a homogeneous acetic

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[*] Corresponding author. Tel./fax: +86 411 39893638.
E-mail address: binyz@dlut.edu.cn (Y. Bin).

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doi:10.1016/j.polymer.2009.10.004

aqueous phase by using ceric ammonium nitrate as an initiator [17]. In another work, graft copolymerization of AN and MMA onto chitosan using potassium persulfate as an initiator was studied [18]. As a kind of high efficient initiator, the compound of salt persulfate and cerium ammonium nitrate were more investigated compared with the thermal initiator AIBN [19]. Fenton's reagent is another frequently used initiator for graft copolymerizing vinyl monomers onto chitosan, which involves the redox initiating system. Comparative studies of graft copolymerizing MA and MMA monomers onto chitosan using potassium persulphate (KPS) alone and KPS coupled with various cocatalysts ($MnCI_2$ or oxalate) were made and the effects on the grafting rate were different [20]. KPS alone can initiate the radical reaction with forming a redox pair with the anhydroglucose units of the polysaccharide to yield the macroradicals, which sometimes results in the degradation of chitosan [21].

Among the many vinyl monomers grafted, AN has been the most frequently used one due to its high grafting efficiency and easy to hydrolyze to introduce varied subsequent derivatives [17,22]. Ammonium persulfate or potassium persulfate was used as the initiator alone in most other literatures [16,18,20,21], which belongs to the peroxy initiator system. But the initiator of ammonium persulfate and sodium thiosulfate can consist of the redox system, which can generate two free radicals thus decrease the decomposition activation energy with faster polymerization rate. However, there are few reports about graft copolymerization for modification of chitosan using the redox system of ammonium persulfate and sodium thiosulfate as the initiator.

The aim of this study was to conduct a kind of chemical modification of chitosan by using the method of graft polymerization of acrylinitrile onto the backbone of chitosan. In the current work, the products of chitosan-g-polyacrylonitrile were characterized by FTIR, XRD, ^{1}H NMR and TGA, which elucidated the structure changes in comparison with chitosan. The factors affected the graft copolymerization were studied in details and the mechanism of graft reaction was proposed. And the solubility of graft copolymer and film-form properties of the graft copolymer blending with PAN in some solvents were investigated.

2. Experimental

2.1. Materials

Chitosan (deacetylation 90%, $\overline{M}_\eta = 35,000$) was supplied by FUNAKOSHI CO, Ltd., Japan. Commercial chitosan was purified by method of dissolved in acetic acid and separated in alkaline solution and then washed by anhydrous alcohol for 3 times and dried at 65 °C in vacuum for 48 h before use. AN was treated with 10% NaOH solution for 0.5 h to remove the inhibitor and then distilled under atmospheric pressure in a setup with a total reflux head. The fraction with bp 77 °C was collected. Ammonium persulfate and sodium thiosulfate of analytical grade with purity of 98% were used as the initiators. Glacial acetic acid with purity of 99.5% was provided by Shenglian CO, Ltd., China. NaSCN with purity of 98.5% was obtained by Damao Tianjin CO, Ltd., China. Before use, the powder of NaSCN was dried at 110 °C in oven to constant weight. Other chemicals of analytical grade were used without further purification.

2.2. Graft copolymerization

A 250 ml three necked round bottomed flask, filled with a magnetic stirrer, thermometer, and reflux condenser in a temperature-controlled oil bath, was used for the graft reaction. Firstly, a desired quantity of chitosan was dissolved in 1 wt% of acetic acid aqueous solution at 60 °C. The total volume of the aqueous solution was 80 ml in all experiments. After the chitosan was fully dissolved, temperature of the system was strictly controlled at a required value. Then ammonium persulfate powder was added into the solution. After 5 min, sodium thiosulfate was added followed by dropwise of addition (5 ml) of AN in another 5 min. The time of addition of AN was taken as zero time. The mixture was continuously stirred at the desired temperature until completion of the copolymerization reaction. The concentration of the initiator was 0.002 mol L^{-1}–0.010 mol L^{-1}.

At the end of the graft copolymerization, the mixture was continuously stirred for 15 min at room temperature, and then neutralized to pH = 10 to precipitate the product with 1 M NaOH solution. Then the mixture was centrifuged to obtain the solid. The solid mixture was washed by the distilled water and centrifuged repeatedly to pH = 7, then washed by anhydrous alcohol to remove the salts and centrifuged for 2 times. The centrifugate was dried at 70 °C to a constant weight. Thus, the crude product containing graft copolymer and homopolymer was obtained.

To remove the AN homopolymer, 1.0 g of the crude product was poured in 100 ml of dimethyl formamide (DMF) and stirred gently at 30 °C for 24 h [17]. After filtration and washed by DMF for several times, the pure chitosan-g-polyacrylonitrile (CS-*g*-PAN) was obtained by thoroughly washed with anhydrous alcohol, and dried at 70 °C to reach a constant weight.

All the samples were absolutely dried before used for characterization. Grafting rate (%*G*), which designates the amount of polymer grafted on the substrate backbone (chitosan), and efficiency of grafting (%*E*), which indicates the efficiency of conversion of the initial AN to the grafted PAN, were calculated from the increase in weight of the chitosan after graft copolymerization in the following formula [23]:

$$\%\text{Grafting}\ (\%G) = \frac{W_1 - W_0}{W_0} \times 100 \tag{1}$$

$$\%\text{Efficiency}\ (\%E) = \frac{W_1 - W_0}{W_2} \times 100 \tag{2}$$

where W_1, W_0 and W_2 denote the weight of the grafted chitosan, the weight of original chitosan and weight of the monomer used, respectively. The experiments of graft polymerization were performed with two parallel experiments, and the data was the average value of the two results. When the two data were quite different, we carried out the third one to confirm it.

2.3. Characterization

Fourier transform infrared spectroscopy (FTIR) was recorded on a Nicolet-20DXB Infrared spectrophotometer using quantitative KBr pellets. X-ray diffraction (XRD) was carried out on D/MAX-2400 powder diffractometer, with 2θ from 5° to 60°. TGA was carried out on Perkin–Elmer Pyris TGA in N_2 atmosphere, temperature range of 40–800 °C, heating rate of 10 °C/min. ^{1}H NMR spectra were recorded with a Bruker AvanceII400 MHz spectrometer and the solvent was consisted of D_2O and NaSCN. The products of *E*% 42 were characterized for FTIR, XRD, and ^{1}H NMR, and those of *E*% 42 and *E*% 17 were used for TGA.

3. Results and discussion

3.1. Characterization of the graft chitosan

Structural changes of chitosan and its graft copolymer were characterized by FTIR spectroscopy.

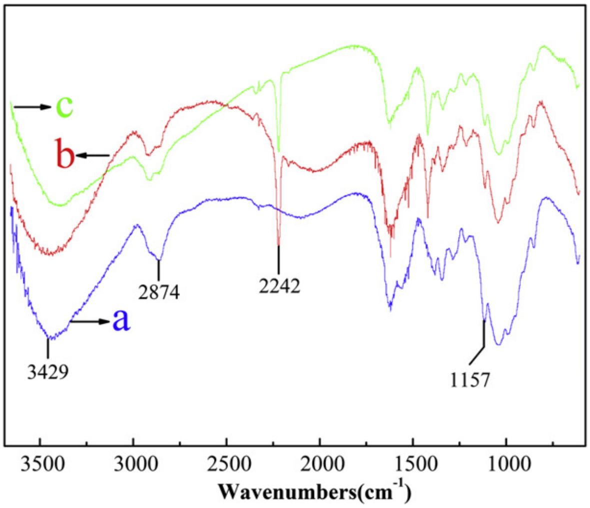

Fig. 1. FTIR spectra of (a) original chitosan, (b) crude CS-g-PAN and (c) purified CS-g-PAN.

Fig. 1 shows the FTIR spectrum of the crude graft copolymer and purified CS-*g*-PAN in comparison with original chitosan. The strong peaks at around 2242 cm^{-1} appeared in spectra (b) and (c) were assigned to the stretching absorption of –CN, which proved the successful graft copolymerization of chitosan and AN [16]. And the obvious difference of peak intensity between (b) and (c) at around 2242 cm^{-1} indicated that there existed the homopolymerization of AN (homo PAN) during the graft copolymerization. Most of other peaks are related to the carbohydrate structure. The broad and strong absorption peak at around 3429 cm^{-1} (O–H and N–H stretching), peak at 2874 cm^{-1}(C–H stretching), the three peaks at range of 1000–1157 cm^{-1} (C–O stretching) were common in spectra due to the chitosan backbone.

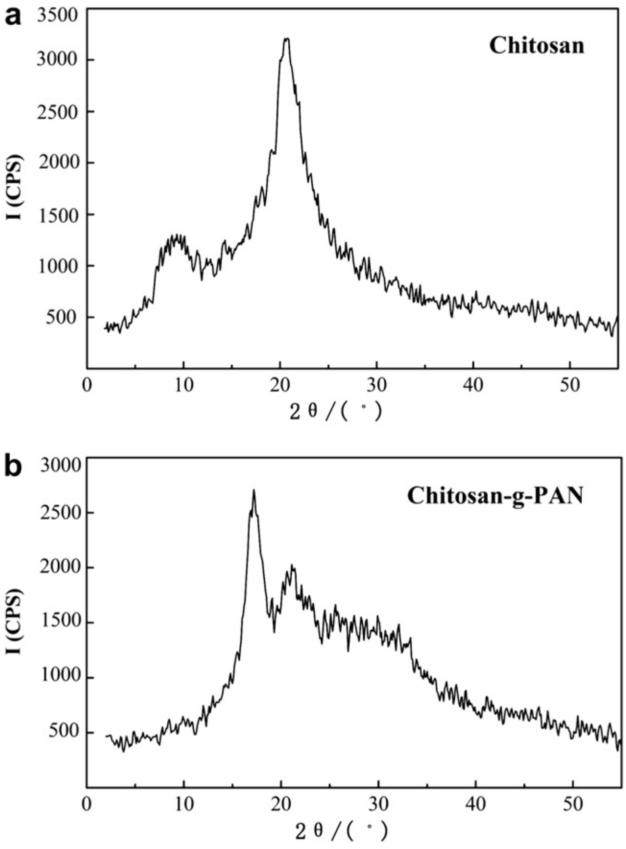

Fig. 2. WAXD intensity distribution for (a) original chitosan and (b) purified CS-*g*-PAN.

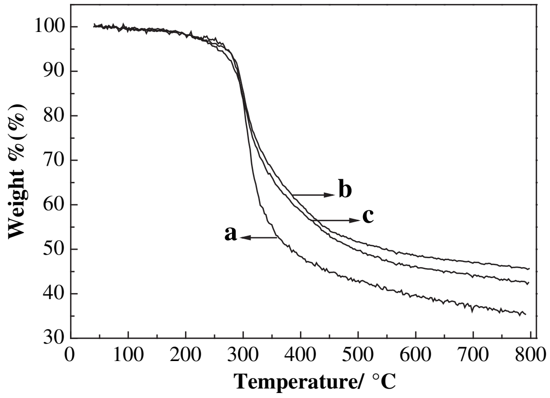

Fig. 3. TGA for (a) original chitosan, (b) CS-g-PAN (%$E = 42$) and (c) CS-g-PAN (%$E = 17$).

The XRD spectra of chitosan (a) and its graft copolymer (b) are showed in Fig. 2. The intensive peak of (a) at around $2\theta = 20^{o}$ was attributed to the overlapped diffraction from the chitosan's crystal planes of (020) and (110), while the more intensive peak of (b) at around $2\theta = 17^{\circ}$ was due to the overlapped diffraction peaks from the PAN's crystal planes of (110) and (200) [24]. In the XRD spectrum of (b), it's observed that diffraction intensity of the peak at around 20° was obviously weakened indicating that the crystallinity of the chitosan decreased after modification. PAN had grew into enough long chain to form the regular crystalline region during the graft copolymerization.

Fig. 3 depicts TGA curves for the original chitosan and the CS-*g*-PAN with different efficiency of grafting. Curves of DTG derived from the derivation of TGA (not shown here) indicated that thermal decomposition temperature of (a) was around 310 °C while (b) and (c) around 300 °C. Thermal decomposability of the three samples had little difference. However, the thermal residual rate of the three was obviously different: (a) 35%, (b) 46% and (c) 42% respectively as shown in Fig. 3. The reason was suggested that the process of TGA in N_2 atmosphere was accompanied with the carbonization of PAN. In the range of 40–310 °C, thermal decomposition in the three specimens all occurred, but in the range of 310–800 °C, carbonization didn't happen in (a) but occurred in the graft copolymer (b) and (c) due to existence of PAN. The more the %*E*, the higher the residual rate. This further confirmed the success of grafting reaction.

The structures of acetylated and deacetylated monomers of chitosan are presented in Fig. 4. And the different protons of chitosan are labeled by Latin letters from (A) to (S).

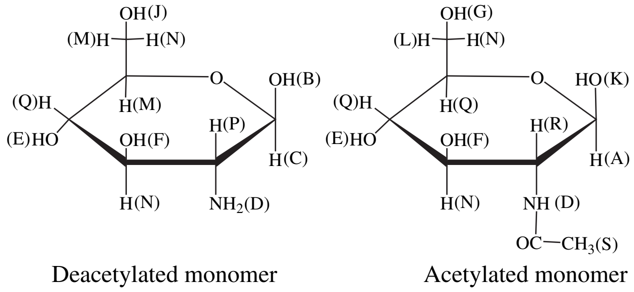

Fig. 4. Acetylated and deacetylated monomers of chitosan.

Fig. 5 shows the ^1H NMR spectra for the original chitosan, PAN homopolymer and the CS-*g*-PAN with $\%E = 42$. In Fig. 5 (a), the weak signals at 1.4 ppm and 2.1 ppm in the ^1H NMR spectrum could be attributed to protons of (D) and (S), respectively. By comparison, the peak intensity at 1.4 ppm in Fig. 5(c) was so weak that it didn't appear, which suggested that the graft copolymerization occurred at the position of the N atom joined by (D).The chemical shifts $\delta = 2.6, 2.8, 3.4, 4.5, 4.7$ and 6.3 ppm corresponded to the protons of (R), (P), (N), (G), (E) and (A), respectively. But the strong signal at 9.2 ppm was unknown. In the spectra of (b) and (c), graft copolymer gave two groups of typical peaks of PAN centered on 3.1 and 3.2 ppm corresponding to β-methylene and α-methine protons, respectively [25]. In the spectra of (c), the signals at 3.6, 3.8 and 4.1 ppm might be due to interaction of chitosan with PAN in the NaSCN solution. However, there are no reports about the ^1H NMR spectrum of CS-*g*-PAN for reference, thus it needs further study to make them clear. Anyway Fig. 5 also confirmed the grafting of PAN chains to chitosan to form copolymer.

3.2. Mechanism of the graft copolymerization

Here we propose a feasible mechanism for the radical polymerization in this reaction system, including graft copolymerization and homopolymerization of AN as Scheme 1. As shown in Scheme 1, virtually all free radical chain reactions require a separate initiation step in which a radical species is generated in the reaction mixture. Redox initiator system possesses the characteristic of decreasing the decomposition activation energy, and is very effective to generate free radicals under mild conditions. Here ammonium persulfate and sodium thiosulfate as redox initiator system was employed to generate the free radicals preferentially. Then the free radicals captured the atom H of –OH and $–NH_2$ on backbone of chitosan [26] to form the macromolecular radicals of chitosan, which initiated the graft copolymerization and homopolymerization. And finally graft reaction was terminated with two macromolecular chain radicals reacting with each other. Meanwhile, homopolymer of PAN was formed, which indicated the important features of graft copolymerization.

3.3. Effect of the reaction parameters on the graft efficiency

The graft reaction conditions were investigated in detail to obtain a high efficiency of grafting, including the concentration of chitosan, reaction temperature, initiator concentration.

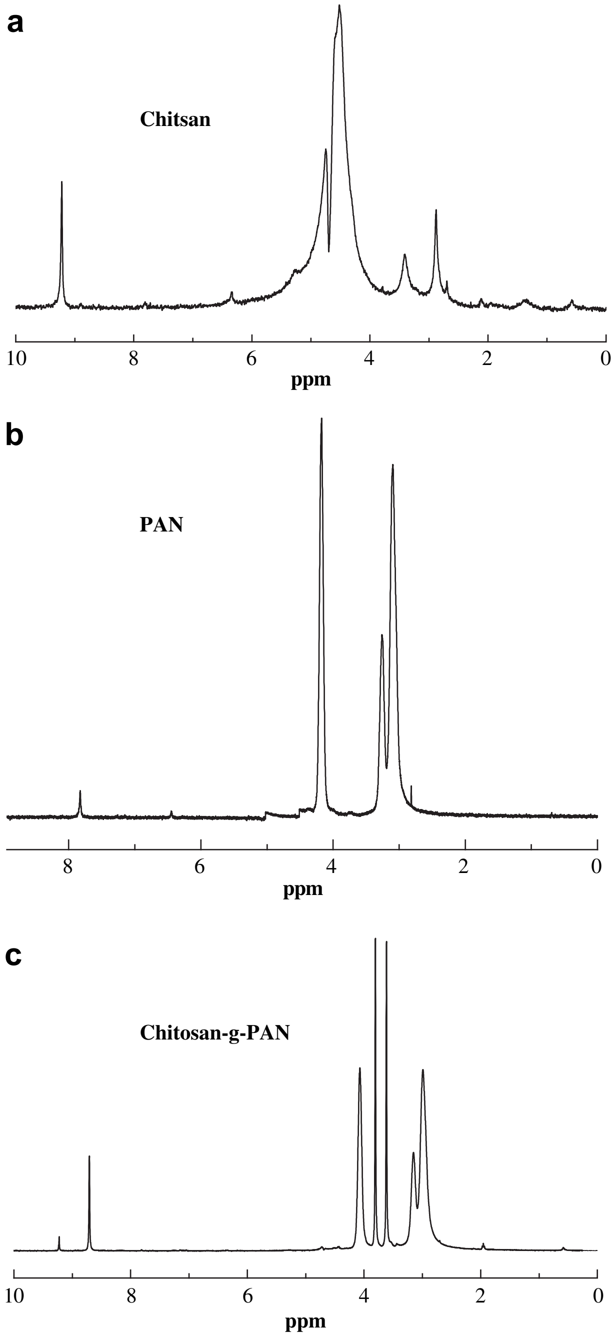

Fig. 5. ^1H NMR spectra for (a) original Chitosan, (b) pure PAN and (c) CS-*g*-PAN ($\%E = 42$).

Grafting at O-H groups of chitosan

Initiation

$$S_2O_8^{2-} + S_2O_3^{2-} \longrightarrow SO_4^{2-} + SO_4^{\bullet-} + S_2O_3^{\bullet-}$$

$$CSOH + SO_4^{\bullet-} + 2S_2O_3^{\bullet-} \longrightarrow CSO^{\bullet} + SO_4^{2-} + S_4O_6^{2-}$$

$$M + SO_4^{\bullet-} \longrightarrow M^{\bullet} + SO_4^{2-}$$

Propagation

$$CSO^{\bullet} + M \longrightarrow CSOM^{\bullet}$$

$$CSOM^{\bullet} + M \longrightarrow CSOMM^{\bullet}$$

$$CSOMM^{\bullet}_{n-1} + M \longrightarrow CSOM^{\bullet}_{n}$$

Termination

$$CSOM^{\bullet}_{n} + CSOM^{\bullet}_{n} \longrightarrow \text{graft copolymer}$$

$$M^{\bullet} + M \longrightarrow MM^{\bullet}$$

$$MM^{\bullet}_{n-1} + M \longrightarrow M^{\bullet}_{n}$$

$$M^{\bullet}_{n} + CSOH \longrightarrow CSO^{\bullet} + M_nH \text{ (homopolymer)}$$

Grafting at N-H groups of chitosan

Initiation

$$S_2O_8^{2-} + S_2O_3^{2-} \longrightarrow SO_4^{2-} + SO_4^{\bullet-} + S_2O_3^{\bullet-}$$

$$CSNH + SO_4^{\bullet-} + 2S_2O_3^{\bullet-} \longrightarrow CSN^{\bullet} + SO_4^{2-} + S_4O_6^{2-}$$

$$M + SO_4^{\bullet} \longrightarrow M^{\bullet} + SO_4^{2-}$$

Propagation

$$CSN^{\bullet} + M \longrightarrow CSNM^{\bullet}$$

$$CSNM^{\bullet} + M \longrightarrow CSNMM^{\bullet}$$

$$CSNMM^{\bullet}_{n-1} + M \longrightarrow CSNM^{\bullet}_{n}$$

Termination

$$CSNM^{\bullet}_{n} + CSNM^{\bullet}_{n} \longrightarrow \text{graft copolymer}$$

Scheme 1. Mechanism of the graft copolymerization of chitosan, where CS represents chitosan and M represents AN monomer.

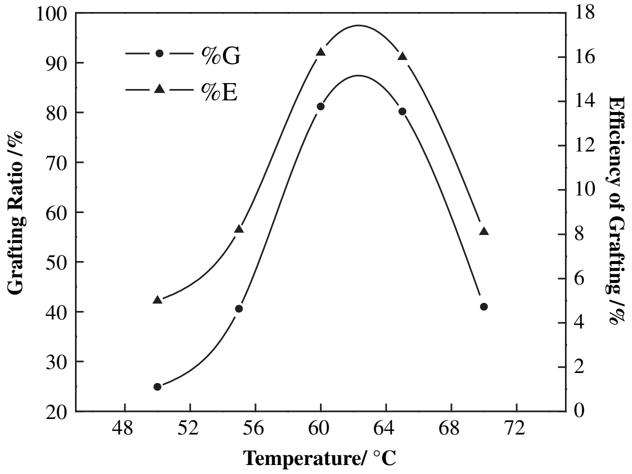

Fig. 7. Effect of the reaction temperature on the grafting efficiency. Reaction conditions: [AN] 0.9 mol/L, [initiator] 0.006 mol/L, [CS] 13.3 g/L, time 2 h.

3.3.1. *Effect of the chitosan concentration*

Fig. 6 shows the effect of chitosan concentration on the grafting efficiency under the indicated reaction conditions. With the increase of concentration of chitosan, both *G*% and *E*% increased continuously. This behavior can be explained from the graft mechanism that under a certain condition of temperature and initiator concentration, the graft reaction involved the graft copolymerization and homopolymerization of AN. With the increase of chitosan concentration, the total number of group $-NH_2$ and –OH on the chitosan increased, resulting in more activated sites of chitosan, which meant that there was more chance for AN attacking the chitosan's radicals. So *G*% and *E*% of the products increased with the increase of concentration of chitosan.

But the excess chitosan would bring an adverse effect because of the high viscosity of the system and thereby being hard to stir. The following experiments were carried out with the chitosan concentration of 13.3 g/L.

3.3.2. *Effect of the reaction temperature*

The influence of temperature on the graft parameters was studied by changing the reaction temperature from 50 to 70 °C, keeping other parameters fixed. As shown in Fig. 7, %*G* and %*E* increased with increasing the temperature from 50–60 °C, and then decreased. The highest %*G* and %*E* were obtained at 62 ± 1 °C. This behavior can be explained as under a certain conditions of chitosan and initiator concentration, the initiating activity increased with the increasing temperature, which was helpful to improve the activity of both graft copolymerization and homopolymerization. But when the temperature exceeded 60 °C, which was the optimum activity temperature for the present redox system, the initiator would generate a large number of free radicals in unit time easily resulting in coupling termination between the free radicals due to the aggravated collision. On the other hand, with the increase of temperature, the mobility of macro radicals would be enhanced and it more easily led to the chain termination at a higher temperature [16]. So, the polymerization activity of the both began to decreased, and %*G* and %*E* of the graft copolymer showed a decrease at the elevated temperature.

3.3.3. *Effect of the initiator concentration*

The effect of the initiator concentration on the graft reaction was studied. As shown in Fig. 8, with the increase of the initiator concentration, *G*% and *E*% had an increase at first, and then decreased. The maximum grafting ratio was achieved at around 0.006 mol/L of the initiator. This behavior can be explained from the graft mechanism that after decomposition, one part of the initiator was used to induce polymerization of the monomer and the other part was consumed away with cage effect and induced decomposition. When the initiator concentration was 0.002 mol/L, the very low initiator concentration of polymerization system made the lower grafting efficiency. Increasing initiator concentration resulted in more radical sites on the chitosan backbone which in turn led to higher *G*% and *E*%. But when the concentration exceeded around 0.006 mol/L, excessive radicals would trigger multiple coupling that made the homopolymerization of AN dominant in the reaction.

3.4. *Tests of solubility of chitosan and its products*

Finally, the solubility of the grafted copolymer product was studied for exploring the applications of the synthesized CS-*g*-PAN. Eight kinds of solvents were selected to detect the solubility of chitosan and its graft products in different conditions. The solubility of grafting copolymer product compared with original chitosan was listed in Table 1. The result indicates that only the

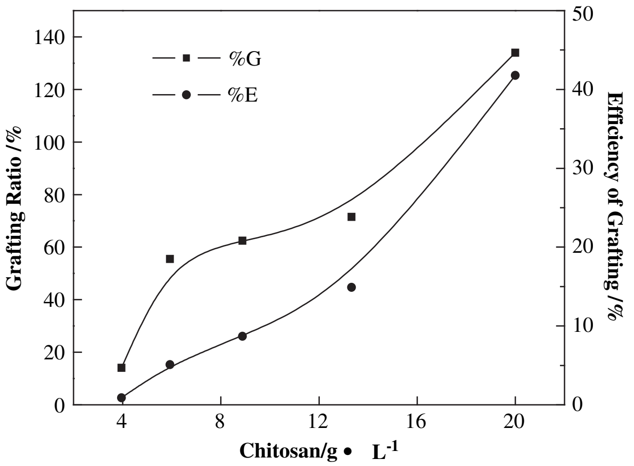

Fig. 6. Effect of the chitosan concentration on the grafting efficiency. Reaction conditions: [AN] 0.9 mol/L, [initiator] 0.006 mol/L, temperature 62 ± 1 °C, time 2 h.

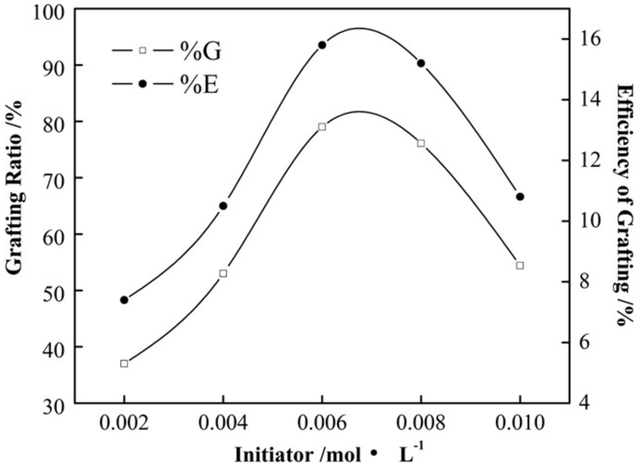

Fig. 8. Effect of the initiator concentration on the grafting efficiency. Reaction conditions: [AN] 0.9 mol/L, [CS] 13.3 g/L, temperature 62 ± 1 °C, time 2 h.

Table 1
The solubility of the chitosan and graft product in eight solvents.

Solvents	HAc	HCl	DMF	DMSO	Acetone	$ZnCl_2$	NaSCN	HNO_3
CS	√	√	×	×	×	√	√	√
PAN	×	×	√	√	√	√	√	√
CS-g-PAN	×	×	×	○	×	○	√	√

Note: "√" represents "soluble"; "×" represents "insoluble"; "○" represents "swelling".

solution of NaSCN and concentrated nitric acid can be adopted as the solvent for the chitosan and its products.

Through the graft reaction, solubility of the products has greatly changed in comparison with original chitosan, which was attributed to the absence of hydroxyl end groups in the polymers obtained with this class of redox pairs [27]. The graft products are insoluble in the solvents, such as acetic acid and DMF, in which the chitosan and PAN are soluble, respectively. And they can only swell in DMSO and aqueous $ZnCl_2$. Similar solubility behavior of chitosan grafted acrylic acid was reported using KPS-ferrous ammonium sulphate(FAS) redox initiating system [28], in which grafted products were not soluble in water and dilute acid solutions but swelled in these media. From Table 1, two solvents, NaSCN and an concentrated nitric acid, were found to dissolve the chitosan and graft product. NaSCN solution has proved a novel solvent for chitosan in our previous patent [29], as well as the common solvent for acrylic fiber industry.

Besides tests of solubility, the film-forming property of composites of graft copolymer and PAN was studied with using NaSCN and HNO_3 as solvent respectively. It's found that composites of graft copolymer and PAN had a good film-forming property, and it is promising for fabrication of acrylic fibers as a kind of functional additive.

4. Conclusions

Graft copolymer of CS-*g*-PAN was successfully synthesized by free radical polymerization using initiator pair of ammonium persulfate and sodium thiosulfate as redox system. The CS-*g*-PAN was characterized by FTIR, XRD, ^{1}H NMR, which elucidated the structure changes in comparison with chitosan, and TGA revealed that copolymer had more thermal stability. The optimum reaction conditions at the highest graft ratio and efficiency of grafting were obtained at [AN] 0.9 mol/L, [CS] 13.3 g/L, [Initiator] 0.006 mol/L, 62 ± 1 °C and 2 h. Additionally, copolymer showed a good solubility in NaSCN and HNO_3 and good film-forming property suggesting possibility for fabricating the functional acrylic fibers as a kind of functional additive. Our future work will focus on the spinning process of the copolymer.

Acknowledgements

This project was sponsored by Opening Fund for Research Program Supported by Ningbo Key Lab of Advanced Textile Technology & Fashion CAD and Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry of China.

References

[1] El-Tahlawy K, Hudson SM. J Appl Polym Sci 2006;100(2):1162–8.
[2] Ravi Kumar MNV, Muzzarelli RAA, Muzzarelli C, Sashiwa H, Domb AJ. Chem Rev 2004;104(12):6017–84.
[3] Keyur D, Kevin K. Polymer 2009;50(15):3661–9.
[4] Wen Jen L, Tze Dan C. Polymer 2009;50(17):4166–74.
[5] Jiankang H, Dichen L. Polymer 2007;48(15):4578–88.
[6] Yinsong W, Qian J. Polymer 2007;48(14):4135–42.
[7] Ying H, Yumin D. Polymer 2007;48(11):3098–106.
[8] Jayakumar R, Prabaharan M, Reis RL, Mano JF. Carbohydr Polym 2005;62(2):142–58.
[9] Chang-Woo N, Young H. J Appl Polym Sci 2001;82(7):1620–9.
[10] Majeti NV, Ravi Kumar. React Funct Polym 2000;46(1):1–27.
[11] Shantha KL, Udaya B, Panduranga RK. Eur Polym J 1995;31(4):377–82.
[12] Ren L, Miura Y, Nishi N, Tokura S. Carbohydr Polym 1993;21(1):23–7.
[13] Singh V, Tripathi DN, Tiwari A, Sanghi R. J Appl Polym Sci 2004;95(4):820–5.
[14] Sen'iYang S, Trimizi SA, Burns A, Barney AA, Risen WM. Synth Met 1989;32:191.
[15] Beck RHF, Fitton MG, Kricheldorf HR. In: Kricheldorf HR, editor. Handbook of polymer synthesis: part B. New York: Marcel Dekker; 1992 [chapter 25].
[16] Sun T, Xu P, Liu Q, Xue J, Xie W. Eur Polym J 2003;39(1):189–92.
[17] Pourjavadi A, Mahdavinia GR, Zohuriaan-Mehr MJ, Omidian H. J Appl Polym Sci 2003;88(8):2048–54.
[18] Prashanth KVH, Tharanathan RN. Carbohydr Polym 2003;54(3):343–51.
[19] Andriyanova NA, Smirnova LA, Drozdov YN, Gracheva TA. J Appl Polym Sci 2005;78(6):962–3.
[20] Retuert J, Yazdani-Pedram M. Polym Bull 1993;31(5):559–62.
[21] Hsu SC, Don TM, Chiu WY. Polym Degrad Stab 2002;75(1):73–83.
[22] Kurita K. In: Salamone JC, editor. Polymeric materials encyclopedia, vol. 2. Boca Raton, Florida: CRC; 1996. p. 1205–8.
[23] Boonstra JD, Bekker A. Ger Pat 1975;2(44):012.
[24] Koganemaru A, Bin Y, Agari Y, Matsuo M. Adv Funct Mater 2004;14(9):842–50.
[25] Verneker VRP, Shaha B. Macromolecules 1986;19(7):1851–6.
[26] Singh V, Tiwari A, Tripathi DN, Sanghi R. Polym 2006;47(1):254–60.
[27] Sarac AS. Prog Polym Sci 1999;24:1149–204.
[28] Yazdani-Pedram M, Retuert J, Quijada R. Macromol Chem Phys 2000;201(9):923–30.
[29] CN2009103011825.