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Synthesis and property of poly(sodium 4-styrenesulfonate) grafted chitosan by nitroxide-mediated polymerization with chitosan-TEMPO macroinitiator

Jianlin Jiang, Daoben Hua*, Jing Jiang, Jing Tang, Xiulin Zhu*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China

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ABSTRACT

Poly(sodium 4-styrenesulfonate) (PSS) grafted chitosan was prepared by nitroxide-mediated polymerization of sodium 4-styrenesulfonate in the presence of chitosan-TEMPO macroinitiater. The results indicated that the graft polymerization was well controlled by the nitroxide-mediated process, and the graft copolymers were successfully synthesized. Chitosan-*g*-PSS could self-assembly into the worm-like or spherical micelles, which might be associated with PSS graft content; and the ion-exchange property of chitosan-*g*-PSS could be controlled by adjusting PSS graft content. The property may promote the graft copolymers to be used in the ion exchange for the environment protection.

1. Introduction

It is known that environmental contamination has been a serious problem that is related to possible serious consequences, including heavy metals contamination of water from various sources. The traditional methods for heavy metal removal from contaminated water involve filtration, flocculation, activated charcoal, and ion exchange resins, which are expensive and can result in toxic exposures of the workers involved. In the past decades, because of its chelating capacity for cations, low price, rich resources and environmental kindness (1→4)-2-amino-2-deoxy-β-D-glucan (i.e. chitosan) has been developed as one of the most popular adsorbents for the removal of metal ions from aqueous solution and is widely used in water treatment applications (Babel & Kurniawan, 2003).

The capacity of the chitosan to complex metallic ions is one of its most important potentialities. However, the adsorption ability of chitosan has not been realized to a satisfying level. Many chemical modifications of chitosan have been made to improve the cation adsorption capacities. For example, carboxymethylation was prepared and regarded as a simple and effective process to facilitate the adsorption ability of chitosan with heavy metals (Chen & Park, 2003; Hon & Tang, 2000). Farag and Kareem (2009) reported that the adsorption capacities of Pb^{2+} increased with increasing the degree of substitution of carboxymethyl chitosan at the range of 0.8–1.5 m mol/g sample, and that the formation of crosslinking between the amino group and aldehyde group improved the adsorption capacity up to maximum before a decrease. In addition, Sousa, Silva, and Airoldi (2009) chemically modified chitosan with ethylenesulfide under solvent-free conditions to give the higher capacity for cation removal from aqueous solution.

On the other hand, great progress has been made in controlled/living free radical polymerizations in the past decade, such as living free radical nitroxide-mediated polymerization (NMP) (Georges, Veregin, Kazmaier, & Hamer, 1993; Hawker, Bosman, & Harth, 2001; Keoshkerian, Georges, & Boilsboissier, 1995), atom transfer radical polymerization (ATRP) (Kato, Kamigaito, Sawamoto, & Higashimura, 1995; Matyjaszewski & Xia, 2001; Wang & Matyjaszewski, 1995) and reversible addition-fragmentation chain transfer (RAFT) (Chiefari et al., 1998; Le, Moad, Rizzardo, & Thang, 1998) process. These techniques would enable a wide variety of molecular designs to afford novel types of tailored hybrid materials composed of natural polysaccharides and synthetic polymers. Using ATRP technique, poly(oligoethylene glycol methacrylate) (Munro, Hanton, Moratti, & Robinson, 2009; Tang, Zhang, Zhu, Cheng, & Zhu, 2009), polyacrylamide (Li, Bai, & Liu, 2005), poly(methoxy polyethyleneglycol methacrylate) (El Tahlawy & Hudson, 2003), poly(methylacrylate) and polystyrene (Lindqvist & Malmstrom, 2006; Liu & Su, 2006) have been grafted onto chitosan or solid polysaccharide substrates. And in the previous work, we reported the methods of controlled graft modification of chitosan via RAFT polymerization (Hua, Tang, Cheng, Deng, & Zhu, 2008; Tang, Hua, Cheng, Jiang, & Zhu, 2008) and via NMP (Hua, Deng, Tang, Cheng, & Zhu, 2008). Among them, NMP is a promising

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* Corresponding author. Tel.: +86 512 65882050; fax: +86 512 65880089.
E-mail addresses: dbhua_lab@suda.edu.cn (D. Hua), xlzhu@suda.edu.cn (X. Zhu).

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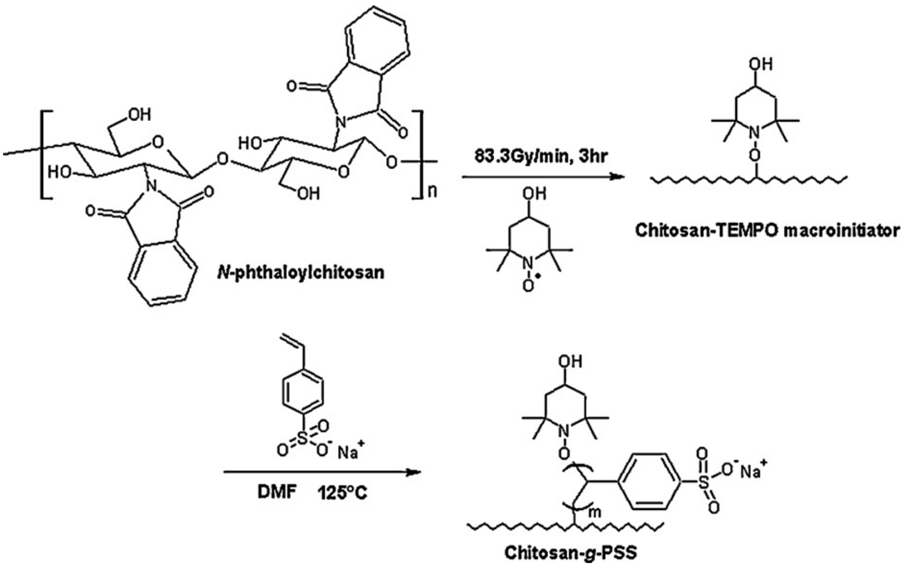


Scheme 1. Synthetic route for the graft copolymer, chitosan-*g*-PSS.

technique, in which a nitroxide radical is used to reversibly terminate the polymer chain radical to control the polymerization. It has been developed as an important synthetic tool for the well-defined polymeric materials with controlled molecular weight, polydispersity, structures and functional groups (Hawker, Bosman, & Harth, 2001).

In this paper, we report the synthesis of poly(sodium 4-styrenesulfonate) (PSS) grafted chitosan by the controlled polymerization in the presence of chitosan-TEMPO macroinitiator. It is known that PSS can be synthesized by NMP (Huang, Charleux, Chiarelli, Marx, Rassat, & Vairon, 2002), and has the good ion-exchange property. Therefore, the graft copolymers would be anticipated to have the improved capacity of cation removal. To our knowledge, this is the first report to synthesize the graft chitosan to improve the capacity by the controlled polymerization. The resultant polymers were characterized by ^{1}H nuclear magnetic resonance (^{1}H NMR), Fourier transform infrared spectrometer (FT-IR), high performance particle sizer (HPPS), and transmission electron microscopy (TEM), field-emitting scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX).

2. Experimental part

2.1. Materials and reagents

Chitosan (degree of deacetylation = 95.2%, determined by elemental analysis, average molecular weight = 200 K) was purchased from Qingdao Haoda Biochemical Co., Shandong, China. 4-Hydroxy-2,2,6,6-tetramethyl piperidine-1-oxyl (4-hydroxy-TEMPO) was purchased from SIGMA Chemical Co., and was purified by recrystallization in n-hexane. Sodium 4-styrenesulfonate was purchased from Alfa Aesar China (Tianjin) Co. Ltd., and was purified by recrystallization from 9:1 (v/v) mixture of methanol and water at 60 °C and dried under vacuum before use. *N*, *N*-dimethyl formamide (DMF) was distilled under reduced pressure from calcium hydride and stored over molecular sieves (4A). *N*-phthaloylchitosan was prepared according to the reported procedure (Kurita, Ikeda, Yoshida, Shimojoh, & Harata, 2002), the degree of substitution of phthaloyl groups was determined by elemental analysis. All other

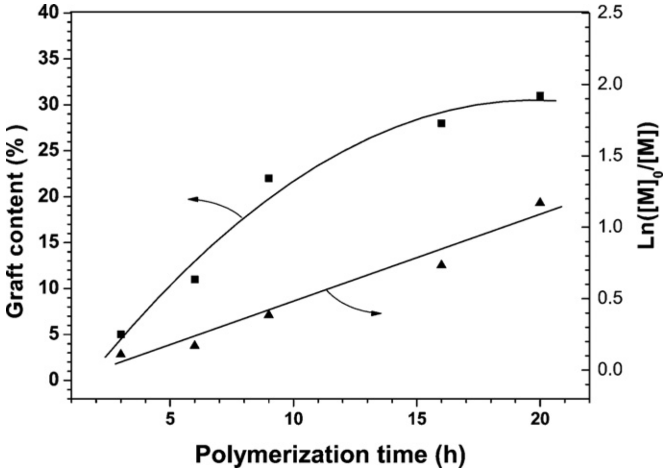


Fig. 1. Graft content of PSS onto chitosan and ln($[M]_0/[M]$) as functions of polymerization time for the graft polymerization.

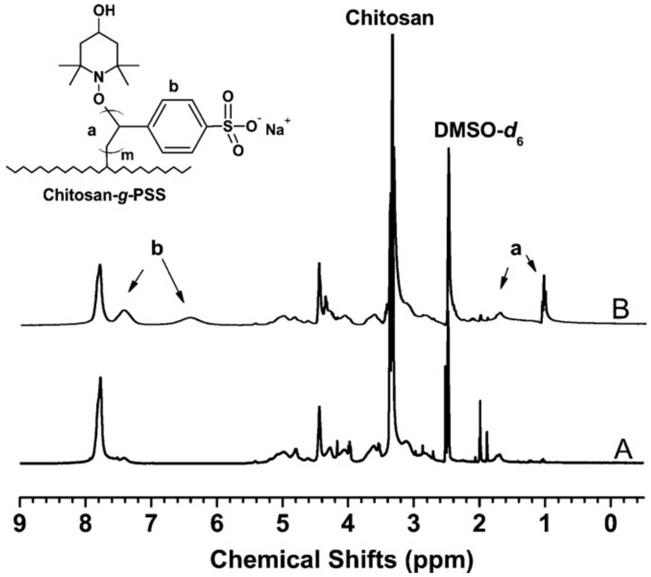


Fig. 2. ^{1}H NMR spectra of (A) chitosan-TEMPO macroinitiator and (B) chitosan-*g*-PSS (t = 6 h) dissolved in DMSO-d_6 at 300 MHz.

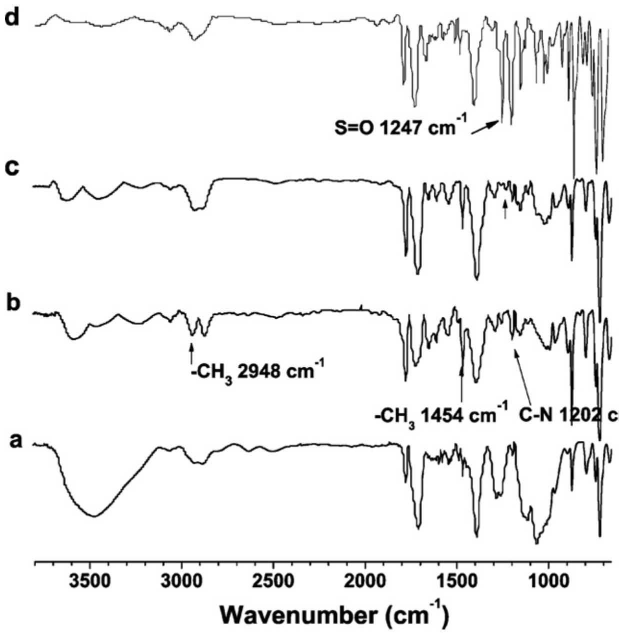


Fig. 3. IR spectra of (a) *N*-phthaloylchitosan, (b) chitosan-TEMPO macroinitiator, (c) chitosan-*g*-PSS (*t* = 3 h), and (d) chitosan-*g*-PSS (*t* = 6 h).

chemical reagents were of analytical grade and used without further purification.

2.2. Synthesis of chitosan-TEMPO macroinitiator

The procedure of chitosan-TEMPO macroinitiator was modified according to the literature method (Hua, Deng, et al., 2008). *N*-phthaloylchitosan (1.168 g, 4.0 mmol repeating unit) and 4-hydroxy-TEMPO (0.688 g, 4.0 mmol) were dissolved in dry DMF (100 mL) under argon atmosphere. Then it was placed in an insulated room with a ^{60}Co source. The reaction was carried out under ^{60}Co γ-ray irradiation at 83.3 Gy/min for 3 h. The resulting mixture was poured into ice water. The precipitate was collected on a filter, and washed completely by Soxhlet's extraction with acetone for 48 h. It was dried in a vacuum oven at 40 °C to give a dark yellow powder (0.984 g, 53% yield). The content of TEMPO group in chitosan-TEMPO macroinitiator was determined to be 0.13 mmol/g according to ^{1}H NMR spectrum. ^{1}H NMR (d$_6$-DMSO), δ: 7.2–8.0 ($-C_6H_5$), 2.8–5.2 (–CH– and $-CH_2-$ of chitosan), 0.8–1.2 ($-CH_3$ and $-CH_2-$ of TEMPO).

2.3. Preparation of graft copolymers

A mixture of chitosan-TEMPO macroinitiator (0.165 g, 0.0212 mmol TEMPO groups) and dry DMF (6 mL) was stirred magnetically under argon atmosphere. After dissolving completely, sodium 4-styrenesulfonate (0.500 g) was added. The polymerization proceeded at 125 °C for a predetermined time. After the polymerization, the reaction mixture was precipitated in 10-fold methanol, and then filtered. The crude copolymer was washed completely by Soxhlet's extraction with distilled water for 48 h. Finally, the copolymer was washed with methanol, and dried in a vacuum oven at 40 °C to constant weight. The graft content (*G*%) was calculated as follows:

$$G\% = \frac{W_g - W_0}{W_0} \times 100\% \qquad (1)$$

And the monomer conversion (Conv.%) was calculated based on Eq. (2):

$$\text{Conv.\%} = \frac{W_g - W_0}{W_M} \times 100\% \qquad (2)$$

where W_g, W_0 and W_M stand for the weights of graft copolymer, chitosan-TEMPO macroinitiator, and monomer, respectively.

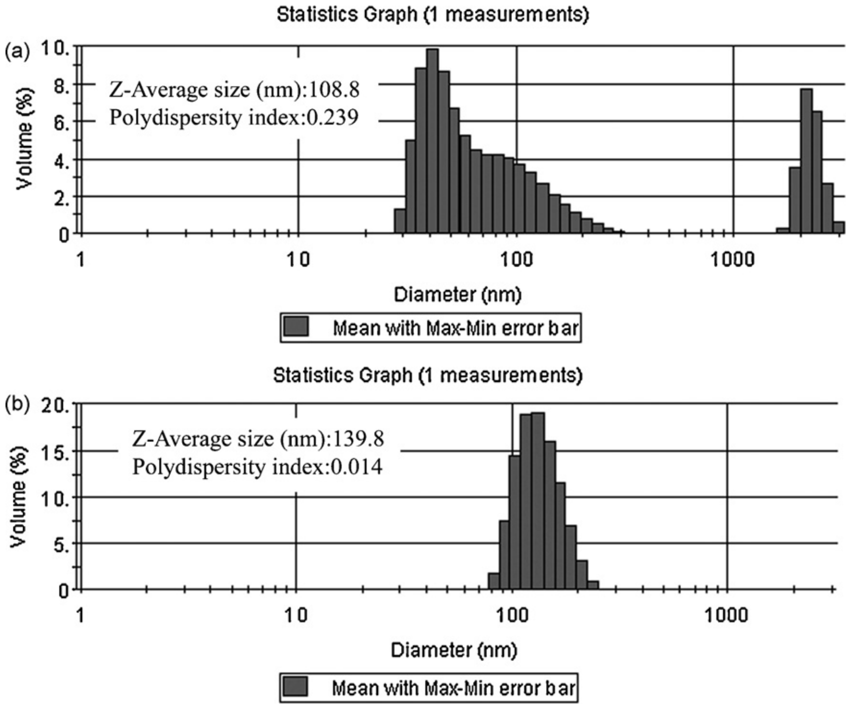


Fig. 4. Particle size distributions of PSS grafted chitosan nanoparticles in distilled water at the concentration of 2 mg/mL: (a) chitosan-*g*-PSS (*t* = 3 h), and (b) chitosan-*g*-PSS (*t* = 6 h).

2.4. Aggregation and adsorption of graft copolymer

Concerning that the graft copolymer can self-assembly in water or aqueous solution due to the amphiphilic structure, the aggregation and ion adsorption experiments were performed as below: a solution of graft copolymer (20 mg) in DMF (10 mL) was dialyzed with distilled water, 10% $FeCl_3$ aqueous solution (pH ~7.0), and 10% $CuCl_2$ aqueous solution (pH ~7.0) for 48 h, respectively. Regarding the adsorption with Fe^{3+} and Cu^{2+}, after stirring for 48 h, the aggregations were further dialyzed with distilled water for 48 h to remove free metal ion. Finally, the complex was separated by centrifugation at 10,000 rpm for 60 min, and dried in a vacuum oven at 40 °C to constant weight.

In order to compare the ion-exchange property, the adsorption experiment of chitosan was also performed under the same condition.

2.5. Characterization

^1H nuclear magnetic resonance (^1H NMR) spectra were obtained on a Varian INVOA-400 instrument with DMSO-d_6 as the solvent. Fourier transform infrared spectrometer (FT-IR) spectra were recorded on a Varian-1000 at room temperature, and the samples were ground with KBr crystals and the mixture was then pressed into a pellet for IR measurement. The *Z*-average size and the polydispersity index of the micelles were measured by Malvern HPP 5001 high performance particle sizer (HPPS). Transmission electron microscopy (TEM) images were taken with a FEI Tecnai G20 electron microscope, using an accelerating voltage of 160 kV. Field-emitting scanning electron microscopy (SEM) images were taken by a HITACHI S-4700 microscope operated at an accelerating voltage of 15 kV. Energy-dispersive X-ray (EDX) analysis was carried out by a Hitachi S570 scanning electron microscope equipped with an EDAX-PV 9100 energy-dispersion X-ray fluorescence analyzer.

3. Results and discussion

In this study, *N*-phthaloylchitosan, the soluble intermediate for the modification of chitosan, was first synthesized according to the related reference (Kurita, Ikeda, Yoshida, Shimojoh, & Harata, 2002), and the degree of substitution of phthaloyl groups was determined to be 0.98 by elemental analysis. Then the irradiation of *N*-phthaloylchitosan was carried out with 4-hydroxy-TEMPO in DMF under argon atmosphere to give the chitosan-TEMPO macroinitiator (Hua, Deng, et al., 2008). The content of TEMPO groups in chitosan-TEMPO macroinitiator was determined to be 0.13 mmol/g according to ^1H NMR spectrum, and the chitosan-TEMPO macroinitiator was used for controlled grafting PSS onto chitosan (Scheme 1).

The graft polymerizations of sodium 4-styrenesulfonate were performed with chitosan-TEMPO macroinitiator in DMF at 125 °C. According to NMP mechanism (Hawker, Bosman, & Harth, 2001), for chitosan-TEMPO macroinitiator, the C–O bond between the

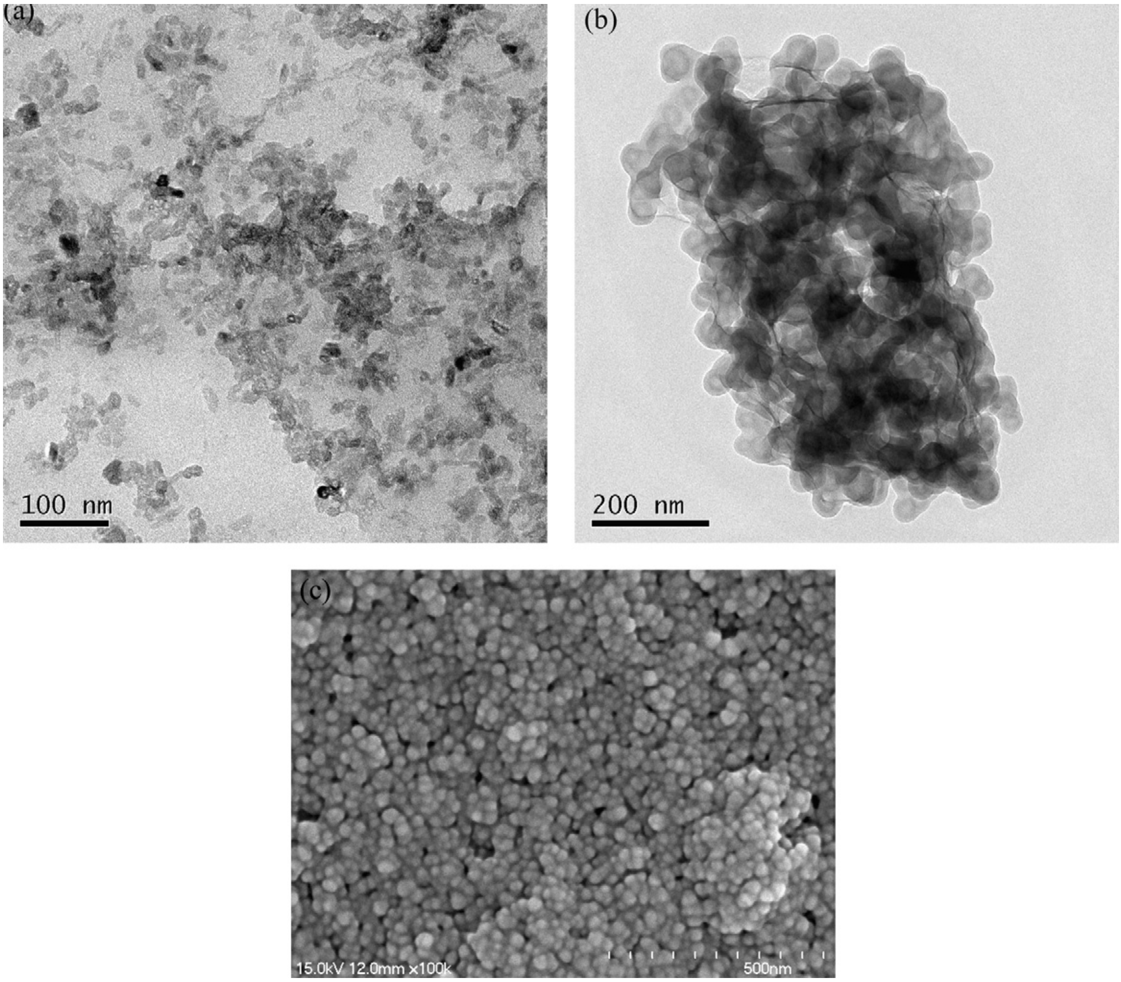


Fig. 5. The morphologies of the graft copolymer casted from dilute H_2O dispersion: TEM images of (a) chitosan-*g*-PSS (t = 3 h) and (b) chitosan-*g*-PSS (t = 6 h); and SEM image of (c) chitosan-*g*-PSS (t = 6 h).

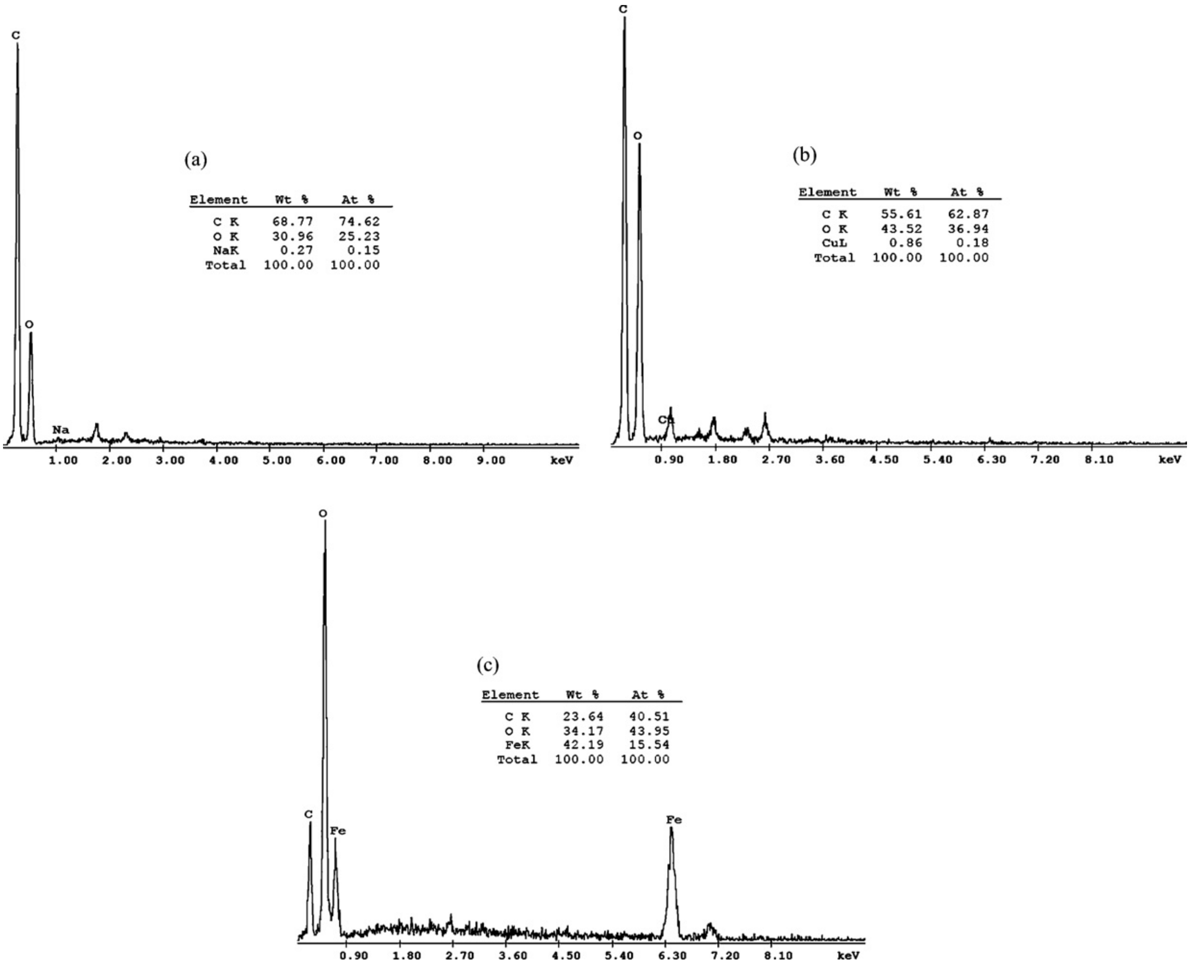
TEMPO and chitosan chain may be thermolytically unstable and first decomposed on heating to give an initiating carbon radical and a stable nitroxide radical. Following the initiation of sodium 4-styrenesulfonate, the stable radical may reversibly terminate the polymer chain radical to control the chain length (i.e. graft content) and give the graft copolymer chitosan-*g*-PSS.

The graft content versus the graft polymerization time is shown in Fig. 1 for the nitroxide-mediated controlled grafting process. In comparison with the graft polymerization of styrene on chitosan reported by Ohya, Maruhashi, Shizuno, Mano, Murata, and Ouchi (1999), the rate of PSS grafting is significantly slower than the conventional free radical grafting polymerization, which may be attributed that TEMPO suppressed the grafting rate considerably and controlled the grafting ratio. In addition, from Fig. 1, the kinetics curve for the graft polymerization is a straight line, which indicates that the graft polymerization is a first order reaction with respect to monomer concentration. All the evidences show that the graft polymerization was well controlled by the nitroxide-mediated process.

The copolymer structures were characterized by ^{1}H NMR and FT-IR spectra. The typical ^{1}H NMR spectra are depicted in Fig. 2. In comparison with that of chitosan-TEMPO macroinitiator (Fig. 2A), the characteristic peaks at $\delta = 7.41$, 6.40, 1.72 and 1.02 ppm are ascribed to phenyl ring, $-CH_2-$ and $-CH-$ respectively (Fig. 2B), which indicated that PSS was successfully grafted onto chitosan. Fig. 3 shows the FT-IR spectra of *N*-phthaloylchitosan, chitosan-TEMPO macroinitiator, and graft copolymers. In comparison with *N*-phthaloylchitosan (Fig. 3a), the characteristic peaks at 2948 and 1454 cm^{-1} ($-CH_3$), and 1202 cm^{-1} (C–N) appear for chitosan-TEMPO macroinitiator (Fig. 3b). Fig. 3c is the graft copolymer of chitosan-*g*-PSS obtained from the polymerization ($t = 3$ h). It can be seen that some characteristic peaks at 1247 cm^{-1} (S=O) occur for PSS when the polymerization time is 3 h, compared to chitosan-TEMPO macroinitiator (Fig. 3b). From Fig. 3d, the characteristic peak is markedly enhanced for the graft copolymer from the polymerization ($t = 6$ h). The results further demonstrated the successful synthesis of the graft copolymer.

Considering that the graft copolymer can self-assembly in water due to the amphiphilic structure, the aggregation in water was investigated. The nanometer sizes and size distributions of the self-assembly of chitosan-*g*-PSS in H_2O medium were characterized by HPPS, and the results are represented in Fig. 4. For chitosan-*g*-PSS ($t = 3$ h), there is the irregular dual peaks for the size distribution (Fig. 4a), while chitosan-*g*-PSS ($t = 6$ h) had a more symmetric size distribution and a narrower size distribution (Fig. 4b). The results may be associated with the PSS graft content for chitosan: in the case of chitosan-*g*-PSS ($t = 6$ h), the more graft content than that of chitosan-*g*-PSS ($t = 3$ h), led to the better self-assembly, i.e. the more symmetric size distribution, and a narrower size distribution.

In order to further clarify this point, the morphologies of the self-assembly of the graft copolymer were investigated by TEM and SEM (Fig. 5). As shown in Fig. 5a, the worm-like micelles were obtained for chitosan-g-PSS ($t = 3$ h); whereas for chitosan-*g*-PSS ($t = 6$ h), the self-assembly was spherical and monodisperse with the diameters of about 40 nm, and the outer shell and core could be clearly observed (Fig. 5b). Similarly, SEM micrograph also shows



(a)

Element	Wt %	At %
C K	68.77	74.62
O K	30.96	25.23
NaK	0.27	0.15
Total	100.00	100.00

(b)

Element	Wt %	At %
C K	55.61	62.87
O K	43.52	36.94
CuL	0.86	0.18
Total	100.00	100.00

(c)

Element	Wt %	At %
C K	23.64	40.51
O K	34.17	43.95
FeK	42.19	15.54
Total	100.00	100.00

Fig. 6. EDX spectra of (a) chitosan-*g*-PSS ($t = 3$ h), (b) chitosan-*g*-PSS ($t = 3$ h)–Cu^{2+} complex, and (c) chitosan-*g*-PSS ($t = 3$ h)–Fe^{3+} complex.

the spherical nanoparticles with a comparatively uniform distribution for chitosan-*g*-PSS ($t = 6$ h) (Fig. 5c). It was reported that the size and morphology of the self-assembly were associated with the contents of grafting polymers on chitosan (Huang, Li, & Fang, 2009; Liu, Xu, Guo, & Han, 2009). In this study, the morphologies should also be attributed to the graft content in the copolymer: small graft content, i.e. short graft chain length of PSS may lead to worm-like micelles for chitosan-*g*-PSS ($t = 3$ h); and chitosan-*g*-PSS ($t = 6$ h) with relatively larger graft content would self-assembly into spherical nanoparticles. The results further demonstrated that the more graft content, the better self-assembly.

It is well-known that sulfonate group had the good ion-exchange property (Muraviev, 1998; Rocha, Pinheiro, & Carapuca, 2006; Silva, Carapuca, Rocha, & Pinheiro, 2009). So in this study, the graft PSS may endow the chitosan with good ion-exchange property. In order to investigate this property of the graft copolymer, the ion adsorption experiments were implemented in aqueous solution. The graft copolymer was dialyzed with ionic aqueous solutions, i.e. 10% $FeCl_3$ aqueous solution (pH ~7.0), and 10% $CuCl_2$ aqueous solution (pH ~7.0), respectively. The ion-exchange equilibrium was reached after stirring for 48 h, since the adsorption amount almost did not change for the longer time. Then the graft copolymers were dialyzed with distilled water for another 48 h to remove free metal ions.

The resultants were characterized by EDX analyses. Fig. 6 shows the EDX spectra of chitosan-*g*-PSS ($t = 3$ h), chitosan-*g*-PSS ($t = 3$ h)–Cu^{2+} complex, and chitosan-*g*-PSS ($t = 3$ h)–Fe^{3+} complex. In comparison with the graft copolymer (Fig. 6a), Cu (0.86%) and Fe (42.19%) elements were clearly observed in Fig. 6b and c respectively, suggesting that ion exchange of chitosan-*g*-PSS ($t = 3$ h) successfully occurred with Cu^{2+} and Fe^{3+}. It should be noted that the complexation of Fe^{3+} is very high (42.19%), which may be ascribed to the sulfonate group's greater affinity for Fe^{3+}. In order to compare the ion-exchange property, the adsorption experiment of chitosan was also performed under the same condition, and the EDX data of 0.42% and 20.55% were obtained for Cu and Fe elements, respectively. It is clear that the ion-exchange property has been markedly improved due to the grafted PSS onto chitosan.

For chitosan-*g*-PSS ($t = 6$ h), there exists a higher content of Na element (Fig. 7a) in comparison with chitosan-*g*-PSS ($t = 3$ h) (Fig. 6a), suggesting the more graft content of PSS; and the ion-exchanges with Fe^{3+} and Cu^{2+} were also enhanced according to Fig. 7b and c. The results indicated that the ion-exchange of chitosan-*g*-PSS could be controlled by adjusting PSS graft content.

It should be noticed that there may be some influence of the morphology on the ion-exchange property. It is well-known that the spherical micelle has the smallest specific surface area, i.e. the smallest area for ion exchange, which should lead to the worse ion-exchange property. However, in this study, there is better ion-exchange property for the spherical micelles in the case of chitosan with longer PSS chain. So it can be ascertained that the better ion-exchange property should mainly be ascribed to the longer grafted PSS chain, and the influence of the morphology may be overlapped. Therefore, it is difficult to evaluate the influence of the morphology on the ion-exchange property in this study. Further investigation is under way in our lab.

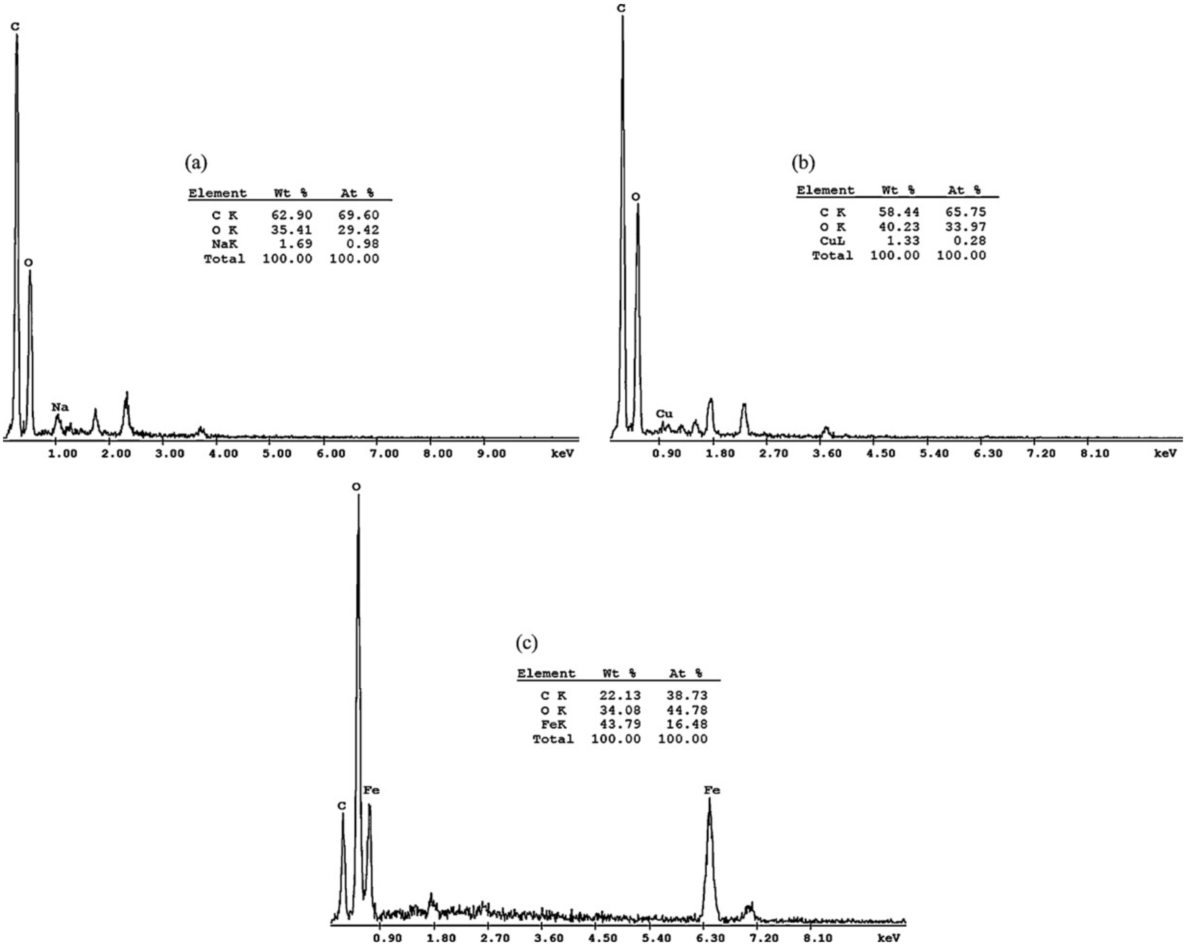


Fig. 7. EDX spectra of (a) chitosan-*g*-PSS ($t = 6$ h), (b) chitosan-*g*-PSS ($t = 6$ h)–Cu^{2+} complex, and (c) chitosan-*g*-PSS ($t = 6$ h)–Fe^{3+} complex.

4. Conclusion

PSS grafted chitosan was successfully synthesized by NMP of sodium 4-styrenesulfonate in the presence of chitosan-TEMPO macroinitiater. Chitosan-TEMPO macroinitiator was obtained from the irradiation of *N*-phthaloylchitosan with 4-hydroxy-TEMPO in DMF under argon atmosphere, and then was used for grafting PSS onto chitosan at 125 °C. The resultants were characterized by ^{1}H NMR, FT-IR, HPPS, TEM, SEM and EDX. The results indicated that the graft polymerization was well controlled by the nitroxide-mediated process, and the graft copolymers were successfully synthesized. The self-assembly of chitosan-*g*-PSS in water might be associated with PSS graft content of chitosan: more graft contents, better self-assembly, i.e. the more symmetric size distribution, and a narrower size distribution. Furthermore, the ion-exchange property of chitosan could be markedly improved due to the grafted PSS, and could be controlled by adjusting PSS graft content. The property may promote the graft copolymers to be used in the ion exchange for the environment protection. To our knowledge, this is the first report to synthesize the grafted chitosan to improve the capacity by the controlled polymerization, in which the chain length and the structure of PSS could be controlled, thereby leading to the controllable capacity.

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