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Grafting of 2-Diethylaminoethyl Methacrylate onto Silk by ATRP

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Abstract. In order to develop silk underwear fabric with good anti-bacterial property, silk was grafted using 2-diethylaminoethyl methacrylate (DEAEMA) by atom transfer radical polymerization (ATRP) method. The amino groups and hydroxyl groups on the side chains of the silk fibroin was reacted with 2-bromoisobutyryl bromide (BriB-Br) to obtain efficient macroinitiator for ATRP. And the macroinitiator was grafted with DEAEMA in water/ethanol media using CuBr/N,N,N',N",N" -pentamethyldiethylenetriamine (PMDETA) as catalyst system. The effects of monomer concentration, the proportion of CuBr and PMDETA, grafting temperature and time on the silk grafting were discussed, and the optimal grafting technology was obtained. FT-IR characterization of the grafted silk showed a peak corresponding to DEAEMA, which indicated that DEAEMA was grafted onto the surface of silk. The quaternized grafted silk had good anti-bacterial property to *S. aureus* and *E. coli.* . And the bacteria repellency of the grafted silk had good washing durability.

Introduction

As a textile fiber, silk exhibits many outstanding properties (handle, luster, dyeability, etc.) that distinguish it from other natural and synthetic fibers. Silk may be regarded not only as a textile fiber but also as biomedical materials for its' good biodegradability. However, for some applications, the properties of silk still need to be improved to meet the corresponding demands. For example, dimensional stability, wrinkle recovery and antimicrobial activity are other examples of properties that can be improved by chemical modification.

Poly(DMAEMA)(dimethylaminoethyl methacrylate) is a useful water-soluble and temperature sensitive polymer. The quaternization of poly(DMAEMA) has been reported by several workers [1,2]. We have reported the work about DMAEMA grafting onto silk using atom transfer radical polymerization(ATRP) method[3]. DEAEMA(2-diethylaminoethyl methacrylate) has the similar structure with DMAEMA. In the present work, silk was grafted with DEAEMA through ATRP in water aqueous. During the copolymerization, CuBr was used as catalyst, and N,N,N',N",N" -pentamethyldiethylenetriamine (PMDETA) was used as ligand. The optimal grafting condition was explored and the anti-bacteria property of grafted silk was tested.

Experimental

Materials. Degummed silk fabrics i.e. Silk (plain woven, 43 g/m^2) were supplied by Suzhou Huasi Silk Printing & Dyeing Co., LTD (Suzhou, Jiangsu Province, China). DEAEMA was kindly supplied by Japan Wako and was distilled under reduced pressure prior to polymerization. Triethylamine (TEA) and tetrahydrofuran (THF) was dried by CaH_2 overnight, and then distilled

under reduced pressure before use. CuBr was stirred in glacial acetic acid, filtered, and washed with acetone three times. PMDETA and 4-(dimethylamino) pyridine (DMAP) were used as received. 2-bromoisobutyryl bromide (BriB-Br) (98%, Alfa Aesar) and all other reagents were used without further purification.

Grafting Procedure and Its Quaternization by Methyl Bromide. The procedures of synthesis of the macroinitiator and quaternization of grafted silk were provided in our previous article of DMAEMA monomer grafting[3]. The procedure of ATRP grafting silk with DEAEMA was as follows: the silk macroinitiator(Silk-Br) was immersed into a reaction mixture containing certain DEAEMA, CuBr/PMDETA and 200 mL of solvent consisting of deionized water and ethanol (volumetric ratio 4:1) in a 250 mL round-bottom flask. After sealing it with a polytetrafluoroethylene three-way stopcock, the flask was evacuated and flushed with nitrogen, which was repeated three times. The mixture was placed in water bath and polymerized under oscillating at certain temperature for some time. After the reaction finished, the sample was rinsed with methanol and water to reach constant weight, and then dried under a vacuum oven. Thus silk grafted DEAEMA(S-g-DEAEMA) sample was obtained.

The weight gain was calculated as:

$$Weightgain\ (\%) = \frac{w_2 - w_1}{w_1} \times 100. \quad (1)$$

where w_1 and w_2 denote the weight of Silk-Br(silk macroinitiator) and S-g-DEAEMA(DEAEMA grafted silk), respectively.

Characterization. The infrared spectra of silk fabrics were recorded on a Nicolet5700 FTIR equipped with a single reflection ATR system.

Fabric Antibacterial Testing. Test for antibacterial effect was performed according to the Method of AATCC 100-1993.The inhibition rate was calculated as:

$$Inhibition\ \ rate\ (\%) = \frac{B - A}{B} \times 100\ . \quad (2)$$

where A denotes the colony number of sample cultivated for 48h; B denotes the colony number of control sample with "0" contact time.

Washing Resistance of Antibacterial Testing. Samples were put into solution with 5 g/L of soaping agent(liquor ratio 1:50) and washed for 10 min at 40 ° C, then the samples were rinsed with cold water and were dried, which was repeated certain times, and the samples were dried at 60 ° C,then the antibacterial property of fabric was tested.

Results and Discussion

Effect of Monomer Concentration. The graft copolymerization of DEAEMA onto silk was carried out by varying the monomer concentrations from 0.08 mol/L to 0.64 mol/L, keeping all other conditions of the reactions constant. As shown in Fig. 1, with increase in the monomer concentrations, the weight gain increased significantly. Since the concentration of macroinitiator was constant, the increase in DEAEMA concentration meant that the reaction opportunities between S-Br macroinitiator and DEAEMA increased and the weight gain increased correspondingly. But the weight gain was as high as 130% when the monomer concentration was 0.64 mol/L, and the handle of the fabric with weigh gain over 60% was poor. In order to achieve higher weight gain and better handle, 0.24 mol/L of monomer concentration was chosen in the following experiments.

Effect of Ratio of PMDETA/CuBr. A typical ATRP system consists of an initiator, a metal halide (at low oxidation state) formed complex with ligand, and a monomer. The ligand can tune the redox property of transition metals, improve the solubility of the related catalysts in reaction mixture and offer the related catalysts suitable selectivity. The ligands for copper-based catalysts are usually bipyridine or multidentage amines. PMDETA is a multitooth ligand and was used in this work. The effect of ratio of PMDETA/ CuBr on the grafting is shown in Fig. 2. It could be observed that with the increase of ratio of PMDETA/ CuBr, the weight gain increased and reached 40.50% at 2:1. By further increasing the ratio of PMDETA/ CuBr, the weight gain decreased instead. This fact was the same as the report of polymerization of styrene and methacrylate, in which the optimum dynamic mol ratio of ligand and CuBr was 2:1[4]. When the ratio was smaller than 2:1, the rate of polymerization was generally slow. When the ratio was bigger than this value, the rate of polymerization nearly had no change. And the optimum ratio was also relative to monomer and medium. In this experiment, for DEAEMA monomer, the optimum ratio of PMDETA/ CuBr was 2:1.

Effect of Reaction Temperature. The effect of reaction temperature on the grafting was also studied keeping all other conditions of the reactions constant (Fig. 3). With the increasing of temperature, the weight gains increased. For conventional chemical initiation, initiator has corresponding half-life under different temperature, and grafting temperature must be over 75 ℃ to finish the grafting in shorter time for those common used initiators like potassium persulphate and ammonium persulphate. However, mild reaction condition advantage of ATRP system made the grafting be run at room temperature. The reaction rate increased with the increase of temperature, and the weight gain reached the maximum value at 80 ℃. High temperature needs more energy sources and would affect the whiteness of silk fabric. Meanwhile, satisfactory weight gain of grafting silk could be obtained at 80℃. Accordingly, the optimum temperature was 80 ℃.

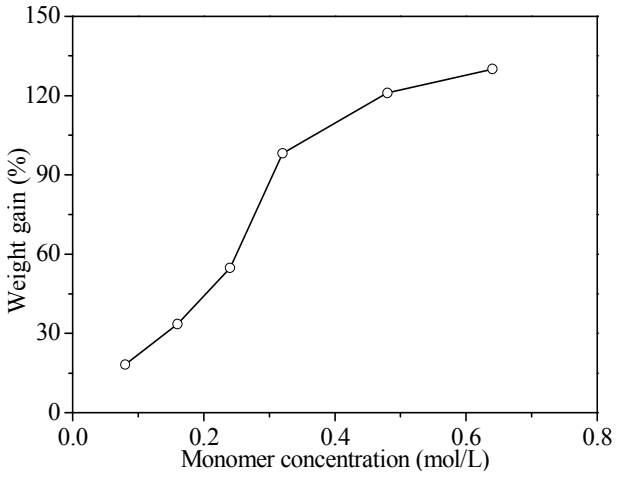

Fig. 1 Effect of [DEAEMA] on weight gain
[CuBr]=0.24 mmol/L; n(PMDETA):n(CuBr) =2:1; pH =8; T =80 ° C; time =1 h

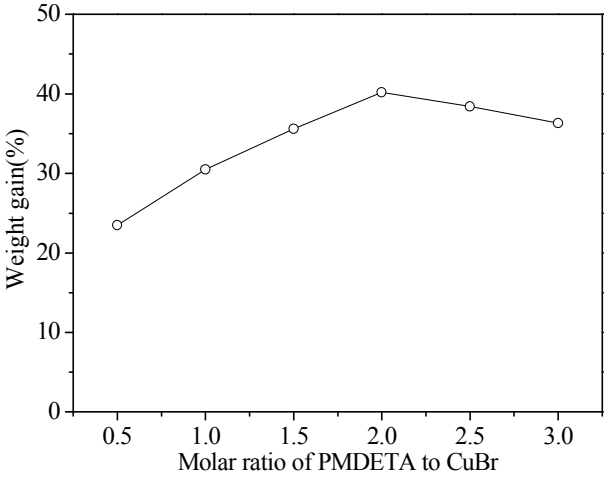

Fig. 2 Effect of ratio of PMDETA and CuBr
[DEAEMA]=0.24 mol/L; [CuBr]= 0.24 mmol/L; T=80 ℃; pH =8; time =1 h

Effect of Reaction Time. The graft copolymerization of DEAEMA onto silk was carried out by varying the reaction time from 10 min to 80 min, keeping all other reaction conditions constant. As shown in Fig. 4, with the increase of reaction time, the weight gain was increased gradually and reached 65.9% at 80 min. Since the copolymerization reaction was carried out at the same temperature and at a fixed concentration of monomer and catalyst, it is possible to assume that the concentration, nature and efficiency of the free radicals and other species generated during the reaction would be the same. By further extending reaction time, the weight gains of silk were

increased. But the handle of grafted silk was not good when the weight gain was over 60%. Thus, the reaction time was chosen as 60 min.

It also can be seen from Fig. 4, there is a linear increase in the weight gain and conversion of monomer with the increase of the polymerizing time. This exhibited the characteristics of a controlled/'living' polymerization[5].

FT-IR Spectra. FT-IR analysis (Fig.5) was used to demonstrate the presence of polymer grafted onto the silk surface. There was no weight gain for the S-Br macroinitiator (0% sample). The spectra of the silk all showed the characteristic absorption peak of amide linkage at about 1631 $cm^{-1}$and 1515 cm^{-1}. However, in case of S-g-DEAEMA samples there were additional peaks of carbonyl of ester groups at about 1732 cm^{-1}, and the peaks at about 1150 cm^{-1} arrtibuted to C-O stretching vibration of ester increased with increasing of weight gain. Thereby DEAEMA monomer was confirmed to be grafted onto silk fabric.

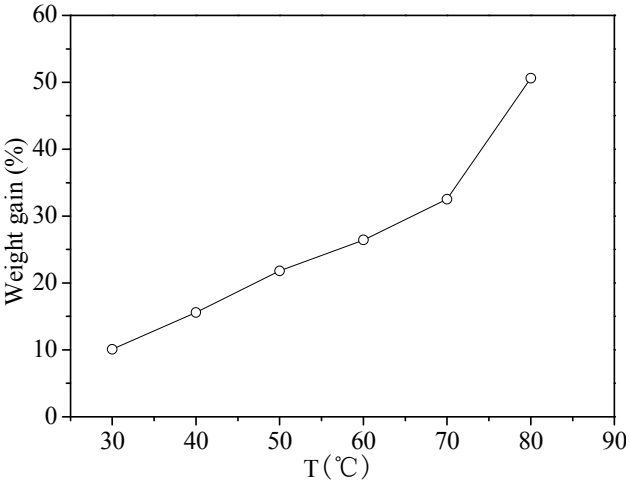

Fig. 3 Effect of temperature on weight gain
[DEAEMA]=0.24 mol/L; [CuBr]=0.24 mmol/L; n(PMDETA):n(CuBr)=2:1; pH=8; time =1 h

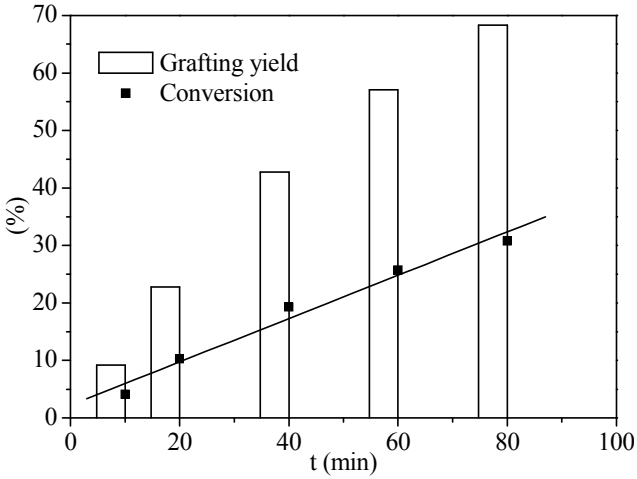

Fig. 4 Effect of time on weight gain and relationship between conversion and time
[DEAEMA]=0.24 mol/L; [CuBr]=0.24 mmol/L; n(PMDETA):n(CuBr)=2:1; pH =8; T=80 ° C

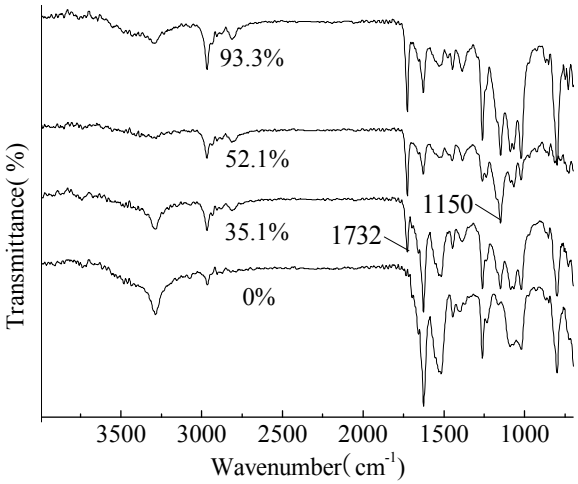

Fig. 5 ATR-FTIR of silk with different grafting yields

Anti-Bacterial Property. The anti-bacterial property of silk to *S. aureus* and *E. coli.* are shown in Table 1. It could be seen that for the control sample (0% weight gain), the bacteria propagate

rapidly. However, the quanternized grafted silk had good anti-bacterial property. And with the increase of weight gain, the inhibition yield also increased. Quaternized grafted silk with different weight gain all had good bacterial inhibition to *S. aureus* and *E. coli.* Furthermore, with the washing times increasing, the inhibition yield had little change and were all over 90%. Accordingly, it could be concluded that the bacteria repellency of the grafted silk had good washing durability.

Table 1 The anti-bacterial effect of quaternized silk with different weight gain

Washing times	Grafting yield (%) / Inhibition yield (%)					
	E. coli	S. aureus	E. coli	S. aureus	E. coli	S. aureus
	0		52.1		93.3	
0	-564	-1950	91.32	94.68	94.56	98.65
20			91.24	93.62	93.29	98.21
50			90.37	93.20	93.06	97.30

Summary

In conclusion, we have successfully developed a method for producing silk fibroin grafted DEAEMA using ATRP. The optimum grafting technology was obtained as follows: [DEAEMA]=0.24 mol/L; [CuBr]=0.24 mmol/L; n(PMDETA):n(CuBr)=2:1; pH=8; T=80 ° C; time =1 h. FT-IR characterization of the grafted silk showed that DEAEMA had been grafted on the silk surface. The quaternized grafted silk had good anti-bacterial property to *S. aureus* and *E. coli.* . And the bacteria repellency of the grafted silk had good washing durability.The described method affords a wide scale of graft copolymers with DEAEMA and grafts of various density, length and chemical structure, having expectedly various application and mechanical properties.

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