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Novel core-shell particles with poly(*n*-butyl acrylate) cores and chitosan shells as an antibacterial coating for textiles

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Abstract

A novel antibacterial coating for cotton fabrics has been developed using core-shell particles that consist of poly(*n*-butyl acrylate) (PBA) cores and chitosan shells. The spherical particles are prepared via a surfactant-free emulsion copolymerization of *n*-butyl acrylate in an aqueous chitosan solution induced by a small amount of *tert*-butyl hydroperoxide. The PBA-chitosan core-shell particles have a narrow particle size distribution with average particle diameter of approximately 300 nm, and display highly positive surface charges. Transmission electron microscopic (TEM) images clearly reveal well-defined core-shell morphology of the particles where PBA cores are coated with chitosan shells. The particle is composed of both the PBA homopolymer and the chitosan-*g*-PBA copolymer, which have been characterized with FTIR and ^{1}H NMR spectroscopes. The cotton fabric is coated with PBA-chitosan particles by using a conventional pad-dry-cure method. Its antibacterial efficiency is then evaluated quantitatively against *Staphylococcus aureus* with the shake flask method. The cotton treated with PBA-chitosan particles demonstrates an excellent antibacterial activity with bacterial reductions more than 99%.

Keywords: Core-shell particles; Chitosan; Antibacterial coating

1. Introduction

Natural textiles such as those made from cellulose and protein fibers are often considered to be more vulnerable to microbe attack than man-made fibers because of their hydrophilic porous structure and moisture transport characteristics. Thus, the use of antibacterial agents to prevent or retard the growth of bacteria is becoming a standard finishing for textile goods. There is, however, an increasing public concern over the possible effects of antibacterial finishing on environmental and biological systems since many antibacterial agents are toxic chemicals. They are also lack of efficiency and durability [1–3]. Thus, an ideal textile antibacterial finishing should be safe and environmentally benign besides killing undesirable micro-organisms.

Chitosan, a β-(1,4)-linked polysaccharide of D-glucosamine, is a deacetylated form of chitin, the second most abundant natural polymer in the world. Obtained from the shells of crabs, shrimps and other crustaceans, chitosan is a non-toxic, biodegradable and biocompatible natural polymer, and has long been used as a biopolymer and natural material in the pharmaceutical, medical, papermaking and food processing industries [4–5]. Because of its polycationic nature, chitosan possesses a good antibacterial property against various bacteria and fungi through ionic interaction at a cell surface, which eventually kills the cell [6–8]. Previous studies have shown that its antimicrobial activity is influenced by molecular weight (M_w) [9], degree of deacetylation [10], temperature, pH and cations in solution [11].

Because chitosan is one of the safest and most effective antibacterial agents, it has been widely applied for cotton and other textile antibacterial finishes [12–15]. But direct coating of chitosan onto textile articles suffers from such drawbacks as its insolubility in most solvents except acidic aqueous solutions, high viscosity of chitosan in aqueous solution causing many handling problems, and poor fabric hand after coating due to chitosan rigidity. To overcome

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these problems, various approaches have been reported to chemically modify the chitosan [16]. For instance, introduction of functional groups, such as quaternary ammonium salts, into the chitosan backbone improved its solubility in water and antibacterial activity [17–19]. Coating cotton with completely deacetylated chitosan in sodium nitrite had better laundry durability [20]. Grafting chitosan onto poly(ethylene terephthalate) fibers or polyhydroxyalkanaote membranes by plasma glow discharge or ozone treatment produced antimicrobial materials [14,21]. Here, a new approach has been developed to address abovementioned problems associated with the use of chitosan through the synthesis of novel core-shell particles that consist of soft polymeric cores and chitosan shells. Their potential application in antibacterial coating of textiles is evaluated.

2. Experimental

2.1. Materials

Chitosan (medium molecular weight, Aldrich) was purified by dissolving it in a 0.6% acetic acid solution at 60 °C, followed by filtration and precipitation in 10% NaOH solution under stirring at room temperature. The chitosan was then filtered and washed with distilled water until neutral, and dried in a vacuum oven at 60 °C. Molecular-weight measurement using a solution viscosity method suggested that the M_v of chitosan was approximately 80,000. Its degree of deacetylation, as estimated by ^{1}H NMR spectroscopy [22], was 74%. *n*-Butyl acrylate (BA, Aldrich) was purified by distillation under reduced pressure. *tert*-Butyl hydroperoxide (*t*-BuOOH, 70% aqueous solution) was obtained from Aldrich and diluted to 20 mM as a stock solution. Acetic acid (Riedel-de Haën, Germany) was used as received. Freshly deionized and distilled water was used as the dispersion medium. Scoured and bleached plain-woven cotton fabric (100%) was rinsed with non-ionic detergent before finishing.

2.2. Synthesis of PBA-chitosan particles

The core-shell particles were prepared via a surfactant-free emulsion copolymerization according to our previously described method with certain modifications [23]. A 250 mL round-bottomed, three-necked flask equipped with a condenser, a magnetic stirrer and a nitrogen inlet was immersed in an oil bath. In a typical run, 100 mL of 0.6% acetic acid solution was added to the flask, followed by the addition of purified chitosan (0.5 g). The mixture was stirred at 60 °C to allow the chitosan to completely dissolve. After mixing in nitrogen at 80 °C for 30 min, *n*-butyl acrylate (2 g) was added drop-wise, followed by a quick addition of 1 mL of *t*-BuOOH solution (2.0×10^{-2} M). Within minutes, the reaction mixture became aggressively white, producing latex particles. The polymerization was continued for 5 h at 80 °C in nitrogen. Upon completion, the white latex dispersion was stored at room temperature for the finishing procedure. The monomer conversion was determined gravimetrically.

2.3. Measurement and characterization

Infrared spectra of graft copolymers were recorded on a Nicolet 750 FT-IR spectrophotometer using KBr disks. Infrared spectra of coated cotton fabrics were recorded on a Perkin–Elmer reflective FT-IR spectrophotometer. ^{1}H NMR spectroscopic determinations were made on a Bruker Advance DPX 400 using $CDCl_3$, acetic acid-d_4, or a mixture of $CDCl_3$/acetic acid-d_4 as solvent. Particle size and size distribution were measured on a Coulter LS-230 particle size analyzer. The zeta-potentials of particles were measured with a Malvern Zetasizer 3000HS (Malvern, UK) with a 1 mM NaCl aqueous solution as the suspension fluid. The core-shell nanostructures of the particles were observed using a scanning transmission electron microscope (STEM, FEI Tachai 12) at an accelerating voltage of 120 kV after treating the particles with 2% phosphotungstic acid (PTA) for an appropriate period. The morphologies of cotton fabrics before and after coating were examined by scanning electron microscopy (SEM, Stereoscan 440, Leica). Cotton fabrics were cut into small pieces and fixed on the standard SEM sample holders with a double-coated carbon conductive tab. All samples were sputter coated with a thin layer of gold in a vacuum.

2.4. Antibacterial finishing

The antibacterial finish was applied through using the conventional pad-dry-cure method. Each fabric sample ($\sim20\times40$ cm) was washed with non-ionic detergent, and immersed it in the latex dispersion for 3–5 min. The sample was then put through a laboratory pad machine (Rapid Vertical Padder, Taiwan) under a nip pressure of 1 kg/cm^{-2} for a complete wet pick-up. The dip-pad procedure was repeated twice, and the padded samples were dried in an oven at 100 °C for 5 min, and cured at 150 °C for 4 min. After rinsing, the treated samples were dried again.

2.5. Antibacterial activity

The antibacterial activity was evaluated quantitatively using the shake flask method [24]. This method is specially designed for specimens treated with non-releasing antibacterial agents under dynamic contact conditions. The test determines the reduction in the number of bacterial cells after placing the sample in a shaking flask for 1 h. *S. aureus* (ATCC 6538), a Gram-positive bacterium commonly found on the human body, was chosen as the tested bacterium. A typical procedure was as follows: 1 ± 0.1 g of sample fabric, cut into small pieces of approximately 0.5×0.5 cm, was

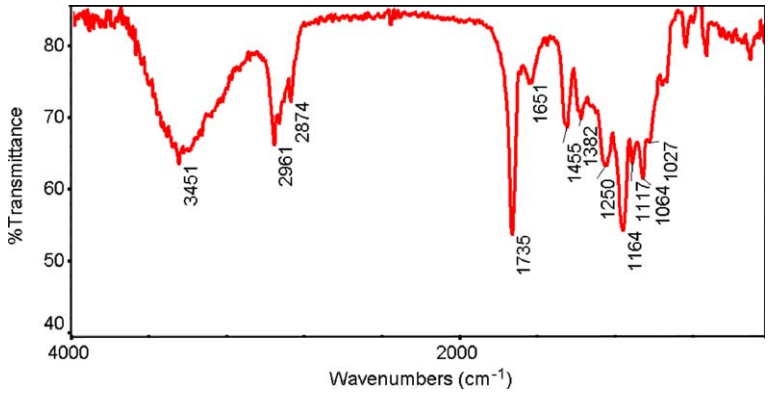

Fig. 1. FT-IR spectrum of chitosan-*g*-PBA copolymer.

dipped into a flask containing 50 mL of 0.5 mM PBS (monopotassium phosphate) culture solution with a cell concentration of $1.0–1.5\times10^4$/mL. The flask was then shaken at 250 rpm on a rotary shaker at 37 °C for 1 h. Before and after shaking, 1 mL of the test solution was extracted, diluted and spread onto an agar plate. After incubation at 37 °C for 24 h, the number of colonies formed on the agar plate was counted and the number of live bacterial cells in the flask before and after the shaking was calculated. Antimicrobial efficacy was determined based on duplicated test results. Percentage bacterial reduction was calculated according to the following equation:

$$R = \frac{(B-A)}{B}\times 100\%$$

Where R is the percentage bacterial reduction, B and A are the number of live bacterial cells in the flask before and after shaking.

3. Results and discussion

3.1. Preparation of core-shell particles with chitosan shells

A new method to prepare well-defined, core-shell particles that consist of hydrophobic cores and hydrophilic shells has been developed via a surfactant-free emulsion copolymerization [23,25,26]. This versatile approach allows us to design and synthesize a variety of core-shell particles for diverse applications [27]. This research aims to synthesize a novel type of core-shell particle consisting of a soft PBA core and the chitosan shell. Thus, textiles treated with the PBA-chitosan core-shell particles are expected to possess notable features including antibacterial property, good fabric hand and durability.

PBA-chitosan core-shell particles were first prepared based on our previously described method [23]. Thus, copolymerization of *n*-butyl acrylate from chitosan (weight

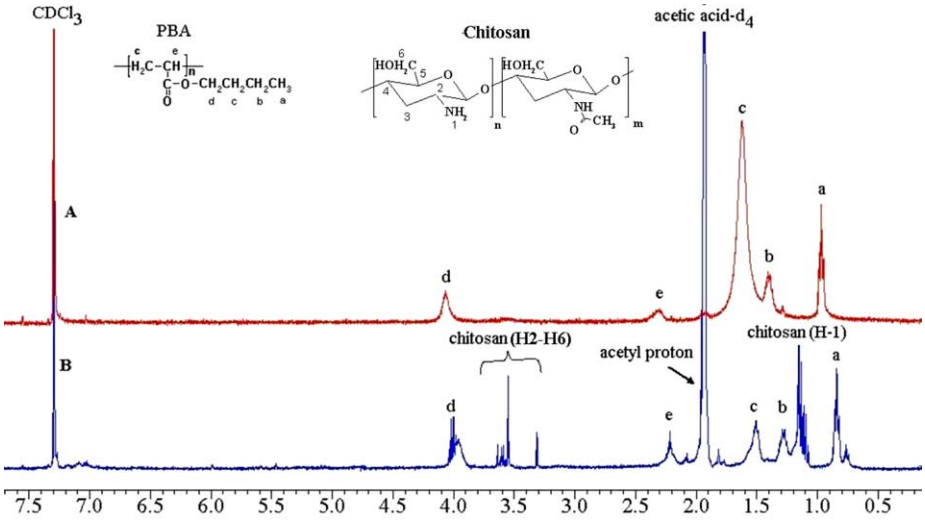

Fig. 2. ^{1}H NMR spectra of chitosan-*g*-PBA copolymer dissolved in (A) $CDCl_3$; (B) a mixture of $CDCl_3$ and acetic acid-d_4.

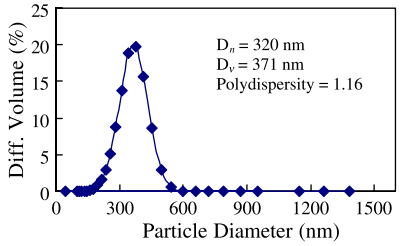

Fig. 3. Dynamic light-scattering measurement of chitosan-PBA particles.

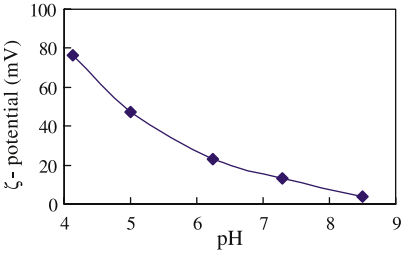

Fig. 4. Surface charges of chitosan-PBA particles as a function of pH in a 1 mM NaCl solution at room temperature.

ratio of BA:chitosan = 4:1) was induced with a small amount of *tert*-butyl hydroperoxide (0.2 mM) in a dilute acetic acid solution. The polymerization was carried out at 80 °C for 5 h in nitrogen to produce graft copolymer and PBA homopolymer concurrently, which phased-separated to form a stable latex emulsion. High monomer conversions up to 95% were generally achieved. However, chitosan concentration had to be maintained below 0.5 wt% for better mixing due to its high viscosity.

3.2. Characterization of polymer

Composition of the particle was determined by isolation both graft- and homopolymer of PBA. It involved a two-step Soxhlet extraction: (a) The adsorbed chitosan on the dry particles was first removed through extraction with 1% acetic acid solution for 48 h; (b) the purified particles were then extracted with chloroform for 48 h to separate the

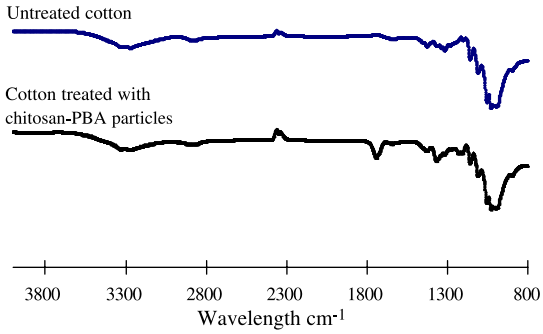

Fig. 6. Reflective FT-IR spectra of cotton fabrics before and after coating with PBA-chitosan particles. IR spectra of cotton fabrics before and after coating with PBA-chitosan particles.

chitosan-*g*-PBA and homopolymer of PBA. Fig. 1 shows the FTIR spectrum of the chitosan-*g*-PBA copolymer, which was insoluble in chloroform. A strong carbonyl peak at 1735 cm^{-1} and C–H stretching peak at 2961 cm^{-1} indicated the presence of PBA. The peaks at 3451 and 1651 cm^{-1} corresponded to the amine and amide groups of chitosan. ^1H NMR spectrum of the chitosan-*g*-PBA in $CDCl_3$ mainly showed the characteristic protons of PBA because of the insolubility of chitosan in $CDCl_3$ (Fig. 2(A)). However, both PBA and chitosan protons were observed in a mixture of $CDCl_3$ and acetic acid-d_4 (Fig. 2(B)). Peaks at 3.3–3.7 ppm indicated the presence of chitosan protons, and a chitin acetyl proton peak appeared at 1.9 ppm. These results clearly proved the formation of chitosan-*g*-PBA copolymer. The grafting efficiency, defined as the weight ratio of the PBA grafts to the total *n*-butyl acrylate monomer polymerized, was 67%. Thus, the PBA core was composed of 67 and 33% of grafted and homo-PBA, respectively. In other words, the chitosan molecules were covalently linked with the PBA cores.

3.3. Determination of particle size and surface

Dynamic light scattering measurement as shown in Fig. 3 indicates that highly monodispersed particles

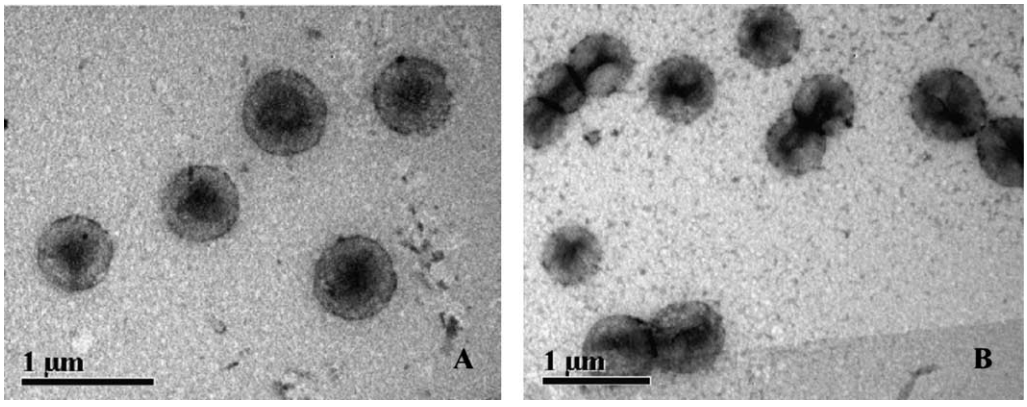

Fig. 5. TEM micrographs of chitosan-PBA particles stained for an appropriate period with 2% PTA solution. (A) Well-defined core-shell particles that consist of PBA cores and chitosan shells; (B) soft PBA-chitosan particles, which deform easily when in contact with each other.

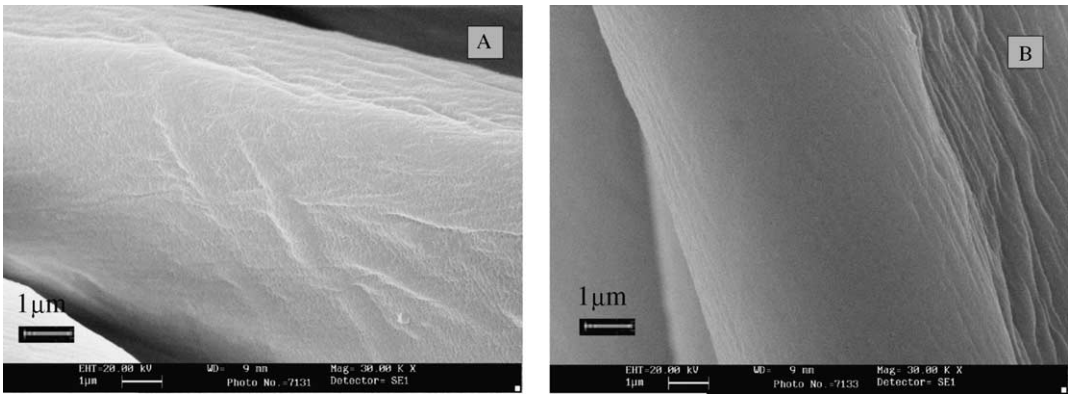

Fig. 7. SEM micrographs of surface morphologies of (A) untreated cotton fabric; (B) particle-treated cotton fabric.

(polydispersity $(D_v/D_n)=1.16$, where D_v and D_n are the volume and number average particle diameters, respectively), with the number average particle diameter of 320 nm are obtained. Surface charges of PBA-chitosan particles were studied through zeta-potential measurement as a function of pH in 1 mM NaCl solution at 25 °C (Fig. 4). The positive potential decreased as the pH increased, indicating that cationic chitosan was coated on the particle surfaces. When pH of the dispersion was higher than 8.5, the particles became unstable due to low surface charge density.

3.4. Particle morphology

Transmission electron microscopy (TEM) micrographs of PBA-chitosan particles (Fig. 5) showed that the particles were spherical and had near uniform particle size distribution. With careful staining of the particles using 2% phosphotungstic acid, the core-shell nanostructure of the particles were clearly revealed where PBA cores were coated with chitosan shells (Fig. 5(A)). The TEM images also indicated that the PBA-chitosan particles were so soft, thus they deformed easily when in contact with each other (Fig. 5(B)).

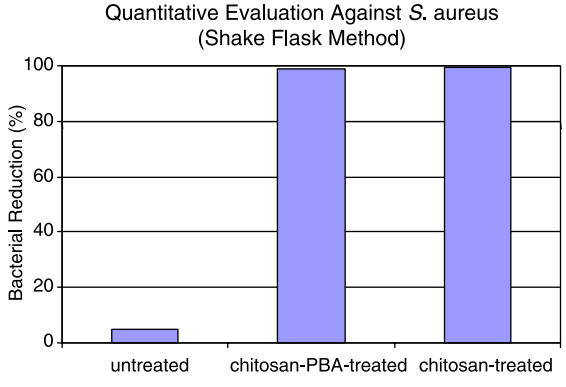

Fig. 8. Comparison of bacterial reduction before and after coating cotton fabrics with chitosan-PBA particles or chitosan solution (after 1 h shaking).

3.5. Characterization of PBA-chitosan treated cotton

Pure cotton fabric was treated with PBA-chitosan latex dispersion by a pad-dry-cure method. The coating of particles onto the fabric is confirmed with Reflective FT-IR spectra (Fig. 6). A small carbonyl absorption peak at 1730 cm^{-1} in the treated cotton sample indicates the presence of ester groups of PBA. Morphology of the coated fabric surface was further examined with SEM (Fig. 7). The SEM images show that there is little difference in surface appearance of the fabrics before and after treatment. Individual particles are not observed on fabric surface. The smooth coating of the PBA-chitosan particles is attributed to the good film-forming property of PBA.

3.6. Antibacterial property

It is well recognized that chitosan has good antimicrobial activity, especially against the growth of *Staphylococcus aureus* (*S. aureus*) [13]. Fig. 8 shows the result of treated and untreated specimens. As expected, the untreated fabric gave a negligible antibacterial activity of less than 5% while all finished cotton showed over 99% bacterial reduction. We also compared samples treated with 0.5 wt% chitosan solution. High bacterial reduction (>99%) was also obtained. Thus chemical modification of the chitosan through the graft copolymerization does not affect its antimicrobial property.

4. Conclusion

Chitosan-based core-shell particle, with chitosan as the shell and a soft polymer as the core, has been designed as a novel antibacterial coating for textiles. The core-shell particles were synthesized via a graft copolymerization of *n*-butyl acrylate from chitosan in aqueous solution. Properties of the particles, including composition, particle size and distribution, surface charge as well as morphology, were characterized. The treatment of cotton with PBA-chitosan

particles confers the fabric with excellent antibacterial property. Other characteristics of particle-coated fabrics including mechanical properties, air permeability, hand feel, and antibacterial durability over repeated launderings are reported separately.

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References

[1] Mao J, Murphy L. AATCC Rev 2001;1:28.
[2] Bohringer A, Rupp J, Yonenaga A. Int Textile Bull 2000;46:12.
[3] Corcoran LM. Determining the processing parameters and conditions to apply antibacterial finishes on 100% cotton and 100% polyester dyed knit fabrics. Charlottesville, VA, USA: Institute of Textile Technology; 1998.
[4] Sashiwa H, Aiba S. Prog Polym Sci 2004;29:887.
[5] Sandford PA. Chitin and chitosan. London and NY: Elsevier Science Publishers; 1989. p. 51–69.
[6] Qi L, Xu Z, Jiang X, Hu C, Zou X. Carbohydr Res 2004;339:2693.
[7] Jolles P, Muzzarelli RAA. Chitin and chitinases. Basel: Birkhauser Verlag; 1999. p. 315–333.
[8] Shin Y, Yoo DI, Min K. J Appl Polym Sci 1999;74:2911.
[9] Shin Y, Yoo DI, Jang J. J Appl Polym Sci 2001;80:2495.
[10] Liu XF, Guan YL, Yang DZ, Li Z, Yao KD. J Appl Polym Sci 2001; 79:1324.
[11] Tsai GJ, Su WH. J Food Protect 1999;62:239.
[12] Oktem T. Color Technol 2003;119:241.
[13] Lee S, Cho JS, Cho G. Textile Res J 1999;69:104.
[14] Huh MW, Kang IK, Lee DH, Kim WS, Lee DH, Park LS, et al. J Appl Polym Sci 2001;81:2769.
[15] Xu Y, Chen J. Fangzhi Xuebao 2001;23:13.
[16] Lim SH, Hudson SM. J Macromol Sci, Part C-Polym Rev 2003;43: 223.
[17] Kim YH, Choi HM, Yoon JH. Textile Res J 1998;68:428.
[18] Kim YH, Nam CW, Chio JW, Jang J. J Appl Polym Sci 2003;88:1567.
[19] Seong HS, Whang HS, Ko SW. J Appl Polym Sci 2000;76:2009.
[20] Seong HS, Kim JP, Ko SW. Textile Res J 1999;69:483.
[21] Hu SG, Jou CH, Yang MC. J Appl Polym Sci 2003;88:2797.
[22] Hirai A, Odani H, Nakajima A. Polym Bull 1991;26:87.
[23] Li P, Zhu J, Sunintaboon P, Harris FW. Langmuir 2002;18:8641.
[24] Yalpani M, Johnson F, Robinson LE. Advances in chitin and chitosan. New York: Elsevier Applied Science; 1995. p 543.
[25] Li P, Zhu J, Sunintaboon P, Harris FW. J Dispersion Sci Technol 2003;24:607.
[26] Zhu J, Li P. J Polym Sci, Part A: Polym Chem 2003;41:3346.
[27] Zhu J, Tang A, Law LP, Feng M, Ho KM, Lee DKL, et al. Bioconjugate Chem 2005;16:139.