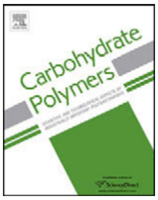
Carbohydrate Polymers 84 (2011) 681–685

Contents lists available at ScienceDirect

Carbohydrate Polymers

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



Short communication

Synthesize and properties of photosensitive organic solvent soluble acylated chitosan derivatives (2)

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ARTICLE INFO

Article history:
Received 18 June 2010
Received in revised form 3 November 2010
Accepted 8 November 2010
Available online 13 November 2010

Keywords:
Chitosan
Ultraviolet absorption
Sunscreen
Photopolymerization

ABSTRACT

A chitosan derivative carrying the benzene group was synthesized by the acylation reaction in the mild conditions. The chemical structures and physical properties of the compounds were characterized in detail. The chitosan derivatives were amorphous comparing with chitosan. The photopolymerization capability of chitosan derivative was also carried out by real-time infrared (RTIR) spectra, and it also has the own ability to photopolymer without photoinitiator under UV irradiation. The derivative had good ultraviolet absorption at 280 nm and good solubility in organic solvents.

1. Introduction

Chitosan has been widely investigated for biomedical applications such as controlled drug and protein delivery (Lin, Liang, Chung, Chen, & Sung, 2005), tissue engineering (Madhumathi et al., 2009), biosensors (Qiu, Deng, Liang, & Xiong, 2008), nerve regeneration (Gingras, Paradis, & Berthod, 2003) and gene delivery (Yoo, Lee, Chung, Kwon, & Jeong, 2005) because of their unique biological properties such as antibacterial and wound-healing property (Hong, Jin, Park, Ahn, & Kim, 2008), low toxicity, and biodegradability (Li, Liu, Tian, Liu, & Fan, 2007).

The applications of chitosan were limited owing to the intra and/or intermolecular hydrogen bonding from the acetamido or primary amino group residues. Low solubility of chitosan in both water and organic solvents resulted in many studies aimed at making water-soluble or organic-soluble chitosan derivatives by chemical modification techniques owing to both the reactive amino and hydroxyl groups. Such as, quaternarization (Murata, Ohya, & Ouchi, 1996), carboxymethylation (Sreedhar, Aparna, Sairam, & Hebalkar, 2007), graft modification (Mun et al., 2008; Makuška & Gorochovceva, 2006), and N- and O-hydroxyalkylation (Huang, Du, & Yang, 2003). Preparation of organic soluble chitosan derivatives could expand its application in many fields (Jeong, Kim, Jang, & Nah, 2008; Ma, Yang, Kennedy, & Nie, 2009; Wang, Jin, & Chang, 2009; Zong, Kimura, Takahashi, & Yamane, 2000). So far, more and more study reported on chitosan derivatives as sunscreen (Rinaudo, 2006). Above all, more and more monomers could react with the free amine groups on deacetylated chitosan units by reversible addition-fragmentation chain transfer RAFT polymerization (Hua, Tang, Cheng, Deng, & Zhu, 2008), high-intensity ultrasound technology (Wang et al., 2009), and immobilization of complexing agents (Justi, Fávere, Mauro, Laranjeira, & Casellato, 2005). The chitosan derivatives could be used as sunscreen because they had the UV-absorption groups (Juthathip, Mitsuru, Toshiyuki, & Suwabun, 2006; Renbutsu et al., 2008). Our research group previously reported the method of chitosan derivatives carrying the benzene group by Michael reaction (Ma, Qian, Yang, Hu, & Nie, 2010). Preparation of organic soluble chitosan derivatives can expand its application in many fields (Jeong et al., 2008; Ma et al., 2009; Wang et al., 2009; Zong et al., 2000).

The present contribution aims at extending the knowledge of the method of organic-soluble and photosensitive chitosan derivative. In the previous work chitosan derivative was got by acylation reaction in mild and convenient conditions, and its structure and properties were characterized in detail by Fourier transform infrared (FT-IR) spectroscope, ^{1}H NMR spectroscopy, and X-ray diffraction (XRD). The solubility of chitosan derivative in organic solvents was also tested. The relationship of conversion double bond of the chitosan derivative with the irradiation time of photopolymerization was revealed by technology of real-time FTIR. The ability between self-photopolymer and photopolymer initiated the benzopheone and ethyl-4-dimethylaminobenzoate (BP/EDMAB) as the photoinitiator under UV irradiation was also distinguished.

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doi:10.1016/j.carbpol.2010.11.013

2. Experimental

2.1. Materials

Chitosan (CS) was purchased from Yuhuan Ocean Biochemical Co. Ltd. (Zhejiang, China). According to the company analysis, its weight-average molecular weight was 200 kDa and its degree of deacetylation was about 88.0%. Cinnamoyl chloride was provided by Acros Organics, Belgium (New Jersey, USA). All other reagents were analytic grade, purchased from Beijing Chemical Reagent Company and used without further purification.

2.2. Preparation of chitosan derivative

Chitosan (2.0 g) was soaked in mixed solvent of triethylamine (60 mL) and acetone (30 mL) for 24 h at room temperature, then cinnamoyl chloride (5.0 g) dissolved in acetone (30 mL) was added dropwise into the mixed solution in 2 h. The reacted solution was filtrated in order to get the solid, and the solid washed with sodium bicarbonate solution to get the precipitate. At last, the precipitate was dried under vacuum at 30 °C overnight.

2.3. Characterization of chitosan derivative

Fourier transform infrared (FT-IR) spectrum was recorded on Nicolet 5700 instrument (Nicolet Instrument, Thermo Company, USA). Samples were prepared as KBr pellet and were scanned against a blank KBr pellet background at wavenumber range 4000–600 cm^{-1} with resolution of 4.0 cm^{-1}.

^1H NMR spectra were carried out on a Bruker AV600MHz (Bruker, Germany). Chitosan was dissolved in a mixed solvent of CD_3COOD and D_2O, and acylated chitosan derivates were dissolved in CD_3Cl. Degrees of substitution (DS) was calculated from the peak area at of H of benzene ring against that of NHAc proton (Hitoshi, Naoki, Yoshifumi, Junzo, & Sei-ichi, 2003).

UV–vis absorption spectra were recorded in chloroform solution on a Hitachi U-3010 UV–vis spectrophotometer (Hitachi High Technologies Corporation, Tokyo, Japan) in the range of 200–400 nm. A cell path length of 1 cm was employed.

2.4. Solubility test

Solubility of the chitosan derivative in the selected solvents was determined by the following procedure. The compound was gradually added to solvent, the mixture was stirred and continued to add the compound till to obtain the saturated solution.

2.5. Real-time infrared photopolymerization

Real-time infrared spectra were recorded on a modified Nicolet 5700 spectrometer (Nicolet 5700, Thermo Electron, USA). Photopolymerizations were conducted in a cell prepared by sandwiching the samples between glass slides and spacers with 15 ± 1 mm in diameter and 1.2 ± 0.1 mm in thickness. The UV light photopolymerization was triggered by a UV spot light source (EFOS Lite, with 300–420 nm filter and crystal optical fiber that the diameter at the fiber exit was 5 mm, Canada). Real-time infrared spectra data were collected with the resolution of 4 cm^{-1} and 0.3985 s sampling interval. The absorbance change of =C–H peak area from 6101 to 6261 cm^{-1} in the near IR range was correlated to the extent of polymerization.

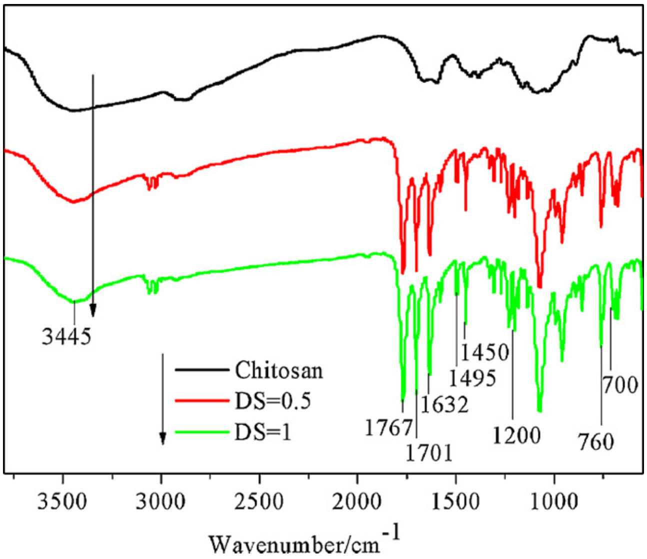

Fig. 1. FT-IR spectra of chitosan and acylated chitosan derivative.

3. Results and discussion

3.1. FT-IR analysis

The FT-IR spectra of chitosan and its derivative were shown in Fig. 1. The spectrum of chitosan presented the following bands. The broad band at around 3443 cm^{-1} attributed to –NH and –OH stretching vibration, as well as inter-molecular and intra-molecular hydrogen bonding of chitosan molecules (VanDeVelde and Kiekens, 2004). $–CH_3$ group symmetrical angular deformation at 1385 cm^{-1}, in addition to other characteristic polysaccharide bands at 1150 and 1080 cm^{-1} (Huang et al., 2003). New peaks at 1720 cm^{-1} and 1765 cm^{-1} appeared which assigned to the C=O of –NCOR group and C=O of –OCOR group, respectively. Another typical peaks at 1600 cm^{-1} and 1520 cm^{-1} were assign to the of benzene group. The typical peaks at 1630 and 810 cm^{-1} was due to the characteristic stretching vibration of double bond. The results also showed that the relative intensities of the absorbance of COO– group depends upon the degree of substitution values.

3.2. ^{1}HNMR analysis

The typical ^{1}HNMR spectrum of the chitosan in D_3CCOOD/D_2O and acylated chitosan in $CDCl_3$ were shown in Figs. 2 and 3, respectively. In Fig. 2, a small peaks at 1.95 ppm existed because of the presence of $–CH_3$ of N-acetylated GlcN residue. A singlet at 3.00 ppm assigned to H_2 of GlcN and N-acetylated GlcN, and multiplets from 3.5 to 3.8 ppm corresponded to H_3, H_4, H_5, H_6 of the methine protons of GlcN and N-acetylated GlcN. The large peak at 4.87 ppm attributed to H_1 of GlcN, N-acetylated GlcN, and few traces of water in the sample. In Fig. 3 a signal of newly formed about from 6.3 to 6.4 ppm attributed to H of double bond. Another signals at 7.3 and 7.5 ppm assigned to H of benzene ring.

3.3. UV–vis spectra

Fig. 4 shows UV–vis spectra of chitosan and its derivatives. The UV spectrum of the chitosan derivatives solution had an absorption band region range from 255 to 320 nm and an absorption peak at 280 nm, while the chitosan solution had no absorption peaks from 220 nm to 400 nm. It was consistent with previous results (Wang et al., 2009; Ma et al., 2010), where two peaks were ascribed to benzene residue group. However, in our work two overlapping peaks

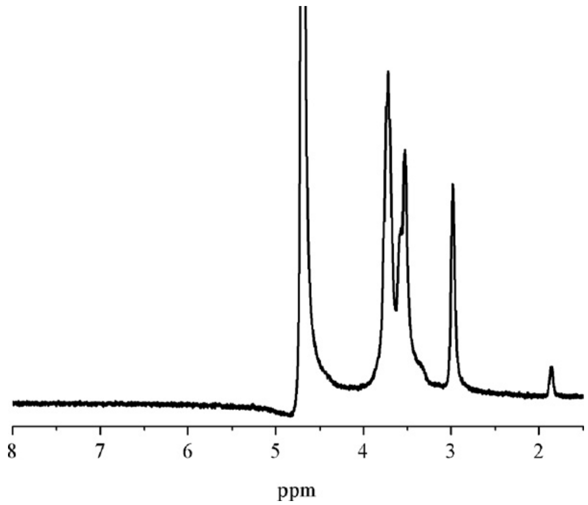

Fig. 2. Typical ^{1}HNMR spectra of chitosan.

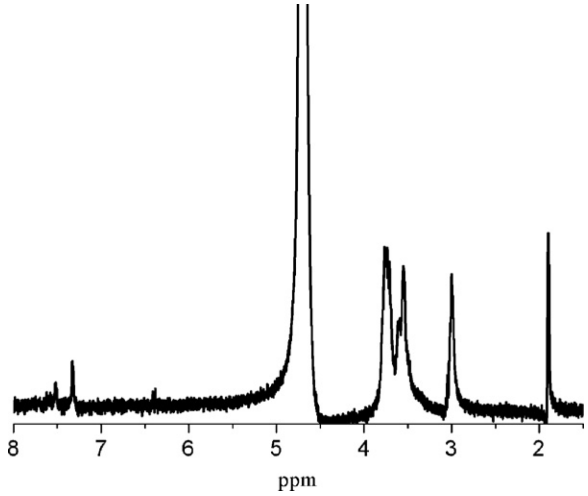

Fig. 3. ^{1}HNMR spectra of acylated chitosan derivative.

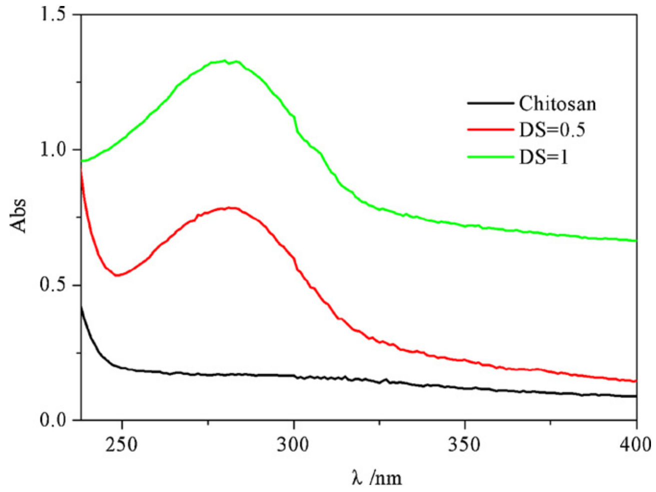

Fig. 4. UV-absorption spectra of chitosan and its derivative at the solution of chloroform.

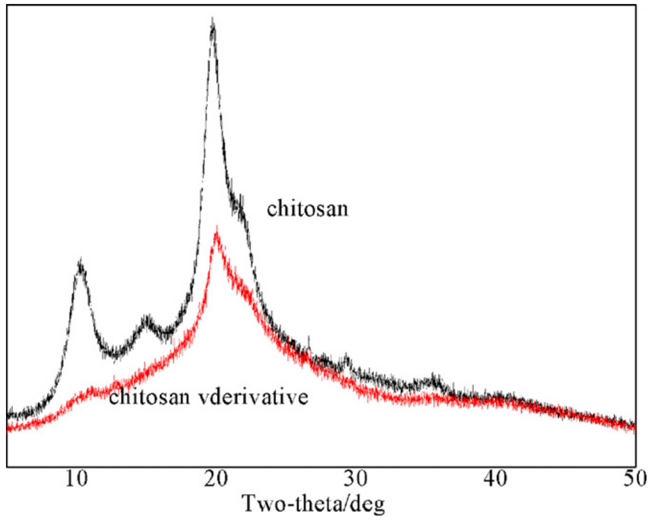

Fig. 5. XRD pattern of chitosan and acylated chitosan derivative.

could be found with slightly shifted absorbance maxima, which could be due to the different degrees of substitution of chitosan. The chitosan derivative was expected to be sensitive to the light at or below 280 nm in the emissions from the sun light and possibly used as sunscreen.

3.4. Solubility analysis

Chitosan derivative could slightly soluble in the solvents such as chloroform and carbon tetrachloride. The solubility in benzene and toluene of chitosan derivative was higher than that of chloroform and carbon tetrachloride. Furthermore, the organic solubility was increased with the increase of degrees of substitution of chitosan. The introduction of benzene group prevented the formation of intra- and inter-hydrogen bonds among the amino groups of chitosan and consequently improved the solubility in organic solvents (Kurita, Ikeda, Yoshida, Shimojoh, & Harata, 2002; Liu, Li, Liu, & Fang, 2004). But the chitosan derivative could not dissolve in ethanol and acetone, it also did not soluble in water.

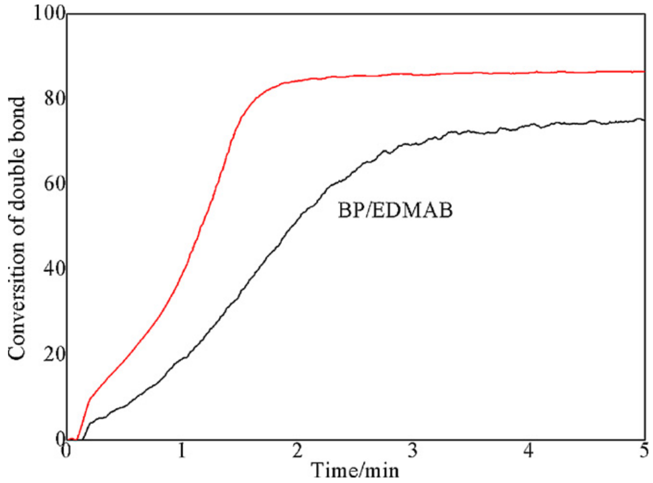

Fig. 6. Conversion of double bond of chitosan derivative, photopolymerized with 1.0 wt.% benzopheone and ethyl-4-dimethylaminobenzoate (BP/EDMAB) and without photoinitiator.

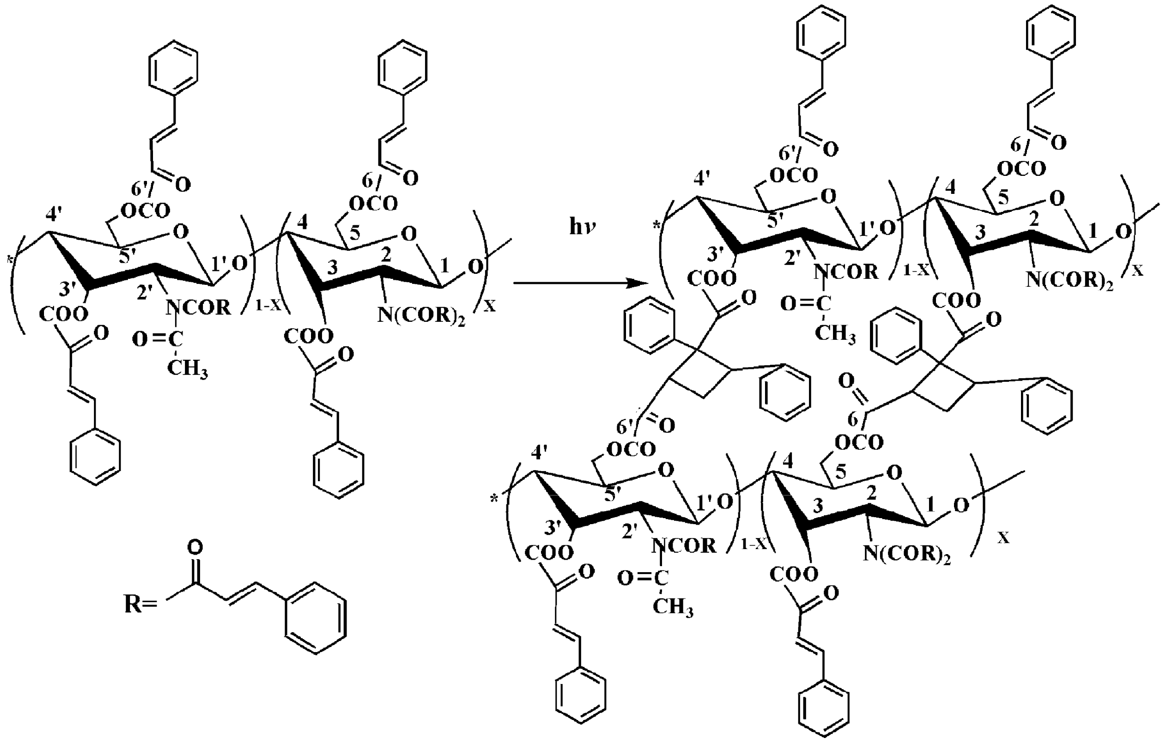

Fig. 7. Scheme of self-photopolymerization of acylated chitosan derivative.

3.5. X-ray diffraction (XRD)

X-ray diffraction analysis of chitosan and its derivative was illustrated in Fig. 4. The strongest reflection appears at $2\theta = 20.0°$, which correspond to crystal forms II, the reflection fall at $2\theta = 10.0°$ was assigned to crystal forms I (Samuels, 1981; Zhang & Neau, 2001). Compared with chitosan, the first peak at $2\theta = 20.0°$ was weaker and became broader, and the peaks at $2\theta = 10.0°$ disappeared which was due to the destruction of hydrogen bonding between amino groups and hydroxyl groups by the incorporated benzene residue group in chitosan derivative. The results showed that benzene residue group caused destruction of the ordered crystal structure of the chitosan.

3.6. Photopolymerization

Fig. 5 shows the degree of double conversion vs. time plots of chitosan derivative initiated by BP/EDMAB and without photoinitiator. The polymerization of chitosan derivative led to constant conversion of double bond within 3 min (Fig. 6). The photopolymerization proceeded in the condition of BP/EDMAB as photoinitiator was slower than that of without photoinitiator, and the final conversion with BP/EDMAB as photoinitiator was lower than that of without photoinitiator. The free radicals from irradiation of BP/EDMAB were away from the rigid chains of chitosan derivative and not easy attack them, but the chitosan derivative could photopolymer by self cross-linking with irradiation of UV light (Fig. 7).

4. Conclusions

The method was studied to introduce benzene group into –OH and $-NH_2$-group of chitosan at mild condition via acylation reaction, the chemical identity of chitosan derivative was confirmed by FT-IR, ^1H NMR spectroscopy, XRD, and UV–vis spectrometry. The chitosan derivative exhibited an excellent solubility in organic solvents and had good ultraviolet absorption at 280 nm which made it could be use as sunscreen. The chitosan derivative both could occur light cross-linking reaction and photopolymerization under UV irradiation with photoinitiator, furthermore, the ability of light cross-linking reaction was higher than that of photopolymerization initiated BP/EDMAB. There was no doubt that it expanded the scope of application of chitosan as biomaterials.

Acknowledgements

The author would like to thank the project supported by the Natural Science Foundation of Jiangsu Province (BK2010190) for its financial support. This study was supported by Key Laboratory for Green Chemical Process of Ministry of Education (GCP201002), Wuhan Institute of Technology, Wuhan 430073, P. R. China.

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