Carbohydrate Polymers 74 (2008) 875–879

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

A novel thermotropic liquid crystalline – Benzoylated bacterial cellulose

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ARTICLE INFO

Article history:
Received 26 March 2008
Received in revised form 28 April 2008
Accepted 7 May 2008
Available online 15 May 2008

Keywords:
Bacterial cellulose
Biofibers
Degree of substitution
Biopolymers
Thermal properties

ABSTRACT

Using the esterification of bacterial cellulose (BC), we have synthesized Benzoylated bacterial cellulose (BBC). The molecular structure of the BBC was characterized by means of Fourier transform infrared (FT-IR) spectroscopy, ^{1}H and ^{13}C nuclear magnetic resonance (NMR). The BBC is found to display thermotropic liquid crystalline feature determined with differential scanning calorimetry (DSC), polarized optical microscope (POM) and wide-angle X-ray diffraction (WAXD). Here, we demonstrate that it is possible to obtain the BBC with degree of substitution (DS) from 0.88 to 2.46 by applying the different molar ratio of benzoyl chloride to the anhydrous glucose unit (AGU). The glass transition temperatures (T_g) of the liquid crystalline phases lie between 281.2 and 281.8 °C and the isotropic melt transition temperatures (T_i) vary from 341.6 to 362.8 °C, depending on the DS.

1. Introduction

Cellulose is one of the oldest and the most abundant natural polymers, which is renewable and biocompatible (Klemm, Heublein, Fink, & Bohn, 2005). Cellulose with a rigid or semirigid backbone facilely forms liquid crystalline phases. Werbowyj and Gray (1976) firstly reported the cholesteric liquid crystalline phase of hydroxypropyl cellulose in aqueous solutions in 1976. Thereafter, investigations have been focused on the liquid crystalline of cellulose and its derivatives. Recently, the study on liquid crystal phases of functional cellulose ester or ether derivative gels or composites becomes attractive owing to their potential advantages in high intensity, toughness, and excellent processability (Huang & Li, 1995; Li, Huang, Hu, Lin, & Yang, 1999; Li, Huang, & Lin, 1996). Meanwhile, the study making use of liquid crystalline properties of cellulose for electro-optical applications opens new horizons for these traditional materials (Godinho, Martins, & Figueirinhas, 1996; Westlund, Carlmark, Hult, Malmstrom, & Saez, 2007). Furthermore, the cholesteric liquid crystalline of cellulose derivative is of great scientific and technological interest in the consequence of its unique selective reflection of light (Huang, Ge, Li, & Hou, 2007; Ifuku, Kamitakahara, Takano, Tanaka, & Nakatsubo, 2004; Wang & Huang, 2004). While a lot of cellulose derivatives have been found to display the liquid crystalline character, all of them derive from plants. Besides plants, some bacteria also can produce cellulose (Brown, 2004; Hestrin & Schramm, 1954). The cellulose produced by bacteria is called “microbial cellulose” or “bacterial cellulose (BC)”, which is an unbranched polymer by β-1,4-linked glucopyranose unit (Jonas & Farah, 1998). Although chemically identical to plant cellulose, BC is distinctly different from the cellulose derived from plants. BC is devoid of lignin, hemicellulose, and other complex carbohydrates. Moreover, BC has unique properties, such as ultrafine network structure, high good mechanical strength and a high degree of polymerization. Owing to these, BC and its derivatives can be used in many fields, such as paper, electronic industries and medical materials (Czaja, Young, Kawecki, & Brown, 2007; Ifuku et al., 2007; Nishi et al., 1990; Shah & Brown, 2005; Yano et al., 2005).

In this paper, we report the preparation of benzoylated bacterial cellulose (BBC) through the esterification of BC with benzoyl chloride. Benzoyl chloride reacts with the hydroxyl groups on the glucopyranose unit of BC, and eventually benzoyl substituents are attached to the BC backbone to form the BBC. With gradual substitution, the molecular chain of the BBC becomes semirigid and display an interesting thermotropic liquid crystalline phase. The BBC is one of potential candidates for sensors, high-level piezoelectric and optical materials.

2. Experimental part

2.1. Materials

Acetobacter xylinum (Hainan-1) was obtained from Hainan University and used to produce the BC pellicles. The *A. xylinum* (Hainan-1) was grown in a sterile liquid medium consisting of 0.4% ammonia sulfate ($(NH_4)_2SO_4$), 0.05% magnesium sulfate ($MgSO_4$), 2% glucose, and 0.1% potassium dihydrogenphosphate (KH_2PO_4) at pH of 4.5, 30 °C for 36 h. The strains were pre-cultured in a tube and then the strain (20 mL) inoculated into the 1 L flask containing 400 mL of the medium described above. The flasks were incubated

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doi:10.1016/j.carbpol.2008.05.007

statically at 30 °C for 7 days. The gel-like pellicles of BC were washed with water, and then boiled in 0.1 M aqueous solution of NaOH for 2 h to remove the impurities. The BC pellicles were again rinsed with water to remove the superabundance of NaOH, and finally dried at 70 °C and pulverized to 40 mesh. Benzoyl chloride, nitrobenzene and pyridine with analytical reagent were used without further purification.

2.2. Measurement

We performed Fourier transform Infrared (FT-IR) spectroscopy at the room temperature by using a G988 FT-IR spectrophotometer with the KBr pellet method. The thermal properties were studied by thermogravimetric analyzer–differential scanning calorimetry (TG-DSC) and polarized optical microscope (POM). TG-DSC curves were recorded with a STA499C DSC in a N_2 atmosphere. The sample with 3 mg mass was heated at a constant rate of 20 °C/min. The birefringence observation was made on an Olympusb × 51 POM. The BBC powder heated on a CSS450 hot stage was placed between a microscope slide and cover glass. Wide-angle X-ray diffraction (WAXD) pattern was performed with a D/max-RB nickel-filtered Cu K_α ($\lambda = 0.154$ nm) the X-ray generator. The voltage and the current were 35 kV and 60 mA, respectively. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker spectrometer of 600 and 74.5 MHz, with deuterated tetrahydrofuran as solvent.

2.3. Typical preparation of benzoylated bacterial cellulose

BC powder and nitrobenzene (14 mL/g) were mixed. After standing for half an hour at room temperature, the above mixture was added weighted benzoyl chloride (12 mL/g) and pyridine (10 mL/g). The mixture was heated at 130 °C for 20 h, a homogenous solution was formed (Choi et al., 2004; Kim, Nishiyama, & Kuga, 2002; Zhou, Zhang, Okamura, Minoda, & Miyamoto, 2001). The solution was subsequently poured into bulky ethanol. The BBC was precipitated as a solid from the solution. The obtained BBC was separated by filtration, alternatively washed with ethanol and acetone, and finally dried at 70 °C.

2.4. Determination of degrees of substitution (DS) for the BBC

The BBC (100 mg) was added into 40 mL of 75% ethanol in a glass bottle, and heated to 60 °C for 30 min. Then 40 mL of 0.1 M NaOH solution was added to the BBC solution. After reheated to 60 °C for 15 min, the solution was cooled to room temperature, and maintained for 48 h. The excessive alkali was titrated with 0.1 M HCl with phenolphthalein as an indicator.

3. Results and discussion

3.1. DS of the BBC vs the molar ratio of benzoyl chloride to the anhydrous glucose unit (AGU)

Fig. 1 shows the DS of the molar ratio of benzoyl chloride to AGU. It reveals that we can obtain BBC with DS from 0.88 to 2.46 by changing the molar ratio of benzoyl chloride to AGU. The DS increases nonlinearly with increasing of the molar ratio of benzoyl chloride to AGU. The probable reason for the nonlinearity is the trace water in the BC (Chen & Wu, 1980).

3.2. The structure of the BBC

As shown in Fig. 2a, the broad peak of the BC at 3435 cm^{-1} assigned to the O–H stretching vibration (ν_{O-H}) model obviously decreases in intensity with benzoyl substitution. The peak of the BC and BBC at 1058 cm^{-1} assigned to the C–O–C stretching vibration (ν_{C-O-C}) model. Meanwhile, three new peaks at 1731, 1606, 711 cm^{-1} assigned to C=O stretching vibration ($\nu_{C=O}$) model, C=C stretching vibration ($\nu_{C=C}$) model and C–H stretching vibra-

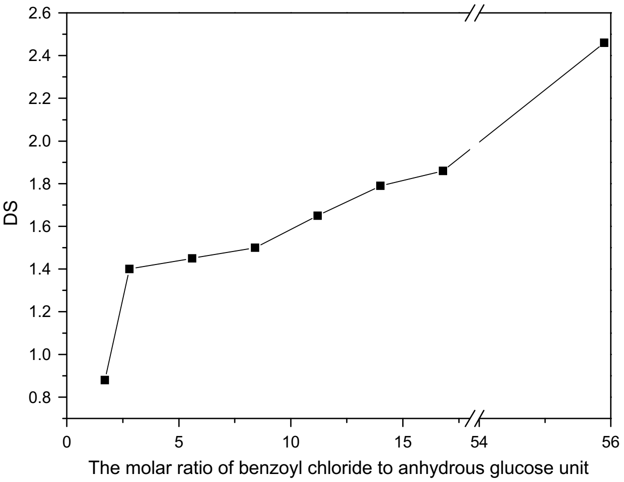


Fig. 1. Plot of DS of the BBC vs the amount of benzoyl chloride.

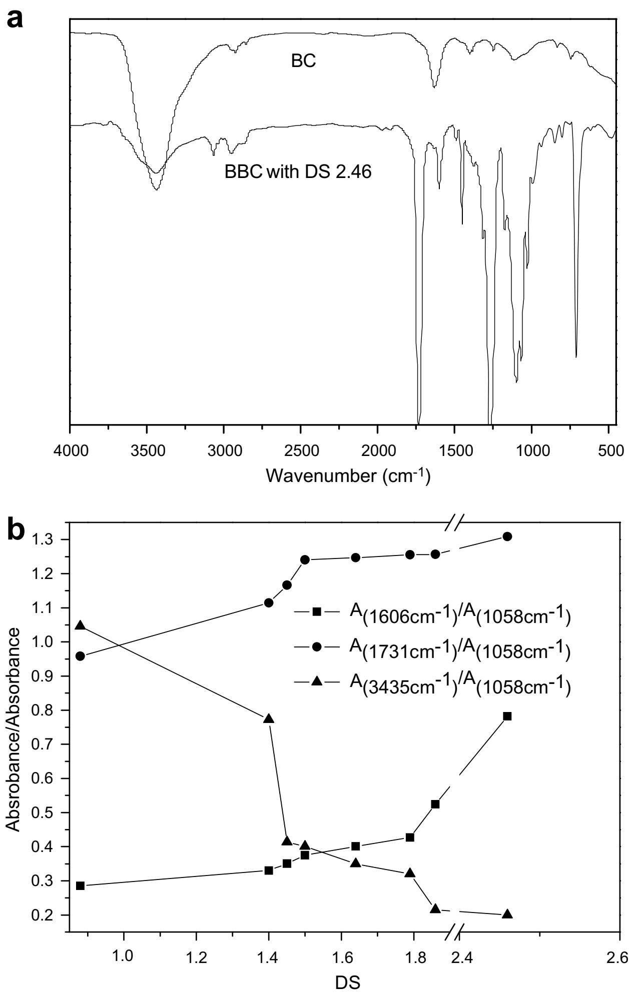


Fig. 2. FT-IR spectra for (a) BC and the BBC with DS 2.46 and (b) the BBC with different DS.

tion ($\nu_{C=H}$) model of the benzene of the BBC. These results indicate that the benzoic acid ester groups were indeed linked onto the backbone of BC after the benzoylated reaction. Fig. 2b gives the relationship between the DS of BBC and the absorbance (A) ratio of the FT-IR. We used the 1058 cm^{-1} (ν_{C-O-C}) for standard and used the absorbance ration of 3435 cm^{-1}(ν_{O-H}), 1731 cm^{-1} ($\nu_{C=O}$) and 1606 cm^{-1} ($\nu_{C=C}$) to 1058 cm^{-1} (ν_{C-O-C}) to investigate the relationship between the DS of BBC and the FT-IR (Morris, Catalano, & Andrews, 1995). With increasing of the DS, the absorbance ratio between $A_{(3435cm^{-1})}$ and $A_{(1058cm^{-1})}$ decreases, and $A_{(1731cm^{-1})}/A_{(1058cm^{-1})}$ and $A_{(1606cm^{-1})}/A_{(1058cm^{-1})}$ increases gradually (Hadano et al., 2004). This shows that the ν_{O-H} peak intensity decreases and the $\nu_{C=O}$ and $\nu_{C=C}$ peak intensity of the benzene of the BBC enhance with increasing of the DS. The formation of the BBC was further confirmed with ^{1}H NMR and ^{13}C NMR spectra. The chemical shifts of the benzoyl were detected at δ 7.96 (aromatic, ortho to ester), δ 7.38 (aromatic, meta to ester) and δ 7.49 (aromatic, pendant to ester). The resonances of the anhydroglucose unit was detected at δ 4.66 (H-1), δ 3.50 (H-2), δ 3.66 (H-3), δ 3.58 (H-4) δ 3.70 (H-5), δ 4.24 (H-6) (the structure of BBC shown in Scheme 1). The ^{13}C NMR spectrum shows the chemical shifts of carbonyl, benzoyl and the anhydroglucose unit at δ 165.9 (carbonyl), δ 130.0 (aromatic carbon-O attached), δ 129.0 (aromatic, ortho to ester), δ 128.1 (aromatic, meta to ester), δ 132.6 (aromatic, pendant to ester), δ 99.8 (C-1), δ 75.6 (C-2), δ 72.5 (C-3), δ 97.2 (C-4), δ 72.1 (C-5), δ 62.4 (C-6). The signals of C-6, C-2 and C-3 were increased comparing with those of the original C-6, C-2, and C-3. The NMR analysis also demonstrates the incorporation of benzoyl group in the main chain of the BC.

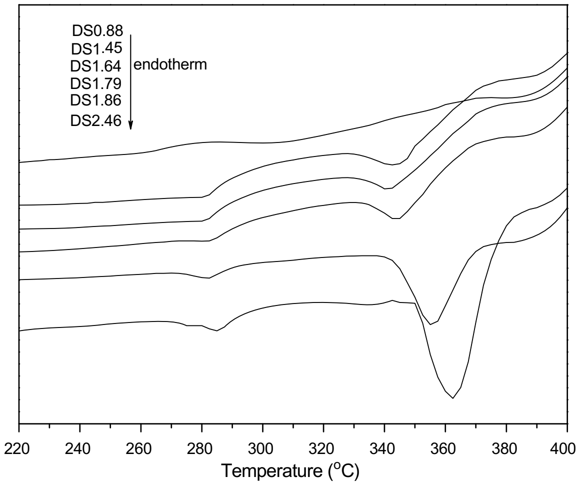


Fig. 3. DSC heating curves of the BBC with different DS.

Table 1
Thermal properties of BBC

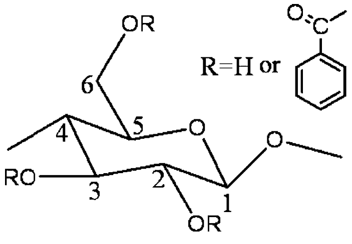
Sample	DS	T_d (°C)	T_g (°C)	T_i (°C)	ΔT (°C)	ΔH_i (J/g)
1	0.88	345.0	–	–	–	–
2	1.45	350.0	281.5	341.6	60.1	7.43
3	1.64	354.7	281.8	343.8	62.0	9.04
4	1.79	357.5	281.2	353.3	71.6	9.43
5	1.86	360.0	281.2	356.0	74.8	22.33
6	2.46	362.8	281.2	362.8	81.6	24.70

3.3. The thermal properties of BBC

DSC measurement allows us to trace the heating behavior of the BBC. Fig. 3 shows the DSC heating diagrams of the BBC with different DS, and Table 1 lists the corresponding transition enthalpy (ΔH_i), T_g, T_i and thermal decomposition temperature (T_d). It is obvious that the ΔH_i, T_i and T_d increase with increasing of the DS, and the T_g remains constant around 280 °C. The enhanced thermal stability may be attributed to the network structure of the BC. Both T_g and T_i are higher than those of the benzoylated plant cellulose that can also form the thermotropic liquid crystalline phase, T_g at 220 °C and T_i at 280 °C (Li & Shen, 1998). In addition, the temperature range between the T_g and the T_i of the liquid crystalline phase become broader with increasing of the DS. The thermal features of the BBC reveal that the backbones of BC and the side chains have the effect on the formation of the liquid crystalline phase transitions (Guo & Gray, 1989; Lenz, 1985; Yamagishi, Fukuda, Miyamoto, & Watanabe, 1988). For the BBC with DS 2.46, the thermal decomposition temperature is the same as its T_i.

3.4. The liquid crystalline characteristics

We used the POM to characterize the liquid crystal phase of the BBC. All the BBC samples displayed the birefringence when the samples were assembled between two glass slides. Fig. 4 shows the temperature dependence of birefringence texture of the BBC with DS 1.79. The birefringence appeared at 275 °C and disappeared at 354 °C, which is a good correspondent to the measured T_g and T_i. The formed liquid crystalline was believed to be the smectic phase.



Scheme 1. The structure of BBC.

The structure of the liquid crystal phase was determined with WAXD. The BBC powder was heated to some temperature between T_g and T_i for 15 min, and then quickly quenched in ice water. Fig. 5 shows a series of WAXD patterns of the treated BBC with different DS. The intense diffraction peak was observed in the range between 5° and 9°, corresponding to 1.30 nm *d-spacing*. The peaks demonstrate that all the BBCs are of short range order structure, which possibly originates from π–π stack interaction among the benzene rings, restraining the molecular chain backbone from random movement. The physical origin of these diffraction peaks may be associated with the smectic layered structure in liquid crystalline phases (Huang et al., 2007). The broad peak at about 19° allowed us to roughly estimate the average lateral distance between the neighboring chains to be 0.47 nm.

4. Conclusion

The BBC was successfully prepared by esterification of BC with benzoyl chloride in nitrobenzene with pyridine as the acid acceptor. Changing the molar ratio of benzoyl chloride to AGU enables us to prepare a series of BBC with different DS ranging from 0.88 to 2.46. The BBC with different DS can form the thermotropic liquid crystalline phase, associated with the smectic layered structure. The T_g was measured between 281.2 and 281.8 °C and T_i varied from 341.6 to 362.8 °C. The temperature difference between the T_g and the T_i become broader with increasing of the DS.

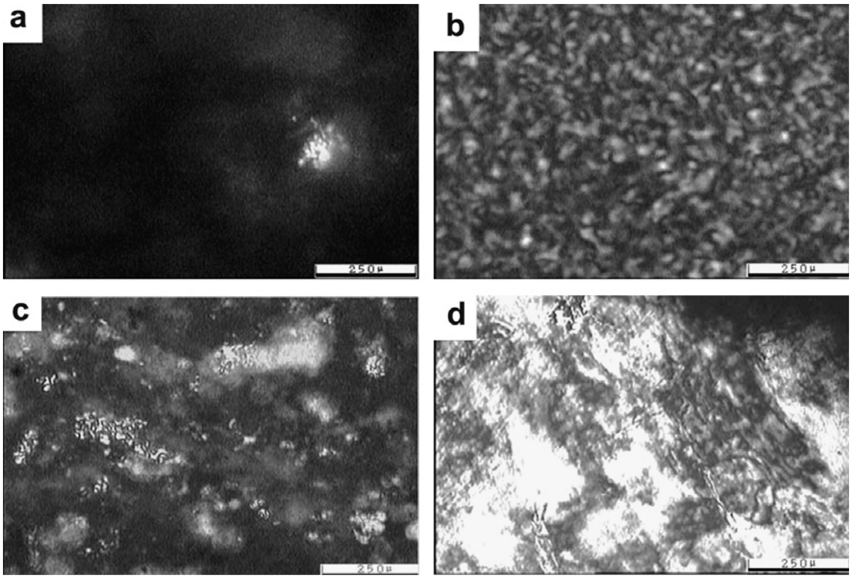


Fig. 4. POM images of the BBC with DS 1.79 (a) 275 °C, (b) 285 °C, (c) 320 °C, (d) 325 °C.

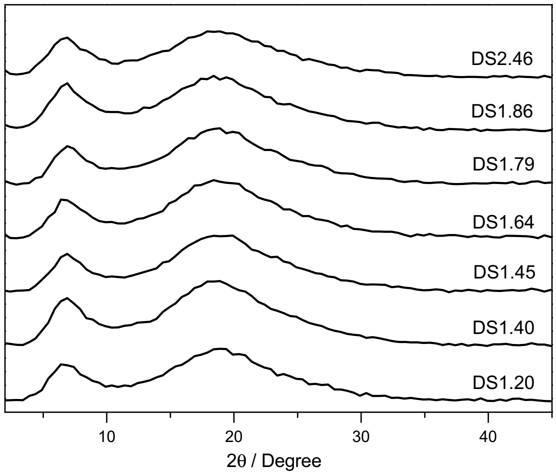


Fig. 5. WAXD patterns of the quenched BBC with different DS.

Acknowledgements

The authors acknowledge Prof. Chaoping Xiao for the BBC measurement. We are also grateful to Dr. Yong Zhou, Dr. Yongjun Ma and Dr. Bo Dai for valuable advice. This investigation was supported by Sichuan Province Science Foundation for Youths (08ZK026-062).

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