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Influence of degree of *N*-butyrylation on critical concentration of *N*-butyrylated chitosan/dichloroacetic acid liquid crystalline solution

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Summary

N-butyrylated chitosan with various degree of N-butyrylation (DB) were prepared by mixing completely deacetylated chitosan and butyric anhydride in mild condition without serious degradation and O-substitution. A standard curve to measure DB was obtained by plotting the infrared absorbance ratio of A_{1560}/A_{2880} against the known DB (from 0%~99%) of eight specimens. The influence of DB on the critical concentration C^* of N-butyrylated chitosan/dichloroacetic acid solutions required to form mesophase was investigated by optical method. A maximum C^* value appeared at medium DB. The effect was explained by the disordering of chain with medium composition ratio of the copolymer of glucosamine and N-butyryl glucosamine.

Introduction

Chitosan is a high molecular weight heteropolysaccharide composed mainly of β -(1,4) -2-deoxy-2-amino-D-glucopyranose units, and partially of β -(1,4) -2-deoxy-2-acetamido-D-glucopyranose units, and thus considered as a binary heteropolysaccharide. [1] Chitosan is commercially manufactured from chitin, the second most abundant natural polymer, by heterogeneous alkaline deacetylation.

Since 1982, the development of lyotropic mesophases for semirigid chitosan and its derivatives has been studied by some groups. Ogura et al. reported that chitosan, (hydroxypropyl) chitosan and (acetoxypropyl) chitosan form cholesteric phase at concentrated solutions. [2] Sakura et al. studied liquid crystal structure in chitosan films and fibers prepared form liquid crystalline solutions. [3-5] Terbojevich et al. determined the persistence length of chitosan to be 22nm in 0.1mol/L CH_3COOH + 0.2mol/L NaCl. [6] Rout et al. found cholesteric solutions in N-phthalolyl chitosan and N-phthaloyl-3,6-di-O-acetyl chitosan dissolved in organic solvents. [7-9] Ratto et al. investigated the mesophase of water/chitosan systems with differential scanning calorimetry. [10] Dong et al. demonstrated lyotropic liquid crystallinity of some chitosan derivatives and studied the structure factors such as molar mass and degree of substitution of these derivatives on critical concentration forming liquid crystal phase. [11-13]

Some literatures have reported the effect of degree of deacetylation (DDA) on critical concentration. Terbojevich et al. [6] have compared persistence length of chitosan A

(DDA=58%) and chitosan B (DDA=85%), and found they are only slightly different, implying these two chitosans may have similar critical concentration. Recently Hu et al. [14] have studied the chitosan samples with DDA from 71% to 89%, and reported they had the same critical concentration (10~11wt%). Nevertheless the DDA scope of these studies are limit. This article concentrates upon the effect of another degree of N-substitution, i.e. the degree of N-butyrylation (DB), on critical concentration. Moreover the research scope of DB is developed to almost whole scope (0~99%).

Experimental

Chitosan (from crab shell) with DDA 84% and viscosity average molecular weight 7.4 X 10^5 was purchased from Xiamen Second Pharmaceutical Factory (China). All commercially available solvents and reagents were used without further purification.

Chitosan raw material was purified by dissolved in 1% aqueous acetic acid solution and precipitated with 10% aqueous NaOH solution. The purified chitosan was then treated with 50% NaOH solution under N_2 at 100 °C for 4h three times to produce completely deacetylated chitosan(DDA=99.8%).

The completely deacetylated chitosan was homogeneously N-butyrylated according to literature method. [15] 1g of this chitosan was dissolved in 50ml 1% aqueous acetic acid. 250ml methanol was mixed with the solution. Different molar ratio of butyric anhydride was added to the solution by strong stirring. After 2h, the mixture was poured into dilute aqueous NaOH solution. The precipitated polymer was filtered off, washed well with ethanol then with acetone and air dried. For the gel-like mixture, the product was immerged in fresh ethanol several times and then dried in vacuo.

The elemental analyses were carried out by means of a CE 1110 CHNS-O elemental analyzer. DB was calculated from N/C ratio according to the formula as follows.

$$\frac{N(Foound)}{C(Found)} = \frac{14}{120 - 48DB}$$

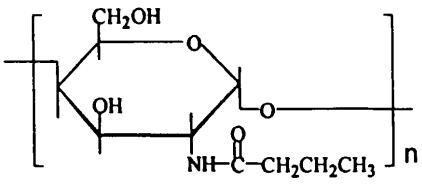
The infrared absorption spectra were measured with a Nicolet avator 360 FTIR by KBr pellet method.

The critical concentration C^* required to form the ordered phase was determined by optical method. N-butyrylated chitosan/dichloroacetic acid solutions with different concentration in an interval of 1wt% were prepared separately in small glass vials. The vials were tightly sealed so that the solvent can not evaporate. The solution were aged for 1 day at 20°C before use, and then sandwiched between two glass slides to form the liquid crystal box. An Olympus polarized microscope was used for observation. The concentration at which the birefringence was just noticed at 20 °C was defined as C^*.

The intrinsic viscosity number [η] was determined in 0.1mol/L CH_3COONa + 0.2mol/L CH_3COOH buffer solution at 30 °C.

Results and discussion

The chemical structure of N-butyrylated chitosan is as follows:



Scheme 1. The chemical structure of N-butyrylated chitosan

Table 1 lists the preparation conditions, phenomena and DB values of eight N-butyrylated chitosan specimens. It can be seen that DB of these specimens covered almost whole DB range.

Table 1. The preparation conditions and DB values of N-butyrylated chitosan specimens

Number of specimen	Molar ratio (Butyric anhydride : chitosan)	State of product in reaction system	DB value[b] (%)
1[a]	—	—	0
2	0.02:1	dissolve	7.4
3	0.10:1	dissolve	12.8
4	0.30:1	dissolve	29.8
5	0.50:1	gelation	54.6
6	0.60:1	gelation	59.8
7	1.00:1	gelation	71.5
8	10.00:1	precipitate	99.1

a. Completely deacetylated chitosan prepared in this lab which was raw material of other specimen.
b. Determined with element analysis.

FTIR spectra of a typical specimen was shown in Figure 1. There was no C=0 stretching band of ester at ~1730cm^{-1}, showing that no substitution occurred on hydroxyl group during butyrylation. The structure difference of these eight N-butyrylated chitosan specimens was only the degree of N-butyrylation.

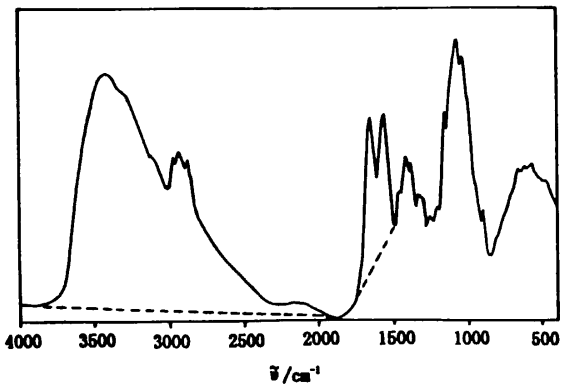


Figure 1. FTIR absorption spectra of N-butyrylated chitosan with DB=54.6%. The dash line shows the drawing method of baseline

The DB values of these specimens can be proved by FTIR determination. The amide II band at 1560cm^{-1} was used as probe band, and the C-H band at 2880 cm^{-1} was used as reference band. A good linear curve was then obtained by plotting the absorbance ratio of A_{1560}/A_{2880} against the known DB of these eight specimens (see Figure 2).

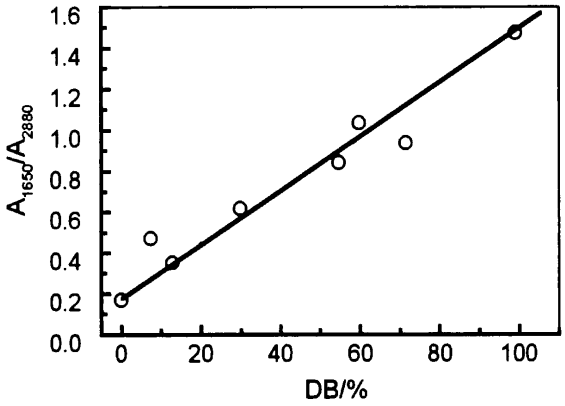


Figure 2. A_{1560}/A_{2880} vs. DB

The FTIR results supported the element analysis determination of DB value. Therefore, Figure 2 can also be used as a standard curve for measuring DB of unknown N-butyrylated chitosan by FTIR.

The eight N-butyrylated chitosan specimens were prepared at very mild N-butyrylation condition, so that no serious degradation of the molecular chain occurred. Table 2 lists the intrinsic viscosity number of some specimens, showing almost no change of [η]. These specimens have been prepared without evident variation of molar mass.

Table 2. The intrinsic viscosity number of N-butyrylated chitosan specimens with different DB

Specimen number	1	2	3	4
DB (%)	0	7.4	12.8	29.8
[η] (ml • g^{-1})	450	484	472	490

Typical liquid crystal texture can be observed in all concentrated N-butyrylated chitosan specimens /dichloroacetic acid solutions. The fingerprint texture formed in some specimens showing that the liquid crystal phase of N-butyrylated chitosan is cholesteric.

Figure 3 illustrated the relationship between DB of N-butyrylated chitosan and C*. From Figure 3, it is of interest to notice that C* did not vary monotonously with DB. A maximum C* value appeared at medium DB. Although C* changed slightly in the DB scope of 58~85% and 71~89% shown by reference [6] and [14] respectively, very strong variation of C* from 10% (for DB=0%) to 18% (for DB=54.6~59.8%) was obtained for N-butyrylated chitosan in this paper.

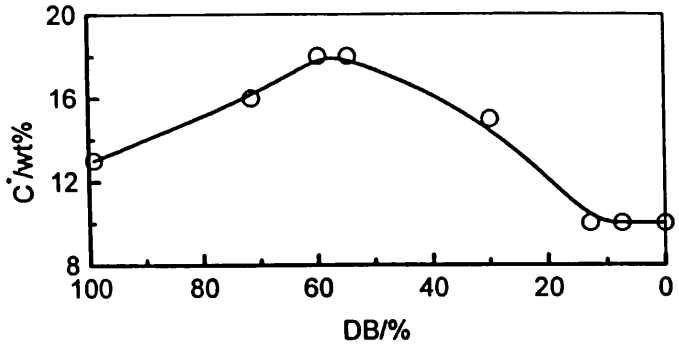


Figure 3 The relationship between DB of N-butyrylated chitosan and C*

The critical volume fraction V'_2 of semirigid chains can be predicted by Flory's well-known equation, [16]

$$V'_2 \cong (8/x)(1-2/x)$$

where x is the axis ratio of rods. x(=2q/d) depends on the persistence length q and the diameter of chain d.

$$d = (M_0/\rho \bullet N_A \bullet L_0)^{\frac{1}{2}}$$

where ρ is density of polymer, M_0 is molar mass of repeat unit, N_A is Avogadro constant and L_0 is the shadow length of repeat unit along chain.

Taken q ≈ 22nm for chitosan with DB=58~85%[6], ρ =1.5g/cm^3[3], M_0=161 and L_0=0.515nm (half of b in unit cell of chitosan crystal [3]), V'_2 can be calculated to be 10.4%(v/v), therefore C^* is 10.0%(w/w) calculated using the density value of 1.5g/cm^3 (for chitosan) and 1.573 g/cm^3 (for dichloroacetic acid).

From Figure 3, it can be seen that only chitosan with DB=0 agreed to the anticipated value. The higher C^* value (13%) for N-butyrylated chitosan with DB=99.1% is due to the destroying of the original hydrogen bond in chitosan.

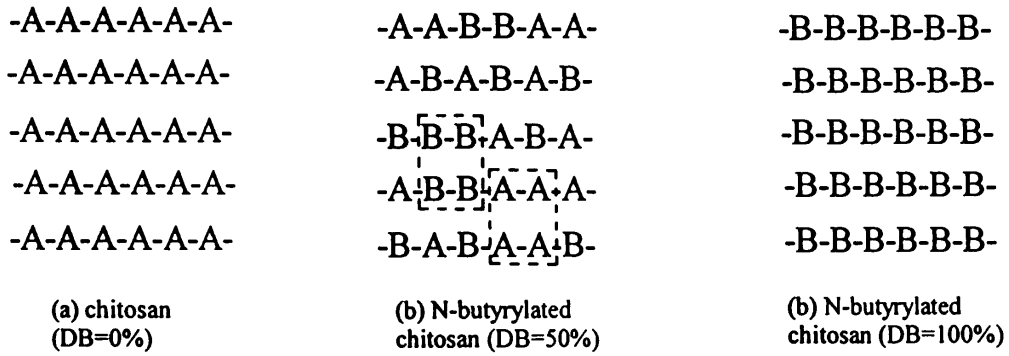


Figure 4 Schematic representation of the possibility of matching for repeat units in chitosan, N-butyrylated chitosan (DB=50%) and N-butyrulated chitosan (DB=100%). "A" represents glucosamine unit and "B" represents N-butyryl glucosamine unit

The maximum C^* value at medium DB (about 54.6~59.8%) may be explained by the disordering of chain in medium composition ratio of copolymer. In this situation, glucosamine unit and N-butyryl glucosamine in random sequence are hard to match each other to form ordered phase (see Figure 4). Generally speaking, the disordering weakens the intermolecular and intramolecular hydrogen bonding, and decreases the rigidity of chain. As a result, C^* rises obviously with the decrease of chain stiffness.

Acknowledgements

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