

Studies on the Effect of Substitution Degree on the Liquid Crystalline Behavior of Cyanoethyl Chitosan

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ABSTRACT: An alkali–chitosan method was employed to prepare cyanoethyl chitosan (CNCS) with different degrees of substitution (DS) from chitosan by controlling the reaction time. The effect of the DS (from 0.36 to 1.21) on the liquid crystalline behaviors of CNCS was investigated. The critical concentration and texture of CNCS liquid crystalline in dichloroacetic acid and formic acid showed no obvious dependence on the DS. However, increase of the DS could enhance the birefringence of liquid crystalline solutions under a polarized microscope, which implied improved liquid crystallinity. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 2057–2061, 2000

Key words: chitosan; cyanoethyl chitosan; lyotropic liquid crystalline; cholesteric phase; degree of substitution

INTRODUCTION

Chitin, a naturally abundant polysaccharide, has attracted much attention in recent decades, due to its unique properties and usefulness in many areas. However, relatively few studies have been conducted on the ability of chitin and its various derivatives to form liquid crystalline phases. Ogura et al. originally reported the liquid crystalline behaviors of chitosan (deacetylated derivative of chitin) and several modified derivatives in 1982.¹ Recently, more derivatives of chitosan were observed to form lyotropic liquid crystalline in suitable solvents. Among them, cyanoethyl chitosan (CNCS) can form typical cholesteric liquid crystalline.^{2,3} Previous work has reported the effect of the molecular weight of CNCS on critical liquid crystalline behaviors.⁴ The present work concentrates on the effect of the degree of substitution (DS) on its liquid crystalline behaviors.

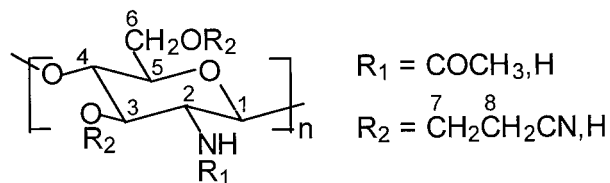
EXPERIMENTAL

Materials

Chitosan was purchased from the Zhejiang Yuhuan Chemical Factory with a claimed viscosity 1000 mPa s (determined with an aqueous solution of 1% chitosan and 1% acetic acid under 20°C), purified and powdered to 40 mesh before use. Acrylonitrile was purified by washing with a 5% NaOH solution. Other reagents were used without further treatment.

Preparation of CNCSs with Different DS

An alkali–chitosan method⁵ was employed to prepare CNCS, where 1 g of chitosan powder was



Scheme 1 Chemical structure of CNCS.

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Table I Element Analysis and FTIR Results of CNCSS

Polymer	Reaction Time	Found %			Calcd % ^a			DS	A_{2250}/A_{1660}
		C	H	N	C	H	N		
Chitosan	—	7.50	42.46	6.82	7.67	43.37	6.90	—	—
CNCS1	10 min	8.71	42.16	7.45	8.67	41.95	7.44	0.36	0.245
CNCS2	30 min	10.78	46.08	7.16	10.80	46.20	6.83	0.81	0.383
CNCS3	1 h	10.59	45.67	6.58	10.66	46.00	6.85	0.77	0.448
CNCS4	2 h	10.93	46.25	6.49	10.98	46.45	6.82	0.86	0.455
CNCS5	3 h	11.09	46.74	6.60	11.05	46.54	6.82	0.88	0.571
CNCS6	4 h	11.68	47.81	6.62	11.54	47.23	6.78	1.03	0.548
CNCS7	24 h	12.56	49.84	7.02	12.54	49.75	6.58	1.21	0.583

^a Calculated for the formula based on 0.5 H₂O (for chitosan and CNCS7), 1 H₂O (for CNCS2 to CNCS6), and 1.5 H₂O (for CNCS1) per glucosamine residue. The degree of deacetylation of chitosan was 70%.

suspended in 5 mL of a freshly prepared NaOH solution (including 0.7 g of NaOH and 10 mg of sodium dodecylsulfate) until swollen, followed by refrigeration at -18°C overnight. Frozen alkali-chitosan was mixed directly with 20 mL of acrylonitrile. CNCSSs with DS from 0.36 to 1.21 were obtained by controlling the reaction time. The products were filtrated and air-dried after washing thoroughly with ethanol.

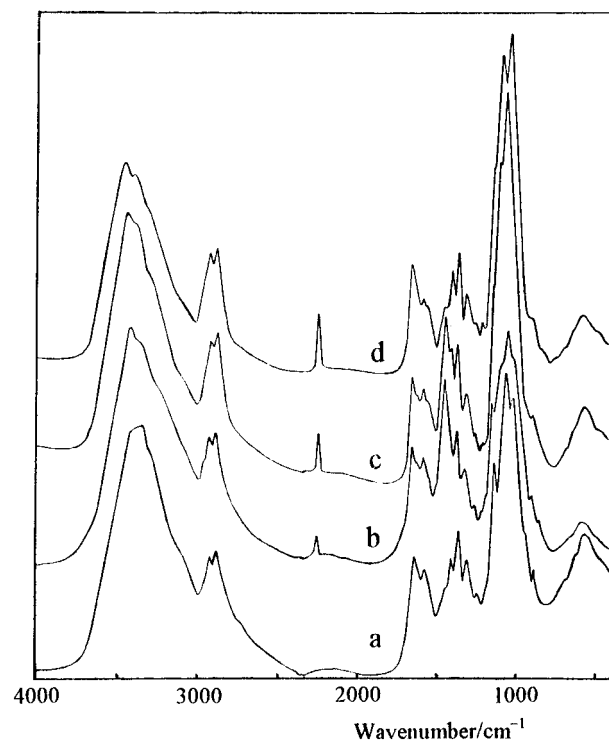


Figure 1 FTIR spectra of CNCSS with different DS: (a) chitosan; (b) DS = 0.36; (c) DS = 0.77; (d) DS = 1.21.

Analyses

IR spectra were measured as KBr pellets for the powder samples using a Nicolet Avatar 360 spectrophotometer. Carbon, hydrogen, and nitrogen contents of the CNCSSs were measured on a Heraeus CHN-O-Rapid elemental analyzer. ¹H-NMR spectra were obtained with a Bruker DRX-400 NMR spectrometer at 400 MHz under room temperature. CD₃COOD/D₂O was used as a solvent. The chemical shifts on the δ scale (ppm) were measured relative to (CH₃)₃Si(CH₂)₃SO₃Na (DSS) in D₂O as an external standard.

Determination of Critical Concentration

CNCS solutions in dichloroacetic acid (DCA) or formic acid (FA) with a concentration interval of 1 wt % were prepared separately in small glass vials. The vials were tightly sealed after stirring.

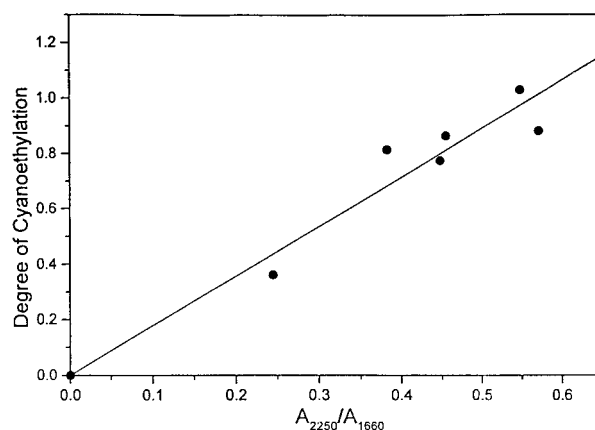


Figure 2 Relationship between DS and A_{2250}/A_{1660} in FTIR spectra of CNCSS.

Table II $^1\text{H-NMR}$ Results of Chitosan and CNCS

Protons	Chemical Shift (ppm)/Integral Intensity							
	CS1	CNCS1	CNCS2	CNCS3	CNCS4	CNCS5	CNCS6	CNCS7
H1 ^a	4.43	4.69	4.68	4.70	4.67	4.68	4.34	4.70
H2	2.78/1.32	2.93/0.19	2.83/0.19	2.89/0.16	2.97/0.15	2.83/0.18	2.79/1.18	2.92/0.17
H3, 4, 5, 6, 6', (7, 7')	(3.38, 3.51) /4.94	3.65/1.00	3.48/1.00	3.54/1.01	3.63/1.00	3.47/1.00	3.42/4.96	3.57/1.00
H8, 8'	—	2.55/0.12	2.44/0.31	2.50/0.31	2.60/0.33	2.44/0.36	2.31/2.83	2.53/0.44
<i>N</i> -Acetyl	1.65/1.00	1.80/0.33	1.67/0.46	1.74/0.38	1.84/0.16	1.70/0.44	1.66/1.00	1.77/0.25

^a The integral intensity of H1 was not presented due to its overlap with the resonance band of HOD or H₂O.

The solutions were aged for 1 day (for DCA) or 1 week (for FA) at room temperature before use. The solutions were then sandwiched between two glass slides to form the sample cells. The cells were observed at 20°C under an Olympus polarized microscope (PLM). The lowest concentration at which birefringence appeared was defined as the critical concentration Cw^* of the liquid crystal–isotropic phase transition.

RESULTS AND DISCUSSION

Structural Characterizations of CNCSs

The chemical structure of CNCS is illustrated in Scheme 1. The elemental analysis results shown in Table I elaborate the DS of the CNCS. IR spectra of chitosan and CNCS are presented in Figure 1. The sharp band at 2250 cm⁻¹ (—CN stretch vibration), which is characteristic of CNCS, increased significantly with increase of the DS. The absorption bands at ~2900 cm⁻¹ (—CH₂ and —CH stretch) and 1000–1200 cm⁻¹ (C—O stretch) increase as well, with the simulta-

neous decrease of the bands at 3300–3500 cm⁻¹ (—OH stretch). Considering that the acetamide groups did not participate in the reaction, the amide I band at 1660 cm⁻¹ was not affected. Therefore, the value of A_{2250}/A_{1660} (using the baseline drawing method described in the literature⁶), can be used as the relative characterization of the DS. Figure 2 depicts a plot of the value of A_{2250}/A_{1660} against the DS of the CNCS. With Figure 2, the DS of the CNCS samples can be estimated rapidly according to the IR spectra.

$^1\text{H-NMR}$ was employed for further confirmation of all samples' DS. Table II presents the $^1\text{H-NMR}$ determination results of chitosan and the CNCS samples. The assignment for the resonance bands of chitosan was reported previously.⁷ Comparison of the spectra of chitosan and CNCS indicates that the resonance band at about 2.5 ppm is characteristic of CNCS due to H8 and H8', while the resonance band of H7 and H7' was included in the wide resonance near 3.6 ppm due to their structural environment's similarity to H6 and H6'. Thus, the DS is evaluated from eq. (1) using the integral intensity of H8 and H8' protons and the integral intensities of H2 whose chemical shift is isolated:

$$\text{DS} = \frac{I_{\text{H8+H8}'}}{I_{\text{H2}} \times 2} \quad (1)$$

The DS calculated from the $^1\text{H-NMR}$ spectra are 0.31, 0.81, 0.94, 1.07, 0.98, 1.21, and 1.27 for CNCS1–CNCS7, respectively, which are generally consistent with those from elemental analysis.

Effect of DS on Liquid Crystalline Behaviors

The critical concentration (C^*) is one of the most important parameters for investigating a lyo-

Table III Cw^* of CNCS with Different DS in DCA

Polymer	DS	Cw^* (%) in FA	Cw^* (%) in DCA
Chitosan	—	4	6
CNCS1	0.36	9	13
CNCS2	0.81	9	13
CNCS3	0.77	9	13
CNCS4	0.86	9	13
CNCS5	0.88	9	13
CNCS6	1.03	9	12
CNCS7	1.21	9	12

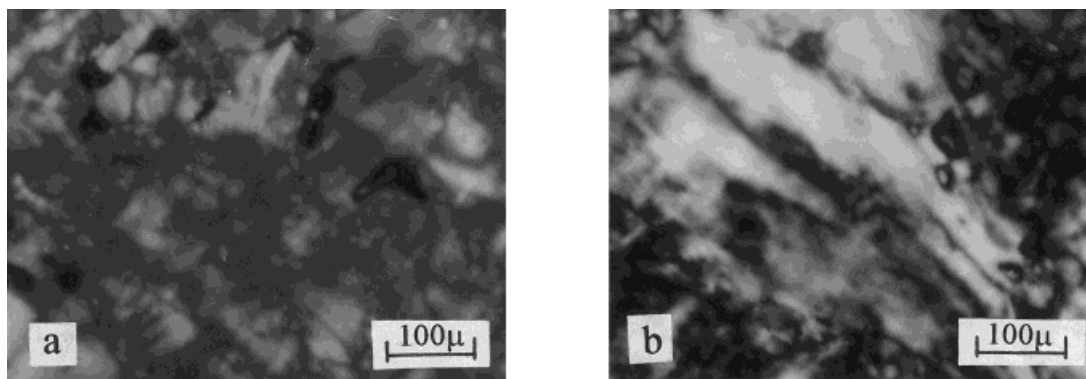
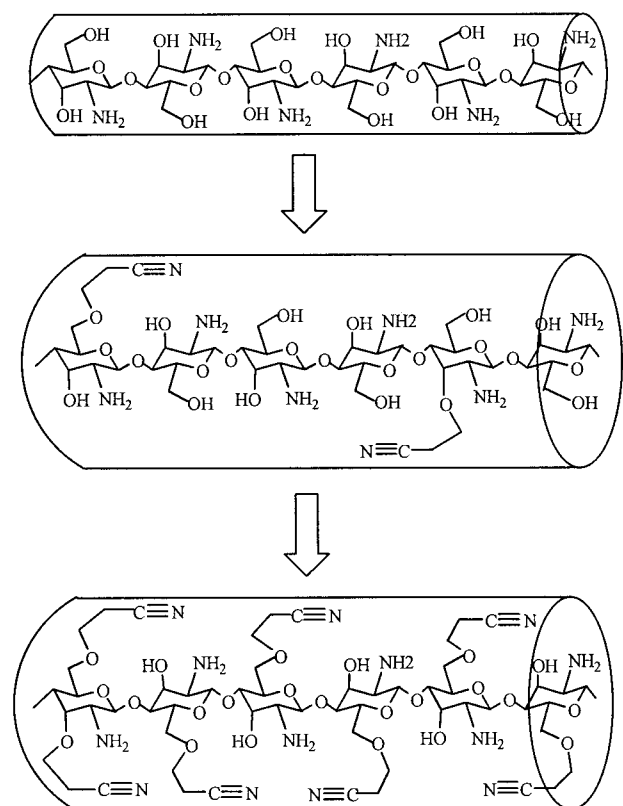


Figure 3 PLM photographs of (a) CNCS4 and (b) CNCS7 in 26 wt % DCA solution (in the same sample thickness and exposure time).

tropic liquid crystal. It was reported to be affected by several factors such as the concentration, temperature, solvent nature, and structural character of the polymer. To study the effect of the structural character on C^* , the relationship between the C^* of the CNCSs and their DS was determined in both FA and DCA solutions. The results are listed in Table III.



Scheme 2 Schematic illustration of the variation of CNCS chain diameters with enhancement of DS.

It can be observed that the influence of the DS was almost the same for these two different solvents. A small substitution degree resulted in a sudden increase of the C^* of chitosan. But, subsequently, further substitution did not change the C^* of CNCS. It is quite similar to the results of cellulose derivatives.⁸ C^* is the function of the persistence length (q) and diameter (d) of a rigid polymer chain, according to Flory's formula⁹:

$$C^* = (4d/q)(1 - d/q)$$

When $q \gg d$, an approximate formula can be deduced as follows:

$$C^* = 4d/q$$

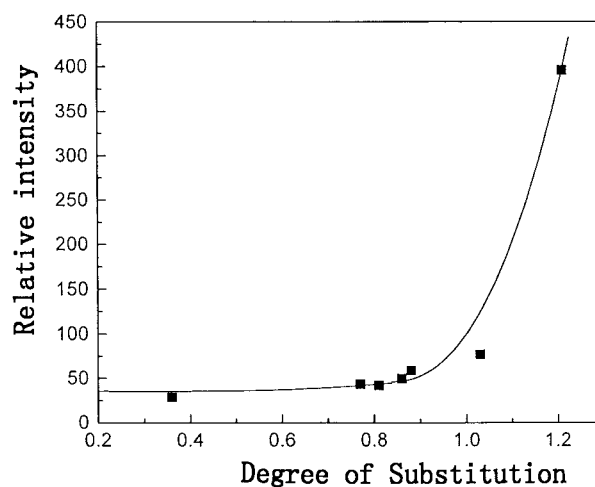


Figure 4 Relationship between depolarized light intensity under PLM and DS of CNCSs which were in a 22% DCA solution with the same thickness.

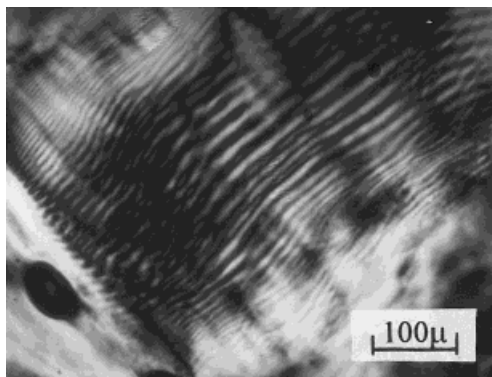


Figure 5 Typical texture of CNCS7 in 20% DCA solution.

meaning that C^* is directly proportional to the diameter and inversely proportional to the persistence length. So, we can explain the variation rule of C^* from these two aspects: First, cyanoethylation decreases the strong inter- and intramolecular hydrogen bond. Hence, q decreases after substitution and the C^* of CNCS became much higher than that of chitosan itself. But a small DS is enough to destroy most of the original hydrogen bond of chitosan. Therefore, when the DS increases subsequently, no obvious variation of CNCS occurs and q remains nearly constant. So, C^* remained unchanged. Second, d may have the same variation rule. An abrupt increase of the chain diameter occurs at the first beginning of substitution. Then, the chain diameter did not grow after further substitution if the rigid chains can rotate and have their fixed rejected volume. This explanation is illustrated in Scheme 2.

Because the critical concentration has no dependence on the DS, it is possible to study the influence of the DS on the liquid crystallinity by

comparing the birefringence intensity of CNCS solutions of the same concentration under PLM by using an optical-electronic apparatus. The results indicated that the intensity of birefringence increases significantly with increase of the DS, as shown in Figures 3 and 4. This implies that the liquid crystalline order, that is, the so-called liquid crystallinity of CNCS solutions, improved with increase of the DS due to the improvement in symmetry of the molecular chains.

The texture of the CNCS lyotropic solutions was not affected by the DS either. PLM studies found a typical cholesteric texture as in Figure 5 in lyotropic solutions of CNCS with different DS.

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