

INFLUENCE OF MOLECULAR WEIGHT OF CHITIN AND ITS THREE DERIVATIVES ON CRITICAL CONCENTRATION OF LYOTROPIC LIQUID CRYSTALLINE PHASE TRANSITION*

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Abstract The critical concentration of lyotropic liquid crystalline phase transition for chitin derivatives was determined using a polarization microscope. The influence of molecular weight on critical concentration of liquid crystalline solution for chitin, chitosan, cyanoethyl chitosan and propionyl chitin successively increases as the chain rigidity decreases. Therefore it can be used as an indicator of the chain rigidity.

Keywords Chitin, Chitosan, Lyotropic liquid crystalline polymer, Critical concentration, Molecular weight

INTRODUCTION

The critical concentration (C^*) of liquid crystal-isotropic phase transition for lyotropic liquid crystalline polymers is affected by the nature of the solvent, the chain rigidity, the degree of polymerization and the temperature of the solution. Some investigations have described the influence of molecular weight (M_w) on C^* for cellulose derivatives^[1, 2]. But the influence of this structure parameter on C^* for chitin and its derivatives, a new kind of liquid crystalline polysaccharide, is unknown. In this paper, it will be shown specifically that the C^* is dependent upon M_w of chitin, chitosan, propionyl chitin and cyanoethyl chitosan in varying degrees.

EXPERIMENTAL

Sample

Four chitins with different M_w (CT1-CT4) were prepared from the shells of four kinds of crustaceans. Four chitosans (CS1-CS4) with same degree of deacetylation ($84 \pm 1\%$) and different M_w were produced from the four chitins respectively by conventional methods. Four propionyl chitins (PCT1-PCT4) with basically the same degree of substitution (1.8 ± 0.2) and different M_w were also synthesized from these four chitins using the methanesulphonic acid method^[3].

CS4 was hydrolyzed by HNO_2 ^[4] to prepare chitosans with different M_w , which were subsequently cyanoethylated by acrylonitrile^[5] to give seven cyanoethyl chitosans with different M_w , which were designated as CNCS1 to CNCS7.

These two series of derivatives PCT and CNCS were mainly *o*-substituted according to synthesis conditions.

The M_w of chitosans were determined by viscometry^[6]. The M_w of chitin and its derivatives were calculated from that of chitosan assuming that no severe decomposition occurred during synthesis, because no K and α values can be used directly. The degree of deacetylation was determined by titrimetry, and the degree of

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substitution (DS) of propionyl chitin and cyanoethyl chitosan was measured by elemental analysis.

Determination of Critical Concentration

Polymer/dichloroacetic acid solutions of different concentration with an interval of 1% (in *W/W*) were prepared separately in small glass vials. The vials were tightly sealed after stirring. The solutions were aged at 20°C for one day and were then sandwiched between two glass slides to form the sample cells. The cells were examined under a polarization microscope. The concentration at which birefringence just appeared was defined as the critical concentration of liquid crystal-isotropic phase transition.

RESULTS AND DISCUSSION

The critical concentration values of chitin (CT), chitosan (CS), propionyl chitin (PCT) and cyanoethyl chitosan (CNCS) with different M_w were listed in Table 1. The related literature values for poly(γ -benzyl-L-glutamate) (PBLG) and cellulose diacetate (CDA) were also listed for comparison. Although the degree of substitution of CNCS series were varied under the same synthesis conditions, it has been proved previously that the critical concentration was not influenced by the degree of substitution within the realm of our experiments. Thus, the samples of this series can be used to reveal the effect of molecular weight.

According to Flory's theory^[7], a semi-empirical formula between critical concentration C^* and persistence length q is as follows:

$$C^* = (8/x)(1 - 2/x)$$

where axial ratio x equals to $2q/d$; d is the diameter of chain. When $x \gg 1$,

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

Table 1. The critical concentration values of chitin and its derivatives, polypeptide and cellulose derivative with different molecular weight

Polymer	Mol. weight ($\times 10^{-4}$)	DS	Solvent	C^* (%)	Ref.
PBLG1	31	—	DMF-MeOH	5	[9]
PBLG2	34	—	DMF-MeOH	5	[9]
PBLG3	79	—	DMF-MeOH	1.8	[9]
CT1	53	—	DCA	5	This work
CT2	94	—	DCA	3.5	This work
CT3	147	—	DCA	1.5	This work
CT4	284	—	DCA	0.5	This work
CS1	44	0.85	DCA	11	This work
CS2	75	0.84	DCA	9	This work
CS3	121	0.85	DCA	6	This work
CS4	234	0.84	DCA	1	This work
CNCS1	7.75	1.35	DCA	25	This work
CNCS2	12.7	1.26	DCA	18	This work
CNCS3	22.2	1.40	DCA	17	This work
CNCS4	52.5	1.15	DCA	12	This work
CNCS5	134.4	0.86	DCA	11	This work
CNCS6	268	0.46	DCA	7	This work
PCT1	67	1.9	DCA	21	This work
PCT2	118	1.8	DCA	20	This work
PCT3	189	2.0	DCA	20	This work
PCT4	349	1.6	DCA	19	This work
CDA1	3.0	2	TFA*	24.5	[1]
CDA2	5.6	2	TFA	22	[1]
CDA3	6.9	2	TFA	16.4	[1]

* trifluoroacetic acid

As the polymer chain is rigid, q is proportional to molecular weight. So C^* is inversely proportional to molecular weight. As shown in Table 1, rigid polymer PBLG belongs to this case. On the other hand, as the

polymer chain is semi-rigid (according to Flory's model^[8], polymer chain consists of rods connected by flexible joints (or spacers)), q basically does not depend on the molecular weight, but relates to the rigidity of chain. Many cellulose derivatives such as cellulose diacetate possess this kind of chain, and its C^* changes less while molecular weight increases. Hence the extent of the molecular weight's effect on C^* can be used to judge the rigidity of liquid crystalline polymer chains.

The rule has been proved by the results demonstrated in Table 1.

For chitin and chitosan, C^* is almost inversely proportional to molecular weight, therefore they can be regarded as rigid macromolecules. The presence of many inter- and intra-molecule hydrogen bonds tends to make chitin or chitosan more rigid than cellulose. For propionyl chitin, C^* varies very little with molecular weight, indicating that it is a semirigid macromolecule. The reason is that the amount of hydrogen bonds decreases after substitution, and concurrently the flexible propionyl groups increase the mobility of chains. For cyanoethyl chitosan, C^* varies distinctly with molecular weight within a wide range, but does not vary as much as chitin or chitosan, indicating that it is a semi-rigid polymer with the rigidity lying between chitin (or chitosan) and propionyl chitin. Although the amount of hydrogen bonding would decrease on substitution, cyano groups could form some new hydrogen bonds to enhance the interaction between molecules. Therefore, CNCS has a medium rigidity.

In short, the critical concentration is influenced by the molecular weight of chitin and its derivatives. Nevertheless, the extent of this influence depends on the chain rigidity, so the former can be used as an indicator of the latter.

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