

## 丁酸壳聚糖液晶的临界行为研究

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**摘 要** 用偏光显微镜法测定了丁酸壳聚糖在四种酸性溶剂中的临界浓度值.发现临界浓度值( $v/v\%$ )与溶剂的酸性无关,都是16%~17%.在以二氯乙酸为溶剂时,不同丁酰化程度的丁酸壳聚糖有相同的临界浓度.用DSC法测定了丁酸壳聚糖/二氯乙酸体系的临界温度,并绘制了相图.结果表明,浓度达60%( $w/w\%$ )后,临界温度基本不再变化,稳定在39℃左右.

**关键词** 壳聚糖,丁酸壳聚糖,溶致液晶,临界浓度,DSC,临界温度

甲壳素是一种蕴藏量最丰富的天然高分子之一,但由于不溶性限制了其应用.壳聚糖是甲壳素的脱乙酰化产物,由于有了易质子化的自由氨基而能溶于酸性溶剂.壳聚糖由于既有氨基又有羟基而很容易进行化学修饰,从而生成一些能直接溶于水或溶于有机溶剂的甲壳素衍生物.本文合成并表征的丁酸壳聚糖就是其中一种.由于它是一种新报道的高分子液晶,本文研究了它的临界液晶行为.

### 1 实验部分

#### 1.1 材料和仪器

丁酸壳聚糖由本实验室按文献[1]方法制备.红外光谱仪为Nicolet 740FTIR.热分析仪为SHIMADZU的DSC-50.偏光显微镜为南京光学仪器厂XPT-7型.

#### 1.2 溶液的配制

在称量瓶中称取一定量的丁酸壳聚糖,再按预订的重量百分比(以2%为间隔)加入溶剂配成各种浓度的溶液,除特别说明外,在室温下密闭静置一周后使用.

#### 1.3 临界浓度的测定方法

在室温(约23℃)下取少许待测溶液于两玻片之间并用力压成薄层,平衡至少5min后,在正交偏光显微镜下观察,用环氧树脂胶封闭玻片边缘,静置过夜后再观察,以显微镜下刚出现指纹状结构或其他有双折射的结构的浓度为临界浓度.

#### 1.4 临界温度的测定方法

取比临界浓度至少高10%的溶液约10mg,装在DSC标准铝样品盘中,以空盘为参比,在氮气气氛下,以10℃/min从25℃扫描至70℃.温度预先用高纯铟校正.

### 2 结果与讨论

#### 2.1 丁酸壳聚糖的液晶性

丁酸壳聚糖能溶于以下溶剂,且在适当浓度时形成液晶相,如水、甲醇、甲酸、乙酸、二

氯乙酸、三氯乙酸、二甲亚砜、丙烯酸、间甲酚、甲酰胺和二甲基乙酸胺等,能形成的典型织构是指纹状织构(图 1),说明是胆甾型液晶。

## 2.2 丁酸壳聚糖溶液的临界浓度

测定了丁酸壳聚糖在四种溶剂中的室温临界浓度值,列于表 1。

Table 1 Critical concentration values of butyryl chitosan solution in various solvents

| Solvent               | $pK_a^{[2]}$ | $C_w^*$ (w/w %) | $C_v^*$ (v/v %) |
|-----------------------|--------------|-----------------|-----------------|
| Trifluoro acetic acid | 0.5          | 12              | 17              |
| Dichloro acetic acid  | 1.26         | 12              | 17              |
| Acrylic acid          | 4.26         | 16              | 17              |
| Acetic acid           | 4.76         | 16              | 16              |

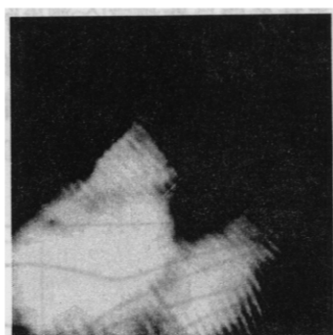


Fig. 1 Typical fingerprint texture of butyryl chitosan in 50% DMSO (468 ×)

结果发现丁酸壳聚糖在各种酸性溶剂中的临界浓度 (v/v %) 均为 16~17%, 此值完全与溶剂的酸值 ( $pK_a$ ) 无关。这一现象在壳聚糖液晶中也能观察到<sup>[3]</sup>, 这与纤维素液晶的  $C_v^*$  随溶剂酸性增加而减少的情况完全不同。原因可能是由于丁酸壳聚糖上存在特有的氨基, 溶剂化作用主要是酸与氨基作用, 此酸碱反应极易进行, 与溶剂酸性关系不大。

溶致性高分子液晶的临界浓度可以通过 Onsager 理论<sup>[4,5]</sup>进行估算。对于刚性高分子链, 临界浓度 (v/v %) 与持续长度  $q$  及 Kuhn 链段直径  $d$  之间有以下关系式:

$$C_v^* = 1.625d/q; \quad d = (M_0/\rho \cdot N_A \cdot L_0)^{1/2}$$

式中  $N_A$  为 Avogadro 常数;  $\rho$  和  $M_0$  分别为密度和重复单元分子量, 对丁酸壳聚糖分别为 1.018g/cm<sup>3</sup> 和 231g/mol (以丁酰化度为 1 计算);  $L_0$  为重复单元沿链轴方向投影的长度 1.03nm, 根据键长键角计算  $d$  为 0.512nm。

壳聚糖的  $q$  值已有报道<sup>[6]</sup>, 丁酸壳聚糖的  $q$  值则可以从实测的  $C_v^*$  值推断。从表 2 可见丁酸壳聚糖比壳聚糖有较高的临界浓度, 预测有较小的持续长度, 说明丁酰化后由于柔性侧基的引入, 分子刚性减小。从数据上看, 丁酸壳聚糖的链刚性与羟丙基纤维素相近。

Table 2 Comparison of calculated and experimental values of persistence length in some chitin derivatives and cellulosic systems

| System                            | $d$ (nm) | $C_v^*$ (exp' l) | $q$ (nm (exp' l)) | $q$ (nm (calc' d)) | Source     |
|-----------------------------------|----------|------------------|-------------------|--------------------|------------|
| Butyryl chitosan/DCA <sup>a</sup> | 0.86     | 0.17             | —                 | 8                  | this paper |
| Chitosan/DCA                      | 0.84     | 0.08             | 22                | 17                 | [3]        |
| HPC <sup>b</sup> /DCA             | 1.04     | 0.15             | 10                | 11                 | [7]        |

a. Dichloro acetic acid; b. Hydroxypropyl cellulose

## 2.3 丁酸壳聚糖溶液的临界温度

Navard 等<sup>[8]</sup>最早将 DSC 用于测定醋酸纤维素的临界温度。本文用 DSC 测定了处于液晶态下的丁酸壳聚糖/二氯乙酸溶液, 见图 2。曲线上出现明显的吸热峰, 这是由各向异

性液晶相转变为各向同性的熔体所致. 以峰前沿的切线与基线的交点  $T_1$  作为临界温度值, 它基本上不受实验条件的影响. 在实验条件相对固定的情况下, 峰结束温度  $T_2$  可用来表征各向异性相完全消失的温度, 于是从  $T_1$  到  $T_2$  之间的温区应视为两相共存区.

根据 DSC 测定结果绘制的相图如图 3 所示. 可见在浓度达到 60% (wt%) 以后临界温度基本不变, 稳定在 39℃ 左右. 总的来说, 丁酸壳聚糖的临界温度值比二醋酸纤维素的数值要低的多, 后者在浓度为 50% 时已达到 77℃<sup>[9]</sup>.

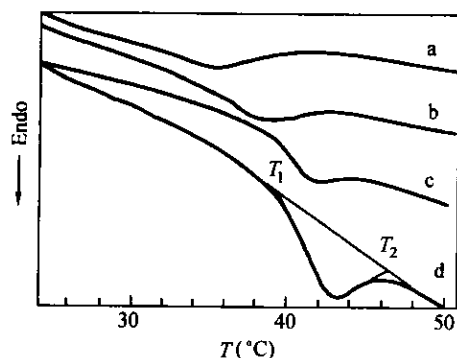


Fig. 2 DSC traces of butyryl chitosan/DCA solution in different concentrations

(a) 35%; (b) 40%; (c) 55%; (d) 70%

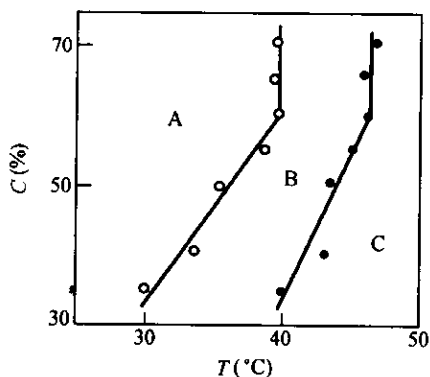


Fig. 3 Phase diagram of butyryl chitosan /DCA lyotropic liquid crystalline system

(○)  $T_1$ ; (●)  $T_2$ ; (A) anisotropic phase; (B) biphasic region; (C) isotropic phase

由于二氯乙酸对丁酸壳聚糖有腐蚀和降解作用, 因而若将配好的溶液静置一周后测定, 几乎没有吸热峰. 实验观察到吸热峰大小与静置时间有关, 在两天内随时间增加而增大, 这是由于溶解以及液晶相的形成需要时间, 两天后热焓值反而降低(图 4 和 5). 因而最佳的观察时间为 48h.

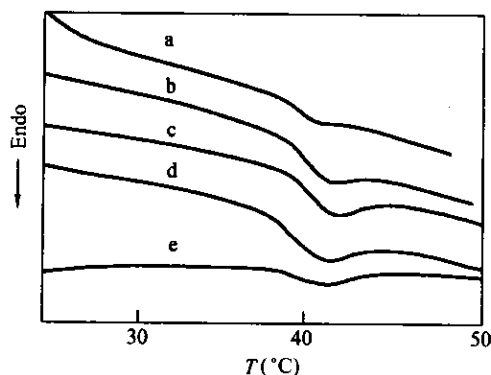


Fig. 4 DSC traces of 55% butyryl chitosan/DCA solution at different staying times of solution after prepared

(a) 12h; (b) 24h; (c) 36h; (d) 48h; (e) 84h

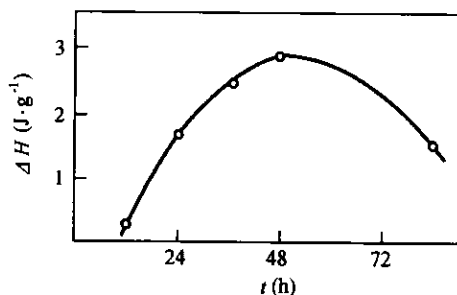


Fig. 5 The dependence of enthalpy of transition on staying time of solution after prepared

## 2.4 丁酰化程度对临界浓度的影响

本文合成了  $B_1$  和  $B_2$  两种不同丁酰化程度的丁酸壳聚糖, 它们的红外谱图示于图 6. 比较壳聚糖的谱图, 新出现了羰基的伸缩振动峰  $1740\text{cm}^{-1}$ .  $1600\sim 1640\text{cm}^{-1}$  的氨基弯曲振动峰没什么变化, 说明氨基没有明显取代. 如果以  $A_{1740}/A_{3450}$  或  $A_{1740}/A_{1600\sim 1640}$  作为取代程度的表征( $3450\text{cm}^{-1}$  为羟基伸缩振动峰), 结果列于表 3, 虽然取代程度的绝对数值根据红外结果尚未能知道, 但可以推断  $B_2$  的取代程度约是  $B_1$  的两倍左右. 从产量估算,  $B_2$  的取代度约为 1.4,  $B_1$  为 0.7.

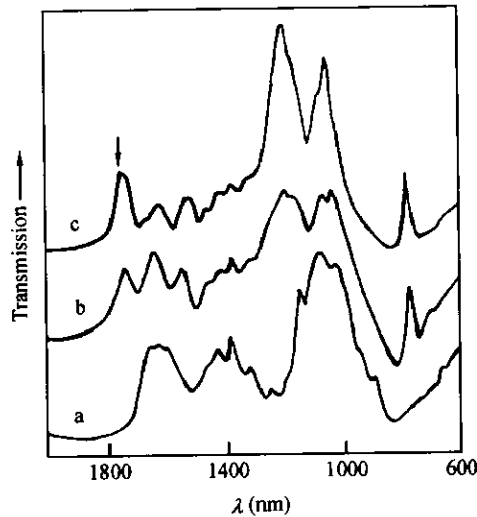


Fig.6 FTIR spectra of (a) chitosan, (b) butyryl chitosan  $B_1$  and (c) butyryl chitosan  $B_2$ . C=O band is shown by arrow

Table 3 IR data and critical concentration values of two butyryl chitosan specimens with different degrees of butyrylation

| Material               | $A_{1740}/A_{3450}$ | $A_{1740}/A_{1600\sim 1640}$ | $C_w^*$ (w/w %) in DCA | $C_v^*$ (v/v %) in DCA |
|------------------------|---------------------|------------------------------|------------------------|------------------------|
| Butyryl chitosan $B_1$ | 0.44                | 0.84                         | 12                     | 17                     |
| Butyryl chitosan $B_2$ | 0.86                | 1.78                         | 12                     | 17                     |

从表 3 的临界浓度测定结果可见, 丁酰化程度对丁酸壳聚糖的临界浓度没有什么影响, 这可能是由于很少的丁酰基取代, 就能使链刚性得到足够降低.

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## STUDIES ON CRITICAL BEHAVIOR OF LIQUID CRYSTALLINE BUTYRYL CHITOSAN

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**Abstract** O-butyryl chitosan which was prepared from chitosan demonstrated lyotropic liquid crystalline behavior in various solvents, for example, water, methanol, formic acid, acetic acid, dichloroacetic acid(DCA), trifluoroacetic acid, dimethyl sulfoxide, acrylic acid, m-cresol, formamide, N, N-dimethyl acetamide. The typical fingerprint texture of cholesteric phase can be observed. Critical concentrations of butyryl chitosan in four acidic solvents were determined using polarized microscopy. All critical concentration values(calculated by v/v%) were 16~17%, independent of the acidity of solvent. This result was similar to that of chitosan. Since the protonation of amine with acid is easy even though the acid is weak, the rigidity of chain(therefore the critical concentration) did not depend on acidity of solvents. Critical temperature of butyryl chitosan/DCA system was measured by DSC. The phase diagram was drawn. Critical temperature reached maximum values of 39°C when concentration was 60% (w/w%). Because butyryl chitosan would degrade in DCA, the enthalpy of transition calculated from DSC traces started to decrease at 48h after the solution was prepared. So the best staying time of solution before DSC determination is 48h. The dependence of butyrylation degree on critical concentration was studied. Two butyryl chitosan samples with relatively different degree of butyrylation which was measured by IR had the same critical concentration values in DCA.

**Key words** Chitosan, Butyryl chitosan, Lyotropic liquid crystal, Critical concentration, DSC, Critical temperature