

学校编码: 10384

分类号_____密级_____

学号: 20720061152067

UDC_____

厦 门 大 学

硕 士 学 位 论 文

基于 *N*-苄基化壳聚糖衍生物液晶性和 T_g 的
分子模拟初步研究

Preliminary Studies of Molecular Simulation on the Liquid
Crystal Behaviors and Glass Transition Temperatures of
N-benzyl Chitosan Derivatives

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专业名称: 高分子化学与物理

论文提交日期: 2009年5月

论文答辩时间: 2009年6月

学位授予日期: 2009年 月

答辩委员会主席: _____

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摘要

壳聚糖结构单元中含有 $-NH_2$ 和 $-OH$ ，因此可对它进行多种化学修饰，这些丰富的化学修饰方法为研究壳聚糖及其衍生物的液晶性提供了很好的条件。利用它进行分子量、取代度和取代基大小等结构因素对溶致液晶行为影响的研究已先后报道，但取代基上特征官能团的位置变化(羟基在苯环的邻、间、对位上)对其溶致液晶性的影响的研究还尚未见有报道。本文拟通过实验合成一系列取代基上特征官能团的位置发生变化的壳聚糖衍生物，对其溶致液晶性进行研究，并通过分子模拟的手段，研究壳聚糖衍生物结构与性质的关系。根据高分子链段的化学结构组成来预测高分子物质的各种性质，对在工业应用中如何进行选择、改性及设计高分子产品具有重要意义。

本文采用壳聚糖同芳基醛反应合成苄基壳聚糖，通过核磁共振法、红外光谱法、紫外光谱法和荧光分析法对产物进行结构表征。利用偏光显微镜法和折射率法测定 *N*-苄基壳聚糖的液晶临界浓度，利用分子模拟的方法对 *N*-苄基壳聚糖分子内与分子间氢键作用力进行了分子动力学模拟，研究氢键作用力与液晶临界浓度的相互关系。通过分子模拟计算不同温度下无定形高分子单元的偏摩尔体积，然后做 *V*-*T* 曲线求得各 *N*-苄基壳聚糖的玻璃化转变温度，与实验用 DSC 测得的玻璃化在转变温度进行比较。通过对树状分子 DOBOB 接枝壳聚糖自组装柱状液晶分子进行分子力学与分子动力学模拟，得到其最优构象，测量其柱直径，并通过改变树状分子的结构，研究树状分子与柱状液晶分子直径大小的关系。对碗型分子 CTV 接枝高分子的自组装结构进行分子动力学模拟，分析碗状小分子能自组装成柱状六方相而其接枝高分子的产物却失去这一特性的原因。

实验成功合成了四种 *N*-苄基化壳聚糖衍生物，它们的取代基上官能团的数目和位置不同，*N*-取代度相近。用偏光显微镜法和折射率法测得各衍生物的液晶临界浓度 (w/w) 分别为 28%、37%、24%和 27%，均比纯壳聚糖的 12%有很大提高，因为取代基的引入破坏了壳聚糖分子内与分子间非常强烈的氢键作用。分子模拟结果表明分子内氢键强或者分子间氢键强都显著提高分子链的刚性，分子链的排列与取向更加规整，因而降低壳聚糖衍生物的液晶临界浓度，这两个因素只要一个即可。相反若两者都不强，则分子链的刚性较小，临界浓度明显较高。对于该体系，氢键的强弱对液晶临界浓度有着决定性的影响。通过分子动力学模

拟出来的高分子的玻璃化转变温度(NOCS:134℃, NMCS:130℃, NPCS:135℃, NMPCS:139℃)与实验测得的玻璃化转变温度(NOCS: 131℃, NMCS: 129℃, NPCS: 138℃, NMPCS: 143℃)相比相差不大, 因此, 分子动力学模拟方法在仅后可能成为预测高分子玻璃化转变温度的一种有用方法。通过分子模拟测得自组装柱状液晶分子直径: DOBOB-CS: 4.8nm, DOVOB-CS: 5.8nm, DOB-CS: 3.1nm, BOB-CS: 4.2nm, 在此柱直径下均能自组装成六方柱相, 由模拟结果可知, DOBOB 分子中柔性的烷基链段对柱直径的贡献最大。对含碗形 CTV 侧基的甲基丙烯酸酯类聚合物的分子结构进行分子模拟, 结果表明当“碗”与主链间的连接链为较短的(CH₂)₂时, 由于碗形侧基过大的体积导致聚合物主链明显弯曲, 分子链失去对称性; 当“碗”与主链间的连接链为较长的(CH₂)₁₁时, 聚合物主链较为伸展, 虽然仍有些弯曲, 但是侧基的“碗”基本上能自组装成柱。但从实验看, 实际上 BPM 并未形成柱状相结构, 液晶性也丧失了。也就是说还需要更长的连接链来实现主链的伸展和 CTV 碗的自组装, 这一点还需要更多实验来进一步证明。

我们利用分子模拟的方法, 对壳聚糖衍生物链进行了分子力学与分子动力学模拟, 以此来预测其各种性质, 并用实验结果对模拟的结果进行了验证, 经过实验验证过的分子模拟方法具有一定的可靠性, 可以用来对实验室未合成出的壳聚糖衍生物的各种性质进行预测进而进行分子结构设计, 从而能够降低实验的成本, 提高科研效率。

关键词: 苜基壳聚糖; 溶致液晶; 取代基; 临界浓度; 氢键; 分子模拟。

Abstract

The structure unit of chitosan contains -NH_2 and -OH , it can be a variety of chemical modification, such a wealth of chemical modification methods provide a very good condition for the study of the liquid crystalline property of chitosan and its derivatives. Researchs use it to study the impact of molecular weight, degree of substitution, substituent size and other structural factors to the lyotropic liquid crystal behavior of chitosan and its derivatives have been reported, but the study of the influence of the position of functional groups in substituents on liquid crystalline behavior of *N*-benzyl chitosan derivatives has not yet been reported. In this paper, we change the position of functional group in substituents and synthesis a series of chitosan derivatives to study the influence of it on the lyotropic liquid crystal property. We use molecular simulation to study the relationship between structure and properties of chitosan derivatives. According to the composition of the polymer chain structure to predict the properties of the polymer, it has great significance on how to choose, modify and design polymer products in industrial applications.

In this paper, we use chitosan and aryl-aldehyde reaction to synthesis the *N*-benzyl chitosan derivatives, characterize the structure of them through NMR, infrared spectroscopy, ultraviolet spectroscopy and fluorescence spectroscopy. Using polarized light microscopy method and refractive index method to determin the liquid crystalline critical concentration of them. Using molecular simulation method to simulate the inter-molecular and intra-molecular hydrogen bonding interaction with molecular dynamics simulation, study the relationship between the hydrogen bonding interaction and liquid crystalline critical concentration. By molecular simulation, we calculate the amorphous polymer unit's running average specific volume at different temperatures, and then draw V - T curve to obtain the glass transition temperature (T_g) of *N*-benzyl chitosan derivatives, compared with the experimental value of T_g which measured by DSC. By the molecular mechanics and molecular dynamics simulation of DOBOB dendrimer grafted chitosan liquid crystalline columnar self-assembly molecules, we got the optimized structure and measured the diameter of their column.

We also want to study the relationship between the structure of dendrimers and the diameter of the columns. By the molecular dynamics simulation of bowl-like molecule CTV grafted polymer molecular self-assembly structure, analysis the reason why CTV small molecule's mesophase belong to hexagonal columnar phase (Φ_h) but the grafted polymer not belong to that.

We synthesized four *N*-benzyl chitosan derivatives in experiment successfully, the number and position of the functional groups in the substituents of which were different. Their degree of *N*-substitution were close, which were 0.72, 0.62, 0.71 and 0.68 respectively. The lyotropic cholesteric liquid crystalline phase was observed in the formic acid solutions of the four chitosan derivatives. Their critical concentration (w/w) were measured to be 28%, 37%, 24% and 27% respectively, by means of both polarized optical microscopy and refractive index method. These values were all much higher than chitosan itself (12%), because the very strong hydrogen bonding interactions of chitosan were broken by the substituent groups. The molecular simulation approach was used to compare the intra-molecular hydrogen bonding interaction and the inter-molecular hydrogen bonding interaction of these four derivatives respectively. It can be seen that if the derivative have a stronger intra-molecular hydrogen bonding (such as NOCS) or a stronger inter-molecular hydrogen bonding (such as NPCS and NMPCS), the rigidity of the molecular chain is significantly improved, the arrangement and orientation of the molecular chain are more regular, as a result, the values of the critical concentration decrease. These two factors require just only one. On the contrary, if both of the two interactions are weaker (such as NMCS), the rigidity of the molecular chain is smaller; the value of the critical concentration becomes evidently higher (37%). For this system, the influence of the strength of the hydrogen bonding on the liquid crystalline critical concentration is definitive. The T_g predicted by molecular dynamics simulation (NOCS:134°C, NMCS:130°C, NPCS:135°C, NMPCS:139°C) is similar with the experimental value (NOCS: 131°C, NMCS: 129°C, NPCS: 138°C, NMPCS: 143°C) measured by DSC, so we think the molecular simulation is a valuable method to predict the T_g of polymers. By molecular simulation measured the diameter of liquid

crystalline self-assembly columnar molecules: DOBOB-CS: 4.8nm, DOVOB-CS: 5.8nm, DOB-CS: 3.1nm, BOB-CS: 4.2nm, the diameter of this column can be self-assembled into hexagonal columnar phase (Φ_h), we can see DOBOB flexible elements in the alkyl chain contribute largest column diameter from the simulation results. We made a molecular dynamics simulation of the methyl acrylate-based polymer which contained the bowl-like CTV as side group. Results show that if the "bowl" connects the main chain with short alkyl chain just like $(CH_2)_2$, the bowl's volume is too large leading the main chain to apparent bending, losing the symmetry of the molecular chain; when the "bowl" connects the main chain with long alkyl chain just like $(CH_2)_{11}$, the polymer main chain is more extended, though there is still some bending, but the side of the base of the "bowl" has been able to self-assemble into a column. However, in experiments BPM did not have a columnar phase, the liquid crystalline property was also lost. It means that there needs to connect a longer chain to come to the realization of the main chain stretching and CTV bowl self-assembly, it also needs more experiments to further prove.

We used the molecular simulation to simulate the chitosan chain with mechanics and dynamics method to predict its properties. The experimental results are used to verify the simulation results. After the experiment is verified, the molecular simulation method has a certain degree of reliability, can be used to guide laboratory synthesis, it can predict the properties of some chitosan derivatives that have not yet been synthesized. Use it for molecular structure design, can reduce test cost and improve the efficiency of scientific research.

Keywords: *N*-benzyl chitosan; lyotropic liquid crystalline; Substituent; Critical concentration hydrogen bonding; Molecular simulation

第一章 绪 论

1.1 甲壳素/壳聚糖的结构与性质

甲壳素(chitin, CT)是一种“古老”的物质,在距今 247 万年前渐新世(Oligocene period)的昆虫化石中就已探测到甲壳素的存在^[1]。同时它也是一种广泛存在的物质,低等动植物体内,尤其是虾、蟹等甲壳纲动物的外壳、昆虫的甲壳、软体动物的壳和骨骼以及真菌和藻类的细胞壁中都含有甲壳素。估计自然界每年生物合成的甲壳素接近 100 亿吨,是含量仅次于纤维素(cellulose)的第二大天然多糖和除蛋白质外数量最大的含氮天然有机化合物,同时也是大量存在的唯一的天然碱性多糖。

甲壳素的化学名称为(1,4)-2-乙酰氨基-2-脱氧- β -D-葡聚糖(2-acetamido-2-deoxy- β -D-glucopyranose, GlcNAc, Chemical Abstracts Registry (CAS) 1398-61-4),是通过 β -(1,4)糖苷键连接的线性高分子,相对分子质量因原料和提取方法的差异而为数十万到数百万不等。甲壳素脱乙酰的产物是壳聚糖(chitosan, CS),其化学名称为(1,4)-2-氨基-2-脱氧- β -D-葡聚糖(GlcN, CAS 9012-76-4)(如图 1)。由于在实际生产过程中,甲壳素会脱掉部分乙酰基,壳聚糖也往往存留部分未脱除的乙酰基,因而,甲壳素和壳聚糖都是 GlcNAc 与 GlcN 的共聚物,只是两者比例不同。甲壳素和壳聚糖一般用在 1%醋酸水溶液中能否溶解进行区分,甲壳素(约 GlcNAc>40%)不溶,能溶的为壳聚糖^[2]。

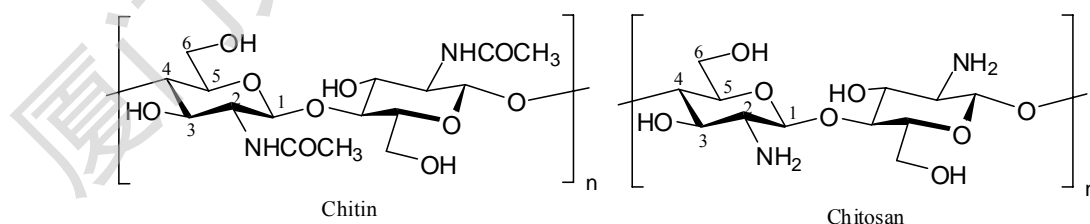


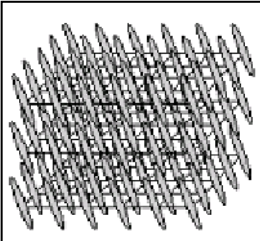
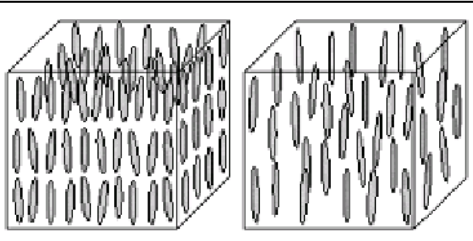
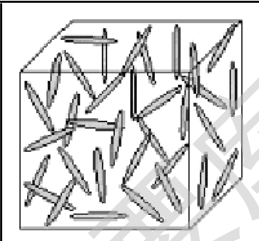
图 1 甲壳素和壳聚糖的结构式

1.2 甲壳素/壳聚糖的液晶性

1.2.1 液晶及聚合物液晶^[3-10]

液晶(liquid crystals, LC), 又称介晶相(mesophases), 简单地说是一种取向有序性流体, 介于各向异性晶体和各向同性液体之间的一种中间态, 兼具液体的流动性和晶体的各向异性(见表 1)。

表 1 晶体, 液晶和液体的性质比较

			
晶体	液晶		液体
三维晶格	一- (二) 维晶格	无晶格	无晶格
有序	有序	有序	无序
固态	液态	液态	液态
各向异性	各向异性	各向异性	各向同性

液晶可按多种方式进行分类:

根据分子量大小, 液晶可以分为小分子液晶和聚合物(高分子)液晶。聚合物液晶是具有液晶性的聚合物, 它们往往由小分子液晶基元键合而成, 按键合方式的不同, 聚合物液晶可分为主链型聚合物液晶(介晶基元处于聚合物主链内)、侧链型聚合物液晶(介晶基元处于聚合物侧链内)及组合式聚合物液晶(主链和侧链均含有液晶基元)。

液晶按来源的不同可分为合成聚合物液晶和生物高分子液晶(如纤维素、甲壳素、多肽、蛋白质和核酸等)。

根据形成过程可分为热致液晶(thermotropic LC)和溶致液晶(lyotropic LC)两大类型。热致液晶是在非溶剂体系中, 在某一温度范围内形成的。通常是在熔融温度(T_m)以后呈液晶态, 当继续加热至清亮点(T_c)时发生相转变而形成各向同性熔体。溶致液晶是纯物质或混合物的各向异性浓溶液, 它只在合适的溶剂中在一定浓度及温度范围内形成。由此可见, 被称为液晶的物质并不总是处于液晶相, 只有在一定的物理条件下才显示出液晶相的物理特征。

根据内部分子排列的有序性不同, 液晶主要分为近晶型(smectic)、向列型

(nematic)和胆甾型(cholesteric)(见图 2)。近晶型具有接近晶体的结构,分子长轴互相平行排列成层状结构,分子指向矢垂直于层片平面。向列型中,分子长轴互相平行排列,其重心排列是无序的,仅保持晶体的一维有序性。胆甾型液晶是最早发现的液晶,其分子长轴也是互相平行排列成层状结构,但它们的长轴在同一层面内,层内分子排列与向列型相似,而相邻两层之间分子长轴的取向绕一螺旋轴依次规则地扭转一定角度。扭转 360° 后实现周期性变化,周期的长度称为螺距(P)。若 P 为无穷大时即为向列型液晶,因而胆甾型液晶也称手性向列相。

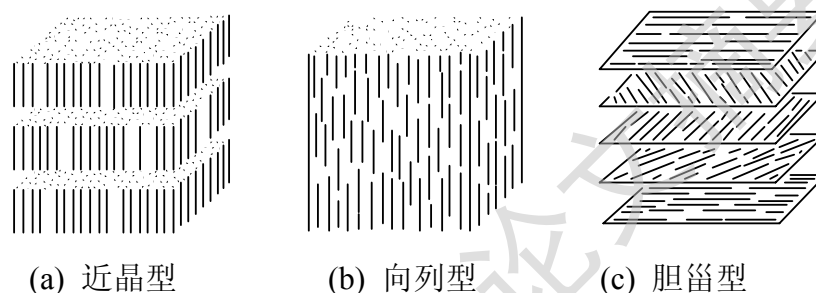


图 2 液晶的结构

1.2.2 甲壳素/壳聚糖及其衍生物的液晶性研究进展

甲壳素/壳聚糖分子链中含有羟基、氨基、羰基等可以形成氢键的基团,特别是形成分子内氢键,分子链难于旋转,因此具有很强的链刚性,可以形成液晶(如图 3)。在一些生物体中,甲壳素就是以胆甾液晶类似物存在的,我们看到蜻蜓的翅膀被膜在阳光下五彩斑斓,类似于胆甾相的光学特征。在螃蟹等节肢动物的外壳中存在的螺旋体(一种胆甾液晶的类似物)是由甲壳素的棒状微晶构造的。在外壳的每一个水平片层中甲壳素的棒状微晶平行排列,水平片层依次堆叠,并且每一个片层的棒状微晶都转过一个小的角度,这种结构看起来很像胆甾液晶的自组装^[11]。

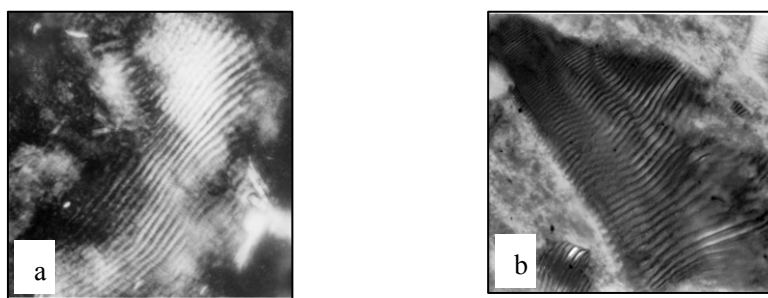


图 3. (a) 甲壳素在甲磺酸溶液中的指纹状织构的偏光显微镜照片

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