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均相酯交换法可控制备纤维素酯类材料
及其应用研究

Controllable Synthesis of Cellulose Esters by Homogeneous
Transesterification and Its Application

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摘要

随着石油、煤炭等不可再生资源的日益枯竭，为了满足社会经济可持续发展的需要，以纤维素生物质为原料制备高附加值化工品及燃料的研究逐渐成为人们研究的热点。本文以多种来源的纤维素为原料，以 N,N-二甲基乙酰胺/氯化锂（DMAc/LiCl）为溶剂体系，建立一种温和快速均相酯交换可控制备纤维素酯的方法，改进了纤维素在 DMAc/LiCl 体系中的溶解过程，优化了酯交换反应制备工艺，分析了纤维素酯类产物特征，探索了一种 SEC 测定纤维素分子量的方法，为纤维素酯的后续研究及应用提供理论基础和依据。

研究微晶纤维素在 DMAc/LiCl 体系中的溶解特性，分析了溶剂交换条件及氯化锂含量等对纤维素溶解过程的影响。通过研究不同浓度氯化锂纤维素分散液的粘度，揭示了溶解过程中局部产生结块的直接原因是活化后的纤维素加入 DMAc/LiCl 溶液中没有得到及时分散，结块表面的纤维素溶液由于 LiCl 浓度的变化而处于溶解过渡态，因其具有较高的黏度，阻碍了结块内纤维素的向外分散。提出了两步加入 LiCl 制备纤维素溶液的方法，即先配制浓度为 4~5 wt% 的 DMAc/LiCl 溶液，加入该溶液后纤维素得到均匀分散，再补充一定量的 LiCl 使其终浓度达到 8.0 wt%，用此方法可快速获得不同种类纤维素的均相溶液。

利用微晶纤维素在均相体系中的酯交换反应制备醋酸纤维素，考察了反应条件对于产物取代度（DS）的影响，并对反应条件进行优化。酯化试剂、催化剂对产物取代度有显著的影响，通过控制两种试剂的添加量可以调节产物取代度。反应可以在常温条件（30 °C）下进行，温度对酯化反应影响较小。通过 FT-IR、¹H-NMR 及 ¹³C-NMR 对纤维素酯进行分析。利用 SEM、XRD 及 TG-DSC 分析了产物的微观形貌、晶相结构及热稳定性，表明制备产物与商品醋酸纤维素具有相似的结构特性。通过分析不同取代度的醋酸纤维素 ¹H-NMR 及 ¹³C-NMR 谱图，揭示该均相酯交换反应中纤维素三个羟基的取代顺序为 C6>C2>C3。制备的醋酸纤维素的热稳定性远远优于原料微晶纤维素。

通过优化醋酸纤维素制备反应条件，合成了不同侧链长的系列纤维素酯（CEs）和三种纤维素混合酯，包括醋酸丙酸纤维素（CAP）、醋酸丁酸纤维素

(CAB) 及醋酸己酸纤维素 (CAH)。均相酯交换法可以高效获得较高取代度的长链纤维素酯，由于侧链的位阻效应，随着目标产物侧链的延长，产物的取代度逐渐降低。利用 FT-IR 对纤维素酯的酯键及亚甲基进行了分析；通过¹H-NMR、¹³C-NMR 对合成产物的结构、取代基位点及混合酯产物取代度的大小进行了分析；利用 XRD 对合成产物的晶相结构进行了分析；TG-DSC 分析显示合成的纤维素酯的热稳定性优于原料纤维素。不同侧链长的系列纤维素酯溶解特性基本相同，但 CE2、CE3 和 CE4 不能在氯仿中溶解，而 CE6、CE8 和 CE10 可以在氯仿中溶解。合成的三种纤维素混合酯具有较好的溶解特性，可在许多常用溶剂中完全溶解。

通过均相酯交换获得的三种纤维素混合酯 CAP、CAB 和 CAH 能快速溶解于多种极性试剂。利用产物溶解性的优势，建立一种以四氢呋喃 (THF) 为流动相，在 SEC 中测定纤维素酯分子量的技术方法，该流动相分子量低、成本低、适应范围广，流动性好。适合该体系进行分子量测定的纤维素酯有醋酸纤维素 (在 DS=2.40~2.55 之间) 和 CAP。本研究中的均相酯交换反应过程几乎不对纤维素造成降解，能真实反映纤维素酯的分子量及聚合度 (DP)，进一步推算原料纤维素的分子量及聚合度。利用优化均相酯交换法分别制备了棉纤维素酯、滤纸纤维素酯、芒草纤维素酯及竹纤维素酯，测定了相应混合酯的分子量，再根据 DS 值计算出多种纤维素及相应纤维素酯的聚合度。

实验证明，以 DBU 作为催化剂在溶剂 DMAc/LiCl 的均相体系中可控合成的各类纤维素酯，不但制备过程取代度及聚合度可控、绿色无污染，而且反应速度快，产物具备热稳定性高、溶解特性好等优异性质，性能均达到文献中的较优水平。这种新型的催化反应体系制备的纤维素酯，在膜材料、光学材料等领域，有着广阔的应用前景。

关键词：纤维素 酯交换 温和条件 可控制备 均相反应

Abstract

Driven by the growing fear of the depletion of oil, coal and other non-renewable resources, and the global need to focus on renewable and earth-abundant resources, high value-added cellulose-based functional materials and polymers are now spotlighted once again and widespread concerned. A series of studies were carried out in this dissertation on the mild and rapid methods of cellulose esters preparation by controllable homogeneous transesterification in N, N-dimethylacetamide/lithium chloride (DMAc/LiCl) system, which includes the dissolution process improvement of cellulose in DMAc/LiCl system, the optimization of the reaction conditions, the analysis of product characteristics and SEC measurement. The ultimate goal is providing a theoretical basis for further research and application.

The influence of solvent exchange and LiCl content on cellulose dissolving process was investigated in order to better understand the solubility characteristics of MCC in DMAc/LiCl system. After comparing the viscosity of cellulose in different LiCl concentration, the reason for the agglomeration in the solution is that the activation of cellulose could not scattered timely in DMAc/LiCl solution, thus the surface of the agglomerate has high viscosity in a certain LiCl concentration which prevent the outward spread of cellulose. By using the method of two-step to add LiCl, the raw materials including MCC, cotton, filter paper, the purified bamboo fiber and *Miscanthus* fiber could dissolved quickly in DMAc/LiCl system. DMAc/LiCl solution with 4~5 wt% LiCl concentration was firstly prepared. The activated cellulose was dispersed uniformly in the solution, and then a certain amount of LiCl was added to make 8 wt% as its final concentration. Finally, the high concentration of cellulose solution was obtained efficiently and the agglomeration was avoided during the dissolving process.

Cellulose acetate (CA) of MCC was prepared efficiently by homogeneous

transesterification in the DMAc/LiCl system with vinyl acetate as acylation reagent and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as catalyst. The affection reaction conditions on the substitution degree (DS) of products were investigated. Among various reaction factors, the ratio of esterification reagent or catalyst to the cellulose has a significant influence on the DS. By controlling the amount of two reagents, the degree of substitution can be adjusted. At the same time, there was nearly no affection of temperature on the reaction, so 30 °C was chosen as the reaction temperature. FT-IR, ¹H NMR and ¹³C NMR analysis confirmed that the successful preparation of cellulose acetate, SEM, XRD and TG-DSC reflected the apparent morphology, phase structure and thermal characteristics, which prove that the structure of the products were similar to the existing cellulose acetates. The priority of reactions in three positions of the cellulose acetate followed the same order of C6>C2>C3 for a homogeneous conversion. Thermal stability of cellulose acetates was better than that of MCC.

Cellulose aliphatic esters (CEs) and three kinds of Mixed Cellulose Esters (MCEs) were synthesized efficiently in an DMAc/LiCl system with vinyl esters (VEs, number of carbon atoms ranging from 4 to 12) as acylation reagent and DBU as catalyst. The existence of ester bond and different number of methylene in FT-IR curve proved that the successful preparation of the cellulose aliphatic esters. The structures and properties of the products have been characterized by various analytical techniques. Generally, the DS of CEs showed a reverse trend with the length of the aliphatic chain increasing due to steric effects. Their thermal stability was also better than that of MCC. CE2, CE3 and CE4 can not be dissolved in chloroform, while CE6, CE8 and CE10 can.

This research provides a novel homogeneous technology to synthesize various CEs efficiently. Cellulose acetate butyrate (CAB), cellulose acetate propionate (CAP) and cellulose acetate hexante (CAH) were prepared homogeneously. There was no decrease of molecular weight under this mild reaction. Mixed cellulose ester also shows good solubility properties in many conventional solvents. We took advantage of the excellent dissolving properties of the cellulose derivatives and dissolved it in

the THF for the SEC determination of THF as the mobile phase. The mobile phase has the advantages of low molecular weight, low cost, wide adaptation, the good liquidity. When the molecular weight of different kinds of cellulose derivatives was obtained, and finally calculated the DP according its DS value.

The results show that using DBU as a catalyst in homogeneous solvent of DMAc/LiCl, the synthesis and preparation process of all kinds of cellulose esters is controlled. In addition to controllable substitution degree and polymerization degree, pollution-free and fast reaction, the product has the excellent properties of high thermal stability and good solubility, and the performance have reached the optimum level in literature. The cellulose ester prepared by this new catalytic reaction system has a great application and development prospect in the field of membrane materials and optical materials.

Keywords: Celluloses; Transesterification; Mild condition; Controllable synthesis; Homogeneous reaction

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