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以离子液体为介质的纤维素均相衍生化

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摘要 纤维素衍生物的均相合成一直是纤维素领域的研究热点之一. 近年来, 能够高效溶解纤维素的非质子型溶剂——离子液体的出现, 为纤维素均相衍生化提供了一个崭新的、多用途的平台. 以离子液体为介质, 几乎所有人们熟知的纤维素衍生物(酯、醚、接枝聚合物等)都已经被合成出来; 同时, 一些新型、功能性纤维素衍生物和合成新技术不断涌现, 以及均相酯化工业化的初步探索、农业废弃物的高值利用等, 这些研究极大地拓展了纤维素资源的应用领域, 促进了纤维素科学的发展. 本文综述了以离子液体为介质的纤维素均相衍生化研究的最新进展.

关键词
纤维素衍生物
离子液体
均相衍生化

纤维素衍生物是一类重要的精细化学品, 广泛应用于涂料、纺织、食品、医药、军工等诸多领域[1~4]. 通过均相反应制备纤维素衍生物不仅可以克服传统非均相法产率低、转化率低、耗时长、产物均一性差等缺点, 而且可以有效地控制反应过程和产物结构, 拓展纤维素衍生物的种类[5]. 但是, 到目前为止, 能够溶解纤维素并提供稳定衍生化环境的溶剂体系很少. 作为一类纤维素的非水溶剂, *N*,*N*-二甲基乙酰胺(DMAc)/LiCl体系用于纤维素的溶解、酯化、接枝等研究被广泛报道, 但这类复合溶剂使用及回收困难, 难以实现大规模工业化应用. 近年来, 人们发现一定结构的离子液体可以高效地溶解纤维素, 为纤维素均相衍生化提供了一个崭新的平台[6~8]. 以离子液体为介质, 几乎所有人们熟知的纤维素衍生物都已经被合成出来; 同时, 一些新型、功能性纤维素衍生物及其合成新技术不断被报道, 特别是适合工业化的合成方法、农业废弃物的高值利用等, 极大地拓展了纤维素资源的应用领域, 促进了纤维素科学的发展. 本文收集整理了近十年间发表在国内外期刊上的相关文献, 综述了以离子液体为介质纤维素均相衍生化研究的最新进展.

1 纤维素酯

作为一类非质子型纤维素溶剂, 离子液体可设计性、高极性和近乎无水的环境非常适合作为纤维素酯化反应介质, 多种传统的和新奇的纤维素酯都已经被合成出来, 常规的合成路线和制得的纤维素酯种类如图1所示.

1.1 纤维素脂肪酸酯

本课题组在国际上最早开展了离子液体中均相合成纤维素酯的相关研究. 以1-烯丙基-3-甲基咪唑氯盐(AmimCl)为介质, 乙酸酐为酰化剂, 在无催化剂存在下, 通过温和的反应条件, 可以一步得到不同取代度(0.5~3)的纤维素醋酸酯, 通过控制反应温度、时间和投料比可以方便地调控产物的取代度, 而且离子液体可以有效地回收使用[9]. 和传统的非均相工艺相比, 以离子液体为介质均相酯化表现出很多优势, 其产物均一性好、结构可控、快速、简单、无需催化剂、溶剂可回收. 基于合成过程中产物结构的可

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Zhang J M, Chen W W, Feng Y, et al. Homogeneous synthesis of cellulose derivatives in ionic liquids (in Chinese). Chin Sci Bull, 2015, 60: 1513–1521, doi: 10.1360/N972014-01405

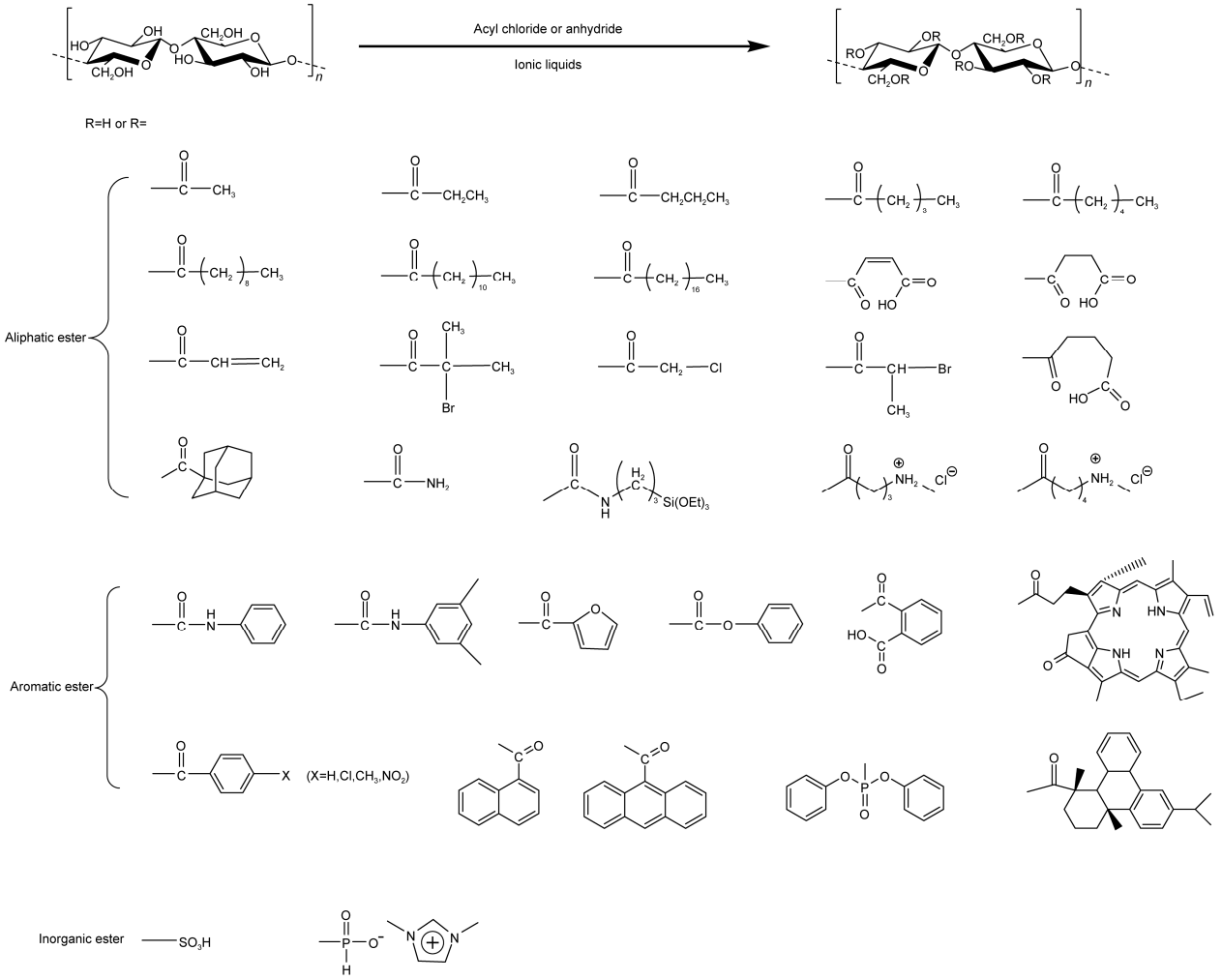

图 1 以离子液体为介质合成纤维素酯的常规路线与合成的纤维素酯结构

Figure 1 Synthesis route and molecular structure of cellulose esters prepared by using ionic liquids (ILs) as reaction media

控性，本课题组[10]详细研究了醋酸纤维素结构与其溶解行为的关系，发现较小分子量和合适取代度范围(DS: 0.5~1.1)的醋酸纤维素可以溶解在水中．此后，以离子液体为介质，合成了一系列的纤维素羧酸酯．Heinze课题组[11~14]在5种离子液体中合成了几乎所有已知的纤维素脂肪酸酯，如乙酸酯、丙酸酯、丁酸酯、己酸酯和月桂酸酯等；并通过引入非离子型含醚键基团[15]和可离子化的有机酸酯[16]得到了水溶性的纤维素有机酸酯．在酯化反应中，酰氯的反应活性往往高于酸酐的反应活性，不同的离子液体也会对反应速率、最终产率产生影响．King等人[17]和Huang等人[18]将2种长链脂肪酸引入纤维素链中，分别合成了纤维素癸酸酯和硬脂酸酯．

在合成纤维素脂肪酸酯过程中，无催化剂条件下，难于得到高取代度的纤维素丙酸酯和丁酸酯．在1-丁基-3-甲基咪唑氯盐(BmimCl)中，纤维素丙酸酯和丁酸酯的最高取代度分别只有0.9和0.4[14]．本课题组[19]发现以4-二甲氨基吡啶(DMAP)为催化剂，在AmimCl中很容易制得各种取代度(0~3)的纤维素丙酸酯和丁酸酯，而且反应条件温和、快速，30℃下反应30 min即可完成实验．酰化试剂转化率极高，大于90%，甚至达到96%．

最近，Yang等人[20]发现一种CO_2开关型离子液体可以溶解纤维素，并可催化纤维素酯化反应．以此离子液体为介质，无需任何催化剂，也可实现纤维素乙酸酯、丙酸酯和丁酸酯的快速、高效合成．

此外，在AmimCl中，本课题组还合成了多种混合酸酯，如纤维素乙酸丁酸酯(CAB)[21,22]、纤维素乙

酸金刚烷酸酯[23]、纤维素乙酸二苯基磷酸酯[24]等. 其中, CAB与Eastman商品相比, 丁酸酯的含量范围更宽(6%~47%, 质量分数), 成膜性更好[21].

在离子液体中, 通过均相酯化可以合成用于活性聚合的纤维素基的大分子引发剂, 如纤维素溴异丁酸酯[25~27]、纤维素溴异丙酸酯[28,29]和纤维素氯乙酸酯[30]. 进而, 通过原子转移自由基活性聚合(ATRP)和可逆加成-断裂链转移聚合(RAFT)可以合成多种新型结构的纤维素接枝聚合物. 另外, 通过纤维素均相酯化引入丙烯酸酯, 进一步利用双键进行自由基接枝聚合离子液体型单体, 得到了对CO_2具有高透气性和高选择性的纤维素基气体分离膜材料[31].

通过在纤维素主链上引入大体积基团, 如金刚烷[23]、树枝状分子[32]和脱氢枞酸[33]等, 可有效地调控纤维素基材料的自由体积、负载能力和生物活性, 得到高透气性或负载能力出色的功能材料.

微波辅助合成是一种"绿色"、高效的合成新技术, 可以加速反应、提高转化率和选择性. El Seoud课题组[34,35]在1-丙烯基-3-丁基咪唑氯盐中通过微波加热方法快速、高效地合成了5种纤维素脂肪酸酯和4种混合酸酯. 和常规加热方式相比, 微波加热可以大大加快纤维素溶解过程和酯化反应速率, 提高酰化试剂转化率.

Zhao等人[36]通过酶催化酯交换反应制得了纤维素甲基丙烯酸酯. Schenzel等人[37]使用1,5,7-三氮杂二环[4.4.0]癸-5-烯作为催化剂, 通过酯交换反应, 成功制得了取代度在0.2~0.7的纤维素丁酸酯和10-癸烯酸酯.

此外, Cao等人[38]证实了使用高浓度、高黏度的纤维素/离子液体溶液制备纤维素酯的可行性, 他们在8%~12%(质量分数)纤维素/AmimCl溶液中同样可以制备取代度0.4~3.0的纤维素醋酸酯, 为纤维素均相酯化的规模化生产做了有益的探索. Kosan等人[39]在一种特殊的垂直捏合机进行酯化反应, 然后直接进行溶液挤出纺丝即可得到醋酸纤维素纤维. Zhang等人[40]在双螺杆挤出机中考察了纤维素与尿素、马来酸酐等多种酰化试剂的原位反应挤出.

1.2 纤维素芳香酸酯

以苯异氰酸酯为原料, Heinze课题组[12,13]合成了纤维素芳香酸酯——纤维素苯基氨基甲酸酯. 在BmimCl中, 不仅棉浆粕可以很好地实现该酯化反应, 而且聚合度很高的细菌纤维素(聚合物6500)也能成功地酯化. 对所得产品进行凝胶渗透色谱(GPC)测试, 发现反应前后纤维素原料的聚合度变化很小, 说明在离子液体中进行该反应不会导致纤维素的降解. 最近, Liu等人[41,42]在AmimCl中合成了全取代和区域选择性取代的纤维素3,5-二甲基苯基氨基甲酸酯, 并制备成涂覆和键合型手性固定相, 可以用于拆分多种农药外消旋体, 同时表现出良好的手性拆分性能.

纤维素苯甲酸酯也是一类重要的手性拆分材料. 在AmimCl中, 本课题组[43]合成了多种纤维素苯甲酸酯, 并考察了苯环上带有取代基团对酰化试剂反应活性的影响, 无论是吸电子基团还是给电子基团都有利于提高反应速率. 所得纤维素苯甲酸酯当取代度大于2.0时表现出较好的手性拆分能力. 特别值得一提的是, 在AmimCl中苯甲酰化反应表现出极高的区域选择性, 优先与6位羟基进行反应. 基于此种现象, 我们通过"一锅法"直接得到了具有区域选择性取代的纤维素混合酸酯.

2014年, 本课题组[24]通过引入大的苯氧磷酯得到了可熔融加工的纤维素酯, 在不加增塑剂的条件下, 通过常规的注塑和压膜得到了高透明性的片状和薄膜状纤维素制品(图2). 通过引入稠环酸酯, 如萘、蒽等, 得到了可溶液加工的纤维素荧光材料, 其中纤维素萘酸酯表现出极好的成膜性, 通过溶液加

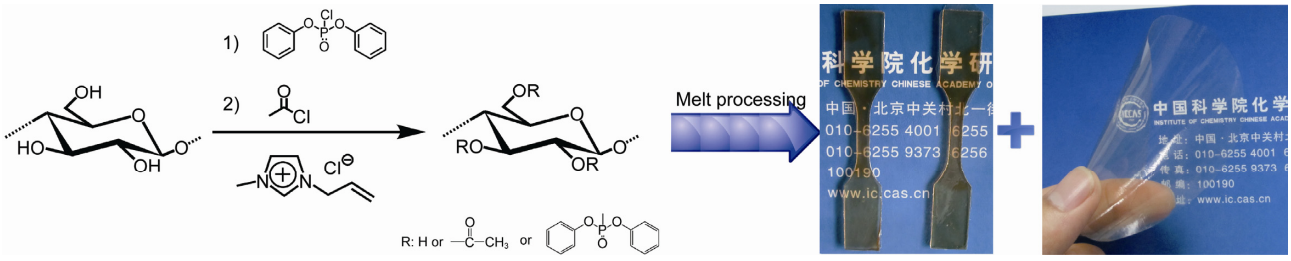

图 2 (网络版彩色)可熔融加工的纤维素乙酸-磷酸二苯酯(C-A-Dp)[24]

Figure 2 (Color online) Meltable cellulose acetate-diphenyl phosphate mixed esters (C-A-Dp)[24]

工得到了高透明性薄膜[44].

以*N*,*N*′-羰基二咪唑(CDI)或吡啶作为催化剂，在BmimCl中，制得了纤维素糠酸酯[45]、苯基碳酸酯[46]和脱镁叶绿酸酯[47]等一系列新型纤维素酯. 其中，以CDI为催化剂时可以直接使用羧酸作为酰化试剂.

1.3 纤维素无机酸酯

纤维素无机酸酯包括纤维素硝酸酯、硫酸酯和磷酸酯等，在军事、医药、涂料、油墨等领域有着不可替代的作用. 在离子液体和有机共溶剂的混合溶剂中, Heinze课题组[48,49]以SO_3/吡啶、SO_3/*N*,*N*-二甲基甲酰胺(DMF)和氯磺酸为酰化试剂，成功地合成了不同取代度的纤维素硫酸酯. 利用制得的纤维素硫酸酯，他们与带正电荷的聚电解质复合得到了聚电解质复合微球(图3)，可包覆葡萄糖氧化酶，并保持其活性. Wu课题组[50]在BmimCl中成功合成了纤维素硫酸酯，并研究了产物的抗凝行为. 他们发现分子量对纤维素硫酸酯的抗凝性能有很大影响，高分子量的纤维素硫酸酯更适合体外使用，低分子量的纤维素硫酸酯更适合体内使用.

Lee课题组[51]发现在1,3-二甲基咪唑亚磷酸甲酯中热处理(温度 > 120℃)纤维素，即可得到水溶性纤维素磷酸酯. 通过调节温度和时间，其取代度可在0.4~1.3调控. 而且，磷元素的引入使所得纤维素酯碳残余量大大提高，达到40%~50%，有望用作纤维素基阻燃材料.

1.4 农林废弃物中纤维素的酯化利用

农林废弃物是一类价格低廉、数量巨大的纤维素资源，如何合理、充分地利用农林废弃物是当前材料、能源和环境领域的研究热点之一. 酯化反应是实现农林废弃物高值化利用的有效途径. 本课题组[52,53]以AmimCl为介质，从秸秆中提取纤维素为原料，一步合成了丙酮可溶的纤维素乙酸酯；随后通过溶液铺膜，得到了力学性能与商品化纤维素醋酸酯相当的膜材料. Hu等人[54]在*N*-乙基吡啶溴盐离子液体中成功实现了棉秸秆纤维素的氨基甲酸酯化. Liu课题组[55~62]以BmimCl, AmimCl和BmimCl/二甲基亚砜(DMSO)共溶剂体系为纤维素溶剂，研究了无催化剂条件下甘蔗渣纤维素与丁二酸酐、邻苯二甲酸酐的均相反应，随后通过使用*N*-溴代丁二酰亚胺、4-二甲氨基吡啶和碘作为催化剂提高所得纤维素酯的取代度，最大取代度值可以达到2.54. Wu课题组[63]利用甘蔗渣纤维素为原料制备了纤维素硫酸酯，产物取代度0.52~2.95，具有显著地抗絮凝活性. Li课题组[64]利用甘蔗渣纤维素为原料制备了2种纤维素混合酸酯：纤维素乙酸丙酸酯和纤维素乙酸丁酸酯. Yu课题组[65]利用超声辅助的方法制备了甘蔗渣纤维素戊二酸酯. 另外，Sun课题组[66]直接将球磨的竹子进行了月桂酸酯化，所得产物在氯仿等有机溶剂中表现出优良的溶解性.

2 纤维素醚

纤维素在离子液体中进行均相醚化反应比较困难，一般所得纤维素醚的取代度较低，且需要加入碱作为催化剂. Heinze等人[11]使用NaOH为催化剂，在BmimCl/DMSO混合溶剂中进行纤维素的均相醚化反应，结果只得到了取代度较低(0.49)的羧甲基纤维素. Abbott等人[67]使用NaOH作为催化剂，在胆碱型离子液体中通过醚化反应制得了阳离子化的纤维素醚，产物取代度也不高. Mikkola等人[68]也使用NaOH作为催化剂研究纤维素在AmimCl和BmimCl中的羧乙基化和羧丙基化，发现NaOH的加入会大大加快纤维素醚化反应速率，羧乙基纤维素的取代度最高可达1.53. 但是，他们指出NaOH的加入会破坏离子液体，使其无法循环使用. 此后，Heinze课题组[69,70]发现含

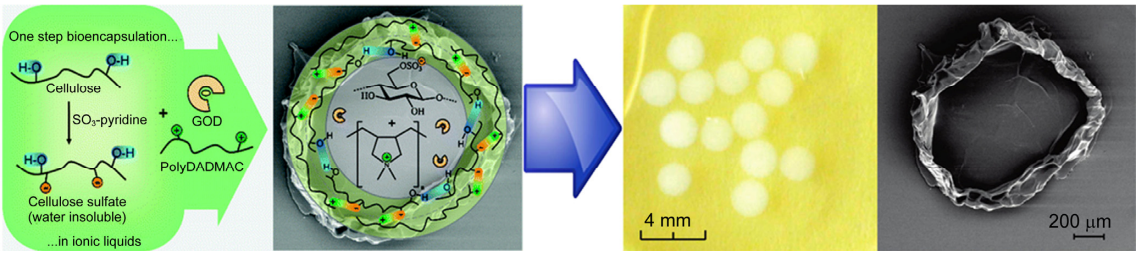

图 3 (网络版彩色)离子液体中制备纤维素硫酸酯及其与正电聚电解质复合微球[49]

Figure 3 (Color online) Polyelectrolyte complex capsules of cellulose sulfates synthesized in ILs[49]

有羧酸根的离子液体对纤维素醚化反应具有很好的催化效果. 在醋酸型离子液体中, 不加入无机碱, 制得了水溶性的羟烷基纤维素醚, 最高取代度可达2.79; 在甲酸型离子液体中, 他们制得了羧甲基纤维素, 最高取代度可达1.55.

Schubert课题组[71,72]在吡啶、三乙胺催化下合成了三苯基甲基纤维素醚, 产物取代度最高可达1.37, 与DMAc/LiCl中合成效果类似, 有望用于保护纤维素6位羟基制备区域选择性纤维素衍生物. Granström等人[73]发现在AmimCl中4-甲氧基-三苯基氯甲烷与纤维素的醚化反应表现出很高的2位和6位羟基选择性, 可以有效地保护纤维素2,6位羟基基团; 在酸性条件下4-甲氧基-三苯基甲基还可以脱保护. 因此该反应可以用于合成具有区域选择性的纤维素衍生物.

此外, 利用对甲苯磺酸基团良好的离去性能, Granström等人[47]在AmimCl中通过两步反应制得了11-溴十一烷基纤维素醚. Heinze课题组[74]以六甲基二硅烷(HMDS)为原料与纤维素反应, 合成了三甲基硅烷纤维素, 取代度可达2.89. Mormann和Wezstein[75]考察了纤维素与六甲基二硅烷在EmimCl, BmimAc和BmimSCN等多种离子液体中的反应, 制得了各种取代度的三甲基硅烷纤维素.

3 纤维素接枝聚合物

在离子液体中, 通过均相接枝聚合的方法可以制备出直接基于纤维素主链的新型接枝共聚物, 并且接枝聚合物的接枝密度、接枝链长以及接枝聚合物种类均可有效地调控. 基于离子液体中纤维素均相酯化的成功经验, 我们在离子液体中合成出了多种纤维素大分子引发剂(纤维素溴异丁酸酯、纤维素氯乙酸酯等), 随后通过原子转移自由基聚合(ATRP)反应得到了纤维素接枝聚甲基丙烯酸甲酯(Cell-g-PMMA)、纤维素接枝聚苯乙烯(Cell-g-PS)、纤维素接枝嵌段共聚物(Cell-g-PMMA-b-PS)和具有温度响应和pH响应的纤维素接枝共聚物(Cell-g-PDMAEMA)[25,76]. 采取相同的办法, Lin等人[30]制得了纤维素接枝聚甲基丙烯酸甲酯(Cell-g-PMMA); Wang等人[26]制得了纤维素接枝聚异戊二烯(Cell-g-PI). Hufendiek等人[29]通过进一步修饰纤维素基大分子引发剂, RAFT聚合合成了温敏性的纤维素接枝共聚物(Cell-g-PDEAAm和Cell-g- PNIPAM).

Shi课题组[77]以过硫酸钾、高锰酸钾等为引发剂, 合成了纤维素接枝聚丙烯酰胺(Cell-g-PAM). Li课题组[78]以过硫酸钾为引发剂, 在微波辅助下, 合成了pH响应和盐响应性的纤维素接枝共聚物(Cell-g-DMAEMA). Fu课题组[79]以过硫酸铵为引发剂, 通过自由基聚合得到了纤维素接枝聚丙烯酸(Cell-g-PAA), 其形成的微球可以吸附重金属离子(Cu^{2+}, Ni^{2+}, Fe^{3+}). 他们进一步的研究发现在微波辅助下仅需3 min就可以很好地合成出Cell-g-PAA[80]. Han课题组[81]以硝酸铈铵为引发剂, 通过双螺杆挤出机原位接枝聚合, 制得了纤维素接枝聚丙烯酰胺(Cell-g-PAM). Peng课题组[82]通过γ-射线辐射诱导聚合制得了纤维素接枝聚*N*-异丙基丙烯酰胺(Cell-g-PNIPAAm).

本课题组以4-二甲胺基吡啶(DMAP)为催化剂, 纤维素上的羟基为引发剂, 在较为温和的条件下, 通过引发丙交酯开环聚合合成出具有较宽聚乳酸含量和链长范围的全生物降解型的纤维素接枝聚乳酸(Cell-g-PLA)[83]和醋酸纤维素接枝聚乳酸(CA-g-PLA)[84], 具有合适接枝聚乳酸含量和接枝链长度的共聚物可以熔融加工, 实现了无外加增塑剂条件下的纤维素基材料的熔融加工. He课题组[85]也采用该方法合成了纤维素接枝聚乳酸, 并考察了其水解和酶解行为. Wang课题组[86,87]以辛酸亚锡为催化剂, 合成了纤维素接枝聚乳酸, 并通过自组装制得了纳米微球. 此外, Wang课题组[88]以辛酸亚锡为催化剂, 通过开环聚合反应合成了纤维素接枝聚对二氧环己酮(Cell-g-PPDO). Huang课题组[89]以4,4′-二苯基甲烷二异氰酸酯为交联剂, 将聚乙二醇接枝到纤维素上, 纤维素接枝聚乙二醇(Cell-g-PEG)具有较高的相变焓, 有望用作相变储能材料.

4 离子液体溶剂的回收

纤维素衍生化反应完成后, 通过加入与离子液体相容性好的极性溶剂(水、醇)将纤维素衍生物和未反应的非极性物质沉淀出来, 过滤后, 纤维素衍生物可通过溶解再沉淀的方式进行纯化, 对滤液可通过旋转蒸发、溶剂萃取等方式回收离子液体[8,9,11,90]. 利用回收离子液体再次作为衍生化介质, 所得纤维素衍生物的取代度与使用新鲜离子液体为介质时所得纤维素衍生物的取代度几乎完全一致[43].

但是, 蒸馏除杂质是一种比较耗费能量的方式. 更重要的是, 一些挥发性差的羧酸, 如长链烷基羧酸等, 很难通过挥发被除去[91]. 因此, 在纤维素均相衍生化的溶剂回收环节, 还需要开发一些有针对性且

高效的回收方法和技术.

5 展望

离子液体为纤维素均相衍生化提供了一个有效的、崭新的平台. 以离子液体为介质, 形形色色纤维素衍生物都已经被合成出来; 通过控制反应条件可以方便地调控反应程度. 与传统的非均相纤维素衍生化方法相比, 以离子液体为介质均相衍生化表现出一些显著的优点: 反应简便、高效, 反应过程中纤维素的降解程度轻, 产物均一性好, 产物结构易于控制, 溶剂可回收并反复使用. 随着越来越多的研究工作者加入到此领域的研究, 可以预计的是, 一方面, 将有更多新型结构的纤维素衍生物被合成出来, 也必将带来更多新奇的功能; 另一方面, 随着离子液体使用量逐渐增大以及工业化合成技术的不断优化, 离子液体价格不断降低, 因此, 以离子液体为介质的纤维素的均相衍生化工业化生产有望在某些品种的纤维素衍生物上获得实现.

需要指出的是, 在以离子液体为介质的纤维素均相衍生化技术获得工业化应用之前, 一些重要的基础理论问题和技术问题迫切需要加强研究: (1) 离子液体在长期反复使用过程中的结构变化与控制方法; (2) 产物分离与离子液体高效回收方法和技术; (3) 均相法制备的纤维素衍生物的结构与性能评价, 特别是与传统的非均相法所得纤维素衍生物结构和性能区别; (4) 更加高效的纤维素均相衍生化的新方法和新体系.

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Homogeneous synthesis of cellulose derivatives in ionic liquids

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Cellulose derivatives are important fine chemicals with a wide range of applications in modern industries, so that cellulose derivatization has been one of hot topics for a long time. However, the existence of numerous hydroxyls in cellulose also generates a well-developed intra- and inter-molecular hydrogen bonding network, thus natural cellulose is neither meltable nor soluble in conventional solvents. Until today, the preparation method for cellulose esters begins with a heterogeneous reaction between cellulose and a large excess of the acylation reagent in the presence of pyridine or sulfuric acid as the catalyst. These heterogeneous reactions cause some problems, such as uneven distribution of substituents, side reactions, time consumption and considerable degradation of cellulose. Homogeneous esterification of cellulose in appropriate media, the alternative procedure for heterogeneous process, has been one focus in cellulose chemistry. It not only provides opportunities to obtain the effective control of degree of substitution (DS), distribution and uniformity of the functional groups along cellulose chains, but also creates more options to induce novel and functional groups. Recently, the advent of ionic liquids that can dissolve cellulose provides a new and versatile platform for the efficient and homogeneous derivatization of cellulose. A variety of well-known, novel and functional cellulose esters have been successfully synthesized in ionic liquids. Meanwhile, development of esterification techniques, utilization of agricultural residues, and pilot scheme of up-scaling esterification in ionic liquids have been in progress continuously. This review summarizes the development in homogeneous synthesis of cellulose esters in ionic liquids published in the recent decade.

cellulose esters, ionic liquid, homogeneous derivatization

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