

·研究简报·

ϵ -己内酯在咪唑型离子液体中开环聚合*

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摘 要 报道 ϵ -己内酯在咪唑型离子液体([bmim][Cl])和氧化苯乙烯中的开环聚合. 离子液体同时起到了溶剂和催化剂的作用, 并且能够回收和循环使用. 氧化苯乙烯(SO)是开环聚合起始剂, 氢核磁谱分析表明聚己内酯(PCL)端基含有一个 SO 单元. 所得 PCL 的数均分子量为 4.22 ~ 6.86 kDa, 分子量分布小于 1.3. 该体系无需金属催化剂, 减少了有机溶剂的使用.

关键词 开环聚合, ϵ -己内酯, 离子液体

作为环境友好材料和生物医用材料的脂肪族聚酯因其生物降解性、生物相容性和低毒性等优点已经得到了广泛的应用^[1]. 制备脂肪族聚酯的途径有很多, 其中内酯、交酯和环状碳酸酯的开环聚合是最重要的方法之一. 这些开环聚合体系都需要金属配合物作为催化剂, 其中金属元素包括铝^[2,3]、锡^[4,5]、锌^[6]、镁^[7]、钙^[8]、稀土^[9~12]和其他金属^[13,14]. 金属催化剂通常对空气和水分敏感, 难以制备和保存. 聚合过程结束后, 消除残留的金属催化剂也是繁琐的步骤. 无金属的催化剂体系有良好的应用前景.

面对日益严重的环境污染问题, 学术界和工业界越来越重视避免有机溶剂的使用与排放. 近年来, 离子液体(IL)因其零蒸汽压、低燃性、低毒性和高热稳定性等特点^[15]引起了化学家们的兴趣, 被誉为绿色溶剂. Gong^[16,17]等报道了 ϵ -己内酯和碳酸三亚甲基酯在氧化锌或辛酸亚锡催化下、在离子液体[bmim][BF₄]₂中微波辅助开环聚合. Okada^[18]等报道了在离子液体[bmim][BF₄]₂、[bmim][PF₆]₂和[bmim][SbF₆]₂中用三氟甲磺酸稀土催化内酯开环聚合. 我们组^[19]曾报道 ϵ -己内酯在氯化稀土催化下、在离子液体[bmim][BF₄]₂和[bmim][PF₆]₂中开环聚合.

本文报道 ϵ -己内酯(CL)在价廉离子液体[bmim][Cl]₂中的开环聚合体系.

1 原料及试剂

ϵ -己内酯(Acros)和氧化苯乙烯(上海晶纯)经 CaH₂ 浸泡后减压蒸出, 氩气保护下保存. 1-丁基-3-甲基咪唑盐酸盐([bmim][Cl])离子液体参照文献方法^[20]制备. 其他试剂直接使用.

2 聚合及聚合物分析

所有聚合操作在氩气保护的无水无氧条件下进行. 聚合物用乙醇沉淀, 过滤, 干燥至恒重. 减压蒸馏除去滤液中的乙醇回收离子液体. 氢核磁共振谱(¹H-NMR)在 Bruker Avance DMX 400 超导核磁共振仪上测定, 氘代氯仿为溶剂, 四甲基硅烷为内标. 聚合物数均分子量及分子量分布由体积排除色谱(SEC)测定, 仪器为 Waters 1525, 分离柱为 Styragel HR4, HR3, HR1, 30℃ 四氢呋喃为流动相(1.0 mL/min), 窄分布聚苯乙烯为标样.

3 聚合结果及聚合物的结构

ϵ -己内酯(CL)在几个条件下的聚合结果列于表 1. 无 IL 或者无 SO 或者二者都不存在时, CL 不能聚合(表 1, run 1, 2 and 3), 离子液体(IL)和氧化苯乙烯(SO)是必要组分. [SO]/[IL] 摩尔比在 1.0 附近聚己内酯(PCL)的收率相对最高(表 1, run 5). 当[CL]/[IL] 摩尔比从 1.45 提高到 3.39, 130℃ 聚合 46 h, PCL 的收率从 4.4% 提高到了 64.2%(表 1, run 7 and 8). 所得 PCL 的数均分子量范围从 4.22 ~ 6.86 kDa, 分子量分布小于 1.3.

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Table 1 Ring-opening polymerization of CL in IL

Run	[CL]/ [IL] ^a	[SO]/ [IL]	Temp. (℃)	Time (h)	Yield (%)	M _n ^b (kDa)	M _w ^b (kDa)	PDI ^b
1	c	d	130	46	e			
2	c	f	130	46	e			
3	4.01	0	130	46	e			
4	4.55	0.55	130	24	14.7	6.50	7.48	1.16
5	4.55	1.29	130	24	33.2	6.80 ^g	7.98	1.17
6	4.55	2.61	130	24	12.1	6.32	7.27	1.15
7	1.45	1.19	130	46	4.4	4.22	5.27	1.25
8	3.39	1.19	130	46	64.2	6.82	8.82	1.29
9	3.51	0.80	130	46	56.7	6.65	7.91	1.19
10	4.22 ^h	0.96	130	46	65.4	6.86	8.41	1.22

^a Molar ratio; ^b Measured by SEC; ^c No IL added; ^d No SO added; ^e No polymer found; ^f [SO]/[CL] = 0.25; ^g M_n = 2.40 kDa by ¹H-NMR;

^h IL was recycled from run 9

PCL 的¹H-NMR 如图 1 所示,δ 7.46 到 δ 7.36 归属于 SO 苯环上的质子,4.07 (t,—COOCH₂—), 2.31 (t,—OCOCH₂—), 1.65 (m,—CH₂CH₂COOCH₂—CH₂—) 和 δ 1.39 (m,—COOCH₂CH₂CH₂—) 归属于 CL 单元. PCL 末端与羟基相连的亚甲基信号在 δ 3.65.

离子液体[bmim][Cl]可以回收和利用,乙醇终止反应得到产物 PCL. 减压蒸馏除去沉淀剂乙醇,回收得到离子液体. 回收的离子液体可以再次

使用(表 1, run 10),并表现出相同的聚合结果.

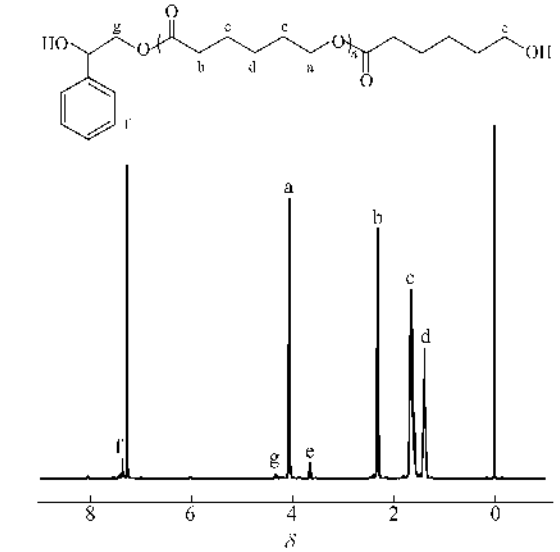


Fig. 1 ¹H-NMR spectrum of PCL (Table 1 run 5) containing a SO unit at one end

4 结论

报道了一种在价廉的离子液体中制备聚己内酯的方法. 离子液体[bmim][Cl]起到了溶剂和催化剂的作用并可以回收使用,氧化苯乙烯作为开环聚合起始剂. 所得到的端基为羟基的聚己内酯可能被用作增塑剂、扩链剂、交联剂等.

REFERENCES

1 Höcker H, Keul H. Adv Mater, 1994, (6): 21 ~ 36
2 Ouhadi T, Stevens C, Teyssié Ph. Makromol Chem Suppl, 1975, (1): 191 ~ 201
3 Liu Y C, Ko B T, Lin C C. Macromolecules, 2001, (34): 6196 ~ 6201
4 Okuda J, Rushkin I L. Macromolecules, 1993, (26): 5530 ~ 5532
5 Kowalski A, Duda A, Penczek S. Macromol Rapid Commun, 1998, (19): 567 ~ 572
6 Barakat I, Dubois Ph, Jérôme R, Teyssié Ph. Macromolecules, 1991, (24): 6542 ~ 6545
7 Yu T L, Wu C C, Chen C C, Huang B H, Wu J, Lin C C. Polymer, 2005, (46): 5909 ~ 5917
8 Zhong Z Y, Dijkstra P J, Birg C, Westerhausen M, Feijen J. Macromolecules, 2001, (34): 3863 ~ 3868
9 Stevels W M, Ankoné M J K, Dijkstra P J, Feijen J. Macromolecules, 1996, (29): 3332 ~ 3333
10 Shen Y Q, Shen Z Q, Zhang Y F, Yao K M. Macromolecules, 1996, (29): 8289 ~ 8295
11 Ling J, Shen Z Q, Huang Q H. Macromolecules, 2001, (34): 7613 ~ 7616
12 Shen Y Q, Shen Z Q, Shen J L, Zhang Y F, Yao K M. Macromolecules, 1996, (29): 3441 ~ 3449
13 Ito K, Yamashita Y. Macromolecules, 1978, (11): 68 ~ 72
14 Endo M, Aida T, Inoue S. Macromolecules, 1987, (20): 2982 ~ 2988
15 Kubisa P. Prog Polym Sci, 2004, (29): 3 ~ 12
16 Liao L Q, Liu L J, Zhang C, Gong S Q. Macromol Rapid Commun, 2006, (27): 2060 ~ 2064
17 Liao L Q, Zhang C, Gong S Q. J Polym Sci Part A: Polym Chem, 2007, (45): 5857 ~ 5863
18 Nomura N, Taira A, Nakase A, Nakase A, Tomioka T, Okada M. Tetrahedron, 2007, (63): 8478 ~ 8484
19 Xiong Yubing(熊玉兵), Fan Ling(樊玲), Shen Zhiquan(沈之荃). Chin J Catal(催化学报), 2006, (27): 75 ~ 78
20 Bohnote P, Dias A P. Inorg Chem, 1996, (35): 1168 ~ 1178

RING-OPENING POLYMERIZATION OF ϵ -CAPROLACTONE IN 1-BUTYL-3-METHYLIMIDAZOLIUM CHLORIDE IONIC LIQUID

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Abstract The ring-opening polymerization (ROP) of ϵ -caprolactone (CL) in 1-butyl-methylimidazolium chloride ([bmim][Cl]) ionic liquid (IL) and styrene oxide (SO) is reported without using any metal compounds. Both [bmim][Cl] and SO were essential in the ROP of CL. No polymerizations were found without [bmim][Cl] or SO or both of them under the same conditions. No poly(styrene oxide) was found by heating IL and SO indicating that the ROP of SO was absent or too slow to be detected. IL acted as both solvent and catalyst. SO was regarded as initiator since a ring-opened SO unit was found at one end of PCL chain according to the $^1\text{H-NMR}$ analysis. The molecular weights of the obtained PCLs were between 4.22 and 6.86 kDa with the molecular weight distributions less than 1.3. The [bmim][Cl] IL could be recycled and reused. The polymerization was quenched and the product was precipitated by the addition of ethanol. After PCL was isolated by suction, the filtrate was a homogeneous mixture of IL and ethanol. The latter was collected by distillation under reduced pressure and thus IL was recovered. The yield and the molecular weight of PCL obtained in the recycled IL were similar to those in the original one.

Keywords Ring-opening polymerization, ϵ -Caprolactone, Ionic liquid