研究论文

洗滤-萃取法去除原子转移自由基聚合法制备 PMMA-*b*-PLLA-*b*-PMMA 嵌段聚合物中的 Cu 离子

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摘 要 采用洗滤-萃取法去除原子转移自由基聚合法(ATRP)制备的聚甲基丙烯酸甲酯-聚 *L*-乳酸-聚甲基丙烯酸甲酯(PMMA-*b*-PLLA-*b*-PMMA)嵌段共聚物中残留金属 Cu 离子。结果表明,采用二氯甲烷(DCM)溶解共聚物,用水或酸水洗滤-萃取,当重复洗滤-萃取 5 次后,Cu 离子的去除率能达到 99%,所得嵌段共聚物的收率高于 80%。与过 Al_2O_3层析柱或溶剂溶解-沉淀方法相比,洗滤-萃取法操作简单、可节省大量的有机溶剂,具有工业化前景。

关键词 原子转移自由基聚合,聚甲基丙烯酸甲酯-聚 *L*-乳酸-聚甲基丙烯酸甲酯,Cu 离子的去除,洗滤-萃取法
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聚 *L*-乳酸(Poly-*L*-lactic acid,PLLA)是优良的可降解的生物材料之一,但 PLLA 质硬,缺乏柔性和弹性,极易弯曲变形[1],且聚乳酸玻璃化转变温度(T_g)低,热稳定差,限制了聚乳酸的应用[2]。近年来对聚乳酸改性方法主要是将 PLLA 进行共聚和共混等[3-4]。原子转移自由基聚合法(Atom transfer radical polymerization,ATRP)制备了聚甲基丙烯酸甲酯-聚 *L*-乳酸-聚甲基丙烯酸甲酯(PMMA-*b*-PLLA-*b*-PMMA)嵌段共聚物,以提高其热稳定性。但产物中残留有催化剂金属 Cu 离子,会降低聚合物的热降解温度[5]。常见的去除金属离子的方法主要有过 Al_2O_3层析柱[6-9]、溶剂溶解-沉淀[10-11]、离子交换法[12]和硅藻土吸附[13]等。Kokorin 等[14]采用了水体系中 SiO_2表面对 Cu 与 Bipy(2,2′-pyridine)、α-甲基吡啶酸混合物的吸附来除 Cu。然而,目前尚未有文献报道采用洗滤-萃取法去除 ATRP 法改性 PLLA 产物中的铜离子。本文比较了过 Al_2O_3层析柱和溶剂溶解-沉淀 2 种方法去除 Cu 离子的效果及对聚合物收率的影响,并提出了采用洗滤-萃取法去除该共聚物中 Cu 离子的新方法。

1 实验部分

1.1 试剂与仪器

PMMA-PLLA-PMMA,实验室自制;*L*-丙交酯(*L*-lactide,LLA),参照文献[15]方法合成和纯化[16],纯度>99%;α-溴丙酰溴,1,4-丁二醇,无水乙醇(EtOH),二氯甲烷(Dichloromethane,DCM),2,2′-联吡啶(2,2′-Bipyridine,Bipy),Al_2O_3,$CuCl_2$,以上试剂均为分析纯;CuCl 经 36% 乙酸清洗至白色,乙醇洗涤 2 次、真空干燥后使用;甲基丙烯酸甲酯(Methyl methacrylate,MMA)使用前未经纯化;四氢呋喃(tetrahydrofuran,THF)(韩国 Burdick & Jackson 化学公司),色谱纯。

凝胶渗透色谱仪(美国 Dionex 公司),色谱柱为 PL gel(Polymer laboratories Inc.,5 μm,300×7.5),工作温度 25 ℃;流动相 THF,流速 1 mL/min,窄分布聚苯乙烯标样(Polymer laboratories Inc.)作相对分子质量校准;PMMA-*b*-PLLA-*b*-PMMA 进样浓度 5 g/L;TAS-986 型原子吸收分光光度计。

1.2 实验方法

1.2.1 催化剂的溶解性实验 分别在 50 mL 锥形瓶中,量取加入 0.0036 g CuCl、0.0036 g $CuCl_2$、

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0.0110 g Bipy 和 0.0036 g CuCl + 0.0110 g Bipy,各加入 10 mL DCM、EtOH 和 H_2O,振荡观察溶解状况。

1.2.2　溶解-沉淀法除 Cu　锥形瓶中加入 0.1 g 粗 PMMA-*b*-PLLA-*b*-PMMA 及 10 mL DCM 完全溶解后,在大量乙醇中沉淀,过滤收集沉淀物,溶解、沉淀 3 次。将收集的固体在 60 ℃下真空干燥至质量恒定。分别计算收率($Y\%$)和除 Cu 率($R\%$):

$$Y = m_0/m_a \times 100\% ,\qquad R = (1 - w_a/w_0) \times 100\%$$

式中,m_0和 m_a分别为去 Cu 处理前后 PMMA-*b*-PLLA-*b*-PMMA 的质量(g);w_0和 w_a为去 Cu 处理前后聚合物中 Cu 的质量分数(mg/kg)。

1.2.3　Al_2O_3层析柱过柱法除 Cu　在砂芯玻璃柱管中装入适量 Al_2O_3制成高 10 cm、直径 1.5 cm 的氧化铝柱。在锥形瓶中加入 0.1 g 粗 PMMA-*b*-PLLA-*b*-PMMA,用 20 mL DCM 使其溶解。将该溶液过柱,每次用 10 mL DCM 荡洗锥形瓶冲洗柱子 3 次。收集滤液,旋转蒸发浓缩至约 5 mL,在大量乙醇中沉淀,滤出沉淀物,真空干燥至恒重。计算收率($Y\%$)和除 Cu 率($R\%$)。

1.2.4　洗滤-萃取法除 Cu　在锥形瓶中加入 1.0 g 粗 PMMA-*b*-PLLA-*b*-PMMA,用 20 mL DCM 使之完全溶解,转移入 250 mL 分液漏斗中,用 50 mL 去离子水或稀酸水溶液(50 mmol/L HCl)萃取多次。最后收集 DCM 相减压浓缩至约 5 mL,在大量无水乙醇中沉淀,过滤、真空干燥至恒重。计算收率($Y\%$)和除 Cu 率($R\%$)。

2　结果与讨论

2.1　溶解-沉淀法除 Cu 分析

CuCl、$CuCl_2$、Bipy 以及 CuCl/Bipy 等固体试剂在几种试剂中的溶解性能,结果见表 1。由表 1 可知,CuCl 在 DCM 中部分溶解,且 CuCl 遇水生成难溶性的黄色固体 CuO、$CuCl_2 \cdot 3H_2O$[17],用 DCM 转移产物时可通过过滤的方法去除一部分催化剂,残留的催化剂则主要为 $CuCl_2$和 Bipy 及 Cu/Bipy。

表 1　CuCl、$CuCl_2$和 Bipy 在几种溶解剂中的溶解性能

Table 1　Dissolubility of CuCl, $CuCl_2$ and Bipy in various solvents

Sample	Solvent		
	DCM	Ethanol	Water
CuCl	Insoluble. CuCl appeared as white powder. Changed a little in 2 days.	Insoluble. CuCl appeared as white powder.	Partly dissolving. Gradually, the CuCl (white powder) turned yellow in the solvent.
$CuCl_2$	Partly dissolving, and further dissolved while adding more solvent. The solution was pale green(almost colorless).	Dissoluble. And the solution turned blue green.	Dissoluble. And the solution turned light green.
Bipy	Dissoluble. The solution was colorless.	Dissoluble. And the solution was colorless.	Partly dissolving. The solution was colorless. A small amount of white powder at the bottom; While completely dissolution of adding solvent.
CuCl/Bipy	Partly dissolving. There was a small amount of white powder at the bottom. The solution was brown. After 1.5 h, the solution turned pale green. At last the green precipitation appeared.	Partly dissolving. And the solution turned black green. while there was a small amount of green powder at the bottom.	Partly dissolving. But there were both some yellow powder and a litter white powder.

Note: $4CuCl + 4H_2O + O_2 \longrightarrow 3CuO + CuCl_2 \cdot 3H_2O + 2H^+ + 2Cl^-$.

用溶解-沉淀法去除相对分子质量为 90317(GPC 法)的 PMMA-*b*-PLLA-*b*-PMMA 嵌段聚合物中 Cu 的效果见表 2。从表 2 可以看出,产物的收率不高(77%),且 Cu 去除率只有 92%,Cu 的残留量高达 54.26 mg/kg。此外,还需耗用大量有机溶剂。

2.2　Al_2O_3层析柱法除 Cu 分析

Al_2O_3的表面具有的大量 Al—OH 基团对铜的配位化合物具有很强的吸附作用[18]。去除 PMMA-*b*-PLLA-*b*-PMMA 中 Cu 的效果见表 2。

通过多次洗涤但产物仍无法洗脱,导致 PMMA-PLLA-PMMA 收率仅为 52%,说明 Al_2O_3对 PMMA-PLLA-PMMA 存在很强的不可逆吸附作用。此外,过柱法也不适于工业化生产。

表2 不同方法去除 PMMA-*b*-PLLA-*b*-PMMA 中 Cu 效果的比较

Table 2 Comparison of Cu removal by different methods from the copolymerization of PMMA-*b*-PLLA-*b*-PMMA

Method	Y/%	w_a(Cu)/(mg·kg^{-1})	R/%
Dissolution-precipitation method	77.10	54.26	92.0
Alumina column chromatography method	52.14	5.55	99.2
Washing-extraction method	83.07	~0	100

Note: $M_{n(PMMA\text{-}b\text{-}PLLA\text{-}b\text{-}PMMA)}$ = 90317 (by GPC); the original mass fraction of Cu-ion is 681.27 mg/kg in the sample.

2.3 洗滤-萃取法除 Cu 分析

PMMA-*b*-PLLA-*b*-PMMA 经洗滤-萃取法除 Cu 后, Cu 残留量接近于零, 且嵌段共聚物的收率(83.07%)在3种方法中最大(见表2)。

Al_2O_3表面的 Al—OH 团因其氢键作用可对 Cu 的配位化合物进行吸附,但 Al_2O_3吸附选择性较差,对目标产物 PMMA-*b*-PLLA-*b*-PMMA 也具有强烈的吸附作用,不利于产物处理;溶解-沉淀法是利用良性溶剂对聚合物的溶解、非良性溶剂对聚合物的沉淀作用,以此达到去除 Cu 离子的目的,但需大量的沉淀剂,成本较高;而洗滤-萃取则利用 Cu 离子在互不相溶的两溶剂间溶解度差异来达到去除的目的。

洗滤-萃取次数和所用溶剂量对除 Cu 的影响见表3。由表3可知,采用洗滤-萃取法,仅用10 mL 的 DCM 萃取5次后所得产物中的 Cu 基本可以完全去除(<10 mg/kg),而且聚合物的损失较小,无需使用大量有机溶剂,工艺简单,成本较低,环境污染较小,具有较好的工业应用前景。

表3 萃取次数、溶剂 DCM 用量的洗滤-萃取法除 Cu 效果

Table 3 Effects of extracting times and the amount of solvent DCM on Cu removal by washing-extracting method

c(DCM)/(mL·g^{-1})	Times	Y/%	w_a(Cu)/(mg·kg^{-1})	R/%	c(DCM)/(mL·g^{-1})	Times	Y/%	w_a(Cu)/(mg·kg^{-1})	R/%
200	3	89.18	48.53	92.9	20	5	87.43	~0	100
200	5	81.85	~0	100	10	5	86.35	7.03	99.0

Note: $M_{n(PMMA\text{-}b\text{-}PLLA\text{-}b\text{-}PMMA)}$ = 90317 (by GPC); DCM as solvent.

3 结 论

洗滤-萃取法可有效去除 PMMA-*b*-PLLA-*b*-PMMA 嵌段聚合物中的 Cu(几乎达到100%),且产物得率收高(>80%),不仅工艺简单,可节省大量有机溶剂,降低了成本,而且减少了环境污染,具有较好的工业应用前景。

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Removal of Cu-ion in Block Copolymer of PMMA-*b*-PLLA-*b*-PMMA Prepared *via* Atom Transfer Radical Polymerization by Washing-extraction Method

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Abstract This paper developed a washing-extraction method to remove the residual Cu-ion from the triblock copolymer of poly(methyl methacrylate)-*b*-poly(*L*-lactic acid)-*b*-poly(methyl methacrylate)(PMMA-*b*-PLLA-*b*-PMMA) prepared *via* atom transfer radical polymerization (ATRP). The result is that, when taking dichloromethane(DCM) as the solvent and water or acid as the extractant, the rate of removing Cu-ion can reach as much as 99% and the yield of the block copolymerization was more than 80% followed by washing and extracting 5 times. Compared with other methods, the washing-extraction method can not only save lots of organic solvent, but is also simple and effective. In addition, the washing-extraction method is a green technology, which might be used in the industry.

Keywords ATRP,PMMA-*b*-PLLA-*b*-PMMA,removal of Cu ion,washing-extraction method