Continuous Microwave-Irradiated Synthesis of Poly (D, L-Lactide)-co-Poly (Ethylene Glycol) Copolymer Under Atmosphere

ZHANG Ying-min, WANG Peng, LI Yue, LEI Hai-fen, JIAO Chun-yan, HAN Ning
(Research Center for Green Chemistry and Technology, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China)

Abstract: Poly (D, L-lactide)-co-poly (ethylene glycol) copolymer (PELA) of intrinsic viscosity 0.51 dL·g^{-1} had been prepared under continuous microwave-irradiation power of 90 W for 8 min at atmosphere. Effects of poly (ethylene glycol) (PEG) content, polymerization time on intrinsic viscosity and yield of PELA had been discussed. Furthermore, temperature rising behavior in reactants system was studied through copolymerization under continuous microwave oven and domestic microwave oven. The results showed that temperature of reactants system evolved smoothly without step under continuous microwave irradiation, which occurred under intermittent microwave irradiation in domestic microwave oven.

Key words: continuous microwave irradiation; polylactide; poly (ethylene glycol); copolymer
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Poly (D, L-lactide)-co-poly (ethylene glycol) (PELA), obtained through copolymerizing PEG into Poly (lactic acid) (PLA) chains, has not only the properties of PLA homopolymer, but also hydrophilicity, toughness, flexibility and so on which are not available in PLA homopolymer[1].

Microwave technology for organic synthesis reaction has been reported[2—3]. Nowadays most research of organic synthesis reaction are still concentrated on the domestic microwave ovens[4]. Because microwave is intermittently irradiated, reaction temperature rises at the presence of microwave irradiation and drops at the absence of it during reaction. Such a heating way is adverse to reaction. Moreover, power adjustment of domestic microwave oven is limited for several intervals and can't meet the actual requirement. In this paper, continuous microwave oven was used (2450 MHz), power output of which was continuous without intermittence and overcome the shortcomings of domestic microwave irradiation.

1 Experimental

1.1 Materials

The synthesis and purification of D, L-lactictide (DLLA) was according to ref[5]. Stannous octoate (Sn(Oct)$_2$) was used as catalyst. PEG-1000 and tetrahydrofuran (THF) were analytically pure.

1.2 Procedure

3 g DLLA and PEG—1000 in a certain proportion were weighed into a 50 mL beaker, Sn(Oct)$_2$ (0.40%) as catalyst then the beaker was placed on the heating-medium and was irradiated under microwave power of 90 W for minutes.

1.3 Measurements

Intrinsic viscosity of PELA was measured with an Ubbelohde viscometer in THF at 37℃. IR spectra were recorded on a Nicolet—670 FT-IR apparatus. ^{1}H-NMR spectra of polymer were recorded with a Bruker AC-P200 MHz apparatus.

2 Results and discussion

2.1 Effect of PEG content

In the Fig. 1, when PEG content was 1%, PELA with maximum intrinsic viscosity of 0.51 dL·g^{-1} was synthesized. It was considered that with PEG content increasing, chain transfer rate increased, which resulted in the halt of the chain growing, thus lowered copolymer viscosity.

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作者简介: 张英民 (1976年生), 男, 博士生; 通讯联系人: 王鹏; E-mail: pwang73@hit.edu.cn

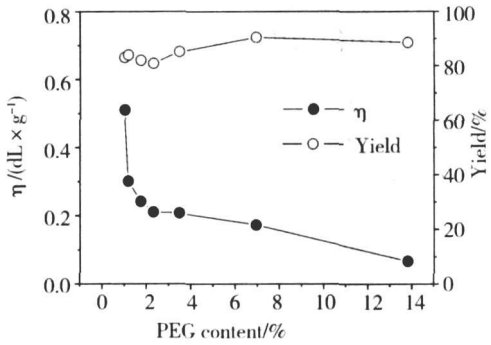

Fig. 1　Effect of PEG content

2.2　Effect of microwave-irradiated time

Fig. 2 shows that when polymerization time was less than 8 minutes, the temperature was not high enough and polymerization was not sufficient. The product had relatively low viscosity. But with polymerization time increasing, reactants temperature gradually rose and the copolymer viscosity increased. When time more than 8 minutes, reactants began to overheat and copolymer began to pyrolysis.

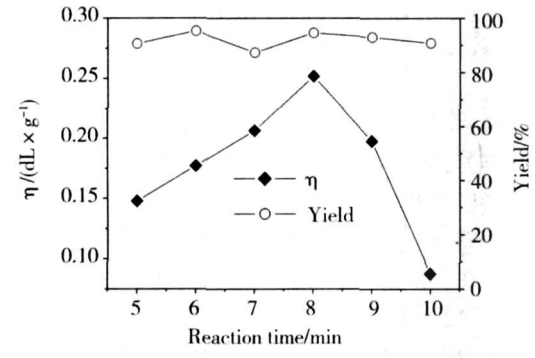

Fig. 2　Effect of microwave-irradiated time

2.3　Temperature rising behavior in reactants system

Fig. 3 shows that temperature of reactants system rose rapidly under continuous microwave irradiation, then kept relatively steady. It was worth to noting that temperature of reactants system evolved smoothly without step. However, under intermittent microwave radiation in domestic microwave oven, temperature of reactants system rose in the presence of microwave irradiation, fell in absence of microwave irradiation, so local temperature change behaved step. So the whole evolving tend of temperature of reactants system took an increasing look, but it was clear to find local temperature step, which led to the ununiformity of temperature field, affected the polymerization process seriously.

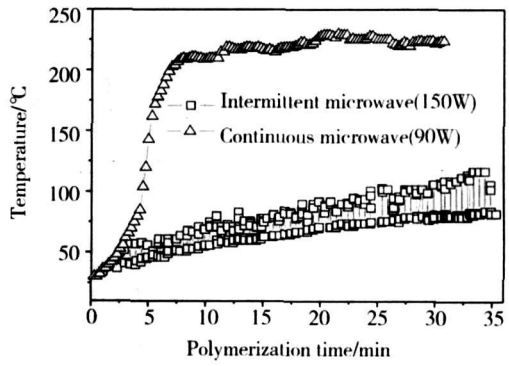

Fig. 3　Evolving of temperature of reactants system

3　Conclusions

(1) PELA was synthesized at atmospheric pressure without vacuum and inert gas under continuous microwave irradiation. This technique was suitable for large-scale preparation of PELA.

(2) In 8 minutes PELA of 0.5 dL·g⁻¹ intrinsic viscosity was obtained under 90 W power continuous microwave irradiation. Under optimum conditions, the yield was about 85%.

(3) Reactants system temperature increased faster and had no step under continuous microwave irradiation. But intermittent microwave radiation in domestic microwave oven did the opposite.

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超滤膜去除地下水中硝基苯的试验研究

赵玉鑫[1], 尹 军[1,2], 王晓玲[1], 刘 蕾[1]
(1. 哈尔滨工业大学 市政环境工程学院, 黑龙江 哈尔滨 150090;
2. 吉林建筑工程学院环境工程系, 吉林 长春 130021)

摘 要: 为解决持久性有机污染物对地下水造成的污染, 以硝基苯为研究对象, 考察了超滤膜对硝基苯的去除效果及影响因素。试验结果表明, 当进水硝基苯浓度为 85 μg/L, 超滤膜可以连续工作 68 h, 出水小于 17 μg/L, 地下水中铁、锰离子对去除效果没有显著影响。进水硝基苯浓度对去除效果有显著影响。当进水硝基苯浓度由 85 μg/L上升至 340 μg/L时, 超滤膜连续工作时间急剧下降, 仅为 14 h。对由硝基苯引起的膜污染, 2% CH_3CH_2OH清洗效果最佳。作为一项应急处理技术, 该工艺可以保障小城镇地区饮水安全。

关键词: 地下水; 持久性有机污染物; 超滤; 硝基苯
中图分类号: X523

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常压连续微波辐射法合成聚乳酸—聚乙二醇共聚物

张英民, 王 鹏*, 李 悦, 雷海芬, 焦春艳, 韩 宁
(哈尔滨工业大学 市政环境工程学院 绿色化学与技术研究中心, 黑龙江 哈尔滨 150090)

摘 要: 常压条件下、连续微波辐射功率 90W, 辐射时间 8min, 合成了特性粘度为 0.51 $dL\cdot g^{-1}$的聚乳酸—聚乙二醇共聚物 (PELA)。考察了聚乙二醇 (PEG) 浓度、聚合时间对共聚物特性粘度和收率的影响。此外, 实验研究了连续微波炉与家用微波炉中反应体系的温升曲线。结果显示, 相比于家用微波炉中的间歇微波辐射, 连续微波辐射下反应体系温度上升平稳无突跃。

关键词: 连续微波辐射; 聚乳酸; 聚乙二醇; 共聚物
中图分类号: TQ316.6+1