蓖　油基多功能单体及其聚酰胺设计

范静静[1] 江桃山[2] 汪钟凯[1,3*]

（1.安徽农业大学林学与园林学院生物质分子工程中心，安徽合肥 230036；2.安徽农业大学生命科学学院，安徽合肥 230036；3. 安徽省高性能生物尼龙工程中心，安徽农业大学轻纺工程与艺术学院，安徽合肥 230036）

摘要：植物油作为一种可再生生物质能源，由于其来源可再生广泛，价格低廉，且本身具有长链烃片段，在长链功能单体及其功能高分子材料设计上越来越受到人们的关注。目前现有合成长链二元单体的化学方法大多存在多步合成、催化剂昂贵、反应条件苛刻和产物分离困难等问题，并且大多缺乏功能性侧基。在这里，我们提出了一种合成长链多功能单体的简单、高效的方法，以蓖麻油衍生物十一烯酸甲酯（MU）为起始原料，通过双键环氧化得到十一烯酸甲酯环氧单体（EMU），再将其在常温常压下通过氨水进行开环反应得到含有羟基和仲胺基团的多功能长链二酯单体（DHMUA）。此单体可直接通过重结晶进行纯化，纯度可达到 98%。将所制备的单体通过熔融缩聚法应用于功能聚合物的制备。对于多功能单体的自缩聚，羟基和仲胺基团可以与酯基反应形成交联聚酰胺，通过调节不同聚合温度，可以得到一系列聚酰胺弹性体，经过 5 次循环拉伸后，其弹性恢复率高达 97%。对于多功能单体的共缩聚，将该多功能单体与 1,6-己二胺进行共聚，通过改变不同投料比，可以得到一系列热学性能可控、且具有优异机械性能的聚酰胺，拉伸强度最高为 43 MPa、断裂伸长率可达 265%。这种环氧-胺开环方法为生物质资源合成多功能单体和功能聚酰胺提供了新的思路。

关键词：蓖麻油；多功能单体；功能聚酰胺

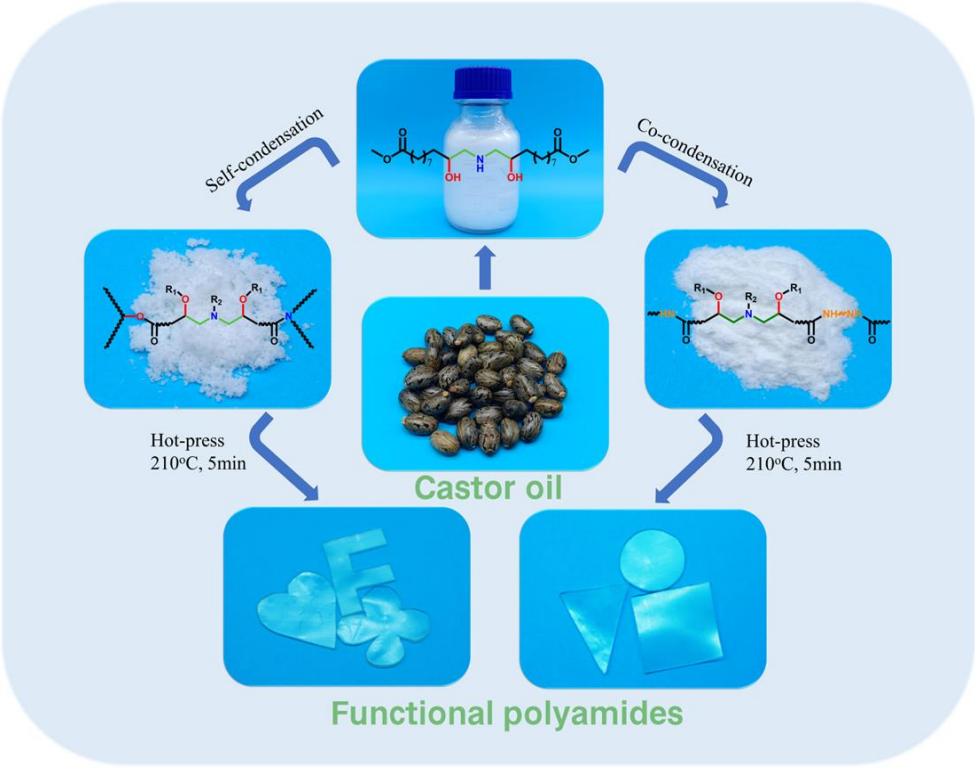

图 1 蓖麻油基多功能单体及其在聚酰胺设计中的应用

Fig. 1 Castor Oil-based Multi-functional Monomers and Their Application in Polyamide Design

Castor Oil-based Multi-functional Monomers and Their Application in Polyamide Design

Jingjing Fan[1], Taoshan Jiang[2], Zhongkai Wang[1,3,*]

(1.*Biomass Molecular Engineering Center, School of Forestry and Landscape Architecture, Anhui Agricultural University, Hefei, Anhui 230036, China;* 2. *School of Life Sciences, Anhui Agricultural University, Hefei, Anhui 230036, China;* 3.*Anhui Provincial Engineering Center for High Performance Biobased Nylons, School of Light Industry-Textile Engineering and Art, Anhui Agricultural University, Hefei, Anhui 230036, China*)

Abstract: As a renewable biomass energy, plant oil has attracted more and more attention in the design of long-chain functional monomers and their functional polymer materials due to its wide renewable source, low price, and have long-chain hydrocarbon fragments. At present, most of the existing chemical methods for synthesizing long-chain binary monomers still suffer problems such as multi-step reaction, expensive catalysts, harsh reaction conditions and difficult product separation, and most of them lack functional side groups. Here, we propose a simple and efficient method to synthesis long-chain multi-functional monomers. Methyl undecylenate epoxy monomer (EMU) was synthesized from the castor oil derivative methyl 10-undecenoate via double-bond epoxidation，and then to obtain long-chain multi-functional diester monomer (DHMUA) with hydroxyl and secondary amine active groups through ammonia ring opening of epoxides at room temperature and pressure. This monomer can be purified directly by recrystallization with a purity of 98%. The prepared monomer was applied to synthesize functional polymers by melt polycondensation. For self-condensation of the multi-functional monomer, the hydroxyl and secondary amine group can react with the ester group to form a series of polyamide elastomers by adjusting different polymerization temperatures, which possess elastic recovery of up to 97% after 5 times of cyclic stretching. For co-condensation of the multi-functional monomer, when the multi-functional monomer was copolymerized with 1, 6-hexamethylenediamine, a series of functional polyamides with controllable thermal properties and excellent mechanical properties can be obtained by changing the different ratios, with tensile strength up to 43 MPa and elongation at break up to 265%. The epoxy-amine ring opening synthesis method provides a new idea for the synthesis of multi-functional monomers and functional polyamide from biomass.

Key words: castor oil, multi-functional monomer, functional polyamide