木本油基 *E*-十八碳-9-烯二 的合成及其聚酰胺性能研究

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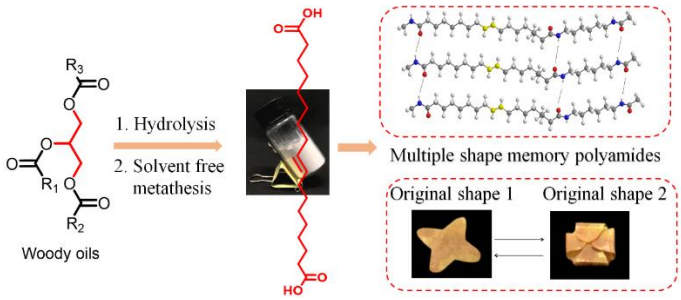
摘 要：尽管人们做出了巨大的努力将木本油转化为有价值的化学品，但大多数已知的实验方案仍然需要繁琐的步骤和严苛的条件。本工作发展了一种将木本油脂转化为长链不饱和二羧酸的简单且高效的方法。这一策略有望开辟木本油脂高值化利用的新途径。由于木本油脂通常含量复杂且含有大量多不饱和脂肪酸，这些特点使其难以通过自复分解合成高纯度二羧酸单体。本研究首次以橡胶籽油（*RSO*）、乌桕梓油（*SSO*）等木本油为原料，通过烯烃自复分解反应合成了 *E*-十八碳-9-烯二酸（C18）功能聚酰胺单体，并用核磁共振波谱（NMR）和傅立叶变换红外光谱（FTIR）对其结构进行表征。作为比较，高油菜籽油（*HOCO*）也被转化为 C18。通过对反应条件进行优化得到最优条件为：在无溶剂条件下，以 1 mol% G Ⅱ进行烯烃自复分解，木本油脂肪酸转化率较高，C18 得率也较高。以不同植物油为原料得到的纯 *E*-十八碳-9-烯二酸单体，与 1，6-己二胺直接溶液缩聚得到不饱和聚酰胺。根据原料的不同，将制备的聚酰胺定义为 *RSO-PA*、*SSO-PA* 和 *HOCO-PA*，并通过 FTIR 和固态碳核磁共振谱（^{13}C CP/MAS NMR）对其结构进行了表征。值得注意的是，通过多种测试方法，例如热力学分析方法（DSC）、热重分析（TGA）、动态力学分析（DMA）和拉伸测试，证实了该长链不饱和聚酰胺具有良好的热力学性能，具有取代石油基聚酰胺成为工程塑料的潜力。有趣的是，由于较宽熔融峰和玻璃化转变的存在，制备得到的长链聚酰胺具有多重形状记忆性能，在航空航天、自动控制系统、火灾传感装置等领域具有广阔的应用前景。



关键词：木本油脂；烯烃复分解；*E*-十八碳-9-烯二酸；长链不饱和聚酰胺；形状记忆

The conversion of woody oils into *E*-octadec-9-enedioic acid and multiple-shape memory polyamides

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Abstract: Although tremendous efforts have been made to convert woody oils into valuable chemicals, most of the known protocols still require multi-step procedures and rigorous conditions. Herein, a highly efficient method for converting woody oils into long-chain unsaturated dicarboxylic acid was reported. Such a strategy holds promises for opening new routes for utilizing woody oils. Firstly, self-metathesis of fatty acids from *Rubber seed oil* (*RSO*), *Sapium sebiferum oil* (*SSO*) and *High oleic Canola oil* (*HOCO*) were optimized. Pure *E*-octadec-9-enedioic acid monomer (C18) was obtained, and confirmed by ^{1}H NMR and FTIR spectra. The prepared dicarboxylic acid was then experienced condensation polymerization with 1,6-hexamethylenediamine. The

chemical structures of the obtained polyamides were investigated by FTIR and 13C NMR spectra. DSC, TGA, DMA, and tensile testing was used to explored their thermal and mechanical properties. Interestingly, due to the existence of broad melting and glass transition, the prepared polyamides possess multiple-shape memory properties. These results indicate that the biobased *RSO-PA* synthesized with a green facile method could be a promising alternative for various applications in aerospace, automatic control systems, fire sensing device, and other fields.

Keywords: woody oil; self-metathesis; *E*-octadec-9-enedioic acid; polyamide; shape-memory