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Synthesis of aliphatic polyesters from a bio derived AB monomer

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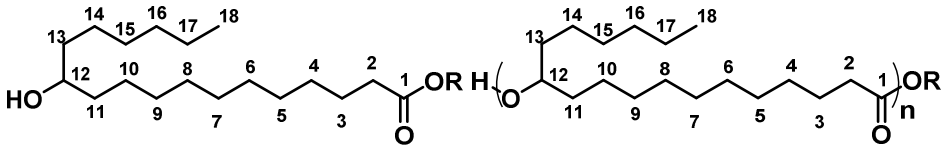
Abstract

12-Hydroxy stearic acid (12-HSA) is a bio-renewable material which is readily available inlarge quantities from castor seed oil [1]. 12-HSA is aα, ω- hydroxy carboxylic acid and can beconsidered as an AB monomer having one carboxylic acid and one secondary hydroxyl group.However, there is very little mention of this compound in the literature as a monomer for melt polymerization[2].

Commercial 12-HSA, as obtained from natural sources, has saturated and unsaturated monocarboxylic acids as impurities. Such monofunctional impurities are not desirable since they actas chain terminators. Therefore, it is necessary to purify 12-HSA prior to studying itspolymerization chemistry.

In this work we have explored several methods for purification of commercial 12-HSA tomonomer grade purity. These include reported methods such as selective extractionas well asconverting 12-HSA to derivatives which can be more readily purified. Such derivatives can beeither polymerized by themselves or can be used to regenerate 12-HSA.

Two derivatives of 12-HSA, namely, methyl-12-hydroxystearate (Me-12HS) [3] and methyl-12-acetoxyoctadecanoate [4] were prepared. These derivatives could be vacuum distilled. The productobtained had high purity as evidenced by the m.p. as well as b.p. and the absence of any extra peaks in NMR.



Where, R=H, -CH_3

Figure 1. Chemical structure of 12-HSA derivatives and its polyesters.

12-HSA, obtained after purification, was subjected to polyesterification using DCC as thecondensing agent. Me-12HS was subjected transesterifcation as well as transesterifcation-polycondensation usingtitanium isopropoxide and distannoxane catalysts. The degree of polymerization increased by 3-4units every 3 h. After 24 h the number average degree of polymerization was found to be 4000-4500 g/mol in both the cases. The rate of polymerization, as evidenced by the change of DP withtime, indicates that the rate is faster with a titanium based catalyst. MALDI-ToF analysis showsthe formation of cyclics along with linear chains.

It is recognized that 12-HSA or its derivatives having a secondary hydroxyl group may besluggish in polycondensation chemistry. This coupled with the fact that intramolecular reactionscan compete with chain growth reaction in the melt phase adds to the complexity ofpolymerizing this monomer.

References :

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