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Synthesis of Polyester from Renewable Feedstock: A comparison between microwave and conventional heating

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Synthesis of polyester using 2-dodecenyl succinic anhydride (DDSA) and renewable glycerol was attempted to generate polymer with control functionality. Conventional (hot plate) and microwave heating were used to accomplish polycondensation reaction. Conventional heating was found suitable to yield polymer whereas microwave heating failed to generate polyester using DDSA and glycerol.

Synthesis of functional polyesters from renewable monomers is of great interest in polymer research[1-3]. Therefore, in this study, we have investigated the synthesis possibility of polyester (with free hydroxyl groups) using glycerol, which offers a selective modification of the available alcohol groups due to the difference in reactivity[4]. A similar approach was utilised previously to synthesise Poly(glycerol adipate) (PGA) polymer[5, 6]. However, to impart hydrophobicity, free hydroxyl groups were substituted with fatty acid chains and thus any further opportunities of post functionalization with additional functional groups of interest is diminished.

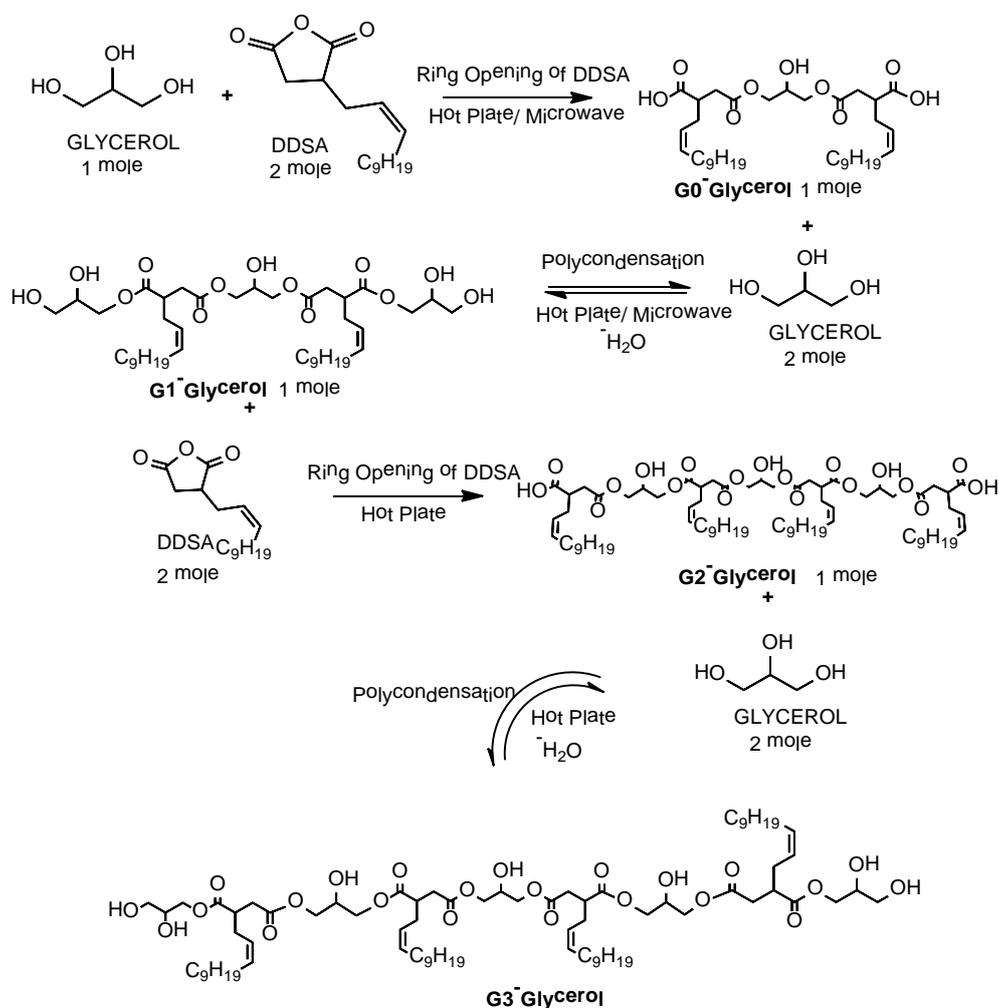
Considering the above mentioned limitation, we have selected a more hydrophobic derivative of succinic anhydride named 2-dodecenyl succinic anhydride (DDSA) to synthesise polyester. DDSA has been widely used to modify biopolymers and resins[7]. The synthesis of alkenyl succinic anhydride was reported from sunflower oil and therefore, it could be a potential

renewable monomer[8]. Use of organic solvents was avoided to generate a solvent free product and to reduce the synthesis cost of the oligomers.

Microwaves as a heat source have been known to lower the reaction temperature and time[9, 10] to make synthesis processes more commercially viable, eco-friendly, and it reduces the potential of the generation of unwanted by-products[11, 12]. Therefore, microwave assisted synthesis was also considered to validate the obvious advantage of this technique. Initially, the synthesis of polyester via polycondensation was tried at high temperature under vacuum but unfortunately, we always got cross-linked material. Therefore, a step-wise approach was selected to synthesise the oligomers and polymers of DDSA in order to increase the level of control that could be exercised over the final polymeric structure. An additional reason behind adopting this strategy was to establish the characterization data of oligomers of different molecular weight with free hydroxyl unit.

Synthesis approach to prepare oligomers of DDSA and glycerol were described in Scheme 1. The G0-Glycerol was synthesised by reacting DDSA with glycerol in bulk without using any catalyst. It was expected that when two moles of DDSA were allowed to react with 1 mole of glycerol, the reaction preferentially occurring at the terminal primary hydroxyl groups. Consequently, the resulting product will have one free secondary alcohol group in its structure due to the latter's higher steric hindrance and low reactivity[13]. It is well known that polyoxyethylenesorbitan monooleate (Tween 80, molecular weight ~1310 Da) is a powerful surfactant[14] and therefore the target molecular weight of 1500 Da was decided for the synthesis of DDSA-glycerol oligomers. Conversion of monomer to oligomer was monitored by ¹H-NMR. The disappearance of the peak at 3.2 ppm (vinyl proton of DDSA and proton associated with anhydride ring, Figure S-1) and appearance of proton peak created after the ester bond formation at 4.0-4.5 ppm suggested the conjugation of DDSA with glycerol *via* an ester bond. 100% conversion of anhydride to acid was observed within 7 hrs at 120 °C. The ¹H-

NMR and MALDI-TOF MASS of the obtained product with the designated peaks were presented in Figure S-2. However, the proton peaks in NMR at 5.1, 5.3 and 3.6-3.8 ppm and additional peaks in MALDI-TOF MASS were also detected which are associated with the tri-substituted and partially substituted glycerol (Table S-1, entry 1, 3 and 5). Therefore, the same reaction was then repeated using a microwave (Sairem miniflow 200SS) heating with the objective of getting the cleaner product in less time. The same level of conversion was achieved in just 2 hrs at 80 °C, but the problem of undesired products remains. Nevertheless, the intensities of these peaks are very low, suggesting that the majority of the sample contains desired structure.



Scheme 1 Schematic presentation of the synthesis of DDSA-Glycerol oligomer via ring opening and polycondensation reaction

Subsequently, the synthesis of a higher generation of DDSA-glycerol polymeric species using phosphoric acid as a biologically acceptable catalyst was first attempted with the aid of microwave heating due to its apparent advantage over hot plate method. However, unfortunately, the oligomer G0-Glycerol was found to reflect almost 90% of supplied microwave power (electromagnetic radiation). To identify the reason behind this, dielectric properties of the oligomer G0-Glycerol and glycerol were measured and loss tangent ($\tan \delta$) value was calculated. $\tan \delta$ is the ratio of dielectric loss (ϵ'') and dielectric constant (ϵ') and thus higher the value of $\tan \delta$, more the ability of a material to absorb microwave heating [15, 16]. Calculated $\tan \delta$ values at different working temperature were plotted (Figure 1) to find the optimum temperature for reaction. It was found that glycerol can able to convert the sufficient amount of stored electromagnetic radiation into heat whereas oligomer G0-Glycerol is not capable of doing the same ($\tan \delta < 0.1$). It was reported that a compound with a $\tan \delta$ value less than 0.1 would not respond better towards microwave heating [17]. The reason for this behaviour of G0 oligomer towards microwave heat might be linked with the decrease in the compound polarity. Since G0 contains 2 units of DDSA, this makes the oligomer very hydrophobic, and thus the microwave radiations might be reflected [18]. Therefore, it was concluded that the microwave heating method was not the best way to synthesise DDSA-glycerol oligomer.

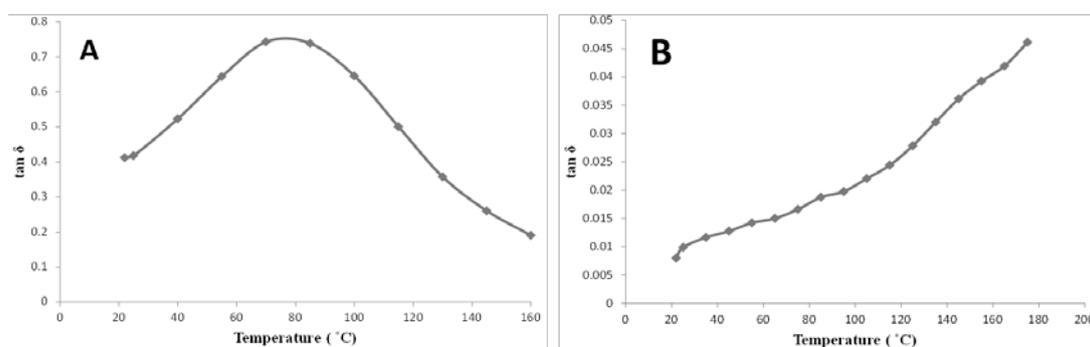


Figure 1 Effect of temperature on loss tangent ($\tan \delta$) (A) Glycerol and (B) G0 Oligomer

Consequently, the oligomers up to G3 was then synthesised using hot plate method and reaction was monitored by $^1\text{H-NMR}$. The increment in the number of protons at position 4.0-4.5 ppm in $^1\text{H-NMR}$ with respect to vinyl peak protons of DDSA chain confirm the conjugation of further moieties of DDSA and glycerol (Figure S-3). Higher molecular weight peaks detected in MALDI-TOF MASS spectra further confirmed the synthesis of desired oligomers (Figure S-4). However, both of the characterisation techniques suggested the presence of undesired species along with the product. It was expected that the presence of long alkyl side chain on DDSA molecules imparts the hydrophobicity to the resultant polymer thus could yield the micelles with low CMC value. However, on the other hand, this alkyl side chain was also responsible for steric hindrance that may have caused an incomplete reaction in the polyesterification processes, which in turn generated side products.

Hence, it was concluded that microwave assisted synthesis to achieve a polymer with free functional groups using DDSA and glycerol is not possible with the reported condition. Though, oligomers of these building blocks had been successfully synthesised *via* conventional heating but with random free hydroxyl groups. Purification at this stage was found to be challenging and therefore synthesis of higher molecular weight polymer is underway, which could have different properties and can be utilized for purifying final product from oligomers. Nevertheless, we have reported a facile synthesis method to generate highly hydrophobic biobased material, and it could be used e.g. to fabricate nanoparticles for biomedical applications and to generate functional amphiphilic polymers.

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