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Synthesis of polyester from renewable feedstock: a comparison between microwave and conventional heating

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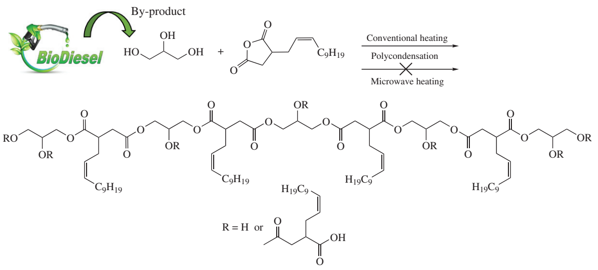
Synthesis of polyester using (dodec-2-enyl)succinic anhydride and renewable glycerol was carried out to produce a polymer with controlled functionality. Conventional (hot plate) heating was found suitable to obtain oligomers, while the microwave heating was useful only at the first step of the process.



Synthesis of functional polyesters from renewable monomers is of great interest in polymer research[1–3] due to the large-scale industrial needs for polymers of this class in addition to a common trend of the replacement of petroleum precursors by renewable ones. In this work, we have investigated the opportunity to synthesize the polyester bearing free hydroxyl groups from glycerol by considering the selective reactivity of alcohol groups.[4] A similar approach was previously reported for the synthesis of poly(glycerol adipate).[5,6] However, to impart hydrophobicity, the free hydroxyl groups in the latter were esterified with fatty acids, which hinders further functionalization with additional functional groups of interest.

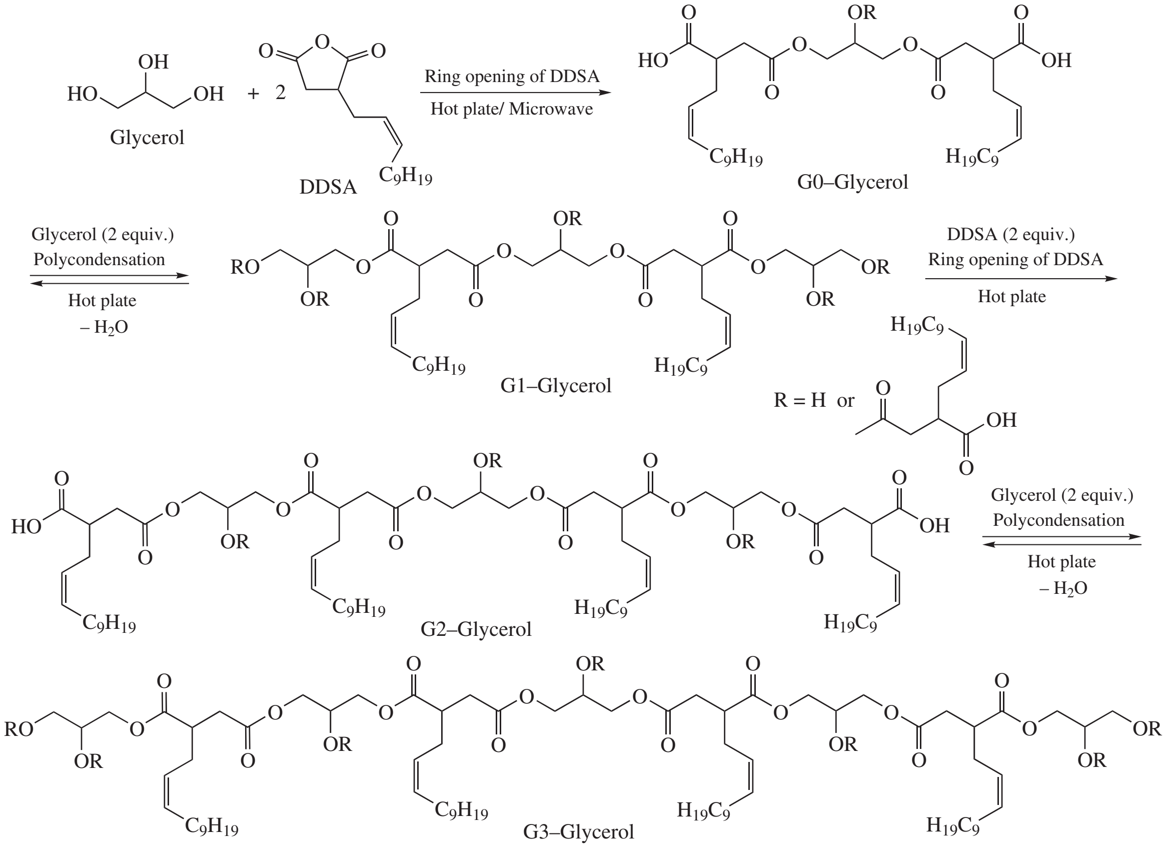
Taking into account the above mentioned limitation, we have selected a more hydrophobic derivative of succinic anhydride, (dodec-2-enyl)succinic anhydride (DDSA), for the polyester synthesis. DDSA has been widely applied for modifications of biopolymers and resins.[7] The synthesis of alkenylsuccinic anhydride from sunflower oil has been reported, which could make DDSA a potentially renewable monomer.[8] In order to generate a solvent-free product and to reduce the cost of oligomer synthesis, reactions were performed in bulk.

Microwave radiation as a heat source has been known to decrease the reaction temperature and time[9,10] to make synthesis processes more commercially viable and eco-friendly and, at the same time, reducing the potential of generation of unwanted by-products.[11,12] Thus, the microwave assisted synthesis was also implemented in this work. The one-step synthesis of polyester at a high temperature *in vacuo*, unfortunately, resulted in a cross-linked material. Therefore, a step-wise approach was selected for the preparation of oligomers and polymers from DDSA in order to increase the level of control over the final polymeric structure. An additional reason behind adopting this strategy was the acquisition of characterization data on oligomers possessing different molecular weights and containing free hydroxyl units.

Scheme 1 shows the synthetic approach to prepare oligomers of DDSA and glycerol. The G0–Glycerol was obtained from DDSA and glycerol without using any catalyst. It was expected that the reaction of two equivalents of DDSA and one equivalent of glycerol would preferentially result in the esterification of terminal (primary) hydroxyl groups of glycerol and the product would contain one free secondary alcohol group due to a higher steric hindrance and low reactivity of the latter.[13]

Since polyoxyethylenesorbitan monooleate (Tween 80, molecular weight of ~1310 Da) is known as a powerful surfactant,[14] the molecular weight of 1500 Da was initially selected as the target value for the DDSA–glycerol oligomers. Conversion of monomers into oligomers was monitored by ^{1}H NMR spectroscopy. A shift in the peak observed between 3.0–3.2 ppm to below 3.0 ppm (proton peak associated with anhydride ring, Figure S1, Online Supplementary Materials) and appearance of a signal at 4.0–4.5 ppm indicating the ester bond formation proposed the attachment of DDSA to glycerol *via* an ester bond. The full (100%) conversion of anhydride into acid was observed within 7 h at 120 °C. However, additional signals were also detected in ^{1}H NMR and mass spectra of the obtained product (5.1, 5.3 and 3.6–3.8 ppm in ^{1}H NMR, Figure S2), which were related to tri-substituted and partially substituted glycerol (Table S1). Thus, to obtain a more clean product in shorter time, the reaction was performed upon the microwave heating. The same conversion was achieved within 2 h at 80 °C, but the undesired products were still present. Nevertheless, the sample mostly contained the desired product since the intensities of impurity signals were very low.

Subsequently, the synthesis of DDSA–glycerol species with an elongated chain using phosphoric acid as a biologically acceptable catalyst was initially attempted upon microwave heating due to its apparent advantages over the hot plate method. Unfortunately, oligomer G0–Glycerol was reflecting almost 90% of the supplied



Scheme 1 Synthesis of DDSA–Glycerol oligomers *via* ring opening and polycondensation reactions.

microwave power. To identify the reason of such behaviour, dielectric properties of this oligomer and glycerol were measured, and the loss tangent (tanδ) value was calculated as the ratio of dielectric loss (ε'') to the dielectric constant (ε'). The higher value of tanδ indicates a higher ability of the material to absorb the microwave radiation.[15,16] The calculated values of tanδ at different operating temperatures were plotted (Figure 1) in order to estimate the optimal temperature for this reaction. It was found that glycerol is capable of converting a sufficient amount of stored electromagnetic radiation into the heat, while oligomer G0–Glycerol was not (tan$\delta < 0.1$). It is known that a compound having value tanδ less than 0.1 would not efficiently interact with microwave heating.[17] This behaviour of oligomer G0–Glycerol might be associated with a decrease in the compound polarity. Since G0–Glycerol contains 2 units of DDSA, which makes the oligomer very hydrophobic, the microwave radiation can be reflected.[18] Therefore, the microwave heating method was not appropriate for the preparation of DDSA–glycerol oligomer.

The hot plate method allowed us to synthesize the oligomers up to G3–Glycerol (^{1}H NMR monitoring). The increments in the number of characteristic protons (at 4.0–4.5 ppm in ^{1}H NMR) with respect to the olefinic protons of DDSA chain confirmed the binding of additional moieties of DDSA and glycerol (Figure S3). The peaks of higher molecular weight observed in the mass spectra have confirmed the formation of desired oligomers (Figure S4). However, both ^{1}H NMR and mass spectra also indicated the presence of undesired species together with the product. It was expected that the presence of long alkyl chain in DDSA molecules imparts the hydrophobicity of the resulting oligomer thus could yield micelles with a low critical micellar concentration. On the other hand, this alkyl side chain was also responsible for a steric hindrance that may cause incomplete polyesterification process, which could also lead to the side products.

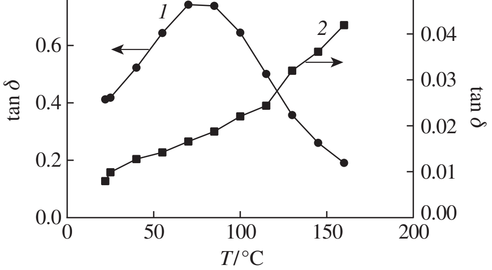


Figure 1 Effect of temperature on loss tangent (tanδ) of (*1*) glycerol and (*2*) G0–Oligomer.

In conclusion, the microwave assisted synthesis is not appropriate for the considered reaction. The desired oligomers have been successfully synthesized from DDSA and glycerol *via* conventional heating, but with random free hydroxyl groups. Since the purification of products was challenging, the synthesis of oligomers with higher molecular weights as well as the desired polymer remains under development. Nevertheless, the developed facile synthetic method allows one to produce the highly hydrophobic material from the renewable precursors, which could be applied, *e.g.*, to design nanoparticles for biomedical applications, to generate functional amphiphilic polymers, *etc*.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.03.021.

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