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To be cited as: *ChemSusChem* 10.1002/cssc.201800446

Link to VoR: http://dx.doi.org/10.1002/cssc.201800446

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FULL PAPER

Lipase Catalysed Synthesis of Furan Based Oligoesters and their Self-Assembly Assisted Polymerization

Kumarasamy Muthusamy,[a] Krishnamoorthy Lalitha,[a] Yadavali Siva Prasad,[a] Ayyapillai Thamizhanban,[a] Vellaisamy Sridharan,[a,b] C. Uma Maheswari[a] and Subbiah Nagarajan[a,c]*

Dedication ((optional))

Abstract: Bio-based polyesters are well-known biodegradable materials that are frequently used in our daily life, which include food industries and biomedical fields. The journey towards the development of sustainable polymer materials and technology postulate the replacement of traditionally using petrochemical-based monomers, transition metal catalyst, and more intensive purification techniques, which do not agree with the green chemistry principles. This contribution investigates the synthesis of bio-based hydrophilic and hydrophobic oligoesters, which in turn derived from easily accessible monomers of natural resources. In addition to the selection of renewable monomers, Novozyme 435, an immobilized lipase B from *Candida antarctica* was used for the oligomerization of monomers. The reaction condition for oligomerization using Novozyme 435 was established to get moderate to good yield. The average number of repeating unit and molecular weight distribution of hydrophilic and hydrophobic oligoester was identified using NMR, GPC and Mass spectral analysis. To our delight, oligoester derived from hydrophilic monomer was found to self-assemble to form a viscous solution, which on further heating resulted in the formation of polymer *via* the intermolecular Diels-Alder reaction. The viscosity of solution and assembly of oligoester to form fibrous structure was investigated by rheological studies, XRD and SEM analysis. Molecular weight of cross linked polymer was identified using MALDI mass spectral analysis. Thermal properties of bio-based polymers were investigated using TGA and DSC analysis. For the first time we are reporting the assembly assisted polymerization of oligoester using intermolecular Diels-Alder reaction, which would initiate a new avenue in polymer science field.

Introduction

From the environmental perspective, particularly the finite availability of fossil resources, increased demand of non-renewable raw materials and CO_2 emission contributing significantly to global warming have emphasized the researchers to focus on renewable feedstock for the fuel, value-added chemicals and monomers for polymer synthesis.[1-4] In the field of polymer chemistry, implementation of strict environmental regulations to reduce the carbon content,[5] pollution and other concerns influenced the demand of biopolymers and plastics, and projected to perceive a CAGR of 12% from 2016 to reach a market size of USD 5.08 billion by 2021.[6] Consequently, there has been an increasing interest in utilization of bio-based monomers derived from renewable resources for developing environmental friendly and renewable polymeric materials.[7-9] Generally, natural resources such as vegetable oils, carbohydrates, lignin, cardanol, catechins, terpenes, rosins and organic acids are used in the production of high performance bio-based polymers.[10] Thus far, polyesters are frequently used commodity polymers in our daily life which include biomedicine for bone fixation, ligament attachment, surgical sutures, food containers, packing, fibers, biodegradable films, surface coatings, composites, plasticizers, membrane filters, wound healing accelerators, controlled drug delivery system and scaffold for cell and tissue growth.[11] In practice, polyesters were derived from petroleum-based diacids and diols with metallic alkoxides or transition metals as catalyst.[12] However, in recent years, as a concern on environmental pollution and energy storage, functional monomers derived from renewable feedstock are promising candidates for bio-based polyester synthesis in both academic and industrial sectors.[13,14] Among the various bio-derived functional monomers available for the synthesis of green polyester synthesis, 5-hydroxymethyl furfural is considered as one of the most promising platform chemical derived from carbohydrates such as glucose, fructose, sucrose and cellulose.[15-17] Continuous effort has been devoted for the synthesis of bifunctional monomers such as 2,5-furandicarboxylic acid (FDCA), 2,5-bis(hydroxymethyl)-furan (BHMF) and 5-oxy(bismethylene)-2-furaldehyde from HMF.[18-20] Recently, US Department of Energy (DOE), DuPont Industrial Bioscience and Archer Daniels Midland Co. has declared FDCA as one of the most important value added chemicals, which is having the potential to generate exciting high-performance renewable materials in the 21st century.[21,22] By employing FDCA as a platform chemical, a wide variety of renewable polymers were generated[23,24] with biocompatibility, good thermal and electrical conductivities, for example, poly(ethylene-2,5-furandicarboxylate) (PEF), structural analogue of poly(ethylene terephthalate) (PET) have excellent thermomechanical and barrier properties than PET.[25,26] Despite the potential application of FDCA based polymers such as polyesters,[27] polyamides,[28] epoxy resins[29] in producing bioplastics,[30] 3D printing,[31] coatings

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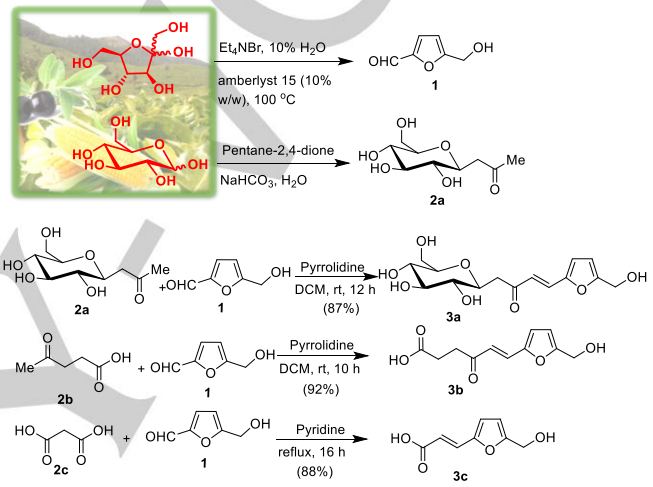
Supporting information for this article is given via a link at the end of the document.

in automotive and marine industries,[32] fabricating biomedical devices,[33] etc., an intensive investigation on environmental friendly synthesis for bio-based polymer and advanced method for generating high molecular weight polymers have not been completely explored. Most of the protocols reported for the synthesis of bio-based polymers displaying various physical and chemical properties involves harsh reaction conditions, metal catalysts and intense purification steps.[24] In order to maintain sustainable society, a widely accepted concept "green polymer chemistry" has to be introduced in each and every step.[35-38] Thus, the enzymatic polymerization is desirable, which allows precise synthesis of bio-based polyesters under mild reaction condition with control in structure, substrate, functional group, stereo- and regioselectivities.[39] Moreover, polymerization using enzymatic reactions show high catalytic efficiency without forming any side products, and after the completion of reaction enzymes can be separated easily either by filtration or centrifugation.[40-42] Eventhough a wide range of enzyme catalysts available for the synthesis of macromolecules, *Candida antarctica* lipase B (CALB) possesses many desirable advantages including compactable with a magnitude of substrate and solvent, regio- and enantioselectivities.[43,44] The immobilized form of CALB, Novozyme 435® displayed high potential in polyester synthesis because of its reusability, enhanced thermal stability, propensity toward bulky substrates and stable catalytic performance in various chemical environment.[45,46] Recently Kobayashi and coworkers have briefly discussed the production of value-added functional macromolecules *via* an environmental friendly enzyme catalysis method.[47] He emphasized the significance on migration of petroleum-based processes to enzymatic renewable-resource based processes, that contribute to the sustainable society for the future. Overall, perceiving the practical application of bio-based polymers in biomedical, drug-delivery, pharmaceutical and other areas, there is a demand to develop functional bio-based polymers using green polymer chemistry.[48] In this study, we present a sustainable approach toward furan-based polyester synthesis *via* the formation of assembled structure. A new class of bifunctional monomers with different hydrophilic and hydrophobic character were generated from HMF using aldol condensation step. Further, furan-based bifunctional monomers were enzymatically polymerized in the presence of Novozyme 435® under optimized reaction condition. The resultant hydrophilic oligoesters undergoes polymerization *via* Diels-Alder reaction. Microstructure, thermal and mechanical properties of furan-based polymers were studied with respect to its molecular structure.

Results and Discussion

The rationale behind the growing interest in bio-based polymers originates from sustainability and exploring the possibility of chemical features associated with the nature of substituents present in the polymers.[49,50] To achieve the target, two main strategies been widely used. First strategy is polycondensation of bio-based monomers in the presence of suitable catalyst and the later one involves Diels-Alder reaction of diene-dienophile combination under thermal condition.[51] However, our approach to synthesize bio-based polymer involves the polycondensation of monomers derived from renewable resources by enzyme catalytic pathway. Precursors for furan-based monomers **3a-d**, such as HMF **1** and *β-C*-glycosidic ketone **2a** were synthesized by following the literature procedure[44,52,53] involving the dehydration of fructose under amberlyst 15 condition and condensation of D-glucose with pentane-2,4-dione in aqueous basic condition respectively. Furan-based monomers with hydrophilic saccharide moiety **3a** and hydrophobic alkyl moiety **3b** and **3c** were synthesized by aldol condensation of **1** with **2a-c** in presence of pyrrolidine as catalyst and DCM as a solvent in good yields (Scheme 1).



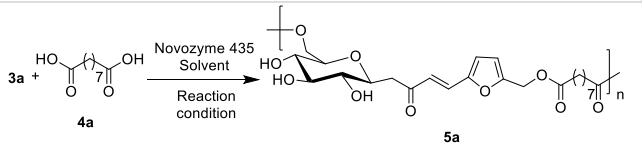
Scheme 1. Synthesis of bifunctional monomers **3a-c**.

The ^{1}H NMR spectrum of furan based monomer **3a-c** displayed the resonance of the alkenic proton around *δ* 7.2 and 6.2 ppm with the coupling constant ranging between 15.2-16.4 Hz, confirms the *trans* isomeric form of alkene. Bifunctional monomer **3a** possesses two primary hydroxyl groups along with three secondary hydroxy groups, whereas **3b** and **3c** has each one primary hydroxy and carboxylic acid groups. Thus, the diol in **3a** undergoes polycondensation with diacids to generate heteropolymer and hydroxyacids self-condense themselves produce homopolymer in the presence of either chemical catalyst or Novozyme 435®. However, to address the global issues on production of polymers and motivation by the general concern about environmental issues, past two decades profound research on the development of bio-based polyester using chemical and biocatalysts has been performed by many research groups.[54,55] Specifically, only few reports were available on lipase catalyzed polycondensation of furan-based monomers. Loos and coworkers have reported the synthesis of bio-based furan polyesters using biocatalyst.[56-59] To ensure the sustainability and regioselectivity in the generation of bio-based polymers, we have chosen the enzymatic polycondensation method.

To explore the possibility of our planned bio-based polymer synthesis using Novozyme 435®,[60] we consecrate our effort to the identification of a suitable reaction condition. It has been reported

that Novozyme 435 displayed prominent catalytic activity in a wide range of solvents such as toluene, acetone, dodecane, isooctane, *t*-butanol, DMF, hexane and diphenyl ether, and the selection of solvent is based on the nature of substrate.[61-63] For the optimization step, we have selected diol **3a** and a non-activated diacid, azelaic acid as a model substrate and studied the polycondensation process in the presence of a variety of solvent under diverse conditions. Reaction was carried out in a wide range of solvents and solvent mixtures. Use of acetone, acetonitrile and dioxane at 50 °C did not afford the product, instead, the reactants remain insoluble even at elevated temperature (Table 1, entries 1-3). Polar protic solvents such as isopropanol, *t*-butanol yielded 10-15% of oligomer, whereas DMSO, water and DMF yielded traces of product (entries 4-8). To our delight, the use of toluene as a solvent at 50 °C furnished 24% of oligomer (entry 9).

Table 1. Optimization of reaction condition for Novozyme 435 catalyzed polymerization.

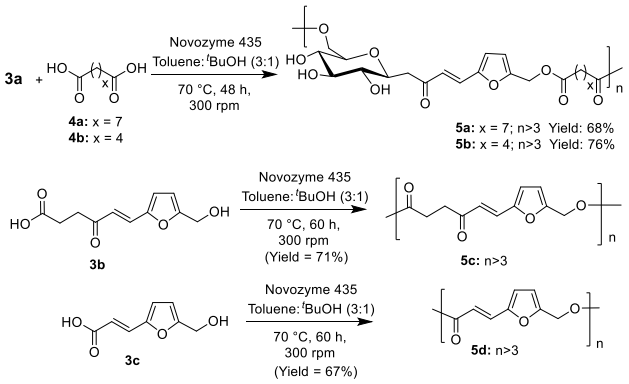


S. No	Solvent [a]	Temperature (ºC)	Time (h)	Yield %[b,c]
1	Dioxane	50	24	NR
2	Acetone	50	24	NR
3	Acetonitrile	50	24	NR
4	Isopropanol	50	24	10
5	*t*-Butanol	50	24	15
6	DMSO	50	24	Traces[d]
7	H_2O	50	24	Traces[d]
8	DMF	50	24	Tracse[d]
9	Toluene	50	24	24
10	Toluene	60	24	30
11	Toluene	70	24	32
12	Toluene	80	24	30
13	Toluene	70	48	42
14	Toluene	70	72	39
15	Toluene + Acetone (3:1)	70	48	30
16	Toluene + Isopropanol (3:1)	70	48	35
17	Toluene + *t*-Butanol (3:1)	70	48	68
18	Toluene + *t*-Butanol (1:1)	70	48	53
19	Toluene + *t*-Butanol (1:3)	70	48	36

NR- no reaction. [a] dry solvents were used. [b] oligomerization was observed. [c] isolated yield. [d] product was not isolated, formation of traces of product was noticed in TLC.…

The increase in temperature and reaction time up to 70 °C and 48 h improved the yield of oligomer (48%), further elevation in temperature and prolonged reaction did not improve the yield substantially, which can be attributed to the loss of activity of Novozyme 435 at 80 °C (entries 9-14). Encouraged by this result, in order to improve the yield, we further moved on to the mixture of solvents. The use of toluene-isopropanol and toluene-acetone mixture in the ratio of 1:3 did not improve the yield (entry 15,16). Gratifyingly, the use of toluene-^{t}BuOH (1:3) mixture at 70 °C and 48 h furnished 68% of oligomer (entry 17). The change of solvent ratio substantially reduce the yield of oligomer (entry 18,19). The enhanced catalytic activity in optimal mixture of solvent is due to the retention of structural integrity of Novozyme 435 and increased solubility of monomers. With the optimized reaction condition in hand, next we turned our attention to study the substrate scope of the established methodology and the results are summarized in the Scheme 2.

First, the utilization of various diacids combining with diol **3a** for the regioselective esterification process to obtain the corresponding furan-based polyester with hydrophilic sugar and hydrophobic flexible alkyl unit has been investigated. The use of glutaric acid as an acid source for regioselective esterification of **3a** did not afford the corresponding oligoester, whereas adipic acid and azelaic acid furnished the respective oligomers **5a** and **5b** in 68 and 76% respectively. Self-condensation of monomers **3b** and **3c** in the presence of novozyme 435 under optimized reaction condition provided the hydrophobic oligoesters **5c** and **5d** respectively in good yield (Scheme 2). Nonetheless, the use of optimized condition for the polymerization of **3b** and **3c** furnished the corresponding low molecular weight oligomer in good yield, whereas the prolonged reaction time yielded the respective furan-based polyester in good yield. Altogether, we have synthesized a series of furan-based oligoesters with a range of hydrophilic-lipophilic character and flexible alkyl units (Scheme 2, Figure 1), which could be potentially used for the synthesis of high molecular weight polymers and self-assembly studies. Formation of oligomeric ester was confirmed by ^{1}H NMR spectral analysis. Before oligomerization, methylene group attached to the furan ring resonate at δ 4.5 ppm, whereas after oligomerization with diacid, methylene protons experienced deshielding and resonate at δ 5.1 ppm. A careful analysis of ^{1}H NMR spectra and integral value of methylene group attached to the furan moiety of oligomeric esters **5a** and **5b** revealed that the oligomer was formed by involving three units of monomer **3a** and two units of **4a** or **4b**. Oligomeric ester formed by the self-condensation of **3b** and **3c** at 70 ºC, 48 h displayed a signal of equal intensity at δ 4.5 ppm and δ 5.1 ppm respectively for furan-CH_2 group. Further the prolonged reaction time furnished the high molecular weight oligomeric ester with the signal ratio of 3:1 (Figure S18, S19). The number average molecular weight (M_n), weight average molecular weight (M_w) and dispersity (Đ) of the oligoesters were determined by gel permeation chromatography (GPC) using DMF as a solvent. GPC analysis of oligoesters **5a**-**5d** displayed M_n of 674, 561, 649 and 495 g/mol, and M_w of 1145, 904, 899 and 638 respectively. The higher polydispersity value ranging from 1.3-1.7 revealed the existence of uneven molecular distribution due to the spontaneous intermolecular Diels Alder reaction of oligoesters (Table S1). Mass spectral analysis of compound **5a**-**d** shows the formation of oligoesters having repeating units n>3 *via* the effective condensation of monomers, which is in good agreement with ^{1}H-NMR spectral studies (Figure S20-S22). However, all the synthesized oligomers possess alkenic and furan moiety with a range of hydrophilic to hydrophobic character.



Scheme 2. Synthesis of furan-based oligoesters **5a-d**.

It is worth mentioning that recently Chen and coworkers have reported the difuranic polyesters with alkenic unit and their self-curing ability *via* Diels-Alder reaction.[64] It has been observed that oligomeric ester **5a** and **5b** displayed self-curing ability and formed crosslinker polymer, whereas **5c** and **5d** exhibited tolerance. The presence of hydrophilic sugar moiety in **5a** and **5b** facilitates the molecular self-assembly *via* the intermolecular hydrogen bonding, allow the alkene to approach furan ring in a close proximity, resulted in the formation of cross-linked polymer *via* Diels-Alder reaction.

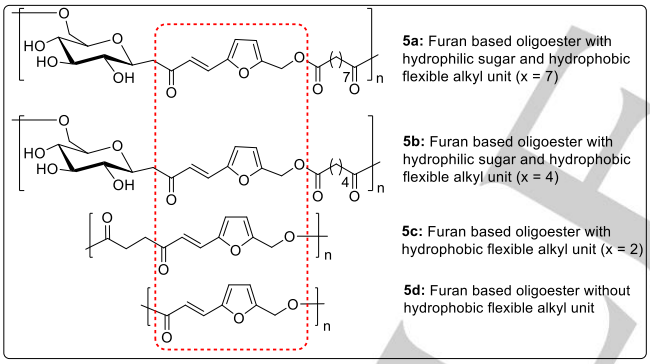


Figure 1. Furan-based oligoesters **5a-d** and their structural features.

Molecular Self-assembly assisted crosslinking behavior of oligoester was confirmed by various techniques. Small angle X-ray diffraction (SAXD) is considered as a valuable technique to study the molecular assembly phenomenon involving H-bonding, π-π interaction and van der Waals interaction.[66,67] Recrystallized oligoesters **5a** and **5b** displayed sharp peaks at 2θ = 7.2 (*d* = 1.2 nm), 10.1 (*d* = 0.87 nm), 17.6 (*d* = 0.53 nm), 21.6 (*d* = 0.41 nm), 23.9 (*d* = 0.37 nm), 27.1 (*d* = 0.33 nm), 29.9 (*d* = 0.30 nm) and 34.17 (*d* = 0.26 nm) suggested the formation of well-organized structure (Figure 2). A careful analysis of diffraction pattern of **5a** and **5b** in the lower angle region propose the existence of various degree of hydrophobic interaction. Hydrophobic oligoester **5c** with flexible alkyl unit displayed peaks at 2θ = 15.6 (*d* = 0.57 nm), 19.8 (*d* = 0.45 nm), 20.9 (*d* = 0.42 nm), 23.5 (*d* = 0.38 nm), 25.80 (*d* = 0.35 nm), 27.5 (*d* = 0.32 nm) corresponds to the (010), (010), (103), (100), (100) and (100) planes and similar XRD diffraction pattern was reported for furanic polyesters (Figure 2).[56-59] However, hydrophobic oligoester **5d** lacking with flexible methylene unit displayed broad peak at 2θ = 10 and 22 evoked the amorphous behavior. Though SAXD result suggest the aggregation behavior of oligoester, it is mandatory to analyze the self-curing by well-established method. Oligoesters **5a-d** were not freely soluble in polar and nonpolar solvents. In order to record NMR spectra, compound **5a-d** were dispersed in DMSO-d_6 followed by heating the mixture to 120 °C for 5 min. Upon heating, oligoesters **5a** and **5b** slowly get dissolved in DMSO-d_6 and the solution becomes more viscous, whereas such phenomenon was not observed in case of **5c** and **5d**. This result clearly indicates the existence of hydrogen-bonding assisted cross-linking between the furan ring and unsaturated double bond in **5a** and **5b**. In this context, oligoesters **5a-5d** after heating at 120 °C in DMSO for about 15 min, the contents were poured in methanol and the precipitated solid were investigated using FT-IR.

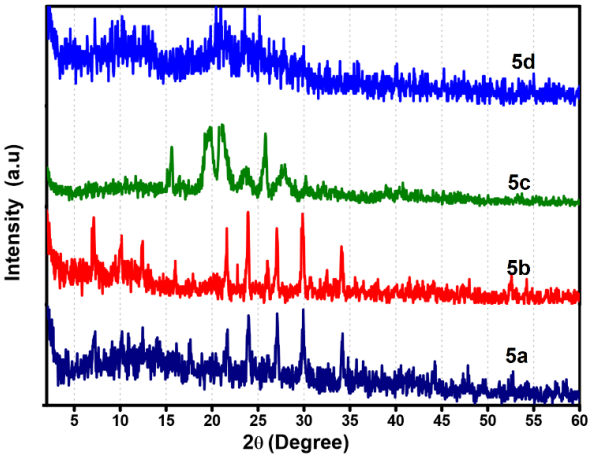


Figure 2. SAXD of self-assembled oligoesters **5a-d**.

The existence of intermolecular hydrogen bonding in oligoethers has also been identified using FT-IR spectroscopy. The bands appear around 2930, 2840, 1400 and 1150 cm^{-1} were assigned to asymmetric and symmetric stretching vibrations of the CH_2 groups, stretching vibrations of C=C and alkenyl ether (C-O) linkage of furan ring respectively (Figure 3).[56-59] In **5a** and **5b**, stretching band appeared for furan ring around 1150 cm^{-1} got shifted to 1085 further confirms the formation of cross-linked polymer *via* intermolecular Diels-Alder reaction (Figure 3,6d).[67] Even though monomer of **5b** and **5c** contains furan ring and alkene, it failed to form Diels-Alder product because of the absence of molecular self-assembly.

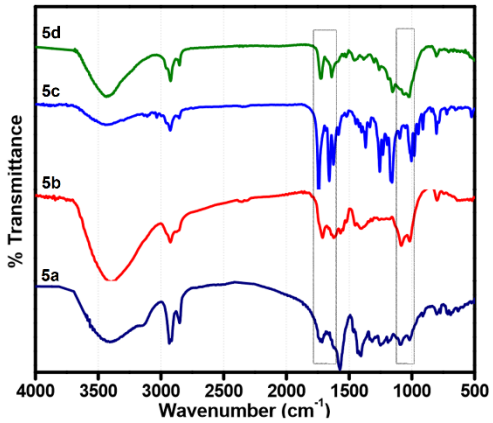


Figure 3. FT-IR spectra of crosslinked hydrophilic oligoesters **5a, 5b** and hydrophobic oligoesters **5c** and **5d**.

Molecular self-assembly assisted crosslinking of alkene to furan moiety *via* the intermolecular Diels-Alder reaction was further confirmed by NMR spectral technique. In ^{1}H NMR spectra of oligoester **5a**, alkenic protons (H_a and H_b) resonate at δ 7.4 and 6.6 ppm (J=15.9 Hz), furan protons (H_c and H_d) resonate at δ 6.9 and 6.5 ppm (J=3.3 Hz) and methylene protons (H_e) attached to the furan moiety resonate at δ 5.1 ppm respectively (Figure 4a, 4e).

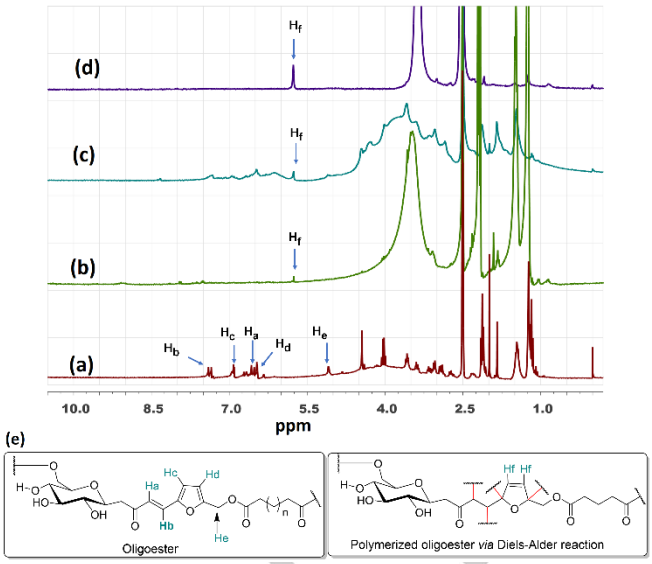


Figure 4. ^{1}H NMR spectra of (a,c) oligoester **5a** and **5b** in DMSO-d_6; (b,d) crosslinked polymer obtained from oligoesters **5a** and **5b** *via* the self-assembly assisted intermolecular Diels-Alder reaction respectively. Broadening of signal is due to the increased viscosity of oligoesters and poor solubility of polymers in DMSO-d_6.

After self-assembly assisted crosslinking of oligoester **5a**, signals corresponding to alkenic and furan protons (H_a-H_d) disappeared and new signal representing the formation of Diels-Alder adduct (H_f) was observed at δ 5.7 ppm (Figure 4b, 4e). Similar trend was observed in case of oligoester **5b** and its corresponding cross-linked polymer (Figure 4c, 4d). However, it is worth mentioning that oligoester **5b** is insoluble in DMSO-d_6 at room temperature and upon heating the mixture to 120 ^{o}C for about 3-5 min attained a viscous character, which displayed signal corresponding to H_f proton along with the expected H_a-H_d protons (Figure 4c). In figure 4d, the appearance of signal for H_f proton in cross-linked polymer derived from oligoester **5b** further confirms the self-assembly assisted polymerization. Eventhough oligoesters **5c** and **5d** possesses alkene and furan in its core structure, it fails to undergo crosslinking owing to the lack of molecular self-assembly.

Morphological analysis of self-cured polymer derived from oligoester **5a** were examined by using optical microscopy and FESEM (Figure 5). Optical microscopy image of viscous solution obtained from **5a** in DMSO-water (1:1 ratio) displayed the formation of fibrous structure. In order to have the further insight of cross linked polymer, we have performed FESEM analysis (Figure 5c-f). The formation of uniformly entangled fibrillar structure with the dimension ranging from 100-200 nm has been observed. This result clearly depicts that self-assembled oligoester **5a** and **5b** undergoes cross linking *via* intermolecular Diels-Alder reaction to form supramolecular architecture.

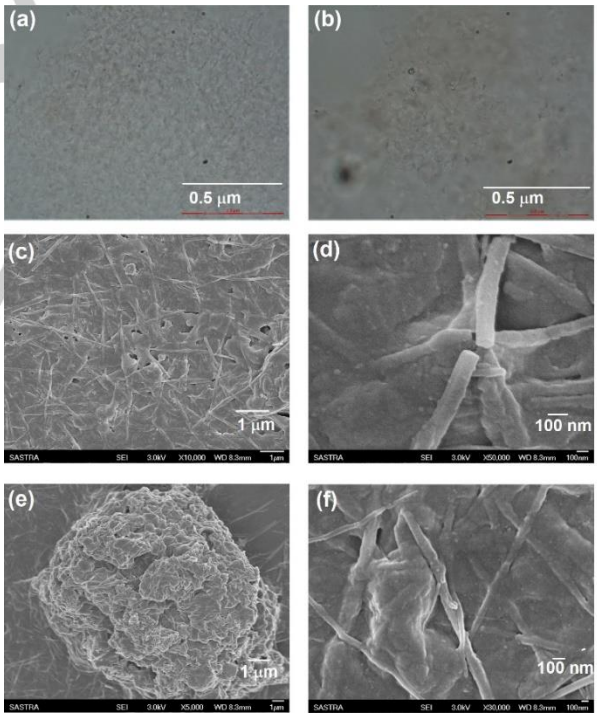


Figure 5. Optical microscopy image of self-cured oligoesters (a) **5a** and (b) **5b**. FESEM images of self-cured oligoesters (c and d) **5a** and (e and f) **5b**.

Nano fibrous polymer solution[68] are versatile materials play an important role in industrial and biomedical applications including cell adhesion, proliferation, tissue engineering and regeneration, etc. Rheological studies correlate the formulation phenomenon

with the product performance, thereby act as a bridge that link laboratory scale preparation and process to the product development.[68] Generally, rheology of nano fibrous polymer solution is governed by the volume of fibers dispersed in the bulk solution, which increase the viscosity by flow line distortion and friction of the particles. The response of viscosity as a function of applied shear rate for **5a** and **5b** is shown in Figure 6. When compared to the solvent, the effective viscosity of **5a** and **5b** displayed higher value because of the formation of fibrous network. At a higher shear rate, however, **5a** and **5b** behave like a Newtonian fluid.

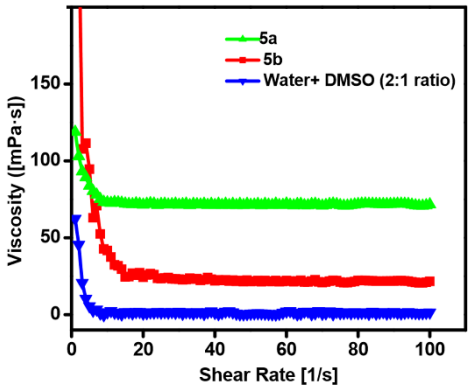


Figure 6. Viscosity *vs* shear rate characteristics of polymer solution (1% wt/v) derived from **5a** and **5b**.

The thermal stability of the furan-based oligoester **5a-d** was investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).[69] The thermal degradation profile of the furan based oligoesters **5a-d**, measured between 30 to 900 °C at a heating rate of 10 °C/min under a nitrogen atmosphere is shown in figure 6. The onset of thermal decomposition (T_{start}) between 100 and 200 °C displayed weight loss of ~5 to 30% of the initial weight. However, furan-based oligoester displayed two stages decomposition mechanism with respect to the temperature and molecular structure.[69] A plot of derivative weight (%/°C) *vs* temperature was used to study the decomposition behavior of oligoesters. Self-assembled hydrophilic oligoester **5a** and **5b** displayed single-stage decomposition, whereas the hydrophobic oligoesters **5c** and **5d** showed the two-stage decomposition. It is worth mentioning that oligoesters **5a** and **5b** displayed higher T_{start} value than **5c** and **5d**, which attributes the perfect molecular assembly of oligoesters *via* H-bonding and van der Waals interaction (Figure 7a, 7b). A complete decomposition of oligoesters was not seen even after heating to 900 °C and the weight percentage of stable residue around 19-55% of initial weight was still remained. The amount of stable carbonaceous materials generated by the polyesters was 15%, 54%, 18% and 38% for the oligoesters **5a, 5b, 5c** and **5d** respectively. DSC curves of the polymers **5a-d** recorded during the first heat cycle is shown in Figure 7c. In DSC thermogram of oligoesters **5a** and **5b**, the existence of a broad exothermic peak in the range of about 45-180°C is ascribed to the evaporation of adsorbed moisture and self-assembly assisted intermolecular Diels-Alder reaction between the alkene and furan moiety (Figure 7d). In oligoester **5a** and **5b**, apart from broad exothermic peak, clear sharp peak indicating the melting point and crystallization was not observed. The schematic representation of the existence of molecular assembly in **5a** and **5b** *via* H-bonding and van der Waals interaction to facilitate the cross linking through Diels-Alder reaction is shown in Figure 7d. However, **5c** displayed sharp melting peak at 250°C and **5d** displayed a broad exothermic peak along with the melting peak at 240°C respectively. DSC analysis of oligoesters also confirms the proposed mechanism of crosslinking without any disputation.

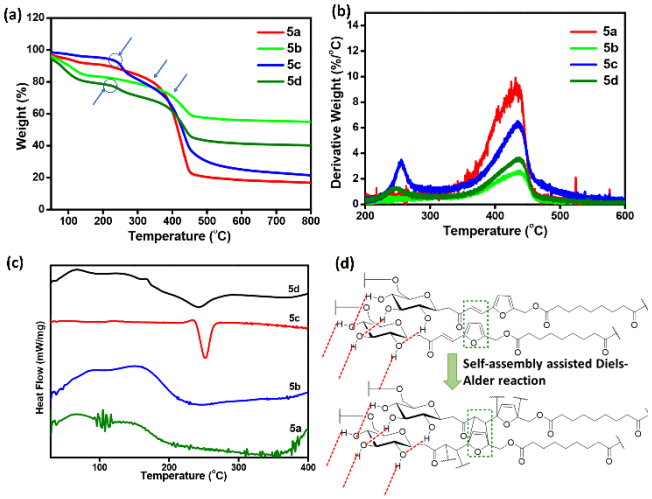


Figure 7. Thermal analysis of **5a-d**. (a) TGA traces of oligoesters **5a-d**; (b) a plot of derivative weight (%/°C) *vs* temperature; (c) DSC curves of oligoesters **5a-d** and (d) schematic representation of self-assembly assisted polymerization of **5a** *via* intermolecular Diels-Alder reaction.

Conclusions

In this study, we have developed a simple and green protocol for the synthesis of bio-based hydrophilic and hydrophobic oligoesters directly from the easily accessible natural monomers using a biocatalyst, Novozyme 435, an immobilized lipase B from *Candida Antarctica* in moderate to high yields. The average number of repeating unit and molecular weight of hydrophilic and hydrophobic oligoester was identified using NMR, GPC and mass spectral analysis. SAXD analysis revealed that hydrophilic oligoesters were prone to self-assemble *via* H-bonding and van der Waals interactions, whereas hydrophobic oligoesters displayed amorphous structure. The self-assembled oligoesters in DMSO at 120 °C undergoes intermolecular crosslinking via the Diels-Alder reaction to form viscous polymer solution. The viscosity of solution and the morphology of self-cured polymer was investigated by rheological studies and SEM analysis. Morphological analysis of polymer showed the formation of fibrous structure. The robust thermal properties of bio-based oligoesters were investigated using DSC and TGA analysis. For the first time, we present the self-assembly aided polymerization

of bio-based oligoesters, derived via "green polymer chemistry" using intermolecular Diels-Alder reaction. The reported method may initiate a new avenue in the development of sustainable polymer materials and technology of commercial interest.

Experimental Section

Materials and General Methods

All reagents and solvents needed for the synthesis of furan-based monomers **3a-c** and polyesters **5a-d** were purchased from Sigma Aldrich, Merck, Alfa aesar, TCI chemicals and Avra chemicals and were used as such without further purification. For purification of compounds, LR grade and distilled solvents were used, when necessary. The reaction progress was monitored by thin-layer chromatography using TLC silica gel 60 F_{254} purchased from Merck and visualized by UV detection, molecular iodine, *p*-anisaldehyde stain or sulphuric acid spray. Column chromatography was performed on silica gel (60-120 mesh) or neutral alumina purchased from Avra chemicals and Merck respectively.

Characterization Methods

^{1}H- and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz instrument in $CDCl_3$ or DMSO-d_6 or D_2O at room temperature. Chemical shifts (δ) are reported in parts per million (ppm) with respect to internal standard TMS and coupling constants (J) are given in Hz. Proton multiplicity is assigned using the following abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m). Infrared spectrum was obtained using FTIR Shimadzu 8000 Spectrometer in the spectral range of 4000 cm^{-1} to 400 cm^{-1}. Matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS) measurement was recorded on Voyager-DE PRO Biospectrometry with dithranol matix. The spectrum was recorded using DMF solvent in positive and linear mode. Thermal stability and the thermal transitions of the polyester were characterized by SDT Q600V20.9 Build 20 thermogravimetric analyzer under nitrogen atmosphere with a heating rate of 10 °C/min. Small angle X-ray diffraction (SAXD) spectra were obtained at room temperature using a BRUKER-binary V3 diffractometer in the angular range of 2-70° (2θ).

Synthesis

Synthesis of HMF 1 and □-*C*-Glycosidic ketone 2a.

HMF was synthesized in batch process reported by Simeonov and Afonso,[42] which include the dehydration of fructose using tetraethylammonium bromide and amberlyst 15 as catalyst. In this method reaction media and catalyst can be effectively recycled. β-*C*-Glycosidic ketone **2a** was synthesized by the condensation of unprotected sugar, D-glucose with pentane-2,4-dione in alkaline aqueous media.[41]

General Procedure for the synthesis of bio-based oligoesters 3a and 3b.

To a stirred solution of suitable methyl ketone (1 mmol) in DCM were added pyrrolidine (1-2 drops) and HMF (1 mmol) and stirring was continued for 10-12 h at room temperature. The progress of the reaction was monitored using TLC. After completion of the reaction as identified by TLC, the reaction mixture was diluted with water and extracted with ethyl acetate (3 x 20 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography.

Compound 3a

Yellow viscous liquid; Yield: 87 %; ^{1}H NMR (300 MHz, D_2O) δ = 7.37 (d, J = 15.9 Hz, 1H, Alk-H), 6.76 (d, J = 3.3 Hz, 1H, Fur-H), 6.60 (d, J = 16.2 Hz, 1H, Alk-H), 6.42 (d, J = 3.6 Hz 1H, Fur-H), 4.50 (s, 2H, Fur-CH_2), 3.74-3.35 (m, 5H, Sac-H), 3.31-3.23 (m, 2H, Sac-H), 3.17 (t, J = 9.3 Hz, 1H, Sac-H), 3.06 (dd, J = 14.4, 3.0 Hz, 1H, Sac-H), 2.80 (dd, J = 15.3, 9.0 Hz, 1H, Sac-H). ^{13}C NMR (75 MHz, D_2O) δ = 201.9, 157.3, 150.40, 131.6, 122.4, 118.9, 111.2, 79.5, 77.3, 75.77, 73.22, 69.68, 60.75, 55.97.

Compound 3b

Yellow solid; Yield: 92%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.35 (d, J = 15.9 Hz, 1H, Alk-H), 6.69 (d, J = 15.6 Hz, 1H, Alk-H), 6.66 (d, J = 3.3 Hz, 1H, Fur-H), 4.68 (s, 2H, Fur-CH_2), 2.97 (t, J = 6.6 Hz, 2H, CH_2), 2.74 (t, J = 6.6 Hz, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 202.5, 179.3, 163.1, 154.9, 133.6, 127.3, 121.8, 114.6, 61.6, 40.3, 32.9.

Synthesis of bio-based monomers 3c.

To a solution of HMF **1** (1 mmol) in 3 mL of pyridine was added malonic acid (1.2 mmol) and the mixture was refluxed with stirring for 16 h. The progress of the reaction was monitored periodically using TLC. After the completion of the reaction as identified by TLC, the reaction mixture was cooled to room temperature and acidified with 5N HCl to precipitate the product. The yellow solid thus precipitated was filtered, washed well with water and dried under vacuum.

Yellow solid; yield: 88%; ^{1}H NMR (300 MHz, D_2O) δ = 7.35 (d, J = 15.3 Hz, 1H, Alk-H), 6.66 (d, J = 3.0 Hz, 1H, Fur-H), 6.39 (d, J = 3.0 Hz, 1H, Fur-H), 6.18 (d, J = 16.5 Hz, 1H, Alk-H), 4.50 (s, 2H, Fur-CH_2). ^{13}C NMR (75 MHz, D_2O) δ = 170.7, 156.5, 150.2, 132.5, 117.1, 113.9, 110.6, 55.8.

General procedure for the synthesis of bio-based oligomers 5a and 5b.

To a solution of compound **3a** (1 mmol) in 5 mL toluene:*t*-BuOH (3:1 ratio) was added fatty acid (2 mmol) and Novozyme 435® (100 mg). The reaction mixture was kept in an orbital incubator shaker at the temperature of 70 °C and 300 rpm for the given period of time. Progress of the reaction was monitored using TLC by following the consumption of compound **3**. After completion of the reaction as identified by TLC, the reaction mixture was cooled to room temperature and filtered to remove Novozyme 435® and washed with acetone. The filtrate was concentrated by rotary evaporator at reduced pressure and the product was precipitated by adding methanol. Bio-based polymers **5a** and **5b** were stored in refrigerator for further studies.

Compound 5a:

Pale brown solid; mp: >250 °C; ^{1}H NMR (300 MHz, DMSO-d_6)* δ = 7.38 (d, J = 15.9 Hz, 1H, Alk-H), 6.93 (d, J = 3.3 Hz, 1H, Fur-H), 6.58 (d, J = 15.9 Hz, 1H, Alk-H), 6.47 (d, J = 3.3 Hz, 1H, Fur-H), 5.09 (s, 2H, Fur-CH_2), 4.44 (s, 2H, Fur-CH_2), 4.03 (q, J = 7.1 Hz, 2H, Sac-H), 3.59–3.43 (m, 1H, Sac-H), 3.41-3.35 (m, 1H, Sac-H), 3.21-3.16 (m, 2H, Sac-H) 3.11–3.04 (m, 2H, Sac-H), 2.93 (m, 1H, Sac-H), 2.72 (dd, J = 16.2, 8.4 Hz, 1H, Sac-H), 2.34-2.28 (m, 1H, Sac-H), 2.15–2.06 (m, 4H, $COCH_2$), 1.49-1.44 (m, 4H, CH_2), 1.26–1.23 (m, 6H, CH_2). ^{13}C NMR (75 MHz, DMSO-d_6) δ = 197.5, 175.1, 158.6, 149.8, 128.9, 122.9, 117.6, 109.9, 80.6, 77.9, 75.9, 73.5, 70.2, 61.0, 55.7, 43.4, 39.8, 39.2, 38.9, 34.4, 33.2, 28.5, 28.5, 28.4, 28.2, 24.7, 24.3, 21.9. *owing to the formation of oligomer, broadening as well as shift in signals were observed.

Compound 5b:

Pale brown solid; mp: >250 °C; ^{1}H NMR (300 MHz, DMSO-d_6)* δ = 7.35-5.85 (m, 4H, Alk-H, Fur-H), 5.07-4.91 (m, 5H, Sac-H, Fur-H), 4.44-4.32 (m, 4H, Sac-H, Fur-H), 3.56-2.73 (m, 3H, Sac-H), 2.37-2.19 (m, 4H, CH_2), 1.49 (s, 4H, CH_2). ^{13}C NMR (75 MHz, D_2O) δ = 180.9, 176.5, 149.6, 148.6, 130.7, 118.0, 110.3, 108.2, 78.7, 78.6, 76.4, 75.0, 74.5, 72.4, 72.2, 68.8, 68.6, 59.9, 59.7, 55.2, 54.9, 51.6, 48.9, 48.2, 44.6, 35.1, 29.5, 24.9, 24.2, 23.9, 23.2, 22.8, 22.7, 21.7. *owing to the formation of oligomer, broadening as well as shift in signals were observed. Saccharide peaks were merged with solvent peak.

General procedure for the synthesis of bio-based oligomers 5c and 5d.

To a solution of compound **3b/3c** (1 mmol) in 5 mL toluene:^{t}BuOH (1:3 ratio) was added Novozyme 435® (100 mg). The reaction mixture was kept in an orbital incubator shaker at the temperature of 70 °C and 300 rpm for the given period of time. Progress of the reaction was monitored using TLC by following the consumption of compound **3**. After completion of the reaction as identified by TLC, the reaction mixture was cooled to room temperature and filtered to remove Novozyme 435® and washed with acetone. The filtrate was concentrated by rotary evaporator at reduced pressure and the product was precipitated by adding methanol. Bio-based polymers **5c** and **5d** were stored in refrigerator for further studies.

Compound 5c

Polymer obtained from compound **3b**. Pale brown solid; mp: >250 °C; ^{1}H NMR (300 MHz, DMSO-d_6)* δ = 7.41 (d, J = 15.9 Hz, 1H, Alk-H), 6.95 (d, J = 3.3 Hz, 1H, Fur-H), 6.67 (d, J = 3.3 Hz, 1H, Fur-H), 5.90 (d, J = 16.2 Hz, 1H, Alk-H), 5.09 (s, 2H, Fur-CH_2), 4.44 (s, 0.5H, Fur-CH_2-OH), 2.96 (s, 2H, CH_2), 2.62 (t, J = 5.4 Hz, 2H, CH_2) ^{13}C NMR (75 MHz, DMSO-d_6) δ = 197.5, 171.9, 152.2, 150.8, 128.6, 123.2, 117.2, 113.3, 57.6, 55.7, 34.7, 27.5.

* In addition to the linear oligoester, trace quantity of cyclic oligoester formation was also observed.

Compound 5d

Polymer obtained from compound **3c**. Pale brown solid; mp: >250 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ = 7.51-7.28 (m, 1H, Alk-H), 6.79 (d, 1H, Fur-H), 6.60 (s, 1H, Fur-H), 6.39-6.18 (m, 1H, Alk-H), 5.18 (s, 2H, Fur-CH_2), 4.48 (s, 1H, Fur-CH_2OH). ^{13}C NMR (75 MHz, DMSO-d_6) δ = 167.2, 165.4, 152.3,150.7, 131.7, 130.5, 117.6, 114.5, 113.4, 113.0, 109.8, 57.7, 55.7. *because of the formation of oligomer, broadening as well as shift in signals were observed.

Self-assembly studies

In a round bottom flask, 25 mg of compound **5a-5d** was dissolved in 10 mL of DMF, if not soluble, the mixture was warmed on water bath until getting a clear solution. The clean solution is cooled room temperature and 25 mL of double distilled water was added slowly until to get a soft precipitate. The precipitate thus formed was filtered, dried and stored under refrigerator. Dried solid was subjected to SAXD analysis to identify the self-assembly behaviour. This experiment has also been carried out in both acidic and basic pH levels.

Polymerization of oligoesters

A dispersed solution of self-assembled oligoesters (10 mg) in DMSO (5 mL) was heated to 120 °C for about 15-25 min. Upon heating, dispersed oligoesters slowly get dissolved and the solution became viscous in nature. The clear viscous solution thus formed was cooled to room temperature and 10 mL of methanol was added to generate solid cross-linked polymers. Cross linked polymer formed by Diels-Alder reaction was not soluble in any of the solvent. Cross linking was confirmed by FTIR analysis. Morphology was identified using optical microscopy and FESEM analysis. Viscous nature of the polymer solution was identified by rheological measurements

Rheological studies

Flow behavior of polymer solution was identified using a stress controlled rheometer (Anton Paar 302 rheometer) implemented with a steel-coated 25 mm diameter parallel-plate geometry. The gap between two plates for rheological testing of polymer solution was fixed as 0.5 mm and experiments were carried out at 23 °C.

Acknowledgements

This work was financially supported by the Department of Science and Technology (IFA11-CH-04 and #SB/FT/CS-024/2013), India and Board of Research in Nuclear Science (#37(1)/20/47/2014), Department of Atomic Energy. S.N. sincerely thanks SASTRA University for financial support under DESH-VIDESH scheme.

Keywords: Renewable Resources • Enzyme catalysis • Biopolymers • Self-Assembly • Diels-Alder Reaction

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10.1002/cssc.201800446

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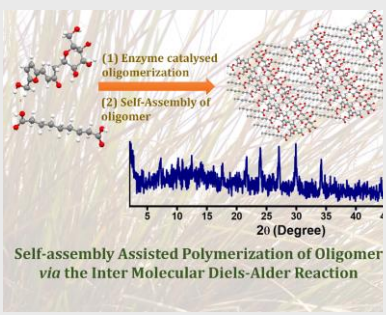
FULL PAPER

This contribution investigates the synthesis of bio-based hydrophilic and hydrophobic furan-based oligoesters, which in turn derived from easily accessible monomers of natural resources by biocatalysis. For the first time we are reporting the self-assembly assisted polymerization of C-glycosyl furan-based oligoester using intermolecular Diels-Alder reaction, which would initiate a new avenue in the field of polymer science.



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Lipase Catalysed Synthesis of Furan Based Oligoesters and their Self-Assembly Assisted Polymerization