

# Lipase catalysed synthesis of bio- based reactive polyester



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TITLE OF THE RESEARCH PAPER: Green polymer chemistry: lipase catalysed synthesis of bio-based reactive polyester employing itaconic anhydride as renewable monomer.

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## 1. INTRODUCTION

### 1. SUMMARY

2. This paper is about the lipase catalysed synthesis of reactive polyester.

In this synthesis lipase used as natural catalyst. The synthesis of reactive polyester was done by ring opening addition condensation polymerization (ROACP) reaction with dehydration. Cyclic anhydride and diol were used. Itaconic anhydride (IAN) is renewable biomass material so it was ideal monomer for synthesis of reactive polyester. IAN is five membered cyclic anhydride. ROACP did not possible between IAN and diol so the monomer succinic anhydride (SAN) or glutaric anhydride (GAN) were used with IAN and diol. The diol used were 1, 4-butanediol (BD), 1, 6-hexanediol (HD), 1, 8-octanediol (OD) and 1, 10-decanediol (DD). ROACP reaction of IAN with the diols in the ratios of IAN: diol with lipase as a catalyst in presence of molecular sieves were studied at 25°C in toluene for 120h. From the GPC analysis it is observed that all the reaction remained inhomogenous during the reaction and gave only low-molecular weight product with  $M_n$  between 150 and 390. The NMR result show that starting IAN completely consumed in ring opening reaction so IAN alone does not show RCACP so the addition of other component or changing reaction condition necessary. For these regioselectivity and substrate selectivity

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examination of IAn done by using model reaction of IAn and n-octyl alcohol. For regioselectivity observation ROA reaction was performed with Novoenzyme 435 catalyst without molecular sieve in toluene at 25°C with stirring. The  $\beta$ -selectivity value without lipase was 90% and with lipase catalysis was 49%. It was because the  $\beta$ -carbonyl group is sterically more favourable than  $\alpha$ -carbonyl group adjacent to the vinylidene group so it confirmed that reaction catalysed by lipase. In ROACP reaction first ring opening addition (ROA) reaction between cyclic anhydride and diol and after that dehydration condensation reaction between alcohol group and carboxylic acid group occur. Out of four diol OD gives good result in terms of yield, molecular weight and number of unit per molecule. ROACP using IAn, SAn or GAn and diol produced polyester in good yield. From the SAn polyester with  $M_n$  value of 650-3510 with 1.3-2.6 units per molecule were obtained and from GAn these value were 560-3690 and 1.2-3.1 respectively. The polymer synthesized have application as macromonomer, telechelic or crosslinking reagent.

## 2. LITERATURE SURVEY

The review of this manuscript and presentation of perspectives has been conducted based on an extensive survey of the manuscripts describing similar or related research.

1. Renewable biobased polymeric materials: facile synthesis of itaconic anhydride-based copolymers with poly(L-lactic acid) grafts (Okuda et. al, 2012)

Biobased material are environmental friendly so these material now a days used mostly for synthesis organic compound. Current paper used itaconic anhydride (IAN) and lactic acid (LA) as a renewable starting material for synthesis of biobased polymeric material of poly (lactic acid) (PLA)-graft copolymer. Synthesis of Poly (lactic acid) (PLA) was done by two way; ring-opening polymerization of lactide with a variety of metal or nonmetal catalysts and direct polycondensation of lactic acid (LA) with acid catalysts. Poly (lactic acid) (PLA)-graft copolymer were synthesized by two way macromonomer approach and copolymer approach. First the using IAN the methacryloyl-type polymerizable PLA macromonomer (IAN-PLA Macro) were formed and then its copolymerization with n-butyl methacrylate (BMA), n-butyl acrylate (BA), methyl methacrylate (MMA) or ethyl methacrylate (EMA) to give graft copolymer with molecular weight  $M_n$  up to  $1.61 \times 10^5$  and biomass content more than 34wt%. When copolymer approached employing IAN as comonomer for radical polymerization with BMA used then IAN-BMA copolymer with  $M_n 5.76 \times 10^4$  obtained. These two approaches are used for synthesis of PLA-graft copolymer as " biomass plastic" having various application.

## 2). Enzymatic Polymerization: A New Method of Polymer Synthesis (kobayashi 1999)

Enzymatic polymerization refers to polymerization using an isolated enzyme outside the biological system through non-biosynthetic pathways. The present article gives idea about development of enzymatic polymerization technique. Hydrolases and oxidoreductase types of enzyme were used for polymerization. By using these enzymatic polymerization method various <https://assignbuster.com/lipase-catalysed-synthesis-of-bio-based-reactive-polyester/>

material synthesized including polysaccharide like chitin, cellulose, xylan and amylose and un-natural polysaccharide by glycosidase through various monomer. Oxidoreductase initiated vinyl polymerization. The polymerizability was depend on ring size, opposing to chemical catalysis where ring strain is operative. Enzymatic polymerization has advantages of high selectivity, ability to operate under mild condition, catalyst recyclability, and biocompatibility.

### 3. Dehydration polycondensation in water for synthesis of polyesters by lipase catalyst. (Suda et al., 1999)

Lipase is natural catalyst used for synthesis of polyester . In the present paper aliphatic polyester was synthesized by dehydration polycondensation in water by using lipase as catalyst. Polymerization was carried out at 45°C for 24 h . size exclusion chromatography (SEC) was used for molecular weight determination. Methanol was used for isolation by reprecipitation. Effect of reaction parameter and the lipase origin on the molecular weight and the polymer yield have been systematically measured in the combination of sebacic acid and 1, 8-octanediol. When the experiment was carried without the lipase (control experiment) then the polymerization did not occur indicating that polymerization takes place due to lipase as catalyst. The effect of temperature, solvent and amount of enzyme and monomer were systematically measured. When enzyme concentration increased it was observed that the yield was increased. It was seen that monomer amount also affected polymerization behaviour . The polymerization behaviour depended on chain length of the monomer in the polymerization of a co-

dicarboxylic acid and glycol. NMR and MALDI-TOF mass spectrometry was used for terminal structure analysis.

#### 4 . Enzymatic polymerization towards biodegradable polyester nanoparticles (Taden et al., 2003)

Biodegradable polymer nanoparticles synthesized from the direct enzymatic polymerization of miniemulsion consisting of lactone nanodroplets. For polymerization of lactone lipase as catalyst was very efficient. Lipases were amphiphilic molecule and they adsorb onto the hydro-phobic lactone nanodroplets. Ultrasonication was used for the miniemulsification until reaching equilibrium and measure by turbidity measurement. When DSC measurements was done it was observed that the dynamic crystallization point of the synthesized polyester were shifted much down that crystallization inside the droplets was suppressed when polymerization condition applied. The melting point of dried polymer was determined by DSC method. Non-spherical aggregate was formed when crystallization carried out at low temperature. The pH of the minemulsion shifted to 5-6 after polymerization from 7.

#### 5. Green Polymer Chemistry Using Nature's Catalysts, Enzymes (Pukas et. al, 2009)

Enzyme are the natural catalyst. The use of enzyme as a catalyst increases as substitute to chemical catalysis method of organic synthesis. The advantage of enzyme were ability to operate under mild condition, high selectivity, biocompatibility and recyclability. The polymer synthesis was done by enzyme and the most common example are polycondensation, <https://assignbuster.com/lipase-catalysed-synthesis-of-bio-based-reactive-polyester/>

oxidative polymerisation and ring opening polymerization. The use of enzyme as a catalyst in polymer science is important methodology for the synthesis of novel polymeric structure, which are impossible or difficult to prepare.

### 3. CRITICAL REVIEW

#### 3. 1 ORIGINALITY

The present paper is about the lipase catalysed synthesis of bio-based reactive polyester employing itaconic anhydride as a renewable monomer. For reducing carbon dioxide emission polymeric material was produced from biobased renewable material. Thus poly-lactic acid has been produced using biobased renewable material. Work on the ring opening polymerization using enzyme catalyst was already done. The work on the lipase catalysed ring opening polymerization of dicarboxylic acid was first done in 1993 for the ring opening addition condensation polymerization (ROACP) involving dehydration already carried out. The work on the “dehydration in water” using lipase catalysed polymerization to form polyester in water was also done. From the extension of all these studies the current paper includes lipase catalysed synthesis of reactive polyester employing itaconic anhydride (IAN), succinic anhydride (SAN) or glutaric anhydride as starting monomer with diol. Even though the concept was not new but the work done was novel. The author did the work with using new monomer IAN and four diols. ROACP between two monomers itaconic anhydride and diol was not possible so the author added one extra polymer so that the reaction completed. Author

carried out model reaction for getting information about the regioselectivity and substrate selectivity of itaconic anhydride using n-octyl alcohol.

### 3. 2 TECHNICAL CORRECTNESS

Technically, this paper is almost correct. All the obtained results have been represented through lucid graphs.

#### DATA REPRESENTATION

All the employed methods have been well-described by the authors. This enabled easy and correct interpretation of some of the related plots and enabled the understanding of the associated concepts. The spectra included in the manuscript clearly represent the results obtained via various experiments and the theoretical discussion supports the results represented in these spectra; which enabled better understanding of the experiments and the concepts.

#### FLOW OF EXPERIMENT

The flow of the experiments conducted is logical. In the initial part of this paper, the scientists have given a brief introduction about biobased renewable material. The authors used some references to state the method for poly lactide synthesis using two method ring opening polymerization of lactide and direct polycondensation of lactic. Lipase catalysed ring opening polymerization of dicarboxylic acid anhydride involving dehydration. The reference also included the “dehydration in water” and have conducted green polymer chemistry. To the extension of these work done current paper



utilised the itaconic anhydride as a starting biobased monomer to produce a poly (lactic acid) macromonomer.

The strategy of synthesis of biobased reactive polyester from itaconic anhydride was like that itaconic anhydride does not react with diol alone so it is necessary that the monomer added so that the reaction was completed therefore succinic anhydride or glutaric anhydride was used in combination. During the synthesis all reaction were remained inhomogenous and gave only low molecular weight product with  $M_n$  values between 150 and 390 as determined by GPC analysis. The  $H^1$  NMR studies show that the itaconic anhydride was completely consumed during ring opening reaction. In addition to these EIS-TOF MS analysis show that reaction of itaconic anhydride with diol reaction gives mixture of 1: 1 and 2: 1 adduct of IAn: diol. From these it was conclude that in addition to main ROA reaction small extent of condensation and dehydration occurred.

After these study the author pointed out why the itaconic anhydride alone does not initialised expected ring opening addition condensation polymerization reaction. The reason behind these was that itaconic anhydride is less reactive than succinic anhydride in dehydration step. The author gives the information from result that ROACP involves two different types of reaction a ROA between diol and cyclic anhydride and dehydration condensation between carboxylic acid group and alcohol group.

Author carried out model reaction before the study of the ROACP reaction to obtain valuable information about the product polyester structure and fundamental aspects of itaconic anhydride. The model reaction carried out

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using n-octanol instead of a diol. The regioselectivity information obtained from reaction carried out with novoenzyme 435 catalyst without molecular sieve in toluene at 25°C. The author interpreted from result that was obtained from  $H^1$  NMR. The  $\beta$ -selectivity value with lipase catalysis was 49% and without lipase catalysis was 90% and thus demonstrate that reaction was governed by lipase catalysis. Author also focus on the substrate selectivity in the reactant in order to prepare reactive polyester. The result from  $H^1$  NMR studies show that after 3h the IAn and SAn were 13% and 27% consumed respectively and without lipase catalyst these reaction did not occur.

Author carried ROACP reaction under different condition using IAn, SAn and diol. IAn: SAn: diol were 2. 5: 2. 5: 5. 0 and 1. 4. 0: 5. 0 taken for synthesis of polyester. When reaction carried out in without novoenzyme 435 no product was formed which insoluble in n-hexane. When the reaction carried out with the lipase but without the molecular sieve, reaction system becomes homogenous to synthesized polymeric product with low  $M_n$ . When the molecular sieve were added ROACP was increased and gave the polyester with higher  $M_n$  values. Out four diol 1, 8-octanediol was the most favourable diol in terms of molecular weight, yield and number of units per molecule. Then paper ended with a detailed discussion on various parameters studied and results observed, which was followed by an appropriate conclusion.

### 3. 3 CLARITY

In this paper, the authors have lucidly explained the background of the topic, which gives a clear dogma of the researched topic. Explanation of some

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concepts enables better understanding of the experiments and reveals the authors' logical approach towards the work conducted. Each of the sub-topics well describe the basic concepts covered within them. There is no repetition of matter. Therefore paper is reasonably easy to follow and understand.

### 3. 4 BIBLIOGRAPHY

Authors have provided 38 references; all the references have been cited in course of the discussion. All references are formatted as per guidelines mentioned for authors by the publishers of this scientific journal. Statements in paper can be correctly interpreted by referring to the cited references.

### 3. 5 TITLE AND ABSTRACT

Title of the paper is“ Green polymer chemistry: lipase catalysed synthesis of bio-based reactive polyester employing itaconic anhydride as renewable monomer”. It is self-explanatory. By looking at the title we can get clear idea that the experiment includes synthesis of biobased reactive polyester using itaconic anhydride as a renewable monomer and lipase as a natural catalyst.

The abstract of the paper presents an overview of the various studies conducted in the manuscript and briefly presents experimental framework and the most important results obtained by the authors. The abstract of paper is of appropriate length and sufficient to give clear idea about what work has been done. The abstract brings out all the main points of paper.

### 3. 6 ILLUSTRATION AND TABLES

The spectra and graphical representations as well as the table represented in the paper are appropriate. The results discussed in the text are accurately represented in the graphs and spectra. They are self-explanatory and simple to understand. These researchers have provided the analytical data of material synthesized during their research. This included Mass spectra, proton NMR spectra and IR spectra of precursor material and intermediate synthesized to point out the differences between the various polymer synthesized during the work using different combination of a monomer in different ratio using different diol and different reaction condition as a proof of the polymer being synthesized varies according to a reaction condition and monomer and its concentration.

### 3. 7 ALTERNATIVE INTERPRETATION

No alternative interpretation can be made from the obtained results. All the conclusions made by the author are correct and justify the results obtained.

### 4. REFERENCES

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