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3PMF PG .JYJOH BOE 5FNQFSBUVSF PO .PMFDV 1PMZDBQSPMBDUPOF 4ZOUIFTJ[FE GSPN

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Abstract

7KH HIIHFW RI WHPSHUDWXUH DQG PL[LQJ RQ 5LQJ 2SHQLQJ 3RO\PHUL]DWLRQV by using lipase enzyme Novozym 435 (immobilized form of lipase B from Candida antarctica) as biocatalyst. The SRO\PHUL]DWLRQ RI 0 FDSURODFWRQH ZDV FDUULHG RXW DW YDULRXV LPSHOOHU the temperature of the reactor were maintained at 60°C, 70°C and 80°C. The maximum molecular weight out of all the experiments carried out is 310000 KDa which was obtained at a temperature of 70°C and 3 hours for an impeller speed of 500 rpm. The results also indicate that increasing the speed reduces the molecular weight distribution. The conclusion is that 500 rpm is found to be the most appropriate speed for the impeller that needs to be maintained for the enzymatic catalyzed polymerization process because when the impeller speed is increased to 1000 rpm the trend seems to vary which might be due to degradation occurring or in other words an increase in impeller speed could lead to killing of the enzymes.

Keywords: Enzymatic Polymerization; Ring Opening Polymerization (ROP); Polycaprolactone Synthesis; Mixing; Temperature; Molecular Weight Distribution.

Introduction

Recently a large amount of focus has been in the eld of enzymatic catalyzed polymerization, the reason being that enzymes as catalyst have been more eco-friendly when compared to that of conventional polymerization where in the inorganic catalysts which are of toxic and precious materials. Even though enzymatic polymerizations seem to be a very good alternative process, its high cost has taken it to the back seat as the cost of production and puri cation has taken the toll. Hence a polymerization process to produce a polymer like polyester with commercial enzyme as catalyst at a cheaper price would be our objective and to achieve this, the rst step would be to optimize the parameters involved in the process. e commercial lipase enzyme (Novozym435) is used as a catalyst in converting -caprolactone to polycaprolactone using Ring Opening Polymerisation (ROP) in an enzymatic catalyzed polymerization process where optimization of the reactor parameters namely temperature, impeller speed are taken into consideration in the present study.

Poly (e-caprolactone) is an important environment-friendly polymer. e ROP of 5-keto-e-caprolactone has attracted attention for several reasons: the monomer can be synthesized in high yield, it has su cient ring strain to enable homopolymerization and either the monomer or polymer can be further derivatized. e e cient monomer synthesis was a very important factor, Poly e-caprolactone (PCL) is semi-crystalline in nature and has several important properties such as biodegradability, biocompatibility, good mechanical properties and its molecular weight can easily be controlled to ensure optimum performance. e aliphatic polyester PCL and its copolymers are of great interest for applications in biological and biomedical areas.

Hence this novel approach has been dealt by Gross & Kumar [1] and also of Madras & Sivalingam [2]. eir worbility, biocompatibility, biocompaibility, biocompaibility, biocomaaio0myoad, either

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prepared by the ROP process are used for a wide range of applications. In practice it is very important to synthesize polymers with a targeted molar mass. It is well known, that the nal molar mass of a polymer prepared using the ROP process is de ned by the monomer/initiator molar ratio [9-10]. In addition, other factors have also been reported to in uence the ROP polymerization process. ese include type of polymerization techniques (melt, bulk or solvent) [11], initiator [12], type and concentration of catalyst [13-14], temperature [15], monomer concentration [16], stirring speed [17] and impurities (water and hydroxyl containing substances) [18] (Figure 1).

In order to optimize the conditions of synthesis, there is a ne>BDCnT1_0 1 Ty(ne>BDCnT09 0 0 tor)]y(ne>BDCnT09 0 0 tor)]y(ne>BD

the reactor. e reactor was started and the reactor temperature was allowed to rise to the desired value. e stirrer was started and set to the desired speed. As the mixture starts to react and the sample were removed according to the time interval.

Zeta-sizer analyser was used for the molecular weight analysis for this research which was performed using Zeta-sizer 1000 HS, Malvern Instruments Ltd., Worcestershire, United Kingdom (UK). e measurement of molecular weight is explained in ve di erent stages.

1. Manual measurement: First the con guring of manual measurement is carried out. en selection of molecular weight measurement is done. is is followed by entering of sample name, selection of appropriate material and solvent and choosing of standard.
2. Performing of measurement: e reference material set consists of scattering standard and three concentrations of polycaprolactone sample.
3. Measurement: e measurement is started by measuring dark count right which is the count right with no laser. is is followed by measurement of scattering standard which is toluene. ese are for the calibration of molecular weight measurement.
4. Next is the analysis of rst sample with a speci c concentration. e more accurate the concentration is known for molecular weight measurement, the more accurate the results are likely to be.
5. Viewing the results: e record view shows the results of molecular weight measurement. e report shows the trend plot and also the second varial coe cient.

Results and Discussion

Temperature e ects

Figure 3, 4, 5 shows the variation of molecular weight with reaction time at various temperatures (60°C, 70°C and 80°C respectively) with a volume ratio of 1:2 of-caprolactone /toluene being taken. Figure 3 indicates that for an impeller speed of 250 rpm and 1000 rpm, the polymerization rates are initially very high at the beginning of the reaction but as the time proceeds the values of molecular weight is found to decrease. But for 500 rpm the polymerization is found to be highest at the 2

organic media, subjecting the reacting mixture to di erent temperature enzyme e ect, dilution e ect, not much of interest has been shown ir the mixing. But when a large scale production of polycaprolactone i required, an important factor that comes into limelight is the mixing. e reason is that in the small scale where magnetic stirrer was use [20] the control over the speed is impossible as the provision fo control of speed is not available, but when the bioreactor is used, t role of impeller speed has to be taken into consideration and as a res varying the impeller speed from 250 rpm to 1000 rpm provides a interesting analysis which is explained in details. ese results have given a new perspective of the enzymatic catalyzed polymerizatic eld. e conclusions are alarming and as a result will intrigate the researchers to shi their focus to this new parameter or rather a ne phenomena.

Figure 6,7,8,9 indicates the variation of molecular weight with reaction time at various impeller speed (250,500, 750, 1000 rpm respectively) with a volume ratio of 1:2 of caprolactone /toluene being taken at a constant temperature that have been considered for th previous set of temperatures namely 60°C, 70°C, 80°C. Figure 6, sh the e ect on molecular weight at a particular impeller speed of 25 rpm, the trend followed is the same which indicates that as the reactic starts the process of polymerization at all the temperatures consider namely 60°C, 70°C, 80°C is found to be maximum initially at the 1st hr as the time proceeds the molecular weight is found to decrease stead

In Figure 7 as well the trend is very much uniform where in the plo

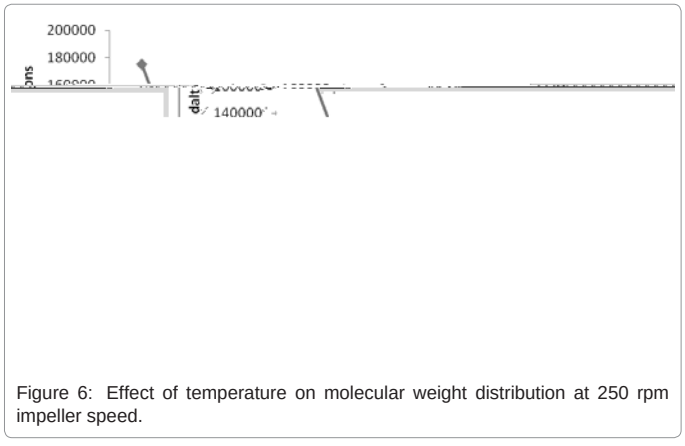


Figure 6: Effect of temperature on molecular weight distribution at 250 rpm impeller speed.

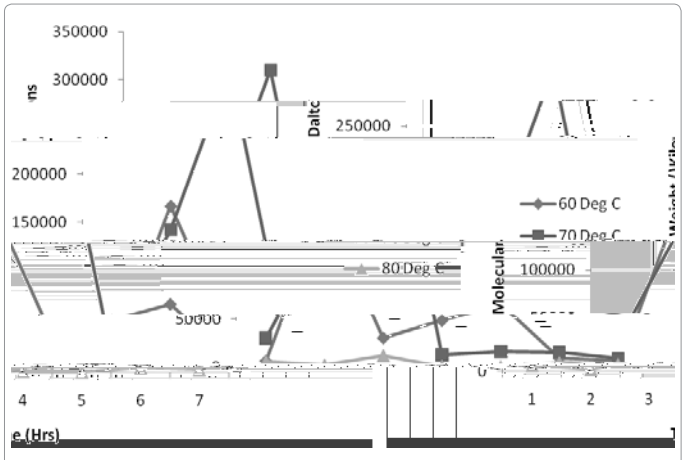


Figure 7: Effect of temperature on molecular weight distribution at 500 rpm impeller speed.

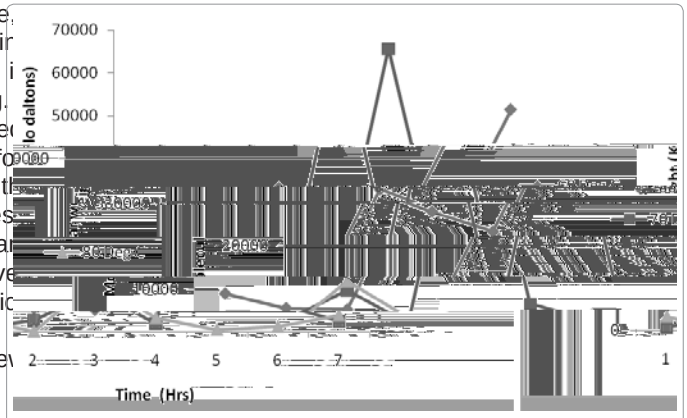
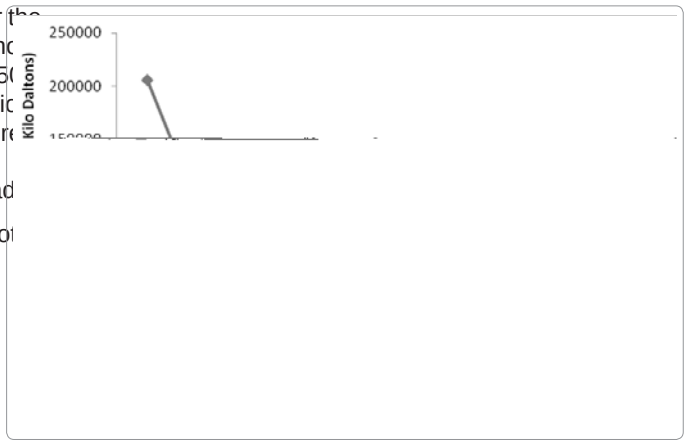


Figure 8: Effect of temperature on molecular weight distribution at 750 rpm impeller speed.



indicates that maximum molecular weight is achieved at the 3 hrs a er maintaining a lower values at the begining of the reaction. Later a er the 3 hrs there is a gradual steady decrease in the molecular weight an nally attaining the least value at the end of 7 hours.

Figure 8 indicated that there is a very low value of molecular weight polymer produced at a particular impeller speed of 750 rpm for all the three temperature considered namely 60°C, 70°C, and 80°C.

Figure 9 indicates the variation of molecular weight for a particular impeller speed of 1000 rpm for various temperatures considered. For all the temperatures considered the maximum value of molecular weight is found to be at the initial reaction time of 1 hr. is was followed by a steady decrease. For 80°C the value of molecular weight throughout the process is found to be very minimal.

Conclusions

In this paper the e ects of temperature and mixing on Ring-Opening Polymerizations (ROP) of -caprolactone was studied by using lipase enzyme Novozym 435 (immobilized form of lipase B from Candida antarctica) as biocatalyst where in for an increase in reaction time the conversion increases steadily and a er a gradual increase there is a decrease which is found uniform for all the temperature showing a uniform trend. e maximum molecular weight out of all the experiments carried out is 310000 KDa which was obtained at a temperature of 70°C and 3 hours for an impeller speed of 500 rpm. e results also indicate that increasing the speed reduces the molecular weight distribution. But the results also have provided a unique trend