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Synthesis of polycaprolactone using tin catalyst: a comparison between dibuthyltindilaurate and tin(II)2-ethyl hexanoate catalyst

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Abstract: In this article tin(II)2-ethyl hexanoate and dibutyltindilaurate catalysts were compared in catalytic preparation of Polycaprolactone. The effects of various parameters such as temperature, reaction time, the molar ratio of monomer to initiator, the molar ratio of catalyst to monomer, the presence and absence of nitrogen, the presence and absence of the initiator has been studied. Consequently, it was found that dibutyltindilaurate catalyst needs shorter time for polymerization and led to higher molecular weight of the polymer than tin(II)2-ethyl hexanoate.

Keywords: Dibuthyltindilaurate, Tin(II)2-ethyl hexanoate, Polycaprolactone, Polymerization.

Introduction

Polycaprolactone (PCL) is an aliphatic polyester with interesting chemical and physical properties which have a variety of industrial applications . PCL is a biodegradable polyester which may be readily synthesized by cationic [1], anionic [2] and coordination polymerization [3]. Biodegradable polymers attract a lot of attention due to their applications as surgical sutures, bone fracture internal fixation devices and drug carriers [4,5]. PCL is the most attractive polymer in biodegradable polymer family, due to its excellent thermal property and permeability to drugs.

The synthesis of PCL has been reported many times with various catalysts. A cationic co-polymerization of caprolactone (CL) and glycerol catalyzed by borontrifluoride increased the molecular weight (Mw) of the products [6]. Lanthanide tris[2,4,6-tri-tert-buthylphenolate]s are highly active catalysts for ring-opening polymerization of CL to give PCL

with average molecular weight [7]. Synthesis of PCL using Zn-Al-and Mg-based organometallic complexes is also reported [8]. Titanium based Lewis acid catalyst was also applied in ring opening polymerization of CL [9]. Polymerization of CL is also reported by double metal cyanide compounds [10]. Many other catalysts such as hydrolase [11], yttriumtriflate [12] and free enzymes [13] have been reported. Several initiators such as diamines [14] and a monohydric or polyhydric alcohol [15] have been used for the preparation of PCL. Microwave irradiation was also used for preparation of PCL in a green way [16].

In this research PCL polymer is synthesized by dibutyltindilaurate catalyst and confirmed by Fourier transform infrared (FT-IR) and nuclear magnetic resonance spectrometer (NMR).Two catalysts tin(II) 2-ethyl hexanoate and dibutyltindilaurate are compared and the effect of different parameters such as temperature, time, the molar ratio of the initiator to the monomer, the molar ratio of the catalyst to monomer are investigated.

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Results and discussion

The ring-opening polymerization of e-caprolactone:

Polymerization of CL catalyzed by dibuthyltindilaurate complex DEG system is well-known. The anionic polymerization occurs through a compelexation of DEG with dibuthyltindilaurate. Mechanism of complex formation and polymerization is shown in Scheme **1**.
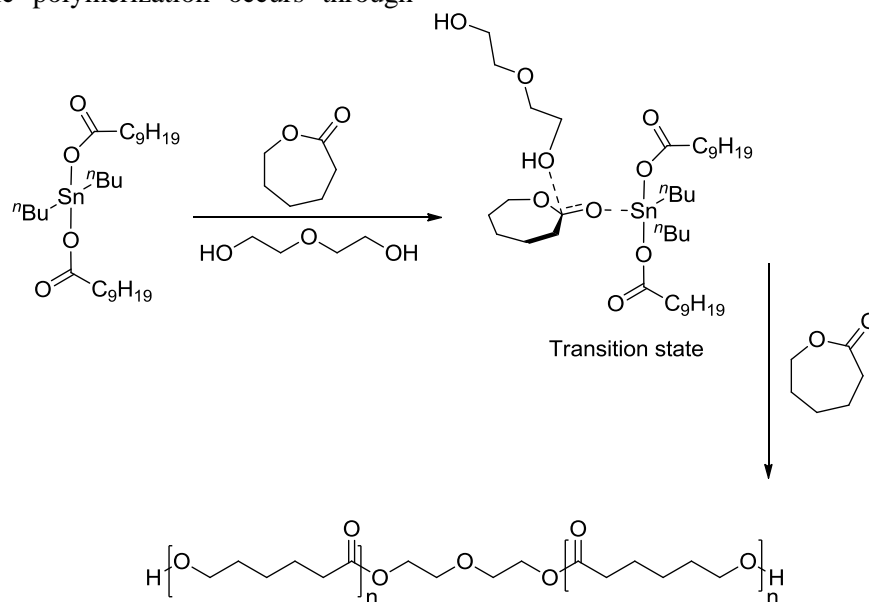
Scheme 1: The mechanism of the polymerization of PCL by using dibuthyltidilaurate catalyst.

The FT-IR spectrum of product is in a good agreement with PCL structure (Fig 1). The characteristic vibration band of ester carbonyl groups (C=O) and the absorption bands of C–O are observed at $1720 cm^{-1}$ and $1192 cm^{-1}$, respectively.
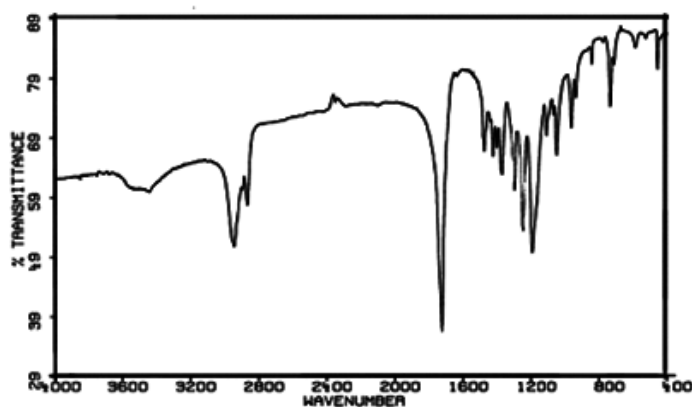

Figure 1: FT-IR spectrum of PCL.

Figure **2** shows the ^1H NMR spectrum of PCL with characterization peaks at 1.4 ppm (H_c), 1.7 ppm ($H_{b,d}$), 2.4 ppm (H_e), 3.7 ppm (H_f), 4.25 ppm (H_a). The ^1H NMR spectrum indicates that the initiator attacks to the carbonyl of the monomer (anionic mechanism).

The effect of initiator/monomer mole ratio:

The influence of catalyst and molar ratio of monomer/initiator is summarized in Table **1**. As seen in Table **1** when the molar ratio of monomer/initiator increased, poly disparity index (PDI) of polymer decreased. Also, increasing the molar ratio of monomer/initiator, molecular weight of polymer is increased. It can be attributed to this fact that increasing the amount of initiator generates more

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active sites for initiating of polymerization therefore shorter polymer chains are obtained.
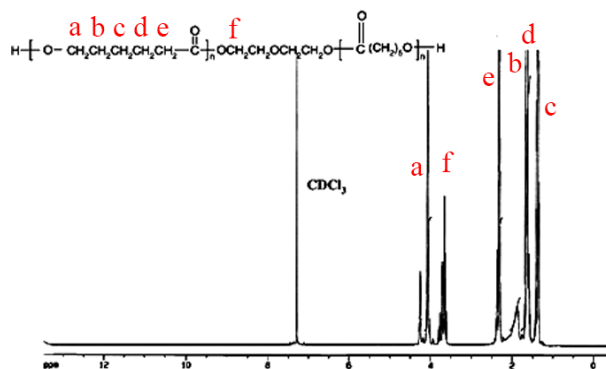

Figure 2: ^{1}H NMR spectrum of PCL.

Comparison between hexanoate and laurate catalyst shows that PDIs are smaller for hexanoate than laurate. However, molecular weights are larger when hexanoate catalyst is used than laurate. Normally, the broader PDI may mainly contributes to the transesterification reaction during the polymerization process.

Table 1: Effect of hexanoate and laurate catalyst on polymerization of CL.

	Hexanoate				Laurate	
Mole ratio[a]	PDI	M_w(g/mol)	Con.(%)	Con. (%)	Mw(g/mol)	PDI
10/1	1.459	1300	76.6	90.3	2192	1.824
20/1	1.258	3076	90.4	96.5	3200	1.621
30/1	1.248	3557	96.6	96.7	4134	1.473
40/1	1.237	4231	80.3	98.1	4998	1.452
50/1	1.202	5328	98.2	98	5100	1.431
60/1	1.191	5327	98.9	98.3	5871	1.413
70/1	1.181	6198	99.8	80.0	6900	1.321
80/1	1.182	7320	100	78.3	7999	1.212
90/1	1.183	8200	98.2	100	9100	1.181

[a] Molar ration of monomer/initiator

Figure 3 shows that the relation between Mw of PCL and molar ratio of CL/DEG for both catalysts are linear. As mentioned, when laurate catalyst is used molecular weights of PCL are higher. *Amount of catalyst:*

Table **2** shows the effect of molar ratio of monomer/catalyst in the synthesis of PCL in the presence of Tin(II)-2-ethyl hexanoate or dibuthyltindilaurate. When the molar amount of the catalysts is low (0.0049 and 0.0032 mmol for hexanoate and laurate catalysts, respectively) the rate of the ring opening reaction of CL slowed down.
The effect of initiator:

Generally, an alcohol can be used with a nucleophilic site as an initiator for controlled synthesis of the polymer. In the absence of an initiator, impurities in Tin(II)-2-ethyl hexanoate (around 1.8 mol% of OH groups) even after two consecutive distillations (high vacuum) appears to play the role of initiator. But, without adding the initiator, in laurate catalyzed polymerization, no polymer was obtained. It shows that laurate catalyst has less impurity than hexanoate catalyst. The mechanism is shown in Scheme **2**. The results confirm the ring-opening polymerization of CL with hexanoate in the absence of initiator proceed via a coordination-insertion mechanism. The monomer coordinated to the transition metal (Sn),

and opened the ring via acyl-oxygen bond cleavage to form a growing chain. The following monomer repeats the steps to insert in to the Sn-O bond in the propagation step (Scheme **2**).

Table **3** shows the effect of initiator on PDI and M_w of PCL. As seen in Table **3**, in the absence of initiator higher molecular weight is obtained when hexanoate catalyst is used. It can be attributed to this fact that without initiator small amount of impurities in catalyst imitates the polymerization and longer polymer chains are generated. But Laurate catalyst has smaller amount of impurity and polymerization did not occur well in the absence of initiator.
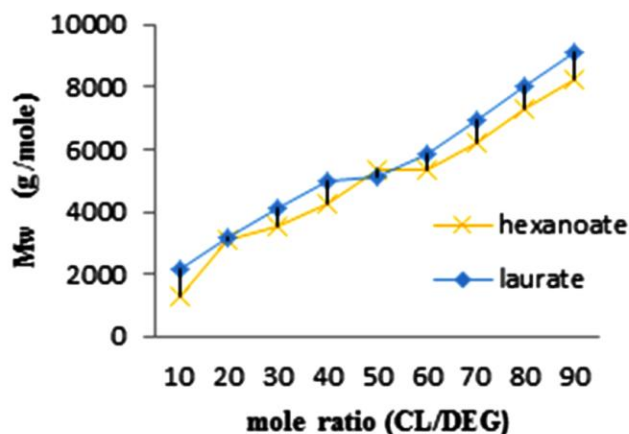

Figure 3: The relation between the Mw and molar ratio(CL/DEG).

The effect of time and temperature:

The effect of time and temperature on CL conversion and M_w of PCL and investigated and results are listed in Tables **4** and **5**. The results show that 15, 19 h of time is preferable for polymerization of CL catalyzed by laurate and hexanoate catalyst, respectively. The monomer conversion and Mw of the polymer reach to a maximum value when the reaction temperature keep at 120 °C. On the other hand, the Mw of the prepared polymer and monomer conversion decrease when the temperature increases up to 120 °C which can be attributed to thermal degradation of catalyst or polymer. It can be noted that in the temperature of more than 120 °C, PDI of the resulting polymer was broad which shows that thermal degradation of the polymers occurred at this temperature (over 120 °C). Based on these results, subsequent polymerizations were occurred at 120 °C. It can be seen that Mw of PCL increases gradually, within 19 h for hexanoate and 15 h for laurate. In suggests that intramolecular trans esterification, i.e., ''back-biting'', which causes degradation and formation of cyclic oligomers and may cause a decrease in the Mw [17-18].

Table 2: The effect of molar ratio(CL/Cat) on the polymerization.

Hexanoate			
Mole ratio(Cat/CL)	**Con. (%)**	**M_w(g/mol)**	**PDI**
5/10	95	2000	1.912
2/52	100	3557	1.248
1/69	98	3000	1.312
1/26	96	2500	1.721
Laurate			
7/81	80	1000	2.911
3/97	100	4134	1.473
2/63	99	4100	1.510
1/97	98	4000	1.551

[a] Reaction condition: molar ratio (CL/DEG):30/1
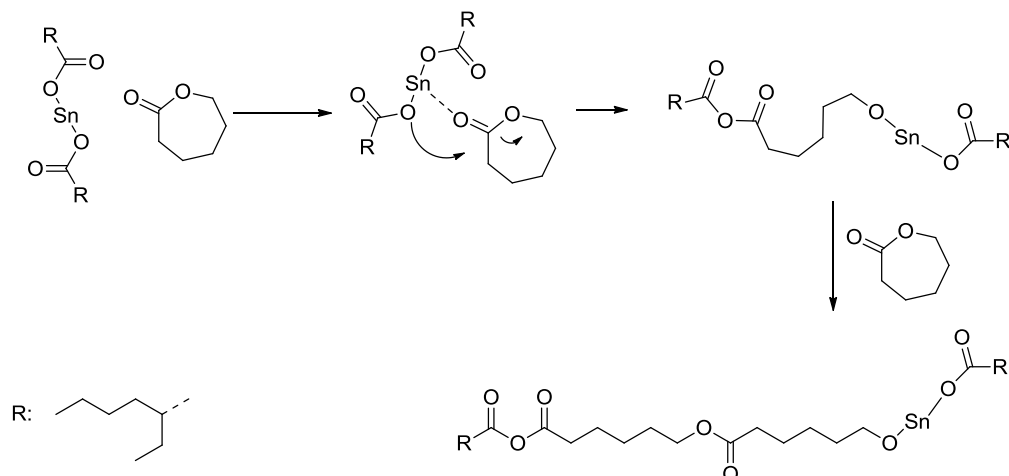
Scheme 2: Mechanism of the polymerization in the absence of initiator.

Table 3: The effect of the initiator on the polymerization [a].

Hexanoate			
Initiator	**m.p (^{o}C)**	**M_w (g/mol)**	**PDI**
Present	53.5-55	3557	1.248
Absent	58.2-60.7	5000	3.121
Laurate			
Present	52-54.2	4134	1.473
Absent	42-47.5	1000	2.011

[a] Molar ratio (CL/DEG):30/1

Table 4: The effect of reaction temperature and time on the polymerization.

hexanoate				
Temperature (^{o}C)	**Time (h)**	**Con. (%)**	**Mw (g/mol)**	**PDI**
100	19	0	-	-
110	19	48	1011	2.10
120	19	100	7320	1.182
130	19	98	7150	1.780
140	19	96	7000	1.99
120	15	20	200	3.00
120	18	99.9	7300	1.181
120	25	93.1	7150	1.3
Laurate				
100	15	0	-	-
110	15	40	2000	2.00
120	15	98	8900	1.31
130	15	100	9100	1.18
140	15	99	900	1.20
130	10	20	99	3.00

130	14	99.9	9098	1.171
130	19	97	9090	1.19
130	25	96	9000	1.21

Condition: Molar ratio (CL/DEG):30/1

The effect of nitrogen atmosphere:

The presence of N_2 atmosphere in the reaction medium was investigated and it was found that N_2 atmosphere can remove water steam in reaction medium. The presence of water can degrade polymer chains in high reaction temperature. Also water can act as an initiator and reduce polymer chain length and increase the PDI of polymer The effect of presence of N_2 atmosphere in the reaction medium has shown in Table **5**.

Table 5: Effect present and absent of N_2 on the polymerization.

Hexanoate				
N_2	**m.p (^{o}C)**	**Con. (%)**	**M_w(g/mol)**	**PDI**
Present	53-55	100	3557	1.248
Absent	50.3-52.4	97	2980	1.712
Laurate				
Present	51.6-54	100	4134	1.473
Absent	49-51	98	3000	1.99

Condition: mole ratio (CL/DEG):30/1

Conclusion

In this paper PCL polymer was synthesized using dibutyltindilaurate catalyst. The effects of different parameters on the M_w of the polymer have been investigated. Also, a comparison of tin (II) 2 – ethyl hexanoate and dibuthyltindilaurate catalysts is done. It can be concluded that hexanoate catalyst needs a long reaction time for the CL polymerization and it is more sensitive to various reaction conditions than laurate catalyst. These can be considered as disadvantages for hexanoate as a catalyst for the synthesis of the PCL. Therefore, the dibuthyltindilaurate is introduced as a desirable catalyst for PCL polymerization and it can be used for large scale application.

Experimental

Materials and methods:

Tin(II)-2-ethyl hexanoate and dibuthyltindilaurate were purchased from Alfa Aser company. CL (Acros 99%) was distilled under reduced pressure. Diethylene glycol (DEG) (99.9%) was purchased from Merck. ^{1}H NMR were recorded on a Bruker Av-500 MHz in CDCl$_3$ as solvent with TMS as internal standard. Average molecular weight and molecular weight distributions (PDI) of PCL were measured by gel permeation chromatography (GPC) Agilent 1100 (THF as solvent, flow rate 1mL/min) with a refractive index detector, calibrated using polystyrene standard. The melting point was determined with a Gallenkamp instrument. Infrared spectra were recorded on a Shimadzu FT-IR instrument.

Preparation PCL using tin(II)2-ethyl hexanoate:

0.68 mmol distilled DEG, 0.025 mmol stannous 2-ethylhexanoate and 20.4 mmol freshly distilled CL was placed in a 250 mL round bottom flask. The temperature of flask was increased to 120 ^{o}C over a period of 3h and the reaction was stirred for 19h under nitrogen atmosphere. After cooling to room temperature a waxy solid was formed that was washed with diethyl ether three times and dried at 40 ^{o}C.

Preparation of PCL using dibuthyl tin dilaurate catalyst:

Same procedure was performed for preparation PCL catalyzed by dibuthyl tin dilaurate except 0.016 mmol catalyst was used.

Acknowledgement

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