

Novel and Efficient Catalyst for the Synthesis of Polycaprolactone

Somayeh Mazloom Darbandy¹, Alireza Bakhtiary² and Hossein Taheri²⁺

¹ Islamic Azad University, North Tehran Branch, Tehran, Iran

² University of Tehran, Tehran, Iran

Abstract. Ring-opening polymerization of ϵ -caprolactone is catalyzed by proton exchanged organically-modified nanoclay (ONC-H⁺) as an initiator. As a result, polycaprolactone (PCL) polymer is produced and its formation is confirmed using FTIR and NMR spectroscopy. It is found that cationic polymerization of ϵ -caprolactone is initiated by ONC-H⁺ at 90°C (in toluene), further, the effect of the temperature on the reaction is studied. Some ONC-H⁺ catalysts with different basal spacing are prepared and the effect of basal spacing and polarity of catalysts on polymerization yield are investigated. Mechanism-based studies showed that the monomer is inserted into the growing chains through breaking the acyl-oxygen bond scission rather than the alkyl-oxygen bond.

Keyword: polymerization, polycaprolactone, organically-modified nanoclay (ONC-H)

1. Introduction

Biodegradable polymers have been extensively investigated for temporary therapeutic applications such as surgical sutures, bone fracture internal fixation devices, drug delivery systems, as well as tissue engineering scaffolds [1,2]. In recent years, some researches are focused on using new modified natural clays as catalysts or initiators for polymerization of vinylic and hetero-cyclic monomers [3,4,5]. In this work, we would like to report a new and efficient catalyst which is a protonated organically-modified nanoclay (ONC-H⁺) in order to synthesis PCL. It contains both Bronsted and Lewis acid sites and when exchanged with cations having a high charges density such as protons, it is converted to a highly-active catalyst for acid-catalyzed reactions [6]. ONC is nanoclay modified by dimethyl di(hydrogenated tallow) ammonium chloride to become organophilic. The nanoclay used in this process is a type of bentonite produced by Iranian companies, and it is purified (for montmorillonite) and nanosized in laboratory. ONC is then protonated (ONC-H⁺) to become more active as catalyst for acid-catalyzed reactions. ONC is organophilic compared to montmorillonite, moreover, the spacing between the layers are increased so that it can be dispersed through the organic reaction media freely producing a homogenous environment. Therefore, the highly polarized sites for catalyzing the ring opening polymerization are easily accessible by caprolactone monomer. The product (polymer) is very soluble in chloroform and can be extracted from the reaction media easily.

This paper includes two parts:

- Experimental
- Results and Discussion

2. Experimental

2.1. Materials

Caprolactone (grade 99%) used in this study is purchased from Aldrich chemical company. Toluene and tetrahydrofuran solvents are distilled over blue benzophenone-Na complex. Other solvent, Dichloromethane,

⁺ Corresponding author. Tel.: + 98.912.4398109
E-mail address: darbandysanaz@yahoo.com

is dried over CaH_2 and distilled just before the beginning of experiment. Also, Methanol is dried over magnesium sulphate MgSO_4 and distilled.

2.2. Measurements

^1H NMR spectra of PCL are recorded on a Bruker Av-500 MHz spectrometer in CDCl_3 at the room temperature with TMS as internal standard. Average number of the molecular weight (M_w) and molecular weight distributions (PDI) of PCL are measured in THF at $30\text{ }^\circ\text{C}$ by Gel permeation chromatography (GPC) Agilent(1100 flow 1ml/min) with a refractive index detector and a set of columns(PL gel $10\text{ }\mu\text{m}$ mixed-B $300\text{mm}\times 7.5\text{mm}$)($500, 10^3, 10^4\text{ \AA}$ in series) which are calibrated using polystyrene standard. The melting point is determined with a Gallenkamp instrument, and Infrared spectra are recorded on a Shimadzu FTTR instrument to confirm PCL formation.

2.3. Preparation of “Organically-Modified Nanoclay”

To prepare the nanoclay, raw bentonite is placed in a beaker together with 1000 ml of distilled water. The bentonite/water mixture is stirred for 2hr and then centrifuged for montmorillonite purification. The obtained mixture is homogenized using homogenizer (at 20000 rpm) to produce a stabilized suspension. Dimethyl di(hydrogenated tallow) ammonium chloride (DMDHT) is added to the montmorillonite/water suspension while stirring and heating (about 80°C) for 1hr. ONC is filtered, washed with distilled water thoroughly and dried at $100\text{ }^\circ\text{C}$.

2.4. Preparation of “ONC-H+ ”

ONC-H⁺ is prepared according to the process reported in previous studies [7,8]. Organically-modified nanoclay (20g) is crushed for 20 min using a prolabo ceramic balls grinder. It is then dried for 2 hr at $105\text{ }^\circ\text{C}$. The organically-modified nanoclay is placed in an Erlenmeyer flask together with 500 ml of distilled water. The mixture is stirred using a magnetic stirrer and combined with 0.25 M sulfuric acid solution, until saturation is achieved over 2 days at room temperature. The mineral is then washed with distilled water to become sulphate free and then dried at $105\text{ }^\circ\text{C}$.

2.5. Preparation Polycaprolactone Polymer

The ring-opening polymerization of ϵ -caprolactone is carried out in 25 cc flasks. Each flask contains a mixture of ϵ -caprolactone monomer (1gr) and catalyst of ONC-H+-15 or ONC-H+-25 (0.1gr) and solvent of toluene (0.2gr). These flasks are equipped with a magnet stirrer, nitrogen atmosphere and the mixture is allowed to heat up to $85\text{ }^\circ\text{C}$ in the oil bathroom. The increase of the temperature occurs gradually over a three-hour period. The reaction temperature is maintained between $85\text{ }^\circ\text{C}$ and $90\text{ }^\circ\text{C}$ for 10 hr. The reaction is terminated by methanol. The resulting polymer is extracted with dichloromethane, precipitated in Methanol, washed for several times, dried at $40\text{ }^\circ\text{C}$ in vacuum and weighed. The monomer conversion is determined gravimetrically by weighing the precipitated polyester chains.

3. Results and discussion

3.1. Ring-opening polymerization of ϵ -caprolactone

The ϵ -caprolactone is well known to be polymerized by protonic acid [9,10]. Cationic Polymerization of ϵ -caprolactone is examined in the presence of ONC-H⁺ (15,25) powder at different temperatures. It is clear that the ending methyl ester group is introduced into the growing chain only at the termination stage. Result of ^1H NMR indicates that the monomer is inserted into the growing chains through the acyl-oxygen bond scission rather than breaking of alkyl-oxygen bond (Fig 1,2). The IR measurements of product are in a good agreement with polycaprolactone structure. The vibrational characteristics of linear ester carbonyl groups ($\text{C}=\text{O}$) and C-O bonds are observed respectively at 1720 cm^{-1} and 1192 cm^{-1} respectively.

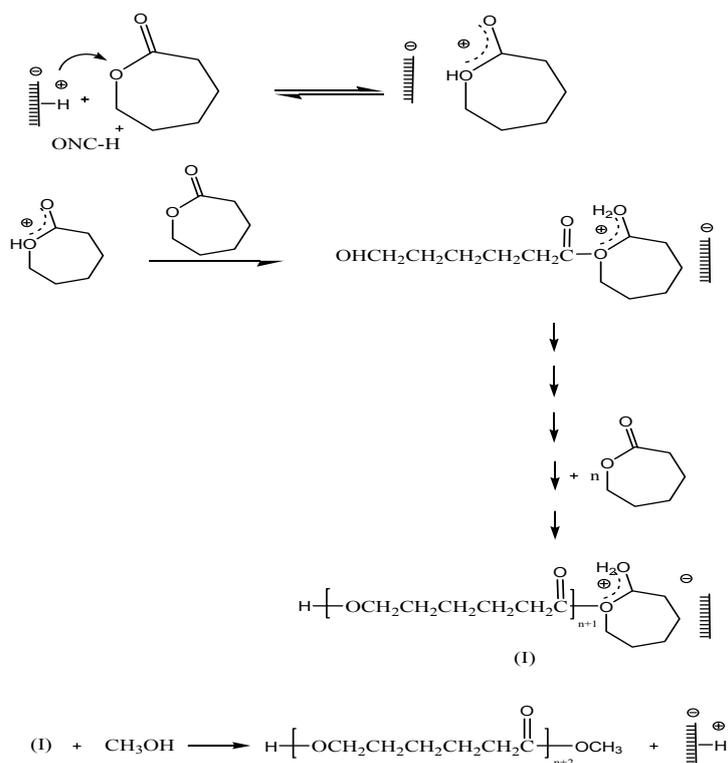


Fig. 1: Mechanism of ϵ -caprolactone Polymerization catalysed by ONC-H⁺

In the ¹H NMR spectrum, signals are assigned as follows: δ 4.06 ppm (Ha), δ 2.31 ppm (Hb) δ 1.39 and 1.66 ppm (Hc), which characterize the polymer chain. Overlapping resonances are related to methyl of ending ester group (s, δ 3.66 ppm) and the -CH₂-OH ending group (t, δ 3.63 ppm) (Hd).

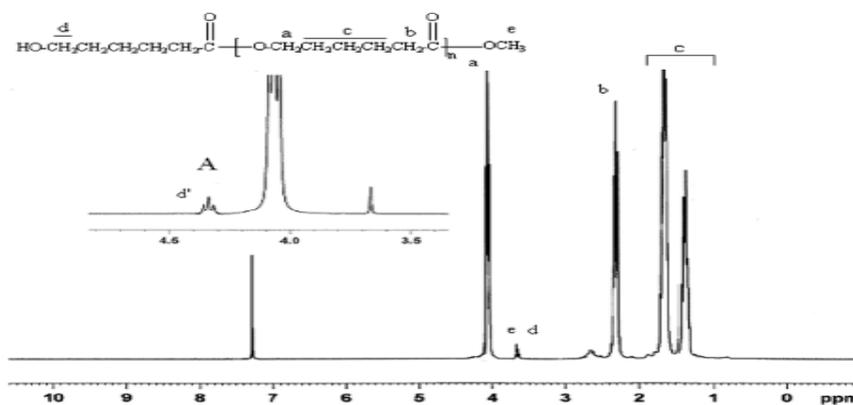


Fig. 2: ¹H NMR spectra of poly (ϵ -caprolactone)

3.2. Effect of Temperature

Table 1 presents the experimental results for the ϵ -caprolactone polymerization initiated by (ONC-H⁺-15,25) at different temperatures. It is found that ONC-H⁺-15,25 themselves possesses appropriate activity as initiator in ϵ -caprolactone polymerization reaction. The monomer conversion and molecular weight of polymer reach maximum values around temperature of 90-100 °C. On the other hand, with the increase in the reaction temperature above 110 °C, the molecular weight of the obtained polymer and monomer conversion decrease progressively suggesting the possible occurrence of thermal degradation. It can be noted that above 110 °C, PDI of the resulting polymer is broad which is also resulted from the same reason. On the basis of these results, subsequent polymerizations are carried out at 90 °C.

Table. 1: Effect of reaction temperature on the \square -caprolactone polymerization^a

T (°C)	ONC-H ⁺ -25			ONC-H ⁺ -15		
	PDI	Mn (g/mol)	Conv (%)	PDI	Mn (g/mol)	Conv (%)
70	1.348	2516	75	1.773	2150	70
80	1.212	3000	88	1.510	2700	82
90	1.121	3850	96	1.351	3500	90
100	1.372	3200	87	1.421	3000	83
110	1.411	3120	85	1.524	2785	80
120	1.526	2700	70	1.609	2400	65

^a ONC-H⁺/ \square -caprolactone weight ratio = 10%. Reaction time 10h.

3.3. Comparing ONC-H⁺-15 and ONC-H⁺-25 and their efficiency as catalyst

ONC-15 and ONC-25 are two kinds of organically-modified nanoclay which are different in basal spacing. It is possible to have various kinds of ONC by changing the reaction conditions. The spacing between the layers in ONC-15 is about 21.1 Å and in ONC-25 is about 17.1 Å (XRD patterns). The organic ammonium salt (DMDHT) used in the reaction is the same in both of them. Consequently, the spacing between the layers in ONC-H⁺-15 and ONC-H⁺-25 are increased to about 39.7 Å and 27.5 Å respectively (according to XRD patterns).

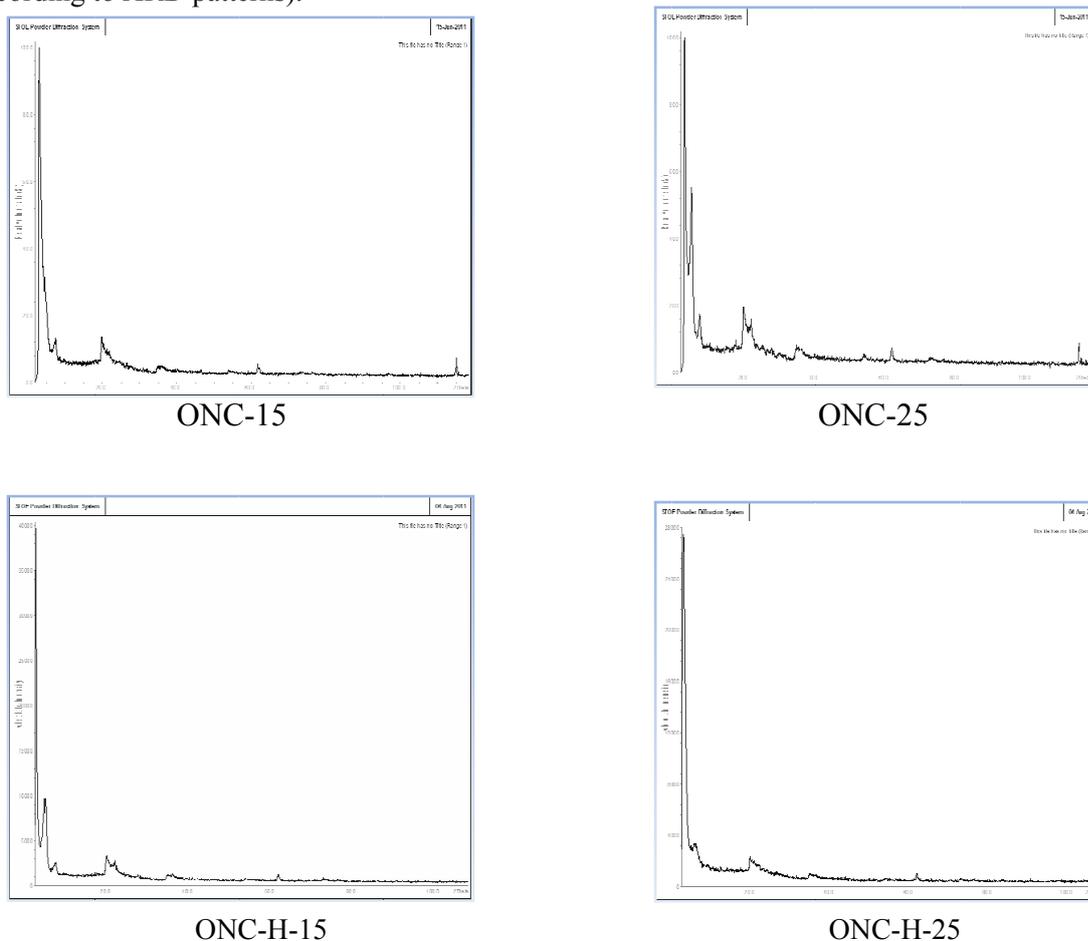


Fig. 3: XRD patterns of ONC and ONC-H⁺ samples

The polymerization yield is about 95% when using ONC-H⁺-25 while it is decreased to about 80% when using ONC-H⁺-15. ONC is organophilic compared to montmorillonite and the spacing between the layers has been increased (11.8 Å for montmorillonite) so it can be dispersed through the organic reaction media

freely producing a homogenous environment. By protonating the samples, basal spacings will increase more causing the highly polarized sites for the purpose of catalyzing the ring opening polymerization to be easily accessible by caprolactone monomers.

4. References

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