



## Preparation and characterization of polyesters with controlled molecular weight method

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### Abstract

*p*-Toluene sulfonic acid (*p*-TSA) as an efficient catalysts has been used for the preparation of various polyesters via controlled molecular weight method using of adipic acid, mono /di/triethylene glycol, 2-ethyl-2-(hydroxymethyl)propane-1,3-diol and 1,4 Butanediol as starting materials. The resulting polyesters were prepared in high yields and were characterized by the using of FT-IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy. The effect of the catalysts on the rate of the reaction has been investigated.

**Key words:** Controlled molecular weight, *p*-Toluene sulfonic acid (*P*-TSA), Aliphatic polyesters, Biodegradable, Synthesis.

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### 1. Introduction

Polyurethanes (PU) are a class of polymers that have found a widespread use in many fields related to man life such as production of furniture, coatings, adhesives, constructional materials, fibers, padding, paints, elastomers and synthetic skins [1,2]. For example: polyurethane-maleamides (PUMAs) for cardiovascular applications [3], Biodegradable injectable polyurethanes for orthopedic applications [4], polyurethane foams are proposed as new polymeric phases for stir bar sorptive extraction (SBSE) [5], Polyurethane networks based on hyper branched polyesters (these polymer have potential applications in a variety of fields, such as biomedical applications, catalysis commercial coatings) and other applications [6]. Polyesters are based materials for preparing of polyurethane [7]. The family of polyesters comprises all polymers with ester functional groups in the polymer backbone. The chemistry of the structural units connecting the ester group can be varied over an immensely broad range, making the polyesters a diverse group covering everything from labile biomedical matrices to liquid crystals, fibers and temperature resistant performance materials. Polyesters were historically the first family of synthetic condensation polymers [8-10]. Polyesters can typically be formed by a stepwise condensation reaction from difunctional monomers such as diols and acids [9]. For example: sebacic acid (SA) is an intermediate product of  $\alpha$ -oxidation of long-chain aliphatic acid [11].

However, it was very difficult to prepare aliphatic polyesters by direct polycondensation because of the thermal degradation at high temperature and low hydrolytic stability in one step [7]. Therefore, a tedious chain extension is needed using diisocyanates and diphenyl carbonates [12,13]. Aliphatic homo and copolyesters prepared by polycondensation of diols and diacids such as ethylene glycol or 1,4 butanediol and adipic acid are biodegradable [8]. Biodegradable polymers with good biocompatibility, nontoxicity and environmental acceptability have attracted much attention in the various fields. Recently, Ishihara et al. reported that the  $\text{HfCl}_4$  (THF)<sub>2</sub> complex more efficiently catalyzed the direct polycondensation of diols and dicarboxylic acid compounds, in which the procedure was a solution polycondensation in *o*-xylene with reflux (ca. 144 °C) for 24h [7, 14]. We believed that it is still a challenging subject to seek other excellent catalysts for the aliphatic polyesters in order to achieve the one-step synthesis of aliphatic polyesters under milder conditions (lower temperature and short time). Polycondensations under mild conditions are very important from an environmental technology viewpoint [15]. Recent concern toward environmental problems prompted us to explore an ideal polycondensation system taking (1) low temperature, (2) avoiding organic solvent, (3) atomic economy, (4) lack of catalyst toxicity after use, and (5) catalyst recyclability and reuse  $\text{Sc}(\text{OTf})_3$  catalyzed direct Esterification of aliphatic alcohol with

carboxylic acid at room temperature [16]. The present work describes the synthesis of aliphatic polyesters with controlled molecular weight that obtained from utilizable primary matters of reaction (Adipic acid, Mono-Di-Triethylene glycol, Trimethylolpropane and 1,4 Butanediol) by polyesterification process at presence of PTSA(*p*-toluensulfonic acid), Ti(OBu)<sub>4</sub> and Sn(oct)<sub>2</sub> catalysts. These aliphatic polyesters also described based on changing the arrangement of primary matters for reaction. Optimum condition at the reaction, through the increasing of Trimethylolpropane determined, in order to producing of polyesters with controlled molecular weight and also reaction rate determined by using neutral and biocompatible catalysts.

## 2. Materials and methods

### 2.1. General

All materials have been purchased from Aldrich chemical company. The NMR spectra were recorded on a Bruker Avance DPX 300 MHz instrument. The spectra were measured in CDCl<sub>3</sub> relative to TMS (0.00 ppm). IR spectra were recorded on a Tensor 27, Bruker spectrophotometer.

### 2.2. Polymer synthesis

Poly-esters were prepared by poly-condensation reaction of stoichiometric quantities of acids and alcohols in the presence of a catalytic amount of *p*-toluene sulfonic acid. The synthesis of aliphatic polyesters was performed following the two-stage melt poly-condensation method (Esterification and poly-condensation) in a glass batch reactor. The polycondensation reactor was a three necked flask equipped with thermometer, separator, mechanical stirrer, distillation head and dropping funnel.

#### 2.2.1. Synthesis of polyesters via two-component condensation reaction

A mixture of adipic acid (14.8 g), diethylene glycol (10.6 g) and *p*-TSA (0.1 g) as catalyst were mixed with constant stirring and charged into the reactor and was electrically heated until the temperature raised to 160 °C.

#### 2.2.2. Synthesis of polyesters via three-component condensation reaction

In this method, polyesters 2-4 were prepared via changing in the arrangement of utilizable primary materials (Adipic acid, Ethylene glycol, Diethylene glycol and 1,4-butanediol).

**Polyester 2:** To a mixture of adipic acid (44.4 g, 0.3 mol), ethylene glycol (21.1 g, 0.3 mol) and 1,4-butanediol (9 g, 0.1 mol), *p*-TSA (0.1 g) as catalyst were added and mixed with constant stirring. Then mixture was charged into the reactor and was electrically heated up to 170-180 °C for 6h.

**Polyester 3:** To a mixture of adipic acid (44.4 g, 0.3 mol), diethylene glycol (10.6 g, 0.1 mol) and 1,4-butanediol (18 g, 0.2 mol), *p*-TSA (0.1 g) as catalyst were added and mixed with constant stirring. Then mixture was charged into the reactor and was electrically heated up to 170-180 °C for 6h.

**Polyester 4:** To a mixture of adipic acid (44.4 g, 0.3 mol), triethylene glycol (6.7 g, 0.1 mol) and 1,4-butanediol (9 g, 0.1 mol), *p*-TSA (0.1 g) as catalyst were added and mixed with constant stirring. Then mixture was charged into the reactor and was electrically heated up to 170-180 °C for 6h.

**Polyester 5:** To a mixture of adipic acid (44.4 g, 0.3 mol), ethylene glycol (21.1 g, 0.3 mol) and diethylene glycol (13 g, 0.1 mol), *p*-TSA (0.1 g) as catalyst were added and mixed with constant stirring. Then mixture was charged into the reactor and was electrically heated up to 160-170 °C for 6h.

### 2.2.3. Synthesis of polyesters via four-component condensation reaction

**Polyester 6:** To a mixture of Sebacic acid (6.0 g, 0.3 mol), Diethylene glycol (10.6 g, 0.1 mol), 1,4butanediol (18.0 g, 0.2 mol) and 2-ethyl-2-(hydroxymethyl)propane-1,3-diol (13.4 g, 0.1 mol), *p*-TSA (0.2 g) as catalyst were added and mixed with constant stirring. Then mixture was charged into the reactor and was electrically heated up to 160-170 °C for 6h.

### 2.2.4. Synthesis of polyesters via five-component condensation reaction

**Polyester 7:** *p*-TSA (1 g) as catalyst was added to a mixture of adipic acid (45.47 g, 0.3 mol), triethylene glycol (10.6 g, 0.1 mol), 1,4butanediol (18.0 g, 0.2 mol) and ethylene glycol (21.2 g, 0.3 mol) and mixed with constant stirring. Then mixture was charged into the reactor and was electrically heated at 110 °C until the first drop of water was appearing in the separator. The mixture was cooled to room temperature and 2-ethyl-2-(hydroxymethyl) propane-1, 3-diol (1.34 g, 0.01 mol) was added to mixture. In continue the mixture was charged into the reactor and was electrically heated at 110 °C until the reaction was completed.

## 2.3. Analysis of samples

### 2.3.1. Acid value (AV):

The acid value is a measure of the amount of free acid groups in the polymer melt and is expressed in terms of the number of milligram of potassium hydroxide required to neutralist 1g of sample using a phenolphthalein indicator, or in mathematical terms:

$$AV = \frac{56.1VN}{W} \quad (1)$$

Where AV= acid value (mg KOH/g of polymer), V= volume of potassium hydroxide used for titration (ml), N= normality of potassium hydroxide solution (mol dm<sup>-3</sup>), and W= weight of test sample (g).

### 2.3.2. Hydroxyl number (HN)

The hydroxyl number is expressed in terms of the number of milligram of potassium hydroxide required to neutralist 1g of sample using a phenolphthalein indicator, or in mathematical terms.

$$V(\text{OH}) = [(K-X) \times 40 \times N(\text{NaOH})/m] \quad (2)$$

Where X= the obtained capacity of base test (ml), K= comparative capacity (ml) and m= the weight of sample.

$$HN = \frac{56.1VN}{W} \quad (3)$$

### 2.3.3. The number of average molecular mass ( $M_n$ )

The number average molecular mass can be found from empirical formula.

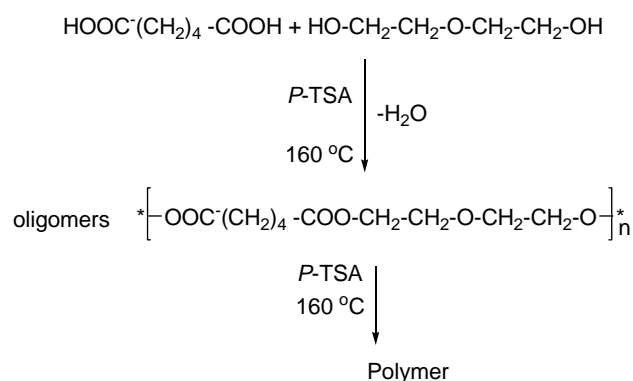
$$M_n = \frac{112220}{AV+HN} \quad (4)$$

$$\text{or} \\ M_n = \frac{56000}{AV} \quad (5)$$

Where  $M_n$  = number average molecular mass ( $\text{g mol}^{-1}$ ), AV = acid number of the melt ( $\text{mg KOH/g polymer}$ ) and HN = hydroxyl number of the melt ( $\text{mg KOH/g polymer}$ )

### 3. Results and Discussion

The polymerisation process for of aliphatic polyesters preparation with controlled molecular weight involves two steps according to the well-known process used for polyester synthesis [2, 3]. In the first stage (esterification), adipic acid reacts with diethylene glycol and water is eliminated as byproduct. *P-TSA* catalysis the reaction process and the reaction takes place at elevated temperature ( $160^\circ\text{C}$ ). In this condition water that was formed in the reaction media can be easily removed from the reactor and oligomers are prepared. In order to increase the molecular weight in the second (polycondensation), the prepared oligomers are condensed at high temperature ( $160^\circ\text{C}$ ). The reactions that take place during these stages and the procedure that was used for the synthesis of aliphatic polyesters are presented in Scheme 1.



Scheme 1

Some of the physical properties of polyesters 2-9 such as acid values (AV), hydroxyl numbers (HN) and molecular weights ( $M_n$ ) are presented in Table 1. The prepared polyesters have average molecular weights between  $1785\text{-}2380 \text{ g mol}^{-1}$  as indicated in Table 1.

The slope of acid number curves has been shown in Table 2. As can be seen from Table 2, the slope of acid number curves at 30 hours in the beginning of the reaction decreased intensively about from 30 to 50 hours that diminished very slowly, as the time that spent in order to decreasing of the acid value from 4 to  $1.5 \text{ (mg KOH /g Polyester)}$  was 2 hours. Significant increase in the reaction rate has been achieved by decrease the time of the reaction from 50 to 40 hours.

**Table 1:** Acid value (AV), Hydroxyl number (HN) and ( $M_n$ ) Molecular weight of aliphatic polyesters 2-9

Polyester Number	AV acid number (mg KOH/g Polymer)	HN; hydroxyl number (mg KOH/g Polymer)	$M_n$ molecular mass ( $\text{g mol}^{-1}$ )
2	16.0	40	1785
3	10.0	46	1785
4	19.0	16	2857
5	9.0	46	1818
6	13.0	41	2364
7	2.0	40	2380
8	1.3	43	2257
9	1.0	45	2173

FT-IR spectra of polyester 8 presented significant bands representative of the groups present (Fig. 1). ( $-\text{OH}$ ,  $-\text{COOH}$ ) stretching were located at  $3400\text{-}3550 \text{ cm}^{-1}$ , stretching vibration bond of ( $-\text{CH}_2$ ) were observed at  $2800\text{-}2950 \text{ cm}^{-1}$  and the carbonyl stretching band appeared at  $1700\text{-}1750 \text{ cm}^{-1}$ .

**Table 2:** Acid value (AV)

Entry	Time (h)	AV (mg KOH/g Polymer)
1	5	45.0
2	10	35.0
3	13	30.0
4	20	19.0
5	25	16.0
6	30	13.0
7	35	10.0
8	40	7.0
9	45	5.0
10	50	3.0
11	55	2.0
12	60	1.3

$^1\text{H-NMR}$  spectra of the samples show the expected characteristic peaks. The peak at  $7.27 \text{ ppm}$  belonging to the  $-\text{CH}_2$  of the trimethylolpropane (b). the peaks at  $4.20\text{-}4.39 \text{ ppm}$  belonging to the  $-\text{CH}_2$  in the ethylene glycol (e). The peaks between  $4.06\text{-}4.20 \text{ ppm}$  were assigned to  $-\text{CH}_2$  belonging to triethylene glycol. The peaks at  $3.41\text{-}3.71 \text{ ppm}$  were identified as  $-\text{CH}_2$  in 1, 4 butanediol (g). The peaks at



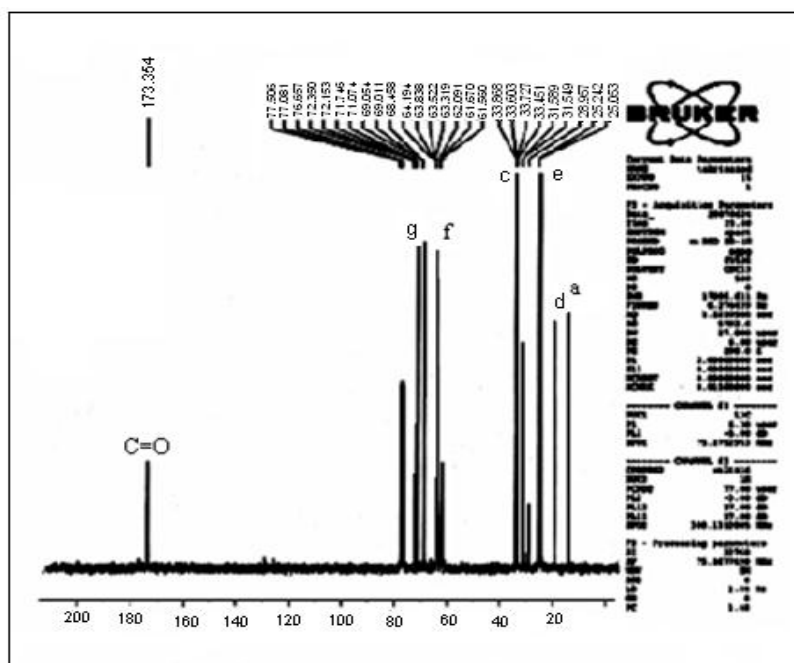


Figure 3.  $^{13}\text{C}$ -NMR spectra of polyester 8

#### 4. Conclusion

The polyesters with controlled molecular weight were synthesized. The synthesis of these polyesters with controlled molecular weight was time consuming using *P*-TSA catalyst than  $\text{Ti}(\text{O}i\text{Bu})_4$  and  $\text{Ti}(\text{OC}_4\text{H}_9)_4$ , the acid number was obtained at the short time. The advantages of this catalyst are low-cost, non-toxicity after use and availability. Therefore, these polyesters are certainly useful for preparing high quality products at different industries.

#### Abbreviations

- P*-TSA : *p*-Toluene sulfonic acid  
 LDPE : Low-density polyethylene  
 AV : acid value  
 V : volume of potassium hydroxide used for titration (mL)  
 N : normality of potassium hydroxide solution ( $\text{mol dm}^{-3}$ )  
 W : weight of test sample (g)  
 HN : hydroxyl number  
 X : the obtained capacity of base test (ml)  
 K : comparative capacity (ml)  
 m : the weight of sample (g)  
 $M_n$  : The number of average molecular mass ( $\text{g mol}^{-1}$ )

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