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Low cost and less toxic p-Toluene sulfonic acid catalysed ecofriendly and extremely rapid synthesis of aliphatic poly esters

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ABSTRACT

Herein we demonstrate a rapid, environmentally benign method for aliphatic polyester synthesis by direct condensation of equimolar quantities of dicarboxylic acid and diol with commercially available, cheap, and less toxic *p*-Toluene sulfonic acid monohydrate as catalyst. In the presence of microwave irradiation at 230°C, Poly (butylenesuccinate) with $M_w = 2.50 \times 10^4$ was synthesized in 20 minutes. The methodology was also extended for the synthesis of various other aliphatic polyesters.

KEYWORDS

Aliphatic polyesters;
Solvent free;
Microwave irradiation;
p-Toluene sulphonic acid;
Poly condensation;
Ecofriendly.

INTRODUCTION

Governments in various countries have adopted policy targets that involve making optimal use of “biomass” (organic materials derived from renewable and living organisms as opposed to fossil resources) as a source of energy and raw materials to realize a society that is capable of sustainable development. The worldwide demand for biocompatible polymers is said to be growing by about 30% per year. Some of the biobased polymers available includes poly lactic acid, poly(alkylene succinate), starch and cellulose based polymers. Poly butylene succinate gains considerable attention as it can be produced from natural resources. Succinic acid can be industrially produced by fermentation process using renewable sources and 1,4-Butane diol has been produced by the reduction of succinic acid. Therefore PBS can be regarded as a bio-based plastic with biodegradability, acceptable mechanical strength and softening temperature that mimic those of traditional plastics such as low density poly ethylene (LDPE). When materials derived from biomass are used to synthesize polymers by polycondensation, the products are often claimed to be carbon neutral, because the source of the carbon and oxygen in the material is atmospheric CO_2, but in reality it is actually difficult to achieve an equimolar reaction and there is a hidden problem in terms of atom economy. Furthermore, a large amount of process energy derived from fossil fuels is still required because of the need for a high reaction temperature and a prolonged reaction time.

Generally aliphatic polyesters for commercial use are prepared by the polycondensation of aliphatic dicarboxylic acid (0.4 mol) and diol (0.52 mol) by a two step process, the first step involves the formation of oligomers at 200° C for 3 h and in the second step the temperature was raised to 250° C under highly reduced pressure in the presence of catalysts like $Ti(OBu)_4$ and $Ge(OBu)_4$[1]. Polycondensation is an equilibrium reaction and, to shift the balance toward the products and to obtain polymers with a high degree of polymerization, eliminated components such as water must be completely removed from the system. Industrially, an excess of the diol or dicarboxylic acid component is used in most cases to compensate for the loss of the lower-boiling component as a result of the depressurized or azeotropic conditions that are required to remove the eliminated components and suppress the reverse reaction.

However, direct polycondensation using equimolar amounts of diacids with diols in the presence of catalyst is gaining considerable attention from the economical point of view. Since the beginning of the 21st century, several attempts have been made to synthesize aliphatic polyesters efficiently by an equimolar reaction. These have resulted in dramatic improvements on conventional methods and involve the use of hafnium (IV) or zirconium (IV) salts[2,3], rare earth triflates[4,5], distannoxane[6], or tin (II) chloride[7] as catalysts. Zhu et al.[7] described the use of Tin (II) chloride (59 h) as a catalyst for the PBS synthesis. They also screened the use of *p*-Toluene sulfonic acid monohydrate (*p*-TSA · H_2O) as one of the catalysts for PBS synthesis and found that the $M_N \times 10^4$ was obtained in 55 h. However, all the synthetic reactions reported still require more than 10 hours of reaction time, so there remains a need for a simple but rapid, economical, and environmentally benign manufacturing process. Development of more efficient and sustainable synthetic procedures for the synthesis of biocompatible polymer is one of the important focal aspects in polymer industry since the real environmental issue of biodegradable polymers is energy consumption in polymer production and the associated green house emissions. The proposed aim of developing biodegradable polymers will be attained only by developing cleaner chemical processes, which do not affect the ecosystem.

To solve these problems, we propose a microwave (MW)-assisted polycondensation process in which MW radiation provides the driving force for the reaction. MW-induced reactions form a promising area of study in which many recent examples in organic chemistry and macromolecular chemistry illustrate abilities of MW radiation beyond its simple heating effect, such as rate enhancements and an improvement in selectivity[8]. As a part of our ongoing research in the field of MW assisted synthesis of polymers and organic molecules[9-11] we wish to report a highly efficient and direct polycondensation of stoichiometric amounts of a dicarboxylic acid and a diol by using MW irradiation in the presence of p-TSA as a catalyst. Green catalysts not only require a high catalytic activity and atom efficiency, but also a low toxicity, a low cost, and an ease of handling. The commercially available *p*-TSA. H_2O is a non-metal catalyst thus eco friendly and also *p*-TSA. H_2O is cheaper than the other metal salts and is not considered particularly poisonous. The LD_{50} [oral, rat] value of *p*-TSA. H_2O is 2480 mg. Kg^{-1}. It is also a well known esterification catalyst[12] and finds application in Poly (lactic acid) synthesis in combination with $SnCl_2$[13]. However, only a few reports are available in the direct condensation of dicarboxylic acid and diol using *p*-TSA as a catalyst[14]. *p*-TSA was found to be a best catalyst for esterification reaction even under MW conditions[15]. Despite its potential application utilization of *p*-TSA in PBS synthesis under conventional and MW heating was not studied in detail. In the present study, PBS was obtained with $M_w = 2.50 \times 10^4$ in a short time of 20 minutes. The effect of various other reaction parameters in the synthesis of PBS is described in detail.

EXPERIMENTAL SECTION

Materials

Succinic acid was purified by recrystallization from acetone. Sebacic acid was purified from water. 1, 4-Butanediol was distilled under reduced pressure. *p*-TSA H_2O was obtained commercially and used as received. All the other reagents like Ethylene glycol, 1, 3-Propane diol, Cyclohexane-1, 4-dimethanol were purchased from Aldrich® and used as received. Analytical grade chloroform and methanol were used as received.

Synthesis of poly (butylene succinate) (PBS)

Typically, 1, 4-Butanediol (5 mmol, 0.450 g), succinic acid (5 mmol, 0.590 g), and the catalyst *p*-TSA H_2O (0.005 mmol, 0.004 g) were placed in a flask and kept in the CEM focused MW synthesis system (model Discover). The mixture was stirred at 230°C for 20 minutes under reduced pressure of 30 mm Hg at maximum microwave power of 200W. (Note: Since, the system was set at constant temperature mode, 50-70 W of MW power was used to keep the reaction temperature constant.) Then the reaction mixture was cooled to room temperature. The polymer formed was dissolved in chloroform (20 mL) and precipitated in methanol (200 mL).

For comparison polymerization under conventional heating was carried out in an oil bath preheated to 230° C. Equimolar quantities of monomers and 1 mol % of catalyst were placed in a round-bottomed flask fitted with a condenser and a three way take off adapter connected to the vacuum pump. The reaction mixture was heated at 230° C for20 minutes. After the completion of reaction, reaction mixture was cooled and the polymer formed was dissolved in choloroform and precipitated with methanol.

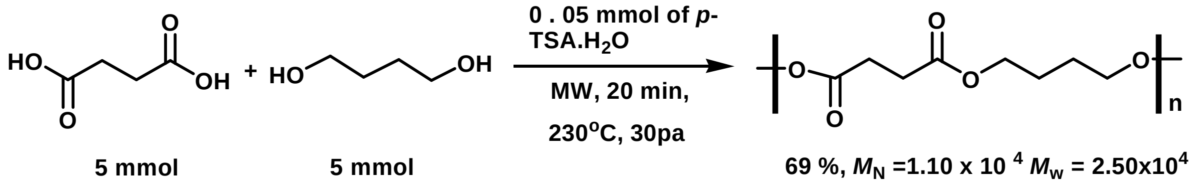
Analytical measurements

The polymer formed was characterized using NMR, IR, SEC, DSC and MALDI-MS analyses. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL LA600 in $CDCl_3$ with tetramethylsilane as internal standard. FT-IR spectra were measured on a Perkin-Elmer FT-IR spectrometer as KBr plates. SEC measurements were performed with a JASCO GULLIVER system coupled with a Shodex K-407L column and an RI detector. The mobile phase was $CHCl_3$ and the data were recorded at the flow rate of 0.3mL/minute. Average molecular weights of the polymerization products were determined with polystyrene as standard. Mass spectrometric analysis was done with a Shimadzu- KRATOS MALDI III MALDI-TOF mass spectrometer equipped with a nitrogen laser (la 337 nm) in the reflectron mode

IR (KBr) νcm^{-1}: 1720 (–CO–), 1160 (C–O–C). ^{1}H NMR, (400 MHz, TMS, δ ppm, $CDCl_3$): = 171 (m, 4H,–CH_2. 2.63 (s, 4H, –$COCH_2$–), 4.12 (t, 4H, –CH_2O), ^{13}C NMR (100 MHz, TMS, δ ppm, $CDCl_3$: = 253 (–CH_2–), 29.1 (–CH_2CO), 64.2 (–OCH_2–) and 172.3 (–CO–).

RESULTS AND DISCUSSION

We first investigated the polymerization of succinic acid and 1,4-butanediol under MW irradiation (Scheme 1). An efficient direct polycondensation process requires two factors: effective removal of water, and suppression of depolymerization. Polyesterification is a reversible reaction and the rate of the reverse reaction increases if water is not efficiently removed from the reaction mixture. The usual route adopted for efficient removal of water is azeotropic removal with *o*-xylene or toluene; however, the slight solubility of water in these hydrocarbons hinders the effective removal of water. Thus in the present study, polyesterification was carried out by the bulk polymerization method (because the best solvent is no solvent) under a vacuum of 4.0 × 10^3 Pa for effective removal of the water eliminated during the reaction (Scheme 1).



Scheme 1 : Synthesis of poly (butylene succinate) under MW irradiation

To optimize the reaction condition to achieve high molecular weight, polymerization reaction was explored in detail with *p*-TSA. H_2O catalyst. The recent concern towards environmental problems prompted us to explore the most ideal polycondensation route, which involves stoichiometric quantities of monomers, no waste (except water as the only byproduct), and solvent free conditions. PBS synthesis was carried out with equivalents of succinic acid and butane diol.

First the influence of temperature was studied and the results are presented in (TABLE 1, runs 1-5). Poly condensation was studied at various temperatures from 220-260 °C. Reaction time was fixed to be 20 minutes and the catalyst concentration of 2 mol%. The results are shown in TABLE 1. The molecular weight of the polymer obtained decreased with increasing reaction temperature. At 230 °C, the *M*w of PBS was 2.13 × 10^4 and the isolated yield was 89 % (run 2). The reaction was quantitative; no monomers were isolated from the reaction mixture. The polyester that was obtained was white in color. The maximum reaction temperature was limited to 260°C to avoid any discoloration of the resulting polyester

TABLE 1 : Influence of temperature, time and catalyst concentration using *p*-TSA catalyst under vacuum 30 mm Hg

Runs[a]	Catalyst Conc. (mol%)	Time (Min)	Temp. (°C)	Yield (%)[b]	$M_N \times 10^4$	$M_w \times 10^4$
1	2	20	220	65	0.72	1.70
2	2	20	230	89	0.96	2.13
3	2	20	240	79	0.84	1.79
4	2	20	250	74.4	0.62	1.50
5	2	20	260	73.2	0.46	1.14
6	2	10	230	84.8	0.39	1.01
7	2	30	230	76.7	0.57	1.60
8	2	40	230	76	0.58	1.70
9	0	20	230	---[c]	0.10	0.19[d]
10	0.1	20	230	37.2	0.16	0.30
11	0.5	20	230	84.4	0.47	1.22
12	1	20	230	69	1.10	2.50
13	10	20	230	----[c]	0.21	0.38[d]
14	1	20	230	----[c]	0.20	0.40[d]

[a]Reaction condition: Even though the MW power was fixed to be 200W, Since, the system was set at constant temperature mode, microwave power was not always 200W; [b]Isolated yield; [c]No polymer was precipitated into methanol; [d]Reaction mixture was dissolved in $CHCl_3$ and GPC was performed

Next, the effect of the MW irradiation time on the molecular weight of the PBS formed was studied by varying the MW irradiation time (10, 20, 30, and 40 min) while keeping the other parameters constant (runs 2, 6-8). It is evident from the table that an excessive increase in the reaction time resulted in a decrease in the molecular weight of the PBS formed. This may be due to degradation of the polymer as a result of prolonged MW irradiation.

Finally the influence of catalyst concentration in the M_n and M_w of the PBS formed was studied by varying the catalyst concentration from 0 to 10 mol%. The reaction time was fixed to be 20 minutes. In the absence of p-TSA, no polymer was isolated indicating that a catalyst is necessary for the polymerization reaction to proceed (run 9). At low concentration of catalyst like 0.1-0.5 mol% only oligomer formation was observed (runs 10, 11). But with 1 mol% of the catalyst PBS with M_w = 2.50 x10^4 was achieved using microwaves (run 12). However, further increase in the catalyst concentration up to 10 mol% (run 13) has resulted in the decrease of the M_w of the polymer obtained. Under atmospheric pressure the reaction resulted in oligomers only (run 14); this may be due to the lack of removal of water eliminated from the reaction medium, and thus the predomination of the reverse reaction. Thus, the optimum condition which, produced high molecular weight PBS with *p*-TSA H_2O catalyst was found to be reaction temperature of 230°C, 20 minutes of MW irradiation, 1:1 stoichiometry of diacid:diol, 1 mol% of catalyst and 30 mm Hg reduced pressure.

End group analysis

To gain understanding of the terminal groups, MALDI-TOF mass analysis was carried out. MALDI-TOF mass spectrum of the polymer is given in Figure 1. It showed a series of ion peaks at *m/z* 172n + α where 172 is the repeat unit of the PBS, 'n' is the number of repeat unit and α represents the residual mass of the end group and adducted cation. The major series was identified as ions corresponding to M + Na^+ where M is polymer with OH groups at both ends of the polymer chain.

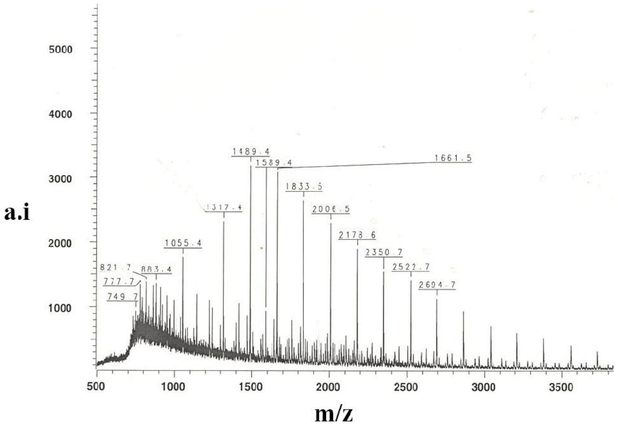


Figure 1 : MALDI-MS spectrum of poly (butylene succinate)

Comparison of microwave vs. oil bath heating

MW assisted chemical reactions have been studied with great interest for the past three decades. Since then there has been considerable debate over the true rate enhancement mechanism of MW assisted reactions as rapid increase in reaction temperature could result in significant rate enhancement. Recently, Jachuck *et al*[16] investigated the influence of MW irradiation in the benzyl alcohol oxidation reaction under isothermal conditions and found that MW does invigorate the molecules to achieve higher reaction rate.

In order to prove the efficiency of the microwave assisted polymerization reactions, PBS synthesis was studied using *p*-TSA. H_2O catalyst under conventional oil bath heating. Two reactions were done simultaneously. Reaction conditions were set as 1 mol% of *p*-TSA. H_2O catalyst, reaction temperature of 230°C, reaction time of 20 minutes, 30 mm Hg reduced pressure and 1:1 stoichiometry of dicarboxylic acid: diol. All reaction conditions were set identical except for the heating mode. One reaction flask was kept under MW irradiation and the other reaction flask was kept in the oil bath preheated to 230° C after the stipulated reaction time PBS was isolated by dissolving the reaction mixture in $CHCl_3$ and precipitating it into methanol. Under conventional heating PBS was obtained with $M_w = 1.22 \times 10^4$ whereas PBS produced by MW heating was with $M_w = 2.50 \times 10^4$. Figure 2 will clearly explain the potential of MW in producing PBS with high molecular weight. It is evident from the figure that under identical reaction conditions, MW activates the reacting molecules and enhances the reaction rate.

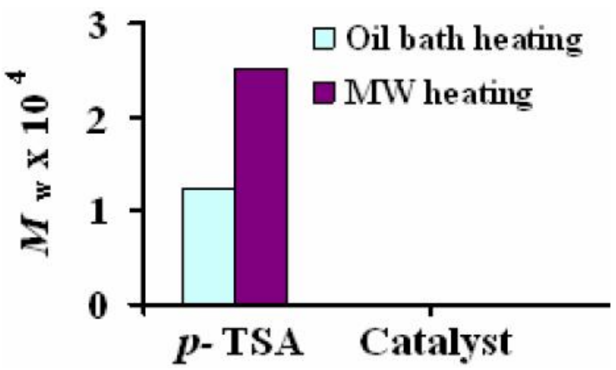


Figure 2 : Comparison of MW vs. oil bath heating

To explore the generality and scope of the *p*-TSA. H_2O catalyzed polyesterification, we extended the reaction to the synthesis of various other aliphatic polyesters. The results are given in TABLE 2. In most cases, the polycondensation proceeded quantitatively; however, with sebacic acid, the M_w of the polymer obtained was slightly lower than that of succinic acid-based polymers. This may be attributed to the difference in chain length of the monomers[14].

TABLE 2 : Synthesis of aliphatic polyesters with *p*-TSA catalyst

Polyester	Yield (%)^a	$M_N \times 10^4$	$M_w \times 10^{4\,b}$
Poly(propylene succinate)	49.0	0.44	0.94
Poly(butylene succinate)	83.7	1.05	2.50
Poly(1,4-cyclohexanedimethylene succinate)	57.5	0.34	0.91
Poly(Ethylene sebacate)	59.6	0.34	0.83
Poly(propylene sebacate)	41.4	0.20	0.40
Poly(butylene sebacate)	78.1	0.58	1.49
Poly(1,4-cyclohexanedimethylene sebacate)	20.1	0.33	0.98

^{a}Isolated yield; ^{b}Measured by GPC in $CHCl_3$, based on standard polystyrene.

Thus, we succeeded in synthesizing aliphatic polyesters by direct polyesterification of a dicarboxylic acid with a diol using *p*-TSA. H_2O as a catalyst under MW irradiation. By conventional heating at 230°C PBS with $M_w = 1.22 \times 10^4$ was achieved in a reaction time of 20 minutes. But in the presence of MW irradiation at 230°C, PBS with $M_w = 2.50 \times 10^4$ was synthesized in 20 minutes.

CONCLUSION

In this article, we describe the synthesis of PBS by direct esterification of dicarboxylic acid and diol using simple and cheaper *p*-TSA. H_2O catalyst under microwaves. The advantages of this method like, short reaction time, solvent free reactions conditions makes it possible to synthesize aliphatic polyesters in a rapid and eco-friendly manner without any solvent and under mild conditions compared to the conventional methods. This study is also extended to synthesis of other aliphatic polyesters. Given that the biodegradable polymer market is emerging, the price of biodegradable polymers is comparatively higher than that of conventional polymers. “The price is expected to decrease due to innovative manufacturing processes and distinctive product features that are likely to create demand in the market,” Thus MW assisted synthesis of biodegradable aliphatic polyesters, is a cost effective process, in terms of catalyst cost, energy utilized and time saved. Application of this innovative procedure will decrease the price of biodegradable polyesters, which in turn will result in more consumers. More the usage of biodegradable polymers safer is the environment and earth.

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