Diphenylammonium Triflate as an Effective Catalyst for Polyesterification Reactions

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Received 6 February 2006; accepted 30 September 2006

ABSTRACT

The direct polycondensation of dicarboxylic acids with diols using diphenylammonium triflate (DPAT) as catalyst is described. We investigated the solvent effect on molecular weight in the polyesterification reactions, influence of the reaction period for a fixed catalyst amount. Also, to determine the effect of catalyst the reaction between succinic acid and 1,6-hexanediol using different catalyst amounts for the constant time was examined. Different types of polyesters were synthesized via solution polycondensation using DPAT catalyst. Molecular weights of the synthesized polymers were determined using GPC and an Ubbelohde viscosimeter. It is found that the molecular weights of polyhexamethylene succinate, polyhexamethylene adipate, polyhexamethylene sebacate, polybutylene adipate and polyethylene adipate, are 12900 g/mol, 13300 g/mol, 8400 g/mol, 8100 g/mol, 2750 g/mol and 2600 g/mol, respectively. The polyesters were characterized by 1H NMR and FTIR spectroscopy. DPAT gave the highest yields of polyhexamethylene succinate and polydecamethylene adipate (93%). It is found that toluene is the best solvent, an appropriate reaction period is 12 h and the optimum catalyst amount is 0.25 mol% for polyesterification. DPAT is efficient for the synthesis of aliphatic polyesters under mild conditions because of the polycondensation, it was revealed that DPAT seems to catalyze not only the esterification but also etherification is catalyzed as a side reaction.

INTRODUCTION

Polycondensation is one of the most fundamental and important reactions in polymer chemistry. Examples of condensation polymers are polyamides, polyesters, phenolic resins, polyurethanes, etc. There are several methods for polyester synthesis but generally polyesters can be synthesized following three methods. The first method is direct condensation of diacid and dialcohol. Secondly, they can be made from acid chlorides and finally by transesterification. Tartaric acid-glycerol polyesters were first reported in 1847 by Berzelius and those of ethylene glycol and succinic acid were reported by Lorenzo in 1863. By the end of 1929, Carother group had synthesi-
zed large molecules with molecular weights in the range 1500-4000 from dicarboxylic acid and dialcohols (glycols) in the presence of an acid catalyst [1]. Carothers and Van Natta [2] clarified the understanding of the polyesterification reaction in light of the knowledge of polymer chemistry at their time.

Higashi et al. reported a convenient method for the preparation of high-molecular-weight polyarylates from aromatic dicarboxylic acids and aromatic diols using thionyl chloride (SOCl₂)/pyridine (Py) [3-4] and tosyl chloride (TsCl)/DMF/Py as condensing agents. However, the reaction was not applicable to the preparation of polyesters from primary aliphatic dicarboxylic acids, such as adipic acid and aromatic diols, because the activated acids became gradually coloured probably due to their instability [5]. Recently Mallakpour et al. [6], successfully prepared a series of optically active and thermally stable poly(ester-imide)s, by direct polycondensation of an optically active aliphatic diacid and various aromatic diols using TsCl/DMF/Py as a condensing agent.

Polyesters are synthesized by the typical esterification reaction, which is generalized by the reaction shown in eqn (1).

\[
\begin{align*}
\text{RCO} & \text{X} + \text{nu} \rightarrow \text{RCO} \text{nu} + \text{X} \\text{(1)}
\end{align*}
\]

where nu: is a nucleophilic reagent such as -OR\(^{-}\), the rate of reaction is dependent on the structure of R, R\(^{-}\), X, nu and on whether a catalyst is used. (R and R\(^{-}\) are -H, -CH\(_3\), -t-butyl, ph-, etc.). The reactivity of alcohols and carboxylic acids toward esterification primarily depends on the steric hindrance of both the alcohol and the carboxylic acid. The basic method remains the equimolar combination of a carboxylic acid and an alcohol. The reaction is equilibrium with an equilibrium constant near unity. The shift of the equilibrium in favour of the ester requires appropriate reaction conditions which consist usually of removal of the water produced, whereas the esterification rate is accelerated in the presence of a catalyst. Well known catalysts for esterification are p-toluenesulfonic acid (PTSA) and the salts of Ti (IV) and Sn (IV). Ishihara et al. [7], reported that HfCl\(_4\)(THF)\(_2\) complex catalyzed the direct polycondensation of diols and dicarboxylic acid compounds, more efficiently than conventional catalysts in o-xylene at reflux (ca. 144°C) for 24 h. Recent esterification processes have taken advantage of the use of mild catalysts, 4-(nitro)-diphenylammonium triflate (NDPAT) [8] and diphenylammonium triflate (DPAT) [9]. In this way, equimolar amounts of monoalcohol and monoacid in toluene solution could react without removal of water to form the corresponding ester in excellent yield. Sterically hindered esterification reactions are best performed in specific fluorous media in the presence of catalytic amounts of DPAT [10].

In general, the synthesis is commercially produced by the polycondensation of aliphatic dicarboxylic acid and diol compounds at 200-250°C under highly reduced pressure. However, it was very difficult to prepare aliphatic polyesters with a high molecular weight by direct polycondensation because of the thermal degradation at high temperature and low hydrolytic stability in one step [11]. Therefore, a tedious chain extension is needed using diisocyanates and diphenyl carbonates as the chain extenders at high temperature [12]. Although a survey of new Lewis acids is urgently required [7], most Lewis acid catalysts are liable toward protic substances including carboxylic acids, alcohols, and water.

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 mild conditions. Polycondensations under mild conditions are very important from an environmental technology viewpoint.

Although DPAT has been widely used in esterification processes we found no detailed literature reports of its application as a catalyst for aliphatic polyesterification reactions. According to Brönsted theory, DPAT is an acid [13], and it may catalyze polyesterification reactions. Therefore we decided to use it as a catalyst to synthesize polymers.

\[
\begin{align*}
\text{OH} + \text{R'O} & \rightarrow \text{R'OH} + \text{H}_2\text{O} \\text{(2)}
\end{align*}
\]

The effectiveness of DPAT in esterification encour-
aged us to investigate the reactivity of DPAT for polyesterification reactions with continuous removal of water under mild conditions.

EXPERIMENTAL

Materials
DPAT was synthesized and purified according to a procedure previously described [9]. Unless otherwise mentioned, all chemicals and solvents used in this study were analytical grade. The main chemicals used in this study were as follows: succinic acid (Merck) pure, hexamethylene glycol (Merck) 97%, 1,4-butandiol (Merck) 99%, adipic acid (Merck) 99%, sebacic acid (Merck) 98%, chloroform (Merck) spectroscopy, p-toluene sulphonic acid across 97.5%, 1,10-decanediol (Merck) 99%, ethylene glycol (Merck) 99.5%, methanol (Reidel de Haen) 99.9%, acetone (Symras) 99.5%, methanol (Symras) 99.5%, p-xylene (BDH), xylene (Analar), decalin (merck), o-xylene (BDH), diphenylamine (Riedel de Haen) pure, trifluoromethane sulphonic acid (Aldrich) 99%.

Polymer Synthesis
All polymers were prepared by direct polycondensation using the following general procedure. A 25 mL three-necked round bottom flask was equipped with a teflon-coated magnetic stirring bar and a specially designed 1 mL capacity (0.02 mL graduated) Dean-Stark apparatus surmounted with a reflux condenser and was charged with 5 mL toluene and α,ω-dicarboxylic acid (20 mmol) and α,ω-diol (20 mmol) as substrates. To define the effect of catalyst, solvent and reaction period to polymerization, two parameters were fixed while the other was changed. After the reaction was completed, products were cooled to ambient temperature, dissolved in chloroform and precipitated with methanol to furnish pure polyester as a white or yellow solid in quantitative yields.

Measurements
IR Spectra of polyesters were recorded on a Mattson 1000 FTIR spectrophotometer (Figure 1). Proton nuclear magnetic resonance spectra (1H NMR) of polyesters were recorded with a Varian AS-400 using CDCl3 as a solvent. An example of 1H NMR spectra of PHMA is given in Figure 2. The reduced viscosity...
of solutions of polyesters in chloroform was measured in an Ubbelohde viscometer at 20°C or 30°C. Molecular weights measurements were obtained using a GPC apparatus (Shimadzu and Waters 410 model). GC Analyses were carried out within HP 5890 gas chromatographer.

RESULTS AND DISCUSSION

To identify reaction conditions we first investigated the solvent effect on molecular weight in the poly-esterification reactions of adipic acid with 1,4-butanediol and of succinic acid with hexamethylene glycol catalyzed by DPAT (0.5 mol%) at 105-110°C. The results are shown in Table 1. The reaction was carried out in xylene, o-xylene, m-xylene, p-xylene, decalin and toluene. If toluene is compared with other solvents structurally, it is similar to xylenes but quite different from decalin. Compared to the other solvents, it can be said that toluene facilitate polyesterification forming less steric hindrance in the reaction medium. Polyesterification reactions proceeded in all solvents but the highest molecular weights were obtained in toluene for polybutylene adipate (PBA) and polyhexamethylene succinate (PHMS). We did not obtain high molecular weight polyesters especially for PBA. To investigate why not, after the reaction is completed, toluene samples were taken from toluene collected in a trap then it was analyzed by gas chromatography. According to this investigation we found THF in the toluene samples. This can be attributed to cyclodehydration of diols because cyclic products may form under acidic conditions [14]. Therefore, the chain growth of the polyesters may be limited because of formation of an ether group. We think that this situation is reflected in the molecular weight of the polyesters.

Secondly, to determine the influence of the reaction period for a fixed catalyst amount and volume of solvent, the polyesterification reaction was brought to reflux for different periods (results are shown in Table 2). The increase in reaction time resulted in an increase in molecular weight of polymers with times up to 18 h. Polymerization reactions were almost completed at a reaction time of 12 h.

Polyesterification is a relatively slow process [16]. To obtain high molecular weight polyesters, a very long time and high temperature are required.

Next, to determine the effect of catalyst we examined the reaction between succinic acid and 1.6 hexanediol using different catalyst amounts for constant times. The obtained results are shown in Table 3. It can be said that molecular weights of polyesters were found to increase with an increase in catalyst amount up to 0.5 mol% while yields of polyesters did not change. This situation was also confirmed by conversion curves versus reaction time. For this, we fol-

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**Table 1.** The effect of solvent type on the molecular weight and yields in polyesterification reaction between adipic acid and 1,4-butanediol and between succinic acid and hexamethylene glycol catalyzed by DPAT (0.5 mol%) at 105-110°C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Yield (%)</th>
<th>(PBA)</th>
<th>(PHMS)</th>
<th>Mv (g/mol)</th>
<th>[η]a</th>
<th>Mv (g/mol)</th>
<th>[η]b</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Xylene</td>
<td>80</td>
<td>89</td>
<td>1150</td>
<td>17.2</td>
<td>3264</td>
<td>14.5</td>
<td></td>
</tr>
<tr>
<td>Xylene</td>
<td>82</td>
<td>87</td>
<td>2209</td>
<td>14.8</td>
<td>2929</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>86</td>
<td>92</td>
<td>2750</td>
<td>17.2</td>
<td>5477</td>
<td>21.9</td>
<td></td>
</tr>
<tr>
<td>m-Xylene</td>
<td>85</td>
<td>86</td>
<td>1390</td>
<td>10.7</td>
<td>2641</td>
<td>12.3</td>
<td></td>
</tr>
<tr>
<td>Decalin</td>
<td>82</td>
<td>80</td>
<td>1826</td>
<td>13.0</td>
<td>1735</td>
<td>8.84</td>
<td></td>
</tr>
<tr>
<td>p-Xylene</td>
<td>87</td>
<td>87</td>
<td>1747</td>
<td>12.6</td>
<td>1441</td>
<td>7.63</td>
<td></td>
</tr>
</tbody>
</table>

[η] = intrinsic viscosity; \( aK=73.3\times10^{-3} a=0.69 \) for PBA at 20°C, \( aK=24.4\times10^{-3} a=0.79 \) for PHMS at 30°C [15].

**Table 2.** Change of molecular weight with time: Direct polyesterification between succinic acid and hexamethylene glycol catalyzed in the presence of 0.5% mol DPAT in toluene.

<table>
<thead>
<tr>
<th>Polyester</th>
<th>Time (h)</th>
<th>Mv (g/mol)</th>
<th>[η]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyhexamethylene</td>
<td>6</td>
<td>14123</td>
<td>46.3</td>
</tr>
<tr>
<td>Succinate</td>
<td>12</td>
<td>20523</td>
<td>62.2</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>20065</td>
<td>61.1</td>
</tr>
</tbody>
</table>
Table 3. The effect of catalyst amount on the molecular weight and yield in the synthesis of PHMS for 12 h in toluene.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst (%) mol</th>
<th>Yield (%)</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (g/mol)</th>
<th>[η]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPAT</td>
<td>0.125</td>
<td>91</td>
<td>15240</td>
<td>49.2</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>93</td>
<td>22022</td>
<td>65.8</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>93</td>
<td>21978</td>
<td>65.8</td>
</tr>
</tbody>
</table>

followed conversion versus time at 135±1°C (oil bath temperature). The reaction temperature was recorded as 112°C (Figure 3).

Kinetic analysis results which were dependent on different catalyst amounts are shown in Figure 3. P-Values for polyesterification catalyzed by DPAT and PTSA were determined by the amounts of collected water. The conversion of polymerization was remarkably improved in the presence of catalysts. The catalyst promoted the esterification. DPAT gave the highest yields of polyhexamethylene succinate and polydecamethylene adipate (93%). Also it can be concluded from Figure 3 that DPAT is an active catalyst for polyesterification.

To demonstrate the effectiveness of DPAT as a catalyst and to compare DPAT with the standard catalyst (p-toluene sulphonic acid) for different polyesterification reactions we synthesized polyesters with various structurally diverse carboxylic acids and alcohols in the presence of 0.25 mol% of DPAT in toluene with removal of water for 12 h. FTIR Spectra of polymers exhibited the following characteristic absorption bands that are indicative of aliphatic polyesters (Figure 1): IR (KBr disk, cm⁻¹): 2965 ± 10 (ν C-H), 705

![Figure 3. Conversion versus time at 112°C for PHMS at reflux with 5 mL of toluene.](image)

Table 4. The results from solution polyesterification reactions in the presence of DPAT (0.25 mol%) for a reaction time of 12 h in toluene.

<table>
<thead>
<tr>
<th>Polyesters</th>
<th>Yield (%)</th>
<th>M&lt;sub&gt;n&lt;/sub&gt;×10&lt;sup&gt;4&lt;/sup&gt;</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;×10&lt;sup&gt;4&lt;/sup&gt;</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt;</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO(CO(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;)CO&lt;sub&gt;2&lt;/sub&gt;(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; (Polyhexamethylene sebacate) (PHS)</td>
<td>91</td>
<td>1.33</td>
<td>3.03</td>
<td>2.27</td>
<td>DPAT</td>
</tr>
<tr>
<td>HO(CO(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;)CO&lt;sub&gt;2&lt;/sub&gt;(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; (Polyethylene adipate) (PEA)</td>
<td>66</td>
<td>0.26</td>
<td>0.6</td>
<td>2.28</td>
<td>DPAT</td>
</tr>
<tr>
<td>HO(CO(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;)CO&lt;sub&gt;2&lt;/sub&gt;(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; (Polyhexamethylene sebacate) (PHS)</td>
<td>91</td>
<td>1.33</td>
<td>3.03</td>
<td>2.27</td>
<td>DPAT</td>
</tr>
<tr>
<td>HO(CO(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;)CO&lt;sub&gt;2&lt;/sub&gt;(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; (Polyethylene adipate) (PEA)</td>
<td>66</td>
<td>0.26</td>
<td>0.6</td>
<td>2.28</td>
<td>DPAT</td>
</tr>
<tr>
<td>HO(CO(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;)CO&lt;sub&gt;2&lt;/sub&gt;(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; (Polyhexamethylene sebacate) (PHS)</td>
<td>91</td>
<td>1.33</td>
<td>3.03</td>
<td>2.27</td>
<td>DPAT</td>
</tr>
<tr>
<td>HO(CO(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;)CO&lt;sub&gt;2&lt;/sub&gt;(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; (Polyethylene adipate) (PEA)</td>
<td>66</td>
<td>0.26</td>
<td>0.6</td>
<td>2.28</td>
<td>DPAT</td>
</tr>
</tbody>
</table>

(a) Molecular weight was determined in THF at 40°C with polystyrene standard; (b) Molecular weight was determined in DMF at 25°C with polystyrene standard; (c) Reaction was carried out in the presence of 0.25 mol PTSA for 12 h in toluene.
1730 ± 5 [ν C=O(ester)], 1450 ± 10 (ν C-H), 1250 ± 10 and 1160 ± 10 [ν C-O(ester)]. In most cases polycondensation proceeded quantitatively and a higher yield and molecular weight were obtained in the polycondensation of PHMS and PBA catalyzed by DPAT than catalyzed by PTSA. The highest molecular weight and lowest polydispersity were obtained for polyhexamethylene adipate. Molecular weights of polymers increased with growth in the chain length of the diols in the solution polymerization reactions of different diols with adipic acid as seen in Table 4. However, a lower molecular weight was obtained for 1-10 decanediol in comparison to polyhexamethylene adipate for the same reaction conditions. This result must be related to increased solution viscosity, decreased reaction rate and difficulty in removal of water. It can be said from Table 4 that polydispersity of PTSA seems to be better than that of DPAT.

CONCLUSION

The effectiveness of DPAT as a catalyst for polyesterification reactions was studied. Different types of polyesters were synthesized via solution polycondensation by using DPAT catalyst. We found that DPAT is an active catalyst for polyesterification reactions and at least as effective as PTSA. Reactions proceeded in all solvents but the best results were in toluene. An appropriate reaction period was found to be 12 h. The optimum catalyst amount was found to be 0.25% mol. We acquired polymers, which are between 2600 g/mol and 13300 g/mol. Consequently, DPAT is an efficient catalyst for polyesterification reactions but the drawbacks of DPAT are cyclization, which occurs by ether formation of alcohol groups of the monomer. Polyesters that have high polydispersity were obtained.

REFERENCES
