Production of Polyethylene Terephthalate using a Nonmetallic Catalyst

Dr. Marsha Winston1, Jared Langson2, Angus Ferguson2, Dr. Robert Posey2

1Christ Church Episcopal School, 2Furman University Department of Chemistry

Introduction

Polyethylene terephthalate (PET) is a condensation polymer of terephthalic acid (HOOC-C6H4COOH) and ethylene glycol (CH2CH2OH) that is used for fibers and films and has been made for decades using a variety of metallic catalysts based on antimony, titanium, germanium, or tin (Figure 1). The catalyst most commonly used is SnBr2 because of performance and cost.

\[\text{HOOC-C_6H_4COOH} + \text{C_2H_4OH} \rightarrow \text{C_12H_4O_4CO} + \text{H}_2\text{O}\]

Figure 1: The PET polymerization reaction of terephthalic acid (TA) and ethylene glycol (EG)

Metal catalysts is a growing concern because of the possibility of negative environmental and health effects from use during processing and from trace amounts remaining in polyester end products. Use of antimony is banned in Europe in food packaging and regulatory issues will likely occur in the future in the rest of the world. Consequently, it would be advantageous if Lewis metal catalysts could be replaced with nonionic organic catalysts without the potential for negative effects.

The purpose of this study is to investigate the viability of producing PET using a novel organic catalyst and to develop a working formulation to run a larger trial at a U.S. film manufacturer. The identity of the catalyst is proprietary and is called "OrgCat" herein. The PET must have properties that it can be processed into stable film. In this study, PET produced from experimental trials has been evaluated for appearance, elasticity, and presence of low molecular weight impurities such as PET oligomers and related terephthalate esters.

Methods

Chemicals used in the experiments were BHET (bis(hydroxyethyl)terephthalate), shown in Figure 2, TA (terephthalic acid), OrgCat, a second proprietary chemical which is called PC herein, and buffer TMAH (tetramethylammonium hydroxide). BHET is a starting material mimics latter stages of the terephthalic acid and ethylene glycol reaction used in industrial operations.

About 1250 g of PET are made in each synthesis using the established lab-scale batch apparatus shown in Figure 3. BHET and/or TA are added, insolated reactor vessel with a stirrer. The temperature of the vessel is gradually raised to 280–300°C using a mantle and the stirrer is set at 20 rpm. Pressure is reduced to low pressures (0.03–0.3 mmHg) as the reaction proceeds. The reaction time, reactor wall and interior temperatures, amps needed to maintain the stirring rate, and pressure are recorded. The OrgCat and TMAH are added early in the process. PC is usually added at 1-1.5 amps more than the lowest amps to increase polymerization by reaction with carbonyl acid end groups generated by polymerization of BHET. The reaction is stopped when the amps equal 2-2.5 more than the lowest amps read during the reaction as this point indicates sufficiently high molecular weight.

Additional syntheses were performed in this study in order to select a formula to recommend as a reasonable trial in a 30 kg reactor at an industrial film manufacturer. The Table summarizes reactant concentrations of each run and properties of the PET produced. Appearance is evaluated for color, clarity, and glossiness using a subjective 1-3 scale.

Table: Reactant concentrations of PET syntheses and properties of PET produced

<table>
<thead>
<tr>
<th>Run</th>
<th>OrgCat, ppm</th>
<th>TMAH, ppm</th>
<th>TA, g</th>
<th>PC, g</th>
<th>Slope1 (Reaction Rate)</th>
<th>Appearance (Rank: 1-Best to 3-Poorest)</th>
<th>Elasticity at °C</th>
<th>Xylene Extractibles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1000</td>
<td>0</td>
<td>0</td>
<td>11</td>
<td>0.027</td>
<td>pale gold (1) somewhat clear (2) glossy (3)</td>
<td>Elastic at 20°C</td>
<td>2.0%</td>
</tr>
<tr>
<td>2</td>
<td>750</td>
<td>20</td>
<td>0</td>
<td>11</td>
<td>0.014</td>
<td>medium gold (2) translucent (3) dull (3)</td>
<td>Inelastic at 20°C</td>
<td>3.0%</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>100</td>
<td>104</td>
<td>11</td>
<td>0.020</td>
<td>pale gold (1) almost clear (1) glossy (1)</td>
<td>Inelastic at 20°C</td>
<td>3.0%</td>
</tr>
<tr>
<td>4</td>
<td>900</td>
<td>10</td>
<td>52</td>
<td>33</td>
<td>0.017</td>
<td>medium gold (3) somewhat clear (2) glossy (1)</td>
<td>Inelastic at 20°C</td>
<td>2.2%</td>
</tr>
<tr>
<td>5</td>
<td>1200</td>
<td>20</td>
<td>0</td>
<td>33</td>
<td>0.025</td>
<td>pale gold (1) almost clear (1) glossy (1)</td>
<td>Inelastic at 20°C</td>
<td>2.1%</td>
</tr>
<tr>
<td>6</td>
<td>1000</td>
<td>0</td>
<td>175</td>
<td>0</td>
<td>0.029</td>
<td>pale gold (1) almost clear (1) glossy (1)</td>
<td>Inelastic at 20°C</td>
<td>2.0%</td>
</tr>
</tbody>
</table>

*Runs 1-5 stopped at Amps of-run at 2. Run 6 stopped at Amps of-run at 2.5.*

*Lot data = polymerization with Jamps 10.5.*

*Added in gourmets during reaction.*

To further evaluate the samples, polymers from each run were drawn, that is they were warmed and stretched to maximum length and allowed to cool. All can be drawn extensively but return to an unstretched state when reheated. Interestingly, Runs 4, 5, and 6 are observed to crystallize when drawn as shown by the formation of a white, opaque area and evolution of heat. This observation suggests these runs produced PET with lower DEG and is a promising indication of the potential for process improvement.

The observed variations in properties show the potential of alterations in the process to affect PET properties. These alterations include reactant, catalyst, and buffer concentrations and timing of addition, heating rate, stopping point, and length of reaction.

Conclusions

The most important conclusion of this study is that OrgCat performs as a catalyst for PET polymerization. The PET syntheses performed indicate it is possible to modify reactant and catalyst concentrations and reaction conditions to improve polymer properties.

Exact conclusions from this study on optimum reaction parameters are not possible because of the multiple variations in trial runs. More trials using the small batch process and varying conditions would provide more information to assist in reaction optimization. More detailed characterization of the PET produced, especially measurement of incorporated DEG, would be beneficial in this regard.

It is possible however to use this information to select formulas for larger trials in an industrial setting. The industrial process which user TA and EG as the reactants and has sophisticated process controls are the next level of development.

With the demonstration of the ability of OrgCat to catalyze PET polymerization, future work includes detailed analysis of the formulation variables to optimize PET quality and production and investigation of the catalysis mechanism.