Unsaturated Polyesters from Benzofuro[2,3-b] benzofuran-2,9-dicarboxylic Acid

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ABSTRACT

Unsaturated polyesters because of their valuable applications and versatile preparation are the most interesting resins among the cross-linkable polymers and a huge volume of works is completed or currently running on this type of polymers. This work is of those kinds resembling the incorporation of new monomers into the ordinary unsaturated polyester resins and investigating the influence of this monomer on the resin properties. By this way the monomer, which is of interest in this work constitutes benzofuro[2,3-b]benzofuran-2,9-dicarboxylic acid. This monomer was synthesized by the authors in 1996 for first time. For polymerization, this molecule, maleic anhydride and several diols were reacted in a polycondensation reaction to yield the unsaturated resins. The produced resins were characterized subsequently by $^1$H NMR and IR spectra, measuring molecular weight, and inherent viscosity. On the other hand, thermal and environmental resistance (resistance to acidic and alkaline moiety) was investigated on the cured resins with styrene 30% (by weight), as are described in the paper. Their thermal and chemical stability show an acceptable range of properties.

Key Words: unsaturated polyester, benzofuro-benzofuran, polycondensation, curing, thermal stability

INTRODUCTION

Unsaturated polyester resin is the reaction product of an unsaturated dibasic acid or a mixture of them with a saturated dibasic acid and a polyhydric alcohol. The product is then thickened with a vinyl monomer, mostly styrene to go to curing. Curing process takes place by the help of organic peroxide [1]. Because of their valuable applications, a large number of works are carried out by focusing on introduction of new kinds of monomers [2–5], curing and processing conditions [6–8] and even their modification to reach better processing condition and properties [9–11]. The reader can find plenty of general information about these unsaturated resins [12–16] but among them reference 17 is a distinguished cite because of its
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(*) Part of this paper was introduced in the 5th Iran. Seminar on Polym. Sci. & Technol, Amir Kabir University of Technology, 12–14 Sep. 2000, Tehran
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useful information especially given for the production of these resins.

The aim of the present work is to use a molecule namely benzofuro[2,3-b]benzofuran-2,9-dicarboxylic acid (diacid I) into the structure of unsaturated polyesters resins as a saturated dibasic acid. The diacid I, as presented below, is a relatively new molecule which was synthesized firstly in 1996 by the author at the University of Shiraz, Iran [18–19]. After that time, the diacid I or its derivatives have been used in several interesting works by several workers. The diacid I, for example, was introduced into polyamides by reacting with several diamines [20] or was converted to its corresponding diamine, and then reacted with several diacids (also including diacid I) to produce another series of polyamides [20–21]. Several other works are published or are currently under investigation.

According to the aim of this research work diacid I, maleic anhydride and several diols including ethylene glycol, diethylene glycol, triethylene glycol, were reacted in a polyesterification reaction and the isolated resins were investigated by several means thereafter.

EXPERIMENTAL

Materials and Instruments
Solvents and reagents were purchased from Merck and Fluka Co. and were used without further purification. IR Spectra were recorded by a Unicam Matteson 1000 and 1H NMR spectra by a Bruker 200 MHz Spectrospin instruments.

Benzofuro[2,3-b]benzofuran-2,9-dicarboxylic Acid (Diacid I).
The diacid I was synthesized by the previously published method [19–20].

Polyesterification
In a 100 mL three-necked flask, equipped with stirrer, N2 inlet and Dean-Stark reflux condenser, diacid I (7.4 g, 25 mmol), diol (55 mmol) and maleic anhydride (2.65 g, 27 mmol) were placed. Xylene (4 mL) and p-toluene sulphonic acid (1 g as catalyst) were added and stirring was started. The stream of N2 was installed and temperature was raised and controlled at 170–180 °C. Xylene-water mixture was distilled off as azeotropic mixture and collected in Dean-Stark receiver as a two-phase liquid. Xylene (upper phase) was recycled to the reaction mixture. Due to the lower amount of used xylene it is necessary to use a small scale Dean-stark condenser. The type, which was used had a receiver of size 10 cm height with a diameter of 2 cm.

Scheme I. Polyesterification and structure of prepared unsaturated polyesters.
Table 1. Polyesterification reaction conditions and physical properties of the polyesters.

<table>
<thead>
<tr>
<th>Polyester</th>
<th>Reac. time (h)</th>
<th>Acid number</th>
<th>Physical state</th>
<th>Mol. weight&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Int.η&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI</td>
<td>2.5</td>
<td>9.5</td>
<td>solid</td>
<td>5x10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.035</td>
</tr>
<tr>
<td>PII</td>
<td>3</td>
<td>6.9</td>
<td>viscous material</td>
<td>4.4x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>0.148</td>
</tr>
<tr>
<td>PIII</td>
<td>2.5</td>
<td>15.6</td>
<td>viscous material</td>
<td>1.1x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>0.086</td>
</tr>
</tbody>
</table>

a) Determined by end group analysis method (acid numbers after purification).
b) at 30 °C for solutions of polyesters in DMF(dL/g).

Table 2. IR Characteristic peaks for the polyester resins.

<table>
<thead>
<tr>
<th>Polyester</th>
<th>-OH, -COOH (end groups)</th>
<th>C=C-H (stretching)</th>
<th>C=O (esters)</th>
<th>Peaks assigned to diacid I</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI</td>
<td>3446 – 3142</td>
<td>3089</td>
<td>1726</td>
<td>1618,1495,777,553,661</td>
</tr>
<tr>
<td>PII</td>
<td>3500 – 3107</td>
<td>3071</td>
<td>1725</td>
<td>1618,1495,777,551,661</td>
</tr>
<tr>
<td>PIII</td>
<td>3589 – 3116</td>
<td>3071</td>
<td>1725</td>
<td>1618,1495,553,669</td>
</tr>
</tbody>
</table>

0.5 cm. In order to reach better efficiency and easier recycling of xylene, an initial volume of water may be placed in the receiver part of Dean-stark. Acid numbers were checked on small sample of reaction mixture over period of 0.5 h. The polyesterification reaction stopped when the subsequent acid values had remained unchanged.

The polyesters prepared were purified twice from chloroform solution by precipitation with light petroleum ether (bp 60–70 °C).

Curing Conditions
A mixture of polyester/styrene (70/30, w/w) and benzoyl peroxide (1 % by weight) was prepared. The prepared mixtures then were applied on small glasses (Lams) as thin films and cured at 70 °C for 24 h.

RESULTS AND DISCUSSION

In the present work, the unsaturated polyesters were synthesized by reaction of diacid I, maleic anhydride and several diols (Scheme I).

In the early part of the experiments polyesterification reactions ran without p-toluene sulphonic acid, (i.e., without catalyst). All were unsuccessful and we had to use catalyst. A solventless system has preference in the polyesterification reactions, in order to reach higher molecular weight and a product easier for purification. In this way the reaction was difficult to proceed at the initial stage because all the
Table 3. $^1$H NMR Characteristic peaks of the polyesters.

<table>
<thead>
<tr>
<th>Polyester</th>
<th>$\delta_{\text{aromatic}}$</th>
<th>$-\text{OCH}_2\text{-CH}_2\text{O}-$</th>
<th>$\delta_{\text{vinyllic}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI</td>
<td>6.7 - 8</td>
<td>3.3 - 4.0</td>
<td>6.8</td>
</tr>
<tr>
<td>PII</td>
<td>6.6 - 8</td>
<td>4.0 - 4.5</td>
<td>6.0 - 6.4</td>
</tr>
<tr>
<td>PIII</td>
<td>6.4 - 8</td>
<td>3.5 - 4.8</td>
<td>6.1 - 6.3</td>
</tr>
</tbody>
</table>

Table 4. Film properties of the cured polyesters in terms of resistance to alkali and acid solutions and also elevated temperatures.

<table>
<thead>
<tr>
<th>Test</th>
<th>PI&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>PII&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>PIII&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>PIV&lt;sup&gt;a&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid solution (HCl 0.1 N)</td>
<td>7 (A)</td>
<td>88 (B)</td>
<td>(D)</td>
<td>5 (A)</td>
</tr>
<tr>
<td>Alkali solution (NaOH 0.1 N)</td>
<td>20 (A)</td>
<td>20 (B)</td>
<td>65 (B)</td>
<td>38 (A)</td>
</tr>
<tr>
<td>Elevated temp. 180 °C</td>
<td>35 (A)</td>
<td>10 (C)</td>
<td>4 (B)</td>
<td>24 (A)</td>
</tr>
<tr>
<td>Elevated temp. 250 °C</td>
<td>40 (A)</td>
<td>15 (C)</td>
<td>10 (B)</td>
<td>30 (A)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Percent of weight lost after 24 h.

(A) The film remained unchanged and saved excellent mechanical properties; (B) The film had poor mechanical properties, broke and separated from the glass substrate; (C) The film undergoes breaking but did not separate from the glass substrate; (D) The film was removed completely after 2h.

CONCLUSION

It can be concluded that diacid I may be replaced for phthalic acid in the conventional unsaturated polyester resins and the resins could have enhanced thermal and chemical properties as the results showed. However, many works, which are published in concern with the diacid I show that it has a potential to become a commercial molecule, but it is necessary to find a procedure to produce it more conveniently and by a higher yield.

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REFERENCES


