Synthesis of Copolymers Based on Benzene and Biphenyl and their Characterization by XRD and DSC

Despina Triantou* and Spyridon Soulis

Laboratory Unit “Advanced and Composite Materials”, School of Chemical Engineering, National Technical University of Athens, 9 Heroon Polytechniou str., Zografou Campus, 157 73 Athens, Greece

Abstract: In this work the crystallinity and the thermal transitions of soluble and insoluble in chlorobenzene polyphenylene copolymers (synthesized by oxidative cationic polymerization) were studied. All copolymers had a degree of crystallinity between 44.6 and 66.7 %. With Differential Scanning Calorimetry (DSC) measurements it was found that the copolymers exhibited endothermic peaks in the region 268 up to 286 oC. These peaks in the case of soluble polyphenylenes were attributed to the melting of their crystallites, whereas in the case of insoluble polyphenylenes were attributed to liquid crystal transitions.

Keywords: Polyphenylenes, conducting polymers, XRD, DSC.

1. INTRODUCTION

Conducting polymers, due to their low cost, low density, mechanical flexibility and easy processability are promising candidates for electronic, electrooptical and electrochemical applications [1]. Poly(p-phenylene), PPP, has attracted much interest among various conducting polymers, because of its high stability in air even at high temperatures, due to the aromatic repeat units [2]. Polyphenylenes can be prepared using benzene or other aromatic compounds, such as biphenyl, chemically in the form of powder or electrochemically as film. A principal advantage of chemical polymerization compared to the electrochemical one is the possibility of mass production at a reasonable cost. The para-coupling of the benzene ring leads to poly(p-phenylene), which is infusible and insoluble. Fusible and soluble polyphenylenes can be prepared from several aromatic compounds, such as biphenyl, since the resulting isomeric polyphenylenes have ortho-, meta- and para- couplings and therefore they are easier to be processed compared to PPP [2, 3]. In order to improve the processability of PPP, apart from the isomeric polyphenylenes, other approaches have been developed, where copolymerization is one of the most important [4].

The aim of this work is the synthesis of copolymers based on benzene and biphenyl and their characterization by XRD and DSC.

2. EXPERIMENTAL

Benzene (Benz) or biphenyl (Biph) were polymerized by oxidative cationic polymerization based on Kovacic method in order to produce poly(paraphenylene) (H-PPP) and o,m,p-polyphenylenes (H-PP), respectively. In the polymerization, copper chloride was used as oxidizer and aluminum chloride as catalyst [5, 6]. Concerning the copolymerization of benzene with biphenyl, a series of preliminary experiments were carried out, in order to define the copolymerization conditions. The optimum molar ratio of raw materials was determined as: [sum of the monomers] / [CuCl2] / [AlCl3] = 1/ 2 / 1.5 and the optimum copolymerization temperature as 55 °C. Two copolymers, C1 and C2, were produced using the molar ratio of benzene to biphenyl, [Benz] / [Biph] = 0.5 / 0.5 and 0.7 / 0.3, respectively [6]. The polyphenylenes produced were separated in the insoluble (H-PPP, H-PP-I, C1-I, C2-I) and the soluble (H-PP-S, C1-S, C2-S) in chlorobenzene polyphenylenes by extraction with chlorobenzene.

X-Ray Diffraction (XRD) diffractograms were recorded on a Siemens D5000 diffractometer using samples in the form of powder, with CuKα radiation and scan rate of 0.02 degrees per second. Differential Scanning Calorimetry (DSC) measurements were carried out using a Netzch DSC 200 apparatus, in inert atmosphere of nitrogen, with a heating and reheating rate of 10 °C/min and cooling rate of 5 °C/min.

3. RESULTS AND DISCUSSION

Figure 1 shows the X-Ray diffractograms of insoluble polyphenylenes. C1-I has been synthesized using equal amount of benzene and biphenyl, whereas C2-I using excess of benzene. According the FTIR
measurements [6], C2-I contains more para-linkages of aryl rings than C1-I and therefore it has higher electrical conductivity (one order of magnitude higher) when doped. The insoluble polyphenylenes have three main reflections, namely in the regions 19.1- 20.4°, 21.0-22.8° and 26.3 - 28.0° (the latter reflection for C1-I and C2-I is a double peak). Additionally, H-PP-I has three less intense reflections at 16°, 32° and 39°. From the X-Ray diffractograms the degree of crystallinity, $x_c$ (%) was determined.

Table 1 presents the endothermic peaks of polyphenylenes at the temperature range from 268 up to 286 °C and their $x_c$. All polyphenylenes (homopolymers and copolymers) exhibit an endothermic peak, except from homopolymer H-PPP which is infusible (due to its extremely rigid structure) [2, 3]. Moreover, they have $x_c$ between 34.4 and 66.7 %, apart from H-PP-S which has a low value. In order to interpret the endothermic peaks, it was investigated whether the polymers melt at temperatures below 300 °C. For this reason, polyphenylenes in the form of discs were placed into furnace at 300 °C for 1.5 h, where it was observed that the soluble ones (i.e. H-PP-S, C1-S and C2-S) did melt. Therefore, the endothermic peak of soluble polyphenylenes (which have crystallinity), can be attributed to the melting of their crystallites. On the other hand, insoluble polyphenylenes that had crystallinity they did not melt. There are not any data reported in the literature on the transitions of C1-I and C2-I, so there is need for further studying the DSC peaks. The first subject that needs to be examined is whether the endothermic peak is reversible or not. This can be examined by cooling with low rate and then reheating. If the transition is reversible, an exothermic peak will appear during cooling at the same temperature region (or slightly lower), and during reheating the endothermic peak will appear again. Irreversibility indicates relaxations or generally

<table>
<thead>
<tr>
<th>Polyphenylene</th>
<th>Endothermic peak (°C)</th>
<th>Degree of crystallinity, $x_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-PPP</td>
<td>-</td>
<td>47.5</td>
</tr>
<tr>
<td>H-PP-I</td>
<td>268.9</td>
<td>34.4</td>
</tr>
<tr>
<td>H-PP-S</td>
<td>278.0</td>
<td>practically amorphous (3.0 %)</td>
</tr>
<tr>
<td>C1-I</td>
<td>280.0</td>
<td>66.1</td>
</tr>
<tr>
<td>C1-S</td>
<td>281.4</td>
<td>57.1</td>
</tr>
<tr>
<td>C2-I</td>
<td>277.8</td>
<td>66.7</td>
</tr>
<tr>
<td>C2-S</td>
<td>286.4</td>
<td>44.6</td>
</tr>
</tbody>
</table>
phenomena that depend on time (kinetical phenomena).

Figures 2 and 3 show the DSC curves for the copolymers C₁-I and C₂-I, respectively. C₁-I during heating exhibits an endothermic peak at 280 °C, during cooling an exothermic peak at 236 °C and during reheating an endothermic peak at 265 °C. Similarly, C₂-I during heating exhibits an endothermic peak at 277.8 °C, whereas during cooling an exothermic peak at 241 °C. Thus, both C₁-I and C₂-I exhibited an endothermic peak during their heating, an exothermic peak during cooling and again an endothermic peak during reheating. This behavior corresponds to 1st order thermodynamic transition (not a 2nd order transition such as glass transition, which appears in the DSC as a knee of the curve) [7,8]. However, as already mentioned, the insoluble polyphenylenes did not melt in this temperature, even though they are crystalline.

According to data reported in the literature [8], the DSC oligophenylenes exhibit thermal transitions near or above their melting point, which are endothermic and were attributed to liquid crystal transitions. Thus, the endothermic peaks exhibited in the DSC of insoluble polyphenylenes in the region 268 up to 286
ºC can be attributed to liquid crystal transitions, whereas those of soluble polyphenylene phases are attributed to the melting of their crystallites.

REFERENCES


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