Synthesis and Characterization of Poly [2-(3,7-dimethyloctyloxy)-5-methoxy-p-phenylenevinylene] (MDMO-PPV) by Gilch Polymerization

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Abstract

Semi conducting polymers, especially those of the poly phenylenevinylene (PPV) family are promising candidates as emission material in light emitting devices such as light emitting diodes, and photovoltaic devices. In the present study, MDMO-PPV samples were synthesized at 98 °C, 80 °C, 60 °C, 40 °C by anhydrous 1,4-dioxane and 60 °C, 40 °C, 25 °C by tetrahydrofuran (THF) via Gilch polymerization procedure. The polymer samples were found to be fully soluble in common organic solvents. Effect of the polymerization temperature and polymerization solvent were examined. In order to understand these effects ¹H-NMR, UV-Vis and GPC analyses were studied. According to results, polymerization yield doesn’t change much with changing of temperature and solvent type under same reaction conditions. Moreover absorption peaks of polymers synthesized by 1,4-dioxane at 98 °C and THF at 25 °C were found 511 nm and 531 nm, respectively. The weight-average molecular weights (Mₖ) and number-average molecular weights (Mₙ) of the polymers were 50000-82000 and 48000-75000 respectively with a polydispersity index (PDI) of 1.03-1.08, as determined by GPC.

Keywords: Gilch polymerization; semi conducting polymers; PPV; MDMO-PPV.

1. Introduction

A general and most widely used synthesis of PPV derivatives was introduced by Gilch [Gilch and. Wheelwright, 1966]. This method avoids high temperature conditions and
occurs through base-promoted 1,6-elimination of 1,4-bis(chloro-methyl)benzenes. For device applications, the as-synthesized PPV materials need to be soluble in organic solvents, otherwise the as-formed polymer powder is completely unprocessable. Alkyl-, alkyloxy- and other substituted monomers giving soluble PPVs can be employed in this reaction. The mechanism of the Gilch polymerization is still a subject of some controversy [Wiesecke and Rehahn, 2003; Hsieh et al 1997; Neef and Ferraris, 2000].

The molecular weight of the polymers can be controlled (from ca. 50,000 to above 1,000,000) by changing the reaction temperature and time, the solvent, the concentration of the monomer, and the amount of base equivalent [Swatos and Gordon, 1990; Johansson et al. 2001].

For the last decade, MEH-PPV has been one of the most studied electroluminescent materials. The 2-ethylhexyl substituent (EH) became a very popular side-chain group for synthesis of soluble conjugated polymers of different classes, but other branched alkylloxy substituents have been also introduced in the PPV backbone. MDMO-PPV substituted with a 3,7-dimethyloctyl-1 group (DMO) showed a very similar electronic behavior to that of MEH-PPV, but an additional branching further improved its solubility and the film-forming properties [Lutsen et al, 1999; Spreitzer et al., 1998]. The molecular structure of MDMO-PPV is shown in Figure 1.

![Figure 1](Image)

**Figure 1**: The molecular structure of MDMO-PPV polymer.

2. **Experimental**

2.1 **Materials**

All reagents were commercially available and used as received. The monomer 2,5-bis(chloromethyl)-1-methoxy-4-(3’,7’-dimethyloctyloxy)benzene was obtained from Sigma Aldrich. Polymerization reactions were carried out under nitrogen atmosphere.

2.2 **Polymerization of MDMO-PPV**

A 500 mL three-neck glass reactor fitted with Teflon stirrer, reflux condenser and dropping funnel were dried with hot air and flushed with N₂. The solvents (dry 1,4-dioksan, dry THF) at volume of 82 mL was added in reactor and degassed by passing N₂ through it for about 15 minutes. The solvent was heated to polymerization temperature (98 °C, 80 °C, 60 °C, 40 °C and 25 °C) with an oil bath. 0.5 g 2,5-bis(chloromethyl)-1-methoxy-4-(3’,7’-dimethyloctyloxy) benzene was added as solid. 0.405 g of potassium tert-butoxide was dissolved in 3.675 mL of solvent and was added dropwise to the reactor from the dropping funnel over a period of 5 minutes. During this addition, the reaction mixture changed color from colorless to yellow and the viscosity increased significantly. The mixture was stirred further for 5 min at
polymerization temperature. 0.31 g of potassium tert-butoxide was dissolved in 2.75 mL of solvent and it was added into reactor over a period of 1 min. The solution was stirred at polymerization temperature for 2 hours (24 hours for THF) and then cooled to room temperature. Finally, the reaction mixture was mixed with 0.5 mL of acetic acid (diluted with the same amount of solvent) and stirred further for 20 min. The solution was then deep orange and the viscosity increased. After that, the reaction solution was slowly poured into 89.5 mL of intensively stirred water and the resulting mixture was stirred further for 10 min. After 7.15 mL of methanol was added in solution, the precipitated polymer was filtered off. The precipitated polymer was washed with 7.15 mL of methanol and dried under reduced pressure at room temperature. A sample of crude polymer was obtained as red fibers.

The polymer was purified by dissolving it in 39.5 mL of THF at 55-60 °C, cooling the solution to 40-45 °C, and precipitating polymer by drop wise addition of 43 mL of methanol. After the polymer was washed with 7.15 mL of methanol, it was dried at room temperature under reduced pressure. This procedure was repeated once more using 35.5 mL of THF and 35.5 mL of methanol. Finally MDMO-PPV was obtained as dark orange-red fibers Figure 2.

![Figure 2](image-url): Synthesis of MDMO-PPV polymer.

2.3 Characterization methods

$^1$H spectra were recorded using Bruker 500MHz NMR spectrometer. Chemical shifts were reported in δ ppm relative to internal solvent standards (CDCl$_3$). UV-Vis spectra were recorded in THF (10 ppm) using Aquamate UV-Visible spectrophotometer. Molecular weights and polydispersities were determined by gel permeation chromatography (GPC) in THF relative to polystyrene standards. GPC data were collected using PLgel 3 μm MIXED-E column (300 x 7.5 mm).

3. Results and Discussion

3.1 Effect of temperature and solvent type on production yield of MDMO-PPV

Polymerization yields were calculated by amounts of using monomer and obtained polymer and shown in Table 1. According to results, polymerization yield doesn’t change much with changing of temperature and solvent type under same reaction conditions.

3.2 Characterization studies

Absorption peaks of Polymer A and Polymer G were found 511 nm and 531 nm, respectively. The results are fairly typical of alkoxy-substituted PPVs in solution.
Polymer G have absorption maxima shifted slightly towards the red more than Polymer A, Figure 3.

### Table 1: Yield of obtained polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temperature (°C)</th>
<th>Solvent type</th>
<th>Monomer (g)</th>
<th>Polymer (g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer A</td>
<td>98</td>
<td>1,4-dioxane</td>
<td>0.5093</td>
<td>0.169</td>
<td>33.2</td>
</tr>
<tr>
<td>Polymer B</td>
<td>80</td>
<td>1,4-dioxane</td>
<td>0.69</td>
<td>0.216</td>
<td>31.3</td>
</tr>
<tr>
<td>Polymer C</td>
<td>60</td>
<td>1,4-dioxane</td>
<td>0.5</td>
<td>0.165</td>
<td>33.0</td>
</tr>
<tr>
<td>Polymer D</td>
<td>40</td>
<td>1,4-dioxane</td>
<td>0.62</td>
<td>0.198</td>
<td>31.9</td>
</tr>
<tr>
<td>Polymer E</td>
<td>60</td>
<td>THF</td>
<td>0.5</td>
<td>0.159</td>
<td>31.8</td>
</tr>
<tr>
<td>Polymer F</td>
<td>40</td>
<td>THF</td>
<td>0.52</td>
<td>0.162</td>
<td>31.2</td>
</tr>
<tr>
<td>Polymer G</td>
<td>25</td>
<td>THF</td>
<td>0.53</td>
<td>0.172</td>
<td>32.5</td>
</tr>
</tbody>
</table>

The common peaks for Polymer A and Polymer E are obvious: $^1$H NMR shows peak at 7.5 ppm and it belongs to vinylic bonds. The signals between 7.0-7.3 ppm are certainly represent aromatic/vinylic bonds. The peaks for all other protons appeared below 4.2 ppm. The multiplets around 4.0 ppm and between 0.7 and 2.0 represent the alkoxy side chains. All peaks showed good correspondence with the chemical structures of the polymers.

Comparing the $^1$H NMR spectra of Polymer A and Polymer E, two major differences are certain. Polymer E has more alkoxy side chains than Polymer A. Also tolane-bisbenzyl (TBB) defect has been detected at 2.9 ppm for Polymer E but not for Polymer A, Figure 4.

$M_w$ and $M_n$ of the synthesized polymers were 50000-82000 and 48000-75000 respectively with a PDI of 1.03-1.08, as determined by GPC. The low polydispersity values of the MDMO-PPV suggest that the molecular weight distribution of the polymers were uniform. These high molecular weights are in part responsible for the superior performance of GILCH PPVs in PLED applications, Table 2.
Figure 4: 1H-NMR spectra of Polymers, a-polymer A, b- polymer G.

Table 2: Gel permeation chromatogram results of polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M_w</th>
<th>M_n</th>
<th>PID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer A</td>
<td>53510</td>
<td>51666</td>
<td>1.04</td>
</tr>
<tr>
<td>Polymer B</td>
<td>62777</td>
<td>58939</td>
<td>1.07</td>
</tr>
<tr>
<td>Polymer C</td>
<td>55263</td>
<td>53292</td>
<td>1.04</td>
</tr>
<tr>
<td>Polymer D</td>
<td>58671</td>
<td>55364</td>
<td>1.06</td>
</tr>
<tr>
<td>Polymer E</td>
<td>50318</td>
<td>48868</td>
<td>1.03</td>
</tr>
<tr>
<td>Polymer F</td>
<td>56466</td>
<td>53750</td>
<td>1.05</td>
</tr>
<tr>
<td>Polymer G</td>
<td>82225</td>
<td>75840</td>
<td>1.08</td>
</tr>
</tbody>
</table>

4. Conclusion
In this present study high molecular weight of MDMO-PPV samples synthesized by Gilch polymerization procedure. Comparison between lower molecular weight material and GILCH PPVs showed inferior electro-optical results obtained with those polymers [Beck et al., 2001]. The absence of saturated defects was confirmed by 1H-NMR spectroscopy. UV-Vis absorption spectra of polymers in THF showed the broad absorption band with between \( \lambda_{\text{max}} = 510-531 \text{ nm} \).

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References


