Acid Catalyzed Polymerization of Phenyl ethane 1,2-diol for One-Pot Synthesis of Organosoluble Poly(phenylene vinylene)

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Abstract

Acid catalyzed polymerization of phenyl ethane 1,2-diol is realized for the first time via a novel one-pot coupling reaction to produce organosoluble poly(phenylene vinylene). A variety of experimental conditions were investigated. PPV structure was confirmed by 13C-NMR and 1H-NMR chemical shifts. Fluorescence spectra of the polymer showed emission in the visible range, as to be expected. Average PPV molecular weights ranged from 670 to 6200 Da. The methanesulfonic acid (MesOH) catalyzed syntheses were shown to produce higher molecular weight and purity PPV than the sulfuric acid (H2SO4) counterparts, although both are able to produce organosoluble products.

π-Conjugated polymers have been of particular significance as organic semiconductors due mostly to their use in the fabrication of a wide range of electronic and optical de-
There is an increasing demand for these materials, specifically in the areas of organic light emitting diodes (OLEDs), photovoltaic cells, thin film transistors (TFTs) and electrochromic devices. Poly(phenylene vinylene) (PPV) and its derivatives, in particular, have found marked interest for the production of OLEDs possessing color tunability and high photoluminescence.

As a result of these unique applications, several different methods have been applied for the synthesis of \(\pi\)-conjugated polymers. For instance, dehydrochlorination of p-xylylidene dichloride can produce PPV with partially chloride bearing moieties and requires subsequent pyrolysis to obtain the pure polymer. On the other hand, many of the techniques, including the Heck, Stille, and Suzuki coupling reactions, utilize palladium catalysts which require the use of complex ligands. Suzuki reaction offers a stereospecific cross-coupling of vinyl or aryl halides with organoboronic compounds. However, the more common phosphine ligands used in the above reactions, can often become integrated into the desired products. To add to the process complexity, the monomers frequently require synthesis prior to the reaction since they are not always commercially available. Besides, residual metal defects, originating from catalyst degradation during the polymerization, can not be entirely removed by physical methods. These defects are known to severely impact the polymer’s electroluminescent, field-effect transistor and photovoltaic cell performances. In addition, the previous synthetic routes were incapable of yielding soluble PPV, which limited its processability.

The precursor route offers commercially available reagents for PPV synthesis and requires post-treatments after the polymerization. These routes involve thermally-driven reactions such as dehydrochlorination and elimination of sulfonium salts. This, however, limits the product purity to that of the extent of reaction, which hinders the polymer’s electroactivity and reduces its effectiveness in OLED, TFT, and photovoltaic applications.

In this paper, the synthesis of organosoluble poly(phenylene vinylene) through an acid catalyzed condensation reaction of a single monomer is outlined. The presented scheme is a
novel coupling route starting from an aryl vicinal diol and, as such, is the first polymerization of its kind for phenyl ethane 1,2-diol (PED). Although only a base case is demonstrated in this work, syntheses for PPV derivatives and other conjugated polymers appear promising. The bare PPV obtained in this work is soluble in solvents such as tetrahydrofuran (THF) and dichloromethane (DCM). The presented condensation reaction allows for one-pot synthesis of PPV, which makes the potential for industrial production of significant interest.

Acid catalyzed polymerization of PED was successfully realized through various synthetic conditions, the details of which are given in the SI. The corresponding reaction is drawn in Scheme 1. The broad patterns in the $8 - 6$ ppm range in the $^1$H-NMR spectrum (Figure 1) and in the $130 - 125$ ppm range in the $^{13}$C-NMR spectrum (Figure 2) clearly indicate the presence of both vinylene and phenylene groups in the synthesized polymer.

Table 1 summarizes data for the polymerization of PED under six different conditions. In the first attempt (Entry I.), sulfuric acid was used to catalyze the reaction in dichloromethane at room temperature. The resulting polymer was readily soluble in a number of solvents such as THF, DCM, chloroform, and toluene. In an effort to separate the H$_2$O product and thus to favor the polymerization, the reaction was carried out at elevated temperatures (130 – 170°C) under bulk conditions (Entry II); however, no significant change in either the molecular weight or percent yield was observed. The reaction was also conducted in the presence of P$_2$O$_5$ to act as a water scavenger and sulfuric acid as the catalyst (Entry III), however, the polymer product was difficult to isolate due to its water-miscibility.

It is well-known that P$_2$O$_5$ can convert H$_2$SO$_4$ to SO$_3$ which might easily cause sulfonation of the benzene ring present in the medium. Hence, to prevent any possible sulfonation reaction, we also experimented with methane sulfonic acid (MesOH) as the catalyst in the presence of P$_2$O$_5$ at three different temperatures (Entries IV, V and, VI). Under these reaction conditions, significant increases in the molecular weights and product yields were achieved. Formation of the PPV structure was confirmed by the $^1$H-NMR spectra (see Figures S3-S5). Gilch and Wheelwright reported that the reaction of α-α’-dihalo-p-xylenes
Table 1: Data for the synthesis of PPV via acid catalyzed polymerization of PED in DCM.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>P₂O₅</th>
<th>Temp.(°C)</th>
<th>Time(h)</th>
<th>[Cat./(M₀)]</th>
<th>Mₙ(Da) a</th>
<th>Mₘ(Da) a</th>
<th>%Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>H₂SO₄</td>
<td>-</td>
<td>25</td>
<td>~120</td>
<td>1.0/1.1</td>
<td>760</td>
<td>700</td>
<td>89.5</td>
</tr>
<tr>
<td>II b</td>
<td>H₂SO₄</td>
<td>-</td>
<td>130−170</td>
<td>46</td>
<td>1.0/48</td>
<td>670</td>
<td>650</td>
<td>89.2</td>
</tr>
<tr>
<td>III</td>
<td>H₂SO₄</td>
<td>+</td>
<td>20−25</td>
<td>21</td>
<td>1.0/5.6</td>
<td>-</td>
<td>-</td>
<td>-c</td>
</tr>
<tr>
<td>IV</td>
<td>MesOH</td>
<td>+</td>
<td>20</td>
<td>143</td>
<td>1.0/4.4</td>
<td>2200 d</td>
<td>2000 d</td>
<td>93.5</td>
</tr>
<tr>
<td>V</td>
<td>MesOH</td>
<td>+</td>
<td>45</td>
<td>169</td>
<td>1.0/4.8</td>
<td>6200 d</td>
<td>1600 d</td>
<td>100</td>
</tr>
<tr>
<td>VI</td>
<td>MesOH</td>
<td>+</td>
<td>60</td>
<td>111</td>
<td>1.0/56</td>
<td>2200 d</td>
<td>1200 d</td>
<td>100</td>
</tr>
</tbody>
</table>

a Average molecular weights are determined by GPC (See Figures S7-S11 for the corresponding GPC curves).

b Polymerization is conducted under bulk conditions.

c The product is difficult to isolate. d Two different populations are detected by GPC analysis (See GPC curves in Figures S9-S11). The given averages correspond to the high molecular weight population.

with potassium t-butoxide yields a solid product with 3−4 repeat units of phenylene-vinylene, estimated from end-group analysis.21

![Scheme 1: Synthesis of PPV via acid catalyzed polymerization of phenyl ethane 1,2-diol.](image)

The polymers synthesized using MesOH at 45°C and 60°C, are highly soluble in THF and partially soluble in DCM whereas the one obtained at 20°C is very soluble in both solvents. In contrast, the previous synthetic routes resulted in insoluble PPV, which limited its processability.17,21,22 In those studies, as a remedy, use of soluble precursors affords applicability prior to the final reaction step. However, the thermally-treated insoluble polymer can not be reprocessed.

Photophysics of the PPV was investigated by excitation-fluorescence spectrometry. Figure 3 shows the relevant results for one of the polymers at three different temperatures. The
Figure 1: $^1$H-NMR spectrum of the synthesized PPV.

Figure 2: $^{13}$C-NMR spectrum of the synthesized PPV.
synthesized polymers exhibit photoluminescence, agreeing with the previous observations for PPV synthesized by other synthetic methods,\textsuperscript{23} due most likely to $\pi-\pi^*$ electron transition. A broad excitation pattern ending at nearly 500 nm is observed, which indicates a highly conjugated structure. We attribute the broadness of the curves primarily to the well-known influences of torsion angle around the phenylene unit and the length of the $\pi$-conjugation on the energy of excitation or $\pi-\pi^*$ transition.\textsuperscript{24,25} The polymer being excited at 416 nm, yields a broad emission band peaking at around 480 nm. Very similar results were obtained for the other polymers, as well (see Figures S12-15). Holmes et.al reported an emission peak at a wavelength of 540 nm for PPV.\textsuperscript{26} The difference in the emission wavelengths might be due to differences in the conjugation lengths of the polymers. Moreover, intensity of the fluorescence decreases as temperature increases in the range 25 – 40°C. However, neither the peak wavelength nor the band-width of the fluorescence is affected by the temperature of the polymer solution.

![Figure 3: Excitation-emission spectra of the PPV (from synthesis V) in THF at various temperatures. Dashed curves correspond to excitation and the solid curves correspond to emission.](image)

Thermogravimetric analysis of the PPV shows that the polymer remains stable up to about 190°C (see Figure 4) under nitrogen medium. Moreover, multiple transitions ob-
served at $190^\circ C$, $340^\circ C$ and $575^\circ C$ suggest different types of backbone linkages. This might specifically be attributed to ortho, meta and para type couplings occurring all together during the polymerization. Moreover, as can be inferred from Figure 4, isomeric compositions might vary with the synthetic conditions. It is clear that the benzene ring in the growing molecule does not have any sort of directing group to favor a preferential ortho, meta or para type coupling. However, to extend this work, the synthesis and polymerization of m-alkoxy-phenyl ethane 1,2-diol is under investigation to test the affordability of para-directed condensation.

The X-ray diffraction (XRD) pattern of PPV indicates an amorphous structure (see Figure 5).

![Figure 4: Thermogravimetric analysis of the PPV.](image)

In conclusion, poly(phenylene vinylene) has been synthesized through an acid catalyzed condensation reaction using a PED monomer in a one-pot synthesis. Mass average molecular weights of up to 6200 Da were achieved. The data indicated that MesOH catalyzed syntheses produce larger molecular weight PPV. The synthesis is a novel coupling reaction and the first involving an aryl vicinal diol molecule. Moreover, since the synthesis is a one-pot reaction, scalability to industrial levels is feasible. In addition, the polymer is soluble in a number of organic solvents, which increases its processability. Preliminary TGA results show three
types of polymer backbone linkages, which would suggest a non-stereospecific coupling of PED. To eliminate this limitation, further investigation should be done on PED derivatives consisting of ortho, para, or meta directing groups. In this paper, only the exploratory syntheses of PPV are shown and discussed, however, further research will be done to examine the various capabilities of this coupling reaction, such as construction of different topologies. Initial results from these seem promising and will be analyzed in more depth. In addition, syntheses of PPV derivatives and other aryl vicinal diols will be explored to reveal more about this novel polymerization method.

Supporting Information Available

References


(2) Li, C.; Liu, M.; Pschirer, N. G.; Baumgarten, M.; Mullen, K. Chemical reviews 2010, 110, 6817–6855.


