Synthesis of blue light emitting copolymers by oxidative coupling reaction

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Abstract:

A new series of blue light emitting copolymers with isolated chromophore have been prepared by using di-tert-butyl peroxide (DTBP) as catalyst via oxidative-coupling copolymerization route. Dialkyloxy benzene and dimethyl-bisphenoxy alkane are copolymerized with anthracene and dinaphthalene, respectively. The high yield copolymers have amorphous structures and show excellent solubility in common organic solvents, good thermal stability and high photoluminescence quantum efficiency.

Keywords: blue light-emitting, di-tert-butyl peroxide, ortho-ortho'-coupling, oxidative coupling, photoluminescence.

1. Introduction

Up to the mid 1980s, two main synthetic routes have been used in the synthesis of Poly( para-phenylene) (PPP): the direct route from benzene \cite{1} and the indirect route from precursor polymer \cite{2}. Unfortunately, both routes suffer from serious drawbacks, while the route to soluble PPP using Suzuki aryl–aryl coupling with Pd catalyst is also limited due to its long and tedious monomer synthesis\cite{3}. A few attempts to reach PPP using shorter oxidative coupling routes have been made by using FeCl\textsubscript{3} \cite{4} or molybdenum pentachloride as an oxidative agent\cite{5} and incorporated anthracene moieties \cite{6} into main chain to improve blue light emitting properties.

In this paper, with the aim of finding a simple and efficient synthetic route to structurally defined PPP and its copolymer for large scale production and for high PL efficiency, we embarked upon the synthesis of copolymers with anthracene and dinaphthalene moieties and unconjugated segments, which might increase PL(EL) efficiency by confining the excitons on the conjugated sections\cite{7}, by use of various oxidative agents like FeCl\textsubscript{3} and DTBP. The choice of DTBP is due to its high efficiency of providing predominantly the corresponding ortho-ortho’- coupled results \cite{8}, which might introduce sterically bulky o-aryl substituents to prevent excimer and exciplex formation through polymer chain aggregation.

2. Experimental

Monomers 1, 2 and 3 shown in Scheme 1, were prepared respectively using a modified literature procedure \cite{9}. Copolymer 1-4 (Scheme 1) were polymerized using DTBP from starting monomers (mole ratio =1:1) according modified literature route \cite{8}. FTIR spectra were recorded on a Nicolet Magna-550 spectrometer; UV spectra: Perkin-Elmer UV-240 scanning spectrophotometer; PL spectra: Cary Eclipse(Varian) luminescence spectrometer; Differential scanning calorimetry (DSC): Setaram DSC 92 system; Gel permeation chromatography (GPC): Perkin-Elmer 200 HPLC system and wide-angle X-ray diffraction patterns on a SHIMADZU XRD-6000 X-ray diffractometer.
3. Results and discussion

As an alternative to DTBP, ferric chloride has also been investigated as an oxidative agent in the polymerization of polymer 2, in this case, a large amount of brick-yellow insoluble fraction was observed and only 20% yield of yellow powder was obtained. This powder has a broad melt point of 90-160°C indicating mainly the monomers.

The copolymers using DTBP as oxidative agent are soluble in common organic solvents such as tetrahydrofuran, chloroform, acetone and toluene, completely. These oligomers have DP of about 5 to 10, and high glass transition temperatures as shown in Table 1.

Table 1. Yield and macromolecular characteristics of copolymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Yield (%)</th>
<th>Tg (°C)</th>
<th>Mn</th>
<th>Mw</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>82</td>
<td>153</td>
<td>1980</td>
<td>3280</td>
<td>1.7</td>
</tr>
<tr>
<td>2</td>
<td>76</td>
<td>73</td>
<td>1610</td>
<td>2970</td>
<td>1.8</td>
</tr>
<tr>
<td>3</td>
<td>78</td>
<td>71</td>
<td>2150</td>
<td>3490</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>75</td>
<td>2740</td>
<td>4790</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The IR spectra of copolymers are shown in Fig.1. Polymer 1 and 2 show characteristic absorptions at 760cm⁻¹ due to the typical C-H out-of-plane bending mode of four adjacent hydrogen on the anthracene units, indicating the 9,10-linkage of anthracene moieties in the backbone of the polymers. The typical C-H out-of-plane bending of three adjacent hydrogen on the 1,2,3-trisubstituted benzene at 780(s) and 693(m) in polymer 2,3,4 indicates the formation of ortho-ortho'-coupling results of polymerization.

Fig. 1. FT-IR spectra of copolymers.

Fig. 2. Wide-angle X-ray diffraction of copolymer 2.

The wide-angle X-ray scattering studies (e.g. Fig 2) almost show no sign of crystallization existence. The amorphous structure is caused by the irregular molecular structure, which might be deduced by the statistical copolymerization of the monomers and the highly ortho-ortho'-coupling brakes the symmetry of polymer backbone. Therefore, good solubility and high optical quality are expectable and reasonable.

4. Conclusions

Novel copolymers of high ortho-ortho'-aryl-aryl structure were synthesized with high yields via oxidative coupling reaction by using DTBP. To break conjugation of copolymer decreases the long wavelength absorbance. The copolymers have amorphous structures and show excellent solubility in common organic solvents, good thermal stability and high photoluminescence quantum efficiency.

References