Chapter 3

Chiral Poly(\textit{l}-lactic acid) Driven Helical Self-Assembly of Oligo(p-phenylenevinylene)
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Chiral Poly(\(\alpha\)-lactic acid) Driven Helical Self-Assembly of Oligo(p-phenylenevinylene)

The synthesis and self-assembly of a series of copolyesters incorporating varying mol ratios of an achiral oligo(p-phenylenevinylene) (OPV) into the backbone of a chiral poly(\(\alpha\)-lactic acid) (PLLA) via high-temperature solution-blending is reported. The polymers were characterized by \(^1\)H NMR spectroscopy and size exclusion chromatography (SEC) and their bulk properties were investigated by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WXRD). DSC and WXRD analysis confirmed the crystallinity and \(\pi-\pi\) stacking of the OPV units in the PLLA-OPV copolyester. Absorption, emission and lifetime-decay studies showed that OPV chromophore was highly aggregated in the solid state. The solid powder samples of the copolyesters exhibited intense red shifted aggregate emission beyond 470 nm. Circular dichroism (CD) spectroscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies revealed that the PLLA-OPV copolyester formed self-assembled architecture in which the helical organization of the achiral OPV segments was dictated by the chiral PLLA segments. The observed CD signal and AFM image accounted for right-handed helical self-assembly of OPV chromophore in the solid state. These results confirmed the effect of chiral PLLA segment on tuning the OPV chromophore packing and supramolecular chirality in molecular aggregates. The methodology illustrated here provides opportunities for the design of a new class of hierarchical self-assembled architectures based on organic \(\pi\)-conjugated materials and the manipulation of their optical properties. The nanofibers of copolyester of PLLA incorporating OPV chromophore were successfully constructed by electrospinning technique and the fluorescence microscopy images of these fibers showed both blue and green emission upon excitation at different wavelengths.
3.1. Introduction

Supramolecular π-conjugated materials based on organic molecules and polymers have been widely studied due to their potential applications in electronic devices like photovoltaics, light emitting diodes and chemical and biosensors.\textsuperscript{1-4} Nature controls the architecture of supramolecular assemblies, such as the DNA double helix, the photosynthetic reaction centres and the collagen triple helix etc, which are vital for sustaining life.\textsuperscript{5} Both covalent and noncovalent chemistry play important roles in this creativity and chemists try to mimic the molecular architectures of such functional assemblies. Over the past decade, several noncovalent interactions such as hydrogen bonding, electrostatic interactions, π-π stacking, dipolar interactions, chirality, and so forth, have been identified as enabling the construction of various hierarchical architecture from specially engineered small molecule building blocks.\textsuperscript{6-9} The chiral self assembly of linear π-conjugated systems makes them interesting as optical probe molecules for various applications.\textsuperscript{10-12} The optical and electronic properties of devices made up of these π-conjugated materials are sensitive to conformational changes upon intermolecular interactions.\textsuperscript{13-15} Oligofluorenes, oligothiophenes, oligophenylenes and oligophenylenevinylene were reported for chiral self-organization in π-conjugated materials.\textsuperscript{16-18} High luminescent characteristics, thermal and optical stability, film forming tendency and solubility in organic solvents make oligo(p-phenylenevinylene) (OPV) chromophore very unique compared to other π-conjugates.\textsuperscript{19, 20}

The self organization of oligo(p-phenylenevinylene) (OPV) chromophore via hydrogen bonding, π-π stacking and metal-ion interactions etc has been reported and the resultant structure were tested successfully as active layer in electronic devices.\textsuperscript{21-24} In most of the cases, helicity has been achieved by the use of chiral monomers. Meijer and co-workers have made significant contributions to the helical self-assembly of π-conjugated oligomers derived from phenylenevinylene where the chirality of the attached side chains was translated to the conjugated oligomer backbone at a supramolecular level.\textsuperscript{25, 26} However, the lack of control over the chirality outcome and tedious asymmetric synthesis make the design of chiral monomers a challenging task. A different approach towards helical system is to use host-guest chemistry to induce tunable chirality to the achiral host by specific recognition of appropriate chiral guest molecules, for which a careful design is needed.\textsuperscript{27} Yet another category that has received lot of attention is the helical self-assembly of the achiral π-conjugated oligomers by the chiral peptide segments. Examples are the solid state self-assembly of peptide-functionalized tetraphiophene and the aqueous supramolecular
aggregates of l-lysine branched phenylvinylene derivative.\textsuperscript{28, 29} Synthesis and self-assembly of oligo(p-phenylenevinylene)-peptide conjugates in solution and at the solid-liquid interface was also reported.\textsuperscript{30}

Inspired by the concept of chiral information transfer from the molecular level to macroscopic features, we have designed a series of copolyesters composed of a chiral poly(l-lactic acid) (PLLA) and an achiral oligo(p-phenylenevinylene). Poly(l-lactic acid) (PLLA) is a chiral semicrystalline aliphatic polyester derived from renewable resources such as corn and rice.\textsuperscript{31} PLLA is the depsipeptide counterpart to polyalanine wherein each amide linkage is replaced by an ester. The n→π* interactions between sequential ester carbonyl groups contribute to the conformational stability of PLLA helix.\textsuperscript{32} The helical molecular conformation in PLLA produces large optical activity and this phenomenon is promising for new optical applications utilizing their optical activity.\textsuperscript{31} In the current chapter, we describe the synthesis of a series of PLLA-OPV random copolyesters incorporating varying amounts of oligo(p-phenylenevinylene) (OPV) by high-temperature solution-blending approach and the helical self-assembly of the achiral OPV segments by the chiral PLLA segment was studied. The structure and bulk properties of the PLLA-OPV copolyesters were studied using \textsuperscript{1}H NMR spectroscopy, size exclusion chromatography (SEC), differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WXRD). The photophysical properties were studied using steady-state UV-vis absorption and fluorescence spectroscopy as well as fluorescence lifetime-decay measurements. The helical self-assembly of OPV segments by chiral PLLA was monitored via CD spectroscopy and the morphological features were revealed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The PLLA induced self-assembly of OPV chromophore is reflected in their packing structure, optical properties and morphology. This molecular design can be applied to other π-conjugated chromophores to diversify their self-assembly pattern, morphologies, optical and electronic properties.

Nanofibers of random copolyester incorporating OPV has been successfully produced using the electrospinning technique. Electrospinning is a simple but advanced technique, which has attracted widespread attention for fabrication of micro-/nano fibers in recent years.\textsuperscript{33} Electrospinning possesses great advantages including simplicity of use, potential scale up and versatility in spinning a wide variety of polymeric fibers. This method involves the application of a high voltage source to obtain fibers whose diameters range from several nanometers to microns. These fibers were analyzed using microscopic techniques like scanning electron microscopy (SEM) and fluorescence microscopy.
3.2. Experimental Methods

3.2.1. Materials: (3S)-cis-3,6-Dimethyl-1,4-dioxane-2,5-dione (l-lactide), tin(II) 2-ethylhexanoate (Sn(Oct)₂), 4-methoxyphenol, 2-ethylhexylbromide, triethylphosphite, 4-hydroxybenzaldehyde, potassium-tert-butoxide, titanium(IV) butoxide (Ti(OBu)₄), and ortho-dichlorobenzene (ODCB) were purchased from Aldrich and used without further purifications. HBr in glacial acetic acid, paraformaldehyde, 2-chloroethanol and all other solvents were purchased locally and purified with standard procedures.

3.2.2. Instrumentation: ¹H NMR spectra were recorded using a Bruker Avance 200 MHz spectrometer. Chemical shifts (δ) are reported in ppm at 25 °C with a small amount of tetramethysilane (TMS) as internal standard. The mass spectral analysis of monomer was carried out using a Voyager-De-STR MALDI-TOF (Applied Biosystems, Framingham, MA, USA) instrument equipped with 337 nm pulsed nitrogen laser used for desorption and ionization. The molecular weight of synthesized polymers was determined using size exclusion chromatography (SEC). GPC measurements were carried on a Polymer Laboratories PL-GPC-220 at 25 °C using chloroform (Merck) as the mobile phase. The analysis was carried out at a flow rate of 1 mL/min using a set of three PLgel columns and a refractive index (RI) detector. This column set enabled the determination of a wide range of molecular weight from 10² to 10⁶. Columns were calibrated with polystyrene standards and the molecular weights reported were with respect to polystyrene. The inherent viscosity (ηinh) of the polymers was measured for 0.5 wt % polymer solutions in chloroform. The absorption spectra in a chloroform solution were recorded using a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. The absorption spectra of the powdered polymer samples were recorded using a JASCO model V-570 spectrophotometer in the reflectance mode. Steady-state fluorescence studies and fluorescence lifetime-decay measurements were performed using Horiba Jobin Yvon Fluorolog 3 spectrophotometer having a 450 W xenon lamp for steady-state fluorescence and nanoLED of 390 nm for fluorescence lifetime-decay measurements. For lifetime measurements, decay curves were obtained by the time-correlated single photon counting (TCSPC) technique. The fluorescence quantum yield of the polymers were determined in CHCl₃ using quinine sulphate in 0.1 M H₂SO₄ (ϕ = 0.54) as the standard by exciting at 360 nm. Solid state photoluminescence spectra were recorded using the front face scan mode with the same Fluorolog spectrofluorimeter. The thermal stability of the polymers was analyzed using a Perkin-Elmer thermogravimetric analyzer under nitrogen atmosphere at
heating rate of 10 °C/min. Differential scanning colorimetry (DSC) was performed using TA Q10 differential scanning calorimeter at heating rate of 10 °C/min. Wide-angle X-ray diffraction (WXRD) were recorded by Phillips x’pertpro powder X-ray diffractometer using Cu Kα radiation, and the spectra were recorded in the range of 2θ = 5-35°. Circular dichroism (CD) spectra were measured in JASCO J815 spectrometer from 550-200 nm. Atomic force microscopy (AFM) images were taken by using a Multimode scanning probe microscope equipped with a Nanoscope IV controller from Veeco Instruments, Inc. in the tapping mode using a SiN probe. The electrospinning apparatus consists of a syringe pump, syringe needle, high voltage power supply and a grounded collector. Polymer solution was loaded into a syringe and positive electrode was clipped onto the syringe needle. The flow rate of the polymer solution to the needle tip was kept constant. Solutions were electrospun horizontally onto the target. Scanning electron microscopy (SEM) images were recorded using FEI, QUANTA 200 3D scanning electron microscope with a tungsten filament as electron source. The fluorescence microscopy images were recorded by Epi-fluorescence microscope Leitz Laborlux, Germany, and images were observes by a cannon power shot S80 camera [excitation wavelengths: 350-430 nm (blue) and 488-520 (green)].

3.2.3. Synthesis

**Synthesis of poly(ʟ-lactic acid) (PLLA):** PLLA was synthesized by following the literature procedure.\(^{34}\) ʟ-Lactide was sealed in a silanized glass tube and placed in an oil bath at 180 °C for 3 h. The ring-opening polymerization of the ʟ-lactide was catalyzed by Sn(Oct)\(_2\) in a 1:10000 catalyst:monomer ratio. The polymer was dissolved in chloroform and poured into methanol to separate any residual ʟ-lactide. The polymer was filtered and dried in oven at 60 °C. Yield: 95.60 %; \(^1\)H NMR (200 MHz, CDCl\(_3\)) δ ppm: 5.16 (q, 1H, \(–\text{C}H(\text{CH}_3)–\text{COO}–\)), 1.56 (d, 3H, \(–\text{CH}_3\)).

**Synthesis of copolyesters of PLLA incorporating OPV chromophore by high-temperature solution-blending (PLLA-OPV-x):** PLLA (0.68 g, 9.5 mmol) and OPV-2-Diol (0.28 g, 0.5 mmol) were dissolved in ODCB (0.5 mL) by heating at 160 °C in an oil bath (for PLLA-OPV-4). The mixture was stirred for 30 min using an overhead mechanical stirrer at a constant rate of 100 rpm. To this mixture, Ti(OBu)\(_4\) (34 mg, 1 mol %) solution in ODCB was added and the reactive blending was continued with stirring at 160 °C for 1 h. The product was dissolved in chloroform and precipitated into methanol. The polymer was
filtered and dried in oven at 60 °C. Yield: 70.00 %; \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) ppm: 6.89–7.51 (Ar–H and vinylic H), 5.16 (–CH(CH\(_3\))–COO–), 4.33–4.51 (–COO–CH\(_2–\)CH\(_2–\)), 3.90–4.17 (Ar–O–CH\(_2–\), Ar–O–CH\(_3\), Ar–O–CH\(_2–\)CH\(_2–\)OH end group), 2.69 (–OH), 0.90–1.80 (–CH\(_3\) in PLLA part and aliphatic H from OPV part).

A similar procedure was employed to synthesize the PLLA-OPV-x series of polyesters by changing the molar ratio of OPV-2-Diol in the feed from 0.5 to 5 mol%.

**Synthesis of nanofibers:** Polymer solution was prepared by dissolving 100 mg of polymer in 1 mL of DCM (10 wt % solution). This solution was subjected to a high electric field of about 10 kV for electrospinning. The tip to collector distance was fixed at 12 cm and the feeding rate was 0.5 mL h\(^{-1}\). The fibers thus obtained were dried in an oven at 60 °C for 2 h.

### 3.3. Results and Discussions

#### 3.3.1. Synthesis and Characterization of Polymers

High molecular weight poly(\(\ell\)-lactic acid) (PLLA) was synthesized by the ring-opening polymerization (ROP) of (3S)-cis-3,6-Dimethyl-1,4-dioxane-2,5-dione catalyzed by Sn(Oct)\(_2\) as shown in scheme 3.1.\(^{34}\) The hydroxyl functionalized OPV derivative (OPV-2-Diol) was synthesized as discussed previously in chapter 2.\(^{35}\) The high-temperature solution-blending of OPV-2-Diol with PLLA was carried out by dissolving PLLA and OPV-2-Diol in minimum amount of a high boiling solvent like ODCB and heating in presence of 1 mol % of transesterification catalyst Ti(OBu)\(_4\) as shown in scheme 3.2. The blending was carried out in a cylindrical glass reactor at 160 °C for 1 h with constant stirring using mechanical stirrer, under continuous nitrogen flow. For workup, the polymer was dissolved in chloroform and precipitated into methanol.

![Scheme 3.1. Synthesis of poly(\(\ell\)-lactic acid) (PLLA) using ring-opening polymerization of (3S)-cis-3,6-Dimethyl-1,4-dioxane-2,5-dione.](image)

The copolyesters obtained were named as PLLA-OPV-x where x represented the actual mole % incorporation of OPV calculated from integration of \(^1\)H NMR signal. Table 3.1 gives the sample name, amount of hydroxyl functionalized OPV taken in the feed, the actual
incorporation determined using \(^1\)H NMR spectroscopy, molecular weight determined using size exclusion chromatography (SEC) in CHCl\(_3\) using polystyrene standard, the 10 % weight loss temperature obtained from thermal gravimetric analysis (TGA) as well as the yield of the various copolyesters.

![Diagram](image)

**Scheme 3.2.** Synthesis of PLLA-OPV-x copolyesters by high-temperature solution-blending of OPV-2-Diol with PLLA.

The structures of polymers were confirmed by \(^1\)H NMR spectroscopy and molecular weights were determined using size exclusion chromatography (SEC). Figure 3.1 compares the \(^1\)H NMR spectra of PLLA and OPV-2-Diol with that of the copolyester PLLA-OPV-4. The structure of the molecules is given and the different types of protons are assigned by alphabets. In OPV-2-Diol, the Ar–O–CH\(_2\)–CH\(_2\)– and Ar–O–CH\(_2\)–CH\(_2\)– protons appeared at \(\delta = 4.11\) and 3.95 ppm (labelled e and f) respectively. In OPV incorporated PLLA, a new peak at 4.33–4.51 ppm (labelled e’ and f’) corresponding to –COO–CH\(_2\)–CH\(_2\)– was observed [figure 3.1 (c)]. The formation of new trans-ester linkage involving OPV was confirmed by the shift of the Ar–O–CH\(_2\)–CH\(_2\)– proton in the proton NMR spectra, which transformed into the new –COO–CH\(_2\)–CH\(_2\)–O–Ar linkage. An attempt was made to determine the mol% incorporation of OPV in the different copolyesters by comparing the integration of peaks corresponding to the OPV aromatic protons (labelled c) with that of –CH(CH\(_3\))–COO–proton (labelled a) of the PLLA. The mol % incorporation of OPV unit in PLLA-OPV-x was determined as 0.5, 1, 2, 3 and 4 mol % corresponding to the intake feed of 0.5, 1, 2, 3 and 5 mol % respectively. Beyond this the molecular weight of the obtained polymer was drastically reduced, so higher incorporation of OPV beyond 4 mol% was not pursued. It was very difficult to accurately determine the low OPV content in the polymers by NMR. More
accurate information regarding the mol% incorporation of OPV into the PLLA backbone was obtained using Beer-Lamberts Law, using the molar extinction coefficient of OPV-2-Diol as 32059 L M⁻¹ cm⁻¹ in chloroform. The mol % incorporation of OPV unit in PLLA-OPV-x was determined as 0.79, 1.27, 2.36, 3.44 and 3.93 mol % corresponding to the intake feed of 0.5, 1, 2, 3 and 5 mol % respectively. These results are well agreement with the mol % incorporation of OPV units calculated from ¹H NMR.

![Chemical structures](image)

**Figure 3.1.** ¹H NMR spectra of (a) PLLA, (b) OPV-2-Diol and (c) PLLA-OPV-4 recorded in chloroform.
Table 3.1. Polymer designation, feed ratio, actual incorporation determined from $^1$H NMR and absorption spectra, molecular weight ($M_w$), polydispersity index, 10 % weight loss temperature ($T_D$) and yield of polymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Feed Ratio (PLLA: OPV)</th>
<th>Composition (PLLA: OPV) a (from H NMR) (mol %)</th>
<th>Mol % incorporation of OPV from absorption spectra b</th>
<th>$M_w$ (g/mol) b</th>
<th>Poly dispersity index ($D_M$)</th>
<th>$\eta_{inh}$ (dL/g) c</th>
<th>$T_D$ (°C) d</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100600</td>
<td>1.8</td>
<td>1.01</td>
<td>268</td>
<td>96</td>
</tr>
<tr>
<td>PLLA-OPV-0.5</td>
<td>99.5:0.5</td>
<td>99.5:0.5</td>
<td>0.79</td>
<td>45700</td>
<td>1.6</td>
<td>0.42</td>
<td>260</td>
<td>92</td>
</tr>
<tr>
<td>PLLA-OPV-1</td>
<td>99:1</td>
<td>99:1</td>
<td>1.27</td>
<td>18100</td>
<td>1.6</td>
<td>0.29</td>
<td>229</td>
<td>85</td>
</tr>
<tr>
<td>PLLA-OPV-2</td>
<td>98:2</td>
<td>98:2</td>
<td>2.36</td>
<td>8500</td>
<td>1.2</td>
<td>0.22</td>
<td>209</td>
<td>81</td>
</tr>
<tr>
<td>PLLA-OPV-3</td>
<td>97:3</td>
<td>97:3</td>
<td>3.44</td>
<td>7700</td>
<td>1.2</td>
<td>0.18</td>
<td>205</td>
<td>75</td>
</tr>
<tr>
<td>PLLA-OPV-4</td>
<td>95:5</td>
<td>96:4</td>
<td>3.93</td>
<td>6100</td>
<td>1.1</td>
<td>0.17</td>
<td>202</td>
<td>70</td>
</tr>
<tr>
<td>OPV-2-Diol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>368</td>
<td>61</td>
</tr>
</tbody>
</table>

a. Measured in chloroform solution.
b. Measured by size exclusion chromatography (SEC) in chloroform (CHCl₃), calibrated with linear, narrow molecular weight distribution polystyrene as standards.
c. Determined in chloroform.
d. Determined by TGA.

3.3.2. Molecular Weights of Polymers

The polymers were soluble in common organic solvents such as chloroform and dichloromethane at room temperature. The molecular weights of the polymers were determined by size exclusion chromatography (SEC) in CHCl₃ using polystyrene standards. Figure 3.2 shows the size exclusion chromatogram of the copolyesters along with that of the parent PLLA polymer and corresponding molecular weights are given in table 3.1. Molecular weights of polyesters decreased with increasing OPV content which was a consequence of the chopping of the PLLA chains to incorporate OPV units by transesterification. Exchange reactions can occur inter- or intramolecularly, and can involve ester, hydroxyl and carboxyl
groups. These inter- and intramolecular exchanges lead to the formation of low molecular weight oligomers also. Due to the reversibility of these reactions, the oligomers concentration will be very low. The GPC traces of PLLA-OPV-0.5 and PLLA-OPV-1 showed a peak around 26 min with low intensity is corresponding to these oligomers. Table 3.1 gives the inherent viscosity measured in chloroform solution for all the polymers. The inherent viscosities of the polymer also decreased with increasing mol % of OPV-2-Diol in feed.

![Size exclusion chromatogram of copolyesters recorded in chloroform using polystyrene as standard.](image)

**Figure 3.2.** Size exclusion chromatogram of copolyesters recorded in chloroform using polystyrene as standard.

### 3.3.3. Thermal Properties of Polyesters

Figure 3.3 (a) shows the TGA thermograms for the series of polymers and OPV-2-Diol. The 10 % weight loss temperature is given in the table 3.1. All polyesters were thermally stable up to 200 °C. Figure 3.3 (b) compares the second heating DSC thermograms of PLLA, OPV-2-Diol, PLLA-OPV-0.5, PLLA-OPV-1 and PLLA-OPV-4 heated at a rate of 10 °C/min. All polymers exhibited both glass transitions (T<sub>g</sub>) and melting transition. PLLA exhibited a T<sub>g</sub> around 63 °C, an exothermic crystallization at 108 °C followed by a melting at 181 °C whereas OPV-2-Diol showed a melting transition at 109 °C. The PLLA-OPV-0.5 copolyester showed a T<sub>g</sub> around 57 °C, an exothermic crystallization at 101 °C followed by a melting transition at 168 °C. The DSC thermogram of PLLA-OPV-1 exhibited T<sub>g</sub> around 46 °C, an exothermic crystallization at 103 °C and multiple-melting transitions around 150 °C. Multiple-melting behaviour has been observed for many semicrystalline polymers, which are
explained by the melt-recrystallization model.\textsuperscript{37} PLLA-OPV-2 and PLLA-OPV-3 also exhibited both \(T_g\) and multiple-melting. PLLA-OPV-4 showed \(T_g\) around 39 °C and two melting transitions at 110 and 122 °C. The sharp endotherm at 110 °C and the broad endotherm around 122 °C are ascribed to the melting of OPV and PLLA segments respectively. The temperature corresponding to the melting transition of PLLA-OPV-\(x\) copolyesters decreased with increasing mol % incorporation of OPV chromophore into the PLLA backbone. This trend is well understood in literature also i.e higher incorporation of rigid units resulted in reduction in the melting point of PLLA copolyester.\textsuperscript{31}

![Figure 3.3](image)

**Figure 3.3.** (a) TGA thermograms of polymers and (b) the second heating DSC thermograms of PLLA, OPV-2-Diol, PLLA-OPV-0.5, PLLA-OPV-1 and PLLA-OPV-4 at the heating rate of 10 °C/min.

### 3.3.4. Wide-angle X-ray Diffraction (WXRD)

The polyesters were analyzed for their bulk packing using wide-angle X-ray diffraction (WXRD) in the range of \(2\theta = 5-35^\circ\) at room temperature (25 °C). Figure 3.4 compares the WXRD patterns of PLLA-OPV-\(x\) copolyesters along with that of PLLA. The
diffraction peaks at $\theta = 12.5^\circ$, $15.0^\circ$, $16.9^\circ$, $19.1^\circ$ and $22.6^\circ$ were assigned to the (103), (010), (200 or 110), (203) and (015) diffractions of the $\alpha$-form crystal of PLLA respectively according to the literature report.\(^{38}\) The peak around $\theta = 24.1$ (3.69 Å), (circled in figure 3.4) visible only for the highest OPV incorporated copolymesters (PLLA-OPV-2, PLLA-OPV-3 and PLLA-OPV-4) was attributable to the average $\pi$-$\pi$ stacking distance of the OPV aromatic core.\(^{39}\) This result was in agreement with the observation of melting transition at 110 $^\circ$C corresponding to the melting of OPV chromophore in the DSC curve of the highest OPV incorporated PLLA-OPV-x copolyester (PLLA-OPV-4). Such an evidence for crystallinity and $\pi$-$\pi$ stacking of the OPV units in a main chain polymer scaffold is very rare in literature. The PLLA segment could be expected to play a role in helping the OPV units to align properly resulting in improved $\pi$-$\pi$ stacking.

![WXRD patterns of polymers in powder form at room temperature.](image)

**Figure 3.4.** WXRD patterns of polymers in powder form at room temperature.

### 3.3.5. Photophysical Properties

The optical properties of the polymers were investigated by UV-Vis and fluorescence spectroscopy in both solution and solid state, which are summarised in table 3.2. Figure 3.5 (a) and (b) shows the normalized absorption spectra of PLLA-OPV-x copolymesters in chloroform solution and in powder state respectively. The copolymesters exhibited $\lambda_{\text{max}} \sim 390$ nm in chloroform solution indicating that all polymers were molecularly dissolved. Similar optical characteristics have been reported for other molecularly dissolved OPVs.\(^{26}\) The absorption spectra in the solid state was broad and the absorption maxima was red shifted from 390 to $\sim 430$ nm, which was an indication of the strong aggregation of OPV
chromophore.\textsuperscript{35} This was in accordance with the OPV aromatic core $\pi-\pi$ stacking observed in WXRD.

\textbf{Table 3.2. Absorption and emission data of polymers in solution and solid state (powder form) along with fluorescence quantum yields $\Phi_{FL}$ in solution.}

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Absorption $\lambda_{\text{max}}$ (nm) (In CHCl$_3$)</th>
<th>Emission $\lambda_{\text{max}}$ (nm) (In CHCl$_3$)</th>
<th>Absorption $\lambda_{\text{max}}$ (nm) (In powder)</th>
<th>Emission $\lambda_{\text{max}}$ (nm) (In powder)</th>
<th>$\Phi_{FL}$ (In solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA-OPV-0.5</td>
<td>390</td>
<td>445</td>
<td>431</td>
<td>476</td>
<td>0.62</td>
</tr>
<tr>
<td>PLLA-OPV-1</td>
<td>391</td>
<td>445</td>
<td>434</td>
<td>485</td>
<td>0.58</td>
</tr>
<tr>
<td>PLLA-OPV-2</td>
<td>388</td>
<td>445</td>
<td>432</td>
<td>489</td>
<td>0.57</td>
</tr>
<tr>
<td>PLLA-OPV-3</td>
<td>388</td>
<td>445</td>
<td>434</td>
<td>490</td>
<td>0.54</td>
</tr>
<tr>
<td>PLLA-OPV-4</td>
<td>387</td>
<td>445</td>
<td>431</td>
<td>494</td>
<td>0.41</td>
</tr>
</tbody>
</table>

a. Excitation at 390 nm.
b. The fluorescence quantum yield for polymers in CHCl$_3$ was obtained upon excitation at 360 nm and was measured using quinine sulphate in 0.1 M H$_2$SO$_4$ solution as standard.

Figure 3.5 (c) and (d) shows the emission spectra of PLLA-OPV-x copolyesters in solution and solid state respectively. All polymers emitted strongly with emission maximum at 445 nm with a shoulder peak at 470 nm in chloroform solution.\textsuperscript{26} These PLLA-OPV copolyesters were highly fluorescent with quantum yields of 0.62, 0.58, 0.57, 0.54 and 0.41 for PLLA-OPV-0.5, PLLA-OPV-1, PLLA-OPV-2, PLLA-OPV-3 and PLLA-OPV-4 respectively in chloroform solution (see table 3.2). The quantum yield decreased with increasing incorporation of OPV suggesting aggregation induced self quenching. In the solid (powder) state, the OPV monomer emission at 445 nm was suppressed and a red shifted intense aggregate emission was observed. The copolyesters PLLA-OPV-0.5, PLLA-OPV-1, PLLA-OPV-2, PLLA-OPV-3 and PLLA-OPV-4 showed emission maximum at 476, 485, 489, 490 and 494 respectively. The strong $\pi-\pi$ stacking of the OPV aromatic units in the solid state was responsible for the strongly red shifted emission.\textsuperscript{35}
Figure 3.5. Normalized absorption spectra of copolyesters (a) in the solution (chloroform) and (b) in the powder form; emission spectra of polymers (c) in the solution (chloroform) [0.1 OD at 390 nm, $\lambda_{ex} = 390$ nm] and (d) in the powder form [$\lambda_{ex} = 390$ nm].

Figure 3.6. Fluorescence lifetime-decay profiles of polymers in (a) chloroform at room temperature (0.1 OD at 390 nm, $\lambda_{ex} = 390$ nm, monitored at 445 nm) and (b) solid state ($\lambda_{ex} = 390$ nm, monitored at emission maxima) at room temperature.

The aggregation of OPV chromophore in the solid state was further supported by fluorescence lifetime-decay studies. The fluorescence lifetime-decay profiles of all the polymers in chloroform solution are given in figure 3.6 (a). The fluorescence lifetime-decay profiles of PLLA-OPV-x copolyesters ($\lambda_{ex} = 390$ nm) in chloroform exhibited mono-
exponential decay with lifetime of 1.29 ns when monitored at 445 nm (see table 3.3). The fluorescence lifetime-decay profiles of all the polymers in powder state are given in figure 3.6 (b). In the solid state, the fluorescence lifetime-decay profile of PLLA-OPV-0.5 (λex = 390 nm) also could be fitted to a mono-exponential decay with lifetime of 1.33 ns when monitored at 476 nm. This suggested the existence of a single luminescent species. On the other hand, all the other copolyesters (PLLA-OPV-1, PLLA-OPV-2, PLLA-OPV-3 and PLLA-OPV-4) exhibited biexponential decay confirming the existence of two types of luminescent species corresponding to the aggregated and isolated chains. The dominant fluorescence lifetime in the solid state decreased with increasing mol % incorporation of OPV chromophore in the copolyesters (see table 3.3). The fluorescence lifetime-decay measurements confirmed the presence of strong aggregation in solid state and also the enhancement of aggregation with increase in OPV content in the random copolyester.

Table 3.3. Fluorescence lifetime-decay data of polymers in solution as well as in powder state using nanoLED 390 nm for excitation.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>In chloroform</th>
<th>In powder state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>τ (ns)</td>
<td>χ²</td>
</tr>
<tr>
<td>PLLA-OPV-0.5</td>
<td>1.29</td>
<td>1.24</td>
</tr>
<tr>
<td>PLLA-OPV-1</td>
<td>1.29</td>
<td>1.20</td>
</tr>
<tr>
<td>PLLA-OPV-2</td>
<td>1.29</td>
<td>1.24</td>
</tr>
<tr>
<td>PLLA-OPV-3</td>
<td>1.29</td>
<td>1.07</td>
</tr>
<tr>
<td>PLLA-OPV-4</td>
<td>1.29</td>
<td>1.05</td>
</tr>
</tbody>
</table>

a. Parameters (τ: decay time and χ²: chi-squared value) retrieved from the mono-exponential fit for polyesters in chloroform solution (0.1 OD at 390 nm). The decay was collected at 445 nm.
b. Parameters (τ: decay time, α: pre-exponential factor and χ²: chi-squared value) retrieved from the biexponential fit for polyesters in powder state. The decay was collected at the emission maxima of polymers.
3.3.6. Helical Self-assembly of Copolyesters

Circular dichroism (CD) spectra of the polymers were recorded in both solution (chloroform) and solid state (powder form) to gain more insight into the self-assembly of OPV chromophore. It is reported that PLLA is a depsipeptide analogue of polyalanine which has a helical structure that resembles a polyproline II helix.$^{32}$ The n→\(\pi^*\) interactions directs the folding of PLLA chain into a helical conformation. In an n→\(\pi^*\) interaction, the filled \(p\)-type lone pair of carbonyl oxygen overlaps with the empty \(\pi^*\) antibonding orbital of a nearby carbonyl group. This overlap allows for orbital mixing and the subsequent release of energy contributes to the conformational stability of the PLLA helix.$^{32}$ PLLA exhibited a strong, positive CD band with a maximum at 231 nm corresponding to the ester n→\(\pi^*\) transition in chloroform solution [figure 3.7 (a)]. The large positive cotton effect exhibited by PLLA has been correlated with the helical conformation of PLLA chain in chloroform solution.$^{40}$ No CD signal was observed for all other copolyesters (PLLA-OPV-X) in chloroform solution where the polymers were molecularly dissolved.$^{30}$

![CD spectra of copolyesters](image)

**Figure 3.7.** (a) CD spectra of copolyesters in solution state (2 mg/mL) recorded in chloroform at 25 °C; (b) CD spectra of copolyesters and (c) normalized (at 213 nm) CD spectra of PLLA-OPV-2 and PLLA-OPV-3 in solid state recorded at 25 °C.
In the solid state (powder), all the polymers showed a positive CD band with a maximum at 213 nm corresponding to the ester $\pi-\pi^*$ transition [Figure 3.7 (b)]. Interestingly, one more sharp exciton-coupled bisignated CD signal with a first positive cotton effect with a maximum at 441 nm and a second negative cotton effect with maximum at 370 nm, through a zero crossing close to the absorption maximum (421 nm) of OPV chromophore was observed for PLLA-OPV-3 corresponding to the $\pi-\pi^*$ transition indicating the right-handed helical self-assembly of achiral OPV segments [figure 3.7 (c)].23,41-45 The chirality information of the PLLA segment was transferred to the self-assembled OPV chromophore as evidenced by the exciton-coupled CD signal corresponding to the absorption maximum of the OPV chromophore. These results confirmed the effect of chiral PLLA segment on tuning the OPV chromophore packing and supramolecular chirality in molecular aggregates. The right-handed self-assembly of OPV segment by the chiral PLLA segment was further confirmed by the morphology of PLLA-OPV-3 observed by SEM and AFM analysis. PLLA-OPV-2 also showed weak exciton-coupled bisignated CD signal. No bisignated Cotton effect was observed in the case of PLLA-OPV-0.5 and PLLA-OPV-1 because of the low mol % incorporation of OPV chromophore in the PLLA backbone. In the case of PLLA-OPV-4, the chain length of PLLA segment may not be sufficient enough to induce helical arrangement to OPV chromophore because of chopping of PLLA backbone to incorporate more OPV chromophore.

![Figure 3.8. Scanning electron microscope images of the solution-precipitated aggregate of PLLA-OPV-3 in different magnifications.](image)

The morphology of the solution-precipitated aggregates of PLLA-OPV-3 was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The solution-precipitated aggregate was prepared by injecting 1 mL of the polymer solution (1 mg/mL) in dichloromethane (DCM) into 10 mL of methanol. The resulting mixture was aged
at room temperature for overnight and the suspension of the aggregate was transferred to silicon wafer by a dropper. After the solvent was evaporated at room temperature, the sample was examined for its morphology. The SEM images of PLLA-OPV-3 (figure 3.8) showed the formation of self-assembled bundles of twisted ‘leaf-like’ structures. The AFM height image of PLLA-OPV-3 (figure 3.9) showed right-handed helical structure, in agreement with the observed CD spectrum.

![AFM Height Image of PLLA-OPV-3](image)

**Figure 3.9.** Tapping mode AFM height images of the solution-precipitated aggregate of PLLA-OPV-3 under different magnifications. The corresponding height section analysis is also shown.

### 3.3.7. Microscopic Characterization of Electrospun Nanofibers

Electrospinning is a very versatile technique for making 1D elongated structure. Figure 3.10 shows the scanning electron microscopy (SEM) and fluorescence microscopy images of the electrospun fibres of PLLA-OPV-0.5. SEM images revealed the presence of nanofibers of 150-500 nm diameters. Fluorescence microscopy images of this polymer showed strong blue and green emission upon excitation at 350-430 nm (blue filter) and 488-520 nm (green filter) respectively.
Figure 3.10. (a) SEM; (b) and (c) fluorescent microscopy image of PLLA-OPV-0.5 with excitation at wavelength of 350-430 nm and 488-520 nm respectively.

3.4. Conclusion

A novel series of copolyesters incorporating varying mol ratios of an achiral oligo(p-phenylene vinylene) (OPV) into the backbone of a chiral poly(l-lactic acid) (PLLA) was synthesized by high-temperature solution-blending of PLLA with hydroxyl group functionalized OPV molecule (OPV-2-Diol). This approach is extendable to a variety of chromophores after suitable end functionalization for transesterification. The chemical incorporation of OPV chromophore into the polyester backbone was proved by $^1$H NMR spectroscopy. The differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WXRD), absorption, emission and lifetime-decay studies showed that OPV chromophore was aggregated in the solid state. The right-handed helical self-assembly of the achiral OPV segments driven by the chiral PLLA segments in the solid state was proved by CD investigation and AFM analysis. The chemistry described here is applicable as a general method to create helical self-assemblies of a variety of π-conjugated system, which have applications in organic electronic devices. Blue and green fluorescent nanofibers of random copolyester incorporating OPV were successfully constructed by electrospinning technique.
3.5. References


43) Mason, S. F.; *Molecular Optical Activity and the Chiral Discrimination*; University Press, 1982.
