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Random Copolyesters Containing Perylene Bisimide: Flexible Films and Fluorescent Fibers

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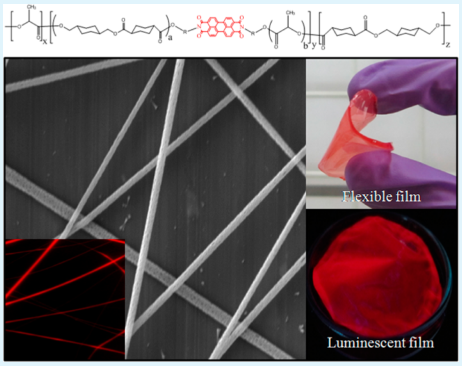
Supporting Information



ABSTRACT: Random copolyesters of poly(L-lactic acid) (**PLLA**) and [poly(1,4-cyclohexylenedimethylene-1,4- cyclohexanedicarboxylate)] (**PCCD**) incorporating varying mol ratios of perylene bisimide (PBI) were developed via a high-temperature solution-blending approach. **PCCD** incorporating PBI was developed by melt polycondenzation followed by a polyester-polyester transesterification reaction between **PCCD**−PBI and **PLLA**. The polymers exhibited good solubility in common organic solvents and formed free-standing films, which showed bright red emission upon irradiation with ultraviolet radiation. A solid state fluorescence quantum yield of 10% was observed for this PBI based polyester, which was much higher than that reported in literature for PBI based polymers in the solid state (<1%). Strong red fluorescent nanofibers of these polymers were successfully constructed by electrospinning technique. A random copolyester incorporating donor based on oligo(*p*-pheneylenevinylene) (OPV) and PBI as acceptor chromophore was also synthesized and fluorescence microscopy images of the electrospun fibers of this polymer exhibited blue, green and red emission upon excitation at different wavelengths. The high temperature solution blending approach involving a high molecular weight polymer and a suitably functionalized π conjugated molecule described here is a unique method by which 1D nanostructures of a wide range of π-conjugated chromophores could be fabricated having strong fluorescence, with the scope of application in nanoscale optoelectronics, biological devices, as well as sensing.

KEYWORDS: *fluorescent nanofibers, perylene bisimide, oligo(p-phenylenevinylene), flexible film, luminescent film*

■ INTRODUCTION

Semiconductor material based nanowires and nanofibers are considered to be extremely useful for miniaturized device applications and also in optoelectronics.[1−5] Traditionally inorganic materials have been the most preferred for such applications, while the organic semiconductors have not found widespread acceptance. Organic and polymeric semiconducting materials have wide structural tunability to suit optoelectronic property requirements and also involve low fabrication costs.[4,6] However, fabricating organic 1D nanostructures have proved to be quite challenging due to various constraints like a lack of proper structure−property understanding, unavailability of easy and scalable routes to produce the 1D nanomaterial over large length scale, etc. Most of the miniaturized device applications involving 1D nanomaterials demands solid state fluorescence as a property requirement.[7,8] This is quite challenging as far as organic π-conjugated systems are concerned due to their tendency to undergo aggregation in the solid state leading to considerable quenching of fluorescence.[6,9] One successful approach of achieving solid state emission from π-conjugated molecules was recently reported from our research group where we developed cross-linked fluorescent polystyrene (PS) microbeads based on fluorophores as cross-linkers.[10] In addition to providing mechanical stability to the polymer, the strategy of incorporating fluorophore as cross-linker had the added advantage of almost complete absence of aggregation induced quenching of fluorescence resulting in intense solid state emission from the polymer beads.

Perylene bisimides (PBI) belong to a class of n-type chromophores exhibiting relatively high electron mobility, large molar absorption coefficients, fluorescence quantum yield, as well as good thermal and photochemical stabilities.[11−15] Well-defined nanowires have recently been fabricated from various symmetric and asymmetric PBIs, none of which demonstrated sufficient fluorescence emission.[16−18] Würthner and co-workers reported highly fluorescent perylene bisimide based gelator with substituents at the bay positions; however they were observed to form less regular structures, probably due to the twisted conformation of the backbone.[19] Recently, Nagarajan and co-workers successfully prepared *N*,*N*′-bis(1-dodecyl)perylene-3,4,9,10-tetracarboxylic diimide (D-PTCDI), which was made to self-assemble into nanofibers by a solution

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Table 1. Polymer Designation, Feed Ratio, Actual Incorporation of Chromophores Determined from Absorption Spectra, Molecular Weight (M_w), Polydispersity Index, Viscosity Data (η_{inh}), 10% Weight Loss Temperature (T_D), and Yield of Polymers

polymer	feed ratio (**PLLA: PCCD−PBI-10**/OPV-2-diol) (wt %)	mol % of PBI/OPV incorporation from UV[a]	M_w (g/mol)[b]	poly dispersity index ($Đ_M$)	η_{inh} (dL/g)[c]	T_D (°C)[d]	yield (%)
PLLA			100600	1.8	1.01	268	95
PCCD−PBI-10		3.42	23700	1.9	0.30	420	76
PLLA−PCCD-PBI-10	90:10	0.33	99100	1.7	0.90	299	98
PLLA−PCCD-PBI-30	70:30	1.02	79400	1.9	0.75	300	98
PLLA−PCCD-PBI-50	50:50	1.69	56600	1.7	0.68	296	98
PLLA−PCCD-PBI-70	30:70	2.92	35700	2.2	0.37	307	98
PLLA−PCCD-PBI-90	10:90	3.29	18400	2.2	0.22	307	98
PLLA−PCCD-PBI-10-OPV-5	85:10:5	0.32 (PBI) 0.67 (OPV)	79200	2.0	0.74	252	96

[a] Measured in chloroform solution. [b] Measured by size exclusion chromatography (SEC) in chloroform ($CHCl_3$), calibrated with linear, narrow molecular weight distribution polystyrene as standards. [c] Determined in chloroform for 0.5 wt % solutions. [d] 10% weight loss temperature determined by TGA.

based phase-transfer method.[20] The fibers exhibited intense red fluorescence as observed by fluorescence microscope imaging; however, the solid state quantum yield was not reported.

Recently we reported the chemical incorporation of PBI in the backbone of an insulating engineering thermoplastic polymer like [poly(1,4-cyclohexylenedimethylene-1,4-cyclohexanedicarboxylate)] (**PCCD**) by melt polycondensation.[21] However, the copolyester showed low mechanical stability because of its low molecular weight. On the other hand, poly(L-lactic acid) (**PLLA**), which is a renewable resource based thermoplastic aliphatic polyester, has similar mechanical properties as PET (polyethylene terephthalate) and it can be processed like most thermoplastics into fiber and film.[22] We were successful in incorporating p-type π-conjugated chromophores based on oligo(*p*-phenylenevinylene) (OPV) into the backbone of chiral **PLLA** via high temperature solution blending.[23] The chirality of the **PLLA** segments could be translated to the achiral OPV segments resulting in right-handed helical self-assembly of OPV chromophore in the solid state. The **PLLA-OPV** polyesters exhibited intense red-shifted OPV aggregate emission in the powder form. Inspired by the self-assembly and solid state emission properties of the OPV based **PLLA** polyesters, we attempted incorporation of suitably functionalized PBI chromophores into PLLA backbone. However, poor solubility of the functionalized PBI in **PLLA** made this approach not feasible. Herein we report the synthesis of a strongly fluorescent PBI based polymer, which could be easily fabricated into well-defined nanofibers over a large length scale. The aim of the work is to provide new insight into molecular design and material fabrication so as to make them desirable for nanoscale device applications. High molecular weight random copolyesters of **PLLA** and **PCCD** incorporating varying amounts of PBI chromophore could be successfully synthesized by a facile polyester/polyester high-temperature solution-blending method.[24] The ester-exchange reaction in this polyester/polyester reactive blending was confirmed using size exclusion chromatography (SEC), ^{1}H NMR spectroscopy and differential scanning calorimetry (DSC). The mol % incorporation of PBI chomophore in these copolyesters was calculated by using Beer−Lamberts Law.[25] The polymers formed transparent and flexible films with high luminescent efficiencies. Nanofibers of these polymers were successfully constructed using electrospinning technique.[26−28] Nanofibers of copolyester incorporating both OPV and PBI chromophores were also fabricated by electrospinning and fluorescence microscopy images showed blue, green and red emission from the nanofibers just by exciting at appropriate wavelength. The simple and versatile approach described here is easily adoptable for a wide range of π-conjugated chromophores, whether n-type or p-type, to achieve the goal of easy fabrication of fluorescent 1D nanostructure which may find application in future nanoelectronic devices that require high solid state light emission.[29] These copolyesters could also serve as polymeric model systems for understanding one-dimensional charge transport with well-defined charge percolation pathways in π-conjugated materials.

EXPERIMENTAL SECTION

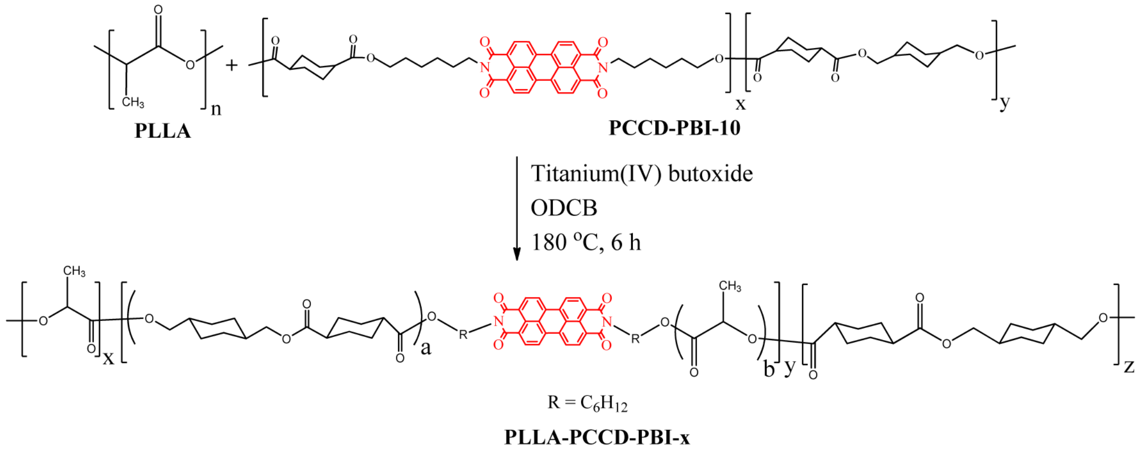
Materials. The starting materials required for the synthesis of the perylene bisimide derivative PBI-6-Diol like perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), 6-aminohexan-1-ol, and zinc acetate were purchased from Aldrich. 1,4-Cyclohexanedimethanol (CHDM) (cis + trans), 1,4-dimethylcyclohexane dicarboxylate (DMCD) (cis + trans), titanium(IV) butoxide [$Ti(OBu)_4$], and 1,2-dichlorobenzene (ODCB) were used for the synthesis of PCCD polymers. (3*S*)-*cis*-3,6-Dimethyl-1,4-dioxane-2,5-dione (L-lactide) and tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) were used for the synthesis of PLLA polymers. All these starting materials were purchased from Aldrich and used without further purifications.

Instruments. The structural characterization of the π-conjugated diols and polymers were carried out using characterization tools like ^{1}H NMR spectroscopy, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimeter (DSC), wide-angle X-ray diffraction (WXRD), and scanning electron microscopy (SEM) as described in detail in our earlier report.[23] The details of the instrumentation for measuring the absorption, emission, as well as lifetime decay profiles were also reported earlier. The solid state quantum yield was measured using a model F-3029, Quanta-Phi 6″ Integrating Sphere connected with Horiba Jobin Yvon Fluorolog 3 spectrophotometer. The electrospinning apparatus consisted of a syringe pump, syringe needle, high voltage power supply, and a grounded collector.[30] 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. 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 filter), 488−520 (green filter) and 500−550 nm (red filter)].

The synthesis of PBI-6-diol,[21] OPV-2-Diol,[31] **PCCD−PBI-10** polymer,[21] **PLLA**,[23] and **PLLA-OPV-5**[23] polymer have already been reported. The details of synthesis of the **PCCD−PBI**-x polymers are given in the Supporting Information.

Synthesis of Random Copolyesters of PLLA and PCCD Incorporating PBI Chromophore (PLLA−PCCD-PBI-50) Using

Scheme 1. Synthesis of Copolyesters of PLLA and PCCD Incorporating PBI Chromophore (PLLA−PCCD-PBI-x) by the high-Temperature Solution-Blending of PLLA with PCCD−PBI-10



High-Temperature Solution-Blending Method. A total of 0.5 g of **PLLA** (50 wt %) and 0.5 g of **PCCD−PBI-10** (50 wt %) was dissolved in 0.5 mL of ODCB in a tubular glass reactor and heated at 180 °C with constant stirring (100 rpm) using an overhead mechanical stirrer. A total of 2.9 mg of $Ti(OBu)_4$ (0.1 mol % solution in ODCB) was added as the catalyst to the above mixture and heating was continued at 180 °C for 6 h with stirring. The reaction mixture was cooled to room temperature and the contents dissolved in chloroform. The polymer was then precipitated into methanol. The filtered polymer was dried in oven at 60 °C. Yield: 98.0%; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.61−8.66 (perylene **H**), 5.17 ($-CH(CH_3)-COO-$ from **PLLA** unit), 3.87−4.19 ($-CH_2-CH_2-O-CO-$, imide $-CH_2-$, cis and trans $-CH_2-$ in **PCCD**), 3.66 ($-CO-O-CH_3$ end group), 3.43 and 3.53 ($-CH_2-OH$ end group), 2.26 and 2.45 (cis and trans $-CH-CO-$ in **PCCD** part), 0.99−2.02 ($-CH_3$ in **PLLA** part, cyclic−**H** in **PCCD** and $-CH_2-$ in PBI part).

A similar procedure was employed to synthesize the **PLLA−PCCD-PBI-x** series of polyesters by varying the wt % of **PCCD−PBI-10** in the feed from 10 to 90 wt %. The yield of the polymers is reported in Table 1.

Synthesis of Random Copolyester of PLLA and PCCD Incorporating Both PBI and OPV Chromophores (PLLA−PCCD-PBI-10-OPV-5) through High-Temperature Solution-Blending Method. A total of 0.85 g of **PLLA** (85 wt %), 0.1 g of **PCCD−PBI-10** (10 wt %), and 0.05 g of OPV-2-Diol (5 wt %) were dissolved in 0.5 mL of ODCB in a tubular glass reactor and heated at 180 °C with constant stirring (100 rpm) using an overhead mechanical stirrer. A total of 4.1 mg of $Ti(OBu)_4$ (0.1 mol %) solution in ODCB was added to this mixture and heating was continued with stirring for 6 h at 180 °C. The reaction mixture was cooled to room temperature and the contents dissolved in chloroform. The polymer was then precipitated into methanol. The filtered polymer was dried in oven at 60 °C. Yield: 96%.

Construction of Nanofibers. 100 mg of polymer was dissolved in 1 mL of dichloromethane (DCM) to make a 10 wt % solution. This solution was subjected to a high electric field of 10 kV for electrospinning using a set up described elsewhere.[30] 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.

■ RESULTS AND DISCUSSION

Synthesis and Structural Characterization of Polymers. Hydroxyl group functionalized perylene bisimide derivative (PBI-6-Diol) was synthesized as reported previously.[21] The melt polycondensation of 1,4-cyclohexanedimethanol (CHDM) and 1,4-dimethylcyclohexane dicarboxylate (DMCD) with varying mol % of PBI-6-Diol (Scheme S1) to obtain **PCCD−PBI-x**, (x represented the mol % of PBI-6-Diol taken in the feed, was carried out as reported earlier.[21] The mol percentage of the monomer DMCD was kept fixed at 100% and that of PBI-6-Diol: CHDM was varied from 5:95 to 30:70. The actual mole % incorporation of PBI chromophore was calculated from absorption spectra by using the molar extinction coefficient of symmetrical N, N′-bis(2-ethylhexyl)-perylene-3,4,9,10-tetracarboxylic diimide as 83006 L M^{-1} cm^{-1} and the details are given in Table S1. Figure S1 shows the size exclusion chromatogram of the polymers while the complete characterization details including the molecular weight, inherent viscosity, as well as 10% weight loss temperature obtained from thermogravimetric analysis (TGA) is given in Table S1. It could be seen that the molecular weight and inherent viscosity of the polymers decreased with increasing mol % incorporation of PBI in the copolyester. The increased incorporation of rigid units in the polymer backbone is known to result in lower molecular weights.[21] None of these polymers formed free-standing film due to their low mechanical stability. **PCCD−PBI-10**, which had reasonably high molecular weight with high PBI incorporation was selected from the polymer series and subjected to high-temperature solution-blending with high molecular weight **PLLA**. High molecular weight **PLLA** was synthesized as described in literature.[23,32]

Random copolyesters of **PLLA** and **PCCD** incorporating varying amounts of PBI was synthesized by the high-temperature solution-blending of **PLLA** with varying amounts of **PCCD−PBI-10** under conditions described previously as shown in Scheme 1.[31] The transesterification reaction was continued for 6 h, after which the polymer was dissolved in chloroform and precipitated into methanol. The polymers were named as **PLLA−PCCD-PBI-x,** to indicate that they were random copolyesters of **PLLA** and **PCCD** with x amount of PBI incorporated where x represented the weight % of **PCCD−PBI-10** taken in the feed. The mol % incorporation of PBI in the polymers was estimated from the absorption spectra in chloroform and the values are given in Table 1.

The scrambling of the **PLLA** and **PCCD** backbones was confirmed by the ^{1}H NMR spectroscopy. Figure S2 compares the labeled ^{1}H NMR spectra of **PLLA, PCCD−PBI-10** and **PLLA−PCCD-PBI-50.** The ^{1}H NMR spectrum of **PLLA** showed two signals at 5.16 and 1.56 ppm assigned to **CH** and CH_3 protons (labeled as “a” and “b”) [Figure S2 (a)]. The ^{1}H NMR spectrum of **PCCD−PBI-10** showed a peak at 8.53 ppm corresponding to PBI aromatic protons (labeled as “c”) and peaks at 2.43 and 2.24 ppm corresponding to the cis and trans proton in −CHCO− attached to DMCD (labeled as “d”) from **PCCD** part [Figure S2 (b)]. The ^{1}H NMR spectrum of **PLLA−PCCD-PBI-50** [Figure S2 (c)] showed peaks corresponding to all three repeat units; namely, PBI aromatic protons (labeled as “c”), protons of **PLLA** (labeled as “a”), and protons of **PCCD** (labeled as “d”). The encircled peak around 3.43 and 3.53 ppm corresponded to the methylene proton of the CH_2OH end group, while another singlet at 3.66 ppm (asterisk) corresponded to the methyl ester (−COO−CH_3) end group from the DMCD component.[21] The observation of these end groups were characteristic of the melt condensation route of polymerization adopted for synthesizing the **PCCD−PBI-x** polymers.

A hydroxyl functionalized OPV derivative (OPV-2-Diol) was synthesized as reported in the literature.[31,33] One random copolyester incorporating both PBI and OPV was synthesized by the high-temperature solution-blending of **PLLA** (85 wt %) with **PCCD−PBI-10** (10 wt %) and OPV-2-Diol (5 wt %) as shown in Scheme S2. The mol % incorporation of OPV and PBI units in the donor−acceptor random copolyester was calculated as 0.7 and 0.3 mol % respectively, using the molar extinction coefficient of symmetrical *N*,*N*′-bis(2-ethylhexyl)-perylene-3,4,9,10-tetracarboxylic diimide as 83006 L M^{-1} cm^{-1} and that of OPV-2-Diol as 32059 L M^{-1} cm^{-1} in chloroform. For comparative studies, a random copolyester of **PLLA** incorporating 0.7 mol % of OPV was also synthesized using 5 wt % of OPV-2-Diol as reported previously (Scheme S3).[23]

Table 1 gives the molecular weight details of all the PLLA polymers determined by size exclusion chromatography (SEC) in $CHCl_3$ using polystyrene standards (SEC plots given in Figure S3) along with the inherent viscosity also measured in chloroform.[23] The M_w of **PLLA** was 100 600[23] and that of **PCCD−PBI-10** was 23 700. The M_w of **PLLA−PCCD-PBI-10**, **PLLA−PCCD-PBI-30**, **PLLA−PCCD-PBI-50**, **PLLA−PCCD-PBI-70**, and **PLLA−PCCD-PBI-90** were 99 100, 79 400, 56 600, 35 700, and 18 400, respectively. The molecular weight as well as inherent viscosities of the **PLLA−PCCD-PBI-x** series of polymers decreased with increasing weight % of **PCCD−PBI-10** in the feed. This indicated chopping of the polymer chains to incorporate **PCCD** and PBI chromophore during the transesterification reaction with PLLA.[34] The M_w of **PLLA−PCCD-PBI-10-OPV-5** was determined as 79 200.

Thermal and X-ray Diffraction Properties of Polymers. The 10% weight loss temperature of the polymers are summarized in Table 1, with the Figure S4 showing the corresponding TGA thermograms. The 10% weight loss temperature for **PLLA** was 268 °C, while that for the **PCCD−PBI-10** was higher at 420 °C. The 10% weight loss temperatures of **PLLA−PCCD-PBI-x** series of polymers were around 300 °C. TGA thermograms of **PLLA−PCCD-PBI-x** series of polymers showed stepwise degradation between 275 to 450 °C. These degradations originate from the scission of aliphatic and cyclic aliphatic polyester segments.[35] Figure 1 shows the stack plot of the second heating scans in the DSC thermograms of the polymers with the data for **PLLA**[23] and **PCCD−PBI-10** also included for comparison. The step transition at 63 °C was attributed to the glass transition temperature (T_g) of **PLLA** with a crystallization peak at 108 °C and a melting peak at 181 °C.[36] **PCCD−PBI-10** was characterized by only T_g around 46 °C as this was an amorphous polymer. All **PLLA−PCCD-PBI-x** series of polymers showed T_g, crystallization, and melting transition (Table 2). **PLLA−PCCD-PBI-10-OPV-5** showed glass transition (T_g) at 53 °C, crystallization peak at 98 °C, and melting at 168 °C. A single T_g was observed for **PLLA−PCCD-PBI-x** series of polymers and **PLLA−PCCD-PBI-10-OPV-5**, indicative of miscible blends formed by ester−ester exchange reaction.[34,37]

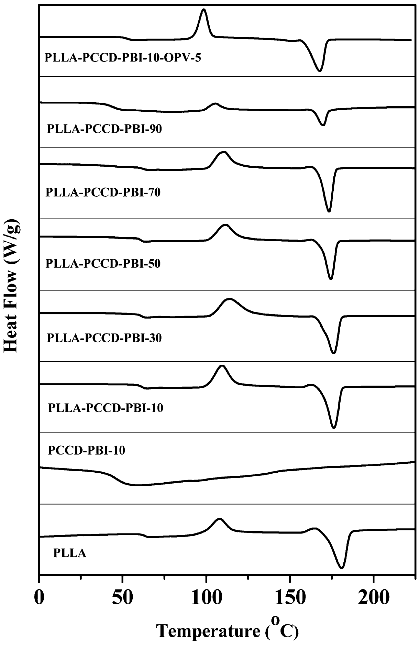


Figure 1. Second heating DSC thermograms of polymers at the heating rate of 10 °C/min.

Table 2. Glass Transition Temperature (T_g), Melting Temperature (T_m), Crystallization Temperature (T_c), and Crystallinity (%) of the Polymers

polymer	T_g (°C)[a]	T_m (°C)[a]	T_c (°C)[a]	crystallinity (%)[b]
PLLA	63	181	108	49
PCCD−PBI-10	46			
PLLA−PCCD-PBI-10	61	176	109	45
PLLA−PCCD-PBI-30	61	176	114	32
PLLA−PCCD-PBI-50	61	174	112	26
PLLA−PCCD-PBI-70	62	173	111	18
PLLA−PCCD-PBI-90	45	170	105	3
PLLA−PCCD-PBI-10-OPV-5	53	168	98	41

[a] Determined by DSC. [b] Calculated from 100% crystalline **PLLA** reported in literature.

The degree of crystallinity of **PLLA** and copolyesters were calculated using the equation:

$$\text{crystallinity}(\%) = (\Delta H_f/\Delta H_f^0) \times 100$$

where ΔH_f is the melting enthalpy and ΔH_f^0 = 93 J/g is the heat of fusion for 100% crystalline **PLLA** reported in literature.[36] The ΔH_f values were obtained from the melting curves of the second heating scans of the DSC. The calculated crystallinity (%) of the **PLLA** and **PLLA−PCCD-PBI-x** series of polymers were summarized in Table 2. Figure S5 compares the crystallinity (%) of **PLLA−PCCD-PBI-x** series of polymers as a function of increased weight % of **PCCD−PBI-10** in the feed. The crystallinity (%) of synthesized **PLLA** was calculated as 49% and it was observed that the crystallinity (%) decreased with increasing weight % of **PCCD−PBI-10** in feed.

Figure 2 shows the wide-angle X-ray diffraction (WXRD) data collected for the **PLLA−PCCD-PBI-x** series of polymers in the range of 2θ = 5−35° at room temperature (25 °C). The XRD patterns of the parent **PLLA** and **PCCD−PBI-10** polymers are also given in the figure for comparison. As reported in literature, **PLLA** exhibited the characteristic diffraction peaks at 2θ = 12.5°, 15.0°, 16.9°, 19.1°, and 22.6° which were assigned to the (103), (010), (200 or 110), (203), and (015) diffractions of the α-form crystal of **PLLA**, respectively.[23,38] The **PCCD−PBI-10** copolyester had a broad reflection in the region 2θ = 15−20° with sharp reflections at 2θ = 9.49° (9.31 Å), 12.41° (7.12 Å), and 24.94° (3.57 Å). The intensity of all the peaks corresponding to the α-form crystal of **PLLA** decreased with increasing weight % of **PCCD−PBI-10** in the **PLLA−PCCD-PBI-x** series of polymer, in conformation with observation from DSC.

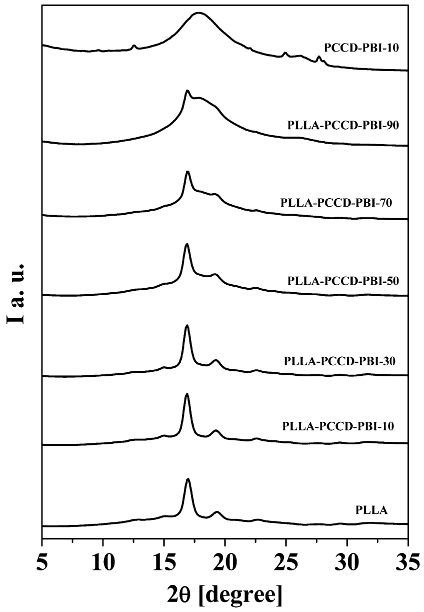


Figure 2. WXRD patterns of **PLLA**, **PCCD−PBI-10**, and **PLLA−PCCD-PBI-x** series of polymers in powder form at room temperature.

Thin Film Formation. The ability to form free-standing films signifies high mechanical stability in the polymers. The **PPCD−PBI-10** polymer could not form free-standing films and were brittle. On the other hand, upon formation of random copolyesters with **PLLA**, the **PLLA−PCCD-PBI-x** series of polymers with $x < 70$ could form free-standing films that were transparent and flexible. The polymers with higher PBI content namely, **PLLA−PCCD-PBI-70** and **PLLA−PCCD-PBI-90** formed nonpeelable brittle films. Figure 3 shows photograph of the free-standing films formed by the polymers from 0.5 wt % $CHCl_3$ solutions. The figure also shows strong red colored emission from the films under a hand-held UV lamp. PBIs are well-known for their aggregation tendency in the solid state which leads to quenching of their fluorescence.[16−18] Our current report of intense red emission from PBI incorporated polymer films is one of the few successful reports of solid state emission from PBI based polymers.

Microscopic Characterization. Electrospinning is a very versatile technique for making polymer based 1D elongated

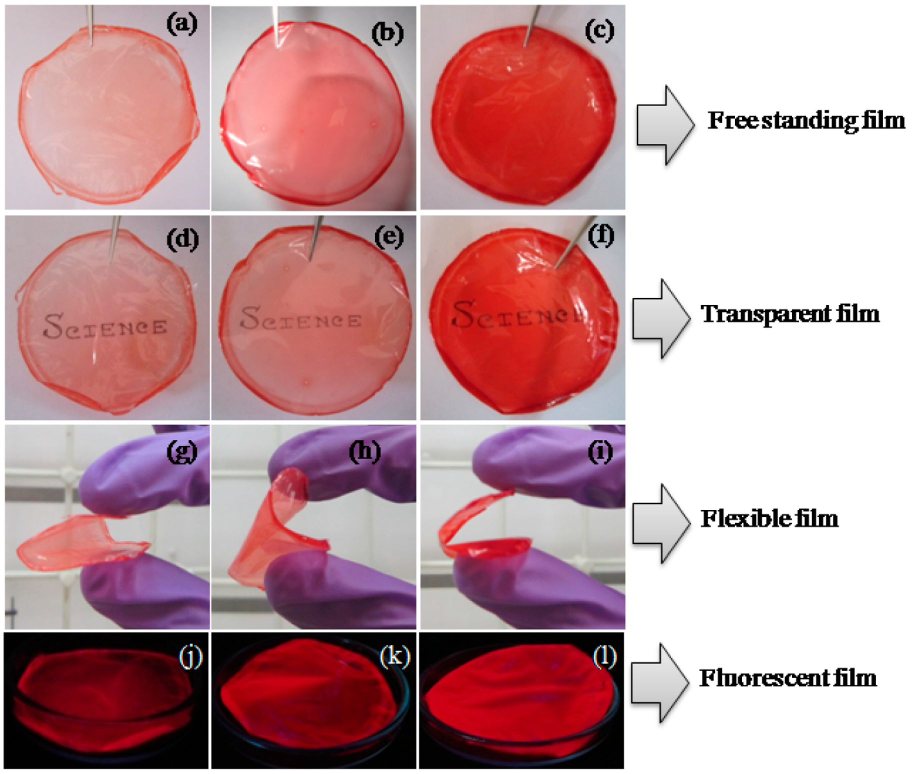


Figure 3. Photographs of the free-standing films of **PLLA−PCCD-PBI-10** (a, d, g), **PLLA−PCCD-PBI-30** (b, e, h), and **PLLA−PCCD-PBI-50** (c, f, i) drop casted from 0.5 wt % solution in chloroform. The respective films upon observation under UV lamp (365 nm) [(j) **PLLA−PCCD-PBI-10**, (k) **PLLA−PCCD-PBI-30**, and (l) **PLLA−PCCD-PBI-50**].

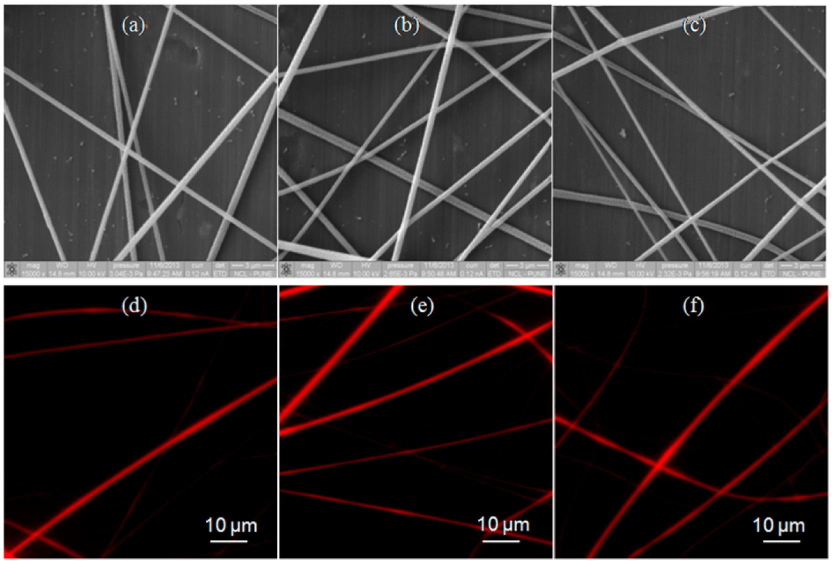


Figure 4. SEM images of the electrospun fibers of (a) **PLLA–PCCD-PBI-10**, (b) **PLLA–PCCD-PBI-30**, and (c) **PLLA–PCCD-PBI-50** (top) and (d–f) the respective fluorescence microscopy images (bottom) with excitation at wavelength of 500–550 nm.

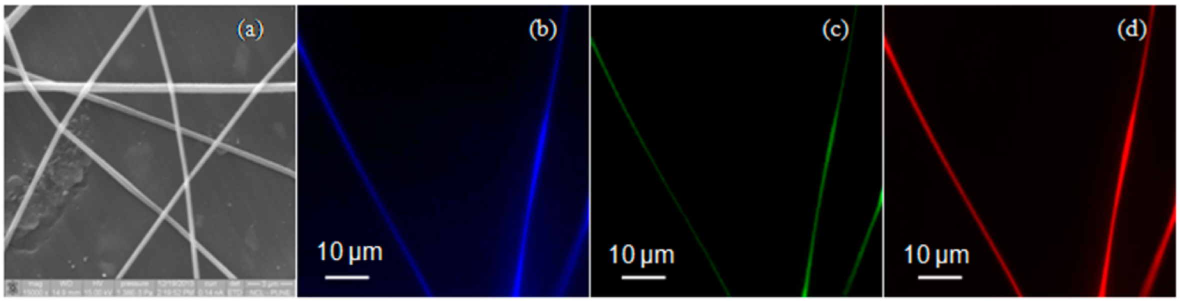


Figure 5. (a) SEM; (b, c, and d) fluorescent microscopy image of **PLLA–PCCD-PBI-10-OPV-5** with excitation at wavelength of 350–430, 488–520, and 500–550 nm, respectively.

structures.[26−28] Figure 4 shows the scanning electron microscopy (SEM) (top) and fluorescence microscopy images (bottom) of the electrospun fibers of **PLLA–PCCD-PBI-10**, **PLLA–PCCD-PBI-30**, and **PLLA–PCCD-PBI-50**. SEM images revealed the presence of nanofibers of 150–500 nm diameters. Fluorescence microscopy images of these nanofibers showed strong red emission upon excitation at wavelength of 500–550 nm. The formation of beaded fibers was observed from the SEM images of **PLLA–PCCD-PBI-70** and **PLLA–PCCD-PBI-90** due to the low viscosity of polymer solutions. Figure S6 shows the SEM and fluorescence microscopy images of the nanofibers fabricated from **PLLA-OPV-5** through electrospinning process. Fluorescence microscopy images of this nanofibers showed strong blue and green emission upon excitation at 350–430 nm (blue filter) and 488–520 nm (green filter) respectively. The nanofiber fabricated from **PLLA–PCCD-PBI-10-OPV-5** showed blue, green, and red emission with excitation at three different wavelengths (Figure 5). Thus, one could access three different emission regions from the nanofiber of **PLLA–PCCD-PBI-10-OPV-5** just by exciting at the appropriate wavelength.

Photophysical Properties. The absorption and emission characteristics of the random copolyesters were studied in solution from chloroform and in the solid state as thin films spin coated from chloroform. Figure 6 (a) and (b) shows the normalized absorption spectra of **PCCD–PBI-10** and **PLLA–**

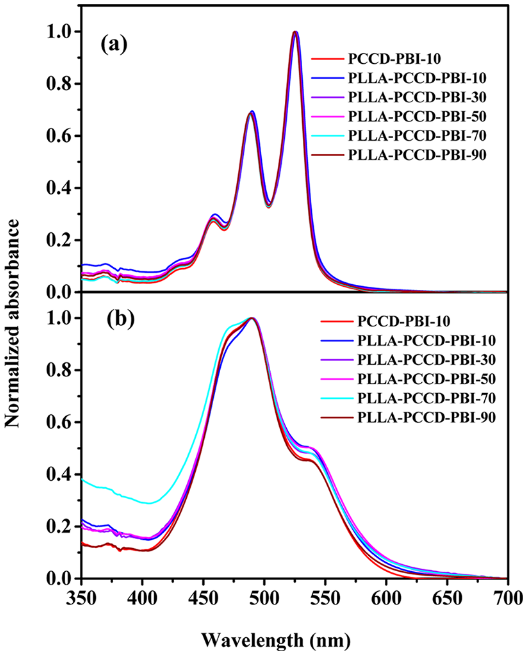


Figure 6. Normalized absorption spectra of polymers in (a) chloroform solution and (b) film spin-coated from chloroform solution.

PCCD-PBI-x series of polymers in solution and in film, respectively. The absorption spectra in solution were all identical and showed characteristic features of molecularly dissolved PBI with peaks in the range of 400−530 nm.[17] The absorption spectra in the solid state was broad with the peak onset red-shifted and the peak maxima blue-shifted by 35 nm ($\lambda_{max} \approx 490$ nm) compared to that in solution. The ratios of peak intensities were also different to that in solution. These were typical features of H type aggregates;[39,40] however, a new red-shifted band emerged at 538 nm. The appearance of the red-shifted peak along with a blue shift of the absorption wavelength maxima is indicative of H type aggregation with rotational offset.[11,29,41−43] Emission from the polymers were studied in solution and in film states by exciting at 490 nm, which is shown in Figure 7a,b respectively. In solution, typical emission of PBI with peaks at 534, 576, and 625 nm was observed for **PCCD−PBI-10** as well as **PLLA−PCCD-PBI-x** series of polymers, indicating absence of PBI aggregation in solution in all polymers, which was in confirmation with the observation from their absorption spectra. In the solid state a clear difference was observed in the behavior of PBI chromophore emission from **PCCD−PBI-10** and **PLLA−PCCD-PBI-x** series of polymers. In **PCCD−PBI-10**, monomeric perylene emission at 534 nm was completely absent; only red-shifted aggregate emission was observed at 638 nm. On the other hand, the emission spectra in the solid state for **PLLA−PCCD-PBI-x** series of polymers was conspicuous by the appearance of PBI monomeric emission at 530 and 570 nm, especially for **PLLA−PCCD-PBI-10**. The aggregate emission intensity at 638 nm also was higher for all the **PLLA−PCCD-PBI-x** series of polymers compared to **PCCD−PBI-10**. The emission intensity of **PLLA−PCCD-PBI-x** series of polymers decreased with increasing mol % incorporation of PBI chromophore, which could be attributed to aggregation-induced quenching.[17,44] The appearance of PBI monomeric emission peaks from film samples of **PLLA−PCCD-PBI-x** polymers indicated PBI chromophore site isolation due to segmentation by the blocks of **PLLA** units. This reduced self-aggregation resulted in the increased overall emission intensity in the **PLLA** series of polymers compared to the parent **PCCD−PBI** polymer.

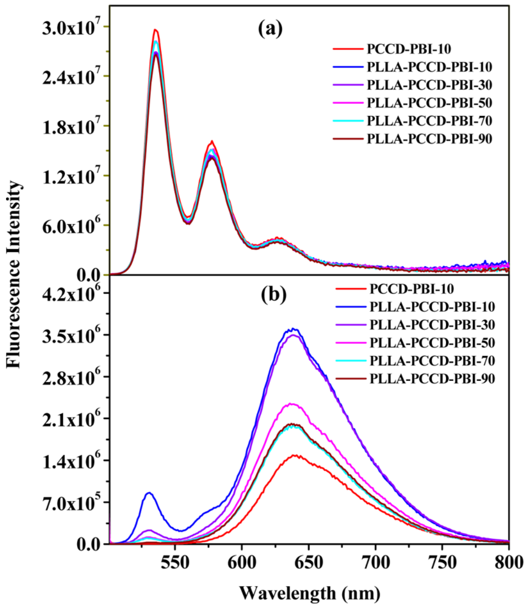


Figure 7. Emission spectra of polymers in (a) chloroform solution [0.1 OD at 490 nm, λ_{ex} = 490 nm] and (b) film state [0.1 OD at 490 nm, λ_{ex} = 490 nm] spin-coated from chloroform solution.

The relative fluorescence quantum yield for all the polymers was determined in $CHCl_3$ by exciting at 490 nm. The absolute fluorescence quantum yield in the powder state was also measured using Integrating Sphere. The quantum yield values along with the photophysical characteristics of all the polymers are given in Table 3. All **PLLA−PCCD-PBI-x** series of polymers were highly fluorescent in chloroform solution with quantum yields of ∼80%. Compared to the solution, the quantum yield values were much lower in the solid state due to aggregation-induced quenching.[17] **PCCD−PBI-10** had solid state quantum yield of 2%, whereas **PLLA−PCCD-PBI-10** had a higher quantum yield of 10%. The solid state fluorescence quantum yields of **PLLA−PCCD-PBI-30**, **PLLA−PCCD-PBI-50**, **PLLA−PCCD-PBI-70**, and **PLLA−PCCD-PBI-90** were 9%, 7%, 6%, and 2%, respectively. The solid state fluorescence quantum yields of **PLLA−PCCD-PBI-x** series of polymers decreased with increasing mol % incorporation of PBI units due to aggregation-induced quenching. The solid state quantum yield of 10% observed for the PBI incorporated polymer reported herein is quite high compared to the normally weak values (<1%) reported in literature for aggregated PBIs.

Table 3. Absorption and Emission of Polymers in Solution As Well As in Solid State (Film Spin-Coated from Chloroform Solution) along with Fluorescence Quantum Yields (Φ_{FL})

polymer	absorption λ_{max} (nm) (in $CHCl_3$)	emission λ_{max} (nm) (in $CHCl_3$)	absorption λ_{max} (nm) (in film)	emission λ_{max} (nm) (in film)	ϕ_{FL} (solution)	ϕ_{FL}^{f} (%) (powder)
PCCD−PBI-10	526	534^{a}	490	638^{a}	0.84^{d}	2
PLLA−PCCD-PBI-10	526	534^{a}	490	638^{a}	0.80^{d}	10
PLLA−PCCD-PBI-30	526	534^{a}	490	638^{a}	0.82^{d}	9
PLLA−PCCD-PBI-50	526	534^{a}	490	638^{a}	0.82^{d}	7
PLLA−PCCD-PBI-70	526	534^{a}	490	638^{a}	0.81^{d}	6
PLLA−PCCD-PBI-90	526	534^{a}	490	638^{a}	0.82^{d}	2
PLLA-OPV-5	390	445^{b}	392	440, 469^{c}	0.62^{e}	63
PLLA−PCCD-PBI-10-OPV-5	390, 526	$445,^{b}$ 534^{a}	392, 490	$441,^{c}$ $467,^{c}$ 638^{a}		23(OPV),^{c} 8(PBI)^{a}

[a] Excitation at 490 nm. [b] Excitation at 390 nm. [c] Excitation at 392 nm. [d] The fluorescence quantum yield for polymers in $CHCl_3$ was obtained upon excitation at 490 nm and was measured using rhodamine-6G in ethanol as standard (ϕ = 0.95). [e] The fluorescence quantum yield for polymer in $CHCl_3$ was obtained upon excitation at 360 nm and was measured using quinine sulfate in 0.1 M H_2SO_4 solution as standard (ϕ = 0.54). [f] Absolute fluorescence quantum yields in the powder form were determined with an integrating sphere.

The absorption and emission characteristics of the donor−acceptor (D-A) polymer **PLLA−PCCD-PBI-10-OPV-5** was also determined in solution and in thin films. The normalized absorption spectra in solution and film are given in Figure S7 (a) and (b). The corresponding spectra of the donor alone polymer **PLLA-OPV-5** and acceptor alone polymer **PLLA−PCCD-PBI-10** are also plotted together for comparison. **PLLA-OPV-5** had absorption maximum at 390 nm. The absorption spectrum of the D−A polymer was almost similar to that of the individual components, OPV and PBI, which indicated the absence of charge transfer in the ground state.[45] The spectral features in the solid state was similar to that of the aggregated donor and acceptor in the solid state.[46] Figure 8a,b compares the emission spectra of the three polymers **PLLA−PCCD-PBI-10-OPV-5**, **PLLA-OPV-5**, and **PLLA−PCCD-PBI-10** in chloroform solution and as spin coated films from chloroform, respectively. In solution, the polymers **PLLA−PCCD-PBI-10-OPV-5** and **PLLA-OPV-5** were prepared to have 0.1 OD at the donor absorption wavelength maxima of 390 nm, while **PLLA−PCCD-PBI-10** was made to have 0.1 OD at 490 nm. All three polymers were excited at 390 nm. **PLLA-OPV-5** exhibited typical emission features of the OPV chromophore with strong emission centered at 445 nm. Excitation of D−A polymer resulted in 27.82% quenching of the OPV emission at 445 nm compared to that of donor alone polymer (**PLLA-OPV-5**). The PBI alone polymer **PLLA−PCCD-PBI-10** did not have noticeable emission. The D−A polymer and the acceptor alone polymer were also excited at the acceptor absorption wavelength maximum of 490 nm. D−A polymer exhibited a slight (16.96%) quenching of emission from PBI compared to that of the acceptor alone polymer (**PLLA−PCCD-PBI-10**) [Figure 8a]. The observation of the OPV and PBI emission without much reduction in their intensity upon selective excitation suggested that photoinduced energy transfer was not a prominent feature in this donor−acceptor system. This was also supported by the excitation spectrum of **PLLA−PCCD-PBI-10-OPV-5** and **PLLA−PCCD-PBI-10**, which were collected while monitoring the PBI emission at 575 nm (Figure S8). The absence of the OPV absorption band in their excitation spectra supported the absence of energy transfer channels between the OPV and PBI units.[47] This was further confirmed by fluorescence lifetime-decay studies conducted on **PLLA−PCCD-PBI-10-OPV-5** and **PLLA-OPV-5** by probing at 445 nm using LED 390 nm [Figure S9 (a)]. A similar fluorescence lifetime-decay values of 1.3 ns was observed for the OPV emission in the donor alone polymer as well as the D−A polymer. This fact was further proof for the absence of energy transfer between donor and acceptor in **PLLA−PCCD-PBI-10-OPV-5**. However, the occurrence of small extent (~28%) of quenching of donor emission observed in the D−A polymer could be attributed to radiative transfer by the trivial mechanism resulting from reabsorption of the donor emission by the acceptor moiety.[47]

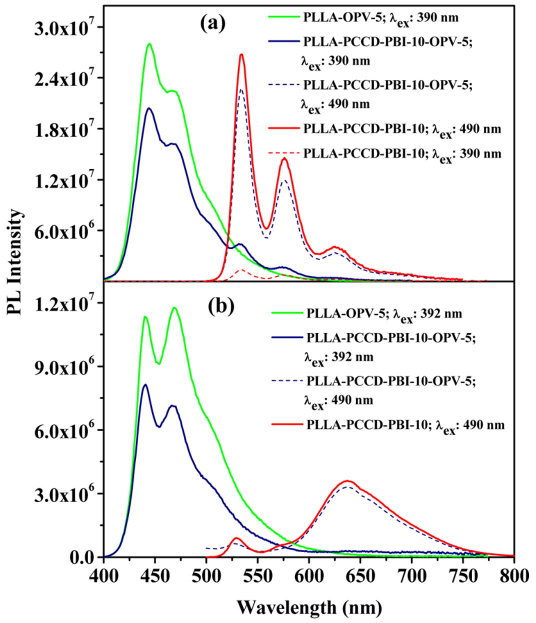


Figure 8. Emission spectra of **PLLA−PCCD-PBI-10**, **PLLA-OPV-5**, and **PLLA−PCCD-PBI-10-OPV-5** in (a) chloroform solution and (b) film spin-coated from chloroform solution.

Figure 8b compares the solid state emission spectra of the polymers. D−A polymer exhibited strong emission intensity for OPV and PBI unit upon excitation at 392 nm (absorption maximum of OPV unit) and 490 nm (absorption maximum of PBI unit) respectively. Compared to the donor alone polymer (**PLLA-OPV-5**), D−A polymer exhibited 36.14% quenching of donor emission. Similar to the observation in solution, the OPV absorption band was not visible in the excitation spectra collected for **PLLA−PCCD-PBI-10-OPV-5** and **PLLA−PCCD-PBI-10** while monitoring the PBI emission at 638 nm (Figure S10). Figure S9 (b) shows the fluorescence lifetime-decay profiles collected for films of **PLLA-OPV-5** and **PLLA−PCCD-PBI-10-OPV-5** at 440 nm using LED 390 nm. Similar fluorescence lifetime decay values of 1.28 ns for both donor alone polymer and the D−A polymer confirmed the absence of energy- or electron transfer occurring in the solid state also.[47]

Previously we had explored the energy and electron transfer characteristics of **PCCD** based donor−acceptor polyesters involving OPV-2-Diol and PBI-6-Diol.[21] Photoexcitation of thin film samples of the **PCCD** based D−A copolyester had exhibited complete quenching of both OPV and PBI emission, which indicated efficient photoinduced charge transfer occurring after photoexcitation of either D or A units. This was in complete contrast to the observation in the current **PLLA−PCCD-PBI-OPV** polymers. This observation brings forth the importance of structure design in materials, which can be tailor-made to suit the application requirements. The previous **PCCD−PBI-OPV** polymers were synthesized by melt condensation polymerization of the PBI-6-Diol and OPV-2-Diol with 1,4-cyclohexanedimethanol (CHDM) and 1,4-dimethylcyclohexane dicarboxylate (DMCD) to obtain random incorporation of the D and A units in the **PCCD** backbone. On the other hand, in the current work the OPV units were incorporated into **PCCD−PBI** polymer backbone by a blending approach in the presence of another polyester, **PLLA**. Scrambling of the **PLLA** polymer occurs with incorporation of donor and acceptor units, along with **PCCD** units by transesterification process. This leads to the segmentation of the OPV and PBI units by blocks of **PLLA** units, which prevents interaction among them. Therefore, energy and/or electron transfer between OPV and PBI moiety was not observed in the **PLLA−PCCD** based D−A polymer. The solid state (powder form) quantum yield of OPV and PBI emission in **PLLA−PCCD-PBI-10-OPV-5** was 23% and 8% respectively. **PLLA−PCCD-PBI-10-OPV-5** could be excited independently without energy transfer occurring between them, and therefore one could access two different emission regions from **PLLA−PCCD-PBI-10-OPV-5** just by exciting at appropriate wavelength, which was confirmed by fluorescence microscopy studies.

■ CONCLUSION

A series of random copolyesters of **PLLA** and **PCCD** incorporating varying mol % of perylene bisimide (PBI) was successfully synthesized by high-temperature solution-blending. A donor−acceptor random copolymer incorporating OPV as the donor and PBI as the acceptor component was also developed by incorporating both donor and acceptor into the **PLLA−PCCD** backbone by a polyester/polyester transesterification process. All polymers exhibited good solubility and film forming ability with strong emission observed from the films. A solid state fluorescence quantum yield of 10% was observed for **PLLA−PCCD-PBI-10** polymer, which was one of the highest reported in the solid state for PBI incorporated polymers. Red fluorescent nanofibers of the PBI based polymers were successfully constructed by electrospinning technique. The electrospun fibers of the OPV based polymer showed both blue and green emission under fluorescence microscopy upon excitation at different wavelengths. This approach was extended for the construction of the nanofibers of copolyester incorporating both OPV and PBI chromophore. Blue, green and red emission from this polymer was observed under fluorescence microscopy upon excitation at different wavelengths. These interesting emission properties make them potential candidates in various nanodevice applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table containing the characterization data of **PCCD−PBI-x** series of polymers, scheme for the synthesis of polymers, ^{1}H NMR spectra, size exclusion chromatogram and TGA thermograms of the polymers, SEM and fluorescence microscopy images, fluorescence lifetime-decay profiles, and excitation spectra of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Law, M.; Goldberger, J.; Yang, P. Semiconductor Nanowires and Nanotubes. *Annu. Rev. Mater. Res.* **2004**, *34*, 83−122.

(2) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. One-Dimensional Nanostructures: Synthesis, Characterization, and Applications. *Adv. Mater.* **2003**, *15*, 353−389.

(3) Huang, M. H.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. Room-Temperature Ultraviolet Nanowire Nanolasers. *Science* **2001**, *292*, 1897−1899.

(4) Ner, Y.; Asemota, C.; Olson, J. R.; Sotzing, G. A. Nanofiber Alignment on a Flexible Substrate: Hierarchical Order from Macro to Nano. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2093−2097.

(5) Agarwal, R.; Barrelet, C. J.; Lieber, C. M. Lasing in Single Cadmium Sulfide Nanowire Optical Cavities. *Nano Lett.* **2005**, *5*, 917−920.

(6) Zang, L.; Che, Y.; Moore, J. S. One-Dimensional Self-Assembly of Planar π-Conjugated Molecules: Adaptable Building Blocks for Organic Nanodevices. *Acc. Chem. Res.* **2008**, *41*, 1596−1608.

(7) Zhao, Y. S.; Fu, H. B.; Hu, F. Q.; Peng, A. D.; Yang, W. S.; Yao, J. N. Tunable Emission from Binary Organic One-Dimensional Nanomaterials: An Alternative Approach to White-Light Emission. *Adv. Mater.* **2008**, *20*, 79−83.

(8) Quochi, F.; Cordella, F.; Mura, A.; Bongiovanni, G.; Balzer, F.; Rubahn, H.-G. Gain Amplification and Lasing Properties of Individual Organic Nanofibers. *Appl. Phys. Lett.* **2006**, *88*, 041106/1−041106/3.

(9) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. About Supramolecular Assemblies of π-Conjugated Systems. *Chem. Rev.* **2005**, *105*, 1491−1546.

(10) Sonawane, S. L.; Asha, S. K. Fluorescent Crosslinked Polystyrene Perylene Bisimide/Oligo(p-Phenylenevinylene) Microbeads with Controlled Particle Size, Tunable Colors and High Solid State Emission. *ACS Appl. Mater. Interfaces.* **2013**, *5*, 12205−12214.

(11) Würthner, F. Perylene Bisimide Dyes as Versatile Building Blocks for Functional Supramolecular Architectures. *Chem. Commun.* **2004**, 1564−1579.

(12) Vercelli, B.; Zotti, G.; Berlin, A. Alternate Monolayers of CdSe Nanocrystals and Perylene Tetracarboxylate: Quantum Dot Hypersensitization for Dye-Sensitized Solar Cells. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3233−3238.

(13) Shi, M.-M.; Chen, H.-Z.; Sun, J.-Z.; Ye, J.; Wang, M. Fluoroperylene Diimide: A Soluble and Air-stable Electron Acceptor. *Chem. Commun.* **2003**, 1710−1711.

(14) Lee, S. K.; Zu, Y.; Herrmann, A.; Geerts, Y.; Müllen, K.; Bard, A. J. Electrochemistry, Spectroscopy and Electrogenerated Chemiluminescence of Perylene, Terrylene, and Quaterrylene Diimides in Aprotic Solution. *J. Am. Chem. Soc.* **1999**, *121*, 3513−3520.

(15) Huang, J.; Wang, X.; Zhang, X.; Niu, Z.; Lu, Z.; Jiang, B.; Sun, Y.; Zhan, C.; Yao, J. Additive-Assisted Control over Phase-Separated Nanostructures by Manipulating Alkylthienyl Position at Donor Backbone for Solution-Processed, Non-Fullerene, All-Small-Molecule Solar Cells. *ACS Appl. Mater. Interfaces* **2014**, *6*, 3853−3862.

(16) Che, Y.; Datar, A.; Balakrishnan, K.; Zang, L. Ultralong Nanobelts Self-Assembled from an Asymmetric Perylene Tetracarboxylic Diimide. *J. Am. Chem. Soc.* **2007**, *129*, 7234−7235.

(17) Balakrishnan, K.; Datar, A.; Naddo, T.; Huang, J.; Oitker, R.; Yen, M.; Zhao, J.; Zang, L. Effect of Side-Chain Substituents on Self-Assembly of Perylene Diimide Molecules: Morphology Control. *J. Am. Chem. Soc.* **2006**, *128*, 7390−7398.

(18) Balakrishnan, K.; Datar, A.; Oitker, R.; Chen, H.; Zuo, J.; Zang, L. Nanobelt Self-Assembly from an Organic n-Type Semiconductor: Propoxyethyl-PTCDI. *J. Am. Chem. Soc.* **2005**, *127*, 10496−10497.

(19) Li, X.-Q.; Zhang, X.; Ghosh, S.; Würthner, F. Highly Fluorescent Lyotropic Mesophases and Organogels Based on J-Aggregates of Core-Twisted Perylene Bisimide Dyes. *Chem.—Eur. J.* **2008**, *14*, 8074−8078.

(20) Boobalan, G.; Imran, P. K.; Manoharan, C.; Nagarajan, S. Fabrication of Highly Fluorescent Perylene Bisimide Nanofibers through Interfacial Self-assembly. *J. Colloid Interface Sci.* **2013**, *393*, 377−383.

(21) Nisha, S. K.; Asha, S. K. Donor-Acceptor Random Copolyesters containing Perylene Bisimide (PBI) and Oligo(*p*-phenylenevinylene) (OPV) by Melt Condensation Polymerization: Energy Transfer Studies. *J. Phys. Chem. B* **2013**, *117*, 13710−13722.

(22) Auras, R.; Lim, L.-T.; Selke, S. E. M.; Tsuji, H. *Poly(lactic acid): Synthesis, Structures, Properties, Processing, and Applications*; Wiley & Sons: Hoboken, NJ, 2010.

(23) Nisha, S. K.; Asha, S. K. Chiral Poly(L-lactic acid) Driven Helical Self-Assembly of Oligo(*p*-phenylenevinylene). *J. Mater. Chem. C* **2014**, *2*, 2051−2060.

(24) Asha, S. K.; Nisha, S. K. *Perylene Bisimide - Polyester Blend*. WO 2012111026 A1, August 23, 2012.

(25) Avlasevich, Y.; Li, C.; Müllen, K. Synthesis and Applications of Core-Enlarged Perylene Dyes. *J. Mater. Chem.* **2010**, *20*, 3814−3826.

(26) Wu, J.; Wang, N.; Zhao, Y.; Jiang, L. Electrospinning of Multilevel Structured Functional Micro-/Nanofibers and their Applications. *J. Mater. Chem. A* **2013**, *1*, 7290−7305.

(27) Bedford, N. M.; Steckl, A. J. Photocatalytic Self Cleaning Textile Fibers by Coaxial Electrospinning. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2448−2455.

(28) Liu, H. A.; Zepeda, D.; Ferraris, J. P.; Balkus, K. J., Jr. Electrospinning of Poly(alkoxyphenylenevinylene) and Methanofullerene Nanofiber Blends. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1958−1965.

(29) Marty, R.; et al. Hierarchically Structured Microfibers of "Single Stack" Perylene Bisimide and Quaterthiophene Nanowires. *ACS Nano* **2013**, *7*, 8498−8508.

(30) Naphade, R. A.; Tathavadekar, M.; Jog, J. P.; Agarkar, S.; Ogale, S. Plasmonic Light Harvesting of Dye Sensitized Solar Cells by Au-Nanoparticle Loaded TiO_2 Nanofibers. *J. Mater. Chem. A* **2014**, *2*, 975−984.

(31) Nisha, S. K.; Asha, S. K. A Facile One-Pot Reactive Solution Blending Approach for Main-Chain Donor−Acceptor Polymeric Materials. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *51*, 509−524.

(32) Thakur, K. A. M.; Kean, R. T.; Hall, E. S.; Kolstad, J. J.; Lindgren, T. A.; Doscotch, M. A.; Siepmann, J. I.; Munson, E. J. High-Resolution ^{13}C and ^{1}H Solution NMR Study of Poly(lactide). *Macromolecules* **1997**, *30*, 2422−2428.

(33) Jayakannan, M.; Deepa, P. Polyurethane-Oligo-(phenylenevinylene) Random Copolymers: π-Conjugated Pores, Vesicles, and Nanospheres via Solvent-Induced Self-Organization. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5897−5915.

(34) Fakirov, S. *Transreactions in Condensation Polymers*; Wiley-VCH: Weinheim, Germany, 1999.

(35) Pielichowski, K.; Njuguna, J. *Thermal Degradation of Polymeric Materials*; Rapra Technology Limited: U.K., 2005.

(36) Haynes, D.; Abayasinghe, N. K.; Harrison, G. M.; Burg, K. J.; Smith, D. W. In Situ Copolyesters Containing Poly(L-lactide) and Poly(hydroxyalkanoate) Units. *Biomacromolecules* **2007**, *8*, 1131−1137.

(37) Jayakannan, M.; AnilKumar, P. Mechanistic Aspects of Ester-Carbonate Exchange in Polycarbonate/Cycloaliphatic Polyester with Model Reactions. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3996−4008.

(38) Li, X.; Zhong, G.; Li, Z. Non-isothermal Crystallization of Poly(L-lactide) (PLLA) Under Quiescent and Steady Shear Conditions. *Chin. J. Polym. Sci.* **2010**, *28*, 357−366.

(39) Neuteboom, E. E.; Meskers, S. C. J.; Meijer, E. W.; Janssen, R. A. J. Photoluminescence of Self-Organized Perylene Bisimide Polymers. *Macromol. Chem. Phys.* **2004**, *205*, 217−222.

(40) Gallaher, J. K.; Aitken, E. J.; Keyzers, R. A.; Hodgkiss, J. M. Controlled Aggregation of Peptide-Substituted Perylene Bisimides. *Chem. Commun.* **2012**, *48*, 7961−7963.

(41) Chen, Z.; Baumeister, U.; Tschierske, C.; Würthner, F. Effect of Core Twisting on Self-Assembly and Optical Properties of Perylene Bisimide Dyes in Solution and Columnar Liquid Crystalline Phases. *Chem.—Eur. J.* **2007**, *13*, 450−465.

(42) Chen, Z.; Stepanenko, V.; Dehm, V.; Prins, P.; Siebbeles, L. D. A.; Seibt, J.; Marquetand, P.; Engel, V.; Würthner, F. Photoluminescence and Conductivity of Self-Assembled π−π Stacks of Perylene Bisimide Dyes. *Chem.—Eur. J.* **2007**, *13*, 436−449.

(43) Narayan, R.; Asha, S. K. Solvent-Induced Self-Assembly of Hydrogen Bonded P4VP-Perylene Bisimide Comb Polymer. *J. Mater. Chem. C* **2013**, *1*, 5925−5934.

(44) Würthner, F.; Kaiser, T. E.; Saha-Möller, C. R. J-Aggregates: From Serendipitous Discovery to Supra-molecular Engineering of Functional Dye Materials. *Angew. Chem., Int. Ed.* **2011**, *50*, 3376−3410.

(45) Neuteboom, E. E.; van Hal, P. A.; Janssen, R. A. Donor-Acceptor Polymers: A Conjugated Oligo(*p*-Phenylene Vinylene) Main Chain with Dangling Perylene Bisimides. *Chem.—Eur. J.* **2004**, *10*, 3907−3918.

(46) Bauer, P.; Wietasch, H.; Lindner, S. M.; Thelakkat, M. Synthesis and Characterization of Donor-Bridge-Acceptor Molecule Containing Tetraphenylbenzidine and Perylene Bisimide. *Chem. Mater.* **2007**, *19*, 88−94.

(47) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 3rd ed.; Springer: New York, 2010.