# Synthesis of Water-Soluble Perylenediimide-Functionalized Polymer Through Esterification with Poly(vinyl alcohol)

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**ABSTRACT:** A new material has been prepared by covalent attachment of a perylene derivative, *N*-(carboxyphenyl)-*N'*-(8-pentadecyl)perylene-3,4:9,10-bis(dicarboximide) (PDI-COOH), to poly(vinyl alcohol) (PVA) by esterification. The perylenediimide (PDI)-modified PVA polymers are soluble in water and dimethylsulfoxide (DMSO). This solubility is conferred to the insoluble perylene derivative by the water-soluble polymer. The materials have been characterized by hydrogen-nuclear magnetic resonance, Fourier transform infrared spectra, X-ray diffraction, and X-ray photoelectron spectroscopy confirming the covalent attachment of the PDI to the polymer chains. The sig-

nificant changes in the crystalline parameters and the thermal stability observed for the polymer after the esterification also confirm the covalent linkage with PDI. In addition, the PDI-modified PVA shows good fluorescence both in solution (quantum yield ~0.2–0.25) and in solid suggesting that the PDI retains largely its photochemical and photophysical properties after immobilization. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 3613–3622, 2010

**KEYWORDS**: esterification; fluorescence; perylenediimide; PVA; water solubility

**INTRODUCTION** Perylene tetracarboxylic acid bisimide, in short perylenediimide (PDI)-based colorants have received a great deal of attention not only in academic but also as industrial dye and in pigment research.<sup>1</sup> More recently, PDI derivatives have developed into one of the best n-type semiconductors available to date<sup>2</sup> and have found application in different areas such as organic solar cells,<sup>3</sup> fluorescent labels,<sup>4</sup> sensors,<sup>5</sup> lasers,<sup>6</sup> sensitizers for photodynamic therapy,<sup>7</sup> field effect transistors,<sup>8</sup> or color tunable light-emitting diodes.<sup>9</sup> In parallel with the different applications found for PDI derivatives, a broad range of derivatives have been synthesized including multi-PDI derivatives,<sup>10</sup> supramolecular architectures, <sup>11–12</sup> derivatives with extended  $\pi$ -conjugation, <sup>13</sup> and a number of PDI derivatives covalently linked to electroactive moieties such as ferrocene,<sup>14</sup> anthraquinone,<sup>15</sup> and [60]fullerene<sup>16</sup> among others. Additionally, a number of conjugated oligomers and polymers have been linked to the PDI moiety through covalent or supramolecular bonds for electrochemical and photophysical studies mainly focused on the investigation of their photoinduced energy and/or electron transfer processes.<sup>17-19</sup>

A very well-known characteristic of aromatic polyimides is their poor solubility in organic solvents, especially those derived from rigid anhydrides such as PDI. This property makes them generally intractable or difficult to process, thus restricting sometimes their applications.<sup>20</sup> It its known that perylene modified with carboxylic acids are versatile and very reactive compounds that can accept a wide number of functionalities, being 3,4:9,10-perylene tetracarboxylic acid, the most employed. Thus, several synthetic strategies<sup>21–23</sup> have been used to prepare water-soluble<sup>21</sup> and organo-soluble<sup>22,23</sup> PDI dyes. As PDI dyes have high quantum yield of fluorescence, the preparation of water-soluble PDIs makes them ideal as high-performance fluorescent labels for biologically active probes.

Considering their excellent thermal and photo stabilities, their electron acceptor and photoconductive properties, the syntheses of soluble, processable, and thermally stable polymers containing PDI moieties is highly desirable for different photonic and optoelectronic applications. With this aim, attempts to incorporate PDI derivatives into polymers have been already carried out. Although the direct incorporation of dyes into an appropriate soluble polymer is difficult because of the low reactivity and solubility of the aromatic blocks used as monomers, different strategies have been followed to incorporate PDI moieties into polymer chains either as side chains or as part of the main chain.

In 1994, Ghassemi and  $Hay^{24}$  reported a seminal paper describing the synthesis of red pigmentary polyimides made by polymerization of *N*,*N*'-diamino-3,4,9,10-perylenetetracarboxylic acid diimide with suitable bisanyhydrides. Other

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### PDI-COOH

PDI-COOR

**SCHEME 1** Chemical structure of the PDI-COOH employed in the esterification reaction with PVA and PDI-COOR used for comparison purposes in quantum yield measurements.

stable polyimides were prepared by Icil et al.<sup>25</sup> based on perylene-3,4,9,10-tetracarboxylic acid-bis(*N*,*N*'-dodecyl polyimide) and by Wang et al.,<sup>26</sup> who investigated their xerographic electrical properties. Nevertheless, most of these polymers were soluble only in strong polar solvents as a consequence of the strong  $\pi$ - $\pi$  interaction between the PDI moieties. In more recent years, different strategies have allowed to obtain PDI-based soluble polyimides,<sup>27</sup> polyesters,<sup>28</sup> polyurethanes,<sup>29</sup> and polyazomethines.<sup>30</sup>

An alternative approach for the incorporation of PDI moieties in polymers involves the synthesis of PDI derivatives covalently linked to polymers as side chains. Thus, PDI moieties have been incorporated as side chain in polyacrylate<sup>31</sup> and polyisocyanide.<sup>32</sup> Thus, inducing the solubility of PDI trough covalent modification with a soluble polymer could be a great advance. Even more, the immobilization of PDI into polymeric matrices can be used to avoid the spontaneous intramolecular aggregation in solution. In that sense, polyisocyanodipeptides have been employed as scaffolds to tailor the chromophorechromophore interactions among PDI dyes covalently linked to the aliphatic side-chains.<sup>33</sup> Compared with blending, the covalent linkage of PDI to a polymeric matrix gives homogeneous materials without phase segregation where the PDI moieties are fixed inside the polymer matrix, avoiding selfassociation.9

However there exist a few examples of common polymers covalently modified with PDI dyes. Homopolymers or block copolymers from butyl acrylate, styrene, isoprene, and butadiene have been labeled with one perylenediimide per polymer.<sup>34</sup> Also, poly(methyl methacrylate) has been polymerized in presence of perylene derivatives.<sup>35</sup> Finally, short poly(ethylene oxide) tails have been covalently attached to perylene giving soluble materials in common solvents ranging from alcohols to toluene.<sup>36</sup>

Poly(vinyl alcohol) (PVA) is a water-soluble biodegradable polymer with excellent film forming properties. Recently, a

water-soluble PDI derivative has been dispersed into vinyl alcohol (VA)-containing polymers by blending and their properties studied.<sup>37</sup> The authors used a *N*,*N*'-bis(2-(1-piper-azino)ethyl)-3,4,9,10-perylene tetracarboxylic acid diimidedichloride, that can interact with the VA by hydrogen bonding. However, it has been reported that planar objects, as big as graphene nanosheets<sup>38</sup> and graphite oxide (GO) laminates,<sup>39</sup> can be covalently attached to PVA by simple esterification remarkably altering the crystallinity of the polymer.<sup>39</sup> Therefore, the inclusion of smaller units should present no difficulty.

Here, we report the esterification of PVA with a water-insoluble PDI, which has a carboxylic acid group in one of its nitrogen and long aliphatic chains in the other (Scheme 1). The reactions reach up to 20% w/w of modification and the obtained products show water solubility due to the PVA. The esterified products retain the absorption and emission properties of the PDI dye giving photoluminescence in both solution and solid state.

#### **RESULTS AND DISCUSSION**

PDI-COOH is composed of a terminal carboxylic group that can react with alcohols or amines giving ester or amides. The esterification of PVA with PDI-COOH was carried out as described in the experimental section. Special care was taken in the purification of the products to ensure that no traces of nonreacted PDI-COOH remained. Samples with different degree of modification were prepared varying the molar fraction of PDI and PVA in the reactor obtaining degrees of modification of 22, 21, and 8 wt % for samples 1, 2, and 3, respectively (Table 1). The products were soluble in water at 90 °C and dimethylsulfoxide (DMSO) due to the interaction of the solvents with the hydroxyl moieties in the polymer. The solubility depends on the final composition but solutions, as concentrated as 15 mg mL<sup>-1</sup>, has been prepared for all samples. Taking into account that samples PVAPery1 and 2 have very

TABLE 1 Composition of Different Samples of PVA Esterified with Perilenediimide

Samples	f <sub>p</sub> <sup>a</sup>	% C	% H	% N	N/C	$F_p^{b}$
PVAPery1	$6.9  imes 10^{-3}$	53.70	10	0.58	$1.1 \times 10^{-2}$	0.22
PVAPery2	$5.4  imes 10^{-3}$	52.9	9.8	0.56	$1.1 \times 10^{-2}$	0.21
PVAPery3	$1.7 \times 10^{-3}$	52.9	9.2	0.2	$3.8 \times 10^{-3}$	0.08

<sup>a</sup>  $f_p$  is defined as the molar fraction of perylenediimide in the reactor.

<sup>b</sup>  $F_{p}$  as the molar fraction of perylenediimide in the products.



FIGURE 1 FTIR transmission spectra of PVA and PDI-modified PVA.

similar composition, henceforth, we will base the discussion on the results of samples PVAPery1 and 3 (Table 1).

To prove the success of the esterification reaction, the products were characterized by Fourier transform infrared spectra (FTIR), hydrogen-nuclear magnetic resonance (<sup>1</sup>H NMR), and X-ray photoelectron spectroscopy (XPS). The FTIR spectra of the PDI-esterified PVA retained most of the bands of PVA, some of them changed in intensity, and show additional bands (Fig. 1). There are two features to remark. First, the most intense bands of PDI-COOH<sup>40</sup> appear weakly in the esterified product PVAPery1, due to the low content of PDI with respect to the polymer. Thus, a doublet centered at 1688 and 1648  $\mbox{cm}^{-1}$  assigned to the symmetric and antisymmetric stretching vibrations of the carbonyl group can be perceived. These bands seem to be displaced  $\sim 10 \text{ cm}^{-1}$  at lower energy with respect to PDI-COOH, due to the possible interaction with the polymer matrix. In addition, a detailed examination of the spectra reveals the presence of a very weak band at 1260  $\text{cm}^{-1}$  in PVAPery1. This band can be assigned to the C-O stretching of the ester group, which appears as a strong band in aromatic esters. Here is only perceived in PVAPery1

due to the actual composition of the samples (PVAPery3 does not have the necessary content of PDI to observe this band). Consequently, the intensity of the mentioned bands diminishes as the content of PDI decreases (Fig. 1).

Second, a variation in the relative intensities of the characteristics bands of PVA in the 1200–1000 cm<sup>-1</sup> region can be clearly observed, resembling the results reported for the esterification of PVA with GO.<sup>39</sup> These bands are attributed to the C—O of doubly H-bonded OH in crystalline regions (1144 cm<sup>-1</sup>) and C—O unbounded in amorphous zones (1096 cm<sup>-1</sup>).<sup>41</sup> The intensity ratio of these bands ( $I_{1144}/I_{1096}$ ) diminishes markedly for the esterified products, suggesting a large decrease in the degree of crystallinity of the modified polymer. These results were also confirmed by X-ray diffraction (XRD; Supporting Information, Fig. S1).

The <sup>1</sup>H NMR spectrum of the soluble PVAPery3 in DMSO- $d_6$  is compared with that of neat PVA (Fig. 2). The latter exhibits the polymer backbone signals at ~3.82 ppm (methine) and ~1.38 ppm (methylene) and the hydroxyl signals at 5–4 ppm from which the stereoregularity of PVA is estimated as isotactic (mm): heterotactic (mr): syndiotactic (rr) of roughly



**FIGURE 2** <sup>1</sup>H NMR spectra of PVA and PVAPery3 at room temperature in DMSO- $d_6$ .

2:5:3.42 Upon the attachment to PDI-COOH the PVA proton signals become much wider maintaining similar chemical shifts. This behavior resembles the observation of PVA covalently modified with carbon nanotubes<sup>43</sup> and GO.<sup>39</sup> However, the effect is more noticeable in our case suggesting that a higher degree of functionalization was achieved. Especially interesting are the changes in the zone corresponding to the hydroxyl protons resonances, which are resolvable in terms of configurational sequences (inset in Fig. 2). Several authors have concluded<sup>44</sup> that the hydrogen-bonding tendency, which is dominant for hydroxyl units in a mesoconfiguration, predominantly determines the hydroxyl proton shielding. As hydrogen bonding leads to downfield shifts, the chemical shifts of hydroxyl sequences resonances increase when passing from iso (4.7 ppm) to hetero (4.5 ppm) and from hetero to syndio (4.2 ppm) triad. On the other hand, it has been demonstrated that the reactivity of substituent groups along the polymer chain can be influenced by tactic sequence,<sup>39,45</sup> where the substituent at mm sequence exhibited higher reactivity than those at the rr counterpart. Here, although the signals are broadened and even overlap, it seems clear that exists, an increase in the rr signal in detriment of the mm one for PVAPery, which suggests that esterification reaction occur at isotactic configuration.39

In addition, the presence of PDI units is confirmed by the low signals at 5.1, 6.6, 6.8–7.8, 8.2, and 8.7 ppm (Supporting Information, Fig. S2). These signals are in agreement with those observed for the PDI-COOR (Experimental section). Because of the low intensity of these signals and the error associated with their quantification, they could not be used to estimate the extent of modification. Therefore, we have used elementary analysis, despite its uncertainties, to roughly estimate the degree of modification (Table 1).

XPS results are summarized in Table S1 (see Supporting Information). It is very interesting to note the changes in the C1s signal with the increase of the content of PDI (Fig. 3). In the product with lower content (PVAPery3), the C1s signal was deconvoluted into only two peaks. The most intense peak at 284.8 eV corresponds to the C—C bonds, whereas the peak at 286.5 eV is assigned to the C—OH of the polymer. However, an additional peak seems at 288.4 eV in the sample with higher content of perylene (PVAPery1). This new peak can be assigned to carboxyl carbon groups in PDI (Scheme 1), and it only appears when a critical concentration of PDI is achieved. The XPS results for O1s reinforce the above hypothesized [Fig. 3(c,d)]. The O1s signal for PVAPer3 was fitted to one peak centered at 532.7 eV, while the same signal for PVAPery1 was deconvoluted into two peaks at



FIGURE 3 C1s XPS spectra of PVAPery1 (a) and PVAPery3 (b) and 1s spectra of PVAPery1 (c) and PVAPery3 (d).

**TABLE 2** Thermal Parameters for PVA and PVA Esterified with

 Perylenediimide Obtained by DSC

Samples	<i>T</i> <sub>g</sub> (°C)	<i>T</i> <sub>m</sub> (°C)	$\Delta H$ (J g <sup>-1</sup> )	<i>X</i> <sub>c</sub> (%)
PVA	82	225	83	51
PVAPery1	90.5	178	33.2	20.4
PVAPery2	91.4	182.6	32.8	20.1
PVAPery3	90.8	179	40	24.5

531.6 and 533 eV (Table S1), suggesting the presence of oxygen atoms in at least two different environments. Finally, the N1s signal was fitted to one peak with maxima at 400.5 eV in both cases, which is logical as nitrogen atoms in perylene are not involved in the esterification reaction (Supporting Information, Fig. S3).

Once confirmed the covalent linkage of PDI units to PVA, it would be interesting to study the effect of this modification on the properties of the polymer as remarkable changes in the crystalline parameters have already been observed in similar systems.<sup>39</sup> We have analyzed the melting and glass transition ( $T_{\rm g}$ ) of the esterified polymers and compared it with PVA.

Regarding the heating scan, it can be observed that the melting temperature  $(T_{\rm m})$  and the melting enthalpy  $(\Delta H_{\rm m})$  are dramatically influenced by the presence of PDI moieties (Table 2). In the modified products, the melting peak broadens and shifts to much lower temperatures (ca. 45 °C), and the crystallinity ( $X_{\rm C}$ ) decreases remarkably (from  $X_{\rm C} = 0.51$  for neat PVA to  $X_{\rm C} = 0.2$ –0.25 for the products), supporting the existence of covalent linkage between the PVA and the PDI (Table 2). However, these changes are less marked than those obtained for PVA with GO.<sup>39</sup> Although, in this case, the degree of functionalization is higher (and, therefore, the presence of PDI groups) the steric factor has no significant contribution as in the case of the huge GO laminates.

It is interesting to remark that the noticeable changes described above are nearly independent on the degree of functionalization because similar behaviors are obtained for all the esterified products.

In addition, the mobility of the polymer chains is also affected by the covalent linkage of PDI groups (Table 2). The  $T_{\rm g}$  shifts to higher values for the esterified products due to the effective covalent attachment of the PDI to the polymer that prevents the segmental motions of the polymer chains. Once more, the effect caused by the incorporation of PDI ( $T_{\rm g}$  shifts ~8–10 °C) is less important than the obtained by GO-modified PVA (35 °C shift). Obviously, the presence of huge rigid graphitic structures in the polymer chains restricts more the movement than the smaller perylene.

As occurred with crystallinity and melting enthalpy, the  $T_{\rm g}$  displacement does not depend on the degree of functionalization. It seems that above a threshold of modification, the polymer becomes independent on the degree of functionalization.

Also, the thermal stability of this kind of polymers changes when they are covalently modified. To investigate the effects of the PDI groups on the thermal stability of the polymer matrix, TGA were performed (Supporting Information, Fig. S4). For the PVA, two processes were observed; the first one due to the evolution of water from the polymer giving polyenes; and the second one correspond to the evolution of aromatic hydrocarbons coming from the rearrangement of these polyenes.<sup>46</sup> TGA results for PVAPery suggest that the presence of PDI improves the thermal stability remarkably. It is clear that the temperature of maximum degradation rate for the PDI-modified polymers increases more than 100 °C as occurred with PVA/GO systems.39,47,48 Figure S4 (Supporting Information) also shows that despite a weight loss is observed  $\sim 200$  °C common in these systems, the onset of decomposition for PVAPery is retarded. In addition, it seems that the second process appears almost simultaneously with the first one. That is, the presence of PDI stabilizes the water elimination making the polyenes rearrange to aromatic hydrocarbons as soon as they are generated.

Because of that one of the most interesting properties of PDI derivatives is their fluorescence; it is interesting to study whether the immobilization within the polymeric matrix affect the fluorescence behavior. Figure 4(a) shows that the absorption spectra of PVAPery in DMSO solution are almost identical to those obtained for the PDI-COOH, suggesting that the electronic absorption of the immobilized PDI is not altered. All PVAPery samples show absorption bands at 528, 491, and 460 nm associated to the vibrational progression  $(0 \rightarrow 0, 0 \rightarrow 1, and 0 \rightarrow 2, respectively)$  of the  $S_0 \rightarrow S_1$  electronic transition.<sup>49</sup> The same absorption spectra are obtained for perylene-modified polymers in water solutions (Supporting Information, Fig. S5). It has been reported that the absorbance ratio between the  $0 \rightarrow 0$  (528 nm),  $0 \rightarrow 1$  (491 nm) transitions give information about aggregation by  $\pi$ -stacking.<sup>49</sup> From Figure 4(a), the calculated  $A_{528}/A_{491}$  ratio is 1.57, 1.42, and 1.41 for the PDI-COOH, PVAPery1, and 3, respectively. Although the variation of the ratio  $A_{528}/A_{491}$  is low, the values obtained for the polymer-linked PDI are lower than that for PDI-COOH, suggesting that the immobilization does not diminish the association, as one might expect. However, for systems involving polymers, intramolecular association or folding should be considered in addition to the intermolecular self-association.<sup>50</sup> Therefore, the system can be seen as composed by rigid blocks of PDI and dynamic segments of PVA. For the PDI-modified PVA in water solution, the  $A_{528}$ /  $A_{491}$  ratio was 1.36 suggesting that folding can also take places in this case. Therefore, it can be concluded that the solvents has not influence in the absorption behavior.

Comparing the two PVAPery samples, the  $A_{528}/A_{491}$  values are identical although the concentration of chromophore is higher in PVAPery1. Probably, the intermolecular self-assembling in the sample with higher concentration of chromophore (PVAPery1) is compensated by the intramolecular folding on the PVAPery3, which has longer polymeric segments. Thus, the chromophore has higher probability to meet other chromophore units in the same polymer.



**FIGURE 4** Absorption and emission spectra of PDI-COOH (solid), PVAPery1 (dots) and PVAPery3 (dash) in DMSO solutions. Concentrations are 0.005 mg mL<sup>-1</sup> for PDI-COOH and 9 mg mL<sup>-1</sup> for the PDI-modified polymers.

Figure 4(b) shows the emission spectra of PVAPery1, PVAPery3, and the corresponding to PDI-COOH in DMSO solution ( $\lambda$ = 470 nm). It can be seen that the immobilized chromophore has retained the photoluminiscent properties as it has emission at  $0\rightarrow 0$  (540 nm),  $0\rightarrow 2$  (584 nm), and  $0\rightarrow 3$  ( $\sim 625$  nm). In similar systems, it has been demonstrated that as the folding increases, the photoluminescence favors emissions to higher vibronic ground states, thereby red-shifting the spectra. Therefore, emission peaks at lower energy appear. The spectra in Figure 4(b) can be deconvoluted into three main bands with an important contribution of the band  $\sim$ 630 for PVAPery samples (Supporting Information, Fig. S6). From the integration of the deconvolution, bands can be observed that the relative intensity of the band at 630 nm is 0.25, 0.16, and 0.07 for PVAPery1, PVAPery3, and PDI-COOH, respectively, suggesting higher degree of aggregation for the polymeric samples. As expected, the emission spectra of PDI-modified PVA in water solution are identical to those obtained in DMSO.

Using these solutions, the quantum yield of the PDI-modified PVA were measured by using afford *N*,*N*'-(9-heptadecyl)perylene-3,4:9,10-bis(dicarboximide) as reference (quantum yield  $\sim$ 1) and by using the comparative method of Williams et al.<sup>51</sup> We obtained the values of 0.18, 0.25, and 0.2 for reference PDI-COOR (Scheme 1), PVAPery 1, and 3, respectively. These similar values confirm that in the PVA-functionalized polymers, the PDI units retain their electronic nature, which is not influenced by the presence of the polymer matrix and can be seen as closed chromophores.

From a practical point of view, to be applied in devices, these materials need to retain their photoluminiscent properties in the solid state. Figure 5 shows the absorption and emission spectrum of a film of PVAPery1. The film was prepared by casting 0.5 mL of a DMSO solution (8 mg mL<sup>-1</sup>) over a glass slide and evaporation at 50 °C under vacuum. The concentrations were varied to find similar absorbance values. Qualitatively, it can be seen that the solid sample displays identical absorption spectrum than that in solution as electronic bands at 467, 495, and 532 appear. Thus, the per-ylene-modified PVA retains its electronic properties in the solid state.

The solid-state emission has been collected using the frontface illumination method [Fig. 5(b)]. As it can be perceived, the emission spectrum is similar to that obtained in DMSO solution showing slightly wider bands at 543 and 583 nm. Therefore, the film retains its emission property, and good photoluminescence is obtained that could be useful in applications.

## EXPERIMENTAL

### Materials

4-Aminobenzoic acid, *n*-propyl 4-aminobenzoate, PVA (99+% hydrolyzed,  $M_{\rm w} \sim 89,000-98,000$ ), *N*,*N*-dicyclohexylcarbodiimide (DCC), and 4-dimethylaminopyrydine (DMAP, 99%) were purchased from Aldrich. Methanol (OHCH<sub>3</sub>) and



**FIGURE 5** Solid state absorption and emission of a PVAPery1 film on glass.

tetrahydrofuran were purchased from Panreac, Spain. *N*-(8-Pentadecyl)perylene-3,4:9,10-tetracarboxylic acid monoimide monoanhydride was prepared according to literature.<sup>52</sup>

## Synthesis of *N*-(Carboxyphenyl)-*N*'-

(8-pentadecyl)perylene-3,4:9,10-bis(dicarboximide)

Under argon atmosphere, a well-stirred mixture of *N*-(8-pentadecyl)perylene-3,4:9,10-tetracarboxylic acid monoimide monoanhydride (615 mg, 1.03 mmol), 4-aminobenzoic acid (0.98 g, 7.21 mmol), zinc acetate dihydrate (108 mg, 0.5 mmol), and imidazole (4 g) was heated at 180 °C for 2 h. After cooling to room temperature, the resulting solid was disaggregated with water and 1 M aqueous hydrochloric acid solution. The resulting precipitate was filtered, thoroughly washed with additional hydrochloric acid solution, water, and methanol. The collected solid was then dried under vacuum and purified by column chromatography (silica gel, dichloromethane/methanol 8/2) to afford *N*-(carboxyphenyl)-*N*'-(8-pentadecyl)perylene-3,4:9,10bis(dicarboximide), PDI-COOH, as a deep red solid in 68% yield with *m.p.* > 300 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta = 8.75$  (d, 2H, Pery), 8.69–8.64 (m, 6H, Pery), 8.10 (d, J = 8.8 Hz, 2H, Ph), 7.42 (d, J = 8.8 Hz, 2H, Ph), 4.94 (bs, 1H, -N-CH), 1.95–1.77 (m, 4H,  $-CH_2-$ ), 1.65–1.50 (m, 4H,  $-CH_2-$ ), 1.40–1.15 (m, 16H,  $-CH_2-$ ), 0.95–0.77 (m, 6H,  $-CH_3$ ).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  = 167.86 (C=0, w), 143.46, 139.68, 138.57, 136.26, 135.37, 135.30, 134.05, 133.14, 130.59, 127.92, 127.58, 127.11, 59.20 (-CH-N-), 36.60, 36.05, 33.74, 33.47, 31.24, 26.85, 18.22. FTIR (KBr, cm<sup>-1</sup>)  $\nu$  = 2952, 2922, 2850, 1698, 1658, 1594, 1579, 1343, 811. MS (FAB): 720 (M<sup>+</sup>, 45), 511 (M<sup>+</sup>-CH(C<sub>7</sub>H<sub>15</sub>)<sub>2</sub>, 100). Anal. Calcd. for C<sub>46</sub>H<sub>44</sub>N<sub>2</sub>O<sub>6</sub>: C: 76.63%; H: 6.16%; N: 3.89%; found: C: 76.42%; H: 6.36%; N: 3.56%.

## Synthesis of *N*-((Ethoxycarbonyl)phenyl)-*N*'-(8-pentadecyl)perylene-3,4:9,10-bis(dicarboximide)

Under argon atmosphere, a well-stirred mixture of *N*-(8-pentadecyl)perylene-3,4:9,10-tetracarboxylic acid monoimide monoanhydride (250 mg, 0.42 mmol), *n*-propyl 4-aminobenzoate (450 mg, 2.50 mmol), zinc acetate dihydrate (60 mg, 0.23 mmol) and imidazole (3 g) is heated at 180 °C for 2 h. After cooling to room temperature, the resulting solid is disaggregated with water and a 1-M aqueous hydrochloric acid solution. The resulting precipitate is filtered, thoroughly washed with additional hydrochloric acid solution, water and methanol. The collected solid is then dried under vacuum and purified by column chromatography (silica gel, dichloromethane/hexane 9/1) to afford *N*-((ethoxycarbonyl)phenyl)-*N'*-(8-pentadecyl)perylene-3,4:9,10-bis(dicarboximide) (PDI-COOR) as a deep red solid in 80% yield with *m. p.* > 300 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta = 8.72-8.64$  (m, 8H, Pery), 8.22 (d, J = 8.8 Hz, 2H, Ph), 7.53 (d, J = 8.8 Hz, 2H, Ph), 5.21 (bs, 1H, -N-CH), 4.37 (bs, 2H, -CH<sub>2</sub>-0), 2.29 (bs, 4H, -CH<sub>2</sub>-), 1.88 (bs, 6H, -CH<sub>2</sub>-), 1.25-1.09 (m, 16H, -CH<sub>2</sub>-), 0.95-0.77 (m, 9H, -CH<sub>3</sub>).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  = 163.50, 139.42, 135.75, 134.65, 135.32, 132. 34, 132.13, 132.09, 132.00, 129.73, 129.54, 129.44, 129.00, 128.88, 126.92, 126.58, 125.42, 124.77, 124.53, 124.16, 123.09, 67.46 (-CH<sub>2</sub>--0), 55.32 (-CH--N--), 32.70, 31.92, 30.17, 30.03, 27.64, 23.00, 22.82, 14.62, 11.92. FTIR (KBr, cm<sup>-1</sup>)  $\nu$  = 2925, 2856, 1702, 1660, 1591, 1344, 1260, 702. Anal. Calcd. for C<sub>49</sub>H<sub>56</sub>N<sub>2</sub>O<sub>6</sub>: C: 76.52%; H: 7.34%; N: 3.64%; found: C: 76.36%; H: 7.28%; N: 3.63%.

### **PVA-functionalization of PDI-COOH**

Samples of PVA esterified with different amounts of PDI-COOH in the feed were prepared (Table 1). The employed



SCHEME 2 Schematic representation of the esterification reaction of PVA with PDI-COOH.

esterification procedure for PDI-COOH was the following: different amounts of PDI-COOH (43, 35, and 11 mg for PVA-Pery1, 2, and 3, respectively) and 0.4 g of PVA (9 mmol equivalent to OH group) were suspended in DMSO (20 mL). The suspension was gently stirred and maintained at 70 °C under nitrogen for 2 h. Then, a solution of DCC (1.85 g, 9 mmol) and DMAP (0.135 g, 1.1 mmol) in DMSO (20 mL) were added, and the resulting mixture was stirred at 40  $^\circ\text{C}$ for another 3 days (Scheme 2). The coagulation of the product was accomplished by adding the suspension into 400 mL of methanol under vigorous stirring. The solid was filtered, washed with methanol, and dried at 50 °C under vacuum. To eliminate the remainings of nonreacted PDI-COOH, the product was redissolved in hot water, centrifuged at a high speed (16,000 rpm) during 1 h and the supernatant colored solution coagulated with methanol. The procedure was repeated twice.

The actual composition of the samples was calculated by using the N/C ratio from elementary analysis (Table 1). We suppose that the final product can be seen as a copolymer of VA and PDI-modified VA (Scheme 2). Thus, for PVA homopolymers, the N/C ratio is zero, and for PVAPery, the theoretical N/C ratio is  $4.9 \times 10^{-2}$ .

### **Physical and Analytical Methods**

The <sup>1</sup>H NMR spectra were recorded at 400 MHz on a Varian Inova 400 spectrometer at room temperature with dimethyl sulfoxide- $d_6$  (10 wt % solutions) as a solvent.

FTIR of the samples in the transmission mode were obtained in KBr pellets by using a Perkin–Elmer System 200 spectrometer with a 4  $\text{cm}^{-1}$  resolution.

XPS spectra were recorded using an Escalab 200R spectrometer (ICP-CSIC, Madrid) with a hemispherical analyzer operated on a constant pass energy mode and nonmonochromatized Mg K $\alpha$  X-ray radiation (h $\nu = 1253.6$  eV) at 10 mA and 12 kV. Data analysis was performed with the "XPS peak" program. The spectra were decomposed by the least-squares fitting routine using a Gauss-Lorentz product information after subtracting a Shirley background.

The thermogravimetric analysis (TGA) was done in a TGA Q500 equipment from TA instruments. Samples were dried under dynamic vacuum before the experiments and then placed in a platinum pan. The loss of weight was monitored from room temperature to 950 °C using a heating rate of 10 °C min<sup>-1</sup> in a nitrogen atmosphere.

The crystallization and melting behavior were investigated by DSC using a Mettler TA4000/DSC30. The experiments were carried out in nitrogen atmosphere by using  $\sim$ 5 mg of

sample sealed in aluminum pans. The samples were heated from room temperature to 240 °C, maintained at this temperature during 5 min, and then cooled to room temperature and heated again to 240 °C. The heating and cooling rates were 10 °C min<sup>-1</sup> in all cases. The transition temperatures were taken as the peak maximum in the calorimetric curves.

UV-vis absorption spectra were recorded on a Perkin–Elmer Lambda 40 spectrophotometer and photoluminescence spectra on a JASCO FP6200 spectrometer. For these measurements, 8 mg mL<sup>-1</sup> solutions of the PDI-modified polymer were prepared by using DMSO as solvent. Fluorescence quantum yields were measured using *N*,*N*'-(9-heptedecyl)3,4:9,10-perylenediimide as reference (quantum yield  $\sim$ 1) by means of the comparative method of Williams et al.<sup>51</sup>

Fluorescence spectra of films were measured with front-face geometry at angles of  $40^{\circ}$  and  $50^{\circ}$  to the excitation and emission beams, respectively. The holder position was that the scattered light was eliminated from the emission beam reaching the detector.

Elemental analysis was performed on a LECO CHNS-932 instrument.

#### **CONCLUSIONS**

We have demonstrated that PDI derivatives can be covalently linked to a biocompatible polymer. The incorporation of the chromophore alters remarkably the properties of the polymer. However, the immobilized PDI retains its interesting optical properties, showing photoluminescence in solution as well as in solid state. The fact that the products described here are water-soluble makes PVAPery promising as fluorescent labels for biologically active probes.

A natural extension of this research is to study the dependence of the optical properties on external parameters such as temperature, especially above the  $T_{\rm g}$  of the system. Also, it is our intention to compare these results with physical mixtures and, finally, study the possibility of using these materials as solid-sate lasers.

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