Articles

Synthesis and Chiroptical Characterization of an Amino Acid Functionalized Dialkoxypoly(*p*-phenyleneethynylene)

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ABSTRACT: 2,5-Dialkoxypoly(*p*-phenyleneethynylene) (**3**) functionalized with *N*-*t*-BOC-L-phenylalanine molecules was synthesized by Pd-catalyzed reaction of dioctyloxybis[(trimethylsilyl)ethynyl]benzene (**1**) with aromatic diiodide **2** linked to two amino acid units by six carbon atoms alkoxy chains. Optical properties were investigated both in solution and in the solid state (as thin films) by absorption, fluorescence and chiroptical spectroscopies (CD and CPL). Polymer **3**, that represents one of few fully characterized dialkoxy-substituted PAEs, is also the first example of a poly(aryleneethynylene) (PAE) with amino acidic chiral pendants.

Introduction

Poly(phenyleneethynylene)s (PPEs) and in general poly(aryleneethynylene)s (PAEs) are classes of conjugated polymers[1] with promising applications in the field of optics and electronics.[2] Fine-tuning of the semiconducting features by proper choice of substituents bound to the phenylene rings of main chain allows one to tailor these materials for specific applications. However, as a general rule, properties of organic semiconductors not only depend on the molecular structure but also are strongly influenced by supramolecular ordering and aggregation phenomena,[3] both in solution and in the solid state, which have to be carefully considered in designing novel materials. PPEs show propensity to form aggregates in solution of some solvents or solvent mixtures,[4] with strong influence on properties. A detailed spectroscopic study on the nature of these aggregates has been performed in the case of alkyl substituted PPEs[4a,d,e,h] and, more recently, also for alkoxy substituted counterparts.[4b,c,f,g,i,j] The introduction of chiral nonracemic alkyl[4d,e] or alkoxy[4f,g] groups as substituents in the PPE main chain has at least two consequences. In the first place it will break the symmetry of the PPEs preventing their tendency to form linear aggregates. Second, it gives the opportunity of investigating the structural features of these aggregates by means of chirooptical spectroscopic techniques.

In this respect, some classes of biological molecules represent easily available sources of enantiopure compounds. Indeed, PPEs functionalized with biomolecules such as monosaccharides,[5] oligonucleotides,[6] and biotine[7] have been reported in the literature, as potential semiconducting or highly fluorescent active materials in biosensing applications, but chirooptical studies on the aggregation processes in solution have not been performed. Natural α-amino acids (and their derivatives) have found widespread applications in the field of molecular recognition, owing to their ability to form labile interactions, often responsible for stereodiscriminating structures.[8] Their introduction in PAEs, which are polymers with a strong tendency to autoaggregation, would represent the first step toward novel complex molecular architectures, whose order may be modulated through the judicious choice within the variety of this class of chiral modifiers. Moreover, this passage may be further elaborated with development of PAEs bearing oligopeptides, proteins, and enzymes.

In the frame of our studies dealing with the development of organometallic methodologies for the synthesis of a variety of conjugated polymers,[9] we have recently reported poly(aryleneethynylene)s (PAEs) bearing glucose units as substituents, obtained by a modified Cassar−Heck−Sonogashira coupling reaction of suitable bis(trimethylsilyl)ethynyl arenes and aromatic dihalides[5b] and an application in devices for enantioselective sensing of chiral alcohols.[10]

Therefore, as a contribution in the field of PPEs with chiral biomolecules, we report herein the first synthesis of a poly(phenyleneethynylene) bearing protected amino acid moieties as side groups, linked to the PPE skeleton via oxaalkyl chains. Optical characterization carried out by absorption, fluorescence, and chirooptical techniques reveals aggregate formation typical of PPE systems both in solutions of solvent/nonsolvent mixtures and in solid thin films. The whole set of spectroscopic data allows us to formulate a hypothesis about the structure of the aggregates of alkoxy-substituted poly(aryleneethynylene)s, a class of materials that has been less systematically investigated so far, in comparison to the corresponding alkyl-functionalized

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counterpart. The presence of the chiral amino acid modifier introduces a twist, which seems to have relevant consequences in reducing fluorescence quenching due to aggregation.

Experimental Section

General Remarks. GC analyses were performed on a gas chromatograph equipped with a SE−30 (methyl silicone, 30 m × 0.25 mm i.d.) capillary column. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 500 MHz and at 125,7 MHz, respectively, using the residual proton peaks of $CDCl_3$ at 7.24 ppm as reference for ^{1}H spectra and the signals of $CDCl_3$ at 77 ppm for ^{13}C spectra. Molecular masses were determined with a Hewlett-Packard HP 1050 liquid chromatograph instrument using a Plgel 5μ Mixed-D 300 × 7.5 mm column, THF as the solvent and uniform polystyrene standards. All the solvents were distilled immediately prior to use. Tetrahydrofuran was distilled from benzophenone ketyl. Dichloromethane was distilled over P_2O_5. 2,5-Diiodohydroquinone (**4**),[11] 1,4-dibromo-2,5-bis(octyloxy)benzene (**6**),[12] and 1,4-bis[(trimethylsilyl)ethynyl]-2,5-bis(octyloxy)benzene (**1**)[13] were prepared as reported in the literature. Trimethylsilylacetylene, 6-bromo-1-hexanol, *N-tert*-BOC-L-phenylalanine, $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, Ag_2O, and CuI were commercial products.

Synthesis of 6-[4-(6-Hydroxyhexyloxy)-2,5-diiodophenoxy]-hexan-1-ol (5). A solution of 2,5-diiodo-hydroquinone (**4**) (1.80 g, 4.97 mmol) and NaOH (0.44 g, 11.00 mmol) in 2 mL of THF and 4 mL of DMF was stirred under N_2 atmosphere. After 20 min, 6-bromo-1-hexanol (2.93 g, 16.10 mmol) was added dropwise, and then the system was heated to 50 °C. After 48 h, the reaction was quenched by adding an aqueous saturated solution of NH_4Cl. The product was extracted with dichloromethane. The organic phases were washed several times with a solution of NaOH (10%) and water to eliminate unreacted reagents and DMF and then dried over anhydrous Na_2SO_4. The solvent was evaporated at reduced pressure. The crude product was washed with diethyl ether and the solid purified by means of a short column of silica gel using dichloromethane/petroleum ether (7:3) to elute byproducts and then ethyl acetate to elute 1.49 g (53% yield) of a white solid (mp: 78−81 °C). IR (KBr): ν 3401, 3293, 2938, 2902, 2863, 1626, 1487, 1464, 1392, 1351, 1215, 1058, 1024 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.35 (bs, 2H), 1.40−1.49 (m, 4H), 1.51−1.58 (m, 4H), 1.59−1.66 (m, 4H), 1.78−1.85 (m, 4H), 3.66 (t, 4H, J = 6.7), 3.93 (t, 4H, J = 6.3), 7.16 (s, 2H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 25.31, 25.77, 28.97, 32.44, 62.51, 70.07, 86.23, 122.66, 152.66 ppm. Anal. Calcd for $C_{18}H_{28}I_2O_4$: C, 38.45; H, 5.02, Found: C, 38.24; H, 4.98.

Synthesis of (*S*,*S*)-2-*tert*-Butoxycarbonylamino-3-phenylpropionic Acid 6-{4-[6-(2-*tert*-Butoxycarbonylamino-3-phenylpropionyloxy)hexyloxy]-2,5-diiodophenoxy}hexyl Ester (2). Triethylamine (0.33 g, 3.26 mmol) and DMAP (0.072 g, 0.59 mmol) were added to a solution of *N-tert*-BOC-L-phenylalanine (0.79 g, 2.98 mmol) and **5** (0.75 g, 1.33 mmol) in 10 mL of dichloromethane. The mixture was cooled to 0 °C, and isopropenyl chlorocarbonate (IPCC) (0.42 g, 3.48 mmol) was added dropwise under stirring for 10 min. After 60 min, ethyl acetate was added, and the organic phases were washed with an aqueous solution of potassium hydrogenosulfate (5%, 2 × 10 mL), then an aqueous solution of sodium hydrogenocarbonate (5%, 2 × 10 mL), and brine. The organic phases were dried over anhydrous Na_2SO_4 and the solvent evaporated at reduced pressure. The crude product was purified by chromatography on silica gel using petroleum ether/dichloromethane/ethyl acetate (8:2:2) as eluent obtaining 1.05 g (75% yield) of a dense yellow oil. IR (KBr): ν 3438, 3025, 2938, 2864, 1713, 1493, 1459, 1350, 1211, 1168, 1055, 756 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.32−1.40 (m, 4H), 1.42 (s, 18H), 1.48−1.56 (m, 4H), 1.59−1.67 (m, 4H), 1.75−1.83 (m, 4H), 3.02−3.20 (m, 4H), 3.92 (t, 4H, J = 6.4), 4.04−4.16 (m, 4H), 4.54−4.62 (bm, 2H), 4.98 (bd, 2H, J ∼ 8), 7.13 (d like, 4H, J ∼ 7), 7.17 (s, 2H), 7.23 (t like, 2H, J ∼ 7), 7.28 (t like, 4H, J ∼ 7) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 25.14, 25.35, 27.98, 28.06, 28.59, 38.03, 54.21, 64.87, 69.61, 79.28, 85.97, 122.31, 126.56, 128.11, 128.95, 135.84, 152.42, 154.71, 171.60 ppm. Anal. Calcd $C_{46}H_{62}I_2N_2O_{10}$: C, 52.28; H. 5.91; N, 2.65. Found: C, 52.53; H, 6.22; N, 2.65.

Synthesis of Polymer 3. Compound **1** (0.209 g, 0.396 mmol), Ag_2O (0.184 g, 0.794 mmol), **2** (0.419 g, 0.396 mmol), and $Pd(PPh_3)_4$ (0.046 g, 0.0398 mmol) were dissolved in 7 mL of anhydrous THF under nitrogen atmosphere. The mixture was stirred at 60 °C for 72 h. After evaporation of the solvent at reduced pressure, the crude product was extracted in a Soxhlet apparatus with methanol and hexane for 24 h, to eliminate low molecular mass fractions, and then with $CHCl_3$ to obtain a greenish solid (0.173 g, 37% yield). IR (KBr): ν 3441, 2927, 2856, 1715, 1496, 1427, 1391, 1366, 1275, 1213, 1169, 1023, 756 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (t like, 6H, J ∼ 7), 1.41 (s, 18H), 1.20−1.64 (m, 32H), 1.80−1.89 (bm, 8H), 3.00−3.12 (bm, 4H), 3.96−4.14 (bm, 12H), 4.51−4.60 (bm, 2H), 4.95−5.20 (bm, 2H), 7.02 (bs, 4H), 7.10−7.14 (bm, 4H), 7.20−7.30 (m, 6H), ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): 14.06, 22.61, 25.57, 25.95, 28.23, 28.43, 29.09, 29.26, 31.78, 38.40, 54.40, 65.21, 69.39, 69.67, 79.74, 91.50, 114.31, 117.35, 126.91, 128.43, 129.24, 136.01, 153.37, 153.49, 154.99, 171.88 ppm. Molecular weights: weight-averaged molecular mass M_w = 19 500 Da, number-averaged molecular mass M_n = 13 000 Da determined by gel-permeation chromatography with uniform polystyrene standards and THF as the solvent. Anal. Calcd For $C_{72}H_{98}N_2O_{12}$: C, 73.07; H, 8.35; N, 2.37. Found: C, 72.34; H, 7.85; N, 2.48.

Optical and Chiroptical Characterization. All samples of **3** were prepared by diluting concentrated solutions in chloroform, to a final concentration 0.26 mg/10 mL. Here, 1 cm path length cuvettes and cells were used. Absorption spectra were measured using a Perkin-Elmer Lambda 19 spectrophotometer; CD spectra with a Jasco J-710 spectropolarimeter (conditions: 20 nm/min scan, 2 nm bandwidth, 2 s response time); fluorescence and CPL spectra with a home-built instrument assembled by E. Castiglioni, constituted by a Jasco J-500-based excitation unit with a 150 W Hg/Xe lamp, a Jasco CT-10 emission monochromator, and a preamplified Jasco R376 detector (conditions: 313 nm excitation wavelength, 180° detection, 8 nm excitation bandwidth, 10 nm emission bandwidth, 20 nm/min scan, 2 s time constant). Correction of emission spectra for the self-absorption affected the shape of curves in Figure 4 only to a minor extent, with only the 500 nm band being slightly reduced in its relative intensity.

Results

Synthesis. The synthesis of **3** was performed by Pd-catalyzed cross-coupling reaction of the bis(trimethylsilyl)ethynyl derivative **1** with the suitable diiodoarene **2** in the presence of silver oxide[14] (Scheme 1).

This cross-coupling process has been reported to afford polymers with a lower amount of defects deriving from oxidative homocoupling reactions of the ethynyl derivative,[5b,14] compared to the classic Cassar−Heck−Sonogashira methodology, and it has already been successfully used for the synthesis of various PAEs.[5b,15] In our case, ^{1}H and ^{13}C NMR spectra of polymer **3** demonstrate the complete absence of butadiyne structural defects. Actually, the integration data related to the proton signals of the polymer shows that the two structural units derived from monomers **1** and **2** are present in a 1:1 ratio. Furthermore, the ^{13}C resonances of butadiyne carbon atoms at about 80 ppm are totally absent.

The molecular weights of polymer **3**, measured by GPC with uniform polystyrene standards and THF as the solvent, are M_w = 19500, M_n = 13000, corresponding to a medium polymerization degree DP = 13 and a narrow molecular weight polydispersity (I_p = 1.5).

Monomer **1** was prepared as reported in the literature.[13] The amino acid substituted monomer **2** was obtained in good yield

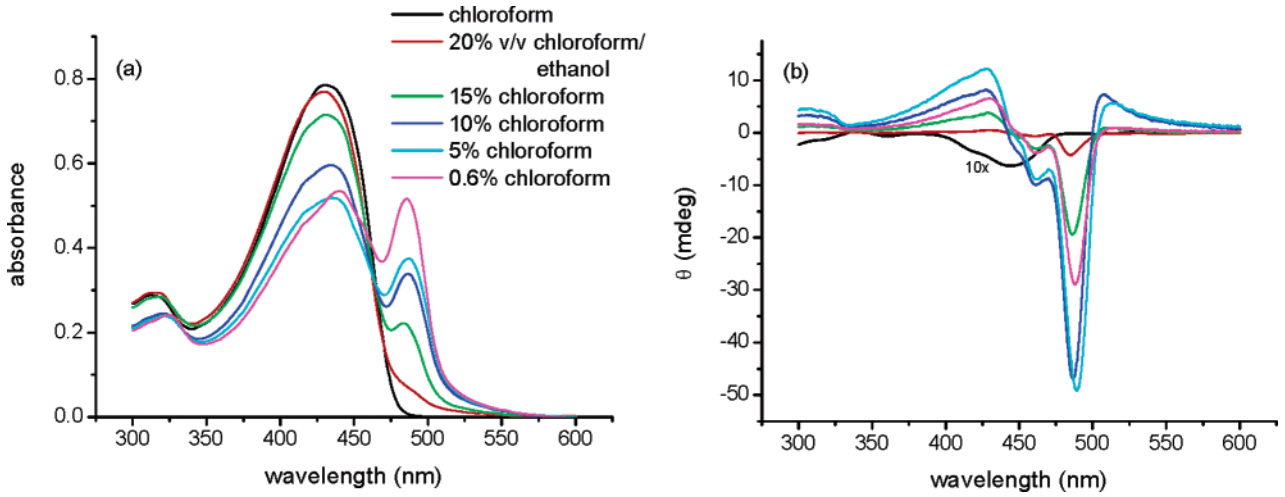
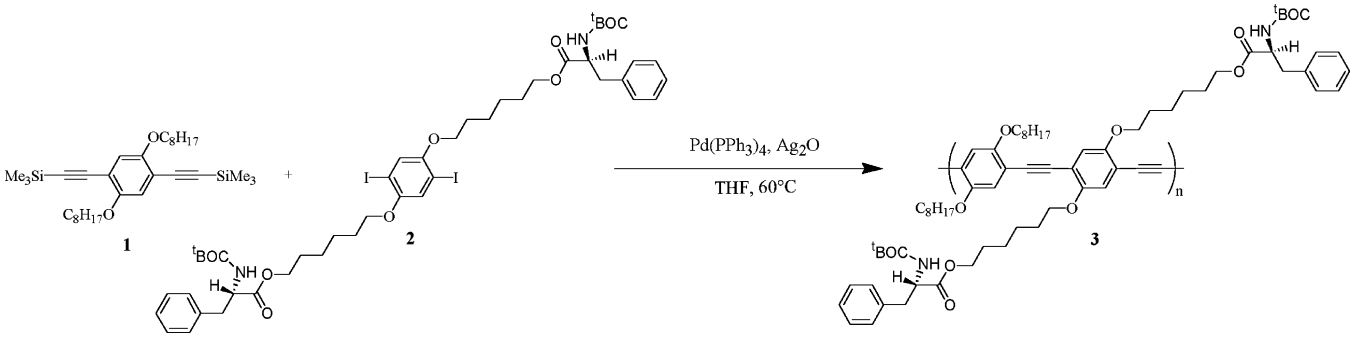
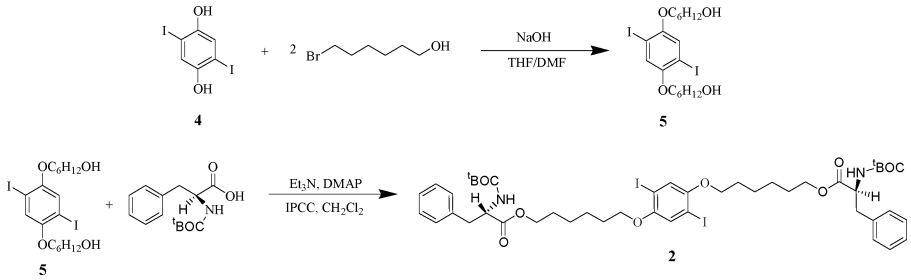


Figure 1. Absorption (a) and CD spectra (b) of **3** in various $CHCl_3$/ethanol mixtures; sample concentration 0.26 mg/mL, 1 cm cell.

Scheme 1. Polymerization Reaction



Scheme 2. Synthesis of Monomer 2



according to the synthetic steps reported in Scheme 2. The esterification reaction of diol **5** with the N-protected phenylalanine, performed using isopropenylchlorocarbonate (IPCC) as condensing agent, occurs without racemization of the amino acid unit.[16]

Optical and Chiroptical Characterization

When dissolved in solvent/nonsolvent mixtures, most poly(aryleneethynylene)s form aggregates and excimers which are usually detected by absorption and fluorescence spectroscopies.[2b,4a−c] Moreover, the presence of chiral pendants[4d−g] as in **3** opens the way to the investigation by chiroptical spectroscopies such as circular dichroism (CD) and circularly polarized luminescence (CPL). The absorption spectrum of **3** in chloroform shows a broad $\pi-\pi^*$ conjugation band with maximum at 430 nm (Figure 1a), in keeping with other 2,5-dialkoxy-substituted PAEs.[2b,4c,f,g] Upon addition of ethanol as a nonsolvent, a manifest solvatochromism is observed: the main band is progressively reduced and red-shifted, and its shape becomes partially structured; moreover, a new, sharp band appears at 483−486 nm which may be assigned to aggregated species dispersed in solution.[2b,4a−d,g,h] Switching from ethanol to different nonsolvents such as methanol, hexane and acetonitrile resulted in similar absorption spectra; in all cases, a minimum amount (0.6%) of $CHCl_3$ was necessary to maintain the solubility required for recording the spectra.

The consequences of aggregation promoted by nonsolvent addition are especially evident in the CD spectra. In chloroform, **3** exhibits a weak negative CD band centered at 444 nm (Figure 1b), with anisotropy g factor [$g = \Delta\epsilon/\epsilon = \theta/(33000A)$, where θ is the ellipticity in mdeg and A the absorbance] around -2×10^{-5}, allied to the electric-dipole allowed transition of the π-conjugated chromophore perturbed by chiral groups at a remote position. Upon aggregation, this weak mono-signed CD is replaced by a complex +/−/−/+ pattern of bands, whose intensities progressively increase passing from 80 to 95% ethanol content; the two strongest bands are the positive one at 428 nm, $g \approx +7 \times 10^{-4}$, and the negative one at 486-489 nm, $g \approx -4 \times 10^{-3}$ (computed for the spectrum in 5% chloroform, Figure 1b). Both the overall appearance of CD spectra and g values for the aggregates compare well with those reported for

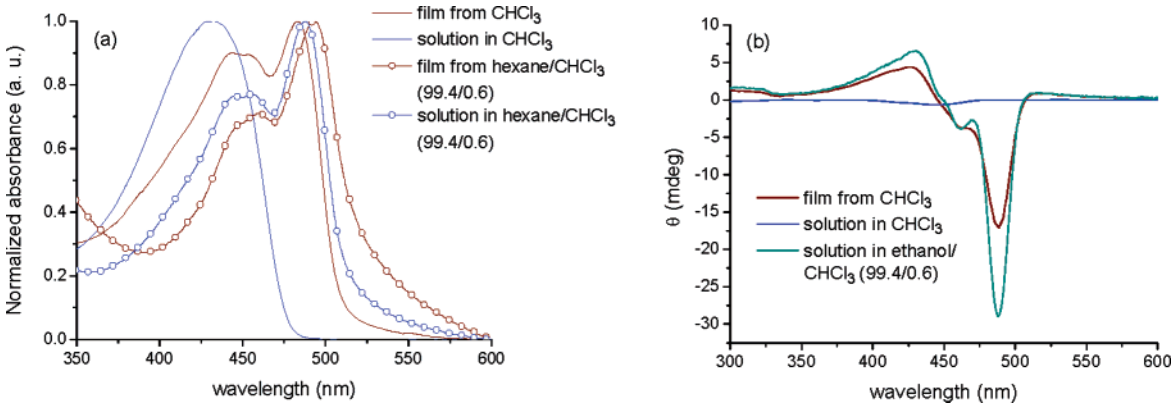


Figure 2. Absorption (normalized) (a), and CD spectra (b) of **3** in solutions and corresponding films.

some other dialkyl-[4d] and dialkoxy-substituted[4g] PPEs in solvent/nonsolvent mixtures.

When hexane was used as the nonsolvent, the aggregates spontaneously precipitated within 30 min from dissolution of the polymer, forming a film on the cell walls. The film precipitated from chloroform-hexane (0.6/99.4) solutions showed a UV−vis spectrum very similar (Figure 2a) to the spectrum recorded in solution before the precipitation. On the contrary, thin film cast from chloroform showed absorption spectra (Figure 2a) different from those of the solution in the same solvent, and more similar to those obtained from aggregates suspended in, or precipitated from, nonsolvent rich mixtures, apart from some differences in the relative intensities of the two main absorptions (Figures 1a and 2a). Similarly, CD spectra of films spun from chloroform resemble those of aggregates suspended in nonsolvent rich mixtures (0.6% chloroform in ethanol) and strongly differ from those recorded in chloroform solutions (Figure 2b). These observations suggest that intermolecular interactions leading to aggregate formation in solvent/nonsolvent mixtures are similarly at work also in the thin films cast from chloroform.

In accordance with the spectral discrepancies between the thin films spun from chloroform and precipitated from hexane/chloroform, AFM images (Figure 3) show some differences in the morphology of the thin films. The former appears more amorphous, with surface roughness RMS = 0.27 nm (Figure 3a), and shows evidences of incipient aggregates, while the presence of embedded aggregates of about 90 nm diameter is evident in the latter (Figure 3b), resulting in a rougher surface (RMS = 0.53 nm). Most likely, in the film cast from chloroform incipient aggregates should have formed directly on the substrate upon solvent evaporation while aggregates grown in solution before the precipitation are present in the film obtained from the solvent-nonsolvent mixture.

The photoluminescence spectrum of **3** in chloroform (Figure 4), upon excitation at 313 nm, displays a main emission band at 486 nm with a long-wavelength (probably vibronic) shoulder. The observed Stokes shift with respect to the main absorption band is 56 nm, a somewhat large value in the dialkoxy−PAE family.[2b] Increasing ethanol percentage causes hypochromism and blue-shift down to 467 nm (34 nm Stokes shift) of the main emission band, plus the appearance of a new band at 502 nm, which can be assigned to aggregated species. As the ethanol concentration is increased, the relative intensity of the two bands changes in favor of the 502 nm one, because of the increased relative concentration of the aggregated form, while the non-aggregate band is progressively blue-shifted according to a concentration-dependent shift already observed in alkoxy−PPEs.[4i] The most striking result of nonsolvent addition is however a marked depression of the overall fluorescence intensity, due to the well-known[4g] quenching side-effect of aggregation of conjugated polymers.

CPL represents a useful technique for investigation of chiral polymers,[17] but applications to PAEs remain rare.[4e] We recorded CPL spectra of **3** in the same conditions used for photoluminescence (see Supporting Information). Both emission transitions at 467−486 and 502 nm are allied with negative CPL effects, in apparent accord with, respectively, the 444 nm CD band in chloroform and the most intense CD band at 486-489 nm in nonsolvent rich solutions. The intensity, shape and solvent dependence of CPL parallel the total emission signal and, in

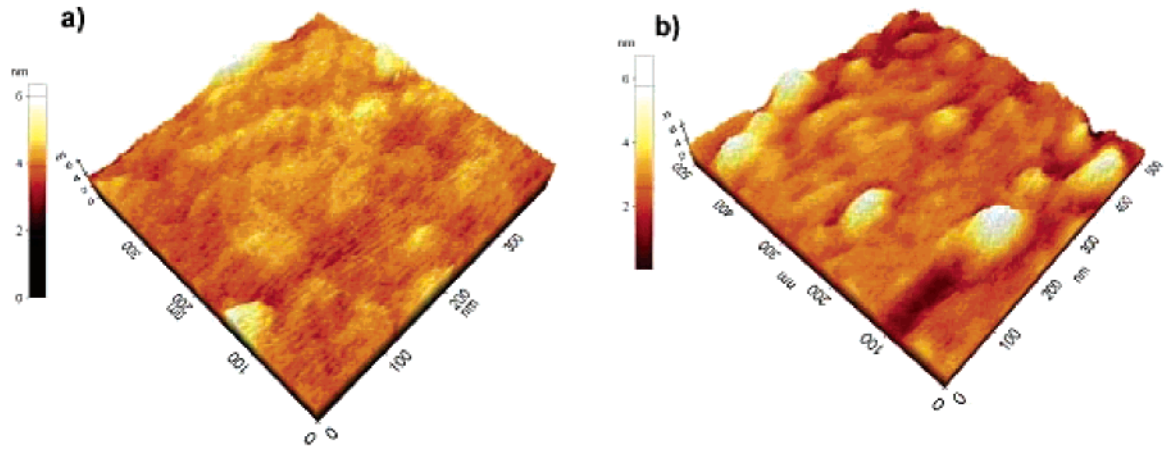


Figure 3. AFM images of thin films of **3**: (a) film cast from chloroform solution; (b) film deposited from hexane/chloroform mixture (99.4/0.6)

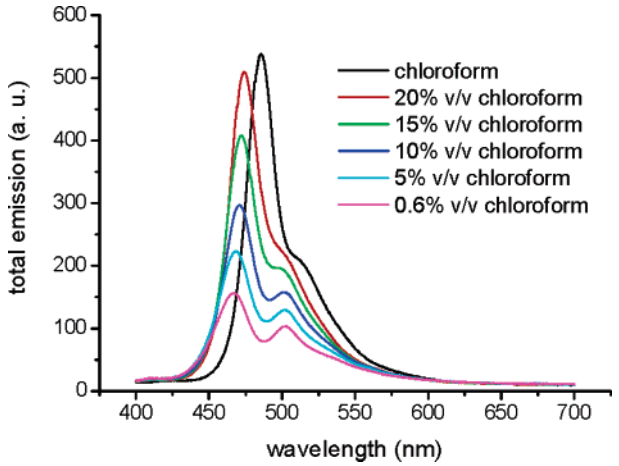


Figure 4. Total emission of **3** upon 313 nm excitation in various $CHCl_3$/ethanol mixtures: sample concentration 0.26 mg/mL; 1 cm cell.

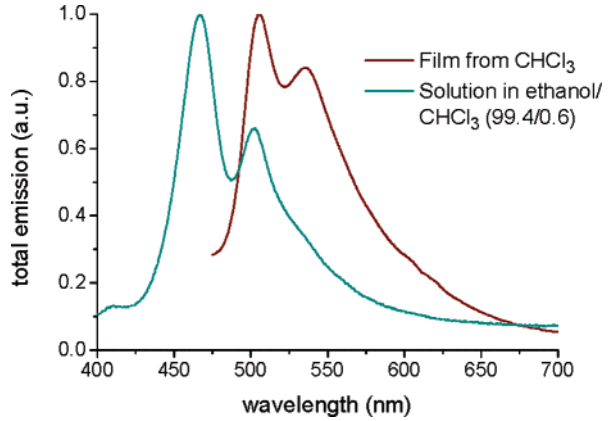


Figure 5. Total emission upon 313 nm excitation of **3** aggregated in solution and as a film.

the current case, they do not seem to offer further structural information.

In Figure 5, the emission spectrum of the film cast from chloroform is reported in comparison with the emission spectrum in 99.6% ethanol. Despite the trend observed upon nonsolvent addition in Figure 4, it is noteworthy that the fluorescence is diminished but not completely quenched both in the nonsolvent rich solutions and in the thin film. While the spectrum in ethanol results from the superimposition of the contributions due to nonaggregated and aggregated species as discussed above, only the emission of the aggregated species is detectable in the thin film, characterized by the red-shifted emission band with a maximum at 505 nm showing a well-resolved vibronic replica at 535 nm. This is faintly visible as a shoulder around 535 nm in the aggregate emission band in ethanol with maximum at 502 nm. The red-shift of about 20 nm for the solid state emission (film from chloroform) compared to the emission from chloroform solution (Figure 4) is comparable to that previously reported for alkoxy-substituted PPE.[4f]

Discussion

Absorption, CD, fluorescence, and CPL spectra demonstrate that phenylalanine-appended polymer **3** undergoes extensive aggregation in solvent/nonsolvent (chloroform/ethanol) mixtures, starting from a minimum 80% amount of nonsolvent. Aggregation-dependent solvatochromism upon nonsolvent addition is a well-known phenomenon for poly(aryleneethynylene)s:[2b,4a−d] however, the few chiral alkoxy-substitued PAEs characterized so far display discordant behavior depending on the materials attributes. For example, Scherf et al.[4f] and Swager et al.[4g] have described two similar 2-(*S*)-methylbutoxy-appended PPEs which, mainly as a function of the molecular weight, exhibit either only a modest effect upon nonsolvent addition (with M_n = 10000, DP = 37)[4f] or, on the contrary, a distinctive solvatochromism (with M_n > 12000, DP≥ 44)[4g] similar to that of our polymer **3**. In this respect, it must be stressed that **3** manifests a marked tendency to aggregation at a much lower DP (M_n = 13000, which corresponds to DP = 13). It must be considered, however, that in the case of polymer **3** the repeating unit consists of two aromatic rings and two triple bonds, due to the different substitutions of the two phenylene units. Therefore, DP = 26 has to be calculated for a correct comparison, taking into consideration only one phenyleneethynylene moiety per repeating unit. Nonetheless, this value is still lower than those of the aforementioned polymers. This suggests a more pronounced tendency to form supramolecular aggregates of PAEs induced by amino acid side groups compared with simple alkoxy substituents, reasonably due to stronger intermolecular interactions between polar protected amino acid moieties.

Both solution aggregates and thin films of **3** display a strong, narrow and red-shifted absorption band around 485 nm (Figures 1a and 2a) which has been similarly found in analogous systems;[2b,4a−e,g,h] its origin has been long disputed, as it may result in principle from two different phenomena.[4h] While the small torsional barrier around the arene-alkynyl bond normally allows free rotation between aryleneethynylene moieties, the packing of polymer chains in the aggregates may force them to assume a more coplanar conformation; thus, a single-molecule (or intramolecular) effect could be responsible of both the red-shifted position (due to increased conjugation) and narrow shape (due to conformational locking) of the aggregate-induced band. In addition, however, the same packing phenomena may improve the electronic communication between polymer chains, and π-stacking may result in charge-transfer transitions; the aggregate band would then follow from an intermolecular mechanism like that involved in charge transport in organic films.[18] Bunz et al. have calculated that, for alkyl-substituted PPEs, the expected red-shift of the main absorption band due to aggregate-induced planarization may fully account for the observed wavelength shift of absorption maxima in chloroform and chloroform/nonsolvent mixtures (around 0.4 eV);[4h] therefore, they concluded that any other—i.e., intermolecular—mechanism does not need to be invoked. In the view of the strong spectral similarities between our polymer **3** and many alkyl−PPEs, including those of Bunz et al.,[4a,d,e,h] it would be tempting to assume a similar interpretation for the origin of aggregate-induced band at 485 nm, red-shifted by 0.33 eV with respect to the maximum in chloroform; however, it must be stressed that several recent reports of dialkoxy−PPEs have argued against the above explanation.[4b,c,g,j] In fact, the evolution of the main absorption band upon ethanol addition, in terms of a small progressive red-shift (from 432 to 440 nm) and change in shape (particularly evident for the thin films spectra, Figure 2a) may be itself well justified as the consequence of the conformational locking and planarization following aggregation (while its hypochromism is probably due to the augmented solvent polarity); on the contrary, the sudden appearance and position of the 485 nm band apparently points to the occurrence of interchain electronic interactions,[4b,c] which also clearly emerges from the analysis of CD spectra.

With respect to the weak CD spectrum exhibited by nonaggregated **3** in chloroform, the CD of its aggregates in nonsolvent

rich solutions and in thin films is characterized by 2 orders of magnitude larger g factors (Figures 1b and 2b). This attribute must be related to the onset of very effective mechanisms generating optical activity in the aggregates. In particular, in some analogy with what recalled concerning absorption spectra, one may invoke different types of intramolecular and/or intermolecular mechanisms.[4d,g] The first is the rise of intrinsic chirality of single helically twisted chains, as a conformational consequence to the hindered rotation around the alkyne units induced by chain packing (intramolecular mechanism); for a hypothetical isolated electronic transition, the intrinsic chirality mechanism would produce a CD band in close wavelength correspondence with the absorption band. The second possible mechanism is the exciton coupling between packed and chirally oriented polymer chains, within the whole aggregate or some determinate domains (an intermolecular mechanism); the exciton coupling mechanism would manifest itself with a more or less symmetric CD-couplet (i.e., two oppositely signed bands of comparable absolute intensity and zero-point in correspondence with the absorption maximum). Third, charge-transfer transitions may occur between packed polymer chains (still an intermolecular mechanism); if so, the same supramolecular chiral aggregation responsible for the exciton coupling would confer these transitions, if sufficiently intense, nonnegligible rotational strengths. Conclusive interpretation of the complex CD spectra in Figure 1b is not easy. However, a qualitative justification may be tried in the light of the three discussed mechanisms and with reference to the existing literature. Each of the three mechanisms alone may well justify g factors around 10^{-3}; however, only a combination of at least two of them may account for the appearance of the CD spectra of the aggregated species. At a first approximation, these can in fact be described as the superimposition of a strong negative band centered at 487 nm, in correspondence with the narrow absorption band at the same wavelength, above a negative couplet-like feature having positive branch with maximum at 427 nm and zero-point (or inflection) around 440 nm, in correspondence with the absorption band with maximum at 440 nm in Figure 1a (spectrum in 99.4% ethanol). In other words, the exciton coupling between $\pi-\pi^*$ transitions of various polymer chains in the aggregates contributes to the 440 nm absorption band, and it is responsible for the corresponding negative couplet in the CD spectra. Concerning the narrow absorption and CD bands at 484−487 nm, these must be associated with electronic transitions distinct from those responsible for the exciton-coupled features. Two possibilities then exist: either they arise from a charge transfer-type transition of the conjugated (and also exciton-coupled) chromophores,[18a] or they are allied to some polymer chains confined within separate domains, which assume an elongated helical shape endowed with extended conjugation[4h] and intrinsic chirality. A sole exciton origin of the whole CD spectra of the aggregates (Figure 1b, from 15 to 0.6% chloroform), as proposed by Swager et al.,[4g] is unlikely in view of their strong asymmetry: the proportion between the integrals of negative and positive bands amounts to about 1:0.6; instead, almost 1:1 proportion is found in the CD spectra of polymers clearly dominated by the exciton coupling mechanism.[19] In fact, the chiral dialkoxy−PPEs with low M_n described by Scherf et al.,[4f] which are less prone to aggregation than **3**, give CD spectra very close to a "classical" exciton couplet. In conclusion, we propose that the red-shifted CD-active transition distinctive of aggregates of **3** arises from strongly interacting polymer chains packed in a fashion endowed with supramolecular handedness. In fact, it is likely that adjacent poly-

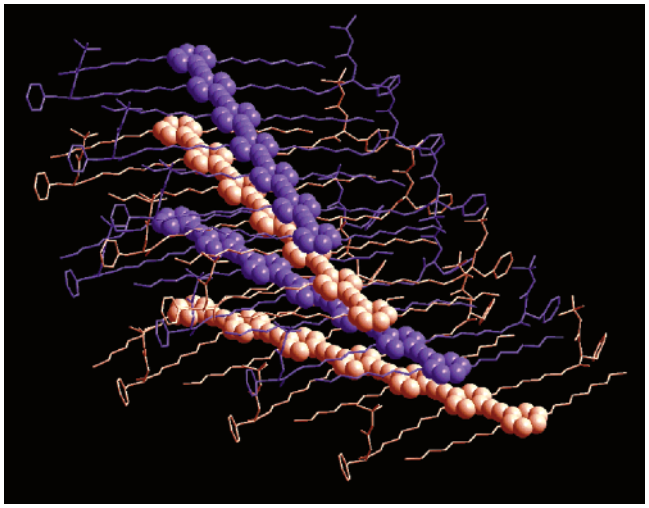


Figure 6. Pictorial model of aggregated chains of **3** evidencing supramolecular chirality adopted by the polymer backbones (represented with spheres).

(aryleneethynylene) chains in aggregates reach short intermolecular distances[4i,20] allowing for a nonnegligible interchromophoric orbital overlap responsible for improved electronic communication,[18] including charge-transfer transitions. A pictorial representation of stacked layers of polymer chains compatible with our reasoning is shown in Figure 6, based on similar models[4g] and on known solid-state structures adopted by PPEs.[4i,20] The fact that the sample with the lowest chloroform content (0.6%, see Figure 1b) shows CD signals actually weaker than two intermediate samples (5−10% chloroform) may be due to a reduced supramolecular chirality adopted by tightly packed polymers, as suggested by Swager.[4g]

In contrast with transmission-based spectroscopies, the evolution of emission (Figure 4) and CPL (see Supporting Information) spectra upon aggregation of **3** is much less remarkable; in fact, addition of nonsolvent causes an overall drop of total and circularly polarized emission signals due to fluorescence quenching in the aggregated state. We notice however that even in the most nonsolvent rich samples (0.6% chloroform), as it is in thin films, fluorescence is not completely quenched, instead, it is reduced to about 30% intensity compared to the sample in chloroform (Figure 4), a fact which may have relevant implications in the development of fluorescent devices based on materials similar to **3**.[4g] Concerning the origin of the aggregate emission band at 500 nm, following the arguments of a recent report,[4j] we may also observe that since aggregates are already present in the ground state (as easily detected by absorption and CD spectroscopies), excimer formation needs not to be invoked in the current case. Interestingly enough, the corresponding CPL signal is also weak due to the diminished quantum efficiency; therefore, no especially strong mechanism of excited-state optical activity seems to be effective for the aggregates. This is opposite to what is seen for the ground-state optical activity sensed by CD, where intense bands result from the aggregation. The CPL activity of thin films of **3** may also find application in novel optoelectronic devices, taking advantage not only of the total emission but also of its circular polarization.

Conclusions

We have synthesized by an operatively simple organometallic methodology a PPE copolymer containing a regular alternation of monomeric units substituted with simple alkoxy chains and

with amino acid units linked to the aromatic ring via an alkoxy linkage. Besides affording the first example of PPE substituted with amino acid units, in principle this approach could be extended to more complex systems functionalized with peptides. The optical properties of the polymer in solution of various solvents and in the solid state have been investigated in detail, using absorption fluorescence spectroscopy and chirooptical techniques. Under this respect, our study represents a progress in the interpretation of the optical behavior of alkoxy-substituted PPE systems, which have been less systematically investigated compared to alkyl-substituted analogues. Despite its reduced degree of polymerization, phenylalanine-appended polymer **3** reveals a remarkable tendency toward aggregation in nonsolvent rich solutions; at the same time, fluorescence is only reduced and not completely quenched in aggregates and films. These facts demonstrate how a proper choice of the chiral pendants can be exploited to modulate supramolecular interactions to a great extent, with the aim to tune material properties. Optical and chiroptical features of thin films of **3** are comparable with those of aggregates dispersed in solution, in accordance with similar mechanisms of supramolecular interactions between polymer chains occurring in the two states.

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Supporting Information Available: Figure S1, showing CPL spectra of **3** in chloroform and chloroform/ethanol mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

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