A Novel L-Tyrosine Derivative of Poly[(fluoren-2,7-diyl)-*alt-co*-(benzen-1,4-diyl)]: Strategy of Synthesis and Chiroptical and Electrochemical Characterization

R. Molina,[†,‡] M. Ramos,[‡] F. Montilla,[†] C. R. Mateo,[†] and R. Mallavia*[,†]

Instituto de Biología Molecular y Celular (IBMC), Universidad Miguel Hernández, Campus de Elche, Edificio Torregaitán, D-0.4, Av. del Ferrocarril, s/n, Elche 03202, Alicante, Spain, and Dpto. de Tecnología Química y Ambiental, Universidad Rey Juan Carlos, 28933 Madrid, Spain

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ABSTRACT: A novel optically active conjugated copolymer of fluorene and phenylene units, modified by tyrosine derivative, was synthesized. Two different methods were probed: Suzuki cross-coupling of chiral monomer and post-modification over halogenous precursor polymer. Only the first strategy was successful in affording the chiral derivative copolymer, while the post-modification route by substitution fails, even into large scale reactions. All monomers and polymers were elucidated and characterized by NMR and FTIR spectrocopies. Molecular weights of the polymers were measured by coupled size exclusion chromatography−evaporative light scattering detector with typical polydispersity values. The optical and chiroptical properties of the new conjugated tyrosine derivative of polyfluorene were studied in a mixture of solvents, where exhibit a significant Cotton effect with respect to the precursors. Fluorescence emission of polyfluorenes was analyzed as a function of different polarity surrounding. Electrochemical doping and degradation studies of new chiral polymer were also performed.

Introduction

Poly(dialkylfluorene) and its derivatives have been revised and classified such that it has become one of the most highly studied and more efficient blue emitters in widely investigated organic devices.[1−5] Thereafter, the research for novel fluorene-based polymer materials with improved properties represents a continuing challenge, and an extensive variety of copolymers were reported and tested in different electrooptical devices.[6−16] Versatile and facile substitution of the remote C9 position provides the possibility of improving the solubility and processability of polymers without significant increase of the steric interactions in the polymer backbone. Polyfluorenes with various functional groups, such as ammonium,[17−20] sulfonic,[21,22] phenol,[23,24] imidazole,[25] phosphonate,[26] and carbohydrates groups,[27] have been reported. A good number of these copolyfluorenes carrying ionic or chiral substituents have attracted much attention because of their potential optolectronic and biological applications, in molecular recognition, such as chemical and biological sensors.[28−30] In this context, the exchange produced by specific groups will provide interesting and unique optical and electronic properties, induced by supramolecular assemblies.[31,32] On the basis of these properties, chiral polymers may be considered and used for the fabrication of polymeric polarized light-emitting devices.

The aim for the present work was to synthesize a new class of optically active conjugated fluorene-based polymers using enantiomerically pure chiral side chains introduced by substitution at the remote C9. Here, we report the synthesis, characterization, and photophysical properties of a novel optically active fluorene copolymer. The Suzuki cross-coupling polymerization has been used in the chemical design to synthesize the chiral polymer, as well as a different strategy based on polymer post-modification, which was evaluated in order to obtain the identical polymer (Scheme 1). The effect of the amino acid end group on the optical and electrochemical properties of the chiral conjugated copolymer has been also investigated.

Experimental Part

General Remarks. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 spectrometer, with tetramethylsilane as an internal reference. FTIR spectra were obtained using a Nicolet model 520P spectrometer with samples prepared as KBr pellets. Optical rotations were recorder on a Perkin-Elmer 241 MC polarimeter, lineally polarized by sodium lamp as light source and DMSO as solvent, at 24 °C. Coupled size exclusion chromatography (SEC) and light scattering measurements were carried out using a HP-1090 liquid chromatograph with autosampler, autoinjector and light scattering detector; ELSD 2000 Alltec. The size exclusion chromatogram was carried out in THF as eluent and data were calibrated using Polymer Laboratories EasiCal PS standards using two column PLGel 5 μm MIXED-C at room constant temperature (see Supporting Information).

Optical and Chiroptical Measurement. Absorption and circular dichroism (CD) spectra of the polymers were recorded in different solvents using a Shimazdzu 1673 spectrophotometer and Jasco J-810 spectropolarimeter, respectively. CD experiments were performed using a quartz cell with a 1 mm path length. Four scan were taken for each sample from 260 to 450 nm at a 50 nm $\times$ min^{-1} and all experiments were completed at a constant temperature of 20 °C. Normal and polarized emission spectra were recorded in a PTI Quantum Master-4 spectrofluorimeter at 90° detection angles Excitation and emission wavelengths are selected by means of auto-calibrated, computer-controlled by FeliX32TM Software package. Corrected steady-state fluorescence emission was performed using low absorption solutions. Anisotropy measurements, recorded in range 380−650 nm of emission, were carried out using Glan-Thompson polarizers controlled automatically. Titration experiments were performed using a stock solution of polymers 0.3 mM (0.17 mg/mL from polymer **5** in chloroform and 0.28 mg/mL from polymer **4** in ethanol). Samples solutions were prepared using 0.1 mL of stock solution by constant volume addition to initial

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[†] Instituto de Biología Molecular y Celular (IBMC), Universidad Miguel Hernández.

[‡] Dpto. de Tecnología Química y Ambiental, Universidad Rey Juan Carlos.

* To whom correspondence should be addressed. E-mail: r.mallavia@umh.es. Telephone: +34-966 658 941. Fax: +34-966 658 758.

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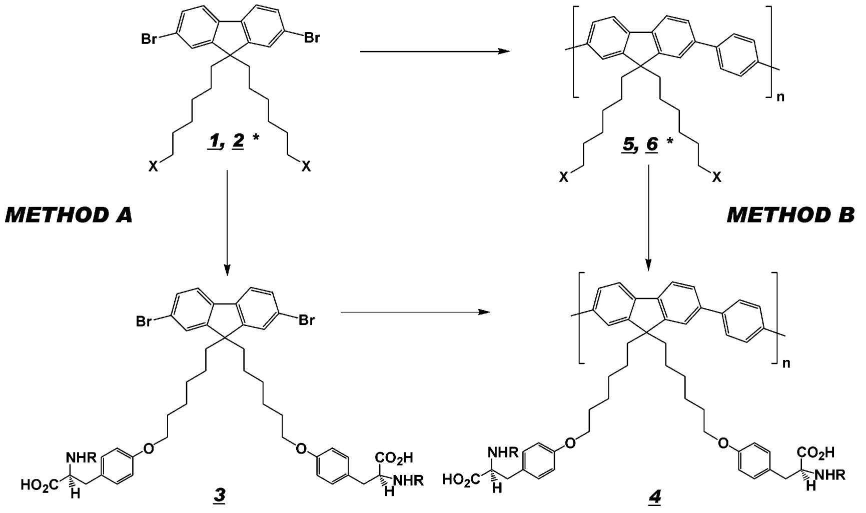
Scheme 1. Synthetic Strategy for the Poly[(9,9′-bis(6″-*N*-acetyltyrosinehexyl)fluorenephenylene)], (4)[a]



[a] Key: The asterisk indicates monomer-X = −Br (**1**), −I (**2**); polymer-X = −Br (**5**), −I (**6**).

2.0 mL just to final volume 4.0 mL in a square Hellma quartz cell (1 × 1 cm). Polymer concentrations were between 1.6 and 0.8 μM (by monomer unit) and solutions were stirred to obtain homogeneous media with a constant temperature, at 25 °C. The integrated area of the fluorescence emission obtained (380−650 nm) was corrected with the corresponding concentration of the polymer studied with appropriate subtraction of the blanks. Polarity surrounding was estimated with tabulated parameters of pure solvents, $E_T(30)^*$, collected by the Catalan group.[33] These values from pure solvent (ethanol, chloroform, and hexane) and the mixture of the solvents were obtained by taking into account and assuming the additive properties; see Supporting Information for details.

Electrochemical Measurement. Cyclic voltammograns were performed with Wenking POS2 potentiostat at a constant sweep rate of 0.1 V s^{-1}. The solvent employed for electrochemical measurement was acetonitrile, and tetrabutylammonium tetrafluoroborate (TBA) was used as the supporting electrolyte. The working electrode was an ITO-glass covered with polymer (drop-cast). A platinum wire was employed as the auxiliary electrode, and the potentials are referred to an Ag/AgCl (3 M KCl) electrode immersed in the same solutions.

Materials. For chemical reaction and electrochemical analysis, all solvents were used as received, without further purification, and were HPLC grade. For optical measurements the solvents were spectroscopy grade (Merck). All starting materials and reagents were purchased from Aldrich Corp.

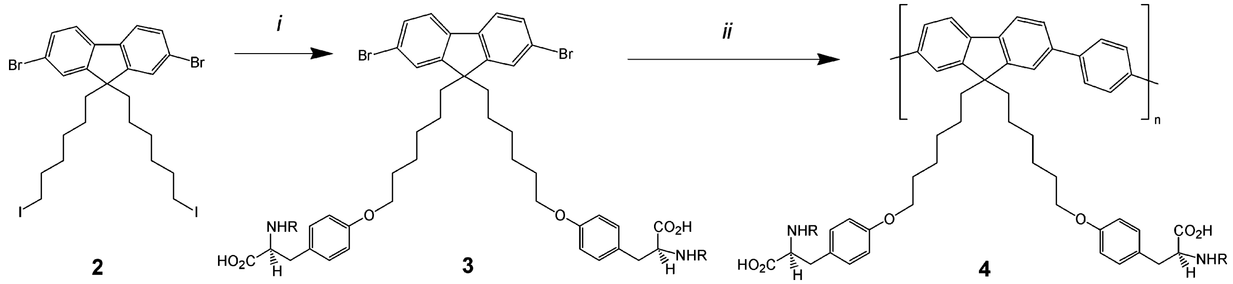
Synthesis. 2,7-Dibromo-9,9′-bis(6″-bromohexyl)fluorene (1), was obtained by transfer catalyst reaction in two phases (1:1 water and 1,6-dibromohexane) according to previous procedure.[18]

2,7-Dibromo-9,9′-bis(6″-iodohexyl)fluorene (2). To a mixture of 2,7-Dibromo-9,9′-bis(6″-bromo-hexyl)fluorene, **1**, (5.0 g, 7.1 mmol) in 50 mL of acetone was added potassium iodide (7.0 g, 42.3 mmol). The reaction mixture was heated at 45 °C for 24 h. The cooled mixture was extracted, with workup in chloroform (2 × 75 mL). The organic phase was washed with water (2 × 100 mL) and brine (2 × 100 mL) and was dried over $MgSO_4$. The solvent was evaporated to afford a white solid (4.6 g, 6.2 mmol). Yield: 87%. ^{1}H NMR ($CDCl_3$): δ = 7.53−7.43 (m, 6H, Ar), 3.07 (t, J = 6.7 Hz, 4H, CH_2(6)), 1.91 (m, 4H, CH_2(1)), 1.63 (qt, J = 6.7 Hz, 4H, CH_2(5)), 1.16 (qt, J = 6.5 Hz, 4H, CH_2(4)), 1.07 (qt, J = 7.4 Hz, 4H, CH_2(3)) and 0.59 ppm (m, 4H, CH_2(2)). ^{13}C NMR (($CDCl_3$): δ = 7.3 (CH_2(6)), 23.5 (CH_2(2)), 28.8 (CH_2(4)), 30.2 (CH_2(3)), 33.4 (CH_2(5)), 40.1 (CH_2(1)), 55.6 (C Fluorene), 121.4 (CH_{Ar}), 121.7 (C_{Ar}), 126.2 (CH_{Ar}), 130.5 (CH_{Ar}), 139.2 (C_{Ar}), and 152.3 ppm (C_{Ar}). IR (KBr): 3430, 2926, 2854, 1464, 1416, 1397,-1168, 1060, 1005, 873, 817, 751, 665, 595, 503 (−CH_2−I), 435 cm^{-1}.

2,7-Dibromo-9,9′-bis(6″-*N*-acetyltyrosinehexyl)fluorene (3). To a mixture of *N*-acetyltyrosine (4.8 g, 21.5 mmol) in 20 mL of DMSO, potassium carbonate (6.0 g, 43.0 mmol) was added. The solution was stirred at room temperature for 15 min. To this solution was added a solution of 2,7-dibromo-9,9′-bis(6″-iodohexyl)fluorene, **2**, (1.6 g, 2.2 mmol) in 10 mL of DMSO. The reaction mixture was stirred at room temperature overnight under N_2 atmosphere. The mixture was extracted workup in ethyl acetate (2 × 75 mL). The combined organic layer was washed with water (2 × 100 mL) and brine (2 × 100 mL) and was dried over $MgSO_4$. The solvent was evaporated to afford a colorless oil (1.8 g, 1.9 mmol). Yield: 90%. ^{1}H NMR ($CDCl_3$): δ = 7.90 (bs, 2H, COOH), 7.50 (d, J = 7.9 Hz, 2H, Ar), 7.43 (s, 2H, Ar), 7.42 (d, J = 1.8 Hz, 2H, Ar), 6.89 (d, J = 8.4 Hz, 4 4H, Ar Tyr); 6.71 (d, J = 8.4 Hz, 4H, Ar Tyr), 6.27 (d, J = 8.0 Hz, 2H, NH), 4.78 (m, 2H, CH Tyr), 3.98 ("t", 4H, CH_2(6)), 3.01 and 2.92 (2 × m, 4H, CH_2 Tyr), 1.94 (s, 6H, CH_3CO), 1.91 (m, 4H, CH_2 (1)), 1.41 (m, 4H, CH_2(5)), 1.06 (m, 8H, CH_2(3 and 4), and 0.58 ppm (m, 4H, CH_2(2)). ^{13}C NMR (($CDCl_3$): δ = 23.0 (CH_3CO), 23.5 (CH_2(2)), 25.4 (CH_2(4)), 28.3 (CH_3(5)), 29.3 (CH_2(3)), 37.2 (CH_2 Tyr), 39.9 (CH_2(1)), 53.5 (CH Tyr), 55.6 (C fluorene), 65.6 (CH_2 (6)), 115.6 (CH_{Ar}), 121.4 (C_{Ar}), 121.6 (CH_{Ar}), 126.2 (C_{Ar}), 126.7 (CH_{Ar}), 130.3 (CH_{Ar}), 130.4 (CH_{Ar}), 139.1 (C_{Ar}), 152.3 (C_{Ar}), 155.9 (C_{Ar}), 170.6 (COOH), and 172.0 ppm (CONH). IR (KBr): 3317, 2927, 2856, 1738, 1657, 1652, 1614, 1516, 1450, 1373, 1269, 1223, 1128, 812, 731, 665, 526 cm^{-1}.

Poly[(9,9′-bis(6″-*N*-acetyltyrosinehexyl)fluoren-2,7-diyl)-*alt*-*co*-(benzen-1,4-diyl)], (4). 2,7-Dibromo-9,9′-bis(6″-*N*-acetyltyrosinehexyl)fluorene, **3** (0.97 g, 1.0 mmol), 1,4-phenyldiboronic acid (0,19 g, 1.1 mmol), $PdCl_2$(dppf) (8 mg, 0.01 mmol) as catalyst, and potassium carbonate anhydrous (1.6 g, 12.1 mmol) were placed in a round-bottom flask under N_2 atmosphere. Then, a mixture of THF:H_2O was added (6 mL:6 mL). The reaction mixture was degassed three times (inert gas and vacuum) and stirred at 80 °C (reflux) for 63 h. After cooling, the reaction was precipitated into methanol. The crude product was filtered and washed with abundant water and acetone respectively. The polymer was dissolved in the minimum amount of chloroform, filtered over celite and precipitated out twice more with methanol. The polymer was obtained as a gray solid (0.38 g, 0.45 mmol). Yield: 44%. ^{1}H NMR ((DMSO-d_6): δ = 9.40 (bs, 2H, COOH), 8.20 (s, 2H, NH), 7.89−7.64 (m, 10H, Ar); 6.92 (bs, 4H, Ar Tyr), 6.63 (bs, 4H, Ar Tyr), 4.30 (m, 2H, CH Tyr), 3.84 (m, 4H, CH_2(6′)), 2.79 and 2.70 (2 × m, 4H, CH_2 Tyr), 2.08 (m, 4H, CH_2 (1′)), 1.74 (s, 6H, CH_3CO), 1.27−1.03 (m, 12H, CH_2(3′, 4′, 5′)) and 0.64 (m, 4H, CH_2(2′)). ^{13}C NMR ((DMSO-d_6): δ = 22.2 (CH_3CO), 23.3 (CH_2(2′)), 24.9 (CH_2(4′)), 27.9 (CH_2-(5′)), 29.0 (CH_2(3′)), 32,2 (CH_2(1′)), 36.1 (CH_2 Tyr), 54.1 (CH Tyr), 55.0 (C fluorene), 64.2 (CH_2 (6′)), 115.1 (CH_{Ar}), 120.0 (C_{Ar}), 121.4

Scheme 2. Synthetic Route of the Poly[(9,9′-bis(6″-*N*-acetyltyrosinehexyl)fluorenephenylene)][a]



[a] Key: (i) *N*-Ac-L-Tyr (10 equiv), K_2CO_3, DMSO, 12 h, room temperature, Ar (92%); (ii) 1,4-phenyldiboronic acid, $PdCl_2(dppf)$, K_2CO_3, THF/H_2O (1:1), Ar, 63 h, 80 °C (46%).

(CH_{Ar}), 125.4 (C_{Ar}) 127.1 (CH_{Ar}), 127.3 (CH_{Ar}), 129.9 (CH_{Ar}), 130.3 (CH_{Ar}), 139.0 (C_{Ar}), 139.4 (C_{Ar}), 151.8 (C_{Ar}), 156.1 (C_{Ar}), 169.4 (COOH), and 171.8 ppm (CONH). IR (KBr): 3286, 2930, 2856, 1734, 1653, 1615, 1516, 1461, 1373, 1237, 813, 738, 528 cm^{-1}.

Poly[(9,9′-bis(6″-bromohexyl)fluoren-2,7-diyl)-*alt-co*-(benzen-1,4-diyl)] (5). The synthesis of the precursor polymer was performed according to previous procedure via Suzuki cross.[34]

Poly[(9,9′-bis(6″-iodohexyl)fluoren-2,7-diyl)-*alt-co*-(benzen-1,4-diyl)] (6). To a solution of polymer, **5** (2.0 g, 3.5 mmol), in 60 mL of THF was added dropwise under stirring a solution of potassium iodide (3.0 g, 18.0 mmol) in 10 mL of acetone. The mixture was at 50 °C during 72 h. When the reaction was cooled at room temperature, methanol was added to precipitate out the polymer. The crude product was filtered and washed with abundant water, methanol and acetone respectively. The polymer was obtained as a yellow solid (2.0 g, 3.0 mmol). Yield: 86%. ^1H NMR (($CDCl_3$): $\delta = 7.83-7.49$ (m, 10H, Ar), 3.06 (t, $J = 7.0$ Hz, 4H, $CH_2(6')$), 2.10 (m, 4H, $CH_2(1')$), 1.65 (m, 4H, $CH_2(5')$), 1.21; 1.14 (2 × m, 8H, $CH_2(4')$, $(3')$) and 0.79 ppm (m, 4H, $CH_2(2')$). ^{13}C NMR (($CDCl_3$): $\delta = 7.5$ ($CH_2(6')$), 23.8 ($CH_2(2')$), 29.0 (CH_2-$(4')$), 30.2 ($CH_2(3')$), 33.5 ($CH_2(5')$), 40.5 ($CH_2(1')$), 55.4 (C fluoreno), 120.4 (CH_{Ar}), 121.5 (CH_{Ar}), 126.3 (CH_{Ar}), 127.7 (CH_{Ar}), 139.9 (C_{Ar}), 140.2 (C_{Ar}), 140.3 (C_{Ar}), and 151.6 ppm (C_{Ar}). IR (KBr): 3437, 2927, 2850, 1462, 1260, 1092, 1013, 888, 811, 753, 592, 497 cm^{-1}.

Results and Discussion

Synthesis and Characterization. Two different routes have been set up to prepare the new chiral fluorene copolymer (Scheme 1). In the first route (Scheme 1, method A), key monomer **3** was previously synthesized and it was polymerized by modified Suzuki-Miyaura coupling.[34] Monomer **3** was obtained with high conversion by aliphatic nucleophilic substitution of the monomer **2**, 2,7-dibromo-9,9′-bis(6″-iodohexyl)-fluorene. The reaction performed in presence of large excess of the aminoacid derivative *N*-acetyltyrosine (10 equiv) dissolved in aqueous potassium carbonate solution as alkaline medium. Previously, the monomer, **2**, was prepared with excellent yield (close to 90%) and total conversion, less than 1% observed by ^1H NMR, from 2,7-dibromo-9,9′-bis(6″-bromohexyl)fluorene, **1**, by reacting it with potassium iodide.[18] Nevertheless, in basic solution, the monomer **1** reacts to give elimination product of the bromo group in the extreme of chain while the desire compound **3** is not found in crude reaction. Conversely, if the iodo monomer **2** is in use, then we obtained the tyrosine monomer **3** with a good yield. The explanation is associated with the different reactivity and behavior for the halogen element as leaving group during a typical mechanism of the aliphatic nucleophilic substitution.[35] The structure of monomer **3** was confirmed by ^1H and ^{13}C NMR spectroscopy. Identification was possible due to the shift of signals assigned to the hydrogen diastereotopics corresponding to the methylene group into tyrosine unit, centered at 3.01 and 2.92 ppm, like starting aminoacid, and also, the methylene group in final chain ($-CH_2-$O-tyrosine) centered at 3.98 ppm, with respect to signals for precursor chain ($-CH_2-X$) at 3.30 and 3.07 ppm from Br and I, respectively. The evolution of the substitution reaction was followed and confirmed by integrated areas of proton corresponding to characteristic methylene group bonded to the new functional group.

The polymer **4** was synthesized via Suzuki coupling polymerization using monomer **3** and 1,4-phenyldiboronic acid with $PdCl_2(dppf)$ as a catalyst in THF/water two-phases system at the refluxing temperature, during 2 days (Scheme 2). The structure of the polymer **4** was also confirmed by ^1H NMR, ^{13}C NMR, and FTIR spectroscopy, and all signals were assigned on the basis of analogy with monomer **3** spectra. Figure 1 shows the ^1H NMR spectra of monomer **3** and polymer **4** and the ^{13}C NMR spectra are in good agreement with structures of similar fluorene polymer derivatives (see Supporting Information). Bidimensional experiments of NMR corroborate these assignments.

In addition to the experiments reported above, we try to obtain chiral polymer **4** by modification over precursor polymer **5** (Scheme 1, method B) using the same reaction conditions for obtaining the homologue monomers. First, bis(6″-iodohexyl) copolymer **6**, was prepared by substitution reaction of polymer **5** with potassium iodide in acetone. Previously, polymer **5** was dissolved in THF to gain solubility before to react respect to the reaction in monomer substitution, again the change in the shifts of the methylene group (side-chain) was the key to control the total transformation (almost 72 h for less of 1% of the initial product). In similar basic conditions, excess of aqueous potassium carbonate, the formation of polymer **6** with *N*-acetyl-L-tyrosine (10 equiv) in DMSO was followed at different reaction times and temperatures. The final reaction of modification to obtain polymer **4** did not take place at room temperature. Employing large time experiments and high-temperature (1 week at 55 °C), the reaction yield of product was low (less than 3%) and no comparable with the other method.

Polymer **4** was soluble in polar solvent as DMSO or DMF at concentration >1 mg/mL. Lower solubility was obtained with protic solvents as methanol or ethanol and other polar organic solvents as chloroform, tetrahydrofuran and dichloromethane, although these solvents were used to dissolve homologue polymers **5** and **6**.

The molecular weight characteristic of chiral polymer **4** was $M_w = 10.8$ kg/mol and polidispersity index (PDI) of 1.5 (DP= 11; $M_p = 9.5$ kg/mol, see table inset of Figure 2). The polymer **6** was also analyzed, with $M_w = 26.1$ kg/mol (PDI = 1.9), obtained from the batch of the polymer **5** ($M_w = 24.8$ kg/mol and PDI = 1.8). Figure 2 shows the chromatograms obtained for all polymers and molecular was determined by SEC-LS. Some overestimation of the molecular weight is an outcome of

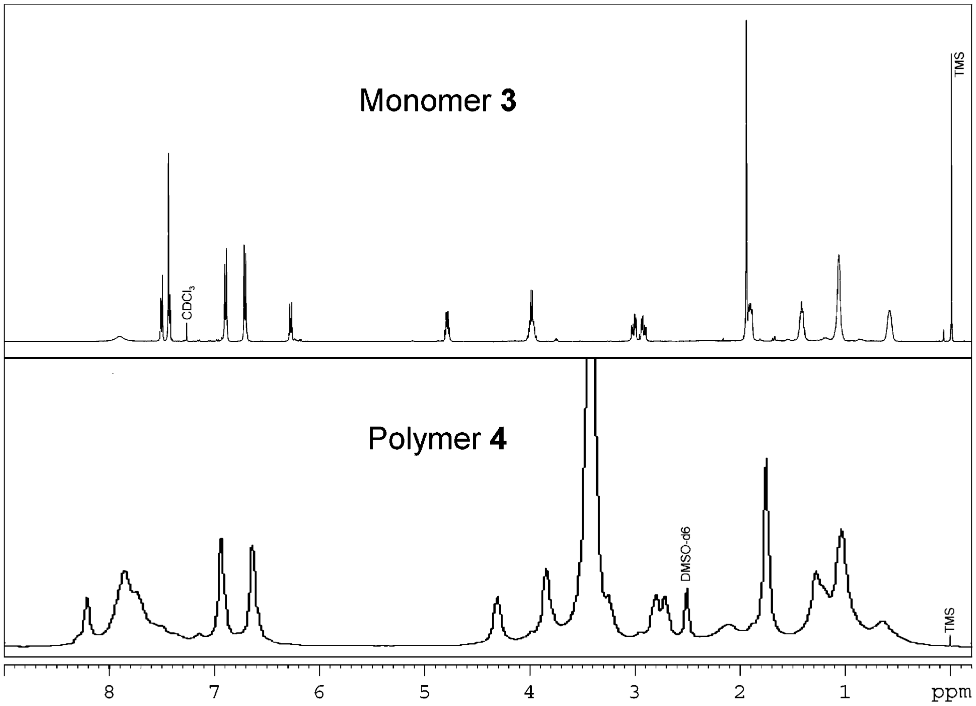


Figure 1. ^{1}H NMR spectra of monomer **3** in $CDCl_3$ (top) and polymer **4** in DMSO-d_6 (bottom).

the calibration with PS standards.[36] We used the maximum peaks to compare and determine the medium polymerization degree (DP). In addition, the PDI corresponding to polymer **4** and **5** were found in the typical range of fluorene-based polymers prepared by Suzuki cross-coupling.[37,38]

Optical and Chiroptical Study. Figure 3 shows the UV−vis absorption and fluorescence emission spectra of monomer **3** and polymer **4** at room temperature. As can be seen, significant modifications in optical spectra were found originated by the conjugation of the polymer. The shape of the absorption spectrum of the monomer **3** is similar to 9,9-dimethylfluorene.[39,40] Monomer **3** presents three characteristics absorptions peaks at 280, 301, and 313 nm, red-shifted with respect to dialkylfluorene, due to bromide aromatic effect in the 2- and 7-positions. The intensity of the λ_{max} at 280 nm could be reinforced by presence of phenolic ring corresponding to amino acid substitution. This same assignation could be attributed for the band appearing in polymer **4** around 280 nm, as broad shoulder respect to the stronger absorption bands of the $\pi-\pi^*$ transition backbone. Absorption maximum in polymer **4** is centered at 375 nm and corresponding with same bandwidths, absorption maximum and intensity presented in others conjugated co-polyfluorenes.[4,34,41]

Emission spectrum of monomer **3** presents a maximum band at 322 nm with a little shoulder close to peak maximum. This band shows a significantly low fluorescence intensity corresponding to the monomer ring of fluorene, as has been observed in oligofluorenes with different backbone lengths.[42,43] However, the emission spectra of the synthesized polymer **4**, in chloroform solution, exhibited a maximum peak at 415 nm with a shoulder peak at 437 nm, again similar to conjugated polyfluorenes. From this data, we observed an apparent red-shift of the maximum wavelength (over 5 nm) respect to the neutral precursor polymer **5** but a blue-shift with respect to the cationic polymer (ammonium salt) in water solution, at 429 nm.[17−20] These optical changes manifest an important key role played by the polarity of the solvent in the excited transition states and associations effects of these polymers (see next section), which is indicative of interchain aggregations or preferential conformations in the experimental conditions, as previously observed in other conjugated polymers like MEH−PPV.[44,45]

Respect to the chiroptical study, first, we calculated the values of the specific optical rotations, $[\alpha]_{D,}$ at room temperature, corresponding to polymer **4**, $[\alpha]_D^{24} = +78.8$ ($c = 0.33$, DMSO) and the monomer **3**, $[\alpha]_D^{24} = +10.0$ ($c = 0.20$, DMSO). The same direction but higher optical rotation for the polymer indicate an enhancement value over the monomer,[46] and this rise cannot be only ascribed to the presence of chiral groups substituted in fluorene. For this reason, we explore the possibility of the contribution of the main chain conformation induced by chiral centers on the side chains at the C9 position, which can be used for probing the helical arrangement of the derivatives polyfluorene backbones.[41,47]

Chiral monomer or terminal chiral residues are usually employed in the polymer architecture, resulting in preference for helix formation in one direction providing main chain chirality.[48,49] Normally, a bisignate Cotton effect can be observed in the circular dichroism (CD) spectrum, and one of the screw senses of the helix is attributed to formation of supramolecular order induced via *interchain* or *intrachain* exciton coupling. Figure 4 shows a noticeable CD spectrum of polymer **4**, in a mixture chloroform/ethanol (1:1), while in pure solvent (chloroform or ethanol) the absence of CD signal evidence that this effect is not due to an aggregated form. CD spectrum of polymer **4** presents a first positive lobe (at 340 nm) and second negative (at 405 nm) Cotton effect and does not correspond to the conjugated polyfluorene backbone absorption at 375 nm (zero crossing point). Also, for comparative reasons, we present the CD spectra of the precursor polymer **5** and monomer **3**, obtained under the same conditions of mixture of the solvent. The absence of a CD response, in neutral polymer **5**, indicates the lack of intrinsic order of the backbone, whereas the chiral monomer **3** does not induce a CD signal. The tyrosine group, in peptides, provides CD activity with a negative signal close to 280 nm,[50,51]

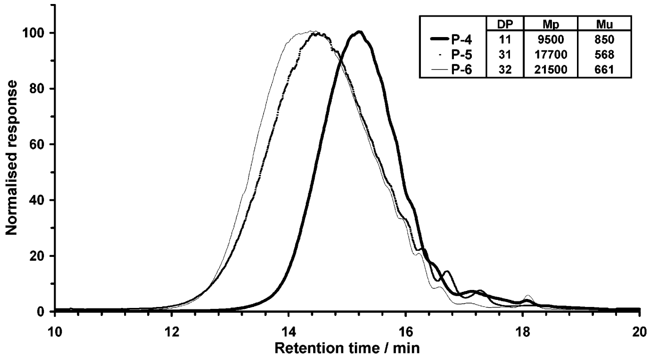


Figure 2. SEC-LS chromatograms of the polymers **4** (thick line), **5** (dashed line), and **6** (solid line) in THF. Inset: medium polymerization degree (DP), calculated over molecular weight in peak (M_p) and molecular weight for unity (M_u), expressed in g/mol.

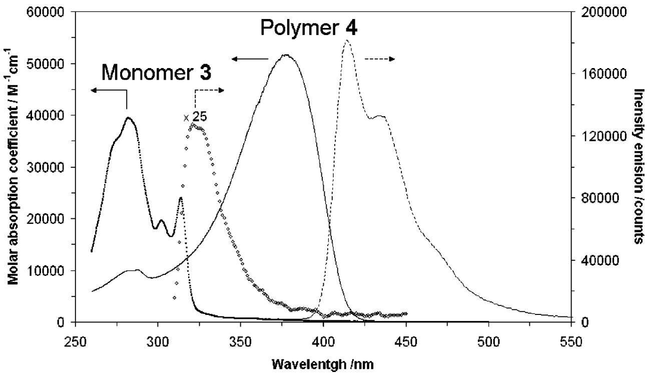


Figure 3. Absorption and fluorescence spectra of synthesized monomer **3** and polymer **4**, in solution.

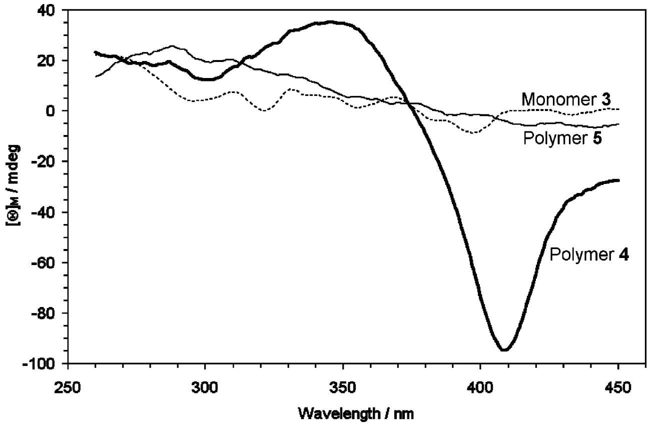


Figure 4. Circular dichroism (CD) spectra of polymer **4** (solid line), precursor polymer **5** (dashed line) and precursor monomer **3** (dotted line) in a mixture of solvents: chloroform/ethanol (1:1).

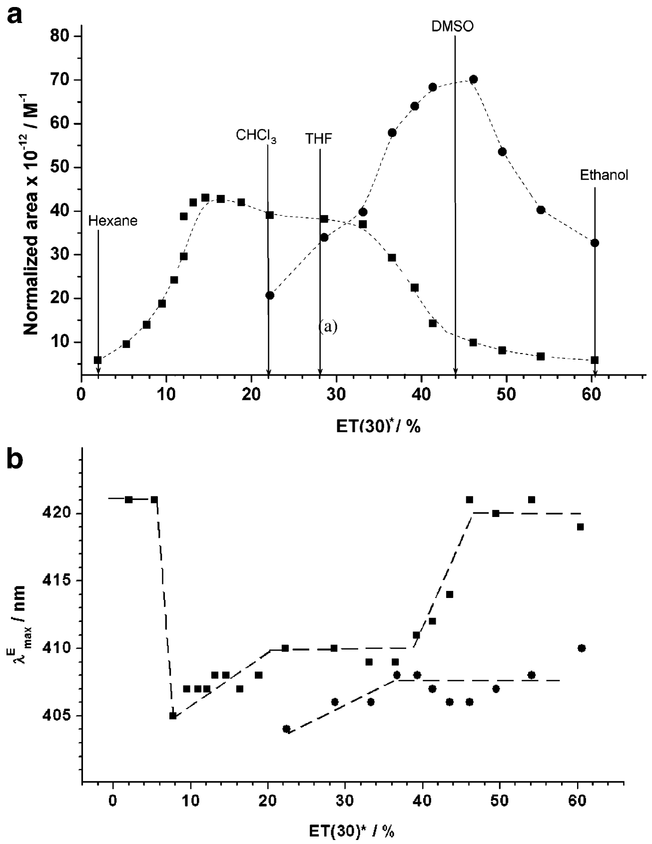


Figure 5. Normalized fluorescence area (a) and maximum wavelength emission, λ^{E}_{max}, (b) vs percentage of solvent polarity values, $E_T(30)^*$. For chiral polymer **4** (circles points) and precursor polymer **5** (squares points), the dashed line represents a provisional guide.

but in this region, we do not find this contribution for our compounds.

The response shows for polymer **4** was previously found in the analogue poly(9,9-bis((*S*)-5-methylheptyl)fluorene-2,7-diyl) (or (*S*)-PF7/1), where the asymmetric carbon is localized close to final chain respect to other chiral polyfluorenes studies. The CD signal obtained for (*S*)-PF7/1 is indicative of *interchain* exciton coupling.[47] Chiroptical effects are attributed to a localization of the asymmetric position in side chain but the dominant effect is not fully understood.[48,52] The unusual transition observed in CD signal for our conjugated polymer implied that a helix transition was supported during the hierarchical evolution via intermediate chiral assemblies in similar effect to that observed for oligo(*p*-phenylenvinylidene).[53] In this work, the authors confirmed a left-handed-helical assembly by AFM image with equivalent CD signals to chiral polymer **4**. Comparable effect of the CD signals are reminiscent of similar helical assemblies than biological macromolecules as DNA, but in the opposite pathway.[54,55]

Conformational and Anisotropy Study on Emission Spectra. In order to understand the structure adopted in the solvent mixture, we study the effect of the polarity solvent on emission fluorescence of conjugated polymers synthesized using a concentration 0.3 mM, respect to unity of the polymer. Figure 5a shows the values obtained for integrated emission area for neutral polymer **5** and chiral polymer **4** with respect to polarity solvent, expressed as $E_T(30)^*$ in percentage (see experimental part). The maximum wavelength of emission, λ^{E}_{max}, was represented in Figure 5b with respect to the same parameter.

The neutral polymer, **5**, in a nonpolar solvent—hexane, $E_T(30)^* = 1.9$—presents a lower emission intensity with a clear red-shift (11 nm) with respect to average λ^{E}_{max} at 410 nm, in good solvent zone ($E_T(30)^* \sim 23$). Red-shift, in poor solvent, is related to the interactions effects in aggregates as overlap structures of type J.[45,56,57] As the solvent polarity is increased at $E_T(30)^* = 9$, by chloroform addition, we observed a huge change on the point of maxima difference of λ^{E}_{max} with respect to the good solvent zone (blue-shift 5 nm), which is associated with intrachain interactions effects in coil-collapsed polymers.[44,45]

The chiral polymer **4** presents a qualitatively similar behavior, but with the maximum plateau displaced to higher polarity values indicative of the variation of the processability induced by the side chain modification, like other cationic polymers

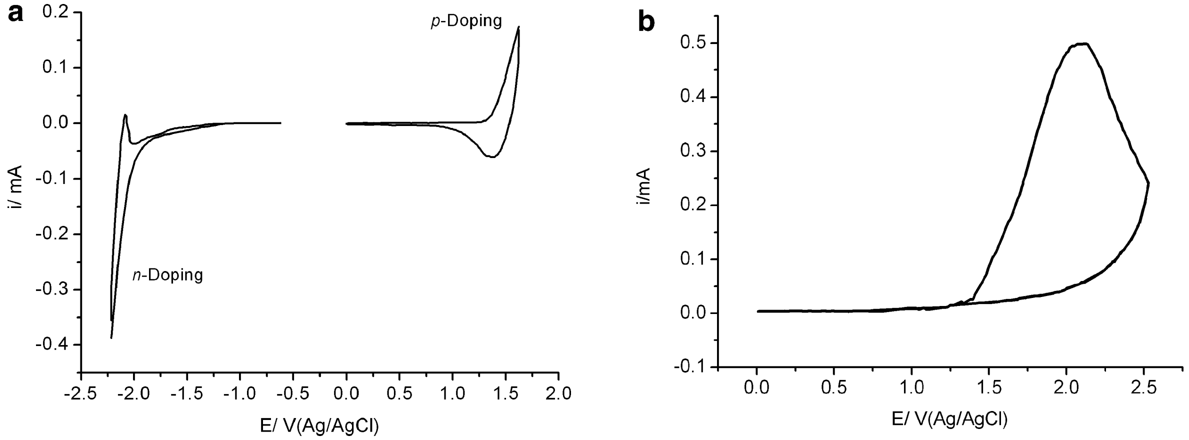


Figure 6. Stabilized cyclic voltammograms (a) and degradation (b) of polymer **4**.

previously analyzed.[17−20] This polymer is highly insoluble in solvents of low polarity—$E_T(30)^* < 10$. The initial value of emission is obtained in pure chloroform where exhibit a red-shift of λ^{E}_{max} (4 nm) respect to value in good solvent. As ethanol is added to the solution, an increase of the emission is observed reaching a maximum at $E_T(30)^* = 40-46$, and at the same value of the polarity, reaching a maximum in λ^{E}_{max}. Further ethanol addition, a decay of the fluorescence intensity getting a minimum for pure ethanol related to a transition state of the conformational associations.[45] Both polymers have maximum values of intensity and a plateau zone in λ^{E}_{max} related to better solubility observed for each polymer. The high emission is a direct consequence of the large distance interchromophore in expanded structure of the backbone.[44,45] For polymer **5**, the maximum corresponds to polarity $E_T(30)^*$ values of pure chloroform (22.2), THF (28.1) or CH_2Cl_2 (28.5) that are excellent solvents in this case, with high interactions with the polymer chains, and therefore high solvent-dynamic volume of the polymer molecules. For chiral polymer **4**, pure DMSO (44.3) is a good solvent, marked in Figure 5a, illustrating the difference of solubility for each polymer studied but also, facilitating the comparison among solvents.

At last, emission anisotropy, *r*, was obtained with the purpose of achieving information about the segment mobility of the polymer in solution.[58] We found $r = 0.19 \pm 0.02$ for polymer **5** and $r = 0.26 \pm 0.02$ for polymer **4**, at 20 °C with the excitation wavelength at 370 nm. The higher value of anisotropy of polymer **4** is correlated to a lower rate of excitation migration along the conjugated chain than in polymer **5**. Similar emission anisotropy values have been measured for poly(9,9-dioctylfluorene).[59] Vaughan et al.,[60] making use of fluorescence anisotropy, observed that the exciton migration along conjugated polymer in solutions involves conformational relaxation by twisting of part of the chain within polyfluorenes of 20 or more repeat units. This result indicates that the conformational relaxation is more impeded in the chiral than in the corresponding bromide substituted polymer.

Electrochemical Study. Finally, in Figure 6a, we present the stabilized cyclic voltammograms (CV) of polymer **4**. The reversible oxidation of the polymer (p-doping) can be observed in the scan to positive potentials emerging at 1.25 V. No well-defined oxidation peak is observed in the scan up to 1.60 V. In the reverse scan, a reduction current appears centered at 1.38 V corresponding to polymer dedoping. The voltammetric charges involved in doping−dedoping processes are similar indicating the reversibility of the process. This polymer can be reversibly n-doped as observed in the left part of Figure 6a. In the scan to negative potentials, a reduction current appears around −1.8 V due to reduction of the polymer up to −2.20 V. The dedoping process can be observed in the positive-going scan with an oxidation peak centered at −2.08 V. The values of the oxidation and reduction onsets were used to estimate molecular orbital energy levels (HOMO and LUMO). The onset potentials of the oxidation and reduction were 1.25 and −1.86 V respectively. The estimated HOMO and LUMO energy levels of polymer **4** are 5.64 and 2.53 eV, respectively. The band gap of the polymer was estimated to be 3.11 eV, which agrees well with the value reported previously for analogous polyfluorenes.[34] Comparing our results with others for alkyl copolymers containing a block of fluorene, it can be found that the new polymer has almost the same LUMO and HOMO energies, which means that the new polymer has similar charge injection properties, with a low influence of the side chain aromatic substituents in the electronic structure of the conjugated chain.

The cyclic voltammogram of a working electrode containing polymer **4** was performed with higher potential limits. At potentials more positive than 1.6 V (Figure 6b), an oxidation peak was observed and centered at 2.10 V. The irreversible character of this oxidation and the absence of electrochemical answer in the successive cycles indicates the loss of conjugation of the main chain (overoxidation). A similar degradative process happens when the electrode is cycled to potentials less positive than −2.20 V (overreduction, not shown). The electrochemical stability of this compound is similar to that of other polyfluorenes.[61]

Conclusion

A novel conjugated optically active from *N*-acetyl-L-tyrosine group in the side chain of poly(2,7-fluorene-1,4-phenylene), **4**, was synthesized. Method A, via Suzuki cross-coupling polymerization above precursor monomer **3**, yielded the chiral polymer with good yield and purity. Method B, via post-modification over a precursor halogenous polymer, was unsuccessful using similar conditions to obtain monomers. The last strategy of polymerization proceeds with poor yield and gives a mixture of polymers. The polymer structure was characterized by conventional techniques to have the conjugated polymer backbone system with designed chiral substituents. This chiral group substituted provides specific optical characteristics that could be explained by *interchain* exciton coupling with 3D-structure of the conjugated polymer. The polymer synthesized have optical activity, and the study of the chiroptical properties points to formation of left-handed-helical conformation due to the localization of the asymmetric carbon in extreme of side chain. Conformational states of polymer **4** and **5** (as model) were analyzed from spectra emission of fluorescence obtained in function of the different polarity. The electrochemical properties of the new polyfluorene show the reversibility and stability of the injected charges (electrons and holes) in conductive polymer layer by n- or p-doping processes.

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Supporting Information Available: Figures showing NMR spectra for synthesized compounds, FTIR spectra of **3** and **4**, plot calibration SEC-LS of PS, and fluorescence polarization, text giving experimental details, and a table of solvent parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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