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Synthesis of Soluble Main-Chain Poly(Quinolines)

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Polyquinoline polymers incorporating a bisquinoline moiety along their polymeric backbones have been synthesized and fully characterized. Two different macromolecular architectures were created; either fully conjugated or rigid-flexible main chains with both cases showing improved solubilities in common organic solvents. The monomers' and subsequent polymers' initial characterization was performed by NMR, as well as GPC and DSC techniques. Additionally, the polymers optical properties were evaluated using UV-Vis and PL spectroscopies. Cyclic voltammetry measurements provided information on the electrochemical properties and energy levels (HOMO-LUMO) of the final polyquinolines in order to determine possible applications in electronic devices.

Keywords quinolines, optical characterization, cyclic voltammetry, synthesis, electron transporters

Introduction

Conjugated polymers with improved semi-conducting properties are of increased scientific interest for applications in light emitting diodes (LEDs), photovoltaic or other electronic devices. Various *p*-type (hole transporting) conjugated polymers have been well-established, presenting desirable optoelectronic characteristics (e.g. polythiophenes, polyphenylene vinylenes, polyfluorenes). On the other hand, *n*-type (electron transporting) polymeric materials are still under intense research not only toward the development of new chemical structures, but also for the improved synthesis, processability and properties' tunability of already existing ones. Among the *n*-type materials, those containing *N*-heterocyclic moieties have been extensively investigated as polymeric semiconductors. Those incorporating the quinoline moiety are particularly excellent candidates due to their interesting properties (1–7) and their ease of synthesis, based primarily on the Friedländer condensation (8). In particular, polyquinolines' unique photonic, electronic and electron transporting properties have allowed their successful incorporation into PLED's, (9–12), organic photovoltaic devices (13, 14), nonlinear optics, (15) electrochromic cells and selective chemosensors (16). Moreover protonation of the amino group, causes these polymers to be pH responsive (17–19), thus opening new uses as tunable molecules.

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However, most polyquinolines reported suffer from poor solubilities in common organic solvents, while they are only soluble in protonic acids (e.g. formic acid) or as Lewis acids in polar aprotic organic solvents. This phenomenon becomes even more intense for main chain polyquinolines for which only a few examples are known with good solubilities in organic solvents, those substituted with long alkyl chains or those copolymerized with fluorene, thiophene or other solubilizing comonomers (20–22). Thus, as early as their initial incorporation into polymers by Stille and co-workers (23–29), great synthetic effort has been devoted towards maintaining the solubility in the synthesized quinoline polymers affording interesting molecules (30, 31).

Herein, we report our efforts in suppressing the poor solubilities of main chain polyquinoline polymeric systems. Thus, we have designed and synthesized two *m*-diquinoline derivatives bearing either two bromo- or hydroxyl- end functionalities, respectively, that are suitable for a variety of polymerization reactions. From the dibromo functionalized monomer, we prepared a fully conjugated polymer through Suzuki Coupling Polymerization with a dialkoxy substituted diboronic acid (32). The two alkoxy chains laterally attached to the rigid polymeric axis were expected to keep the polymeric backbones from aggregating without disrupting the main chain conjugation length.

Alternatively, it is has been realized early on that alternating conjugated–non conjugated polymers, in which the chromophores are regularly separated from aliphatic, silicon, or other non emissive units, are capable in possessing the exact same optoelectronic characteristics as their fully conjugated counterparts. Moreover, such conjugated-non conjugated polymers usually present improved solubilities than analogous wholly aromatic, rigid polymeric structures. Thus, we adopted a phase transfer polymerization (33) of the dihydroxyl functionalized diquinoline monomer with aliphatic dibromides for the preparation of rigid-flexible, conjugated-non conjugated polyethers.

Experimental

Materials and Instrumentation

All solvents and reagents were purchased from Aldrich or Merck and used without further purification unless otherwise stated. DMF was distilled under reduced pressure and stored over molecular sieves. 2-Amino-5-bromobenzophenone (29, 34), 2-tetrahydropyranyloxy-4-phenylboronic acid (35), 2,5-bis(didodecyloxy) phenylene-1,4-diboronic acid (36), tetrakis (triphenylpshosphine) palladium (0) ($Pd(PPh_3)_4$) (37) were synthesized according to literature methods. 1,12-Dibromododecane was recrystallized from methanol.

Optical absorption spectra were recorded on a Hewlett Packard 8452A spectrophotometer. Photoluminescence spectra were recorded using a Perkin-Elmer LS45 luminescence spectrometer, by excitation of the sample at the absorption maxima of the UV-Vis spectra. Polyquinolines' polymeric films were fabricated either from spin coating or drop casting of dilute solutions (0.2 mg, 10 mL). All polymers' solutions were kept at a concentration of 10−5 M.

^{1}H NMR spectra were obtained on a Bruker Avance-DPX 400 MHz with deuterated $CHCl_3$ or CF_3COOH having TMS as internal standard.

Gel permeation chromatography (GPC) measurements were carried out using a Polymer Lab chromatographer with two Ultra Styragel linear columns (10^4, 500 Å), UV detector (254 nm) polystyrene standards and $CHCl_3$ as eluent.

Differential Scanning Calorimetry (DSC) measurements were conducted on a TA Instruments Inc. model DSC Q100 series. The heating and cooling runs were conducted at a rate of $10^\circ C\,min^{-1}$ and were kept constant for all the measurements.

Cyclic voltammetry (CV) studies were performed using a standard 3-electrode cell. Platinum wires were used as counter and working electrodes. Silver/silver nitrate ($Ag/AgNO_3$) was used as a reference electrode.

Tetrabutylammoniumhexafluorophosphate $TBAPF_6$, 98% from Aldrich was used as electrolyte and was recrystallized three times from acetone before use. $TBAPF_6$ was dried in vacuum at 120°C before each experiment. Acetonitrile anhydrous 99.8% (CH_3CN), was also supplied from Aldrich and used without further purification. Before each experiment, the cell was purged with inert gas for 15 min. Before the start of the measurement, the inert gas was turned to "blanket mode". Measurements were recorded using a EG&G Princeton Applied Research potensiostat model 263A connected to a personal computer running PowerCV software.

Monomer Syntheses

1,3-(m-Phenylene)bis(6-bromo-4-phenylquinoline) (1). Under an argon atmosphere, 2-amino-5-bromobenzophenone (5.5 g, 20 mmol), 1,3-diacetylbenzene (1.6 g, 10 mmol), H_2SO_4 (98%) (0.1 mL) and CH_3COOH (10 mL) were placed in a round flask and refluxed for 18 h. After cooling, the mixture was slowly added to a stirred mixture of crushed ice (40 g) and 25% ammonia solution in water (15 mL) to give a precipitate that was filtrated, washed with hot water, EtOH, and $CHCl_3$ affording 1 as a pale yellow solid. Yield 4.1 g, 64% M.p. >310°C. ^{1}H-NMR (CF_3COOD) δ (ppm): 8.81 (s, 1H), 8.68 (s, 2H), 8.47 (d, 2H), 8.35 (m, 6H), 8.13 (t, 1H), 7.77–7.73 (m, 10H).

1,3-(m-Phenylene)bis(6-hydroxylphenyl-4-phenylquinoline) (2). Under an argon atmosphere, 1,3-(m-phenylene)bis(6-bromo-4-phenylquinoline) (1) (1.3 g, 2.0 mmol), 2-tetrahydropyranyloxy-4-phenylboronic acid (0.88 g, 4.0 mmol), $Pd(PPh_3)_4$ (0.19 g, 0.16 mmol), DMF (10 mL) and Et_3N (1.0 mL) were placed in a round flask and heated at 90°C for 48 h. After cooling, the mixture was diluted with DMA and filtrated in order to remove the catalyst. The end-protective groups were removed afterwards with the addition of MeOH (5 mL) and HCl 37% (2 mL) and the resulting yellow-orange solution was stirred for 24 h. The solution was precipitated in 200 g of crushed ice under stirring and thus **2** was obtained as a pale-yellow solid after filtration and subsequent washing with MeOH, $CHCl_3$ and hexane. Yield 0.98 g, 73%. ^{1}H-NMR (CF_3COOD) δ (ppm): 8.82 (s, 1H), 8.53 (s, 2H) 8.50 (d, 2H), 8.45 (d, 2H), 8.31 (s, 2H), 8.14 (t, 1H), 7.76–7.73 (m, 12H), 7.65 (d, 4H), 7.13 (d, 4H).

Polymer Syntheses

Polymer PQ-OR. Under argon atmosphere, 1,3-(m-phenylene)bis(6-bromo-4-phenylquinoline) (1) (1.3 g, 2.0 mmol), 2,5-bis(didodecyloxy) phenylene-1,4-diboronic acid (1.0 g, 2.0 mmol), $Pd(PPh_3)_4$ (0.19 g, 0.16 mmol), DMF (8 mL) and Et_3N (0.8 mL) were placed in a three-necked flask and heated at 90°C for 48 h. After cooling, the mixture was diluted with $CHCl_3$ (50 mL), filtrated and precipitated into MeOH to afford a pale yellow powder (PQ-OR). ^{1}H-NMR ($CDCl_3$) δ (ppm): 9.05 (s, 1H), 8.45 (two d, 4H), 8.18 (s, 2H), 7.96–7.85 (two d, 4H), 7.45–7.78 (m, 11H), 7.02 (s, 1H), 6.97 (s, 1H), 3.89 (d, 4H), 1.65 (m broad, 4H), 1,32 (m, 36H), 0.85 (m, 6H).

Polymer PQ-S

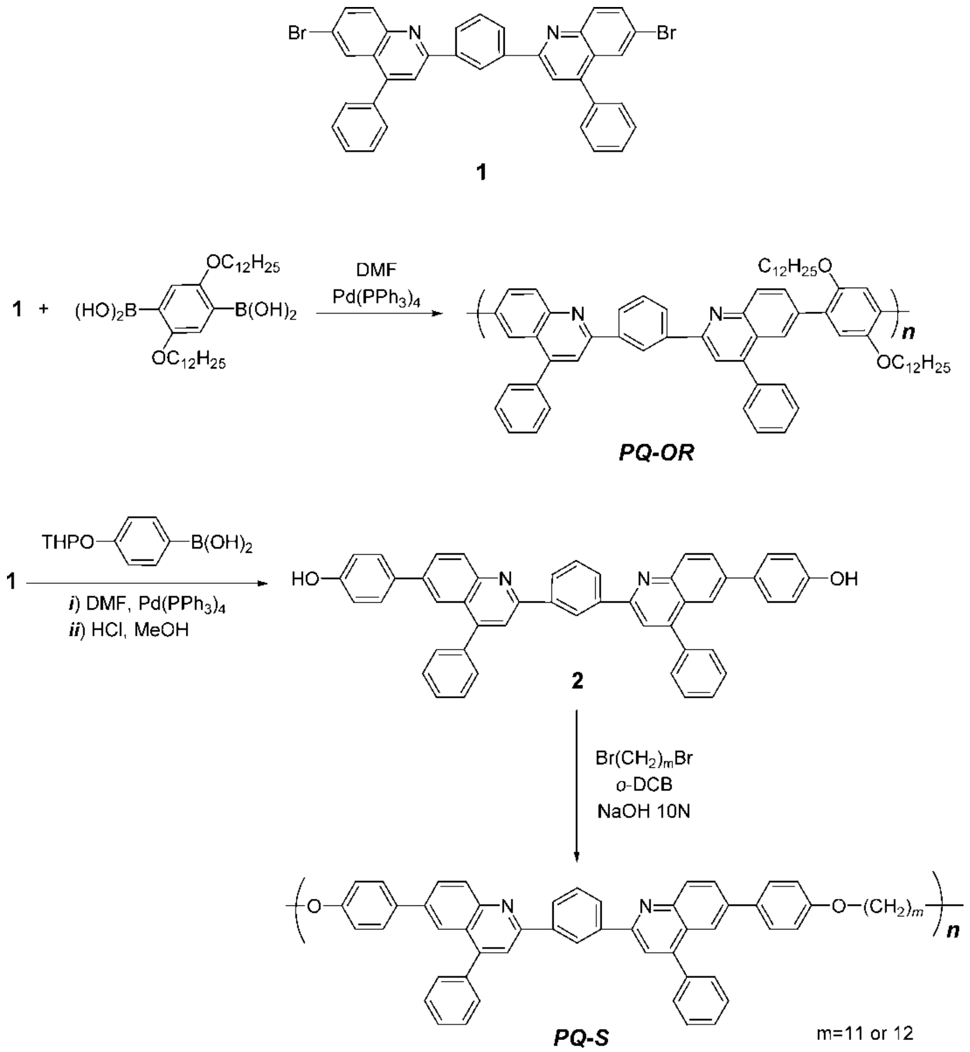
1,3-(m-Phenylene)bis(6-hydroxylphenyl-4-phenylquinoline) (2) (0.17 mmol), 1,11-dibromoundecane or 1,12-dibromododecane (0.17 mmol) and TBAH (0.068 mmol) were placed into a round flask and degassed several times before the addition of *o*-DCB (0.85 mL) and NaOH 10 N (0.85 mL). The reaction mixture was vigorously stirred at 90°C for 48 h under argon. Afterwards, the mixture was diluted with $CHCl_3$, filtrated and precipitated in a ten-fold amount of MeOH. After filtration and drying in vacuum, a pale yellow powder was obtained (PQ-S). ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.98 (s, 1H), 8.33–8.31 (m, 4H), 8.04 (s, 2H), 7.97 (m, 4H), 7.7–7.5 (m, 15H), 6.96 (d, 4H), 3.99 (s, 4H), 1.77 (m, 4H), 1.32–1.46 (m, 14H).

Results and Discussion

Syntheses and Characterization

The synthetic procedure employed herein towards the preparation of fully aromatic or rigid-flexible main chain polyquinolines is outlined in Scheme 1. The initial *m*-phenyl bisquinoline dibromide 1 was prepared from condensation of 2-amino-5-bromobenzophenone and 1,3-diacetylbenzene under acidic conditions. An analogous methodology has been reported previously by Zhan et al. (38) towards the syntheses of a *p*-phenyl bisquinoline dibromide. By altering the substitution pattern of the middle phenylene ring, we tried to reduce the rigid nature of the final main-chain polyquinolines and thus improve their solubilities. Polymers bearing an alkoxy-substituted *m*-phenyl bisquinoline unit have also been reported in the past, but their preparation was based on direct nickel (0) catalyzed coupling or Friedländer polymerization reactions (16, 39). Dibromide 1 was slightly soluble in mild organic solvents, but easily soluble in protonic ones like formic acid as expected. Fortunately, it also presented improved solubilities in dimethylformamide (DMF) or dimethylacetamide (DMA). Thus, we employed a modification of the Suzuki coupling reaction, proposed by Thompson and Gaudino (40), using DMF as the organic solvent for both the preparation of the fully conjugated polyquinoline PQ-OR and of the second diquinoline monomer diol 2. The fully aromatic polyquinolines PQ-OR, due to the side dodecyloxy chains, presented good solubilities in common organic solvents like $CHCl_3$ and could be characterized by NMR and GPC techniques (Figure 1 and Table 1, respectively).

The synthesis of the monomer diol 2 using DMF as solvent and Et_3N as a base (Scheme 1) afforded higher yields than the typical Suzuki coupling reaction using THF or toluene as solvent and aqueous solutions of NaOH or Na_2CO_3 as a base. Moreover, the deprotection step under acidic conditions could be performed directly after the cross coupling reaction, giving quantitative results and reducing the synthetic effort. Polymerization of diol 2 with aliphatic dibromides of 11 or 12 methylene units, affording polyethers PQ-S, was performed in *o*-DCB/NaOH 10 N mixtures using *t*-butyl ammonium hydrogen sulfate (TBAH) as the phase transfer catalyst. The rigid-flexible nature of polyethers PQ-S must be responsible for their good solubilities in $CHCl_3$ which allowed their complete characterization (Figure 2, Table 1). Even though the polymerization reactions were not optimized as far as the reaction time is concerned, both polymeric series, PQ-OR and PQ-S, showed good film forming abilities after solution casting producing stable, self-standing films. Additionally, in their ^{1}H-NMR spectra, no end-groups could be found across the polymeric chains revealing their satisfactory molecular weights.



Scheme 1. Synthetic procedures and the resulting chemical structures of polymers PQ-OR and PQ-S.

Thus, the medium ranged molecular weights obtained from GPC using polystyrene standards must be attributed in the nitrogen atoms of the quinoline moieties interacting with the columns' stationary phase. As expected, both series of polyquinolines were also easily soluble in highly polar solvents like DMF, DMA, and 1,1,2,2-TCE as well as in protonic ones like formic acid.

The polyquinolines' thermal properties were examined by means of differential scanning calorimetry (DSC). Representative thermograms are depicted in Figure 3. Only second heating scans were taken into account while the cooling cycles for both series were almost featureless. The polyethers PQ-S exhibited a T_g at approximately 130°C, which is in the same temperature region as for other quinoline bearing copolymers (38) even though those were of higher molecular weights. As for the conjugated polymer PQ-OR, only an endothermic peak was observed, which can be attributed to

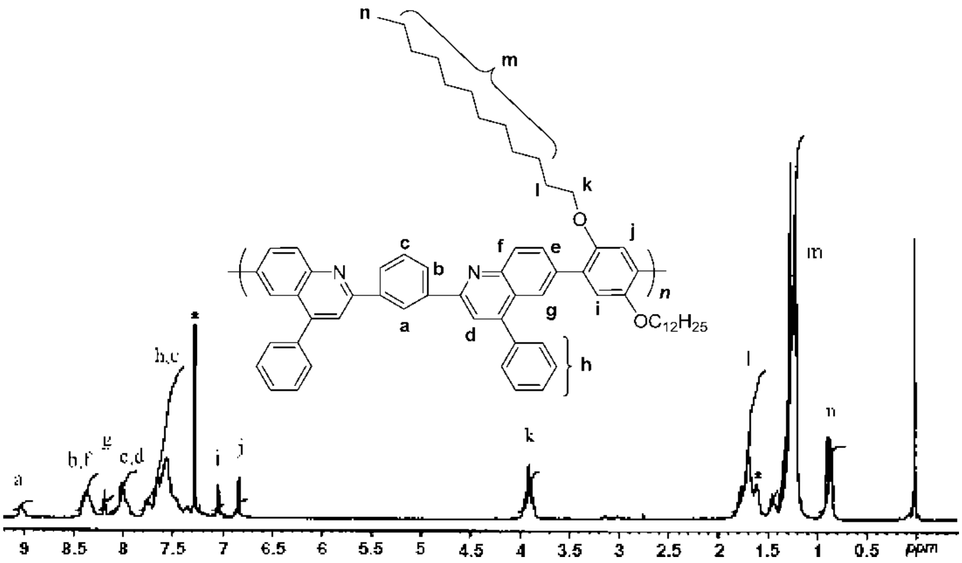


Figure 1. ^{1}H-NMR spectra of polymer PQ-OR 1 in $CDCl_3$.

the side-alkoxy groups' melting, with no glass transition temperature detected for these polyquinolines.

Optical Properties

The optical properties of the main chain quinoline bearing polymers, PQ-OR and PQ-S, were examined, both in solution and in the solid state. The absorption spectra of the two polymers in chloroform solutions consist of a peak at 274 nm for PQ-OR (Figure 4) and at 282 nm for PQ-S (Figure 5), as well as a broad shoulder at 344 nm for both of them. Thus the increase of conjugation when passing from the PQ-S to the PQ-OR structure does not seem to strongly affect the optical characteristics of these polymers, since no additional peaks or other changes were noticeable. This could mean that the presence of the alkoxy- side groups disturbs the conjugation, due to conformational changes imposed on the planarity of the main chain. On the other hand, the UV spectra in formic acid show a differentiation of the first peak located at 273 nm in the PQ-OR polymer

Table 1
Typical molecular weights obtained for the main chain quinoline bearing polymers

Polymer	M_n	M_w	PDI
PQ-OR 1	3540	5380	1.5
PQ-OR 2	2700	9600	3.5
PQ-OR 3	5300	14800	2.8
PQ-S 11	8160	18210	2.2
PQ-S 12	2400	9770	4.0

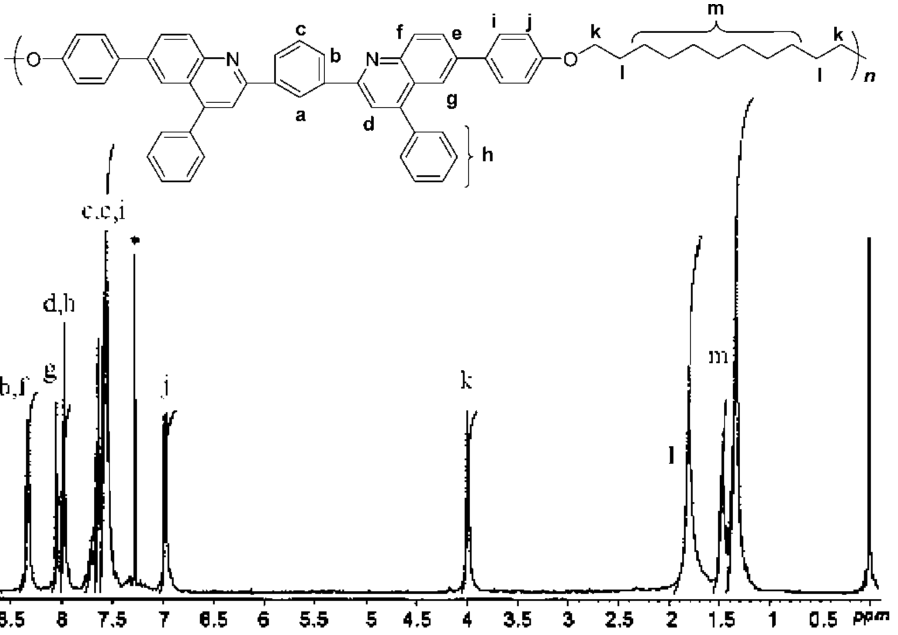


Figure 2. ^{1}H-NMR spectra of polymer PQ-S 11 in $CDCl_3$.

and at 304 nm in the PQ-S one, as well as different relative intensities for the peak at 335 nm for PQ-OR and 357 for PQ-S. This may be attributed to differentiations on the protonation's extend or to the final conformation adopted by the interacting macromolecular chains, between these two polymers. Since the effective conjugation length does not differ as

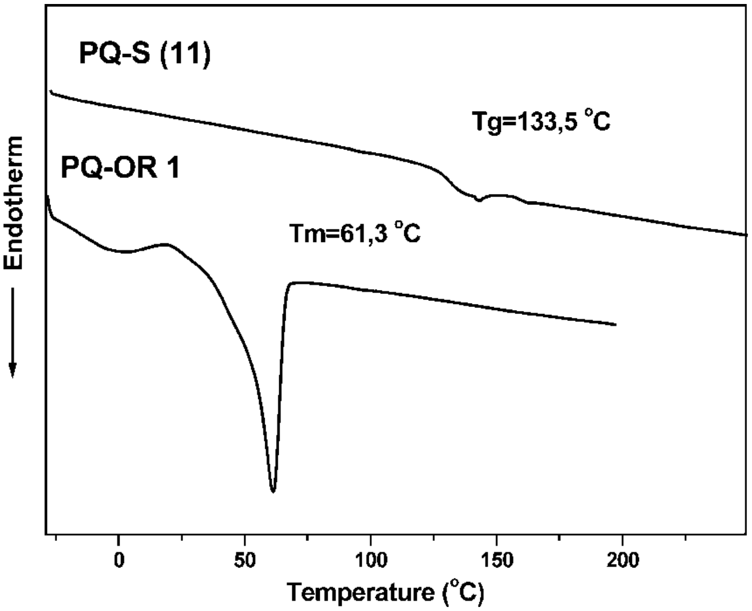


Figure 3. DSC thermograms of the polymers PQ-OR 1 and PQ-S (11).

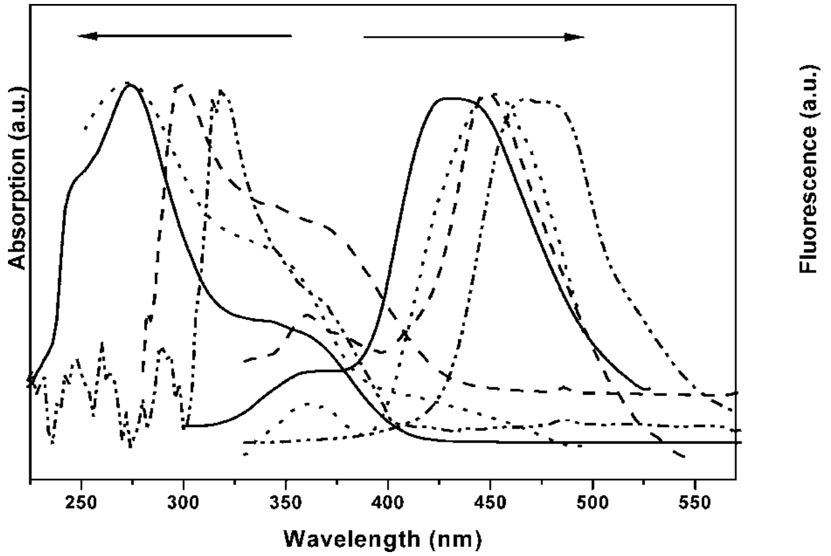


Figure 4. Absorption (left) and fluorescence (right) spectra in $CHCl_3$ solution (solid line), in HCOOH solution (10^{-6} M, dot line) in thin film cast from $CHCl_3$ (dash line), in thin film cast from HCOOH (dash dot dot) for polymer PQ-OR 1.

shown from the UV absorption spectra in chloroform any observed differentiations may be safely attributed to the different effect or extend of protonation. The absorption of thin films is the same for both polymers showing a peak at 300 nm, which is red shifted compared to the solution. This fact is further proof that all the above-observed differences between the

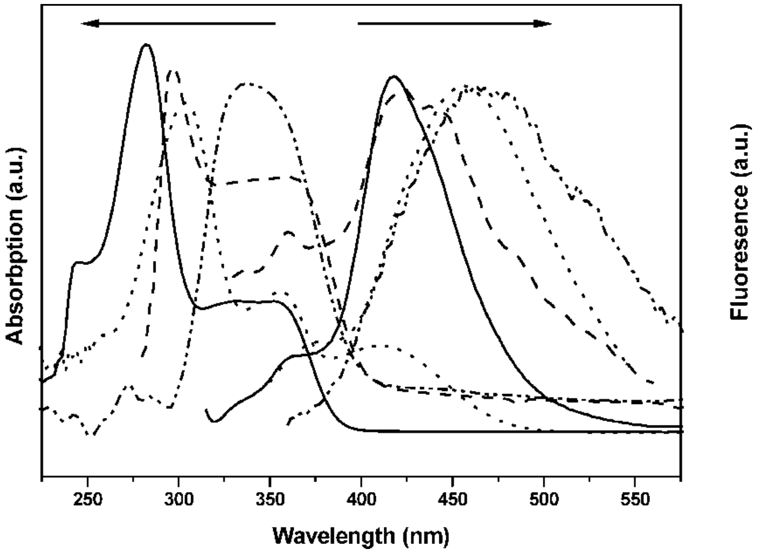


Figure 5. Absorption (left) and fluorescence (right) spectra in $CHCl_3$ solution (solid line), in HCOOH solution (dot line) and in thin film cast from $CHCl_3$ (dash line), in thin film cast from HCOOH (dash dot dot) for polymer PQ-S 11.

Table 2
Contains the electrochemical data for the PQ-OR and PQ-S polymers

	PQ-OR 1	PQ-S 11
$E_{g\ optical}$	2.9	3.0
Oxidation peak	1.2	1.3
Reduction peak	−2.0	−1.9
Eox_{onset}	1.0	1.0
$Ered_{onset}$	−1.9	−1.8
$E_{g\ echem}$	2.9	2.8
HOMO	5.4	5.4
LUMO	2.5	2.6

two solutions should be due to interactions of the protonated and non-protonated groups in the solution. The emission spectrum of the PQ-OR polymer in chloroform, formic acid solution and in thin film are depicted in Figure 4. Apart from the observed peak at 433 nm in chloroform solution, the peaks at 448 nm in thin film along with the 450 nm in formic acid, show that aggregate formation in the solid state and complex formation in the formic acid solution have an equal effect on the optical properties.

The emission spectra of the PQ-S polymer (Figure 5) present a peak at 418 nm (chloroform) and 457 nm (formic acid) while both of them show broad featureless emission bands. The observed red shift, at 457 nm for PQ-S is caused by protonation. Summarizing the results obtained from the main chain quinolines and taking into account our previous findings concerning a side chain polyquinoline (19) PSDPQ, and its behavior

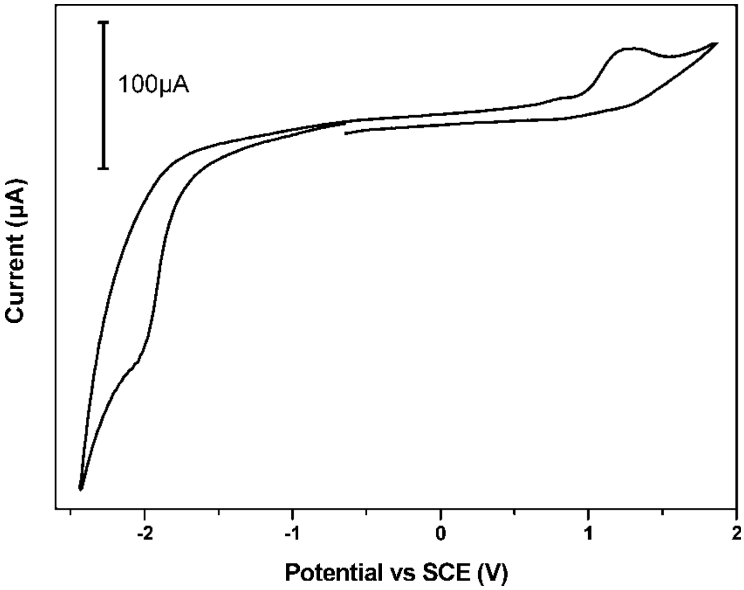


Figure 6. Cyclic voltammogram of the polymer PQ-OR 1 in thin film. Scan rate 100 mV/s.

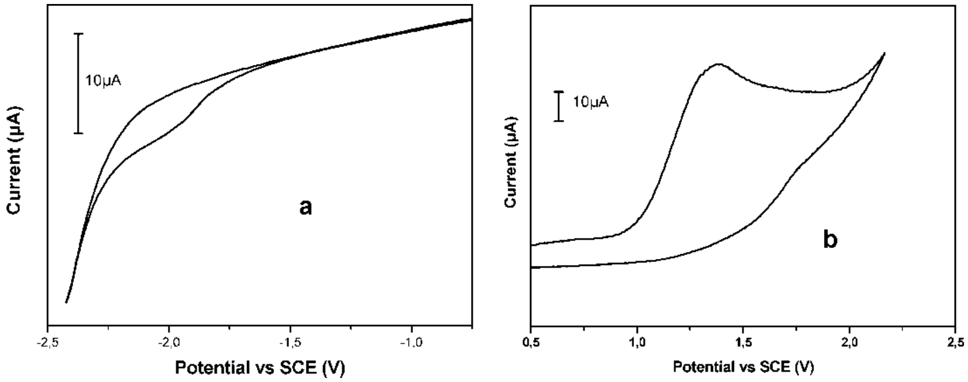


Figure 7. Contains the cyclic voltammogram of the PQ-S 11 polymer in thin film using a scan rate of 100 mV/s. 7a contains the reduction wave and 7b contains the oxidation wave.

when an acidic medium was used, we can clearly deduct that the incorporation of the quinoline group in the main chain results in a reduced tendency for complex formation between protonated and non protonated species as shown by the decrease of the peak maxima from 530 nm to 457 and 447 nm for PSDPQ, PQ-S and PQ-OR, respectively. It is clearly shown that the chemical structure of the polymer plays a critical role in determining the final optical properties of these materials. Most likely, the long alkoxy chains of either the PQ-OR, or the PQ-S prevent intermolecular or intramolecular interactions which are, evidently, responsible for the red shift of the emission maxima.

Cyclic Voltammetry

All the polymers synthesized, were studied using cyclic voltammetry, in an effort to reveal their HOMO and LUMO energy levels. The working electrode was cleaned before each experiment, through sonication in HNO_3 65%, followed by subsequent sonication in absolute ethanol. The reference electrode was a standard $Ag/AgNO_3$ non aqueous electrode, which consisted of a silver wire, immersed in a 0.1 M solution of $AgNO_3$ in acetonitrile and communicated with the electrochemical cell through a salt bridge. In order to calculate the energy levels, ferrocenium/ferrocene was used, before each experiment, as internal standard in order to convert the results versus SCE. All the polymers were studied in thin film, by dipping the Pt electrode in a viscous $CHCl_3$ solution of the polymer. The HOMO energy level was calculated by using the oxidation onset of each polymers and using that value in the empirical equation. $\mathrm{HOMO} = \mathrm{Eox}_{\mathrm{onset}} + 4.4$. Likewise, the LUMO was approximated by determining the onset of the reduction and using that value in the empirical equation. $\mathrm{LUMO} = 4.4 - \mathrm{Ered}_{\mathrm{onset}}$. The data from the cyclic voltammetry are summarized in Table 2. The cyclic voltammograms are depicted in Figure 6 for the PQ-OR and Figure 7 for the PQ-S.

Conclusions

Main chain quinoline based polymers have been synthesized and studied with respect to their optical and electrochemical properties. An emphasis was given towards obtaining polymers soluble in common organic solvents that can be used in applications such as polymeric light emitting diodes. Incorporating alkoxy side chains allowed us to maintain a conjugated polymer backbone while at the same time, greatly improving their solubility. Protonation of the polymers showed a red shift of the emissive properties of the polymers, though, apparently, steric hindrances from the alkyl groups prevent extensive intermolecular or intramolecular interactions. Cyclic voltammetry for the conjugated polymer bearing side chain alkoxy groups and the quinoline polymers bearing alkyl spacers, revealed a LUMO energy level of 2.5 eV and 2.6 eV respectively. The ionization potential was estimated at 5.4 eV for both polymers.

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