Polymer Bulletin

Synthesis and Characterization of Poly(1,4-phenylene vinylene)-co-(2,5-pyridilene vinylene)'s

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Summary

The polymerizability of nitrogen-containing *bis*sulfonium salts was analyzed. The poor homopolymerization results were attributed to sluggish quinodimethane formation. However, copolymerizations with the non-nitrogenated analogue sulfonium salt were successful. We report here the synthesis and characterization of a series of poly(1,4-phenylene vinylene)-co-(2,5-pyridylene vinylene)s. Elemental analysis, FTIR, UV-vis and fluorescence studies demonstrate that the pyridilene units can be incorporated by the water soluble precursor route in PPV-type polymers with free-standing film formation properties.

Introduction

Poly(arylene vinylene) polymers of general formula [-Ar-CH=CH-]$_n$ are one of the most explored class of conjugated polymers that are currently under investigation, both from the viewpoint of understanding fundamental electronic processes and for practical applications in optoelectronics [1,2]. In particular, pyridine-containing conjugated polymers are considered promising candidates for applications in light-emitting devices [3]. Since these nitrogenated polymers have a higher electron affinity as compared to the phenylene-based analogue, PPV, they show better electron transport properties, higher luminescence and are more resistant to oxidation. Moreover, their higher electroaffinity allows the use of more stable metals, i.e. Al or Au, [4] or even sulfonated polyaniline as the electron-injecting electrode in polymer light-emitting diodes [5].

There are two main synthetic approaches for the preparation of arylene vinylene polymers. The ethylene units are formed either in one step or in two steps. The direct synthesis of the conjugated polymer requires the presence of lateral chains to improve the solubility of the rigid conjugated backbone in order to achieve processability [6]. Films are therefore produced by spin casting of organic solutions of the conjugated polymer. Indeed, almost all the reported poly(pyridilene vinylene) homopolymers or their copolymers have been prepared by this approach [6-12]. Alternatively, to circumvent the insolubility of the rigid rod polymers a water-soluble precursor polymer is prepared first by base-promoted polymerization of *bis*sulfonium salts. This

high molecular weight precursor polyelectrolyte can then be cast into films by solvent evaporation or spin-coating techniques. Finally, a thermal elimination generates ethylene units to afford homogeneous films of poly(arylene vinylene)s [13]. This route has been modified so the precursor polymer is soluble in organic solvents [14-16]. Although processability from water solutions is required in certain applications [17] there is only one report describing the synthesis of a rather low molecular weight poly(1,4-pyridylene vinylene), PPyV, from a water-soluble precursor polymer [18].

Therefore, in this article we report a polymerizability study on the nitrogen-containing *bis*sulfonium salts **2** and **3** and the synthesis and characterization of a series of poly(1,4-phenylene vinylene)-co-(2,5-pyridylene vinylene), **5a-e**, PPVPyV. The general structure of the monomer and the polymers is shown in Scheme 1. The purpose of the work was to establish if the pyridilene units could be incorporated by the water-soluble precursor polyelectrolyte route in PPV-type polymers with free-standing film formation properties and how the monomer polymerizability is influenced by the introduction of nitrogen atoms in the aryl moiety.

1; X = Y = CH
2; X = N, Y = CH
3; X = Y = N

1 + 2 → (Et$_4$NOH / H$_2$O:AN/pentane) → 4a-e → (240 °C / 4 h) → 5a-e
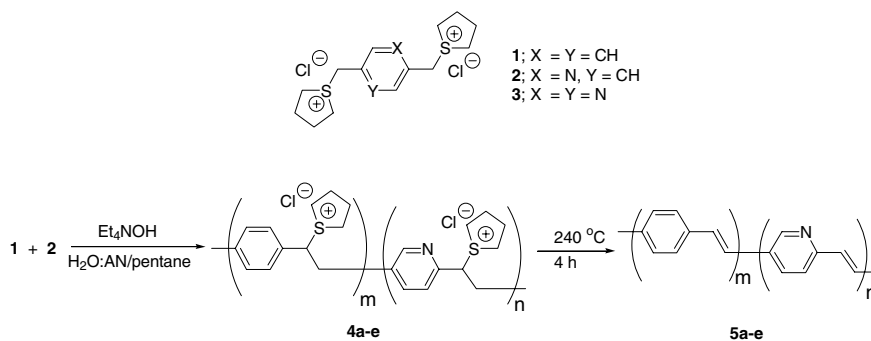
Scheme 1

Experimental

Materials

N-clorosuccinimide (NCS), tetrahydrothiophene (THT), 2,5-dimethylpyrazine, 2,5-dimethylpyridine and α,α-dichloro-*p*-xylene (Aldrich) were used as received. Dibenzoylperoxide (BPO) was recrystallized twice from ethanol. Tetrachloromethane was distilled and kept over molecular sieves.

Instruments

Elemental analysis were made in the INQUIMAE, Universidad de Buenos Aires. Melting points reported are not corrected. ^{1}H spectra were recorded on a Bruker ARX300 spectrometer in D$_2$O using HDO at 4.67 ppm and the sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3-d$_4$ acid at 0 ppm as internal standards in the aqueous media. Gel permeation chromatography (GPC) was carried out on a Waters GPC. Tetrahydrofuran was the eluent solvent, and polystyrene was used as standard. IR spectra were taken on free-standing polymer films using an FTIR Nicolet 520 spectrophotometer. UV/vis and emission spectra were obtained on thin polymer films, which were cast and eliminated on quartz plates, using either a Gilford Response spectrometer or an AMINCO 8100 spectrofluorimeter.

Monomer Syntheses

α,α'-bis(chloromethyl)pyridine and α,α'-bis(chloromethyl)pyrazine were synthesized by radical chlorination with NCS of the appropriate heteroarene compound in yields of 48% and 55% respectively after chromatographic purification. Monomer **1** was prepared from α, α'-dichloro-*p*-xylene and THT following the literature method [19].

2,5-Bis(tetrahydrothiopheniomethyl)pyridine dichloride (**2**). To a solution of α,α'-bis(chloromethyl)pyridine (8.98 g, 51 mmol) in methanol (50 mL) was added THT (13.5 g, 153 mmol). The mixture was warmed to 50 °C, stirred for 24 h and cooled to room temperature. Excess methanol and THT were removed by distillation and the resulting paste was dissolved in a minimal amount of methanol and reprecipitated twice in cold acetone (200 ml). The precipitate was dried to constant weight at 20 °C under reduced pressure (10^{-2} mmHg) to afford a hygroscopic semisolid compound. Yield: 54%. ^{1}H RMN (D^2O): 8.77 (d, J = 2.2 Hz, 2H, aromatic H); 8.22 (dd, J = 8.2 Hz and J = 2.2 Hz, 2H, aromatic); 7.78 (d, J = 8.2 Hz, 2H, aromatic); 4.80 (s, 4H, benzylic H); 3.65 (m, 8H, CH_2-S^+-CH_2); 2.45 (m, 8 H, CH_2-CH_2).

2,5-Bis(tetrahydrothiopheniomethyl)pyrazine dichloride (**3**). The salt was obtained as a semisolid compound from the α,α'-bis(choromethyl)pyrazine by the procedure described above for **2**. Yield: 48%. ^{1}H RMN (D_2O): 8.71 (s, 2H, aromatic H); 4.88 (s, 4H, benzylic H); 3.74 (m, 8H, CH_2-S^+-CH_2); 2.52 (m, 8H, CH_2-CH_2).

Homopolymer and copolymer synthesis and characterization

The polymerization reactions were started by the addition of a nitrogen-purged aqueous solution of tetraethylammonium hydroxide to a nitrogen-purged solution of the *bis*sulfonium salts in acetonitrile:water mixture (1:1) stirred with an amount of pentane such that the volume ratio of the aqueous reacting mixture to pentane was 1:2. Both solutions were first cooled in an ice-water bath and the reaction was carried out at the same temperature under nitrogen atmosphere for 1 h. The reaction mixture was neutralized with HCl. The resulting aqueous solutions of the polyelectrolytes were dialyzed to remove low-molecular-weight by-products and the unreacted monomer using membrane tubing with a molecular weight cut-off of 10.000 Da. Free-standing films or thin films on quartz plates were obtained by solvent evaporation and were stored at -14 °C. The polyelectrolyte films were transformed into the *p*-arylene vinylene films by heat treatment *in vacuo* (10^{-2} torr) at 240 °C for 4 hours. To measure the polymer yield, 20 mL of the polyelectrolyte solutions were cast into films of **4a-e**, which were transformed into the conjugated polymers **5a-e** by heat treatment. From the weight of the resulting film and the volume of the polymer solution, the yield of the polymerization was calculated. Derivatives of the polyelectrolytes, which were soluble in organic solvents, were obtained according to the method of Machado *et al.* [20] in order to obtain molecular weight data for the polymers. The solutions of **4a-e** were treated with sodium thiophenolate as described in ref. 20.
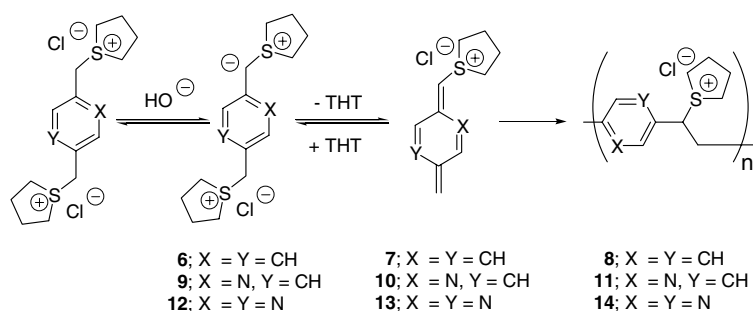
Molecular modeling

Molecular modeling was performed by using first the PM3 MO program to model geometries and then using the ZINDO/S(CI) program to calculate electronic spectra [21]. The minimization operations for close shell molecules (RHF) were performed using the conjugate gradient method where minimization was halted by setting the

gradient option at 0.01 kcal/Å mol. Then, a vibrational spectrum calculation was performed on each of the minimized structures. A local minimum and not a saddle point was assigned to the molecular structure when the spectrum showed only positive vibrational modes.

Results and Discussion

Polymerizability studies

It is well established that a transient reactive quinodimethane **7** is formed *in situ* by the way of an ylide intermediate **6** when the *bis*sulfonium salt **1** is treated with a base and this quinodimethane reacts then to form the precursor polyelectrolyte **8** being the second equilibrium the rate-determining step in the polymerization reaction [22,23].

6; X = Y = CH	**7**; X = Y = CH	**8**; X = Y = CH
9; X = N, Y = CH	**10**; X = N, Y = CH	**11**; X = N, Y = CH
12; X = Y = N	**13**; X = Y = N	**14**; X = Y = N

Scheme 2. Polymerization mechanism of the bissulfonium salts

We found that polymerizability of **2** and **3** are poor even after the polymerization conditions were optimized to increase quinodimethane formation by adding acetonitrile as water miscible cosolvent to favor the sulfide elimination from the ylide [24] and an immiscible organic solvent to form a two-phase solvent system in order to further shift the equilibriums via THT extraction [19]. Thus, the purification of the polymerization mixtures of **2** and **3** with a membrane having a MWCO of 10.000 Da gave films with very poor mechanical properties of the polyelectrolytes **11** and **14** in 8% and 3% yield respectively. No transient UV-vis band, which is usually associated with the quinodimethane generation, was observed after treatment of either **2** or **3** in basic aqueous acetonitrile in the sample chambers of the spectrophotometer. On the contrary, a strong fading band at 317 nm has been observed after basic treatment of the salt **1** [22,23]. Our failure to detect the quinodimethane bands could be due to a very low quinodimethane concentration or to the fact that the quinodimethane band overlaps the sulfonium salt band. The longest wavelength observed for **2** appears at $\lambda_{max} = 266$ nn with a tail up to 290 nm while **3** displays a strong band at $\lambda_{max} = 264$ nm with a shoulder extending up to 320 nm. The PM3/ZINDO/S(CI) computations that predict transitions for **7**, **10** and **13** at 307, 298 and 290 nm, respectively, support the last argumentation. Anyhow, the quinodimethane concentrations should be low since there were no significant changes in the UV-vis spectra of the salts after the base addition. Therefore, the low polymerizability should be due to sluggish quinodimethane formation, which in a number of cases is related to a large aromaticity

loss on the second step of the above reaction [23]. However, experimental measurements and calculations have shown that the energy of resonance of the aromatic ring decreases on going from benzene to pyridine to pirazine [25]. Besides, resonance energies of *p*-quinodimethanes are known to be low [26] and for **7**, **10** and **13** could be assumed to be rather similar to each other. Thus, in our case the reduced aromaticity of **10** and **13** should favor quinodimethane formation as the number of nitrogen atoms in the aromatic ring increases.

In order to shed light upon this matter, the experimental observations were complemented with theoretical calculations at the semiempirical quantum mechanical level using the PM3 MO program to calculate the reaction heats, ΔH_r, from the heats of formation of the quinodimethanes, H_f^{QDM}, and its corresponding ylids, H_f^{YLID}. Thus, the reactions heats for the formation of quinodimethanes **7**, **10** and **13** from the corresponding ylids are 13.1, 15.8 and 17.2 kcal/mol, respectively, showing an increasing energetic demand as the number of nitrogen atoms increases. In this context, it must also be considered that the pKa of the benzylic position decreases as the nitrogen substitution increases. Hence, it seems that the reduced reactivity of nitrogenated-ring bissulfonium salts would rather be due to the enhanced stabilization of the ylids by the electronegative nitrogen atoms relative to the corresponding *p*-quinodimethanes that will outweigh the favorable reduction in aromaticity.

Table 1. PM3 MO molecular modeling[a)]

Salt	H_f^{YLID}	H_f^{QDM}	ΔH_r
1	182.72	206.34	13.1
2	187.63	213.94	15.8
3	198.04	225.71	17.2

a) In Kcal/mol. The H_f of THT needed to calculate ΔH_r is –10.51 Kcal/mol

Synthesis of the poly(1,4-phenylenevinylene)-co-(2,5-pyridylene vinylene)

It is conceivable that the nitrogenated quinodimethanes could react with a growing chain of polyelectrolyte **8** to become part of it. Therefore we tried first to incorporate pyridilene units by copolymerization of **2** with **1** and the attempt was successful. The attempts with the salt **3** will be the subject of a future report. Table 1 summarizes the data for the copolymerization results.

Table 2. Copolymerization reactions results

Polymer	Feed r[a)]	Copolymer yield[b)] in %	M_W[c)]	Actual r[d)]
5a	90/10	42	4800	95/05
5b	80/20	26	5950	85/15
5c	70/30	27	6000	78/22
5d	60/40	30	4650	73/27
5e	50/50	25	6500	64/36

a) Ratio of monomer **1** to monomer **2** in the feed b) Determined gravimetrically c) GPC results by the method of ref 20. d) Actual compositions were estimated from experimentally determined nitrogen contents of the copolymers **5a-e**

Table 3. Elemental analyses of conjugated polymers **5a-e**

Polymer	C	H	N	S
5a	90.79	6.37	0,84	0.72
5b	89,25	6,78	1,97	0.83
5c	88,61	6,54	2,94	0.64
5d	87,71	7,09	3,69	0.43
5e	87,19	6,17	4,94	0.51

The reversible yellow gels that were formed within minutes after the base addition to the reaction mixture were dissolved upon water addition. The light yellow free-standing precursor polymer films, which were cast from these solutions, were homogeneous in appearance, flexible and showed good mechanical properties. These precursor polymer films were converted into the conjugated polymers by thermal elimination at 240 °C. Free-standing films were orange, while the thin films casted on quartz plates showed a light yellow color.
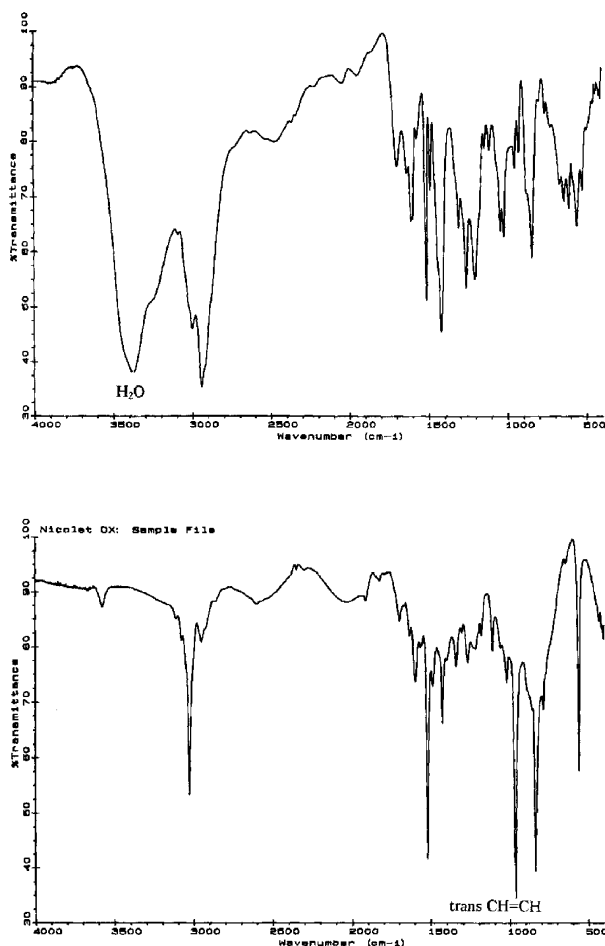
Figure 1. FT-IR spectra for a) polyelectrolyte **4d** (upper) and conjugated polymer **5d** (bottom)

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The polymer molecular weights obtained are strongly influenced by the presence of even small amounts of the *bis*sulfonium salt **2** since they are much lower than those attained with the salt **1**, e.g. ca. 10^5-10^6 Da, [1] but no dependence of the polymer molecular weight on the monomer feed ratio is apparent. The polymer yields suggest the formation of a considerable portion of oligomers and low molecular weight polymers. However, the elemental analysis results indicated that significant amounts of the pyridilene units were incorporated into the polymer films, though in a lower composition ratio than the monomer feed ratio.

The presence the pyridilene units are further evidenced by the FTIR data of free-standing films of the polyelectrolytes and the conjugated polymers. The general features of these spectra are showed in Figure 1. The most noticeable differences between both spectra are the disappearance of the bands showed by the precursor polymer that correspond to H_2O molecules trapped into the film and to the C-H stretch of the saturated units in the polyelectrolyte and the appearance of the band at 964 cm^{-1} in the conjugated polymer that can be assigned to the *trans*-vinylene CH stretch. The small signal at 3600 cm^{-1} indicates that some CH-OH defect remains in the main chain, so a study using TGA is needed to find the optimal thermal elimination conditions. Also significant is the presence in all the spectra of the band at 1599 cm^{-1}, almost absent in PPV, that corresponds to the "quadrant stretching" mode and is originated in the loss of symmetry at the ring center of the PPyV units caused by the nitrogen atom [27,28]. Besides, the detailed analysis of the FTIR spectra of the
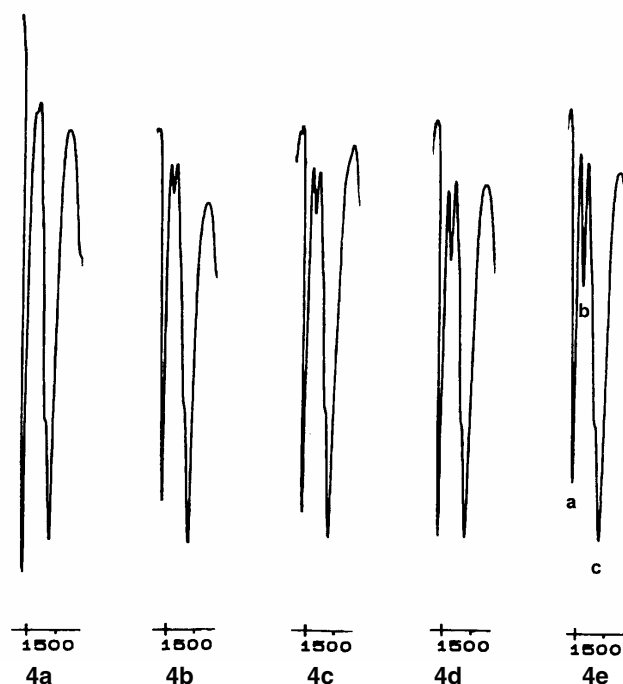

Figure 2. FTIR spectra of the polyelectrolytes **4a-c** in the region around 1500 cm^{-1}.
a) Semicircle stretching mode of the phenylene units, b) first component of the semicircle stretching mode of the pyridilene units, c) second component of the semicircle stretching mode of the pyridilene units

polyelectrolytes **4a-e** showed that they are very similar with insignificant variation in almost all the band intensities. The exception is the region around 1500 cm^{-1} where the semicircle stretching mixed with CH bending of aromatic rings usually appears.

Figure 2 shows that the intensity of the band at 1517 cm^{-1} of the phenylene units and at 1485 cm^{-1} of the pyridilene units vary in qualitative agreement with the composition ratio that was determined by elemental analysis. The relative variation of these two bands can be compared with the band at 1423 cm^{-1} that is rather insensitive to structural changes. This band corresponds to the second component of the semicircle stretching of the pyridilene units.

Figure 3 shows the UV spectra of the precursor polyelectrolyte of **4c** before and after the thermal treatment at 240 °C. The UV spectra for the clear, saturated films displayed a strong absorption band with overlapping maxima associated with both the sulfonium group (λ = 265, 270, 276 nm) and the isolated pyridine group (λ_{max} = 265 nm) and a band with the characteristic vibrational pattern of isolated stilbene units (λ_{max} *ca*. 327 nm) formed by early elimination during the film casting procedure. When the same sample was thermally treated its absorption spectrum shows the broad continuous absorption of fully conjugated polymers centered at ca. 396 nm and a electronic band-gap of 2.39 eV which is very similar to that of PPV (400 nm) but different from that reported for PPyV (419 nm) [15]. The "PPV-like" appearance of the UV/vis spectra of films obtained by copolymerization of **1** with various sulfonium salts has customarily been taken as an indication of the copolymeric nature of these polymers [29-31]. Later, Lathi proved the existence of a random copolymeric microstructure in these polymers by ^{13}C NMR spectroscopy working with ^{13}C-labeled salts [32].

The photoluminescence spectra of copolymers **5a**, **5c** and **5e** are shown offset vertically for clarity in Figure 3. Two strong peaks with a third much weaker that appears as a shoulder at lower energy dominate the spectra. Thus, emission spectra of
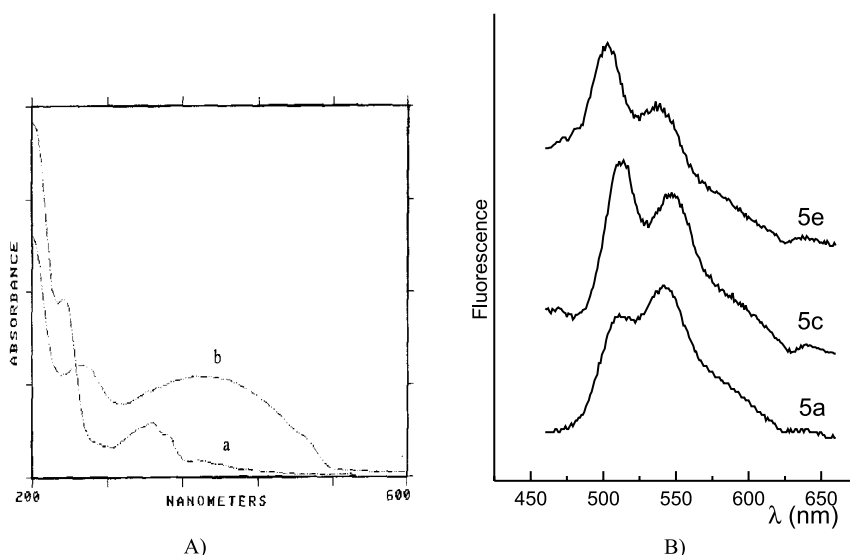

Figure 3. UV-vis spectra of a) polyelectrolyte **4c** and b) conjugated polymer **5c** (left) and photoluminescence spectra of copolymers **5a**, **5c** and **5e** (right)

the copolymers **5a-e** resemble the spectrum corresponding to the homopolymer PPV that shows two distinct bands at 520 nm and 551 nm [1,33]. On the contrary, PPyV shows only a structureless band at 590 nm owing to the regiochemical disorder introduced by the lower symmetry of the pyridine ring [10,16,17]. However, only the polymer with the lower content of pyridilene units, **5a**, shows all the features of PPV where most of the oscillator strength is in the 0-1 transition while for **5c** and **5e**, more weight goes to the 0-0 emission as the number of pyridilene units increases. Moreover, there is a blue shift in emission spectra that is not expected since the incorporation of the pyridilene units should produce a red shift similar to that observed in copolymers of PPV and dimethoxy-PPV [34]. In luminescent polymers where the predominant result of photoexcitation are intra-chain singlet excitons, the absorption is originated in chain segments of a range of different conjugation lengths that leads to a broader absorption spectrum than the emission spectra that is due to luminescence from the longest conjugated segments and therefore has a much better resolved structure [35]. Apparently, the emission of the copolymers **5a-e** is due to PPV-like segments whose lengths are reduced as the amount of pyridilene units increases. Though the shift of the oscillator strength into the 0-0 transition has been attributed to enhanced intrachain order by improved coplanarity in the repeating units and extended conjugation [33,36], the explanation for the shift observed in our system is unclear.

In summary, elemental analysis, FTIR, UV-vis and fluorescence studies demonstrate that the pyridilene units can be incorporated by the water soluble precursor route in PPV-type polymers with free-standing film formation properties.

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