Highly Fluorescent Poly(arylene ethynylene)s Containing Quinoline and 3-Alkylthiophene

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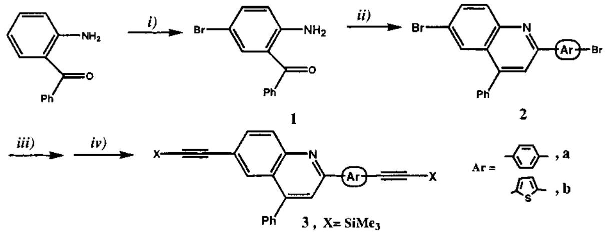
Poly(arylene ethynylene)s are of growing interest due to their π-conjugated rigid rod-like conformation, optical properties, and promising applications in sensors, sheet polarizers, and light-emitting diodes.[1,2] Their syntheses by the palladium cross-coupling and metathesis methods provide access to a large variety of polymers with different moieties in the repeating units.[1−3] Polyquinolines, on the other hand, are characterized by high thermal and oxidative stability and excellent film-forming and mechanical properties.[4,5] The optical and optoelectronic properties of polyquinolines[5] such as electroluminescence[6] and third-order nonlinear optical[7] properties have been studied for photonic and electronic applications. Extensive electrochemical studies of the polyquinolines and their use in light-emitting diodes have shown that they have excellent n-type (electron transport) properties.[6,8] Thus, if incorporated into the poly(arylene ethynylene) architecture, quinoline moieties could impart desired electron transport properties and enhance the prospects of poly(arylene ethynylene)s (PAEs) for electroluminescence[6] and electrogenerated chemiluminescence.[9] Furthermore, the palladium coupling methodology[1−3] could facilitate the generation of quinoline-containing copolymers with many different building blocks selected to enhance properties such as solubility, photophysics, charge transport, and intramolecular charge transfer.

In this paper, we report the synthesis of new highly fluorescent arylene ethynylene copolymers containing quinoline and 3-alkylthiophene by palladium-catalyzed polycondensation of new monomers. The new conjugated copolymers with donor−acceptor architecture have moderate molecular weights and are soluble in organic solvents, and they have improved electrochemical properties and high fluorescence quantum yield in the solid state.

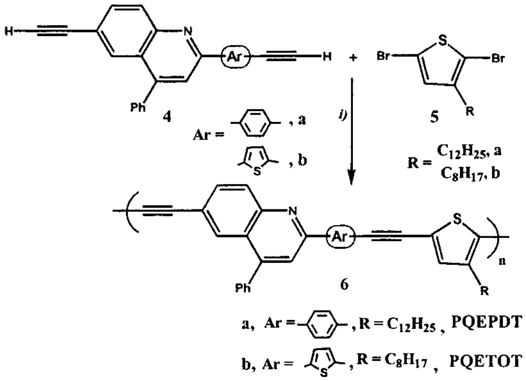
Synthesis and Characterization. The new monomers **4a** and **4b** were prepared in four steps with an overall yield of 62% for **4a** and 50% for **4b** (Scheme 1, see Supporting Information for details). Polymers **6a** (PQEPDT) and **6b** (PQETOT) were obtained in high yields (78−83%) by copolymerization of **4** with 3-alkylthiophene at 60 °C via a Heck coupling[10] in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ and CuI with a mixture of diisopropylamine and THF as solvents (Scheme 2). The weight-average molecular weights, based on polystyrene standards, were 9700 for **6a** and 14 600 for **6b**, and the polydispersity was 1.89−1.95. These polymers are soluble in organic solvents such as 1,1′,2,2′-tetrachloroethane, THF, toluene, and $CHCl_3$. Surprisingly, these polymers are not soluble in formic acid which is known to be a good solvent for the polyquinolines.[6] This is likely due to the presence of the long alkyl side chain that prevent the protonation of the quinoline ring in the present poly(arylene ethynylene)s. The molecular structures of polymers **6a** and **6b** were confirmed by ^1H NMR and FTIR spectra and elemental analysis. Figure 1 shows the ^1H NMR spectra of the polymers. The ratios of integrated peaks among CH_3, $-CH_2-$, Th−CH_2, aromatic Th−H, and phenylene hydrogens agree with the structures of the polymers. The alkyl chains give rise to proton resonances at 0.88, 1.32, 1.7, 2.5, and 2.6 ppm. The resonance of the terminal ethynyl protons at 3.2−3.4 ppm in the monomers (**4a**, **4b**) were not observed in the polymer spectra. The splitting of the Th−H, as well as the Th−CH_2, resonance into two peaks at 7.1 and 7.2 ppm suggests regiorandom coupling between the two monomers.

Scheme 1



i) $^tBuNBr_3$, $CHCl_3$, rt, overnight ii) 4-acetylbromobenzene (a) or 2-acetyl-5-bromothiophene (b), DPP, toluene, 110°C, 24 hours iii)TMSA,$PdCl_2(PPh_3)_2$, CuI, NH^iPr_2, THF, 60°C, 24 hours iv) NaOH, THF, MeOH, rt, 1 hour.

Scheme 2



i) $PdCl_2(PPh_3)_2$, CuI, NH^iPr_2, THF, 60°C, 72 hours

FT-IR spectra of the new PAEs (**6a**, **6b**) were compared with their corresponding monomers (**4a**, **4b**) (not shown). The weak ν(C≡C) band of HC≡C−Ar−C≡CH at 2095 cm^{-1} was shifted to a higher frequency at 2180 cm^{-1} in the polymers, consistent with the known trend that disubstituted acetylenes RC≡CR give rise to the ν(C≡C) band at a higher frequency than monosubstitued acetylenes RC≡CH.[11] The FTIR spectra of **6a** and **6b** do not exhibit an observable ν(C−H) band of the −C≡C−H present in the starting monomers **4a** and **4b** at about 3150 cm^{-1} or a ν(C−Br) band at 980 cm^{-1}. This indicates that polymers with sufficiently high molecular weights were obtained.[12] Peaks observed at 2850−2920 cm^{-1} in the FT-IR spectra of **6a** and **6b** are due to the asymmetric and symmetric stretching of methyl and methylene groups of the alkyl chains. The vibrational bands at 3000−3070 cm^{-1}, assigned to the ν(C−H) of the aromatic rings, were also observed in the polymer

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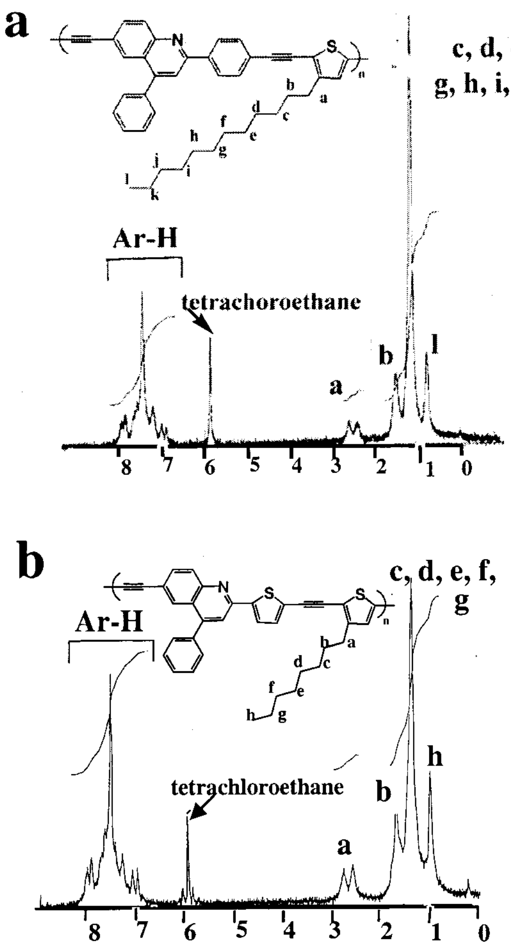

Figure 1. ^{1}H NMR spectra of (a) **6a** and (b) **6b** in 1,1′,2,2′-tetrachloroethane-d_4.

spectra. The FT-IR spectra of both monomers (**4a, 4b**) and polymers also showed the characteristic ν(C=N) stretch of the quinoline ring in the 1580 cm^{-1} region.[5]

The elemental analysis results were in good agreement with the polymer structures, but the analysis for C was lower than expected in the case of **6a**. This difference in C content is likely a result of the much lower molecular weight of **6a** compared to that of **6b**. Thermogravimetric analysis in N_2 revealed that **6a** and **6b** were stable up to 300 °C. Compared to other PAEs with similar side chains which undergo first stage degradation around 180 °C,[13] the present quinoline-containing PAEs have enhanced thermal stability. No glass or melting transition was observed in differential scanning calorimetry scans in N_2 in the 30−375 °C range.

Photophysics. The solution and thin film absorption spectra of the new PAEs are shown in Figure 2a. The absorption maxima (λ_{max}) in THF solution were 430 and 412 nm for **6a** and **6b**, respectively. The absorption maxima of the thin films are red-shifted by about 10−20 nm. Absorption edge optical band gaps determined from the thin film absorption spectra were 2.3 eV for **6a** and 2.4 eV **6b**. The absorption maximum red shift in going from the solution to the solid state may be an indication of either intermolecular interactions (aggregation) or planarization of the PAE backbone conformation.[14] The observed bathochromic shift of the absorption of **6a** from that of **6b** could be a result of improved electron delocalization with the 1,4-phenylene linkage compared to the 2,5-thienylene in the latter polymer or the difference in alkyl chain length (C12 vs C8). We favor the former explanation because of the overall more rodlike conformation of **6a** compared to **6b**.

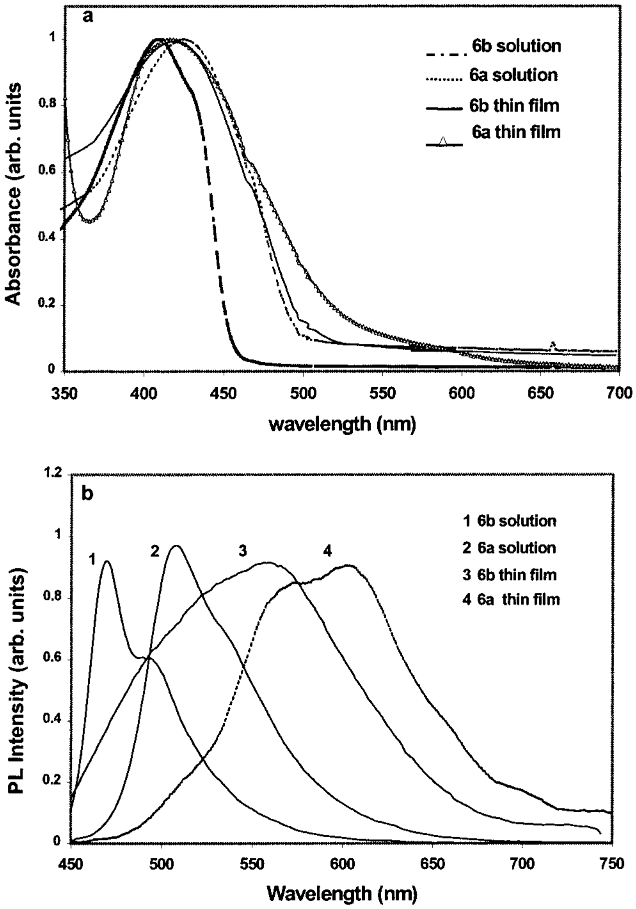

Figure 2. Optical absorption (a) and emission (b) spectra of quinoline-containing PAEs in THF solutions and as thin films.

Figure 2b shows the photoluminescence (PL) spectra of dilute solutions (3.6 × 10^{-5} M) and thin films of the quinoline-containing PAEs. The polymers emit blue and green light in solution, with emission maxima of 470−508 nm. In the solid state, **6b** emits yellow light (λ_{max} = 560 nm) whereas **6a** emits orange light (λ_{max} = 605 nm). The solid-state PL emission spectra are very broad with fwhm of 130 nm for **6b** and 90 nm for **6a** and Stokes shifts of 136−160 nm. These rather large Stokes shifts and broad featureless emission bands in the solid state suggest that the dominant emitting species are intermolecular in nature, namely aggregates and excimers.[14,15] When either **6a** or **6b** was blended with polystyrene at dilute levels (1 wt %), the resulting solid-state PL emission spectrum was identical to that in THF solution, confirming the intermolecular nature of the PL emission from thin films.[15]

The PL quantum yield in solution was 0.46 and 0.64 for **6a** and **6b**, respectively, using dichloroanthracene in hexane as a standard (ϕ = 0.54 at 365 nm).[16a] The PL quantum yield of the new polymers in the solid state was 0.48 for **6a** thin film and 0.69 for **6b** thin film based on a 10^{-3} M diphenylanthracene in poly(methyl methacrylate) standard (ϕ = 0.83).[16b] Although the solid-state PL quantum yields of these quinoline-containing PAEs were not measured with an integrating sphere, they are lower bounds on the absolute values.[6f] Thus, these solid-state fluorescence efficiencies are much higher than those of the polyquinolines[6] and most PAEs.[1,2]

Electrochemical Properties. Cyclic voltammetry in the potential range −2 to 2 V (vs SCE) showed that the new PAEs had a reversible reduction (n-type doping) and an irreversible oxidation (p-type doping) (see Supporting Information). The formal potential ($E°'$) of the reduction wave was −1.6 V for both polymers. The onset potential for the reduction wave was also identical for both polymers at −1.4 V (vs SCE). The electron affinity (LUMO level) for both polymers, estimated from the onset reduction potential by using a value of −4.8 eV as the SCE energy level relative to the vacuum level,[17] is 3.4 eV. The peak oxidation potentials (E_{pa}) were 1.1 and 0.75 V for **6a** and **6b**, respectively. The corresponding onset oxidation potentials were 0.8 and 0.6 V (vs SCE), and from these values ionization potentials (HOMO levels) were estimated to be 5.6 and 5.4 eV for **6a** and **6b**, respectively. The electrochemical band gaps obtained from the onset redox potentials, 2.2 eV for **6a** and 2.0 eV for **6b**, are fairly close to the optical band gaps. The reversible reduction, relatively high electron affinity, and lower ionization potentials of the new PAEs compared to those of most polyquinolines[8] and prior PAEs[18] suggest that they are promising for electroluminescence applications.

Summary. New monomers **4a** and **4b** have been copolymerized with 2,5-dibromo-3-alkylthiophene by palladium-catalyzed polycondensation. The resulting poly(arylene ethynylene)s have a donor−acceptor architecture containing quinoline and 3-alkylthiophene moieties. These polymers combine very high fluorescence efficiency in the solid state with enhanced electrochemical redox properties compared to those of known polyquinolines and prior PAEs.

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Supporting Information Available: Synthetic and characterization details for new compounds, including monomers **4a** and **4b** and polymers **6a** and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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