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Notes

Regioregular Poly(4-alkylquinoline)s: Synthesis, Self-Organization, and Properties

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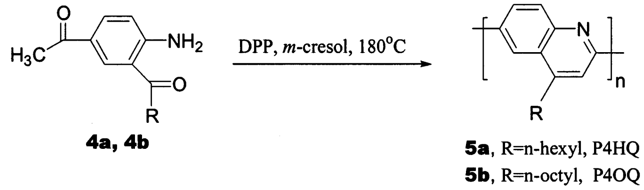
Self-assembly of π-conjugated polymers achieved through head-to-tail, regioregular, alkylated polymer main chains[1] or via block copolymer architectures[2] can lead to highly ordered supramolecular assemblies with interesting electronic and photonic properties. The former approach is exemplified by regioregular poly(3-alkylthiophene)s which self-order into layered crystalline films having high charge carrier mobilities and enhancement in electronic properties.[1,3] They have shown good potential for device applications in field-effect transistors[3] and photovoltaic cells[4] due to their high electrical conductivity and hole mobility. A successful extension of such a strategy to n-type conjugated polymers may prove useful for improving the mobility of electrons and other physical properties. Very few current polymers are known to be capable of showing high field-effect mobility of electrons.[5] We have thus targeted for synthesis and investigation regioregular head-to-tail poly(4-alkylquinoline)s that have the potential to self-organize in ways similar to the regioregular poly(3-alkylthiophene)s.

Numerous phenylated polyquinolines, including poly-(4-phenylquinoline-2,6-diyl) (PPQ), have been synthesized and extensively investigated.[6−9] More recently, the polyquinolines have been explored as emissive and electron transport materials in light-emitting devices.[9] All of the currently known conjugated polyquinolines form amorphous films when solution-cast or spin-coated, lacking long alkyl side chains that can drive the self-ordering of the rigid-rod macromolecules. In this paper, we report the synthesis, characterization, and properties of the first regioregular poly(4-alkylquinoline-2,6-diyl)s exemplified by poly(4-hexylquinoline-2,6-diyl) (P4HQ) and poly(4-octylquinoline-2,6-diyl) (P4OQ). We show that these polymers self-organize into layered ordered structures in solution-cast solid films (Figure 1). The 100% head-to-tail regioregular poly(4-alkylquinoline)s emit blue light in dilute solution and exhibit yellow solid-state photoluminescence and electroluminescence.

Synthesis and Characterization. The synthesis of the regioregular poly(4-alkylquinoline)s, P4HQ (**5a**) and P4OQ (**5b**), is shown in Scheme 1. The new AB-type monomers, 1-(5-acetyl-2-aminophenyl)heptan-1-one (**4a**) and 1-(5-acetyl-2-aminophenyl)nonan-1-one (**4b**), were prepared in four steps by modifying a reported method.[10]

Scheme 1



The molecular structures of P4HQ and P4OQ were confirmed by FT-IR, ^{1}H NMR, and UV−vis spectra (see Supporting Information for details) and by comparison with other polyquinolines.[6−9] The strong FT-IR peaks at 1663 and 1656 cm^{-1} owing to the carbonyl groups in **4a** and **4b** almost completely disappeared in P4HQ and P4OQ. In addition, the two peaks at 3427 and 3314 cm^{-1} in **4a** and 3445 and 3332 cm^{-1} in **4b** corresponding to primary amines were absent in the FT-IR spectra of the polymers. Instead, new strong bands between 1600 and 1400 cm^{-1} due to the imine (C=N) group and characteristic of the quinoline ring were observed.[7] We found that the presence of alkyl side chains in monomers **4a** and **4b** lowered the reactivity compared to the phenyl-substituted monomers.[7] A higher reaction temperature (180 °C) and longer polymerization time were required to achieve the poly(4-alkylquinoline)s compared to the 140 °C normally used in the synthesis of phenylated polyquinolines.[7]

In the ^{1}H NMR spectra, the overall integration ratio between the aliphatic protons and the aromatic protons were consistent with the structures of the polymers. In the aliphatic region, the alkyl chain proton resonances were at 1.01, 1.50, 2.16, and 3.77 ppm in P4HQ and at 0.94, 1.39, 2.14, and 3.76 ppm in P4OQ. The 100% head-to-tail regioregularity of P4HQ and P4OQ automatically follows from the AB-type nature of the condensation polymerization. The presence of only one nonsplitting peak at 3.76−3.77 ppm corresponding to the methylene protons in the α position further confirmed the regioregular structures of the two polymers.[1c] The singlet peak at 3.10 ppm in the ^{1}H NMR spectra of both P4HQ and P4OQ can be assigned as the terminal acetyl protons in the polymer chains. We point out that the elemental analysis results were not in good agreement with the polymer structures, the analytical data for carbon being lower than expected. This is likely due to the incomplete combustion of the two polymers. The rigid main chain structures contributed to their outstanding thermal stability both in inert atmosphere and in air. Stille found a similar large difference in the elemental analysis of poly(4- phenylquinoline-2,6-diyl).[6b]

The two poly(4-alkylquinoline)s were soluble in common organic solvents, such as chloroform, THF, and methylene chloride. The weight-average molecular weights, based on polystyrene standards, were 15 150 for P4HQ and 10 250 for P4OQ with polydispersity indices (M_w/M_n) of 2.79 and 4.02, respectively. The

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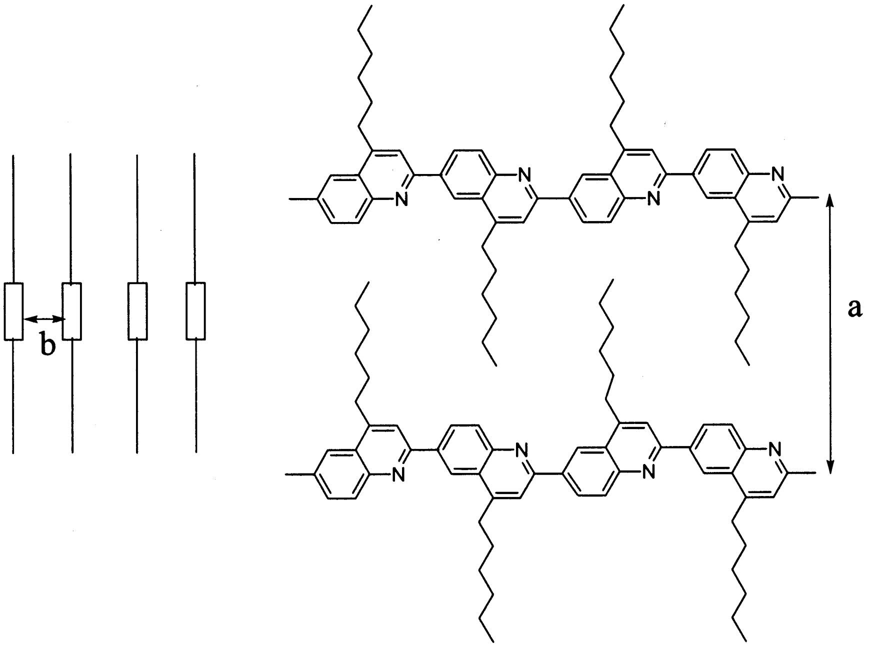

Figure 1. Schematic of layered and $\pi-\pi$ stacking structures of regioregular poly(4-alkylquinoline)s.

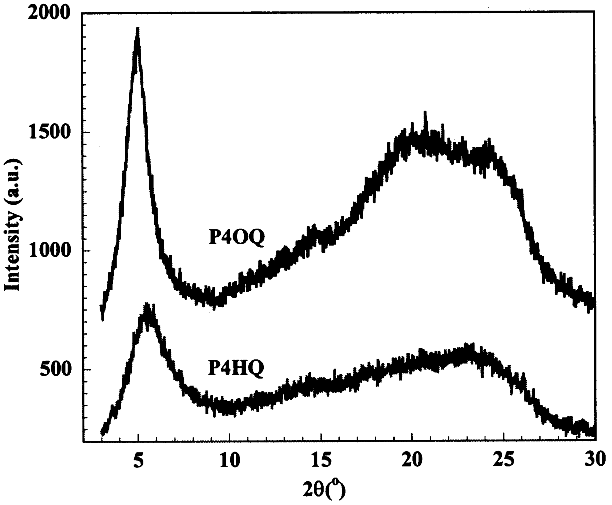

Figure 2. X-ray diffraction pattern of solution-cast films of P4HQ and P4OQ.

corresponding degrees of polymerization were 26 for P4HQ and 11 for P4OQ, respectively. No clear phase transitions were observed in differential scanning calorimetry scans up to 380 °C for both polymers. Thermogravimetric analysis (TGA) revealed that the onset decomposition temperatures of the two polymers under N_2 were about 460 °C. High residual weights of 63% for P4HQ and 57% for P4OQ were observed even at 900 °C under N_2.

Self-Organization in Films. X-ray diffraction patterns of films of P4HQ and P4OQ cast from chloroform are shown in Figure 2. The X-ray diffraction patterns showed a strong first-order reflection at 2θ angle of 5.63° for P4HQ and 5.0° for P4OQ. This corresponded to an interlayer spacing of 15.7 Å for P4HQ and 17.7 Å for P4OQ. In contrast, relatively weak and broad diffractions were observed in the powdered samples. These results show that solution-cast films of poly(4-alkylquinoline)s form layered order structures in which the rigid-rod main chains are spaced by the alkyl side chains (Figure 1). Compared to regioregular poly(3-alkylthiophene)s,[1c] the interlayer spacing is a little shorter in poly(4-alkylquinoline) with the same alkyl side chain. A broad peak in the diffraction pattern centered at 22.4° for P4HQ and 21.6° for P4OQ corresponds to a spacing of 4.0 and 4.11 Å, respectively. This side-chain-length independent spacing is assigned to the $\pi-\pi$ interchain stacking distance. These initial X-ray diffraction results suggest that the new regioregular poly(4-alkylquinoline)s can self-organize in solution processed films.

Photophysical Properties. The optical absorption and emission spectra of P4HQ in THF solution and in the solid state are shown in Figure 3a. Those of P4OQ (see Supporting Information) were almost identical. The two polymers have almost identical lowest energy $\pi-\pi^*$ transitions with a $\lambda_{\max}$ at 389 nm for P4HQ and 395 nm for P4OQ in dilute THF solution and a $\lambda_{\max}$ at 397 nm for thin films of both. The absorption edge band gaps for both polymers is 2.7 eV. They emit blue light in solution with emission peak at 432−435 nm and yellow light in thin films with emission peak at 547 nm. The broad, featureless emission bands with a large Stokes shift in the solid state are characteristic of excimer emission of solid films of many conjugated polymers.[11] The fluorescence quantum yields (ϕ_f) of P4HQ and P4OQ in the solid state were rather low, 2−5%, using a thin film of $\sim 10^{-3}$ M 9,10-diphenylanthracene in poly(methyl methacrylate) as a standard ($\phi_f = 83\%$).[9b]

Electrochemical Properties. Cyclic voltammetry (see Supporting Information for details) showed that the poly(4-alkylquinoline)s have a reversible reduction with onset reduction potential of −1.7 eV vs SCE for both P4HQ and P4OQ. The formal reduction potentials were also identical at −1.82 eV. We estimate the electron affinity (LUMO level) of the two polymers to be 3.1 eV from the onset reduction potential. These results are similar to those of the poly(4-phenylquinoline)s.[8b] However, unlike the phenylated polyquinolines,[8b] P4HQ and P4OQ did not show a clear oxidation, suggesting that the two polymers are more suitable for n-type doping than for p-type doping.

Electroluminescence. Yellow electroluminescence (EL) with emission peak at 552 nm was observed for

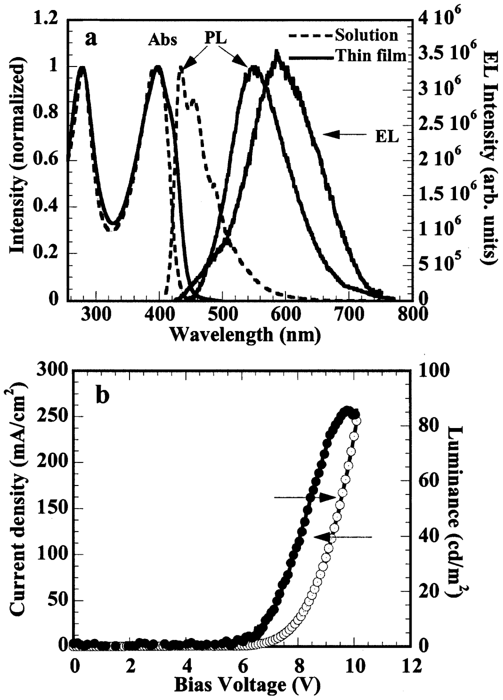

Figure 3. (a) Optical absorption and PL spectra of P4HQ in THF solution (~10^{-6} M) and as a thin film on a silica substrate. Also shown is the EL spectrum of P4HQ. (b) Current−voltage and luminance−voltage characteristics of ITO/PEDOT/PVK/P4HQ/Al LED.

both P4HQ and P4OQ in LEDs of the type ITO/PEDOT/PVK/P4HQ or P4OQ/Al. The EL spectrum of P4HQ is shown in Figure 3a. The nearly identical EL and PL emission spectra mean that the poly(4-alkylquinoline)s function as emissive materials in these diodes. The diodes had a turn-on voltage of 5 V and a luminance of 69−86 cd/m^2 at 10 V for P4HQ and P4OQ. The external quantum efficiencies were 0.6% for P4HQ and 0.22% for P4OQ. Although these LEDs are not optimized, the low performance of P4HQ and P4OQ as emissive EL materials is consistent with their low solid-state PL quantum yield, which in turn originates from their efficient $\pi-\pi$ stacking in films. These polymers are thus more promising as electron-transport materials that could be used in conjunction with other more emissive conjugated polymers for the construction of multilayer and blend LED devices.

Conclusions. Novel poly(4-alkylquinoline-2,6-diyl)s with 100% head-to-tail regioregularity have been synthesized by self-condensation of new AB-type monomers. X-ray diffraction studies confirmed that solution-cast films of these n-type conjugated polymers have self-organized highly ordered lamellar structures. In dilute organic solvent solutions, poly(4-hexylquinoline) and poly(4-octylquinoline) emit blue light, and they exhibit yellow photoluminescence and electroluminescence in the solid state. The synthesis of various regioregular poly(4-alkylquinoline)s and detailed investigation of their structure−self-organization−property relationships are in progress and will be reported in the future.

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Supporting Information Available: Synthetic and characterization details for new compounds, including monomers **4a** and **4b** and polymers **5a** and **5b**. This material is available free of charge via the Internet at http:// pubs.acs.org.

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