Fluorescence Studies of Poly(*p*-phenyleneethynylene)s: The Effect of Anthracene Substitution

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The poly(*p*-phenyleethynylene) molecules, **PI—PIII**, synthesized by a palladium-catalyzed cross-coupling reaction of diiodobenzene derivatives and derivatives of 1,4-diethynylbenzene, are highly luminescent materials. The polymers are soluble by virtue of the $-OC_{16}H_{33}$ groups introduced on the aromatic rings and by controlling their molecular weight. The fluorescent quantum yields are between 0.35 and 0.40 depending on the material. The excited-state lifetimes of the polymers are 1—2 ns, slightly shorter than that of the model compound, 1,4-diphenylethynyl-2,5-dibutoxybenzene, which has a lifetime of 3 ns. Incorporation of anthracene, coupled at the 9,10-positions by using 9,10-bibromoanthracene, into the polymer backbone decreases the quantum yield to between 0.05 and 0.27 depending on the anthracene content. In addition, low-energy electronic transitions and longer wavelength emission bands associated with the anthracene group are produced. The polymers harvest optical energy and transfer it to the anthracene resulting in emission from this chromophore. In the case where only terminal anthracene units, introduced by using 9-bromo-10-phenylethynylanthracene, are present, the process is very efficient with >95% of the energy being transferred to the end groups.

We wish to report investigations on the photoluminescence properties of a series of poly(*p*-phenyleneethynylene) molecules, **PI—PIII** (Chart 1). These polymers are soluble, high molecular weight materials which are highly fluorescent. When anthracene is incorporated into the backbones, the polymers act as antennae which harvest the optical energy and transfer it to the anthracene groups, resulting in emission from these chromophores. The energy-transfer process is particularly efficient even when only the termini of the polymers have anthracene. These results indicate that the polymers may be thought of as large band gap semiconductors with the anthracene inducing a localized narrowing of the band gap.

Our interest in conjugated rigid-rod polymers is due to the fact that they may be thought of as "molecular wires" with well-defined lengths proportional to molecular weight. Conjugated polymers also exhibit unique electronic and photophysical properties, being conductive when doped[1] and photoconductive.[2] These properties make these materials attractive candidates as potential spacer elements in molecular assemblies and as components in electronic and photonic devices.

The inherent insolubility of long, rigid molecules has made them difficult to study. Recently, well-defined, linear, rodlike oligomers have been synthesized in soluble forms by the addition of pendant alkyl or aryl groups to the backbone.[3] Similarly, the attachment of flexible chains to polymer backbones has made it possible to synthesize soluble rigid-rod polymers.[4] Principal interest in much of this work has focused on the liquid crystalline properties of these polymers.[5]

Poly(*p*-phenyleneethynylene) has been made in soluble forms by the addition of long alkoxy chains to the backbone;[6] however, there are still few reports on the optical properties of these polymers. Considering the highly fluorescent nature of phenylethynyl-substituted aromatic compounds[7] and the similar structure of this polymer to other poly(phenylene) molecules already being examined as potential materials in LED devices,[8]

CHART 1
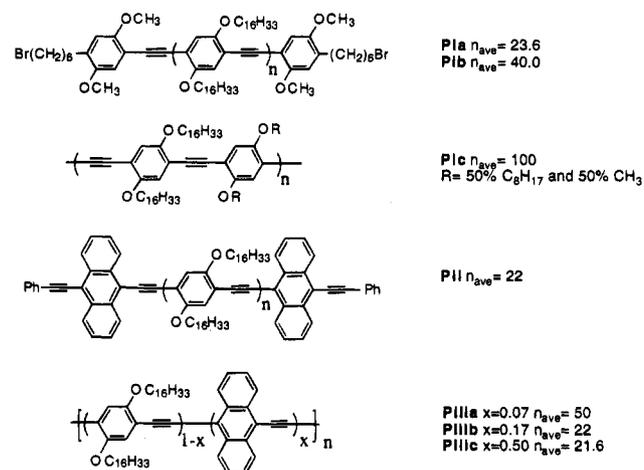
it seemed of interest to examine the photophysical properties of these polymers more closely. Other studies have already shown these polymers to become highly conductive when oxidized and to display liquid crystalline properties and ordered structures in the solid state.[9]

Results and Discussion

Synthesis and Characterization of Polymers. The polymers **PI—PIII** were prepared in good yield by a step growth polymerization employing the palladium-catalyzed cross-coupling of aryl acetylenes and aryl halides (Scheme 1).[10] Several palladium catalyst systems have already been used to synthesize a variety of polymers,[11] including insoluble[12] and soluble[6] low molecular weight poly(*p*-phenyleneethynylene) molecules, by this reaction. The reaction conditions typically used throughout our work involve heating a mixture of the monomers and catalyst (5 mol % of CuI and (PPh$_3$)$_4$Pd) in 30: 70 diisopropylamine:toluene at 70 °C for 14—16 h (Scheme 1). The exclusion of oxygen is necessary to prevent catalyst deactivation and to minimize the copper-catalyzed coupling of acetylenes to diacetylenes which can compete with the desired

Fluorescence Studies of Poly(p-phenyleneethynylene) Molecules

J. Phys. Chem., Vol. 99, No. 14, 1995 **4887**

SCHEME 1: Synthetic Approach to Making Soluble Poly(p-phenyleneethynylene) Molecules

Ia R = C$_{16}$H$_{33}$
Ib R = C$_8$H$_{17}$
Ic R = C$_4$H$_9$
Id R = CH$_3$

II

(PPh$_3$)$_4$Pd/CuI

toluene/diisopropylamine
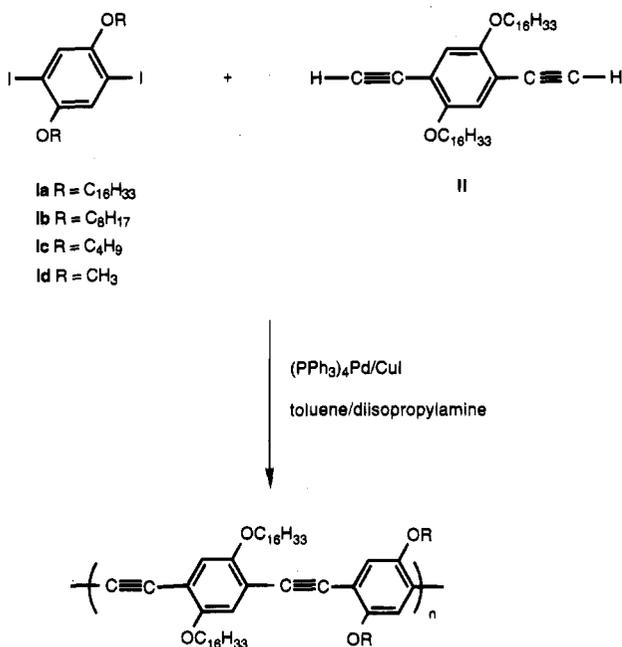
reaction. The high degree of conversion and selectivity of this reaction is also advantageous as it produces material with a high degree of polymerization, DP, and allows for the quantitative incorporation of functionalized end groups. In general, we have found that aryl iodides give better yields than aryl bromides.[13] In order to determine the percent conversion for the monomers used in this study, model cross-coupling reactions with phenylacetylene were performed under typical polymerization conditions and found to proceed quantitatively for monomers of type **I** (Scheme 1 and Table 1) and in 95% (per coupling) yield for 9,10-dibromoanthracene.

As discussed above, the pendant alkyl chains make these materials soluble in organic media. The lower molecular weight materials **PIa** and **PIb**, with mean molecular weights (determined by gel permeation chromatographic (GPC) analysis) of 9400 and 19 200, respectively, are highly soluble in toluene, tetrahydrofuran (THF), and chlorinated solvents. Solutions of **PIa** and **PIb** which contain over 5 wt % polymer form stable gels upon standing but, with heating, redissolve, indicating that only weak physical cross-links are responsible for gelation. By adjusting the monomer stoichiometry closer to unity, soluble high molecular weight polymers may be synthesized. If all the side chains are hexadecyloxy groups, however, solubility is still a problem, and after removal of the solvent only a small amount of these materials redissolve. However, if the side chains are disordered by using monomers with different alkyl substituents, then solubility is increased. For example, **PIc** with a GPC molecular weight of 98 000 is highly soluble in THF, CHCl$_3$, and toluene. The interpolymer interactions which favor the solid state are decreased by the disordered side chains and so solubility is increased. Consistent with this is the observation that even though **PIc** is much higher molecular weight than **PIa** and **PIb**, it does not gel readily.

The anthracene copolymers, **PIIIa−PIIIc**, all have decreased solubilities due to their high molecular weights as well as the small density of alkyl side chains. For example, **PIIIc** is only slightly soluble in CHCl$_3$ but is highly soluble in boiling o-dichlorobenzene. Gels or precipitates are formed when solutions are cooled to room temperature, but dilute solutions (0.01 mg/mL) are stable for long periods.

The ^{1}H NMR handles provided by the end capping group **III** provide a convenient method for determining the degree of

III
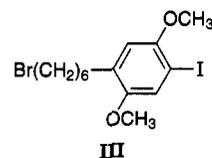
polymerization, DP,[14] or average number of repeat units, of **PIa** and **PIb** which correlates directly with the mean molecular weight of the polymer. The methoxy groups are well resolved from all other polymer signals in the ^{1}H NMR. Also, under the polymerization conditions used, the alkyl bromide group of **III** remains intact and the methylene protons alpha to the bromide are visible in the ^{1}H NMR and integrate correctly versus the methoxy groups. Since the cross-coupling reaction with dialkoxyphenyl iodides is quantitative, all of the polymers (except **PII**) are end capped with **III**, and the DP may be determined by straightforward integration of the end-group and polymer signals. By this method, the DP was found to be 23.6 for **PIa** and 40.0 for **PIb** which are in good agreement with the theoretical values of 20 and 41, respectively.[15] The slightly higher than expected value for **PIa** results from the loss of low molecular weight material during polymer isolation. These values are also self-consistent with the molecular weights of the polymers as determined by GPC, 9400 for **PIa** and 19 200 for **PIb**. ^{1}H NMR analysis of **PIc** gave no sign of any acetylene protons indicating that the polymers are predominantly terminated with the aryl iodide.

The rigid structure of these polymers results in an average polymer length which is proportional to the molecular weight and can be estimated by multiplying the length of the repeat units by the DP. With the length of the repeating unit being 6.75 Å,[16] the average length of **PIa** is 165 Å and **PIb** about 275 Å. Considering that the DP scales linearly with the polystyrene molecular weight, the DP of **PIc** is estimated to be roughly 10 times that of **PIa** or approximately 100 for the expanded repeat unit. This corresponds to an average length of approximately 1300 Å. However, it should be pointed out that these step-growth polymerizations produce materials with broad molecular weight distributions characterized by a polymer dispersity index of about 2.[17]

The cross-coupling reaction of both 9,10-dibromoanthracene and the capping group **IV**, with aryl acetylenes is not quantitative but the anthracene content of the polymers can be determined from ^{1}H NMR integration. In the model compound **V**,

IV

V
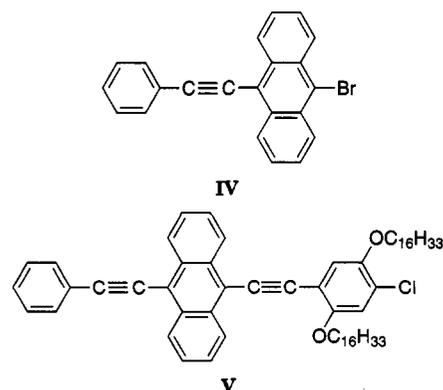
anthracene has well-resolved resonances at 7.4 and 8.9 ppm, a region in which the polymer backbone has no signals. Polymer **PII** displays anthracene resonances with virtually identical chemical shifts as **V**. ^{1}H NMR integration indicates ap-

proximately one phenylethynylanthracene group for 13 polymer repeat units. However, **PII** was produced from the same monomer ratio as **PIa** and has a similar molecular weight as determined by GPC, 9100. This corresponds to a DP of 22 or one anthracene end group for 11 polymer repeat units. The lower than expected anthracene content suggests that 2−5% of the polymer chains are without anthracene end groups.

The anthracene contents of **PIIIa** and **PIIIb** were determined by integration of the downfield anthracene signals at 8.83 and 7.75 ppm and were found to be 6.8 and 17.5 mol %, respectively. These are lower than predicted by the monomer stoichiometries used and is a result of the lower cross-coupling yield with 9,10-dibromoanthracene resulting in lower molecular weight material which is removed during the reaction workup. The lower cross-coupling yield also results in bromoanthracene end groups, as indicated by elemental analysis data which found **PIIIa** and **PIIIb** to have 0.5 and 1.5% bromine, respectively. In addition, a weak broad signal in the ^{1}H NMR at 8.65 ppm for **PIIIb** is similar to the 8.69 ppm resonance for the protons beta to the bromide in 9-bromo-10-phenylanthracene. As a result of the low solubility of these materials, GPC analysis was not performed. However, if it is assumed that all the end groups are bromoanthracene, then the bromine content may be used as a rough estimate of the molecular weight. This analysis yields DP's of 50 for **PIIIa** and 22 for **PIIIb**. For **PIIIb** the DP determined by integration of the 8.69 ppm signal, 24, is also consistent with this analysis. For **PIIIc**, elemental analysis of the bromine end groups yields a DP of 10.8 considering an expanded repeat unit which includes both an anthracene and a phenyl group.

Fluorescence Measurements. The absorption and emission spectra of **PIa** and the model compound **VI** are shown in Figure

VI
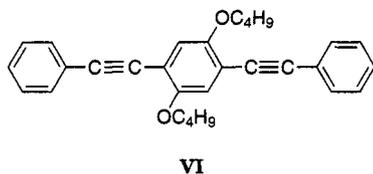
1. The absorption maximum at 446 nm and the emission maximum at 478 nm of the polymer are substantially red-shifted relative to **VI** as a result of the extended conjugation. Both materials are highly fluorescent with quantum yields of 0.35 and 0.74 in CHCl$_3$ for **PIa** and **VI**, respectively. The molar extinction coefficient of the 446 nm band of **PIa** was found to be 19 000 cm^{-1} M^{-1} per repeat unit, which is approximately the same as that of phenylacetylene, indicating that the polymer behaves as if it is composed of isolated chromophores. The emission band of **PIa** is sharper than its absorbance band and even narrower than that of **VI**. This result is surprising considering that **PIa** is composed of a distribution of molecules of different lengths. Increasing the molecular weight above that of **PIa** produces only minor effects in the photophysical properties of the polymer.[18] **PIb** exhibits absorbance and emission spectra which are indistinguishable from those of **PIa** within the resolution of our measurements, even though **PIb** has approximately twice the DP. In addition, **PIc**, which has an estimated DP of approximately 200, has spectra which are red-shifted only slightly from **PIa**, absorbing at 452 nm and emitting at 482 nm. However, the shape of the major absorbance band of **PIc** is slightly different with a more abrupt rise in the absorption on the lower energy side of the absorption. This insensitivity to molecular weight is also revealed in the fact that the emission maximum is insensitive to the excitation wavelength and remains constant with excitation light between
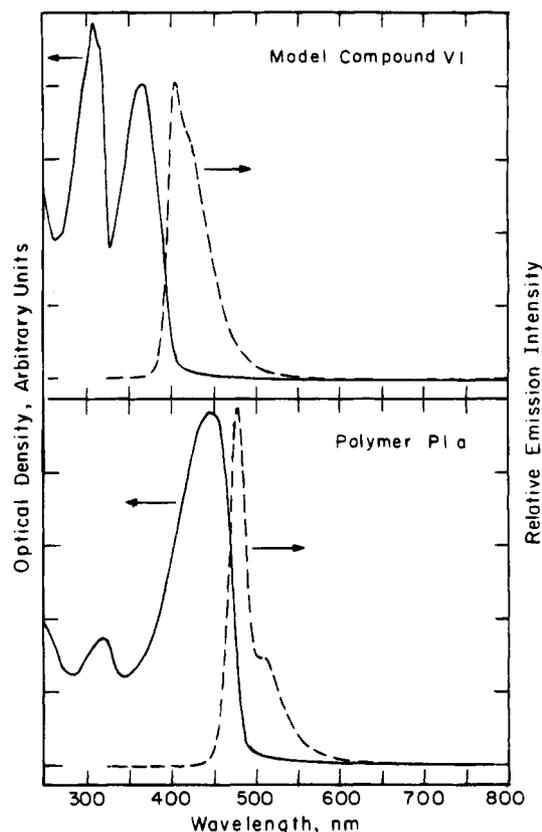
Figure 1. Absorption and emission spectra of **VI** (top) and **PIa** (bottom). The absorption maxima of **VI** are at 308 and 362 nm and those of the polymer are at 318 and 446 nm. The emission maximum of **VI** is at 405 nm with a shoulder at 420 nm, and the maxima for **PIa** are at 478 and 510 nm.

320 and 480 nm, a wavelength region in which one would expect to be exciting different fractions of polymers with varying length. Additionally, corrected excitation spectra match the absorption spectra of the polymers. The emission quantum yields of **PIa** and **PIb** are also the same, within experimental error, but the higher molecular weight polymer, **PIc**, exhibits a slightly higher quantum yield of 0.40. The insensitivity of the optical properties is likely due to polymer conformations which produce conjugation lengths which are shorter than the total polymer length. **PIa**, **PIb**, **PIc**, and model compound **VI** all have relatively short lifetimes as evidenced by their relative insensitivity to quenching by O$_2$. Assuming diffusion-limited quenching of the fluorescence of O$_2$, the approximate excited-state lifetimes are calculated to be 1 ns for **PIa** and **PIb**, 2 ns for **PIc**, and 3 ns for **VI**, using Stern−Volmer quenching data.

In Figure 2 the absorbance and emission spectra of **PII** and model compound **V** are compared. The absorption spectrum of **PII** appears to be a straightforward composite of **PIa** and **V**, with a red shift in the bands attributed to the phenylethynylanthracene end group relative to **V**. Hence, the absorption bands of **PII** at 279 and 498 nm are considered to be similar in nature to the 279 nm and 481 nm bands of **V**, with the red shift resulting from conjugation. Similarly, the polymer bands at 316 and 452 nm are at similar wavelengths as those of **PIa**. The fact that the shape of the absorption spectrum of the polymer appears unchanged indicates that the end group produces a small perturbation resulting in some low-energy electronic states at the termini of the polymer. Nevertheless, these low-energy states have a large effect on the emission spectrum. Almost all the emission occurs in a band at 524 nm with a small amount (ca. <5%) at 478 nm. The latter band is at the same wavelength

Fluorescence Studies of Poly(p-phenyleneethynylene) Molecules

J. Phys. Chem., Vol. 99, No. 14, 1995 **4889**
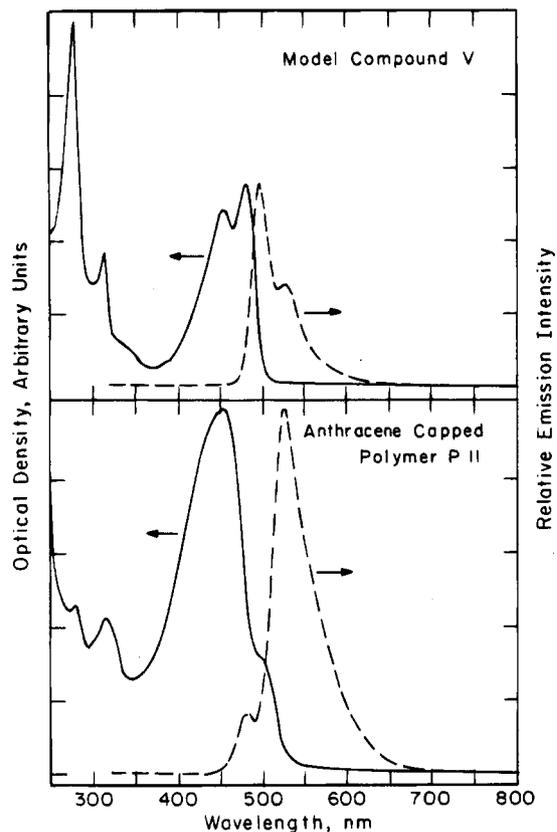
Figure 2. Absorption and emission spectra of **V** (top) and **PII** (bottom). The absorption spectrum of **PII** resembles a composite of **PIa** and **V** where the bands due to **V** are red-shifted due to conjugation. The majority of the emission occurs from the band at 524 nm which is not observed in polymers without anthracene end groups, while a small amount of emission occurs from a band at 474 nm where **PIa** emits.

Figure 3. Absorption and emission spectra of **PIIIa** (top) and **PIIIb** (bottom). For both materials the majority of the emission occurs from low-energy states introduced by the anthracene groups.

as that of **PIa** while the 524 nm band is new. The emission quantum yield of **PII** is 0.28, only slightly lower than that of **PIa**, and emission from the model compound **V** is highly efficient with a quantum yield of 0.90. The emission spectra of both materials are insensitive to the excitation wavelength and corrected excitation spectra match the absorption spectra showing that the 524 nm emission band results from excitation of the bulk material. The emissions of both **PII** and **V** are relatively insensitive to quenching by O_2, and Stern—Volmer analyses give lifetimes of 1 and 3 ns, respectively. The lifetime for **V** is in accord with direct lifetime measurements of 9,10-diphenylethynylanthracene derivatives which vary between 3.17 and 3.4 ns.[7a] Since **PII** and **PIa** have the same molecular weight, the only explanation for the longer wavelength emission of **PII** is that the energy resulting from random excitation of the polymer backbone migrates to the lower energy end-group states producing the 524 nm emission. As discussed previously, a small amount of the material of **PII** does not contain anthracene end groups which may account for the emission at 478 nm.

The anthracene copolymers, **PIIIa**, **PIIIb**, and **PIIIc**, also exhibit low-energy absorbances and emissions not present in **PIa**, (Figures 3 and 4). For **PIIIa** the anthracene concentration is low, 7 mol %, and may be considered a dopant which produces low-energy states within the polymer backbone. The new absorption bands at 494 and 527 nm due to the anthracene are red-shifted with respect to those of the end groups of **PII** due to the increased conjugation obtained by having the anthracene group in the polymer backbone. The majority of the emission from **PIIIa** occurs at 549 nm, although there is
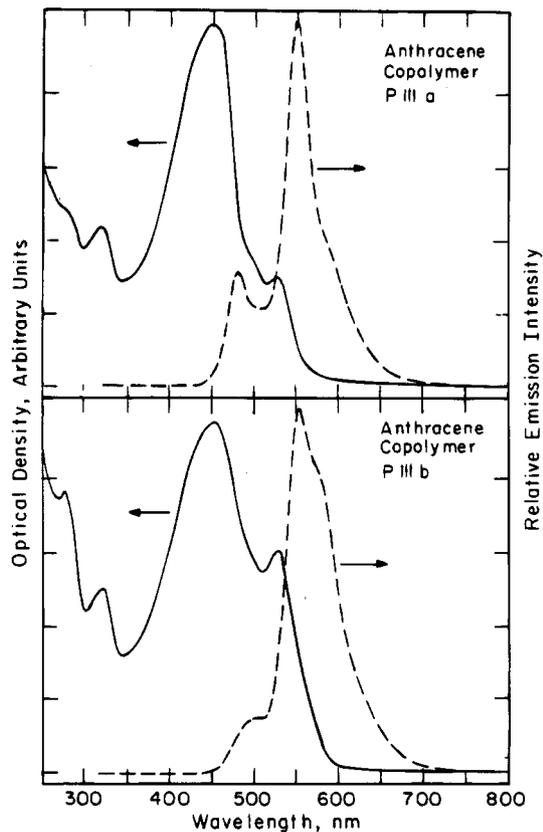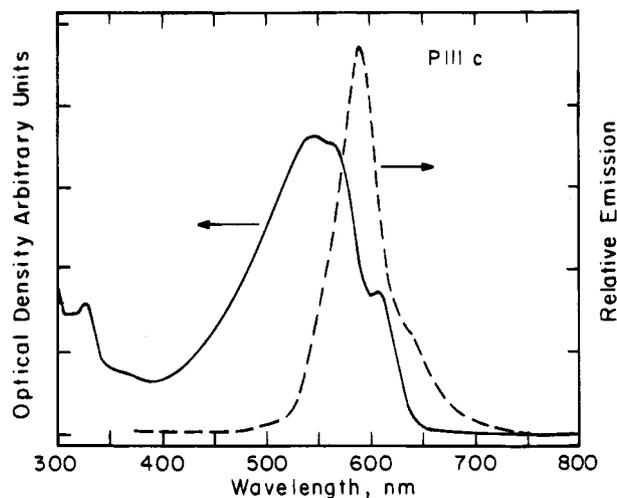
Figure 4. Absorption and emission spectra of **PIIIc**. There is a sizable overlap of these bands and the spectra are red-shifted from those of **PIIIa** and **PIIIb**.

still a peak at 480 nm where **PIa** emits. The quantum yield of **PIIIa** is 0.14, considerably less than that of **PII**. Stern—Volmer analysis for O_2 quenching indicates that the 480 nm band has a short lifetime, <1 ns, while the 549 nm peak has a 1 ns lifetime, indicating that there are two emitting states or molecules present. The results from **PII** suggest that the 480 nm band may be due to material which does not contain anthracene. The 480 nm band accounts for roughly 30% of the emission but, since the quantum yield is less than half that of **PIa**, this band could be produced if <15% of the material does not contain anthracene groups.

For **PIIIb** the anthracene content is increased to 17 mol %. The emission appears very similar to that of **PIIIa**; however,

4890 *J. Phys. Chem., Vol. 99, No. 14, 1995*

Swager et al.

the quantum yield has decreased to 0.09. In this case there is no emission at 480 nm, indicating that all the polymers contain anthracene groups. The main emission band is at 551 nm with an additional band at 502 nm. Stern−Volmer analysis for O_2 quenching shows both bands have similar lifetimes, approximately 2.5 ns, so it is unknown whether these bands originate from different emitting states. However, the 502 nm band may be the result of polymers containing bromoanthracene end groups which are known to be present by ^{1}H NMR and elemental analysis. This is consistent with the fact that 9-bromo-10-phenylethynylanthracene is highly fluorescent, exhibiting an emission maximum at 442 nm and a quantum yield of 0.48.

The absorption and emission spectra for the alternating copolymer, **PIIIc**, are shown in Figure 4. The absorption maximum at 543 nm is substantially red-shifted compared to the longest wavelength absorbances of **PIIIa** and **PIIIb**. The emission is also red-shifted with the maximum at 590 nm. The quantum yield continues to decrease with the increased anthracene content, falling to 0.05 for **PIIIc** with a lifetime of 1 ns.

The effect of anthracenyl groups on the photophysical properties of the poly(p-phenyleneethynylene) molecules is quite interesting. Low-energy emitting states are introduced into the backbone by the anthracene, although the quantum yield for emission decreases with increased anthracene concentration. The polymers function as antennae that harvest optical energy and deliver it to these anthracenyl sites resulting in emission from the anthracene chromophore. For the end-capped **PII** polymer, the process is highly efficient resulting in 95% energy transfer to the end groups. This efficiency is impressive when one considers that, although the polymer chains have an average degree of polymerization of 21−23, the polydisperse nature of this material results in an appreciable fraction of high molecular weight polymer. Hence, it appears that these materials are capable of efficient energy transfer over large distances.

The antenna effect is a key feature in photosynthesis and has also been demonstrated in reasonably high efficiency in other polymeric systems.[19] Previously studied polymeric systems consisted of saturated polymer backbones with pendant naphthalene chromophores and anthracene end groups. However, these materials are different from **PII** in that the chromophores are localized and exhibit little or no interaction with each other. As a result, energy transfer between the pendant chromophores occurs through a Förster energy-transfer mechanism.[19,20] For **PII**, the situation is different, since the conjugated nature of the polymer results in strong interactions which produce energy bands as is evident from the conductive nature of the oxidized polymer[9] and from band calculations.[21] As a result, **PII** is more akin to a semiconductor which is doped with some emitting impurity and photoexcitation produces an electron−hole pair which may be bound together in the form of an exciton.[22] These polymers are also photoconductive[23] which is also consistent with the formation of an electron−hole pair upon photoexcitation. In this model, the carriers migrate through the polymer backbone to the terminal anthracene group which introduces a localized narrowing of the band gap and recombination of the carriers resulting in emission. A schematic representation of this model is shown in Scheme 2.

Conclusions

Soluble conjugated rigid-rod poly(p-phenyleneethynylene) molecules can be made in good yield by a step growth polymerization using the palladium cross-coupling reaction of aryl acetylenes and aryl iodides. Variations in monomer ratios can be used adjust the molecular weights of the polymers and

SCHEME 2: Representation of Energy Migration in a Semiconductive Molecular Wire with a Decrease in Band Gap at the Terminus[a]
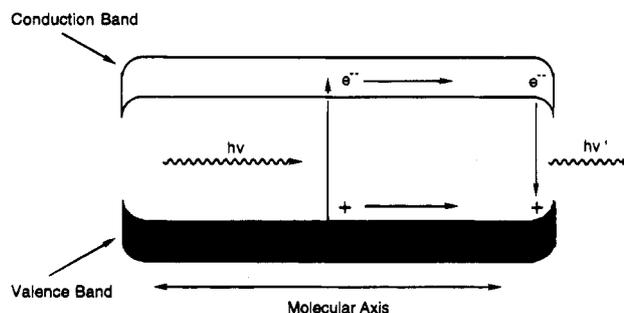
[a] Initial photoexcitation generates an electron−hole pair which migrates to the region of the narrowed band gap and then recombines with emission.

high molecular weight polymers can be synthesized. Functional groups may be incorporated in high yield at the polymer termini by using a monomer with only one reactive bond, typically an aryl iodide or aryl bromide. The polymers are highly fluorescent and the high quantum yields exhibited by these materials are likely due to the rigid structure which limits potential nonradiative deactivation pathways. When low-energy states are incorporated into the polymer backbone by means of anthracenyl groups, energy transfer occurs to these units resulting in emission from the anthracene. When these groups are only at the termini of the polymers, energy transfer is efficient, with >95% of the energy being transferred to the terminal anthracene group.

Experimental Section

Physical Measurements. All absorption and emission spectra were obtained in $CHCl_3$ except for **PIIIc** which was obtained in distilled o-dichlorobenzene. Both solvents were determined to be free of emitting impurities prior to use. The absorption spectra and optical density measurements were obtained on a Hewlett-Packard 8451a diode array spectrophotometer. The emission spectroscopy was performed using a Hitchi Perkin-Elmer spectrophotofluorimeter operating with a 150 W high-pressure xenon arc lamp powered by a Perkin-Elmer 150 Xe power supply and using a Hamamatsu HR777 photomultiplier tube detector. The PMT output was collected on a Nicolet 4094 digital storage oscilloscope. The data was transferred to an IBM PC for plotting and numerical integrations. The spectra presented are uncorrected for detector response but the manufacturer's specifications indicate that response is nearly wavelength independent over the 400−650 nm region. All emission studies were performed on optically dilute solutions with absorption maxima less than 0.1. All quantum yields were measured relative to quinine sulfate in 1 N H_2SO_4 assuming a quantum yield of 0.55 and an excitation wavelength of 320 nm. Corrections for refractive indices and differences in optical densities were applied. All emission measurements were made in four-sided quartz cells and in quantum yield measurements care was taken to use only matched cells. Stern−Volmer investigations were made using an excitation wavelength of 250 nm, assuming an ambient oxygen concentration of 2.6 mM in $CHCl_3$ and 2 mM in o-dichlorobenzene and a diffusional quenching rate constant of 10^{10} M^{-1} s^{-1}. The three-point Stern−Volmer measurements were made after bubbling solvent-saturated argon, air, and oxygen through the sample for 30 min. In all of the reported measurements the three points constituted a straight line with an intercept of 1.

Molecular weight determinations were made at a flow rate of 1 mL/min in toluene with Waters Ultrastyragel columns with

Fluorescence Studies of Poly(p-phenyleneethynylene) Molecules

J. Phys. Chem., Vol. 99, No. 14, 1995 **4891**

10^5, 10^4, 10^3, and 10^2 Å pore sizes. The molecular weights are reported relative to narrow dispersity polystyrene standards. GPC measurements made without the 10^2 Å column gave molecular weights which were approximately twice those reported. All samples analyzed by GPC gave a single broad peak and no bimodal distributions were observed.

^{1}H NMR spectra were obtained in CDCl$_3$ on a Bruker 250 or Varian XL-300 spectrometer and referenced to residual protio CHCl$_3$ at 7.24 ppm. ^{13}C spectra were obtained on a Varian XL-300 spectrometer and referenced to the carbon signal of CDCl$_3$ at 77.0 ppm.

Elemental analyses were obtained from Galbraith Laboratories.

Syntheses. Materials. Diisopropylamine was distilled from KOH and toluene was distilled from CaH$_2$ under a N$_2$ atmosphere. Both solvents were sparged with Ar for 2 h and stored under Ar. CuI, 1-hexadecyl bromide, 1-octyl bromide, phenylacetylene, 9,10-dibromoanthracene, and chloro-p-hydroquinone were purchased from Aldrich Chemical Co. and used without further purification. Trimethylsilylacetylene was obtained from Farchan Laboratories and used without further purification. (PPh$_3$)$_4$Pd and (PPh$_3$)$_2$PdCl$_2$ were obtained from Strem Chemical Co. (PPh$_3$)$_4$Pd was stored and handled in a N$_2$ atmosphere drybox. All cross-coupling reactions using this catalyst used standard Schlenk and vacuum line techniques.

1,4-Dihexadecyloxybenzene: 0.18 mol of K$_2$CO$_3$ and 0.164 mol of 1-hexadecyl bromide were added to a solution of 0.0744 mol of p-hydroquinone in 600 mL of acetone. This mixture was refluxed under N$_2$ for 3 days at which time an additional 0.06 mol of K$_2$CO$_3$ was added and refluxing continued for 2 days. Toluene was added to help dissolve the product and the hot mixture was filtered to remove insolubles. Evaporation of the solvent yielded a brown solid which was recrystallized twice from acetone/toluene to yield a fluffy white material in 76% yield. mp 85−87 °C. ^{1}H NMR (CDCl$_3$) d 6.88 (s, 4 H), 3.71 (t, 4 H), 1.68 (m, 4 H), 1.40−1.25 (br m, 52 H), 0.91 (t, 6 H). Also synthesized by this method were 1,4-dioctyloxybenzene, 1,4-dibutyloxybenzene, and 1-chloro-2,5-dihexadecyloxybenzene. mp 67−70 °C. ^{1}H NMR (CDCl$_3$) d 6.92 (d, 1 H), 6.81 (d, 1 H), 6.70 (dd, 1 H), 3.93 (t, 2 H), 3.87 (t, 2 H), 1.76 (m, 2 H), 1.48−1.20 (br m, 54 H), 0.83 (t, 6 H).

1,4-Dihexadecyloxy-2,5-diiodobenzene (Ia): 0.0286 mol of 1,4-dihexadecyloxybenzene, 0.0114 mol of KIO$_3$, and 0.0315 mol of I$_2$ were combined in 300 mL of acetic acid, 3 mL of H$_2$SO$_4$, and 30 mL of H$_2$O. The mixture was refluxed for 6 h and then 20% aqueous Na$_2$S$_2$O$_4$ was added until the brown iodine color was gone. The precipitate was collected, rinsed with cold EtOH, and recrystallized twice from EtOH/CHCl$_3$ to yield 83% of analytically pure material. Anal. Calcd for C$_{38}$H$_{68}$O$_2$I$_2$: C, 56.3; H, 8.4; I, 31.3. Found: C, 56.41; H, 4.23; I, 30.54. mp 76−77 °C. ^{1}H NMR (CDCl$_3$) d 7.14 (s, 2 H), 3.90 (t, 4 H), 1.89 (m, 4 H), 1.46 (br m, 4 H) 1.24 (br s, 48 H), 0.88 (t, 6 H). ^{13}C NMR (CDCl$_3$) d 153.2, 123.3, 86.5, 70.7, 32.0, 29.7, 29.6, 29.4, 26.7, 26.1, 14.0. Mass spectrum (EI): 812 (6), 811 (24), 810 (72), 362 (100). Other compounds obtained by this procedure: 1,4-dioctyloxy-2,5-diiodobenzene (**Ib**), mp 52−53 °C; 1,4-dibutyloxy-2,5-diiodobenzene (**Ic**), mp 82−83 °C; 1,4-dimethoxy-2,5-diiodobenzene (**Id**) mp 168−169 °C (lit. 167−168 °C);[24] 1-chloro-4-iodo-2,5-dihexadecyloxybenzene (93% yield) mp 77−79 °C. ^{1}H NMR (CDCl$_3$) d 6.84 (s, 1 H), 7.30 (s, 1 H), 3.93 (m, 4 H), 1.6−1.2 (br m, 52 H), 0.90 (m, 6 H).

1,4-Diethynyl-2,5-dihexadecyloxybenzene (II): 0.0123 mol of **Ia**, 0.6 mmol of CuI, and 0.6 mmol of (PPh$_3$)$_2$PdCl$_2$ were dissolved in 150 mL of diisopropylamine at room temperature.

0.0271 mol of trimethylsilylacetylene was added to the mixture over the course of 15 min. A heavy ammonium iodide salt formed immediately and at the end of the addition the solution turned dark brown. This mixture was refluxed for 2 h, diluted with toluene and filtered and the solvent was removed on a rotary evaporator. The remaining brown solid was dissolved in toluene and passed through a 4 cm plug of silica gel. Removal of the solvent yielded a brown solid which was recrystallized twice from EtOH/CHCl$_3$ to give 92% pure 1,4-bistrimethylsilylethynyl-2,5-dihexadecyloxybenzene as a white crystalline solid, mp 61−63 °C. ^{1}H NMR (CDCl$_3$) d 6.86 (s, 2 H), 3.91 (t, 4 H), 1.77 (m, 4 H), 1.46 (m, 4 H), 1.23 (br s, 48 H), 0.87 (t, 6 H). ^{13}C NMR (CDCl$_3$) d 154.3, 117.9, 114.5, 101.3, 100.0, 69.9, 32.0, 29.7, 29.4, 26.1, 22.7, 14.0, 0.01. Mass spectrum (EI): 752 (11), 751 (451), 750 (82), 158 (100). 100 mL of methanol and 2 mL of 20% KOH were added to a rapidly stirred solution of 0.0114 mol of this material in 200 mL of THF at room temperature. The mixture initially gelled and then after a couple of minutes became homogeneous and a white precipitate formed. The mixture was stirred for 5 h and then 200 mL of methanol was added. The mixture was filtered and the solvent removed by rotary evaporation. The remaining solid was recrystallized twice from hexane with charcoal to yield white crystalline material. Anal. Calcd for C$_{42}$H$_{70}$O$_2$: C, 83.11; H 11.62. Found. C, 83.13; H, 11.51. mp 87−88 °C. ^{1}H NMR (CDCl$_3$) d 6.96 (s, 2 H), 3.50 (t, 4 H), 3.07 (s, 2H), 1.6 (m, 4 H), 1.29 (br m, 52 H), 0.92 (m, 6 H). ^{13}C NMR (CDCl$_3$) d 154.0, 117.7, 113.2, 82.4, 79.8, 69.7, 31.9, 29.7, 29.6, 29.4, 29.1, 25.9, 22.7, 14.1. Mass spectrum (EI): 608 (13), 607 (50), 606 (100).

1-Iodo-4-hexyl-6'-bromo-2,5-dimethoxybenzene (III): 0.0256 mol of 1,4-dimethoxybenzene was dissolved in dry, deoxygenated THF and the mixture was cooled to −30 °C. 0.027 mol of n-BuLi (2.5 M in hexanes) was slowly added and the reaction was gradually warmed to room temperature. This solution was slowly added to 0.1 mol of 1,6-dibromohexane kept under Ar and the mixture was stirred at room temperature overnight to give a pale yellow reaction mixture. Excess THF and hexane was distilled off at ambient pressure while excess 1,6-dibromohexane distilled at 50 °C at 5 × 10^{-5} mmHg. 3.8 g of 1-(hexyl-6'-bromo)-2,5-dimethoxybenzene was collected as a clear oil boiling at 125−130 °C at 5 × 10^{-5} mmHg. 2.0 g of this material was combined with 4 mmol of I$_2$, 1.7 mmol of KIO$_3$, 20 mL of acetic acid, 5 mL of H$_2$O, and 0.5 mL of H$_2$SO$_4$ and refluxed for 4 h. A 20% aqueous solution of Na$_2$S$_2$O$_4$ was added to the cooled mixture until the iodine color was gone. The mixture was added to water and the product extracted with CH$_2$Cl$_2$. The organic layer was dried over MgSO$_4$ and filtered, and the solvent was evaporated to give a yellow to brown oil which was chromatographed on silica gel (230−400 mesh, 60 Å) with 40:10 hexane:CHCl$_3$. The second fraction was the product and was isolated as a white solid after recrystallization from EtOH, in 80% yield. Anal. Calcd for C$_{14}$H$_{20}$IBrO$_2$: C, 39.36; H 4.72. Found: C, 38.5; H 4.51. mp 47−48 °C. ^{1}H NMR (CDCl$_3$) d 7.18 (s, 1 H), 6.63 (s, 1 H), 3.82 (s, 3 H), 3.77 (s, 3 H), 3.41 (t, 2 H), 2.55 (t, 2 H), 1.85 (q, 2 H), 1.62−1.23 (m, 6 H). ^{13}C NMR (CDCl$_3$) d 152.4, 152.3, 132.5, 121.5, 113.2, 81.7, 57.1, 56.1, 34.0, 32.7, 30.3, 29.6, 28.5, 27.9. Mass spectrum (EI): 277 (100), 429 (4.0), 428 (36.0), 426 (37.6).

9-Bromo-10-phenylethynylanthracene (IV): 3.0 mmol of 9,-10-dibromoanthracene, 0.03 mmol of CuI, and 0.03 mmol of (PPh$_3$)$_4$Pd were dissolved in 15 mL of diisopropylamine and 35 mL of toluene under an Ar atmosphere. 6.0 mmol of phenylacetylene was then added and the mixture was heated at 70 °C for 15 h. After cooling to room temperature the mixture

was filtered and the solvent removed under vacuum. The resulting solid was chromatographed on silica gel with 70:30 hexane:CHCl$_3$ to give 80% of pure 9,10-diphenylethynylanthracene, mp 254−255 °C (lit. 250−252 °C),[25] and 51 mg of pure 9-bromo-10-phenylethynylanthracene, mp 167−168 °C. ^{1}H NMR (CDCl$_3$) d 8.69 (m, 2 H), 8.55 (m, 2 H), 7.73 (m, 2 H), 7.63 (m, 4 H), 7.42 (m, 3 H). ^{13}C NMR (partial) (CDCl$_3$) d 131.7, 128.8, 128.6, 128.3, 127.5, 127.3, 126.9, 105.1. UV−vis (CHCl$_3$) λ_{max}, nm (log e): 302 (4.15), 410 (4.16), 434 (4.16). Mass spectrum (EI): 359 (30), 358 (98), 257 (26), 356 (100), 276 (87).

Model Compound V. 9-Phenylethynyl-10-[1-chloro-4-ethynyl-2,5-di-hexadecyloxybenzene]anthracene: 6.96 mmol of 1-chloro-4-iodo-2,5-dihexadecyloxybenzene, 0.03 mmol of (PPh$_3$)$_2$PdCl$_2$, and 0.03 mmol of CuI were dissolved in 25 mL of diisopropylamine and 60 mL of toluene. As 8 mmol of trimethylsilylacetylene was added a heavy ammonium iodide salt formed immediately. The reaction mixture was then heated at 70 °C for 5 h. After cooling, the mixture was filtered and the solvent evaporated. Recrystallization of the remaining solid from EtOH/CHCl$_3$ produced white crystals of 1-chloro-4-trimethylsilylethynyl-2,5-dihexadecyloxybenzene in 95% yield. ^{1}H NMR (CDCl$_3$) d 6.94 (s, 1 H), 6.84 (s, 1 H), 3.92 (m, 4 H), 1.77 (m, 4 H), 1.47 (br m, 4 H), 1.23 (br s, 48 H), 0.85 (t, 6 H), 0.23 (s, 9 H). This material was then dissolved in 100 mL of THF and 50 mL of methanol and 1 mL of a 20% aqueous KOH solution was added and the mixture stirred for 5 h at room temperature. 100 mL more of methanol was added, the mixture filtered, and the solvent evaporated. Recrystallization of this solid from CHCl$_3$/toluene gave slightly yellow crystals of 1-chloro-4-ethynyl-2,5-dihexadecyloxy-benzene. mp 73−76 °C. ^{1}H NMR (CDCl$_3$) d 6.98 (s, 1 H), 6.88 (s, 1 H), 3.93 (m, 4 H), 3.25 (s, 1 H), 1.78 (m, 4 H), 1.61−1.20 (br m, 52 H), 0.88 (t, 6 H). ^{13}C NMR (CDCl$_3$) d 154.7, 152.1, 124.8, 118.8, 115.1, 110.6, 81.5, 79.5, 70.1, 69.9, 32.0, 29.7, 29.4, 29.2, 29.1, 25.9, 22.7, 14.1. 0.07 mmol of this material, 0.065 mmol of 9-bromo-10-phenylethynylanthracene, 0.01 mmol (PPh$_3$)$_4$Pd, and 0.01 mmol of CuI were dissolved in 5 mL of diisopropylamine and refluxed for 5 h. The mixture was then filtered, evaporated, and chromatographed on silica gel with 50:10 hexane:THF to give pure **V** in 92% yield as bright orange crystals. mp 87−88 °C. ^{1}H NMR (CDCl$_3$) d 8.78 (m, 2 H), 8.67 (m, 2 H), 7.77 (m, 2 H), 7.61 (m, 4 H), 7.44 (m, 3 H), 7.23 (s, 1 H), 7.00 (s, 1 H), 4.08 (t, 4 H), 2.02 (m, 2 H), 1.87 (m, 2 H), 1.58 (br m, 4 H), 1.25 (br s, 48 H), 0.86 (m, 6 H). ^{13}C NMR (partial) (CDCl$_3$) d 152.2, 132.2, 132.1, 131.7, 128.6, 127.6, 127.2, 126.8, 126.6, 113.9, 102.7, 32.0, 29.7, 29.4, 22.7, 14.1. UV−vis (CHCl$_3$) λ_{max}, nm (log e) 481 (4.65), 452 (4.60), 316 (4.45), 279 (4.88). Mass spectrum (EI): 895 (20), 894 (34), 892 (100).

Model Compound VI. 1,4-Diphenylethynyl-2,5-dibutoxybenzene: 0.33 mmol of **Ic**, 0.016 mmol of (PPh$_3$)$_4$Pd, and 0.016 mmol of CuI were dissolved in 3 mL of diisopropylamine and 7 mL of toluene under Ar. 0.66 mmol of phenylacetylene was added and the reaction was heated at 70 °C for 14 h. The mixture was then filtered and the solvent was evaporated. The solid was redissolved in toluene and passed through a 4 cm plug of silica gel. The toluene was evaporated and the resulting slightly yellowed solid was recrystallized twice from EtOH to give 98% yield of pure product. mp 122−123 °C. Anal. Calcd for C$_{28}$H$_{30}$O$_2$: C 84.38; H 7.59. Found: C, 80.7; H 6.87. ^{1}H NMR (CDCl$_3$) d 7.53 (m, 4 H), 7.34 (m, 6 H), 7.02 (s, 2 H), 4.04 (t, 4 H), 1.85 (m, 4 H), 1.60 (m, 4 H), 1.0 (t, 6 H). ^{13}C NMR (CDCl$_3$) d 153.7, 131.6, 128.3, 128.2, 123.5, 117.1, 114.1, 94.8, 86.0, 69.4, 31.4, 19.3, 13.9. UV−vis (CHCl$_3$) λ_{max}, nm (log e): 362 (4.32), 308 (4.41).

PIa: 0.165 mmol of **II**, 0.150 mmol of **Ia**, 0.0325 mmol of **III**, 0.008 mmol of (PPh$_3$)$_4$Pd, and 0.008 mmol of CuI were combined in 3 mL of diisopropylamine and 7 mL of toluene under Ar. The mixture was heated at 70 °C for 14 h. Ammonium iodide salts were formed immediately and the mixture was highly fluorescent, the emission in the early stages of polymerization being blue and in the later stages more green. After cooling the reaction mixture to room temperature it was added dropwise to 200 mL of rapidly stirred acetone. The orange-yellow precipitate was collected and washed repeatedly with acetone, hot EtOH, hot CH$_3$CN, and hexane. Some lower molecular weight material was removed with the washing as evidenced by the fluorescent nature of the washings. After drying overnight at 40 °C, **PIa** was isolated in 89% yield. DP = 23.6 by ^{1}H NMR. M_n = 9400 by GPC (PDI = 1.6). ^{1}H NMR (CDCl$_3$) d 7.0 (br s, 47.2 H), 6.81 (br s, 2 H), 6.68 (br s, 2 H), 4.00 (br m, 94.4 H), 3.87 (s, 6 H), 3.78 (s, 6 H), 3.39 (t, 4 H), 2.58 (br m, 4 H), 1.82 (br s), 1.49 (br s), 1.23 (br s), 0.83 (br t, 142 H). Anal. Calcd for C$_{972}$H$_{1645}$O$_{49}$Br$_2$: C, 81.75; H, 11.61. Found: C, 81.03; H, 11.15. ^{13}C NMR (CDCl$_3$) d 154.0, 117.9, 114.8, 92.2, 70.0, 32.3, 30.3, 29.8, 29.5, 26.3, 22.8, 14.3. UV−vis (CHCl$_3$) λ_{max}, nm (log e per repeat): 446 (4.28), 318 (3.79).

PIb: This material was prepared with a procedure identical to **PIa** except with 0.157 mmol of **Ia** and 0.157 mmol of **III** and isolated in 93% yield. DP = 40.0 by ^{1}H NMR. M_n = 19 200 by GPC (PDI = 1.5). The NMR spectra are identical to that of **PIa** except that the signal intensities of the end groups are diminished. Anal. Calcd for DP = 41, C$_{1668}$H$_{2828}$O$_{86}$Br$_2$: C, 82.0; H, 11.7. Found: C, 80.93; H, 11.02.

PIc: 0.3295 mmol of **II**, 0.1647 mmol of **Ib**, 0.1647 mmol of **Id**, 0.016 mmol of (PPh$_3$)$_4$Pd, and 0.016 mmol of CuI were combined in 6 mL of diisopropylamine and 14 mL of toluene under Ar. The reactants were heated at 70 °C for 14 h to yield a noticeably viscous, fluorescent mixture. After cooling the material was added to 200 mL of rapidly stirred acetone. The resulting precipitate was collected, rinsed with acetone, hot CH$_3$-CN, hot EtOH, and hexane, and dried at 40 °C overnight to give a light yellow green solid in 96% yield. The ^{1}H NMR gave no signals which could be attributed to end groups. M_n = 98 000 by GPC (PDI = 1.5). Anal. Calcd for (C$_{114}$H$_{180}$O$_8$)$_n$: C, 81.56; H, 10.81. Found: C, 79.89; H, 10.81. ^{1}H NMR (CDCl$_3$) d 7.02 (s), 6.99 (s), 4.03 (br m), 3.89 (s), 1.83 (br m), 1.50 (br m), 1.23 (br s), 0.87 (br t). UV−vis (CHCl$_3$) λ_{max}, nm (log e per repeat): 450 (4.44), 318 (3.86).

PII: This material was synthesized by the same procedure as used for **PIa** except substituting 0.0325 mmol of 9-bromo-10-phenylanthracene of **III**. The precipitated polymer exhibited a more orange color than **PIa** and was obtained in 91% yield. M_n = 9,100 by GPC (PDI = 2.2). Anal. Calcd for DP = 22 (C$_{926}$H$_{1522}$O$_{44}$): C, 83.25; H, 11.48. Found: C, 82.26; H, 11.29. ^{1}H NMR (CDCl$_3$) d 8.83 (m, 2 H), 8.68 (m, 2 H), 7.78 (m, 2 H), 7.62 (m, 4 H), 7.43 (m, 3 H), 6.99 (s, 26.1 H), 3.96 (br t, 52.2 H), 1.49 (br m), 1.23 (br s), 0.83 (br s). UV−vis (CHCl$_3$) λ_{max}, nm: 279, 316, 452, 498.

PIIIa: 0.165 mmol of **II**, 0.132 mmol of **Ia**, 0.0330 mmol of 9,10-dibromoanthracene, 0.0083 mmol of (PPh$_3$)$_4$Pd, and 0.0083 mmol of CuI were dissolved in 3 mL of diisopropylamine and 7 mL of toluene under Ar. The mixture was heated at 70 °C for 16 h to yield an orange-red solution. After cooling, the product was precipitated into acetone, filtered, and rinsed with acetone, hot CH$_3$CN, hot EtOH, and hexane. After drying at 40 °C overnight, **PIIIa** was isolated in 85% yield. Anal. Calcd for 7 mol % anthracene incorporation: C, 83.64; H, 11.18. Found: C, 79.88; H, 11.25; Br, 0.05. ^{1}H NMR (CDCl$_3$) d 8.83

Fluorescence Studies of Poly(p-phenyleneethynylene) Molecules

J. Phys. Chem., Vol. 99, No. 14, 1995 **4893**

(br m, 2 H), 7.75 (br m, 2 H), 7.0 (s, 15.6 H), 3.99 (vbr m, 31.25 H), 2.05 (sh), 1.83 (br s), 1.58 (br s), 1.3 (br s), 0.89 (br t). UV−vis (CHCl$_3$) λ_{max}, nm: 320, 450, 494, 527.

PIIIb: 0.165 mmol of **II**, 0.0823 mmol of **Ia**, and 0.0823 mmol of 9,10-dibromoanthracene, 0.0083 mmol of (PPh$_3$)$_4$Pd, and 0.0083 mmol of CuI were dissolved in 3 mL of diisopropylamine and 7 mL of toluene under Ar. After heating the mixture at 70 °C for 16 h the polymer was precipitated in acetone, filtered, and washed with acetone, hot EtOH, hot CH$_3$CN, and hexane. The polymer was isolated in 83% yield as a red solid. DP = 24 by ^{1}H NMR. Anal. Calcd for 17 mol % anthracene incorporation: C, 84.01; H, 10.09. Found: C, 79.08; H, 11.25; Br, 1.52. ^{1}H NMR (CDCl$_3$) d 8.83 (m, 2 H), 8.65 (m, 0.6 H), 7.75 (m, 2.6 H), 7.0 (s, 6.3 H), 4.00 (vbr m, 12.54 H), 2.07 (sh), 1.87 (br m), 1.52 (br s), 1.28 (br s), 0.89 (br t). UV−vis (CHCl$_3$) λ_{max}, nm: 528, 450, 321, 278.

PIIIc: 0.494 mmol of **II**, 0.543 mmol of 9,10-dibromoanthracene, 0.025 mmol of (PPh$_3$)$_4$Pd, and 0.025 mmol of CuI were dissolved in 6 mL of diisopropylamine and 14 mL of orthodichlorobenzene under Ar. The mixture was heated at 70 °C for 16 h, cooled, precipitated in acetone, filtered, and washed with acetone, hot EtOH, hot CH$_3$CN, and hot hexane. The polymer was isolated in 77% yield as a purple solid. Anal. Calcd for DP = 10.8 (C$_{604.8}$H$_{820.8}$O$_{21}$·6Br$_2$): C, 84.50; H, 9.62; Br, 1.86. Found: C, 83.22; H, 9.79; Br, 1.85. ^{1}H NMR (CDCl$_3$) d 8.85 (br m), 7.67 (br m), 7.28 (br s), 4.11 (vbr m), 2.08 (br m), 1.9−1.0 (br m), 0.85 (br s). UV−vis (o-dichlorobenzene) λ_{max}, nm (log e per repeat): 543 (4.60), 606 (4.27), 326 (4.24), 294 (4.38).

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(15) For a step-growth polymerization the degree of polymerization = 1/1 percent conversion. From ref 13, DP as the number average molecular weight, $X_n = 1 + r/1 − r$ where $r = N_A/N_B$ and N_A and N_B are the monomer equivalents used in the polymerization.

(16) Calculated from standard bond lengths and angles: *CRC Handbook of Chemistry and Physics*, 61st ed.; CRC Press: Boca Raton, FL, 1976.

(17) Reference 14. The polydispersity indices (PDI's) calculated for some of the polymers are less than 2 which may be a result of fractionation of the polymer in the workup or a nonideal relationship between the GPC molecular weight and the actual molecular weight of these materials.

(18) The authors in reference 6 report a λ_{max} of 410 nm for poly(p-phenyleethynylene) with a DP of 13.

(19) (a) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1989**, *22*, 2317. (b) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1989**, *22*, 3903. (c) Guillet, J. E.; Rendall, W. A. *Macromolecules* **1986**, *19*, 24. (d) Holden, D. A.; Guillet, J. E. *Macromolecules* **1980**, *13*, 289. (e) Aspler, J. S.; Hoyle, C. E.; Guillet, J. E. *Macromolecules* **1978**, *11*, 925.

(20) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin Cummings: California, 1978.

(21) The valence bandwidth of unsubstituted poly(p-phenylenethynylene) has been calculated to be 2.5 eV; see: Bredas, J. L., in ref 1.

(22) Kittel, C. *Introduction to Solid State Physics* 5th ed.; John Wiley and Sons: New York, 1976; Chapter 11.

(23) Swager, T. M.; Wrighton, M. S. Unpublished results.

(24) Sargent, T., III; Shulgin, A. T.; Mathis, C. A. *J. Med. Chem.* **1984**, *27*, 1071.

(25) Diphenylethynylanthracene is commercially available from Aldrich.