Poly[bis(pyrrol-2-yl)arylenes]: Conducting Polymers from Low Oxidation Potential Monomers Based on Pyrrole via Electropolymerization

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ABSTRACT: A series of derivatized bis(pyrrol-2-yl) arylenes, specifically 1,4-bis(pyrrol-2-yl)benzene (**1e**, BPB), 1,4-bis(pyrrol-2-yl)-2,5-dimethoxybenzene (**2e**, BPB(OCH$_3$)$_2$), 1,4-bis(pyrrol-2-yl)-2,5-diethoxybenzene (**3e**, BPB(OC$_2$H$_5$)$_2$), 1,4-bis(pyrrol-2-yl)-2,5-didodecyloxybenzene (**4e**, BPB(OC$_{12}$H$_{25}$)$_2$), 2,6-bis(pyrrol-2-yl)-naphthalene (**5e**, BPN), and 4,4′-bis(pyrrol-2-yl)biphenyl (**6e**, BPBP) have been synthesized. Cyclic voltammetry shows these monomers to oxidize at relatively low potentials to form cation radicals. The lowest peak monomer oxidation potential of +0.15 V vs Ag/Ag$^+$ is observed for **2e**, lower than that reported for any other pyrrole-based monomer. Electrochemical polymerization from a 0.01 M monomer, 0.1 M tetrabutylammonium perchlorate (TBAP), and acetonitrile solution was carried out using multiple scanning cyclic voltammetry to yield polymers having $E_{1/2}$ values ranging from −0.1 to +0.1 V. These low oxidation potentials cause the polymers to be quite stable in the electrically conducting form. The electronic band gaps for these polymers (measured as the onset of the $\pi-\pi^*$ transition) occurs between 2.3 and 2.4 eV. Upon electrochemical doping, the intensity of the $\pi-\pi^*$ transition decreases while bipolaron bands appear at lower energy. The intensity of these bands increases upon increasing the anodic potential. The redox doping process was found to be reversible upon electrochemical reduction of the films. The unsubstituted polymer poly[1,4-bis(pyrrol-2-yl)benzene], doped with perchlorate, was found to exhibit an average conductivity of 1 S/cm. When the dopant was the anion of bis[(trifluoromethyl)-sulfonyl]imide, the conductivity increased to 30 S/cm. These polymers are stable to thousands of double-potential steps before 50% loss of electroactivity occurs.

Introduction

The electropolymerization of pyrrole has made a significant impact in the synthesis of stable, highly conducting polymers via a relatively low oxidation potential monomer.[1] Pyrrole oxidizes at significantly lower potentials than that of thiophene or furan, allowing for fewer defects in the polymer formed. The polymer's redox processes are generally found between −0.5 and 0.0 V vs SCE. With this low oxidation potential to form the conducting state, the polymer is quite stable as a conductor and can be subjected to a high number of redox switches with little degradation in charge response.[2] These properties suggest that polypyrrole may prove useful in a number of practical applications which include areas as diverse as solid cell lithium batteries,[3] biocompatable electrodes,[4] and conducting textiles.[5]

The electropolymerization of heterocyclic monomers to form electrically conductive and redox-active polymers is highly dependent of the monomer's oxidation potential. In order for electrochemical polymerization to proceed, the monomer is continually oxidized while the electroactive polymer deposits on the electrode surface. In cases where the monomer oxidation occurs at potentials that cause polymer degradation, defect-containing materials are formed, and in the extreme, polymerization is completely inhibited. In the case of thiophene polymerization, this has been termed the polythiophene paradox.[6]

By extending the conjugation of the monomer, using multiheterocyclic compounds with a discrete number of rings, a significant reduction in the oxidation potential is observed relative to a single heterocycle. In addition, this predetermines most of the main-chain linkages between rings along the backbone. This concept has been successfully applied to the electropolymerization of a number of multi-ring heterocyclic monomers.[7] For example, Ferraris et al. have shown 2,5-(2-thienyl)-pyrrole to electropolymerize with a monomer peak oxidation potential between +0.30 and +0.35 V vs Ag/Ag$^+$ to yield a film exhibiting a conductivity of 280 S/cm.

One of our groups,[8] and others,[9] have utilized these concepts in the synthesis of a series of 1,4-bis(2-furanyl)- and 1,4-bis(2-thienyl)benzenes which form electrically conducting polymers via both chemical and electrochemical polymerization routes. These monomers contain external heterocycles with open α positions to allow for the production of polymers with an alternating 2,2′-biheterocycle/*p*-phenylene repeat unit. They exhibit significantly lower oxidative polymerization potentials than either the parent heterocycle or benzene. Oxidative polymerization of symmetrically derivatized monomers gives isoregically structured polymers with a much higher degree of order.[8d] These polymers exhibit higher electrical conductivities in their doped form than their unsymmetrically substituted analogs.
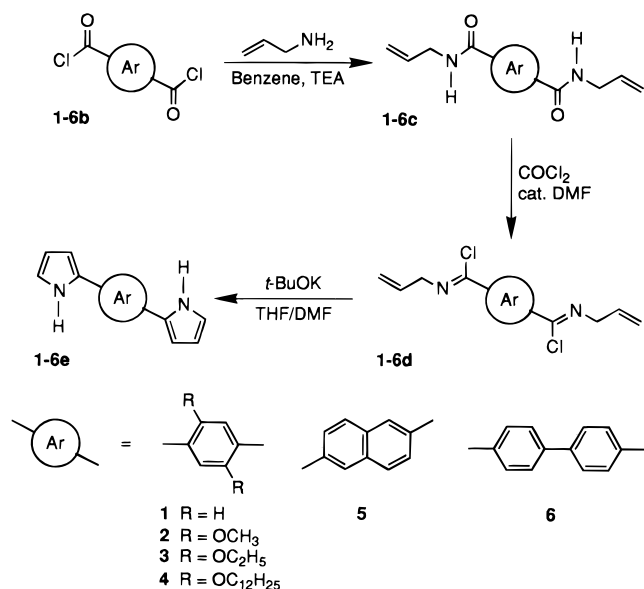
The synthetic procedure used for the syntheses of the 1,4-bis(furanyl)- and 1,4-bis(2-thienyl)benzenes, transition metal-catalyzed coupling of activated heterocycles, cannot be easily applied to the synthesis of 1,4-bis-(pyrrol-2-yl)benzenes due to the acidic nature of the pyrrole hydrogen.[10] We have recently developed a methodology for the synthesis of bis(pyrrol-2-yl)arylenes and have communicated our work on the synthesis and initial redox results of poly[1,4-bis(pyrrol-2-yl))phenylene].[11] Here we report an extension of our synthesis to a series of bis(pyrrol-2-yl)arylenes and their electro-

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Scheme 1

Figure 1. Cyclic voltammetric scanning electropolymerization of 0.01 M BPB(OCH₃)₂ in 0.1 M TBAP/CH₃CN cycled at 100 mV/s.

chemical polymerization, redox properties, band structure, and stability to multiple double-potential-step switchings as required for electrochromic devices[12] and electromagnetic shutters.[13] Polymers having similar repeat unit structures have been prepared using chemical methods.[14,15]

Results and Discussion

Synthesis of Aryl Bispyrroles. The aryl bispyrroles **1e**–**6e** were prepared by modification of the method of Engel and Steglich[16] in accordance with the general pathway set out in Scheme 1. The appropriate acid chlorides **1b**–**6b** were reacted with allylamine to give aryl bis(allylamides) **1c**–**6c** in good yields. Subsequent treatment with phosgene furnished the aryl bis(allylimino chlorides) **1d**–**6d**, which were used without isolation or purification in the following step. **1d**–**6d** were cyclized under basic conditions to form 1,4-bis-(pyrrol-2-yl)benzene (**1e**, BPB), 1,4-bis(pyrrol-2-yl)-2,5-dimethoxybenzene (**2e**, BPB(OCH₃)₂), 1,4-bis(pyrrol-2-yl)-2,5-diethoxybenzene (**3e**, BPB(OC₂H₅)₂), 1,4-bis(pyrrol-2-yl)-2,5-didodecyloxybenzene (**4e**, BPB(OC₁₂H₂₅)₂), 2,6-bis(pyrrol-2-yl)naphthalene (**5e**, BPN), and 4,4′-bis(pyrrol-2-yl)biphenyl (**6e**, BPBP) in moderate yields.

Oxidative Polymerization. Scheme 2 depicts the oxidative polymerization of this family of bis(pyrrol-2-yl)arylenes and the subsequent reversible redox process of the as-made doped polymers using BPB(OCH₃)₂ (**2e**) as an example. The oxidative polymerization of these bis(pyrrol-2-yl)arylenes likely proceeds through an electrochemically activated step-growth mechanism with the initial formation of a monomer cation radical followed by a coupling polymerization. Multiple-scan cyclic voltammetric polymerization of the bis(pyrrole) monomers was carried out to determine monomer oxidation onset and peak potentials, along with monitoring the rate of growth of the electroactive polymer film. The cyclic voltammetric polymerization of BPB-(OCH₃)₂ is shown in Figure 1 and is representative of the other monomers which were successfully electrochemically polymerized. In each case, during the first anodic scan, the monomer exhibited a low potential current onset followed by a single peak due to the formation of the monomer radical cation as shown in Table 1. With the reverse scan, a cathodic process is
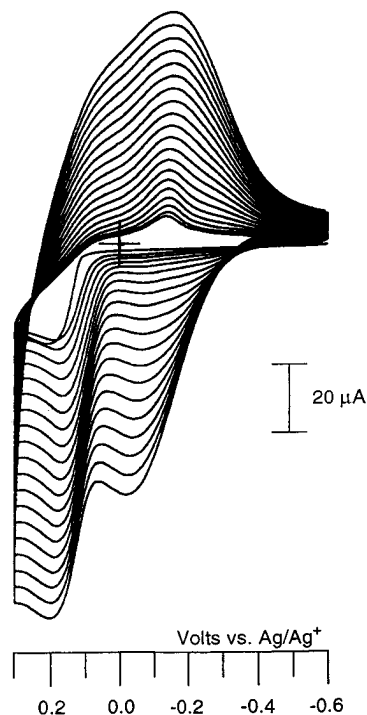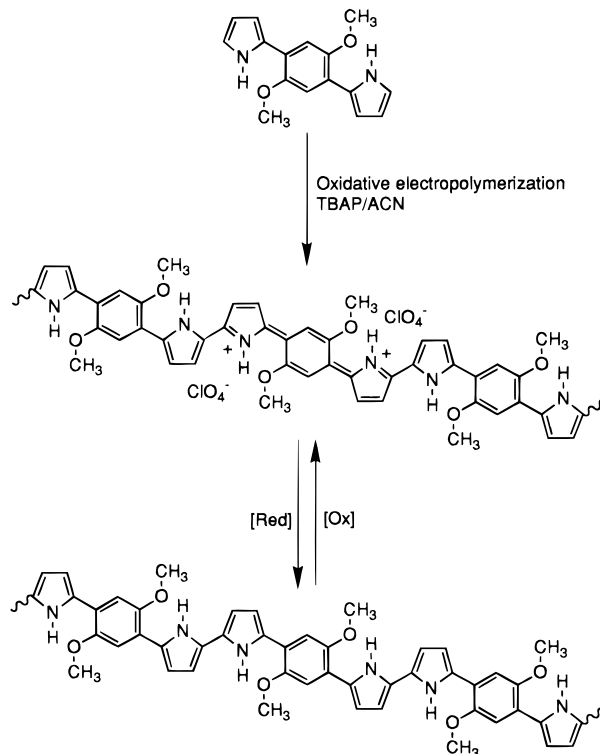
Scheme 2

evident which is indicative of the reduction of the initially formed oxidized polymer. The second scan shows a current onset (∼−0.3 V for PBPB(OCH₃)₂) due to reoxidation of the electroactive polymer followed by the monomer oxidation. Upon repeated scanning, the increased current response of the polymer redox processes illustrates that the electrochemical polymerization is proceeding at the electrode surface to form an electrically conducting electroactive film. It should be noted that the above polymerizations are quite rapid

Table 1

monomer	$E_{onset,m}$ (V)	$E_{p,m}$ (V)	$E_{1/2,p}$ (V)	E_g (V)
BPB	0.30	0.35	−0.10	2.4
BPB(OCH$_3$)$_2$	0.12	0.15	−0.05	2.3
BPB(OC$_{12}$H$_{25}$)$_2$	0.13	0.17	−0.05	n/a[a]
BPN	0.30	0.35	0.05	2.3
BPBP	0.40	0.45	0.10	n/a[a]

[a] Not available.

when compared to pyrrole, which points out a benefit of this class of monomers.[11]

BPB(OC$_2$H$_5$)$_2$ did not undergo electrochemical polymerization. In this instance, the first anodic scan showed an oxidative process occurring at a relatively high potential. Upon subsequent scanning, there was no current response at lower potentials and the current response of the initial anodic process continued to decline upon subsequent cycling. Upon termination of the experiment, there was no film observed on the working electrode. On the other hand, the BPB-(OC$_{12}$H$_{25}$)$_2$ electropolymerized in a fashion nearly identical to the dimethoxy derivative as noted in Table 1. The inability of the diethoxy derivative to electropolymerize was likely due to the instability of this monomer to ambient oxidation as it was obtained as an oil and was difficult to handle.

As noted above, an important property of these monomers is their low oxidation potential. This will limit the amount of side reactions during electropolymerization, such as the formation of β linkages and overoxidation of the polymer.[17] Table 1 lists the onset potentials for monomer oxidation ($E_{onset,m}$), peak monomer oxidation potential ($E_{p,m}$), and the polymer's half-wave potential ($E_{1/2,p}$). Substitution of the methoxy groups onto the benzene ring of BPB significantly lowers the monomer $E_{p,m}$ from +0.35 V for BPB to +0.15 V for BPB(OCH$_3$)$_2$. This can be explained by the enhanced stability of the monomer radical cation contributed by the electron-donating methoxy groups in the 2 and 5 positions on the benzene ring. BPB(ODoD)$_2$ exhibits a monomer oxidation potential slightly higher than that of BPB(OCH$_3$)$_2$.

In order to study the redox processes of the polymers formed from the electrochemical polymerizations, the working electrodes were removed from the monomer/electrolyte solution; the film of the electrode was thoroughly washed with solvent and subsequently placed into a monomer-free electrolyte solution. Figure 2 illustrates the cyclic voltammetry of PBPB(OCH$_3$)$_2$ at various scan rates and is representative of all of the electroactive polymers. As can be seen, the potentials of the anodic and cathodic processes of the polymer film are relatively close (∼100 mV) indicating a reversible redox process. Both anodic and cathodic peak currents are linearly proportional to the scan rate, which is indicative of an electrode-supported electroactive film.

Electrical Conductivity. Continuous films of PBPB have been obtained using 0.1 M TBAP/CH$_3$CN, tetraethylammonium tosylate (TEATOS)/CH$_3$CN, and lithium bis[(trifluoromethyl)sulfonyl]imide (Li−imide salt)/propylene carbonate by potentiostatic deposition onto indium tin oxide (ITO)-coated glass electrodes at +0.4 V. Studies were focused to this monomer as bulk electrolysis requires significant amounts of monomer and BPB has been available in the greatest amounts. The resulting PBPB-ClO$_4$, PBPB-TOS, and PBPB-imide anion exhibited average conductivities of 1, 0.1, and 30 S/cm, respectively. Initial experiments have been at-
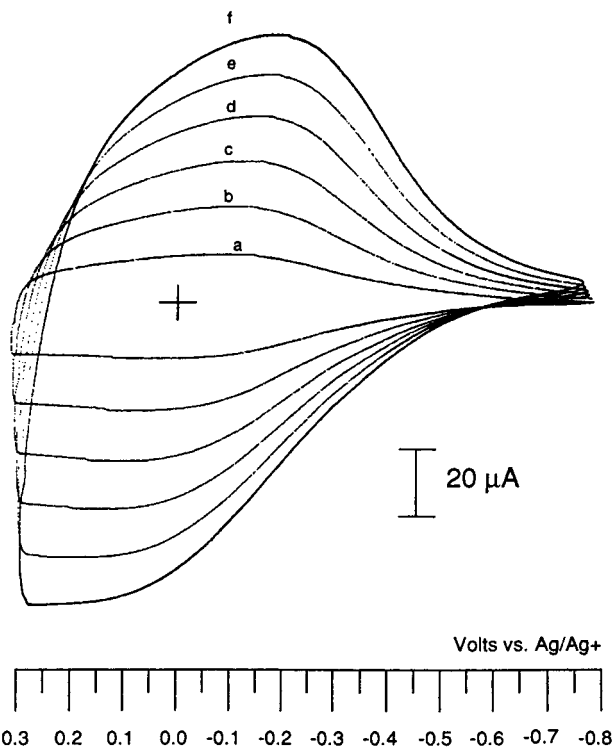

Figure 2. Scan rate dependence of the cyclic voltammetry of PBPB(OCH$_3$)$_2$ in 0.1M TBAP/CH$_3$CN cycled at (a) 50, (b) 100, (c) 150, (d) 200, (e) 250, and (f) 300 mV/s.

tempted for the formation of continuous films of PBPB-(OCH$_3$)$_2$ in 0.1 M TBAP/CH$_3$CN. The deposited polymer was found to be quite powdery in nature and could not be removed from the electrode as a continuous film for measurement. Current−voltage dependencies showed the samples to be ohmic with the current densities varied between ∼4 and 0.04 mA/cm^2. Application of higher currents led to immediate degradation and combustion in air.

Electronic Structure. Optoelectrochemical methods were used to elucidate the effect of the structure of the aryl core unit (*p*-phenylene and 2,6-naphthyl) and pendant substituents on the energy of the π electrons. Polymer films used for optoelectrochemical analysis were prepared potentiostatistically at the $E_{p,m}$ of the monomer on ITO-coated glass plates and their spectra obtained in a quartz cuvette containing electrolyte solution and counter and reference electrodes. The polymers were first fully reduced and the electronic spectrum (310−1600 nm) was obtained. The polymers were subsequently subjected to increasing potentials in 100 mV steps, and the spectrum was obtained at each potential after equilibration. The reversible nature of the redox doping process was confirmed by a similar stepwise reduction. An optoelectrochemical series for the dimethoxy-substituted polymer is shown in Figure 3 and is similar to PBPB-ClO$_4$ and PBPN-ClO$_4$. The optical band gap for each polymer was obtained from the onset of the $\pi−\pi^*$ transition. The unsubstituted BPB exhibits a band gap of 2.4 eV, which is lower than that of polypyrrole (2.7 eV) or poly(*p*-phenylene) (3.0 eV). The band gap of PBPB(OCH$_3$)$_2$ is reduced further to 2.3 eV. We attribute this lowering of the band gap relative to polypyrrole to the increased structural regularity induced by the use of the three-ring-containing bis-(pyrrol-2-yl)benzene monomer. In addition, the oxygens of the methoxy substituent in PBPB(OCH$_3$)$_2$ are expected to hydrogen bond with the pyrrole hydrogen,
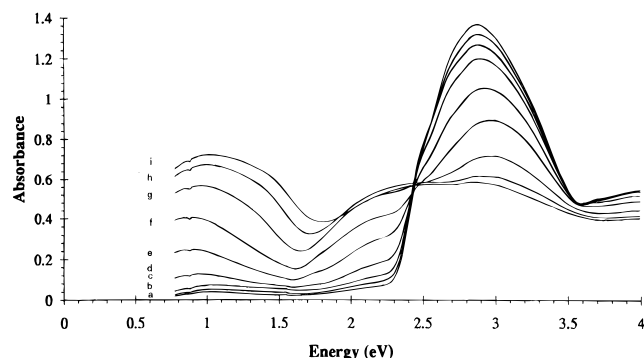
Figure 3. Optoelectrochemical analysis of PBPB(OCH$_3$)$_2$ performed in 0.1 M TBAP/CH$_3$CN. UV−visible−near-IR spectra taken at (a) −0.6, (b) −0.3, (c) −0.2, (d) −0.1, (e) 0.0, (f) +0.1, (g) +0.2, (h) +0.3, and (i) 0.4 V vs Ag/Ag$^+$.

Figure 4. Long-term double-potential-stepping charge retention for PBPB and PBPB(OCH$_3$)$_2$ performed under an argon blanket in 0.1 M TBAP/CH$_3$CN. Twenty seconds constitutes a double-potential step.

causing the repeat unit to attain planarity more easily than unsubstituted BPB. According to Hong and Marynick, PRDDO studies indicated the lowest energy form of BPB(OCH$_3$)$_2$ has a planar conformation between the benzene and pyrrole rings. The energy of the system increases with increased torsional angle as the extent of H-bonding is reduced.[18] The unsubstituted BPB was calculated to have its lowest energy between a torsional angle of 0° and 15°, which increased only 1 kcal/mol at 30°. PBPN exhibited a band gap similar to BPB-(OCH$_3$)$_2$. Upon oxidation, the above polymers exhibited two new midgap absorptions upon oxidation, which is consistent with the formation of delocalized cationic charge carriers.

Long-Term Redox Switching Stability. In order for these polymers to be useful in practical devices where they are switched between charge states, they must sustain a number of sequential oxidative and reductive processes while retaining their electroactivity.[2,13] Double-potential-step experiments were carried out by poising the polymer at an oxidative potential for a period of time, then stepping to a reductive potential, and returning to the original oxidative potential constituting a double-potential step. Multiple redox switching experiments were carried out on PBPB-ClO$_4$ and PBPB(OCH$_3$)$_2$-ClO$_4$ prepared via constant-potential electropolymerization at the $E_{p,m}$ until 2 mC of charge passed (400 mC/cm^2) and subsequently switched in monomer-free 0.1 M TBAP/CH$_3$CN electrolyte. The films were first redox "broken in" by repeated scanning to obtain a constant CV current response. Double-potential steps were carried out by holding the potential at $E_{p,a}$ + 0.15 V for 10 s, stepping to $E_{p,c}$ − 0.15 V for 10 s, and then returning to the original potential. The charge for each half-cycle was monitored and compared to the original charge response as a function of the number of complete double-potential-stepping cycles. Figure 4 shows the long-term double-potential-stepping results for the above polymers. After 2300 double-potential steps, PBPB retained 50% of its original charge. PBPB(OCH$_3$)$_2$ was able to maintain 80% of its original charge after 3000 double-potential steps and 50% electroactivity after 6000 double-potential steps. For comparison purposes, poly(pyrrole chloride), redox switched in 0.1 M LiClO$_4$(aqueous), exhibits 65% retention after 900 double-potential steps.

Experimental Section

General Comments. Melting points are uncorrected. All NMR spectra were performed using a Varian VXR-300 spectrometer operating at 300 MHz in deuteriochloroform as
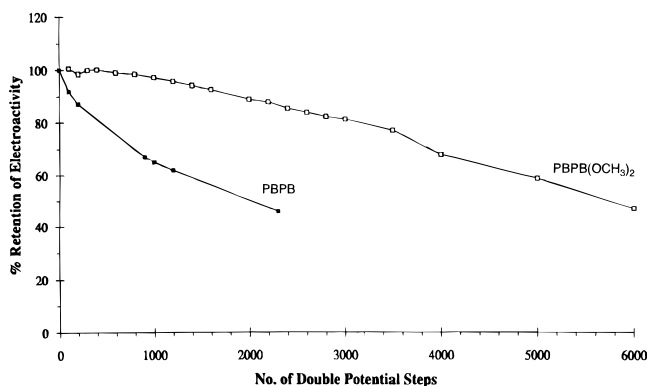
solvent unless otherwise stated. TMS was used as the internal reference. Column chromatography was carried out on Merck Keisel gel 60 (5386) silica gel. Diethyl 2,5-dihydroxyterephthalate, terephthaloyl chloride (**1b**), 2,6-naphthalenedicarboxylic acid (**5a**), and 4,4′-biphenyldicarboxylic acid (**6a**) were purchased from Aldrich.

Synthesis of 2,5-Dialkoxyterephthalic Acids.[19] Typical Procedure for the Synthesis of 2,5-Dimethoxyterephthalic Acid (2a). A mixture of diethyl 2,5-dihydroxyterephthalate (12.2 g, 48 mmol) and powered potassium carbonate (6.18 g, 48 mmol) in acetone (300 mL) was heated at reflux for 10 min. Iodomethane (74.7 mL, 1.16 mol) was added, and heating continued until disappearance of the yellow color. The potassium iodide was filtered and the solvent evaporated to give a solid which was recrystallized from diethyl ether to give diethyl 2,5-dimethoxyterephthalate. Yield 9.47 g (70%); mp 95−97 °C (lit.[20] mp 100.5−101.5 °C). Diethyl 2,5-dimethoxyterephthalate (2.3 g, 8 mmol) was heated at reflux in aqueous potassium hydroxide (30%, 35 mL) for 10 h under nitrogen. The mixture was cooled and acidified with 6 N hydrochloric acid. The precipitate was filtered and recrystallized from benzene to give **2a**: yield 1.2 g (67%); mp 260−262 °C (lit.[20] mp 263−266 °C).

2,5-Diethoxyterephthalic Acid (3a). The title compound was prepared from diethyl 2,5-dihydroxyterephthalate and iodoethane in the same manner as described above for **2a**. Diethyl 2,5-diethoxyterephthalate: yield 76%; mp 66 °C (lit.[19] mp 72 °C). **2,5-Diethoxyterephthalic Acid (3a):** yield 66%; mp 207−209 °C (lit.[19] mp 211 °C).

2,5-(Didodecyloxy)tetraphthalic Acid (4a). The title compound was prepared from diethyl 2,5-dihydroxyterephthalate and 1-iodododecane in the same manner as described above for **2a**. Diethyl 2,5-(didodecyloxy)terephthalate: yield 62%; mp 54 °C (lit.[19] mp 57 °C). **2,5-(Didodecyloxy)-terephthalic Acid (4a):** yield 40%; mp 126 °C (lit.[19] mp 128 °C).

Synthesis of Acid Chlorides 2b−6b.[21] Typical Procedure for the Preparation of 2,5-Dimethoxyterephthaloyl Chloride (2b). A mixture of **2a** (0.7 g, 2 mmol), thionyl chloride (11.8 g, 100 mmol), and DMF (1 drop) under nitrogen was stirred for 24 h at room temperature followed by heating at reflux for 4 h. Excess thionyl chloride was removed by distillation and the residual solid washed with hexane to give **2b**, which was used directly in the next step: yield 0.5g (75%); mp 102−104 °C (lit.[22] mp 97−100 °C).

2,5-Diethoxyterephthaloyl Chloride (3b). The title compound was prepared as above from **3a**: yield 75%; mp 95−97 °C (lit.[19] mp 82 °C).

2,5-(Didodecyloxy)terephthaloyl Chloride (4b). The title compound was prepared as above from **4a**: yield 59%; mp 60−61 °C (lit[19] mp 60 °C).

2,6-Naphthalenedicarbonyl Chloride (5b). The title compound was prepared as above from **5a**: yield 81%; mp 181−182 °C (lit.[23] mp 186 °C).

4,4′-Biphenyldicarbonyl Chloride (6b). The title compound was prepared as above from **6a:** yield 78%; mp 180−182 °C (lit.[24] mp 184 °C).

Synthesis of Aryl Bis(allylamides). Typical Procedure for the Synthesis of *N,N*-Diallylterephthaldiamide (1c). A solution of terephthaloyl chloride (**1b**); (6.9 g, 34 mmol) in dry benzene (60 mL) was added slowly with vigorous stirring to a solution of allylamine (4 g, 70 mmol) and triethylamine (40 mL) in dry benzene. The mixture was stirred at room temperature for 2 h, heated at reflux for 3 h, cooled, and poured into diethyl ether (50 mL). The precipitate was filtered and washed with water and saturated sodium bicarbonate solution. Recrystallization from methanol gave colorless needles of **1c**: yield 7.0 g (84%); mp 210−211 °C (lit.[25] mp 210−213 °C); ^{1}H NMR δ (CDCl$_3$) 3.92 (m, 4 H, NHC*H*$_2$), 5.10 (dd, 2 H, *J* 1.5 and 10.1 Hz, CH=C*H*H *cis*), 5.19 (dd, 2 H, *J* 1.6 and 17.2 Hz, C=C*H*H *trans*), 5.90 (m, 2 H, C*H*=CH$_2$), 7.95 (s, 4 H, aromatic), 8.80 (br s, 2 H, NH); ^{13}C NMR δ (CDCl$_3$) 41.5 (NHCH$_2$), 115.2 (CH=*C*H$_2$), 127.2 (C-2, C-3), 135.2 and 136.6 (C-1 and *C*H=CH$_2$), 165.4 (CONH).

N,N-Diallyl-2,5-dimethoxyterephthaldiamide (2c). The title compound was prepared as above from **2b** except that the reaction mixture was heated under reflux for 10 h: yield 74%; mp 148−150 °C; ^{1}H NMR δ (CDCl$_3$) 3.89 (s, 6 H, OMe), 4.11 (m, 4 H, NHC*H*$_2$), 5.17 (dd, 2 H, *J* 1.3 and 10.3 Hz, CH=C*H*H *cis*), 5.25 (dd, 2 H, *J* 1.4 and 17.3 Hz, C=C*H*H *trans*), 5.95 (m, 2 H, C*H*=CH$_2$), 7.91 (s, 2 H, aromatic), 8.19 (br s, 2 H, NH); ^{13}C NMR δ (CDCl$_3$) 42.1 (NHCH$_2$), 56.5 (OMe), 115.2 (CH=*C*H$_2$), 115.8 (C-3), 124.3 (C-1), 134.0 (*C*H=CH$_2$), 151.4 (C-2), 164.0 (CONH). Anal. Calcd for C$_{16}$H$_{20}$N$_2$O$_4$: C, 63.14; H, 6.62; N, 9.20. Found: C, 63.42; H, 6.69; N, 9.12.

N,N-Diallyl-2,5-diethoxyterephthaldiamide (3c). The title compound was prepared as above from **3b** except that the reaction mixture was heated under reflux for 5 h: yield 75%; mp 163−167 °C; ^{1}H NMR δ (CDCl$_3$) 1.50 (t, 6 H, *J* 7.2 Hz, OCH$_2$C*H*$_3$), 4.10 (m, 4 H, NHC*H*$_2$), 4.24 (q, 4 H, *J* 7.1 Hz, OC*H*$_2$CH$_3$), 5.19 (dd, 2 H, *J* 0.9 and 10.0 Hz, CH=C*H*H *cis*), 5.29 (dd, 2 H, *J* 0.9 and 18.0 Hz, C=C*H*H *trans*), 5.96 (m, 2 H, C*H*=CH$_2$), 7.87 (s, 2 H, aromatic), 8.33 (br s, 2 H, NH); ^{13}C NMR δ (CDCl$_3$) 14.7 (OCH$_2$*C*H$_3$), 42.1 (NHCH$_2$), 65.3 (O*C*H$_2$CH$_3$), 116.1 (CH=*C*H$_2$, C-3), 124.3 (C-1), 134.0 (*C*H=CH$_2$), 150.7 (C-2), 164.0 (CONH). Anal. Calcd for C$_{18}$H$_{24}$N$_2$O$_4$: C, 65.07; H, 7.22; N, 8.42. Found: C, 64.83; H, 7.25; N, 8.32.

N,N-Diallyl-2,5-(didodecyloxy)terephthaldiamide (4c). The title compound was prepared as above from **4b** except that the reaction mixture was heated under reflux for 5 h: yield 42%; mp 105−107 °C; ^{1}H NMR δ (CDCl$_3$) 0.88 (t, 6 H, *J* 6.6 Hz, CH$_3$), 1.27−1.47 (m, 36 H, CH$_2$), 1.89 (m, 4 H, C*H*$_2$CH$_2$O), 4.10 (t, 4 H, *J* 5.6 Hz, NHC*H*$_2$), 4.17 (t, 4 H, *J* 6.3 Hz, OCH$_2$), 5.19 (dd, 2 H, *J* 1.6 and 10.2 Hz, *cis* CH=C*H*H), 5.27 (dd, 2 H, *J* 1.6 and 17.1 Hz, *trans* CH=C*H*H), 5.90−6.00 (m, 2 H, C*H*=CH$_2$), 7.87 (s, 2 H, aromatic), 8.32 (t, 2 H, *J* 5.4 Hz, NH); ^{13}C NMR δ (CDCl$_3$) 14.1 (CH$_3$), 22.6, 26.2, 29.3, 29.5, 29.6, and 31.9 (CH$_2$), 42.3 (NHCH$_2$), 69.8 (OCH$_2$), 116.1 (C-3), 116.4 (CH=*C*H$_2$), 124.4 (C-1), 134.0 (*C*H=CH$_2$), 150.9 (C-2), 164.2 (CONH); HRMS calcd for C$_{38}$H$_{65}$N$_2$O$_4$ 613.4944 (M$^+$ + 1), found 613.4975.

N,N-Diallyl-2,6-naphthalenedicarboxamide (5c). The title compound was prepared as above from **5b:** yield 82%; mp 185−187 °C; ^{1}H NMR δ (DMSO-d_6) 4.00 (m, 4 H, NHC*H*$_2$), 5.13 (dd, 2 H, *J* 1.8 and 10.2 Hz, CH=C*H*H cis), 5.24 (dd, 2 H, *J* 1.8 and 17.2 Hz, C=C*H*H *trans*), 5.95 (m, 2 H, C*H*=CH$_2$), 8.05 and 8.10 (each d, 4 H, *J* 8.6 and 8.5 Hz, H-3 and H-4), 8.54 (s, 2 H, H-5), 8.80 (br s, 2 H, NH); ^{13}C NMR δ (DMSO-d_6) 41.7 (NHCH$_2$), 115.2 (CH=*C*H$_2$), 124.8, 127.2, and 128.9 (C-1, C-3, and C-4), 133.1 and 133.3 (C-2 and C-4a), 135.3 (*C*H=CH$_2$), 165.9 (CONH); HRMS calcd for C$_{18}$H$_{19}$N$_2$O$_2$ 295.1447 (M$^+$ + 1), found 295.1483.

N,N-Diallyl-4,4′-biphenyldicarboxamide (6c). The title compound was prepared as above from **6b** except that reaction mixture was heated under reflux for 5h yield 57%; mp 305 °C; ^{1}H NMR δ (DMSO-d_6) 4.00 (m, 4 H, NHC*H*$_2$), 5.11 (d, 2 H, *J* 10.3 Hz, CH=C*H*H *cis*), 5.20 (d, 2 H, *J* 17.1 Hz, C=C*H*H *trans*), 5.97 (m, 2 H, C*H*=CH$_2$), 8.02 and 8.10 (each d, 4 H, *J* 8.5 and 8.6 Hz, H-3 and H-4), 8.96 (br s, 2 H, NH); ^{13}C NMR δ (DMSO-d_6) 45.3 (NHCH$_2$), 115.1 (CH=*C*H$_2$), 126.6 and 128.0

(C-2 and C-3), 133.7 (C-1), 135.4 (*C*H=CH$_2$), 141.6 (C-4), 162.3 (CONH). Anal. Calcd for C$_{20}$H$_{20}$N$_2$O$_2$: C, 74.90; H, 6.29; N, 8.74. Found: C, 75.16; H, 6.32; N, 8.73.

1,4-Bis(pyrrol-2-yl)benzene (1e). A mixture of **1c** (4 g, 16 mmol), phosgene (20% solution in toluene, 64 mL), and DMF (6 drops) was stirred for 15 h at room temperature under nitrogen. The resulting mixture was heated at 40−45 °C for 2 h and the solvent removed *in vacuo*. The resulting crude bis(chloroimine) **1d** was used without isolation or purification in the next step. A solution of crude **1d** in THF (40 mL) was added dropwise with stirring to potassium *tert*-butoxide (9.42 g, 84 mmol) in THF at 5−10 °C under nitrogen. After stirring for 1 h at this temperature, the reaction mixture was poured into ice water and extracted with chloroform (2 × 50 mL). The organic phase was dried (MgSO$_4$) and evaporated to dryness and the residue subjected to column chromatography (hexane/THF 20:1, 10:1, 4:1) to give **1a**: yield 0.65 g (22%); mp 170 °C; ^{1}H NMR δ (DMSO-d_6) 6.10 (br s, 2 H, H-4′), 6.49 (br s, 2 H, H-3′), 6.83 (br s, 2 H, H-5′), 7.59 (s, 4 H, H-2 and H-3), 11.23 (br s, 2 H, NH); ^{13}C NMR δ (DMSO-d_6) 104.8 (C-4′), 108.7 (C-3′), 118.6 (C-5′), 123.2 (C-2), 129.7 and 130.7 (C-1 and C-2′); HRMS calcd for C$_{14}$H$_{12}$N$_2$ 208.1000 (M$^+$), found 208.1004.

1,4-Bis(pyrrol-2-yl)-2,5-dimethoxybenzene (2e). A mixture of **2c** (1 g, 3.2 mmol), phosgene (20% solution in toluene, 19 mL), and DMF (1 drop) was stirred for 24 h at room temperature under nitrogen. The resulting crude bis(chloroimine) **2d** was used without isolation or purification in the next step. A solution of crude **2d** in THF (30 mL) was added dropwise with stirring to potassium *tert*-butoxide (1.44 g, 12.8 mmol) in THF (30 mL) at 5−10 °C under nitrogen. After being stirred for 20 min at this temperature, the reaction mixture was poured into ice/water and extracted with chloroform (2 × 50 mL). The organic phase was dried (MgSO$_4$) and evaporated to dryness and the residue subjected to column chromatography (hexane/THF 9:1, 6:1, 3:2) to give **2e**: yield 0.17 g (20%); mp 108−110 °C; ^{1}H NMR δ (CDCl$_3$) 3.96 (s, 6 H, OMe), 6.29 (br s, 2 H, H-4′), 6.59 (br s, 2 H, H-3′), 6.87 (br s, 2 H, H-5′), 7.22 (s, 2 H, H-3), 9.88 (br s, 2 H, NH); ^{13}C NMR δ (DMSO-d_6) 60.0 (Me), 108.1 (C-4′), 108.3 (C-3′), 109.7 (C-3), 118.5 (C-5′), 119.1 (C-1), 127.9 (C-2′), 149.1 (C-2); HRMS calcd for C$_{16}$H$_{16}$N$_2$O$_2$ 269.1290 (M$^+$), found 269.1287.

1,4-Bis(pyrrol-2-yl)-2,5-diethoxybenzene (3e). The title compound was prepared as an oil from **3c** in the same manner as **2e**, column chromatography (hexane/THF 5:1, 4:1): yield 0.23 g (29%); ^{1}H NMR δ (CDCl$_3$) 1.53 (t, 6 H, *J* 7.0 Hz, OCH$_2$C*H*$_3$), 4.18 (q, 4 H, *J* 7.0 Hz, OC*H*$_2$CH$_3$), 6.29 (br s, 2 H, H-4′), 6.57 (br s, 2 H, H-3′), 6.87 (br s, 2 H, H-5′), 7.22 (s, 2 H, H-3), 9.98 (br s, 2 H, NH); ^{13}C NMR δ (CDCl$_3$) 29.1 (OCH$_2$*C*H$_3$), 56.4 (O*C*H$_2$CH$_3$), 105.7 (C-4′), 108.9 (C-3′), 110.1 (C-3), 118.0 (C-5′), 119.4 (C-1), 129.8 (C-2′), 149.5 (C-2); HRMS calcd for C$_{18}$H$_{20}$N$_2$O$_2$ 296.1525 (M$^+$), found 296.1504.

1,4-Bis(pyrrol-2-yl)-2,5-(didodecyloxy)benzene (4e). The title compound was prepared as an oil in the same manner as **2e**, column chromatography (hexane/THF-4:1): yield 0.26 g (30%); ^{1}H NMR δ (CDCl$_3$) 0.88 (t, 6 H, *J* 6.6 Hz, CH$_3$), 1.27−1.52 (m, 36 H, CH$_2$), 1.90 (pentet, 4 H, *J* 7.4 Hz, C*H*$_2$CH$_2$O), 4.10 (t, 4 H, *J* 6.6 Hz, OCH$_2$), 6.29 (br s, 2 H, H-4′), 6.57 (br s, 2 H, H-3′), 6.85 (br s, 2 H, H-2′), 7.21 (s, 2 H, H-3), 9.97 (br s, 2 H, NH); ^{13}C NMR δ (CDCl$_3$) 14.0 (CH$_3$), 22.6, 26.2, 29.3, 29.5, 29.6, 29.8 and 31.8 (CH$_2$), 69.4 (OCH$_2$), 105.5 (C-4′), 108.8 (C-3′), 110.9 (C-3), 117.7 (C-5′), 119.2 (C-1), 130.0 (C-2′), 148.8 (C-2); HRMS calcd for C$_{38}$H$_{61}$N$_2$O$_4$ 577.4733 (M$^+$ + 1), found 577.4762.

2,6-Bis(pyrrol-2-yl)naphthalene (5e). A mixture of **5c** (1.0 g, 3 mmol), phosgene (20% solution in toluene, 10 mL), and DMF (2 drops) was stirred for 15 h at room temperature under nitrogen. The resulting mixture was heated at 40−45 °C for 1 h and the solvent removed *in vacuo*. The resulting crude bis(chloroimine) **5d** was used without isolation or purification in the next step. A solution of crude **5d** in THF (20 mL) and DMF (2 mL) was added dropwise with stirring to potassium *tert*-butoxide (0.6 g, 5 mmol) in THF (30 mL) at 5−10 °C under nitrogen. After being stirred for 30 min at this temperature, the reaction mixture was poured into ice/water. The brown solid was filtered and recrystallized from methanol to give **5e**: yield 0.40 g (65%); mp 240 °C; ^{1}H NMR δ (DMSO-

d_6) 6.17 (br s, 2 H, H-4′), 6.64 (br s, 2 H, H-3′), 6.91 (br s, 2 H, H-5′), 7.79 (br s, 4 H, H-3 and H-4), 8.04 (s, 2 H, H-1), 11.44 (br s, 2 H, NH); ^{13}C NMR δ (DMSO-d_6) 106.1 (C-4′), 109.2 (C-3′), 119.6 and 120.1 (C-5′ and C-1), 123.5 (C-3), 127.7 (C-4), 129.6, 131.1, and 131.7 (C-2′, C-4a, and C-2); HRMS calcd for $C_{18}H_{14}N_2$ 256.1157 (M$^+$), found 256.1179.

4,4′-Bis(pyrrol-2-yl)biphenyl (6e). The title compound was prepared from **6c** in the same manner as **5e**: yield 44%; mp 290 °C; ^{1}H NMR δ (DMSO-d_6) 6.14 (br s, 2 H, H-3′), 6.56 (br s, 2 H, H-4′), 6.87 (br s, 2 H, H-5′), 7.69 (br s, 8 H, H-2 and H-3), 11.36 (br s, 2 H, NH); ^{13}C NMR δ (DMSO-d_6) 105.7 (C-4′), 109.1 (C-3′), 119.4 (C-5′), 123.7 (C-2), 126.3 (C-3), 130.7 and 131.8 (C-1 and C-2′), 136.4 (C-4); HRMS calcd for $C_{20}H_{16}N_2$ 284.1313 (M$^+$), found 284.1314.

Electrochemical Methods. Electrochemical polymerizations, cyclic voltammetry, and all other experiments involving the use of a potentiostat were performed on an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat. A 0.006 cm^2 platinum button was used as a working electrode in cyclic voltammetry experiments and long-term double-potential-stepping experiments. For each case, a platinum plate counter electrode and a Ag/Ag$^+$ (Ag wire in 0.01 M AgNO$_3$) was employed as a reference electrode, which has a potential of +0.34 V vs the SCE. All electrochemical potentials are reported and discussed relative to this reference electrode. CH$_3$CN was refluxed and distilled over CaH$_2$ and TBAP was recrystallized from ethanol. TEATOS was used as received from Aldrich. Lithium (trifluoromethyl)sulfonimide was used as received from 3M. Propylene carbonate was used as received from Fisher. All electrolyte solutions were 0.1 M, and monomer solutions were 0.01 M. Prior to electrochemistry, all solutions were purged with argon and during experimentation an argon blanket was held above the solution.

Conductivity Measurements. Film thicknesses were measured on electrode-supported films with a Tencor Instruments Alpha Step 200 profilometer. Films electrochemically polymerized for conductivities were done so on ITO-coated glass plates which were purchased from Delta Technologies, Ltd. Thin films of each polymer were removed from the ITO coated glass plates using transparent adhesive tape, and the conductivities were measured via the four-probe method by utilizing a Keithley Model 224 programmable current source and a Keithley Model 197 autoranging multimeter.

Optoelectrochemical Measurements. The optical spectrum of each polymer, as a function of injected charge, was obtained using ITO-coated conducting glass as a working electrode. Films were electrochemically polymerized onto the ITO-coated glass via constant potential until a desired charge density was obtained. The polymer-coated electrode was placed into a quartz cuvette with monomer-free electrolyte, and the counter electrode was a platinum plate with a 1 cm diameter hole in the center. A silver wire was employed as a quasi-reference electrode. The spectra were obtained on a Varian Cary 5 UV–Vis–NIR spectrophotometer, while the potential at the working electrode was varied. All optoelectronic experiments were carried out in a nitrogen atmosphere.

References and Notes

(1) Diaz, A. F.; Bargon, J. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; p 81.
(2) Pyo, M.; Reynolds, J. R.; Warren, L. F.; Marcy, H. O. *Synth. Met.* **1994**, *68*, 71.
(3) Reynolds, J. R. *CHEMTECH* **1988**, *18*, 440.
(4) Guiseppi-Elie, A.; Wilson, A. M. *Polym. Mater. Sci. Eng.* **1995**, *72*, 404.
(5) Kuhn, H. H.; Kimbrell, W. C.; Fowler, J. E.; Barry, C. N. *Synth. Met.* **1993**, *55–57*, 3707.
(6) Krische, B.; Zagorska, M. *Synth. Met.* **1989**, *28*, C263.
(7) (a) Ferraris, J. P.; Skiles, G. D. *Polymer* **1987**, *28*, 179. (b) Ferraris, J. P.; Hanlon, T. R. *Polymer* **1989**, *30*, 1319. (c) Ferraris, J. P.; Andrus, R. G.; Hrncir, D. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1318. (d) Galal, A.; Lewis, E. T.; Ataman, O. Y.; Zimmer, H.; Mark, H. B., Jr. *J. Polym. Sci., Polym. Chem.* **1989**, *27*, 1891. (e) Joshi, M. V.; Cava, M. P.; Bakker, M. G.; McKinley, A. J.; Cain, J. L.; Metzger, R. M. *Synth. Met.* **1993**, *55–57*, 948. (f) Niziurski-Mann, R. E.; Scordilis-Kelley, C.; Liu, T.-L.; Cava, M. P.; Carlin, R. T. *J. Am. Chem. Soc.* **1993**, *115*, 887. (g) Glenis, S.; Benz, M.; LeGoff, E.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 12519.
(8) (a) Ruiz, J. P.; Nayak, K.; Child, A. D.; Marynick, D. S.; Reynolds, J. R. *Mater. Res. Soc. Symp. Proc.* **1990**, *173*, 369. (b) Reynolds, J. R.; Ruiz, J. P.; Child, A. D.; Nayak, K.; Marynick, D. S. *Macromolecules* **1991**, *24*, 678. (c) Child, A. D.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun.* **1991**, *24*, 1780. (d) Ruiz, J. P.; Dharia, J. R.; Reynolds, J. R.; Buckley, L. J. *Macromolecules* **1992**, *25*, 849. (e) Reynolds, J. R.; Child, A. D.; Ruiz, J. P.; Hong, S. Y.; Marynick, D. S. *Macromolecules* **1993**, *26*, 2095. (f) Child, A. D.; Sankaran, B.; Larmat, F.; Reynolds, J. R. *Macromolecules* **1995**, *28*, 6571.
(9) (a) Danieli, R.; Ostoja, R.; Tiecco, M.; Zamboni, R.; Taliani, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1473. (b) Mitsuhara, T.; Tanaka, S.; Kaeriyama, K. *Makromol. Chem.* **1988**, *189*, 1755. (c) Tanaka, S.; Kaeriyama, K.; Hiraide, T. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 743. (d) Pelter, A.; Maud, J. M.; Jenkins, I.; Sadeka, C.; Coles, G. *Tetrahedron Lett.* **1989**, *30*, 3461. (e) Haynes, P. M.; Hepburn, A. R.; Goldie, D. M.; Marshall, J. M.; Pelter, A. *Synth. Met.* **1993**, *55–57*, 839.
(10) Reynolds, J. R.; Katritzky, A. R.; Belyakov, S.; Soloducho, J.; Sotzing, G.; Pyo, M.; Ruiz, J. P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 676.
(11) Reynolds, J. R.; Katritzky, A. R.; Soloducho, J.; Belyakov, S.; Sotzing, G. A.; Pyo, M. *Macromolecules* **1994**, *27*, 7225.
(12) Yoshino, K.; Onoda, M.; Kawai, T. *Optoelectron.-Devices Technol.* **1990**, *5*, 1.
(13) Stenger-Smith, J. D.; Tipton, A. L.; Marcy, H. O.; Warren, L. F.; Pyo, M.; Sotzing, G.; Reynolds, J. R. *Polym. Mater. Sci. Eng.* **1994**, *71*, 711.
(14) (a) Martina, S.; Schlüter, A. *Macromolecules* **1992**, *25*, 3607. (b) Martina, S.; Enkelmann, V.; Wegner, G.; Schlüter, A. *Synth. Met.* **1992**, *51*, 299.
(15) Pouwer, K. L.; Vries, T. R.; Havinga, E. E.; Meijer, E. W.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1988**, 1432.
(16) Engel, N.; Steglich, W. *Angew. Chem., Ed. Int. Engl.* **1978**, 676.
(17) Tsai, E. W.; Basak, S.; Ruiz, J. P.; Reynolds, J. R.; Rajeshwar, K. *J. Electrochem. Soc.* **1989**, *136*, 3683.
(18) Hong, S. Y.; Marynick, D. S. *Macromolecules* **1992**, *25*, 3591.
(19) Ballauff, M. *Makromol. Chem. Rapid Commun.* **1986**, *7*, 407.
(20) Westfahl, J. C.; Gresham, T. L. *J. Am. Chem. Soc.* **1974**, *76*, 1076.
(21) Ringsdorf, H.; Tschirner, P.; Hermann-Schönherr, O.; Wendorff, J. H. *Makromol. Chem.* **1987**, *188*, 1431.
(22) Diaz, F. R.; Tagle, L. H.; Olivares, J. P. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2277.
(23) Kato, T.; Kabir, G. M. A.; Uryu, T. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 1447.
(24) Work, T. S. *J. Chem. Soc.* **1940**, 1315.
(25) Inata, H.; Morinaga, T.; Matsumura, S. *J. Appl. Polym. Sci.* **1988**, *35*, 1705.