Ultraviolet-Emitting, Alkoxy-Functionalized Poly(*m*-phenylene)

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ABSTRACT: UV-emitting, highly soluble poly(3,5-(dodecyloxy)phenylene) (**2**) has been prepared by the nickel-catalyzed polymerization of 3,5-dichloro(dodecyloxy)benzene (**1**) in the presence of excess zinc, triphenylphosphine, and 2,2′-bipyridine. Structural characterization by ^{1}H and ^{13}C NMR spectroscopy agrees with the proposed polymer architecture of **2** consisting exclusively of *meta*-linkages. MALDI-MS in a dithranol matrix confirms the presence of the 260 g/mol repeat units contained in the polymer backbone. Elemental analysis is consistent with an average polymer chain consisting of approximately 40 monomer repeats capped by one terminal chlorine atom. GPC of **2** indicates an M_n of 9700 g/mol (relative to polystyrene), well in aggreement with the M_n of 8800 g/mol obtained by toluene VPO studies of the same sample. Thermal analysis has shown the polymer to possess high thermal stability with no weight loss in N_2 up to 350 °C. Solution fluorescence studies of the polymer in THF have determined the polymer to be primarily a UV emitter with only a slight tail extending into the visible region.

As has been reviewed by Schlüter and Wegner, initial efforts attempted the direct synthesis of polyphenylenes from unsubstituted benzenes, and these routes typically led to infusible, low molecular weight solids.[1] Thus, the need became apparent to introduce groups onto the rings that would aid in processibility and concomittantly allow higher molecular weight materials to be produced.[2] Since this realization, the synthesis of derivatized polyphenylenes has been the focus of much attention as these polymers can possess many sought after properties such as a rigid-rod backbone, high thermal stability (of the neutral polymers), and an extended π-system, which can be both p- and n-doped. Many of the polyphenylenes have been found to be excellent candidates for electronic devices, especially those applications calling for luminescent or nonlinear optical materials.

Of the side groups that can be affixed to the phenylene monomers, alkoxy-based units are highly useful due to their electron-donating nature and small steric hindrance. Unfortunately, while alkoxy groups are ideal from a properties standpoint, during the polymerization they have proven to be synthetically difficult. The electron-donating effects of the alkoxy groups make the coupling of such substituted rings difficult by standard means (e.g., Yamamoto[3] and Suzuki[4] methods).

In this study, we report the synthesis and characterization of poly(3,5-(dodecyloxy)phenylene), prepared by a nickel-catalyzed polymerization of the corresponding aromatic dichloride. This polymer is of the polyphenylene class; however, being a poly(*m*-phenylene) (PMP), it possesses a backbone with broken conjugation, consisting essentially of biphenyl units. Previous work in our laboratories with unsubstituted PMP showed it to be a blue emitter.[5] Unfortunately the insolubility of the polymer hindered analysis, including important structural characterization of the material. By introduction of the dodecyloxy substituent onto each repeat unit, we have induced a high level of solubility. Also, the use of an electron-donating alkoxy group alters the electronic structure of the polymer, and quantifying this effect is an important addition to the growing library of information concerning the structure/property relationships of conjugated polymers.

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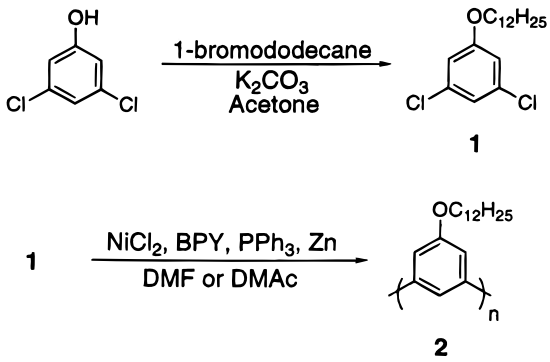
Scheme 1



As illustrated in Scheme 1, the monomer 3,5-dichloro-(dodecyloxy)benzene (**1**) was prepared *via* a classical Williamson ether synthesis, using 3,5-dichlorophenol and 1-bromododecane. Polymerization was accomplished using a nickel-catalyzed homocoupling reaction pioneered by Colon and Kelsey.[6] This methodology has been used by others to prepare a number of polymers, some of which boast relatively high molecular weights.[7] In general, these polymerizations are best suited for electron-withdrawing substituents; however, in this work we illustrate how polymerization has been utilized in conjunction with electron-rich monomers to yield alkoxy-substituted polyphenylenes.

For this reaction the catalyst may be prepared beforehand or *in situ* in the presence of the monomer. Formation of the active catalyst results in a color change from an initial green solution to red/brown. The color returns to green in the presence of uncoupled monomer and persists until the reaction reaches completion, whereby the color of the active catalyst returns. Due to the ambiguity of the green color in the presence of monomer, we selected the slightly more tedious route of preparing the catalyst prior to monomer addition to ensure formation. The choice of coligands for this reaction also proves critical. The use of triphenylphosphine (PPh_3) brings about the undesirable complication of phenyl group transfer to monomer or growing polymer chain. Colon and Kelsey found that addition of 1 equiv of 2,2′-bipyridine (BPY) shuts down this side reaction and also increases the rate of coupling.[6]

We have found the polymerization of 3,5-dichloro-(dodecyloxy)benzene to be relatively insensitive to reac-

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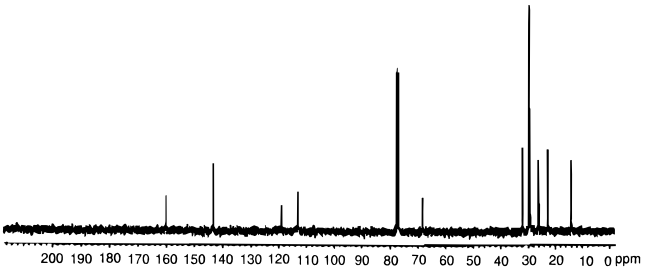

Figure 1. ^{13}C NMR of poly(3,5-(dodecyloxy)phenylene) (**2**) in $CDCl_3$.

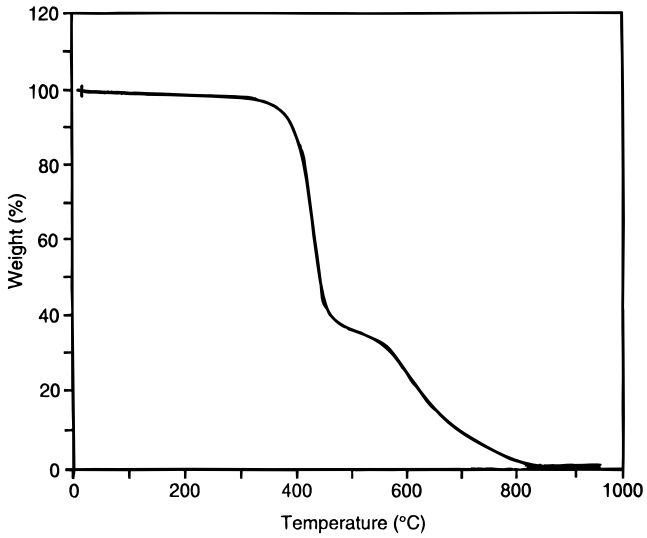

Figure 2. TGA thermogram for poly(3,5-(dodecyloxy)phenylene) (**2**) in N_2.

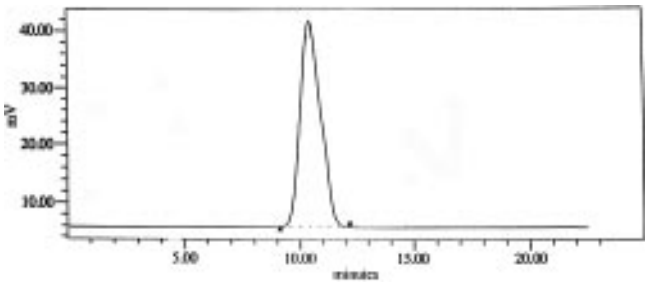

Figure 3. Gel permeation chromatogram of poly(3,5-(dodecyloxy)phenylene) (**2**).

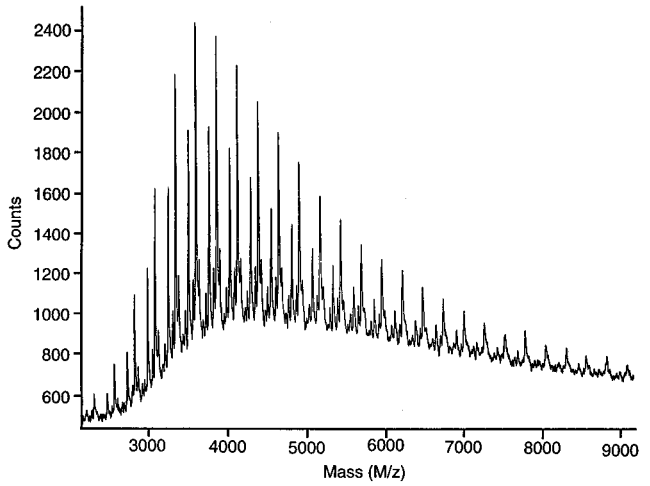

Figure 4. Matrix-assisted laser desorption mass spectral analysis of poly(3,5-(dodecyloxy)phenylene) (**2**) in dithranol matrix. The larger series of peaks correspond to the polymer's 260 g/mol repeat unit.

tion conditions. Catalyst concentrations were varied from 2 to 20 mol %, and the polymerization was carried out in both DMF and DMAc and varying amounts of zinc (from 40 to 80 equiv). In a typical polymerization, monomer **1** is added to the preformed catalyst and stirred at 90 °C for 24 h. The crude polymer is precipitated from the reaction mixture by the addition of H_2O. This resulting tar is dissolved in CH_2Cl_2, filtered to remove zinc metal, and precipitated into CH_3OH. The material is dissolved again in CH_2Cl_2 and reprecipitated in CH_3OH to give poly(3,5-(dodecyloxy)-benzene) (**2**) as a viscous white oil, which slowly converted to a white, flexible solid. This polymer is soluble in various organic solvents such as THF, toluene, and chlorinated alkanes. ^1H and ^{13}C NMR spectra agree with the proposed structure of **2** showing no evidence of coupling defects. Figure 1 shows the ^{13}C NMR spectrum of the polymer in $CDCl_3$. Elemental analysis results are consistent with the repeat unit, showing the presence of a small amount of Cl (less than 1 chlorine atom/40 monomer repeats). Thermogravimetric analysis (TGA) was performed on **2**, and Figure 2 shows the TGA thermogram obtained under a nitrogen atmosphere. The polymer displayed no significant weight loss until a temperature in excess of 350 °C was reached, indicating a relatively high level of thermal stability and the absence of volatile oligomers.

Molecular weight results were obtained by a number of methods including gel permeation chromatography (GPC), vapor pressure osmometry (VPO), and matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS). GPC was performed on 5 mg/mL THF solutions of **2**, using a UV−vis detector set at 313 nm. Figure 3 depicts a typical GPC curve for the polymer. In all cases monomodal distributions were achieved with polydispersity indices (PDI) of approximately 2. The number-average molecular weight (M_n) for **2** was approximated to be 9700 g/mol relative to polystyrene standards. Molecular weight data for each of the respective runs showed little variation between polymers (<1−3 repeat units). As the polymers remain in solution during the polymerization, the reasons for this invariability are not clear. Toluene VPO studies of the same polymer sample used in the GPC analysis were conducted giving an absolute M_n of 8800 g/mol, well within agreement of the GPC data. MALDI-MS studies were performed on the same sample as well, and Figure 4 shows the data obtained for **2**. The key feature of this data is the occurrence of the most intense peaks 260 g/mol apart corresponding to the polymer repeat unit. There is also the presence of a series of peaks of lesser intensity that begin with a mass of 91 g/mol but thereafter retain the 260 g/mol spacing. While the origin of the mass series is not certain, 91 g/mol does coincide with that of a ring missing a single alkyl chain. It has been reported that this coupling reaction is not ideal for electron-rich systems.[4] Given this precedence, perhaps a side reaction, occurring to a very small extent, has resulted in cleavage of the weakened aliphatic carbon−oxygen bond.

While unsubstituted poly(*m*-phenylene) proved to be a blue emitter in the solid state, we were unsure of the total effect that the incorporation of electron-donating groups would impart on luminescence. Irradiating a solution of **2** with a handheld UV lamp resulted in only a faint violet emission detectable by the naked eye. Solution fluorescence studies were performed on THF solutions of **2**. Figure 5 shows the fluorescence spec-

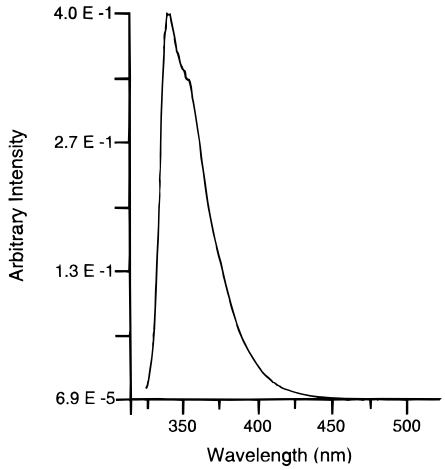

Figure 5. Solution fluorescence emission spectrum of poly-(3,5-(dodecyloxy)phenylene) (**2**) in THF irradiated at 313 nm. The emission maximum for the polymer is at 346 nm.

trum obtained for **2** using a xenon lamp set at 313 nm as the excitation source. The wavelength of maximum emission (λ_{max}) is found at 346 nm, and hence, the majority of the emission lies within the UV region. It is only the tail that trails into the visible spectrum resulting in the faint purple luminescence.

Experimental Section

Materials and Methods. All reactions were performed under prepurified nitrogen or argon, using Schlenk-type techniques. Glassware was dried in an oven overnight or flame-dried and then cooled under a stream of inert gas. NMR spectra were obtained on a 300 MHz spectrometer using $CDCl_3$ as solvent. MALDI-MS was accomplished using a dithranol matrix and a Persptive Biosystems Bench TOF spectrometer calibrated with an insulin standard. Fluorecence spectra were acquired using a SPEX F-112 fluorimeter. Mass spectral anaylses were performed by the University of Florida Mass Spectral Services, Gainesville, FL. Elemental analyses were performed by Robertson Microlabs, Madison, NJ.

3,5-Dichloro(dodecyloxy)benzene (1). A 250 mL round-bottomed flask was charged with 3,5-dichlorophenol (5 g, 0.031 mol), bromododecane (7.65 g, 0.031 mol), potassium carbonate (12.85 g, 0.093 mol), and acetone (100 mL). The mixture was refluxed for 12 h and poured into H_2O (500 mL), and the product was extracted with Et_2O. The organic layer was dried over $MgSO_4$ and the solvent removed. Distillation under reduced pressure (157 °C, 0.02 Torr) afforded **1** as a clear, colorless liquid (8.14 g, 80.0%). ^{1}H NMR: δ 0.91 (t, 3H), 1.30−1.49 (br, 18H), 1.77 (m, 2H), 3.93 (t, 2H), 6.80 (d, 2H), 6.96 (t, 1H). ^{13}C NMR: δ 14.05, 22.66, 25.91, 28.99, 29.29, 29.33, 29.52, 29.56, 29.62, 31.90, 68.62, 113.59, 120.72, 135.27, 160.22. Anal. Calcd for $C_{18}H_{28}Cl_2O$: C, 65.26; H, 8.52; Cl, 21.40. Found: C, 65.49; H, 8.60; Cl, 21.44.

Poly(3,5-(dodecyloxy)benzene) (2). A 50 mL 3-neck, round-bottomed flask was charged with anhydrous nickel(II) chloride (0.13 g, 0.001 mol), 2,2′-bipyridine (0.15 g, 0.001 mol), triphenylphosphine (1.0 g, 0.0038 mol), and zinc powder (3.0 g, 0.046 mol), and the flask was repeatedly evacuated and back-filled with argon (ca. 10 times). Dry *N*,*N*-dimethylformamide (or *N*,*N*-dimethylacetamide) (15 mL) was added, and the mixture was heated with stirring to 50 °C. Heating was continued until a red/brown color appeared in the flask (indicating active catalyst), at which time **1** (3.30 g, 0.01 mol) was added *via* syringe. The reaction mixture was heated at 90 °C with stirring for 24 h. Upon cooling, the mixture was poured into H_2O (150 mL) and the liquid decanted. The tarry residue remaining in the flask was dissolved in CH_2Cl_2, filtered to remove insoluble materials, and added dropwise to a flask containing CH_3OH (300 mL). The precipitate was collected and the process repeated. A white viscous oil was obtained, which, upon standing, gave **2** (2.27 g, 87.3%) as a white flexible solid. ^{1}H NMR: δ 0.88 (t, 3H), 1.28−1.49 (br, 18H), 1.82 (m, 2H), 4.08 (t, 2H), 7.20 (br, 2H), 7.49 (t, 1H). ^{13}C NMR: δ 14.11, 22.68, 26.10, 29.35, 29.44, 29.62, 31.91, 68.30, 112.79, 118.84, 143.09, 159.84. Anal. Calcd for $(C_{18}H_{28}O)_{40}$-Cl: C, 82.74; H, 10.80; Cl, 0.34. Found: C, 82.19; H, 10.74; Cl, 0.19.

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