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Synthesis and Characterization of a Conjugated Copolymer of Poly(phenylenevinylene) Containing a Metalloporphyrin Incorporated into the Polymer Backbone

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ABSTRACT: A chlorine precursor copolymer was synthesized from the monomers 1,4-bis(chloromethyl)-2,5-(dihexyloxy)benzene and the metal complexes [5,15-bis(mesityl)-10,20-bis(4-(chloromethyl)phenyl)-porphyrin] in different ratios with potassium *tert*-butoxide. The precursor copolymers were readily soluble in common organic solvents and were characterized by NMR, IR, UV−vis, elemental analysis, and TGA. A relatively high molecular weight of the precursor copolymer was determined by GPC with a polydispersity of about ∼3. The arylenevinylene copolymer film was formed by thermal conversion and demonstrated higher thermal stability as compared to typical poly(phenylenevinylene)-type polymers. Doping of undrawn films of the copolymer with iodine vapor led to conductivities as high as 2 S cm^{-1}.

Introduction

Incorporation of chromophores such as porphyrins into polymer networks has been investigated for potential applications in sensing,[1−3] magnetic,[4] catalytic,[5] nonlinear optics materials,[6] and artificial photosynthesis in recent years.[7−11] We have initiated a program to explore the photoactivity of chromophores within conjugated systems in order to establish how we can control the optical or electronic properties of polymers with visible excitation. Porphyrins can be incorporated into polymers via nonconjugated bonds[4,5,7] or conjugated bonds.[6,8] Coordination polymers have also been investigated in which the metalloporphyrins are linked face-to-face.[12] Polymeric porphyrins in which the chromophoric units are wired directly within the conjugated molecular chain are very rare.[6] This may be due to synthetic challenges in preparing suitably functionalized porphyrins which can be incorporated into the conjugated polymer. The advantage to this approach is the opportunity to provide further electronic modification of the conjugation and new approaches to ordered molecular level assemblies through stacking interactions of the porphyrins.[4,13,14]

It is well-known that many metalloporphyrins undergo reversible oxidation, yielding stable radical cations.[15] Recently we have demonstrated that chromophores such as metalloporphyrins can be doped into conducting polymers as photoactive conductivity switches.[16] It was hypothesized that the limited efficiency of the intermolecular systems could be improved through covalent attachment of the chromophore. Covalent incorporation of porphyrins could also lead to useful variations in the physiochemical properties of these materials.

Generally, there are three approaches to the preparation of processable conjugated polymers.[17] The first method circumvents the insolubility and infusibility limitations associated with stiff-chain polymers by appending flexible side chains onto the main chain.[17] The second approach relies on the preparation of a soluble precursor polymer which can then be transformed to the final conjugated polymer through thermal or photochemical means.[17−21] One example is the chlorine precursor route reported in 1990 by Swatos et al.,[21] involving the polymerization of 1,4-bis(chloromethyl)-2,5-(dihexyloxy)benzene with approximately 1 equiv of KO^{t}Bu to give a soluble chlorine precursor polymer. This soluble precursor was then converted to conducting poly(2,5-(dihexyloxy)-*p*-phenylenevinylene) [DHPPV] under mild thermal conditions (Scheme 1). The third approach is through surfactant counterion complexation.[22,23]

We report here the design and synthesis of a new series of metalloporphyrin monomers, shown below, and their subsequent copolymerization to form different ratios of 2,5-bis(chloromethyl)-1,4-(dihexyloxy)benzene

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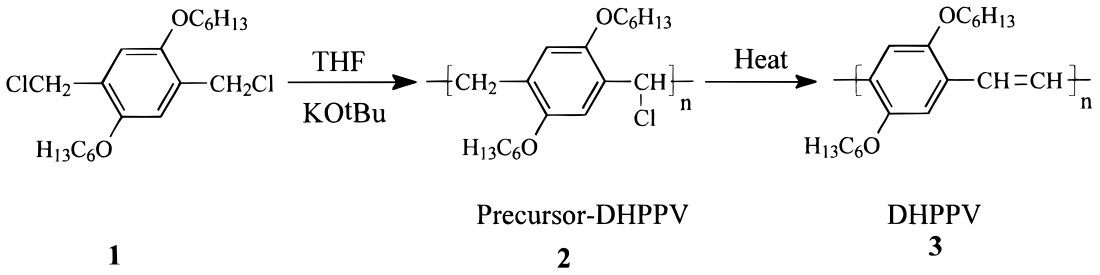
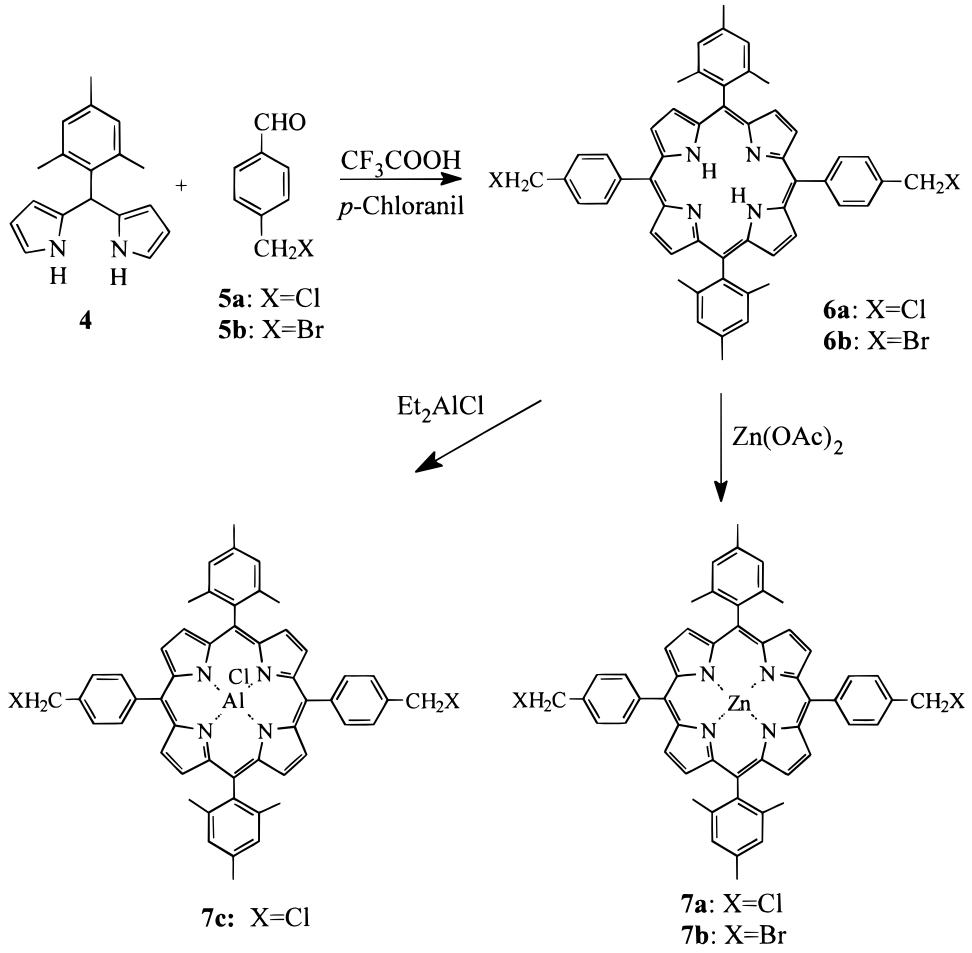
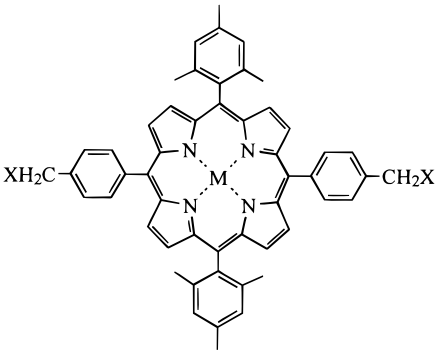
Scheme 1. Synthetic Scheme for DHPPV



Scheme 2. Synthesis of Metalloporphyrin Monomers



and the metalloporphyrins. The porphyrin monomers have been synthesized in large quantity, with reasonable yields, by a simple two-step procedure. The precursor copolymers are all soluble in common organic solvents and can be cast into high-quality films which can then be converted into fully conjugated polymers under mild thermal conditions. The results of thermal and electronic characterization provide insight into the utility of this new material for photonic or electronic applications.



Porphyrin monomers: X=Cl, Br; M=Zn, Al.

Experimental Section

Materials. Pyrrole (Aldrich) was distilled at atmospheric pressure from CaH_2 under N_2. CH_2Cl_2 (Fisher) was distilled from P_2O_5 prior to use. Anhydrous THF and all other chemicals were purchased from Aldrich and were used without further purification. Column chromatography was performed using silica gel (Baker, 60−200 mesh or Aldrich, 230−400 mesh).

The compound 1,4-(dihexyloxy)benzene was prepared from hydroquinone and *n*-hexyl bromide in DMF/KOH solution.[24] Chloromethylation of the 1,4-(dihexyloxy)benzene gave 1,4-bis(chloromethyl)-2,5-(dihexyloxy)benzene (**1**). Meso(mesityl)-dipyrromethane (**4**) was prepared from mesitaldehyde and excess pyrrole according to literature procedures.[25]

Synthesis of 4-Formylbenzyl Chloride (5). Mono(diethylacetyl) terephthaldehyde (21.6 g, 10 mmol) was added to

a 500-mL round-bottom flask equipped with a condenser. The solution was cooled in an ice bath, and 2 g of $NaBH_4$ (52 mmol) was carefully added dropwise. The reaction is highly exothermic, and care should be taken to prevent the methanol from boiling. When the reaction subsided, the ice bath was removed and the flask was stirred overnight. The volume of solvent was reduced by 33%, and the mixture was quenched with 400 mL of 0.2−0.4% aqueous sodium carbonate. The product was extracted with diethyl ether, washed with distilled water, and then dried over $MgSO_4$. The resulting solution was evaporated under reduced pressure to give an oil (19 g). A portion of the oil, 8.4 g (0.04 mol), was dissolved in 3.48 g (0.044 mol) of pyridine in a 100-mL three-neck round-bottom flask equipped with condenser and Ar inlet. The solution was put into an ice bath and purged with Ar for about 10 min. Freshly distilled sulfuryl chloride, 5 g (0.042 mol), was added over 30 min. After 3 h of stirring at room temperature, the solution was poured into 500 mL of water and extracted with diethyl ether (3 × 200 mL). Diethyl ether was evaporated to dryness, and the resulting oil became solid on standing for 10 min. Concentrated HCl (3 mL) and 10% H_2SO_4 (50 mL) were added to the solid, and the solution was refluxed with stirring for 30 min. The solution was cooled to room temperature, resulting in the formation of needlelike crystals that were collected by suction filtration. Recrystallization was achieved from hexane, overall yield 85%. ^{1}H NMR($CDCl_3$) δ 10.01 (s, 1 H, CHO), 7.87 (d, 2 H, aromatic), 7.55 (d, 2 H, aromatic), 4.62 (s, 2 H, CH_2Cl). Anal. Calcd for C_8H_7ClO: C, 62.33; H, 4.58; Cl, 22.70; O, 10.39. Found: C, 62.10; H, 4.60.

Synthesis of 5,15-Bis(mesityl)-10,20-bis(4-(chloromethyl)phenyl)porphyrin (6a).[26] A solution of 4-formylbenzyl chloride, 1.30 g (8.5 mmol), and meso(mesityl)dipyrromethane, 2.24 g (8.5 mmol), in freshly distilled methylene chloride (1.5 L) was cooled in an ice bath and purged with argon for 30 min. Trifluoroacetic acid (0.5 mL) was added, and the solution was stirred overnight. *p*-Chloranil (3.5 g) was added, and the mixture was stirred for an additional 3 h. The solvent was removed under vacuum. Column chromatography (silica, CH_2Cl_2) afforded the porphyrin as the first moving band (0.8 g, 23% yield). ^{1}H NMR ($CDCl_3$) δ 8.73 (dd, 8 H, β-pyrrole), 8.00 (AA′BB′, 8 H, 4-(chloromethyl)phenyl-H), 7.28 (s, 4 H, mesityl-H), 4.94 (s, 4 H, *p*-$ClCH_2$), 2.62 (s, 6 H, *p*-CH_3),1.82 (s, 12 H, *o*-CH_3), −2.62 (br s, 2 H, NH); ^{13}C NMR ($CDCl_3$) 142.18, 139.39, 138.37, 137.78, 136.91, 134.78, 127.78, 126.92, 118.59, 118.48, 46.29, 21.61, 21.45; UV−vis λ_{abs} (THF) 418, 514, 546, 592, 650 nm. Anal. Calcd for $C_{52}H_{44}N_4Cl_2$: C, 78.56; H, 5.58; N, 7.05; Cl, 8.81. Found: C, 78.38; H, 5.71; N, 7.00; Cl, 8.65.

Synthesis of 5,15-Bis(mesityl)-10,20-bis(4-(bromomethyl)phenyl)porphyrin (6b). The porphyrin **6b** was prepared in a similar manner to **6a** in 25% yield. ^{1}H NMR δ 8.73 (dd, 8 H, β-pyrrole), 7.98 (AA′BB′, 8 H, 4-(bromomethyl)-phenyl-H), 7.25 (s, 4 H, mesityl-H), 4.84 (s, 4 H, *p*-$BrCH_2$), 2.62 (s, 6 H, *p*-CH_3), 1.82 (s, 12 H, *o*-CH_3), −2.62 (br s, 2 H, NH); ^{13}C NMR ($CDCl_3$) δ 142.22, 139.39, 138.37, 137.79, 137.24, 134.85, 131.22 (b), 130.17 (b), 127.79, 127.42, 118.51, 33.48, 21.60, 21.45; UV−vis λ_{abs} (THF) 416, 514, 548, 592, 650 nm. Anal. Calcd for $C_{52}H_{44}N_4Br_2$: C, 70.73; H, 5.04; N, 6.35; Br, 17.89. Found: C, 70.52; H, 5.21; N, 6.30; Br, 17.69.

Synthesis of [5,15-Bis(mesityl)-10,20-bis(4-(chloromethyl)phenyl)porphyrin]zinc (7a).[27] The free-base porphyrin **6a** (0.3 g; 0.37 mmol) was dissolved in 10 mL of THF, and then 0.41 g (1.85 mmol) of $Zn(OAc)_2{\cdot}2H_2O$ was added. The solution was refluxed for 1 h, and the solvent was evaporated to yield purple−red crystals. The product was recrystallized from methanol (in 95% yield). ^{1}H NMR δ 8.83 (dd, 8 H, β-pyrrole), 8.00 (AA′BB′, 8 H, 4-(chloromethyl)phenyl-H), 7.28 (s, 4 H, mesityl-H), 4.95 (s, 4 H, *p*-$ClCH_2$), 2.63 (s, 6 H, *p*-CH_3), 1.83 (s, 12 H, *o*-CH_3); ^{13}C NMR ($CDCl_3$) δ 150.03, 142.99, 139.25, 138.95, 137.52, 136.66, 134.70, 132.24, 130.89, 127.69, 126.76, 119.54, 46.36, 21.61, 21.45; UV−vis λ_{abs} (THF) 422, 514, 556, 596, 650 nm. Anal. Calcd for $C_{52}H_{42}N_4Cl_2Zn$: C, 72.69; H, 4.93; N, 6.52; Cl, 8.25. Found: C, 72.40; H, 5.14; N, 6.25; Cl, 8.50.

Synthesis of [5,15-Bis(mesityl)-10,20-bis(4-(bromomethyl)phenyl)porphyrin]zinc (7b). The porphyrin **7b** was prepared in a similar manner to **7a** in 95% yield. ^{1}H NMR δ 8.82 (dd, 8 H, β-pyrrole), 7.98 (AA′BB′, 8 H, 4-(bromomethyl)-phenyl-H), 7.28 (s, 4 H, mesityl-H), 4.84 (s, 4 H, *p*-$BrCH_2$), 2.63 (s, 6 H, *p*-CH_3), 1.82 (s, 12 H, *o*-CH_3); ^{13}C NMR ($CDCl_3$) δ 150.04, 149.95, 143.03, 139.25, 138.94, 137.54, 136.98, 134.77, 132.24, 130.91, 127.86, 127.27, 119.49, 33.62, 21.61, 21.46; UV−vis λ_{abs} (THF) 418, 514, 546, 592, 650 nm. Anal. Calcd for $C_{52}H_{42}N_4Br_2Zn$: C, 66.09; H, 4.48; N, 5.93; Br, 16.72. Found: C, 66.20; H, 5.00; N, 6.01; Br, 16.40.

Synthesis of [5,15-Bis(mesityl)-10,20-bis(4-(chloromethyl)phenyl)porphyrin]aluminum(III) (7c). Free-base porphyrin **6a** (0.02 g) was placed into a 10-mL round-bottom flask and purged with N_2. (Care must be taken to ensure that the porphyrin, **6a**, is anhydrous by drying under vacuum prior to reaction.) Anhydrous methylene chloride (0.5 mL) was added via syringe to dissolve the porphyrin, and then diethylaluminum chloride in toluene (1.2 equiv) was then added by syringe. After about 10 min of reaction at room temperature, the formation of metalated porphyrin was confirmed by the UV−vis spectrum, and the solvent was evaporated under vacuum. The metallic blue compound was used directly as monomer for subsequent polymerization reactions. UV−vis λ_{abs} (THF) 422, 516, 558, 598 nm; ^{1}H NMR δ 8.74 (dd, 8 H, β-pyrrole), 8.53−7.28 (m, 10 H), 5.29 (s, 4 H), 2.6 (s, H), 2.0 (s, 6 H), 1.8 (s, 6 H).

Synthesis of Precursor Copolymers 8a, 8b, and 8c.[21] **General Procedure.** A solution of the monomers **1** and **7a−c** in THF (∼5%) was added to 1.0 M KO^{t}Bu (1:1 molar ratio). The resulting solution was stirred for 10 min at room temperature, and the solid was precipitated by adding methanol. A deep-green, fibrous chlorine precursor polymer was obtained. This precursor copolymer was redissolved in THF and precipitated in methanol several times until no free porphyrin was detected in the methanol by UV−vis. Anal. Found for **8a**: C, 72.06; H, 9.30; N, 0.11. Anal. Found for **8b**: C, 72.00; H, 9.62; N, 0.13. Anal. Found for **8c**: C, 71.78; H, 9.00; N, 0.45.

Conjugated Copolymer 9a, 9b, and 9c. The precursor polymer or copolymer prepared either as a fibrous solid or by spin coating as a polymer film was put into a tube furnace under N_2 flow with catalytic amounts of triethylamine. The temperature was maintained at 150 °C for 2 h. The polymer films turned dark red upon heating, consistent with the formation of the conjugated vinylene copolymer. The conjugated form was insoluble in both organic and aqueous solvents.

Film Preparation. Films of the precursor polymers were obtained by spin coating on glass slides from a concentrated THF solution. Films prepared in this manner were a uniform 2−5 μm based on profilometry. Undrawn films of the copolymer were doped under iodine vapor for periods up to 5 h.

Physiochemical Methods. NMR spectra were recorded on a Bruker AM-360 spectrometer. Elemental analyses were performed by the Oneida Research Services, Inc. The molecular weight of the precursor copolymer in THF solution was measured by GPC (Waters 510) relative to polystyrene calibration with UV and refractive index detectors. The molecular weights were also run by light scattering using a Wyatt Technologies MiniDawn operating in batch mode with a d*n*/d*c* value of 0.290 based on pure DHPPV. All reported molecular weights are weight averages, M_w, unless otherwise noted. UV−Vis spectra were obtained both on the solution and film using a Perkin-Elmer Lambda 2S spectrophotometer. Infrared spectra were recorded on a Nicolet Model 20SXC FTIR spectrometer. Fluorescence measurements were made on dilute solutions of the monomer with an SLM 48000S fluorescence lifetime instrument with 428-nm excitation and 8-nm slits. Solid-state fluorescence measurements were achieved using copolymer films supported on glass substrates and mounted with front-face excitation at an angle of <45°.

The conductivity measurements were carried out using the conventional four-probe technique.[28] The dc current was provided by a programmable Kiethley current source (Model 220). The voltage was measured using a Kiethley voltmeter (Model 182). The temperature was monitored using an Omega e-type thermocouple interfaced to a Kiethley 195 A digital voltmeter. All components were controlled through GPIB communication and software written locally.

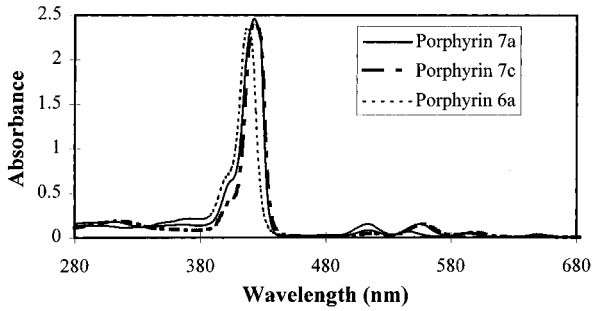


Figure 1. UV−Vis absorption spectra of porphyrin monomers in THF solution at room temperature.

Results and Discussion

Monomer Preparation and Characterization. The preparation of substituted porphyrins for synthetic coupling in macromolecular systems has been an active area of research in recent years.[1−12] In order to facilitate copolymerization of a metalloporphyrin within a conjugated polymer chain, 4-formylbenzyl halide (see Experimental Section) reacted with **4** with catalytic amounts of trifluoroacetic acid yielded the methyl halide substituted free-base porphyrin **6a** or **6b** in 25% yield. The large quantity of **4** can be readily prepared according to Lindsey *et al.*[25] ^{1}H NMR and IR characterization of these new structures provides direct evidence of the porphyrin structure and purity. The free-base porphyrins could then be metalated with $Zn(OAc)_2 \cdot 2H_2O$ or Et_2AlCl to give metalloporphyrins **7a**, **7b**, or **7c**, respectively. Both the metalated and free-base porphyrins were very soluble in THF, CH_2Cl_2, and toluene.

UV−Vis spectroscopy of the porphyrin monomers is shown in Figure 1. Characteristic visible absorptions appear in the 420-nm region for the B-band $\pi-\pi^*$ transitions. Additional electronic transitions appear as sets of peaks in the 500−600-nm region of the spectra, consistent with Q-band transitions. Fluorescence spectroscopy of the porphyrin monomers in THF solution showed two emission peaks in the 600−700-nm region. There was a general shift to lower energy on going from the Zn, $\lambda_{max} = 624$ nm, to the free base, $\lambda_{max} = 670$ nm, consistent with previous reports on porphyrin monomers.[10−12]

Copolymer Characterization. In order to enhance the subsequent solubility of the copolymer, **1** was used as the monomer for copolymerization. Scheme 3 shows the copolymerization of monomer **1** with the metalloporphyrin monomers (**7a**, **7b**, or **7c**) in anhydrous THF solution under N_2 with 1 equiv of KO^{t}Bu. The resulting solution is deep green, as opposed to the light-yellow solution that results from the homopolymer of **3**. The chlorine−precursor copolymer was obtained by pouring the THF solution into methanol several times until no free porphyrin absorptions were observed by UV−vis spectroscopy on the methanol solutions.

Molecular weights determined by both GPC with polystyrene calibration in and by laser light scattering in THF for these systems varied from $M_w = 3.5 \times 10^5$ to 9.0×10^5 for the aluminum and zinc porphyrin copolymer samples, respectively, Table 1. For the laser-light-scattering measurements, the laser wavelength of 690 nm was not absorbed by the solution. The polydispersities observed for these samples were between 3.5 and 2.8. We observed that more efficient incorporation of the porphyrin decreased the final molecular weight. This was most likely due to decreased solubility of the copolymers relative to pure DHPPV. The porphyrin anions may also have been less effective at chain propagation, though we did not see evidence of porphyrin end groups in the ^{1}H NMR.

Scheme 3. Synthesis of Metalloporphyrin-Containing Copolymers

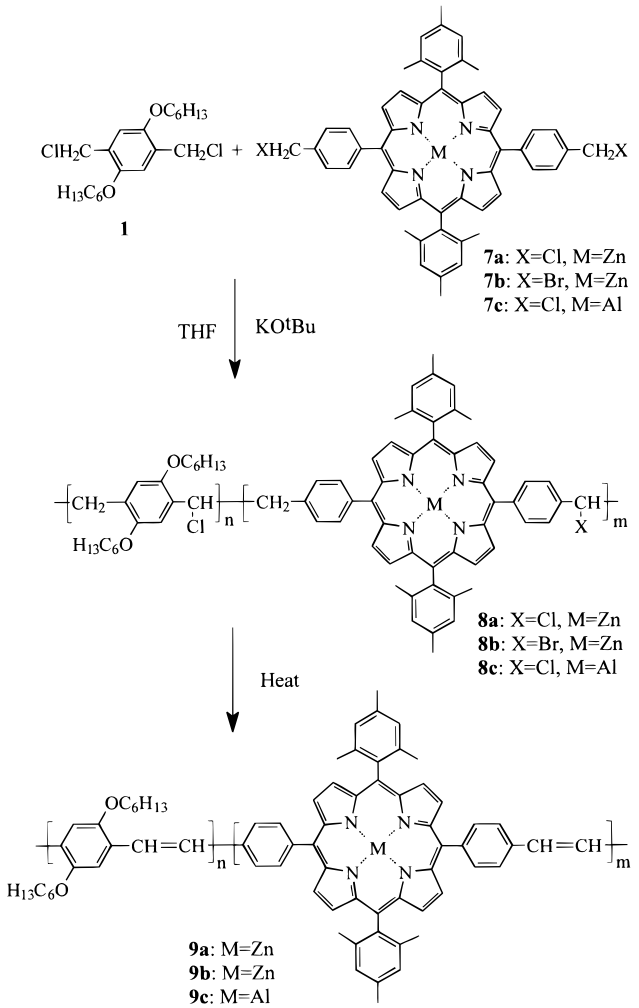


Table 1. Copolymerization of Porphyrins with Conjugated Phenylenevinylene Bridges

	wt % porphyrin			
sample	in monomer	incorpord[a]	% yield	M_w
8a	15	1.7	45	7.8×10^5
8b	15	2.0	40	9.0×10^5
8c	15	7.0	47	3.5×10^5

[a] Calculated based on the content of nitrogen determined by elemental analysis and by integration of ^{1}H NMR.

Shown in Figure 2a are the UV−vis spectra recorded in room-temperature THF solutions of the copolymers prepared from the zinc and aluminum porphyrin monomers. For comparison purposes, the homopolymer of **1** is also shown. The strong absorption at 310 nm in all samples is readily assigned to the $\pi-\pi^*$ transition of aromatic units in the polymer backbone. There was no significant shift in either the energy or the bandwidth of this transition upon incorporation of the porphyrin within the copolymer. Substantial broadening of the metalated porphyrin absorptions occurs as compared to the monomer absorptions in Figure 1, consistent with the formation of the copolymer.

A concern in the characterization of the copolymers was the formation of a mixture of two homopolymers or a mixture of DHPPV and the porphyrin monomers.

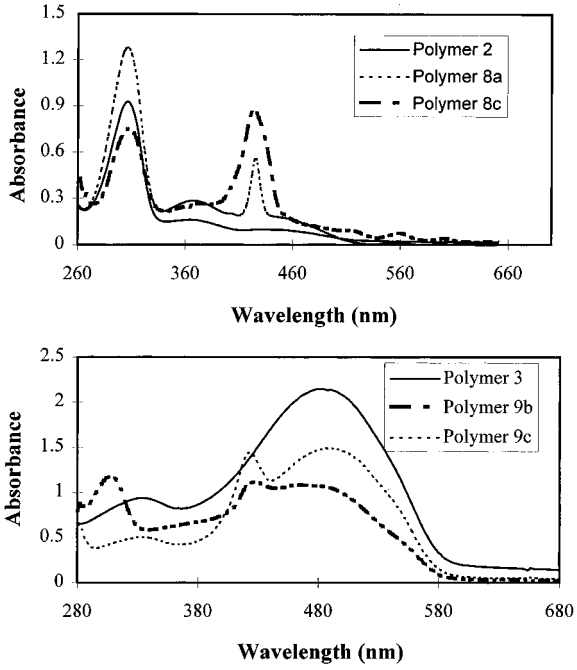


Figure 2. (a, top) UV−Vis absorption spectra of the precursor polymer and representative copolymers **8a** and **8b** in THF solution at room temperature. (b, bottom) UV−Vis absorption spectra of thin polymer films of a conjugated polymer and copolymer on glass slides at room temperature.

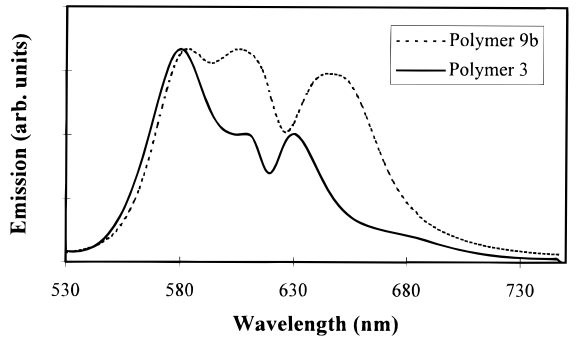
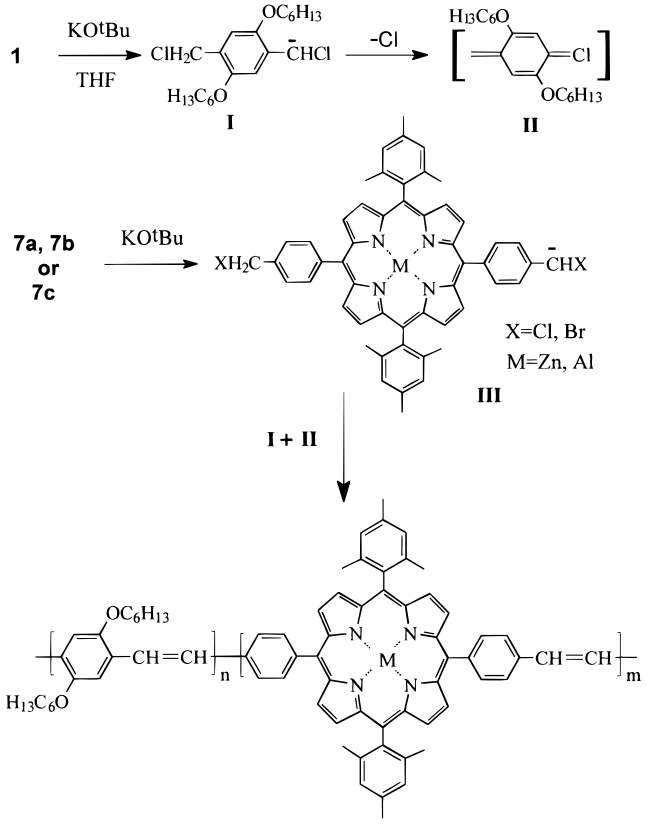


Figure 3. Fluorescence spectra of DHPPV and Zn−porphyrin copolymer as thin films on glass substrates excited at 428 nm.

The latter of these two options is readily disproved by the 5−8-nm shift of the low-bandwidth B-band absorptions of the porphyrin upon incorporation into the polymer. This shift is not observed when mixtures of the porphyrin are prepared as thin films with DHPPV. In addition, the ^{1}H NMR peak at 4.95 ppm due to the CH_2Cl functional group of the porphyrin monomer was not observed following polymerization, even at high concentrations.

The possibility that the product is a mixture of the two homopolymers (DHPPV and the porphyrin homopolymers) is more challenging. Direct evidence of the formation of the copolymers rather than a mixture of the two homopolymers is not available from ^{1}H and ^{13}C NMR spectra due to two complications. At room temperature, the dehydrohalogenation of the precursor polymer occurs continuously, resulting in a mixture of conjugated and nonconjugated products in the NMR.[23] The relatively low concentration of porphyrin within the copolymer, <2 mol %, limits our ability to assign unique peaks to the porphyrin repeating unit. Further, the similarity in the porphyrin repeating unit for either the homopolymer or copolymer, Scheme 3, limits the assignment and would most likely require ^{13}C, which is

Scheme 4. Proposed Mechanism of Copolymerization



even more limited by the low concentration of porphyrin. An attempt was made to prepare the pure porphyrin homopolymer under identical conditions to the preparation of **8**. Under these conditions, no oligomeric or polymeric porphyrin was formed. This suggests that the formation of the homopolymer is not significant under these conditions. Further, careful study of the GPC results shows only one polydisperse peak and no lower molecular weight oligomeric species that could be attributed to a mixture of homopolymers. On the basis of these results, we conclude that the copolymers shown in Scheme 2 are formed.

Copolymerization Mechanism. The mechanism for the homopolymerization reaction of **1** has previously been discussed.[21,29] It was suggested that the monomer loses one proton under basic conditions to form anion I and subsequent loss of chlorine results in the formation of intermediate II (Scheme 4). The anion acts as an initiator by attacking II to form the polymer. The corresponding mechanism for the copolymerization is more complex than that of homopolymerization (Scheme 4). Porphyrin monomers (**7a**−**c**) in the first step can form the anion III by loss of one proton under basic conditions. The anionic form of the porphyrin can act as an initiator, leading to polymer formation.

The final composition of the precursor copolymers provides some insight into the consistency of our results with this mechanism. The amount of porphyrin incorporated into the final copolymer was determined by elemental analysis. In each case, the weight percent of porphyrin monomer incorporated was significantly less than that which was provided stoichiometrically, Table 1. The incorporation of free-base porphyrin into the copolymer was least successful. This was most likely due to the relatively high acidity of the nitrogen protons in the free base. Under basic conditions, free-base porphyrins lose the proton from the porphyrin ring

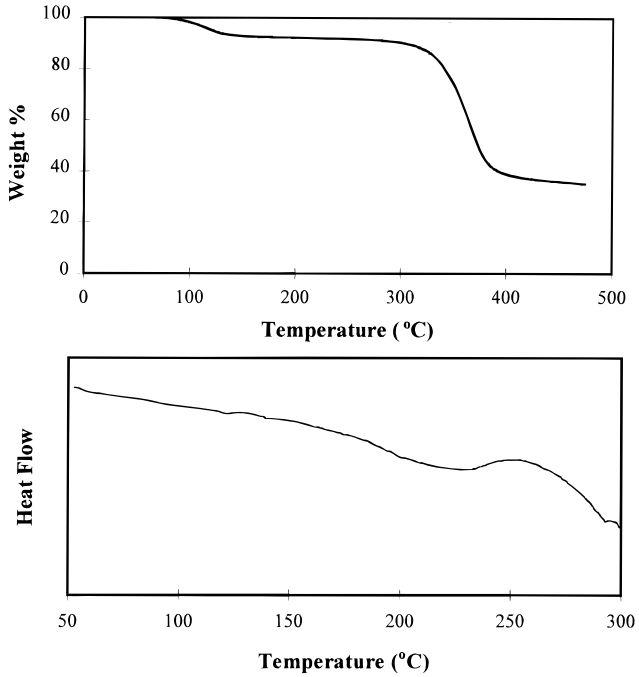


Figure 4. (a, top) TGA thermogram of representative precursor copolymer **8c**. (b, bottom) DSC thermogram of representative copolymer **9b**.

instead of forming the carbanion, which is crucial for initiating the anionic polymerization. The Zn- and Al-metalated porphyrins resulted in about 2.0% and 7.0% incorporation, respectively. The mechanism in Scheme 4 is consistent with the observation that the aluminum monomer is 3 times more reactive toward polymerization since the Al monomer can form the most stable anion (III) under basic conditions, which is critical for the anionic polymerization. Thus, our results support the assignment of the anionic copolymerization mechanism shown in Scheme 4.

Copolymer Conjugation and Conductivity. Dehydrohalogenation of the precursor homopolymer or copolymer took place at approximately 100 °C as determined by TGA, shown in Figure 4a. However, the process proceeds slowly even at room temperature, as mentioned above. When the samples (films or fiber) were allowed to stand in a capped vial for several days, the color changed from light yellow (homopolymer) or green−yellow (copolymer) to red. This color change, combined with IR and NMR data (see below), confirmed the formation of the vinyl-conjugated polymer. In addition, evidence for HCl can be observed upon removing the vial cap. Swatos et al. have reported the same properties for the related precursor DHPPV.[21] The conversion process also occurs in solution, though there was an unexpected stability in THF solutions as observed previously for the homopolymer.[21] Specific solvation of undissolved base may be the reason for the stability in the THF solution.[21]

The solubility of the precursor polymer provides the opportunity to prepare high-quality films by spin coating a THF solution onto a glass slide. Films prepared in this manner were converted to the fully conjugated copolymer **9a** or **9b** in a tube furnace at approximately 150 °C under N_2 flow, with or without basic catalyst, or by subjecting them to a vacuum of 0.1 Torr at 150 °C for 2 h. The maximum electrical conductivity obtained for the unstretched films doped with iodine was 1−3 S cm^{-1} for both DHPPV and the porphyrin-substituted copolymers. The conductivity can be increased by 2 orders of magnitude through the use of base-catalyzed conversion rather than the vacuum conditions reported by Swatos et al.[21] This conductivity is similar to the conductivity reported by Wudl et al.[30] for DHPPV prepared via the sulfonium precursor route. The high conductivity is most likely due to more complete dehydrochlorination under basic catalyst conditions.

The conductivity reaches a maximum after exposure to iodine for 4 h. The iodine-doped copolymers, like DHPPV and its derivatives, are not stable in air. A reversible loss in conductivity upon exposure to air can be monitored by the concomitant color change or electronically. The doped films were stabilized under sealed nitrogen conditions. The conductivity of the porphyrin-substituted polymers was not significantly changed by incorporation of the metalloporphyrin into the main chain relative to DHPPV. This may be due to the low weight percent of the porphyrin unit in the copolymer, based on recent results with related copolymers with 50% porphyrin incorporation.[32]

Infrared spectra of the copolymer and homopolymer were taken before and after thermal conversion. The dehydrohalogenation was evidenced by the appearance of an absorption at 3050 cm^{-1} due to the olefinic C−H stretch and a small absorption due to the trans-substituted olefinic C−H bend at 960 cm^{-1}. There was no apparent difference between the homopolymer and copolymers based on IR spectroscopy.

UV−Vis spectra of the polymers **9a** and **9b** as thin films (2−5 μm) on glass slides are shown in Figure 2b. The UV−vis spectrum of the polymer of DHPPV prepared separately under the same conditions is included for comparison. The absorption at 424 nm due to the porphyrin remains, though the lower energy porphyrin absorptions are masked. The bandwidths of the porphyrin absorptions remain broad. Enhanced conjugation of the polymer thin films should result in further broadening of the porphyrin absorptions. However, conjugation results in a new absorption feature at 484 nm, consistent with the formation of the band gap of the conducting polymer. This new absorption masks any increased broadening which may have occurred. We can estimate the band gap of the homopolymer as 2.10 eV from an extrapolation of the slope of the low-energy edge of the transition. The band gap shifts to 2.12 eV upon incorporation of the metalated porphyrin.

A general interest in PPV derivatives involves their use in light-emitting diode applications (LED).[31] The copolymers prepared here contain the additional porphyrin chromophore that is fluorescent and may provide further opportunities for use in LED applications. Shown in Figure 3 are the fluorescence spectra of 5-μm thin films of DHPPV and and the Zn−porphyrin copolymer **9b** excited at 428 nm. The spectrum for **9b** is a composite of the DHPPV spectrum and the Zn−porphyrin monomer spectrum. Interesting to note in these data is the presence of both fluorescent signatures. If electronic communication between the porphyrin groups and the PPV chain were significant, only the lower energy porphyrin fluorescence would be expected. Further work on the energy-transfer dynamics in these systems is underway.[32]

The thermal properties of the polymers were analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Figure 4a shows the TGA spectrum of a representative precursor copolymer **8c.** The dehydrohalogenation begins at ~100 °C and results

in the loss of 8% of the mass. This is consistent with the formation of the vinylene bridge upon loss of HCl. The structure decomposition temperature occurs at ~330 °C. A representative DSC thermogram of the conjugated samples **9b** is shown in Figure 4b. The most notable feature of the DSC data was the absence of glass transition temperature below 150 °C. The glass transition temperature in typical samples of derivatized DHPPV occurs at <50 °C.[33] This suggests that the incorporation of the porphyrin may decrease the flexibility of the copolymer relative to DHPPV. This may be due to π-stacking interactions of the porphyrins,[4,13,14] though no evidence for long-range order was observed in a preliminary X-ray powder diffraction experiment. The combined DSC and TGA data suggest an increased thermal stability for electronics processing upon incorporation of the porphyrin into the conjugation of the polymer.

Summary

We have prepared conjugated copolymers containing metalated porphyrin complexes through the preparation of a new porphyrin precursor with a methyl halide substituent. Various metal complexes of the porphyrin can be incorporated into PPV or derivatives, e.g., DHPPV. By comparing the relative incorporation of free-base, aluminum, and zinc porphyrin complexes into the polymer, we find support for an anionic polymerization mechanism consistent with previous descriptions of the homopolymerization. The precursor copolymer was soluble in THF solution and could be deposited as uniform thin films prior to dehydrohalogenation and the formation of the conjugated structure. Incorporation of the porphyrins into the conjugation of the polymer backbone resulted in enhanced thermal properties.

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