New Metalloporphyrin Containing Polymers from the Heck Coupling Reaction

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In this paper, we report the synthesis and characterization of novel polymers containing porphyrin moieties. The motivation to carry out this research came from the following considerations: first, processible, well-defined polymers containing transition metal ions have been widely sought because of their potential applications in molecular electronics, electro-optics, and catalytic processes.[1-3] Our major research interest is focused upon the synthesis of new polymers with multifunctional properties, such as photorefractive polymers which combine the photoconductivity and optical nonlinearity to manifest photorefractivity.[4] Polymers containing metalloporphyrin arouse our interest for these purposes due to their unique electronic structures and optical properties. It is known that many porphyrin and metalloporphyrin compounds are responsible for charge separation in natural photosynthetic centers and in many photosynthetic model compounds.[5] These properties are relevant to the design of photorefractive polymers.

Second, the Heck reaction has been successfully applied to synthesize several phenylenevinylene polymers.[6a-c] Recently, we also utilized the Heck coupling reaction to synthesize substituted poly(phenylenevinylene) conjugated polymers, which demonstrated interesting liquid crystallinity.[6d] However, our interest to explore the Heck reaction was directed to utilize the reaction to synthesize multifunctional polymers. This work represents an extension of the polymerization by the Heck reaction and demonstrated the feasibility of the Heck reaction in the synthesis of metal-containing polymers. It also indicated the synthetic and physical basis for the further synthesis of photorefractive polymers.

Experimental Procedure. Monomer **2A** was a new compound and was synthesized in 68% yield from a dipyrromethane 4.[7] Metallation of monomer **2A**, by refluxing with transition-metal acetate in a chloroform/methanol (3:1) solution, yielded monomers **2B–D** quantitatively. Monomer 3 was synthesized according to a literature procedure.[6d]

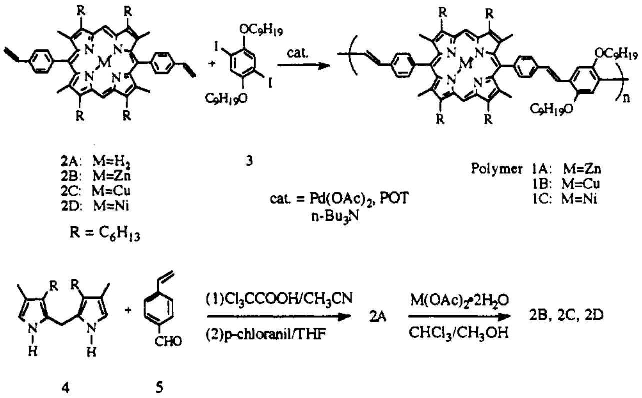
Polymerization. The following is a typical polymerization procedure: Tri-*n*-butylamine (0.15 mL) was added to a mixture of metalloporphyrin monomer (0.12 mmol), 1,4-diiodo-2,5-dinonoxybenzene (compound 3; 0.0718 g, 0.12 mmol), palladium acetate (0.0011 g, 0.0047 mmol), and tri-*o*-tolylphosphine (0.0036 g, 0.012 mmol) in 5 mL of DMF. The reaction mixture was heated in a 100 °C oil bath under a nitrogen atmosphere until the polymer precipitated out from the reaction mixture. It was then poured into acetone (75 mL), and the precipitate was collected. To further purify the polymer, it was redissolved in chloroform or THF, and the solution was filtered to remove any residual palladium precipitate. The filtrate was concentrated and precipitated into acetone. The resulting polymer was collected and extracted with methanol for 24 h in a Soxhlet extractor. The results from the elemental analyses are as follows. Polymer **1A**: Anal. Calcd for $C_{88}H_{116}N_4ZnO_2$: C, 79.63; H, 8.80; N, 4.22. Found: C, 78.36; H, 8.89; N, 4.15. Polymer **1B**: Anal. Calcd for $C_{88}H_{116}N_4CuO_2$: C, 79.74; H, 8.82; N, 4.23. Found: C, 78.36; H, 8.91; N, 4.17. Polymer **1C**: Anal. Calcd for $C_{88}H_{116}N_4NiO_2$: C, 80.04; H, 8.85; N, 4.24. Found: C, 78.69; H, 8.88; N, 4.23.

Table 1. GPC Results for Polymers 1A–C (Polystyrene Standards)

sample	reactn time (h)	yield[a] (%)	M_w	M_n
polymer 1A				
fraction 1	3	73	4.6×10^4	3.0×10^4
fraction 2	3	73	5.3×10^3	4.5×10^3
polymer 1B	4	75	8.3×10^3	4.2×10^3
polymer 1C	4	78	1.3×10^4	6.6×10^3

[a] Yields after purification; the crude yields were almost quantitative.

Scheme 1. Syntheses of Monomers and Polymers



Photoconductivity Measurements. The photocells were prepared by casting a polymer film on an ITO glass followed by evaporating Au electrodes to the film. An Ar^+ laser was used as the light source. The photocurrent was determined by measuring the voltage across a resistor with a lock-in amplifier in conjunction with a mechanical chopper. The intensity of the laser light incident on the sample was 143 mW/cm^2. The positive voltage was applied to the illuminated ITO or Au electrode.

Results and Discussion. A variety of porphyrins with different substituents are known and can be synthesized through well-developed synthetic approaches.[8] We utilized the approach developed by Li et al. and Osuka et al. to synthesize the divinylporphyrin monomer necessary for the Heck reaction (Scheme 1).[9] All of the monomers have been characterized by microanalysis, ^{1}H and ^{13}C NMR, and UV–visible absorption spectra. The results were in excellent agreement with the proposed structures.

The polymerizations were carried out smoothly under the conditions that we previously described.[6d] Due to the mild reaction conditions, the Heck reaction enabled us to incorporate the metalated porphyrin into the polymer chain without affecting the metal chelation. Polymers with reasonable molecular weights were obtained as indicated by GPC studies (THF as eluent and polystyrenes as standards (see Table 1)). The structures of these polymers were confirmed by elemental analysis, FTIR, and ^{1}H NMR.

The ^{1}H NMR spectrum of polymer **1A** (in $CDCl_3$) was dominated by the chemical shifts of the side alkyl chains at the region between 0.80 and 2.55 ppm. The meso proton of the porphyrin appeared at 10.10 ppm and the $-OCH_2-$ protons at 4.19 ppm. The aromatic protons were well separated. The proton from the dialkoxyphenyl ring appeared at 7.34 ppm, while the aromatic protons at the phenyl ring linked directly to the porphyrin unit were found at 7.92 and 8.10 ppm. The vinyl protons were not

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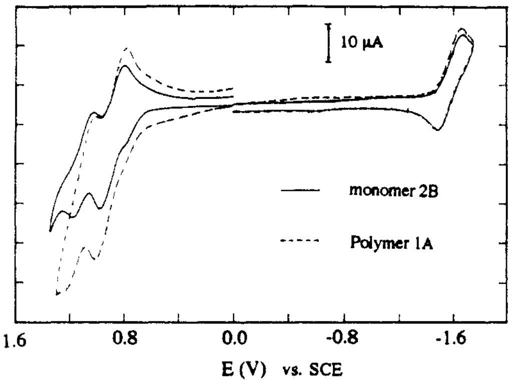

Figure 1. Cyclic voltammetric results for monomer **2B** and polymer **1A**.

equivalent and appeared at 7.73 and 7.82 ppm. The chemical shift of the vinylbenzene end group was visible in the spectrum as a result of the oligomeric fraction. Polymer **1C** gave similar ^{1}H NMR spectral features. The paramagnetic property of Cu(II) severely broadened the spectrum of polymer **1B**. However, a similar spectrum as polymer **1A**, except an additional chemical shift at −2.35 ppm due to the NH proton, was obtained by treating the chloroform solution of **1B** with concentrated hydrochloric acid followed by neutralizing with $NaHCO_3$.

FTIR spectra of all of the polymers showed typical absorptions of the ether linkage at 1208 cm^{-1} after polymerization due to the introduction of the dialkoxybenzene units. The appearance of the absorption at 965 cm^{-1} due to the out-of-plane mode of the =CH of the double bond indicated that their conformations were in a trans form.

All of the polymers were soluble in common organic solvents, such as THF, chloroform, and chlorobenzene. Uniform, optical-quality films were obtained by either casting or spin-coating on glass slides. The TGA studies indicated that the polymers were stable up to 400 °C under a nitrogen atmosphere. There was no melting or glass transition observed in the DSC thermograms between room temperature and 400 °C.

The UV–vis spectra of the polymers were similar with their corresponding metalloporphyrin monomers. A strong Soret band at 408 nm and Q bands between 500 and 600 nm could be clearly identified. The emission spectrum of polymer **1A** also resembled its corresponding zinc porphyrin monomer. For the THF solution of polymer **1A**, the excitation at the Q(1,0) band (550 nm) resulted in an emission spectrum at 585 and 640 nm. These results indicated that the metalloporphyrin moieties in the polymer backbone were kept intact throughout the polymerization and the electron delocalization was limited. No fluorescence was observed for either monomers or polymers with the copper and nickel porphyrin moieties.

The redox properties of these polymers were studied by cyclic voltametry (CV) in THF or chloroform solution (see Figure 1). The results showed that polymerization did not significantly affect the redox properties of the porphyrin moieties compared to their corresponding monomers. For example, two reversible oxidation processes and a reversible reduction process for polymer **1A** were observed at +1.01, +1.22, and −1.66 V, respectively, in THF solution vs SCE reference electrode. The corresponding monomer **2A** showed similar behavior at +0.98, +1.18, and −1.66 V. This result was expected due to the limited conjugation in these systems.

The photoconducting property of these polymers was studied by using an Ar^+ laser as the light source. It was noted that the photocurrent (I_{ph}) increased steadily under a low electric field and increased dramatically at a high electric field (Figure 2). The dark current was small, in the range of 10^{-9} A measured by a Keithley 617 electrometer. A relatively high quantum yield for a photocharge generation was observed, for example, a quantum yield of 2.3% for polymer **1B** at 514 nm with a film thickness of 1.65 μm under an electric field of 620 kV/cm, indicating a promising feature for the design of photorefractive polymers.

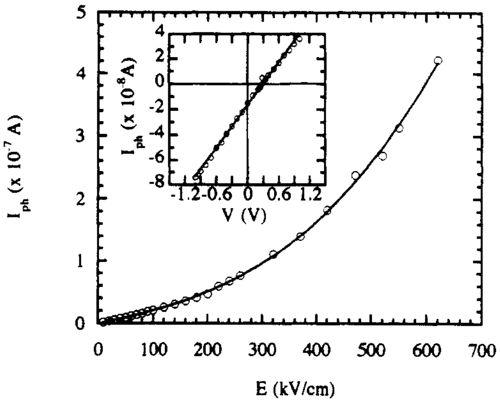

Figure 2. Photocurrent of polymer **1C** as a function of the external electric field. The inset shows the photovoltage effect.

Interestingly, all of the photocells exhibited photovoltage regardless of the type of electrode used, e.g., ITO/polymer/Au or Au/polymer/Au. The illuminated electrode always charged negatively. The dependence of the photocurrent on the applied voltage (Figure 2 inset) showed a displacement from the origin by $V_o = V_{oc}$ (open-circuit voltage). When the ITO/polymer/Au cells of polymers **1A–C** were illuminated with 514.5-nm light, V_{oc} values were obtained to be −0.17, −0.20, and −0.27 V, respectively. Under the same conditions for a Au/polymer/Au cell, V_{oc} was found to be −0.14 V for polymer **1A**. Although the photovoltage was relatively small, the phenomena were encouraging, and further improvements are possible because the synthetic approach is versatile.

In summary, we have demonstrated that the Heck reaction can be utilized to synthesize metalloporphyrin polymers. Although there were efforts to synthesize conjugated porphyrin main-chain polymers that could act as molecular wires,[10] our approach provides flexibility in synthesizing different porphyrin polymers. The reaction conditions were mild, permitting us to incorporate different functional groups. Therefore, the electronic, optical, and magnetic properties of these polymers can be tuned by changing different substituents and by incorporating various metal ions into the porphyrin units. Metal-free porphyrin polymer can also be obtained easily by treating the metalloporphyrin polymers with acids. Moreover, observations of the photovoltaic effect and large photoconductivity assured further studies in the solar cell devices. These observations also provided the basis for the design and synthesis of new photorefractive polymers.[11]

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Supplementary Material Available: Analytical and spectral data for porphyrins **2A–D** (2 pages). Ordering information is given on any current masthead page.

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