J. Am. Chem. Soc. **1996,** *118,* 3777−3778 3777

Synthesis of Conjugated Polymers Containing Ionic Transition Metal Complexes

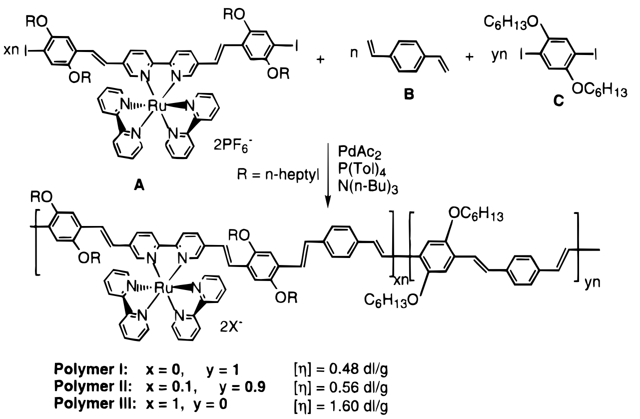
Zhonghua Peng and Luping Yu*

Department of Chemistry and James Frank Institute
The University of Chicago, 5735 S. Ellis Avenue
Chicago, Illinois 60637

Received September 21, 1995

One of our research projects concerns the syntheses and characterizations of new photorefractive (PR) polymers, which are materials that possess both photoconductivity and the electrooptic effect.[1,2] A problem for organic photorefractive materials is their low quantum yield of the photogeneration of charge carriers, which results in a low photorefractive performance, such as low diffraction efficiency.[3] In the process of photogeneration of charge carriers, it is known that there are many pathways by which an excited state can decay before it has the chance to dissociate into a free charge carrier.[4] A solution to this problem is to synthesize materials containing species which can undergo very efficient charge separation processes. Tris(bipyridyl) ruthenium complexes are such species which are known to exhibit interesting electron transfer properties through a metal-to-ligand charge transfer (MLCT) process.[5] They have been extensively studied as light-harvesting materials, materials which can reduce water into hydrogen when coupled with other components.[6] To utilize their interesting charge transfer properties to prepare photorefractive polymers, we designed a new monomer containing the Ru species with diiodo functional groups. It can be polymerized with divinyl monomers via the Heck reaction to generate conjugated polymers.[7] Here, we further implemented the idea by introducing the conjugated system. We expect that the conjugated backbone will act as the electron migration channel after the electron is excited from the Ru center. It is well-known that oxidation or reduction (doping) of conjugated polymer backbones results in a highly conducting state of the polymers (due to formation of so-called polaron or bipolaron species).[8] Photoinduced electron injection from the ruthenium complex to the conjugated backbone is equivalent to n-doping to the conjugated backbone, which will enhance the conductivity of the polymers. Thus, the charge separation efficiency can be further improved. In this paper, we report the preliminary studies on the syntheses and characterizations of the monomer and conjugated polymers without electrooptic components. We think it is interesting that the Heck reaction can be applied to prepare polymers containing ionic transition metal complexes. More interestingly, the resultant conjugated polymers exhibit enhanced photoconductivities and quantum yields of photogeneration of the charge carriers, which is consistent with our design ideas. Further works on the syntheses and characterizations of novel photorefractive polymers based on this system will be reported separately.[9]

Scheme 1. Synthesis of Conjugated Polymers Containing Ionic Ruthenium Complexes



To synthesize the polymers, a new ruthenium complex (compound **A**) was designed and synthesized. There are two approaches which can be applied to synthesize the target polymers: (1) to synthesize polymers bearing the bipyridyl type ligand first and then use them to chelate with transition metal complexes or (2) to synthesize monomers containing ionic transition metal complexes and then polymerize them with other related monomers. Both approaches should work if a proper polymerization method is chosen. However, the first approach lacks certainty as to the amount of transition metal ion chelation due to statitical reasons. The second approach needs a polymerization method which can tolerate the ionic species. We found that the second approach works very well if the Heck coupling reaction is applied in the polymerization. Scheme 1 shows the polymerization conditions.

Our initial polymerization attempt utilized the diiodo-functionalized ligand as the monomer. The polymerization did not proceed, presumably due to the chelation of the Pd catalyst used in the Heck reaction with the bipyridinyl unit. When compound **A** was used as the monomer, the polymerization proceeded smoothly. Soluble polymers (soluble in tetrachloroethane, DMF, NMP) were obtained in excellent yields and reasonable molecular weights (see Scheme 1).[10] The viscosity of polymer **III** is especially high, and long fibers can be prepared from the concentrated NMP solution of this polymer. Apparently, the Ru^{2+} species blocked the chelating site in the monomers so that the palladium catalyst was not deactivated. To our knowledge, this is the first time that the Heck reaction was successfully applied for the synthesis of conjugated polymers containing ionic transition metal complex species.

All of the spectroscopic studies support the proposed polymer structures. ^{1}H NMR spectra of polymers **II** and **III** showed chemical shifts at 8.4 and 7.9 ppm which are due to protons from the two bipyridyl ligands. In comparison to the NMR spectrum of compound **A**, the chemical shifts at 8.1 and 8.3 ppm can be assigned to the bipyridyl protons in the conjugated backbone. All of the other chemical shifts are consistent with the chemical shifts of dialkoxy-substituted PPV (polymer **I**).[7d]

UV−vis spectra show some interesting features of these polymers (Figure 1). Compared to the spectrum of compound **A**, the ligand-centered transition due to the bipyridine still exists at around 285 nm in both polymers **II** and **III**.[5] The metal-

---

(1) Chan, W. K.; Chen, Y. M.; Peng, Z. H.; Yu, L. P. *J. Am. Chem. Soc.* **1993**, *115*, 11735.

(2) Peng, Z. H.; Bao, Z. N.; Yu, L. P. *J. Am. Chem. Soc.* **1994**, *116*, 6003.

(3) Moerner, W. E.; Silence, S. M. *Chem. Rev.* **1994**, *94*, 127.

(4) Mort, J., Pfister, G., Eds. *Electronic Properties of Polymers*; John Wiley & Sons: New York, 1982.

(5) (a) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991. (b) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

(6) Bruuger, Pierre-Alain; Gratzel, M. *J. Am. Chem. Soc.* **1980**, *102*, 2461.

(7) (a) Heitz, W.; Brugging, W.; Freund, L.; Gailberger, M.; Greiner, A.; Jung, H.; Kampschulte, U.; Niebner, N.; Osan, F. *Makromol. Chem.* **1991**, *192*, 967. (b) Suzuki, M.; Lim, J. C.; Saegusa, T. *Macromolecules* **1990**, *23*, 1574. (c) Weitzel, H. P.; Mullen, K. *Macromol. Chem.* **1990**, *191*, 2837. (d) Bao, Z. N.; Chen, Y. M.; Cai, R. B.; Yu, L. P. *Macromolecules* **1993**, *26*, 5281.

(8) Bredas, J. L., Silbey, R., Eds. *Conjugated Polymers*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.

(9) Peng, Z. H.; Gharavi, A.; Yu, L. P. To be submitted for publication in *Appl. Phys. Lett.*

(10) Intrinsic viscosities (NMP, 30 °C) were reported since there is no standard sample for GPC calibration and polymer **III** is not soluble in THF, which is the eluent we used.

0002-7863/96/1518-3777$12.00/0

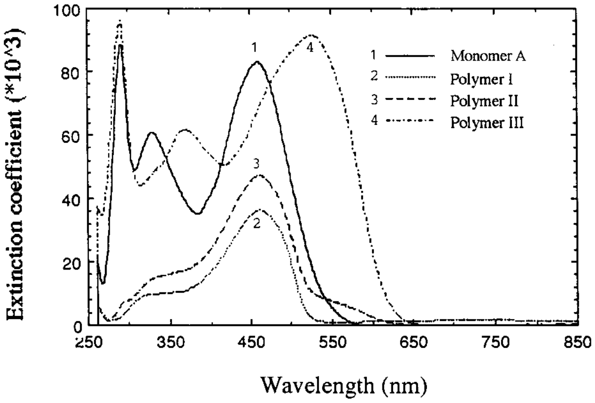


Figure 1. UV−vis spectra of polymers **I**−**III** and compound **A** in THF.

centered transition, however, shifts toward longer wavelengths (from 326 to 370 nm). The metal-to-ligand transition also shifts to longer wavelengths where it overlaps with the $\pi-\pi^*$ transition of the conjugated backbone. Compared to the transitions of the polymer without Ru complexes (polymer **I**), we can tentatively assign that the $\pi-\pi^*$ transition occurs at 470 nm and the MLCT transition at about 550 nm, which is a large red-shift from that of the simple tris(bipyridine) ruthenium complex.[5] This is presumably caused by the more extended π-electronic orbital in the conjugated systems. These results reveal two points: (1) the Ru complex is indeed incorporated into the polymer backbone, and (2) the MLCT transition energy was lowered. The second point is especially relevant to our design idea for its utilization in the synthesis of photorefractive polymers which require photosensitivity for charge separation at longer wavelengths. Another message from these spectra is that the absorption strength of the polymers at longer wavelengths can be adjusted by controlling the ratio of the monomers, as clearly shown by the comparison of the spectra of polymers **II** and **III**. This is a useful feature for the control of the polymer's optical properties.

FTIR spectra provide further evidence of the incorporation of the ruthenium complex into the polymers. It is known that high-frequency vibrations in an IR spectrum of a metal complex (4000−650 cm^{-1}) are sensitive to the nature of the ligands, while low-frequency vibrations (650−50 cm^{-1}) are sensitive to metal ions.[11] Though direct evidence of the metal complex incorporation comes from low-frequency vibration spectra, normal FTIR spectra provide information about ligands. Compared to polymer **I**, both polymers **II** and **III** show typical absorption bands of pyridine moieties at 1590−1630 cm^{-1} (triple absorption bands) and at 760 cm^{-1}. Their peak intensities are well correlated to the ruthenium complex composition, while polymer **I** does not have these absorption features.

The fluorescence emission spectra are interesting but less conclusive due to the instrumental limitation. All of the polymers and the Ru-complex monomer exhibit triple emission peaks at 525, 554, and 600 nm, features typical for poly(phenylenevinylene).[7d] In addition, compound **A** shows an emission transition at around 720 nm which can be ascribed to the ^{3}MLCT state emission.[5] This emission process was not observed within the range 650−900 nm for those polymers containing Ru complexes. There are two possible reasons for this observation: (1) the emission occurred at wavelengths longer than 900 nm, or (2) the emission process was quenched after the Ru complex was incorporated into the polymer backbone. At this stage, we cannot rule out either of these factors.

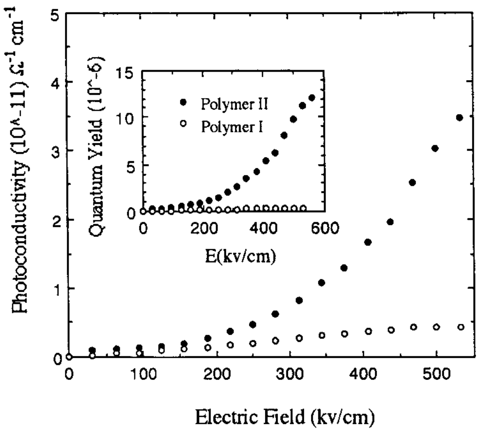


Figure 2. Photoconductivity and quantum yield (inset) of polymers **I** and **II** as a function of the electric field.

As expected, these polymers are photoconductive, demonstrated by a diode laser at a wavelength of 690 nm, which is of interest to our photorefractive polymer studies. It was found that polymer **II** exhibits much higher photoconductivity than does polymer **I**, which proves our design idea that the incorporation of ruthenium complexes into a conjugated backbone will enhance the photosensitivity of the resulting polymers at longer wavelengths and enhance the photoinduced charge separation process (Figure 2). Polymer **III** is also photoconductive, but it posseses a high dark electric conductivity due to its ionic nature, which makes it difficult to measure the photoconductivity at reasonably high external electric fields.

In conclusion, we successfully synthesized conjugated polymers containing ruthenium complexes by utilizing the Heck coupling reaction. These polymers show interesting electro and optical properties which become valuable in our further photorefractive polymer syntheses. As our initial goal, photorefractive polymers based on this Ru-complex system have been synthesized. Photorefractive properties superior to those of our previous PR polymers have been observed. The results will be published in our forthcoming paper.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research and by the National Science Foundation. Support of this work by the NSF Young Investigator Award and the Arnold and Mabel Foundation through the Beckman Young Invesigator Award is gratefully acknowledged.

Supporting Information Available: Details of the synthesis and characterization of monomer **A** and polymers **I**−**III**; ^{1}H NMR and IR spectra of the polymers; TGA traces, cyclic voltammograms, and fluorescence emission spectra of the polymers and monomer **A** (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA953231S

---

[11] Nakamoto, Kazuo; Mccarthy, Paul J. *Spectroscopy and Structure of Metal Chelate Compounds*; John Wiley & Sons: New York, 1968.