5962 *Inorg. Chem.* **1996,** *35,* 5962−5963

Electropolymerization of Macromers Containing Ruthenium(II) Polypridyl Complexes

Robert M. Leasure, Toru Kajita,[†] and Thomas J. Meyer*

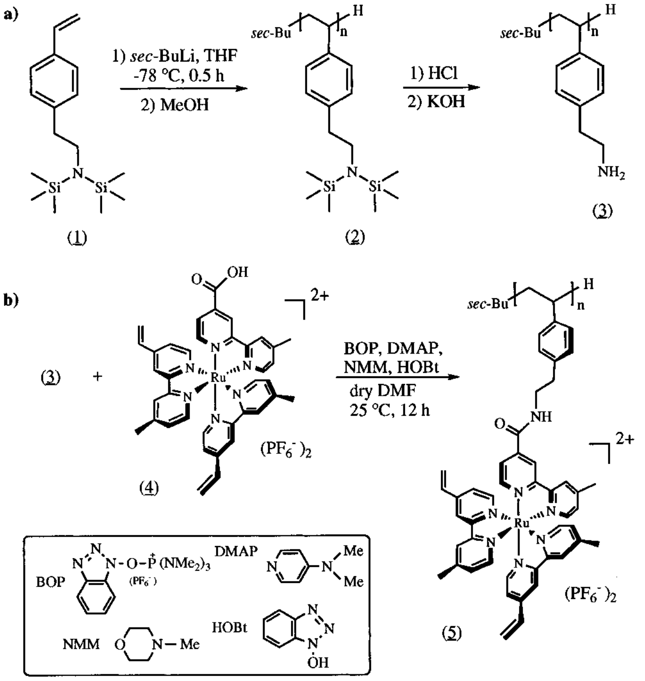
Kenan Laboratories of Chemistry, The University of North Carolina at Chapel Hill, CB No. 3290,
Chapel Hill, North Carolina 27599-3290

Received September 26, 1995

There are well-established techniques for the preparation of redox-active metallopolymeric films on a variety of electrodes.[1] One approach utilizes electropolymerization based on vinyl or pyrrole groups. For example, electrochemical reduction of [Ru(vbpy)$_3$]$^{2+}$ (vbpy is 4-vinyl-4′-methyl-2,2′-bipyridine) leads to stable, electroactive films formed by network polymerization.[2] We are exploring additional dimensions in this chemistry both to develop new structural motifs and to incorporate more complex electro- and photoactive assemblies.[3] We report here that electropolymerization of preformed macromolecular monomers or "macromers"[4] leads to redox-active films with highly open structures.

The parent polymer, poly[4-(2-aminoethyl)styrene] (**3**), was prepared by modification of the living anionic polymerization procedures developed by Nakahama and co-workers.[5] Polymerization of 4-{2-[bis(trimethylsilyl)amino]ethyl}styrene (**1**) was initiated by addition of *sec*-butyllithium and terminated by addition of methanol, Scheme 1a. The average number of repeat units for the trimethylsilyl-protected polymer (**2**) was determined by gel permeation chromatography to be $n \approx 18$ with a molecular weight distribution of $\bar{M}_w/\bar{M}_n = 1.10$.[6] Deprotection was achieved by cleaving the N−Si bonds under mild acidic conditions, followed by treatment with base. Pendant polypyridyl complexes of Ru^{II} containing terminal carboxylic acid groups were loaded onto **3** by amide coupling and use of stoichiometric amounts of common peptide-coupling reagents in dry *N*,*N*-dimethylformamide at room temperature, Scheme 1b.[7] The loading level could be controlled by adjusting the mole ratio of the carboxylic acid derivative and amine groups. Unreacted amines were converted into acetyl amides by reaction of the partially loaded polymers with acetic anhydride. Fully loaded macromolecular assemblies (**5**) were prepared by using an excess of the Ru^{II} complex (**4**). The degree of loading was determined by comparing the integrated resonances for the aromatic (6.2−8.9 ppm), vinyl (5.15 and 6.05 ppm), and side chain ethylene (3.0−3.4 ppm) groups in the ^{1}H NMR spectra vs CD$_3$CN.

Scheme 1



Molecular modeling of the fully loaded, atactic polymer [PS-CH$_2$CH$_2$NHCO-(Ru^{II}$_{18}$)]$^{36+}$ (**5**) was conducted by using CAChe Scientific molecular modeling software and modified MM2 parameters with each pendant Ru^{II} complex treated as a sphere of diameter 14 Å and net 2+ charge.[8] The molecular volume and charge on the complex restrict large-amplitude displacements and constrain the macromolecule to a nearly linear conformation (following diagram). In the lowest energy structures, the center-to-center distance between nearest neighbors is ~18 ± 3 Å with a contact distance of ~4 Å between the peripheries of the complexes.

Electropolymerization of [PS-CH$_2$CH$_2$NHCO-(Ru^{II}$_{18}$)]$^{36+}$ was conducted in acetonitrile solutions ca. 27 μM in the macromer (0.5 mM in Ru^{II} sites) and 0.1 M in tetra-*n*-butylammonium hexafluorophosphate (TBAH) by repeatedly cycling the potential of the electrode past the ligand-based reductions at −1.40, −1.53, and −1.68 V vs SSCE. On platinum, film surface

---

* To whom correspondence should be addressed.

[†] Current address: Japan Synthetic Rubber Co., Ltd. 100 Kawajiri-cho, Yokkaichi Mie 510 Japan

(1) (a) Abruña, H. D. *Coord. Chem. Rev.* **1988**, *86*, 135−189. (b) Merz, A. In *Topics in Current Chemistry—Electrochemistry IV*; Steckhan, Ed.; Springer-Verlag: Berlin, 1990; Vol. 152, pp 49−90. (c) *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; John Wiley & Sons, Inc.: New York, 1992; Vol. XXII.

(2) (a) Denisevich, P.; Abruña, H. D.; Leidner, C. R.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1982**, *21*, 2153. (b) Ikeda, T.; Schmehl, R.; Denisevich, P.; Willman, K.; Murray, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 2683. (c) Ewing, A. G.; Feldman, B. J.; Murray, R. W. *J. Phys. Chem.* **1985**, *89*, 1263.

(3) (a) Gould, S.; O'Toole, T. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 26. (b) Gould, S.; Gray, K. H.; Linton, R. W.; Meyer, T. J. *Inorg. Chem.* **1992**, *31*, 5521. (c) Leasure, R. M.; Moss, J. A.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 1247. (d) Bakir, M.; MacKay, S. G.; Linton, R. W.; Sullivan, P.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 3945. (e) Gould, S.; Gray, K. H.; Linton, R. W.; Meyer, T. J. *J. Phys. Chem*, **1995**, *99*, 16052−16058.

(4) *Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed.; John Wiley & Sons: New York, 1987; Vol. 9.

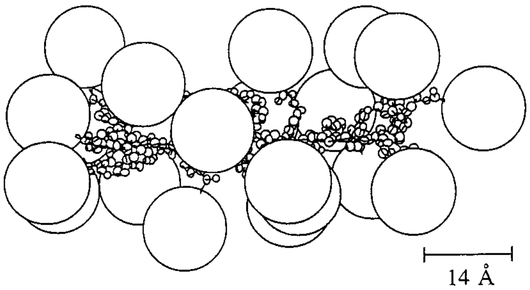
(5) Suzuki, K.; Hirao, A.; Nakahama, S. *Makromol. Chem.* **1989**, *190*, 2893.

(6) Gel permeation chromatography (GPC) was performed on a Waters 150-CV GPC with Ultrastyragel (cross-linked polystyrene) columns of 100, 500, 103, 104, and 105 Å porosities, tetrahydrofuran as the eluent, and polystyrene standards (Showa Denko).

(7) (a) Peptide-coupling reagents were (1-benzotriazolyloxy)tris(dimethylamino)phosphonium hexfluorophosphate (BOP), 1-hydroxybenzotriazole (HOBt), 4-(dimethylamino)pyridine (DMAP), and *N*-methylmorpholine (NMM). (b) Peek, B. M.; Ross, G. T.; Edwards, S.-W.; Meyer, G. J.; Meyer, T. J.; Erickson, B. W. *Int. J. Peptide Protein Res.* **1991**, *38*, 194. (c) McCafferty, D. G.; Bishop, B. M.; Wall, C. G.; Hughes, S. G.; Mecklenberg, S. L.; Meyer, T. J.; Erickson, B. W. *Tetrahedron* **1995**, *51*, 1093.

(8) *CAChe Scientific*, ver. 3.7; CAChe Scientific, Inc.: Beaverton, OR, 1992. Also see: Jones, W. E., Jr.; Baxter, S. M.; Strouse, G. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 7363.

S0020-1669(95)01246-8 CCC: $12.00



$[PS\text{-}CH_2CH_2NHCO\text{-}(Ru^{II})_{18}]^{36+}$

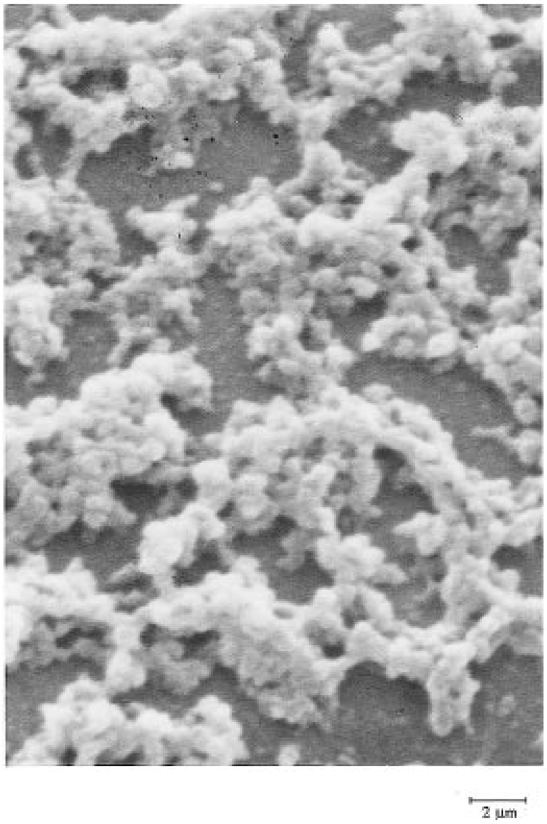


Figure 1. SEM image of an electropolymerized film of the macromer $[PS\text{-}CH_2CH_2NHCO\text{-}(Ru^{II}{}_{18})](PF_6)_{36}$ ($\Gamma \approx 5 \times 10^{-9}$ mol/cm^2) on a Au/Cr/SiO$_2$ electrode.

coverages (Γ in mol/cm^2 of the Ru^{II} complex) were determined by integrating the charge under the cathodic wave of the reversible Ru$^{III/II}$ couple at +1.23 V recorded in fresh electrolyte solution. Unlike films of comparable surface coverages prepared from $[Ru(vbpy)_3](PF_6)_2$, the macromeric films appeared visibly rougher with significant surface topography. In Figure 1 is shown a scanning electron micrograph of an electropolymerized film of the macromer ($\Gamma = 5 \times 10^{-9}$ mol/cm^2) on a Au/Cr/SiO$_2$ electrode.[9] The film appears to be composed of small spheres on the order of ca. 0.5 μm in diameter. The nodular growth is indicative of rapid cross-linking of the macromers and formation of insoluble clusters of polymer. Similar nodular growth has been reported by Murray and co-workers on *thick* films ($\Gamma > 1 \times 10^{-8}$ mol/cm^2) of poly$[Os(bpy)_2(vpy)_2]^{2+}$ (bpy is 2,2′-bipyridine; vpy is 4-vinylpyridine).[10] For the macromers, dendritic film growth is accelerated due to the large number of polymerizable sites ($2n = 36$) and the fact that the macromers are themselves "oligomers". Atomic force microscopic measurements indicate that the surfaces of the macromeric films are approximately 10 times rougher than films of comparable surface coverages prepared from monomeric analogs.[11]

Diffusion coefficients for charge transport, D_{ct}, were measured by potential-step chronoamperometry.[12] Current−time responses for potential steps between 1.13 and 1.33 V gave linear, short-time ($t = 4{-}10$ ms) Cottrell plots with linear regions extending over ~60% of the total charge passed. Assuming a redox site concentration of $C = 1.3$ M,[11b] $D_{ct} = 5.0 \times 10^{-10}$ cm^2/s, which is comparable to diffusion coefficients measured for poly$[Ru(vbpy)_3]^{2+}$.[2a] These measurements demonstrate that electron-transfer hopping within these porous films is facile.

The films retain the characteristic metal-to-ligand charge-transfer (MLCT) emission properties of the constituent monomers, but modified by the film environment. Emission in CH$_3$CN occurs at 680 nm compared to 620 nm for $[Ru(bpy)_3]^{2+}$.

There is an element of synthetic flexibility in forming the macromeric films. Mixed-metal polymers can be prepared by using sequential amide-coupling reactions to vary both composition and extent of cross-linking. To demonstrate this, a macromer was prepared containing ca. 10% $[Ru(vbpy)_2(bpy\text{-}CONH\text{-})]^{2+}$ and 90% $[Ru(bpy)_2(bpy\text{-}CONH\text{-})]^{2+}$ (bpy-CONH- is 4-CH$_3$-4′-(CONH-)bpy attached to the backbone by the amide link. Electropolymerization of the mixed macromer was far slower ($\approx ^1/_{25}$) than electropolymerization of the purely vinyl macromer, a consequence of the fewer number of polymerizable sites.

The results with the mixed polymer are important in demonstrating a means for controlling film composition in a local microenvironment of high porosity. We look forward to application of these structures in electrocatalysis and photochemistry.

Acknowledgment. We gratefully acknowledge the Japan Synthetic Rubber Co., Ltd., and the U.S. Army Research Office under Grants DAAL03-90-G-0062 and DAAL03-92-G-D166 for financial support of this work. The authors also thank Michael O. Hunt for GPC measurements, Wallace A. Ambrose for SEM measurements, Wei Ou for AFM measurements, and Prof. Joseph M. DeSimone for insightful discussions about the polymer synthesis.

IC951246L

---

(9) Electrodes of Au/Cr/SiO$_2$ were prepared by vapor deposition of a gold layer (~2000 Å) over an adhesive layer of chromium (~200 Å) on glass by using locally built equipment which applied resistive electrical heating at reduced pressure (2×10^{-5} Torr). Scanning electron microscopy was performed by using an Etec Autoscan SEM operating at an accelerating voltage of 20 kV. Prior to analysis, the samples were coated with 200−300 Å of a gold/palladium alloy in a Polaron 5100 plasma sputter coater.

(10) McCarley, R. L.; Thomas, R. E.; Irene, E. A.; Murray, R. W. *J. Electrochem. Soc.* **1990**, *137*, 1485.

(11) (a) Atomic force microscope measurements were performed in the "tapping mode" with a Digital Instruments, Inc., Nanoscope III AFM operating at a resonant frequency of ~360 kHz. Surface roughnesses were calculated from the root-mean-square of the *z*-height values from each data point in the image. (b) Musselman, I. H.; Gray, K. H.; Leasure, R. M.; Meyer, T. J.; Linton, R. W. *Microbeam Anal.* **1993**, *2*, 297. (c) Ou, W. Unpublished results.

(12) Daum, P.; Lenhard, J. R.; Rolison, D.; Murray, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 4649−4653.