2756 *Inorg. Chem.* **1998,** *37,* 2756−2762

Preparation and Photophysical Properties of Amide-Linked, Polypyridylruthenium-Derivatized Polystyrene

Duane A. Friesen, Toru Kajita, Earl Danielson, and Thomas J. Meyer*

Department of Chemistry, The University of North Carolina at Chapel Hill, CB #3290 Venable and Kenan Laboratories, Chapel Hill, North Carolina 27599-3290

Received August 19, 1997

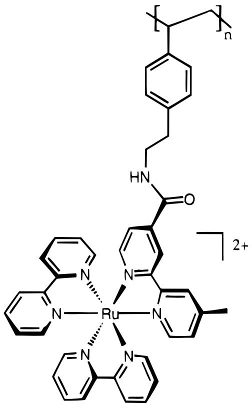
The polymer poly(4{2-[*N*,*N*-bis(trimethylsilyl)amino]ethyl}styrene), prepared by anionic polymerization and of low polydispersity ($M_w/M_n = 1.10-1.18$), has been derivatized by amide linkage to [Ru^{II}(bpy)$_2$(4-(CO−)-4′-CH$_3$-bpy)−]$^{2+}$ (bpy is 2,2′-bipyridine; 4-(CO−)-4′-CH$_3$-bpy is 4-carbonyl-4′-methyl-2,2′-bipyridine). Unreacted amine sites were converted into acetamides by treatment with acetic anhydride to give derivatized polymers of general formula [PS-CH$_2$CH$_2$NHCO(Ru$^{II}{}_n$Me$_m$)](PF$_6$)$_{2n}$, where $m + n = 11$, 18, or 25, PS represents the polystyrene backbone, and Ru^{II} and Me represent the attached complex and acetamide, respectively. Spectral and electrochemical properties of the derivatized polymers are similar to those of the model [Ru(bpy)$_2$(4-CONHCH$_2$-CH$_2$C$_6$H$_5$-4′-CH$_3$-bpy)]$^{2+}$ (4-CONHCH$_2$CH$_2$C$_6$H$_5$-4′-CH$_3$-bpy is 4′-methyl-2,2′-bipyridinyl-4-(2-phenylethylamide)), but emission quantum yields (ϕ_{em}) and time-resolved emission decays are slightly dependent on the level of Ru^{II} loading, with nonexponential, irradiation-dependent decays appearing at high loadings. The decays could be fitted satisfactorily to the first derivative of the Williams−Watts distribution function. These results are discussed with reference to possible structural and multichromophoric effects on excited-state decay.

Introduction

We and others have been interested in the utilization of soluble polymers derivatized by the addition of polypyridyl complexes for the study of photoinduced electron and energy transfer.[1−20] Our previous linkage strategies involved the formation of ether or amide links in 1:1 styrene−4-substituted styrene copolymers. In these studies the polymers were prepared by free radical initiation, which gives samples of high polydispersity. We describe here the preparation and derivatization of a series of polystyrene homopolymers prepared by living anionic polymerization.[21−26] This procedure greatly decreases polydispersity, increasing control over the distribution of chain lengths.

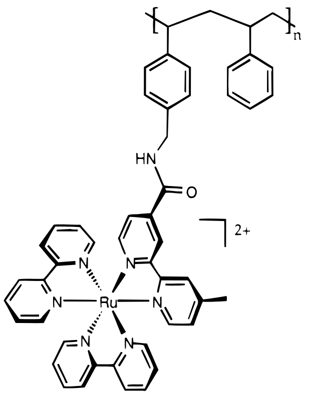
We also report the photophysical properties of the polymers partly or fully derivatized by amide coupling to a polypyridyl complex of Ru(II). The linkage structure is illustrated (**1**) and compared with an amide-derivatized copolymer reported earlier (**2**).[1] Important issues that we wished to address in this work included the role of the linkage chemistry and degree of loading on excited-state properties in these multichromophoric arrays.

1



[PS-CH$_2$CH$_2$NHCO-(Ru$^{II}{}_n$)]$^{2n+}$

2



[*co*-PS-CH$_2$NHCO-(Ru$^{II}{}_n$)]$^{2n+}$

---

* To whom correspondence should be addressed.

(1) Dupray, L. M.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 6299.

(2) Leasure, R. M.; Kajita, T.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 5962.

(3) Jones, W. E., Jr.; Baxter, S. M.; Strouse, G. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 7363.

(4) Baxter, S. M.; Jones, W. E., Jr.; Danielson, E.; Worl, L.; Strouse, G.; Younathan, J.; Meyer, T. J. *Coord. Chem. Rev.* **1991**, *111*, 47.

(5) Younathan, J. N.; Jones, W. E., Jr.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 488.

(6) Worl, L. A.; Strouse, G. F.; Younathan, J. N.; Baxter, S. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7571.

(7) Strouse, G. F.; Worl, L. A.; Younathan, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 9101.

(8) Younathan, J. N.; McClanahan, S. F.; Meyer, T. J. *Macromolecules* **1989**, *22*, 1048.

(9) Olmsted, J., III; McClanahan, S. F.; Danielson, E.; Younathan, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 3297.

(10) Forster, R. J.; Vos, J. G. *Macromolecules* **1990**, *23*, 4372.

(11) Kaneko, M.; Yamada, A.; Tsuchida, E.; Kurimura, Y. *J. Phys. Chem.* **1984**, *88*, 1061.

(12) Ennis, P. M.; Kelly, J. M. *J. Phys. Chem.* **1989**, *93*, 5735.

(13) Kaneko, M.; Nakamura, H. *Macromolecules* **1987**, *20*, 2265.

(14) Hou, X.-H.; Kaneko, M.; Yamada, A. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 2749.

(15) Sassoon, R. E.; Rabani, J. *J. Phys. Chem.* **1985**, *89*, 5500.

(16) Sumi, K.; Furue, M.; Nozakura, S.-I. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 3059.

(17) Kurimura, Y.; Shinozaki, M.; Ito, F.; Uratani, Y.; Shigehara, K.; Tsuchida, E.; Kaneko, M.; Yamada, A. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 380.

(18) Ennis, P. M.; Kelly, J. M.; O'Connell, C. M. *J. Chem. Soc., Dalton Trans.* **1986**, 2485.

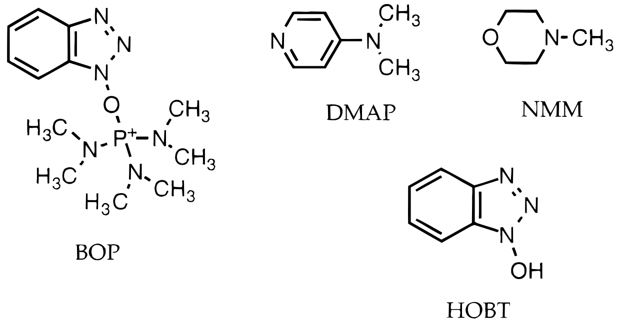
(19) Kelly, J. M.; Long, C.; O'Connell, C. M.; Vos, J. G.; Tinnemans, A. H. A. *Inorg. Chem.* **1983**, *22*, 2818.

(20) Nakahira, T.; Inoue, Y.; Iwasaki, K.; Tanigawa, H.; Kouda, Y.; Iwabuchi, S.; Kojima, K. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 13.

S0020-1669(97)01042-2 CCC: $15.00

Experimental Section

Reagents. *N,N*-Bis(trimethylsilyl)lithium amide (1.00 M in hexane), chloromethyl methyl ether, 4-(dimethylamino)pyridine (DMAP), 4-methylmorpholine (NMM), *sec*-butyllithium, and ammonium hexafluorophosphate were all used as received (Aldrich). Benzotriazol-1-yloxy tris(dimethylamino)phosphonium hexafluorophosphate (BOP) and 1-hydroxybenzotriazole hydrate (HOBT) were also used as received (Nova Biochem). Tetra(1-butyl)ammonium hexafluorophosphate (TBAH) was recrystallized twice from absolute ethanol, dried under vacuum (60 °C) for 2 days, and stored under nitrogen. 9-(Chloromethyl)anthracene was recrystallized twice from *n*-hexane. 4-(Chloromethyl)styrene (Eastman Chemical) was treated with basic alumina via column chromatography (dry diethyl ether eluent) in order to remove inhibitors. Styrene was similarly treated and then distilled from CaH$_2$ under reduced pressure. Cyclohexane was pretreated with concentrated H$_2$SO$_4$ for 1 week and distilled. Tetrahydrofuran and diethyl ether were distilled under an argon atmosphere from Na−benzophenone. Acetonitrile for photophysical and electrochemical measurements was SpectraGrade (Burdick & Jackson) and stored under nitrogen. 1,2-Dichloroethane (Fisher) was dried over CaH$_2$ and distilled under nitrogen. Dimethylformamide (DMF, Fisher) was dried with 4 Å molecular sieves. The concentration of the *sec*-butyllithium solution was determined by using the Gilman double-titration procedure.



Coupling Reagents

Syntheses. *N,N*-Bis(trimethylsilyl)methoxymethylamine. Chloromethyl methyl ether (20 mL, 0.263 mol) was added to an ice-cooled 1.0 M THF solution of lithium *N,N*-bis(trimethylsilyl)amide (250 mL, 0.25 mol) in an Ar-purged 500 mL round-bottomed flask over a 10 min period. The precipitation of LiCl was observed during this procedure. The mixture was stirred for 14 h at room temperature and the LiCl removed by filtration. The solvent was removed by distillation under an argon atmosphere at room pressure, and the pure *N,N*-bis(trimethylsilyl)methoxymethylamine was obtained by subsequent distillation at reduced pressure (bp 74 °C at 24 mmHg; yield: 86%). It was kept under argon and redistilled before further use. ^{1}H NMR (CDCl$_3$): δ 4.26 (s, 2H, CH$_2$), 3.15 (s, 3H, CH$_3$), 0.11 (s, 18H, SiMe$_3$).

4-{2-[*N,N*-Bis(trimethylsilyl)amino]ethyl}styrene (1). A 50 mL dry diethyl ether solution of 4-(chloromethyl)styrene (20 g, 0.131 mol) was added to a dry ether suspension of Mg powder (5.0 g, 0.206 mol) in an ice-cooled, Ar-purged, 250 mL three-necked round-bottomed flask equipped with rubber septa and a condenser. An exothermic reaction ensued, and the reaction mixture turned green due to the formation of 4-(vinylbenzyl)magnesium chloride. The reaction mixture was stirred with ice cooling for 30 min, heated at reflux for 1 h to complete the formation of the Grignard reagent, and recooled in an ice bath. Freshly distilled *N,N*-bis(trimethylsilyl)methoxymethylamine (28 g) was added over a period of 5 min, and the mixture was stirred for 14 h at room temperature. The unreacted magnesium powder and insoluble salts were removed by filtration with a medium-porosity frit. A viscous yellow oil was obtained by evaporation after an ether extraction and was washed with distilled water three times. Distillation under reduced pressure gave pure 4-{2-[*N,N*-bis(trimethylsilyl)amino]ethyl}styrene as a colorless liquid (16.0 g, yield: 42%, bp 142−144 °C at 4.0 mmHg). ^{1}H NMR (CDCl$_3$): δ 6.81−7.25 (m, 4H, aromatic), 6.57 (dd, 1H, CH=), 5.05 and 5.53 (2d, 2H, J = 10.5 and 17.8 Hz, CH$_2$=), 2.60−3.02 (m, 4H, −CH$_2$CH$_2$−), 0.01 (s, 18H, SiMe$_3$).

Poly(4-{2-[*N,N*-bis(trimethylsilyl)amino]ethyl}styrene) (Homopolymer) (2). Glassware used in the following procedure was cleaned with a mixture of HNO$_3$ and H$_2$SO$_4$, rinsed well with distilled water, and dried in an oven before use. Before the synthetic procedure, a septum-sealed round-bottomed flask was heated and purged with argon. Living polymerization in THF was carried out at −78 °C with *sec*-butyllithium as initiator. After termination with deoxygenated methanol, the polymers were recovered by precipitation with excess methanol containing a small portion of sodium bicarbonate. They were filtered, dissolved in THF, reprecipitated three times with methanol, and stored under vacuum in a desiccator.

Poly[4-(2-aminoethyl)styrene] (Deprotection of the Homopolymer) (3). Poly(4{2-[*N,N*-bis(trimethylsilyl)amino]ethyl}styrene) (1.0 g) was dissolved in THF (25 mL). HCl (1 mL) was added over a 5 min period, and the solution was stirred for 1 h at 25 °C. Filtration and evaporation yielded solid, colorless poly(4-[2-aminoethyl]styrene hydrochloride), which was rinsed with THF, subsequently dissolved in 25 mL of water, and added dropwise to 100 mL of a 1 M aqueous solution of Na$_2$CO$_3$. The resulting white precipitate of poly(4-[2-aminoethyl]styrene) was washed several times with water and diethyl ether and stored under vacuum in a desiccator.

Preparation of Polypyridylruthenium-Derivatized Polymers [PS-CH$_2$CH$_2$NHCO(Ru$^{\mathrm{II}}_{18}$)](PF$_6$)$_{36}$ (5). Dry DMF solutions of BOP (4.6 wt %), HOBT (3.2 wt %), NMM (5.1 wt %), and DMAP (3.3 wt %) were freshly prepared before the reaction. The following reagents were added to a 50 mL round-bottomed flask: dry DMF (5.7 g); deprotected polymer (**3**) (21.0 mg, 1.43 × 10^{-4} molar unit); bis(2,2′-bipyridine)-(4-carboxylic acid−4′-methyl-2,2′-bipyridine)ruthenium(II) bis-hexafluorophosphate (**4**) (200 mg, 2.18 × 10^{-4} mol); BOP solution (2.06 g, BOP 95.0 mg, 2.15 × 10^{-4} mol); HOBT solution (1.03 g, HOBT 33.0 mg, 2.15 × 10^{-4} mol); NMM solution (0.425 g, NMM 21.7 mg, 2.17 × 10^{-4} mol); and DMAP solution (0.797 g, DMAP 26.3 mg, 2.15 × 10^{-4} mol). The reaction mixture was stirred vigorously for 12 h. It was poured into 200 mL of dry diethyl ether to form an orange precipitate. This was collected, dissolved in 10 mL of acetonitrile, and reprecipitated with 100 mL of 10% aqueous NaHCO$_3$. The precipitate was collected on a fine-porosity glass frit, washed with water six times, and redissolved in 10 mL of CH$_3$CN. This procedure, starting with the ether precipitation, was repeated until no residual UV−vis absorption from the ruthenium bipyridyl complex was observed in the aqueous wash. At this point, the precipitate was washed with dry diethyl ether and dried in a vacuum desiccator. Ruthenium bis(2,2′-bipyridine)(poly(2-styrylethyl)-4-methyl-2,2′-bipyridinecarboxamide) (**5**) was obtained as an orange solid. IR spectroscopy (ν(C=O) = 1734 cm^{-1} for the acid and 1668 cm^{-1} for the amide) was used to monitor the amount of unreacted ruthenium complex. ^{1}H NMR (CD$_3$CN): δ 6.81−7.25 (m, aromatic). The degree of Ru(bpy) loading was determined by ^{1}H NMR as described in Results.

For partially loaded polymers, an excess of acetic anhydride was added and the solution heated at 60 °C for 2 h in order to cap unreacted amino groups after precipitation. The acetyl-capped polymers were recovered by precipitation from diethyl ether.

Measurements and Instrumentation. ^{1}H NMR spectra in CDCl$_3$, CD$_3$OD, or CD$_3$CN (Cambridge Isotopes) were acquired at 200 MHz with a Bruker AC200 NMR spectrometer. Cyclic voltammetry was carried out with a Princeton Applied Research model 273 potentiostat and Ag/AgNO$_3$ (CH$_3$CN) reference electrode. The potential of this reference was related to the sodium-saturated calomel electrode (SSCE) by comparing the open-circuit potential between the two references or by monitoring the half-wave potential of the Ru$^{\mathrm{III/II}}$ couple for [Ru(bpy)$_2$-

---

(21) Nakahama, S.; Hirao, A. *Prog. Polym. Sci.* **1990**, *15*, 299.

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

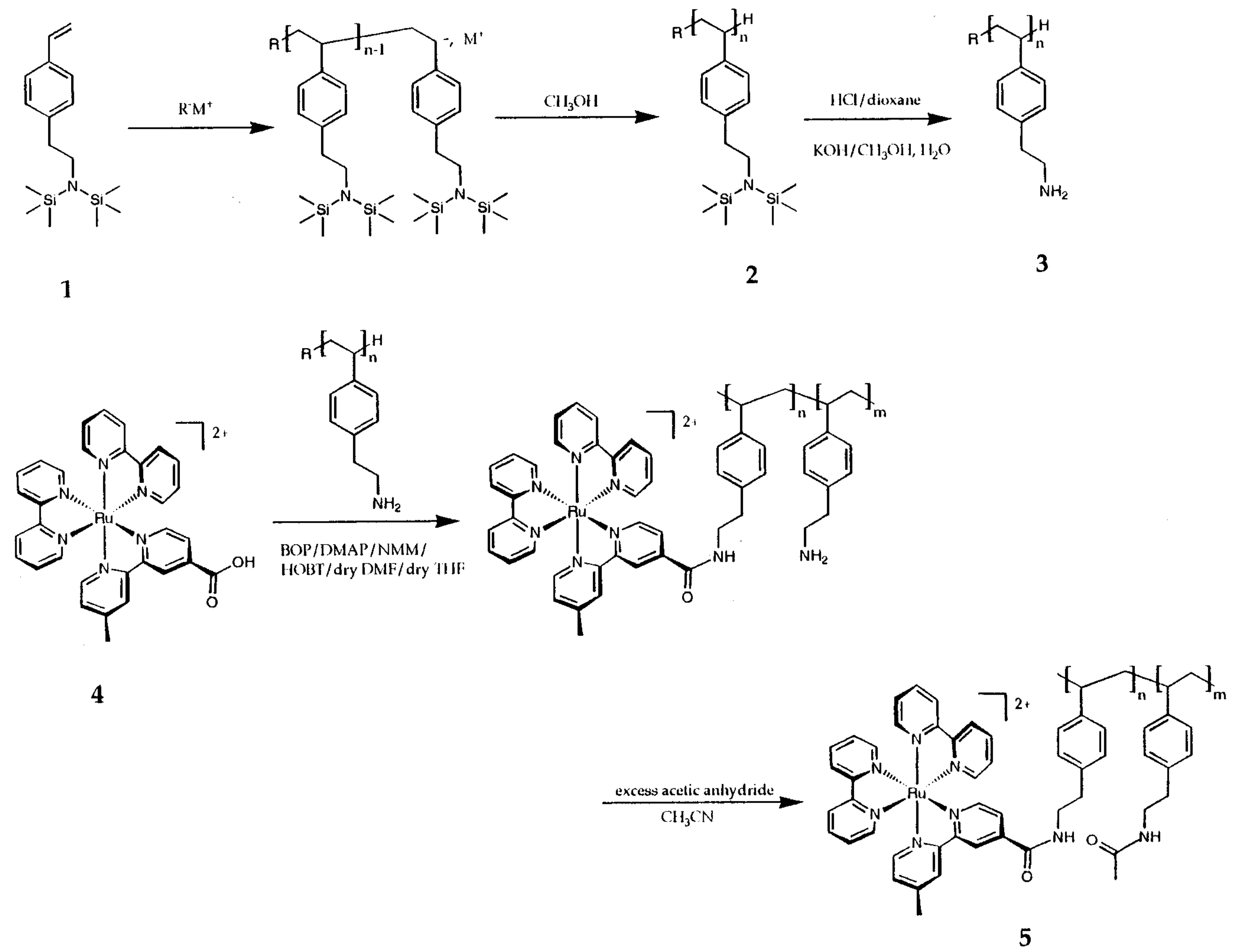
(23) Rempp, P.; Franta, E.; Herz, J. E. *Adv. Polym. Sci.* **1988**, *86*, 145.

(24) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1.

(25) Morton, M. *Anionic Polymerization: Principles and Practice*; Academic Press: New York, 1983.

(26) Szwarc, M. *Carbanions, Living Polymers and Electron-Transfer Processes*; Interscience: New York, 1968.

Scheme 1

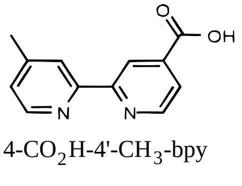


$Cl_2]\cdot 2H_2O$ (+0.34 V vs SSCE in CH_3CN). Infrared absorption spectra were obtained with a Mattson Instruments Inc. Galaxy Series 5000 FT-IR. UV−visible absorption spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer. Polymer molecular weights were determined in THF with a Waters 150-CV gel permeation chromatograph with Ultrastyragel columns of 100, 103, 104, 105, and 500 Å porosities. Polystyrene standards (Showa Denko) were used in the determination of molar mass distributions. Samples for emission and excitation experiments were prepared as optically dilute solutions in acetonitrile. These were deoxygenated by four freeze−pump−thaw cycles (10^{-5}−10^{-6} Torr) or by purging with argon for at least 40 min. Steady-state emission spectra were collected on a Spex Fluorolog F212-A spectrofluorometer equipped with a Hamamatsu R666-10 PMT and corrected for detector response. Emission quantum yields were measured relative to $[Ru(bpy)_3](PF_6)_2$ in CH_3CN ($\phi_{em} = 0.062$).[27,28] Emission lifetimes were determined by using a PRA LN 1000 N_2 laser−LN 102 dye laser combination (coumarin 460 dye, Exciton) for excitation. The emission was monitored at right angles with a Macpherson 272 monochromator and a Hamamatsu R3896 PMT. The signal was processed by a LeCroy 7200A transient digitizer interfaced to an IBM-PC for analysis. The resulting waveforms were fitted by using software of our own design based on the Marquardt algorithm.[29] Beam pulse energies were measured with a Molectron J3-09 power meter.

Results

Synthesis. We used a modification of procedures described by Nakahama and Hirao for the preparation of poly[4-(2-aminoethyl)styrene] (**3**), Scheme 1.[21,22] It involves living anionic polymerization of a vinyl monomer with a protected amine. The trimethylsilyl-protected (aminoethyl)styrene (**1**) was synthesized according to their method. *sec*-BuLi was the initiator. Each polymer prepared had a polydispersity in the range $M_w/M_n = 1.10-1.18$, which is a characteristic of the “living” polymerization procedure.[22] A typical GPC elution curve of **3** is shown in Figure 1. Chain length is controllable to a high degree by controlling the ratio of vinyl monomer to initiator. The average number of repeat units is defined as the ratio of the number average molecular weight (M_n) to the formula weight (fw) of **2**.[30] Subsequent references in this paper to “molecular weight” refer to M_n.

Samples of the amino polymer, characterized as described above, were subsequently derivatized by amide formation with $[Ru(bpy)_2(4\text{-}CO_2H\text{-}4'\text{-}CH_3\text{-}bpy)]^{2+}$ and protection of unreacted



$4\text{-}CO_2H\text{-}4'\text{-}CH_3\text{-}bpy$

---

[27] Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583.

[28] Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

[29] Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*, 2nd ed.; McGraw-Hill: New York, 1992; Chapter 8.

Table 1. Photophysical Properties of $[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_nMe_{m-n})](PF_6)_{2n}$ in CH_3CN at 25−28 °C[a]

salt	ϕ_{em}[b]	$10^2\alpha$[c]	$10^{-5}\,k\ (s^{-1})$[c]	β[c]	$\langle\tau\rangle$ (ns)[d]
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_2Me_9)](PF_6)_4$	0.11	2.6	7.41	0.98	1350
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_7Me_4)](PF_6)_{14}$	0.092	2.0	7.9	0.96	1290
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{11})](PF_6)_{22}$	0.099	1.3	8.3	0.94	1240
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_5Me_{13})](PF_6)_{10}$	0.088	2.6	7.9	0.99	1280
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{13}Me_5)](PF_6)_{26}$	0.053	1.8	8.4	0.97	1200
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{18})](PF_6)_{36}$	0.055	1.7	8.7	0.96	1170
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_8Me_{17})](PF_6)_{16}$	0.090	2.9	7.8	0.99	1280
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{21}Me_4)](PF_6)_{42}$	0.088	0.91	12	0.91	900
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{25})](PF_6)_{50}$	0.058	0.79	13	0.91	820
$[Ru(bpy)_2(4\text{-}CONHCH_2CH_2C_6H_5\text{-}4'\text{-}CH_3\text{-}bpy)](PF_6)_2$	0.11		7.1		1400[e]

[a] $\lambda_{max}(abs) = 458$ nm; $\lambda_{max}(em) = 645$ nm. [b] Emission quantum yield ± 10% relative to $[Ru(bpy)_3]^{2+}$ in CH_3CN (ref 27). [c] Kinetic parameters from emission decay fits to eq 5. [d] Average lifetimes calculated by numerical integration of the first moment of eq 5. [e] Decay is exponential.

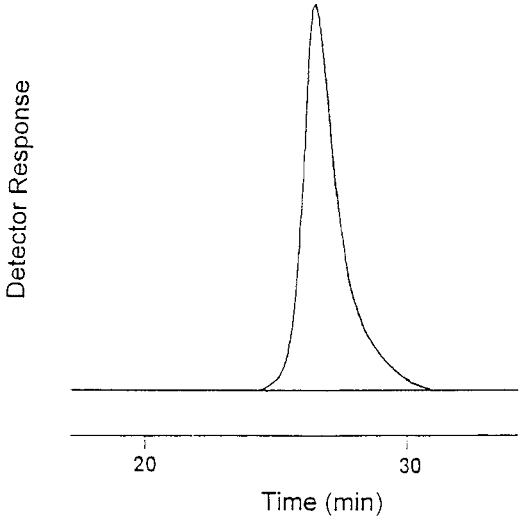


Figure 1. GPC elution curve of poly{4-2-[*N*,*N*-bis(trimethylsilyl)-aminoethyl]styrene} **(3)** in THF.

amines by reaction with acetic anhydride to give acetamides, Scheme 1. Amide coupling has been used in the construction of peptide molecular assemblies for electron transfer studies.[31−34] The abbreviation used for the pure Ru^{II}-derivatized homopolymer is $[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_n)](PF_6)_{2n}$ with n the average number of repeat units and for the mixed Ru^{II}−acetamide polymer $[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_nMe_{n-m})](PF_6)_{2n}$ with n the number of Ru^{II} sites. The loading level of the complex was controlled simply by controlling the reaction stoichiometry. It is assumed that the molecular weight characteristics of the starting amine polymer are retained in the derivatized polymer. The final content was determined by ^1H NMR integrations.[1] Representative spectra are shown in Figure 2. Complete loading of the complex was possible by using an excess of $[Ru(bpy)_2(4\text{-}CO_2H\text{-}4'\text{-}CH_3\text{-}bpy)]^{2+}$ (**4**). These are the first fully loaded homopolymers of styrene derivatives containing ruthenium complexes.

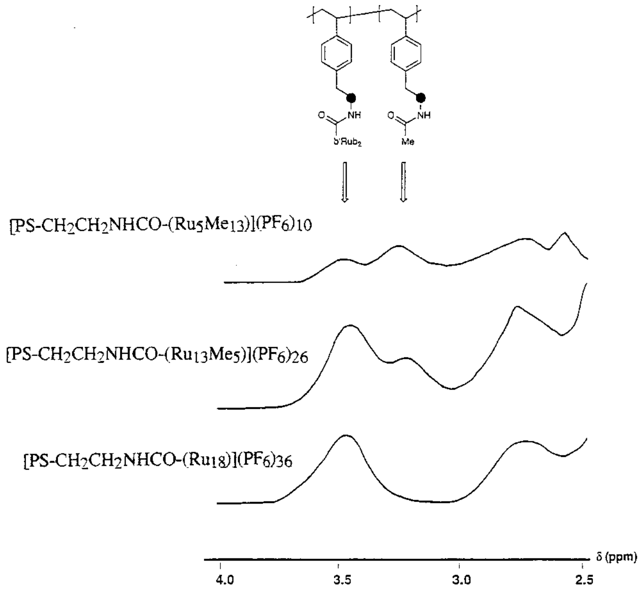


Figure 2. ^1H NMR spectra illustrating resonances for the protons of the ethylenic linkage in $[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_nMe_m)](PF_6)_{2n}$, $m + n = 18$, in CD_3CN.

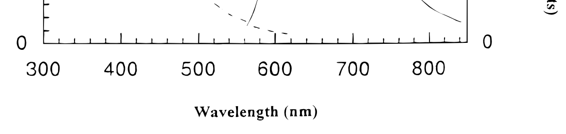


Figure 3. UV−visible absorption and emission spectra for $[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{18})](PF_6)_{36}$ in CH_3CN at room temperature.

Properties. Absorption and emission maxima in CH_3CN (458 and 645 nm) are independent of the number of repeat units, the degree of loading and the excitation wavelength. The absorption is due to $d\pi(Ru^{II}) \rightarrow \pi^*(bpy)$ metal-to-ligand charge transfer (MLCT) bands.[35,36] The emission is from the corresponding MLCT excited states. Representative spectra are shown in Figure 3. From the data in Table 1, emission quantum

---

(30) Tung, L. H. *J. Appl. Polym. Sci.* **1966**, *10*, 375.

(31) McCafferty, D. G.; Bishop, B. M.; Wall, C. G.; Hughes, S. G.; Mecklenburg, S. L.; Meyer, T. J.; Erickson, B. W. *Tetrahedron* **1995**, *51*, 1093.

(32) Mecklenburg, S. L.; McCafferty, D. G.; Schoonover, J. R.; Peek, B. M.; Erickson, B. W.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 2974.

(33) Mecklenburg, S. L.; Peek, B. M.; Schoonover, J. R.; McCafferty, D. G.; Wall, C. G.; Erickson, B. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 5479.

(34) Peek, B. M.; Ross, G. T.; Edwards, S. W.; Meyer, G. J.; Meyer, T. J.; Erickson, B. W. *Int. J. Pept. Protein Res.* **1991**, *38*, 114.

(35) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

(36) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.

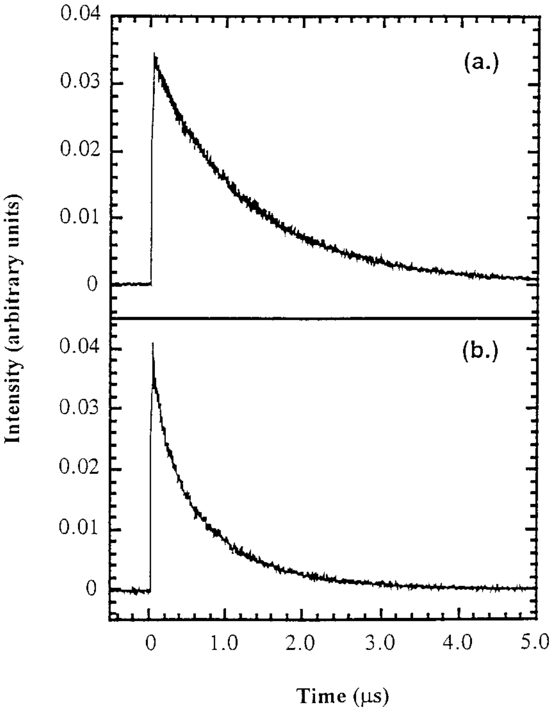
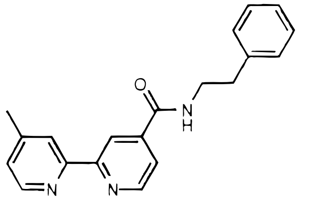


Figure 4. Emission decays at 650 nm for (a) [PS-CH$_2$CH$_2$NHCO-(Ru$^{II}_8$Me$_{17}$)](PF$_6$)$_{16}$ and (b) [PS-CH$_2$CH$_2$NHCO(Ru$^{II}_{25}$)](PF$_6$)$_{50}$ in deoxygenated CH$_3$CN solution at 29 °C. Excitation wavelength = 457 nm; beam irradiance = 0.9 μJ/mm^2.

yields (ϕ_{em}) decrease slightly with increased loading levels and chain length.

The electrochemical properties of the polymers are closely related to those of the model salt [Ru(bpy)$_2$(4-CONHCH$_2$-CH$_2$C$_6$H$_5$-4′-CH$_3$-bpy)](PF$_6$)$_2$.[32] The ligand is illustrated below.



4-CONHCH$_2$CH$_2$C$_6$H$_5$-4'-CH$_3$-bpy

Couples occur for Ru(III/II) oxidation at $E_{1/2}$ = 1.33 V vs SSCE in CH$_3$CN (0.1 M in [N(n-C$_4$H$_9$)$_4$](PF$_6$)) and ligand-based reductions at −1.20, −1.45, and −1.69 V. For [PS-CH$_2$CH$_2$-NHCO(Ru$^{II}_5$Me$_{13}$)](PF$_6$)$_{10}$, oxidation occurs at 1.32 V and reductions occur at −1.22 and −1.40 V. The electrochemical characteristics were largely independent of the extent of loading, although the third reduction was often obscured due to adsorption of the twice-reduced (per Ru) polymer onto the electrode surface.[37]

Emission decays were, in general, nonexponential although the lightly loaded polymers were close to exponential (Figure 4). Attempts were made to fit the decay data to the various functions in eqs 1−5, which included single-exponential (eq 1) and bi- (eq 2) and triexponential (eq 3) functions; the Williams−Watts function (eq 4), which has been used to describe relaxation in disordered media;[38−44] and the derivative of the Williams−Watts function with respect to time (eq 5).[3,4] In these equations

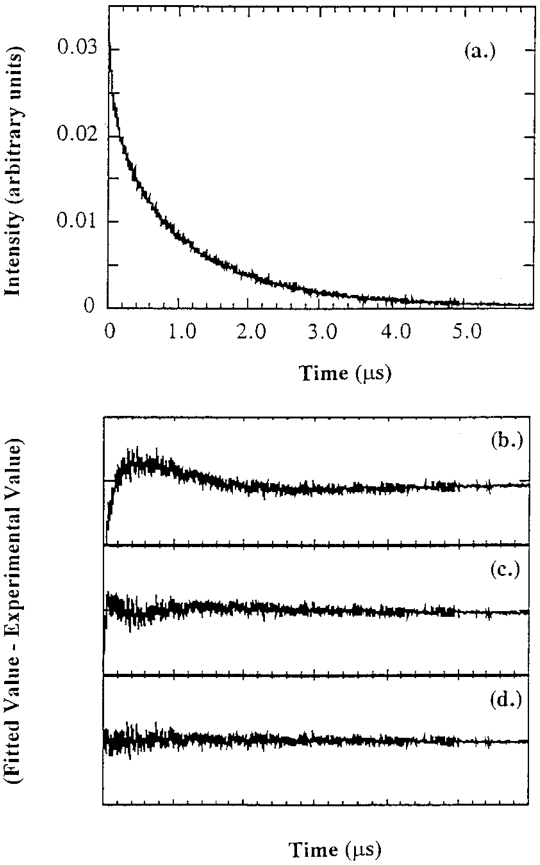


Figure 5. (a) Emission decays at 650 nm for [PS-CH$_2$CH$_2$NHCO-(Ru$^{II}_{18}$)](PF$_6$)$_{36}$ in deoxygenated CH$_3$CN; λ_{ex} = 457 nm, beam irradiance = 8.1 μJ/mm^2. (b−d) Residuals for best fits to (b) eq 1, single-exponential function; (c) eq 2, biexponential function; and (d) eq 5, Williams−Watts derivative function. The parameters for the fit represented by plot d are given in Table 2.

$$I(t) = Ae^{-(kt)} \tag{1}$$

$$I(t) = Ae^{-(k_1t)} + Be^{-(k_2t)} \tag{2}$$

$$I(t) = Ae^{-(k_1t)} + Be^{-(k_2t)} + Ce^{-(k_3t)} \tag{3}$$

$$I(t) = \alpha e^{-(kt)^{\beta}} \tag{4}$$

$$I(t) = \alpha t^{\beta-1} e^{-(kt)^{\beta}} \tag{5}$$

$I(t)$ is the emission intensity at time t, and A, B, C, α, β, and k are fitting parameters for the various functions. In Figure 5 are shown some representative fits. In all cases, the best fits were provided by eq 5. The resulting parameters were virtually independent of fitting limits. The other functions (especially the Williams−Watts function, eq 4) gave fits which were dependent on the fitting range. Table 1 gives fitting parameters for Ru^{II}* decay in a series of derivatized polymers according

---

(37) Abruña, H. D.; Teng, A. Y.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 6745.

(38) Williams, G.; Watts, D. C.; Dev, S. B.; North, A. M. *Trans. Faraday Soc.* **1971**, *67*, 1323.

(39) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80.

(40) Castellano, F. N.; Heimer, T. A.; Tandhasetti, M. T.; Meyer, G. J. *Chem. Mater.* **1994**, *6*, 1041.

(41) Scher, H.; Lax, M. *Phys. Rev.* **1973**, *B7*, 4491.

(42) Blumen, A.; Klafter, J.; Silbey, R. *J. Chem. Phys.* **1980**, *72*, 5320.

(43) Palmer, R. G.; Stein, D. L.; Abrahams, E.; Anderson, P. W. *Phys. Rev. Lett.* **1984**, *53*, 958.

(44) Lindsey, C. P.; Patterson, G. D. *J. Chem. Phys.* **1980**, *73*, 3348.

Table 2. Irradiance Dependence (at 650 nm) of the Kinetic Decay Parameters for Eq 5 in CH_3CN at 25−28 °C[a]

pulse energy (μJ/mm^2)	$10^2\alpha$	$10^{-5}k$ (s^{-1})	β	$\langle\tau\rangle$ (ns)
[PS-$CH_2CH_2NHCO(Ru^{II}_{18})](PF_6)_{36}$[b]				
8.1	0.49	8.6	0.90	1220
5.4	0.69	8.4	0.91	1240
4.1	0.84	8.5	0.92	1220
3.1	0.978	8.4	0.93	1230
1.6	1.0	8.3	0.94	1240
0.8	1.7	8.3	0.96	1230
0.3	1.9	8.1	0.97	1250
[PS-$CH_2CH_2NHCO(Ru^{II}_5Me_{13})](PF_6)_{10}$[c]				
6.2	1.0	8.2	0.95	1250
3.6	1.80	8.2	0.9	1240
2.3	2.0	8.1	0.970	1250
1.4	2.0	8.0	0.97	1260
0.9	2.6	7.9	0.99	1280
0.3	3.3	8.0	0.99	1260
[PS-$CH_2CH_2NHCO(Ru^{II}_2Me_9)](PF_6)_4$[c]				
6.4	2.1	7.2	0.97	1390
0.9	2.6	7.4	0.98	1350

[a] Solution absorbances at 450 nm from 0.04−0.08. [b] At 25 °C. [c] At 28 °C.

Table 3. Dependence of Emission Decay Kinetics (Eq 5) on Monitoring Wavelength in CH_3CN[a]

λ_{monitor} (nm)	$10^2\alpha$	$10^{-5}k$ (s^{-1})	β	$\langle\tau\rangle$ (ns)
[PS-$CH_2CH_2NHCO(Ru^{II}_{18})](PF_6)_{36}$[b]				
600	0.94	8.2	0.93	1250
625	1.8	8.2	0.96	1240
650	1.7	8.3	0.96	1230
675	2.0	8.1	0.96	1250
700	8.0	8.2	0.96	1240
725	1.9	8.1	0.96	1260
750	1.9	8.1	0.96	1260
[PS-$CH_2CH_2NHCO(Ru^{II}_5Me_{13})](PF_6)_{10}$[c]				
600	1.7	8.2	0.97	1230
625	2.8	8.0	0.98	1250
650	2.6	7.9	0.99	1280
675	3.3	8.2	0.99	1230
700	2.8	8.2	0.99	1220
725	3.0	8.0	0.99	1250
750	2.1	8.0	0.98	1260
800	2.8	8.2	0.99	1220

[a] Incident pulse energy was 0.8−0.9 μJ/mm^2 at 457 nm; absorbance = 0.04−0.07. [b] At 25 °C. [c] At 28 °C.

to eq 5. The "average" lifetime $\langle\tau\rangle$ was obtained by numerical integration of the first moment of eq 5.[44]

Emission decay kinetics for [PS-$CH_2CH_2NHCO(Ru^{II})_{18}$]($PF_6$)$_{36}$ were independent of polymer concentration between 2×10^{-4} and 1×10^{-3} mM but were slightly dependent on excitation irradiance. Relevant data are presented in Table 2. The decrease in the β parameter with increasing irradiance is an indication of a broadened distribution of emitters as discussed below. As shown by the data in Table 3, the decays are essentially independent of monitoring wavelength.

Discussion

Synthesis. Living anionic polymerization techniques are well-known and offer the advantage of decreased molecular weight dispersities compared to free radical procedures.[23−26] These techniques also allow for the stepwise preparation of block polymers, telechelic polymers, and graft polymers.[21,22] Only a limited number of vinyl monomers are responsive to these techniques because of the instability of many functional groups under the conditions of polymerization. Nakahama and co-workers have reported living anionic polymerizations for a variety of vinyl monomers with polar functional groups.[21,22] Their approach utilizes suitable protective groups which mask the functional groups during the polymerization step. It has been used for the preparation of polyalcohols, polyphenols, polyaldehydes, polycarboxylic acids, and polyamines of controlled molecular weights and polydispersities. We have exploited their approach to prepare the amino-derivatized styryl polymers.

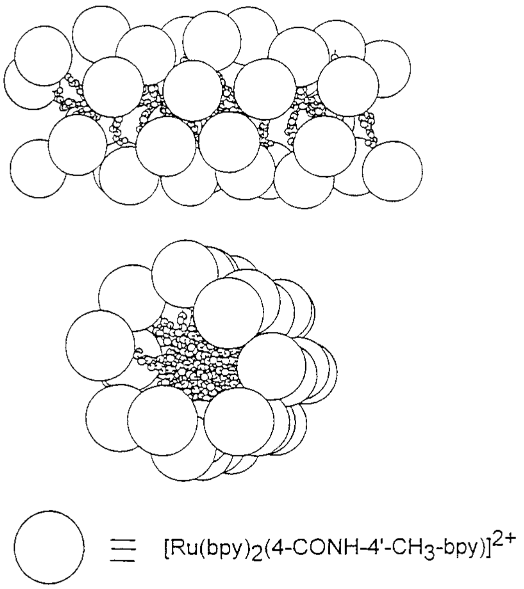


Figure 6. End-on and side views of the energy-minimized structure of [PS-$CH_2CH_2NHCO(Ru^{II}_{18})]^{36+}$ calculated by using modified MM2 parameters and CAChe software.

The second synthetic feature of interest in the current work is utilization of the living polymerization technique to prepare the styryl backbone. There are potentially several advantages associated with polymers prepared by the living anionic polymerization technique for photophysical studies. The narrow polydispersities offer materials with relatively narrow molecular weight distributions. There is no problem arising from a residual radical initiator. Polymers prepared by this method are optically transparent in the visible region of the spectrum. Finally, polymers synthesized by radical initiation can have considerable branching character, while living anionic polymers are linear, without branching.

Use of the silyl protecting groups allows the living anionic polymerization technique to be exploited to give the amine precursor to the derivatized amide polymers, Scheme 1. The amide coupling protocol is notable in its own right as a convenient, high-yield method for derivatizing the polymers by addition of the complexes and, in future studies, a variety of chromophores and electron or energy transfer donors or acceptors.

The amide coupling reaction, which uses BOP, allows easy purification of the polymer.[2,31] The coupling reaction also proceeds under mild reaction conditions at room temperature and therefore has no influence on the polymer main chain except for the amino group. There are no possibilities for ligand scrambling which would increase the molecular weight and/or the degree of cross-linking of the polymer.

In order to appreciate the structural and morphological characteristics of the polymers, the results of a molecular modeling calculation on [PS-$CH_2CH_2NHCO(Ru^{II})_{18}]^{36+}$ are illustrated in Figure 6. The calculations were performed by using the CAChe program with modified MM2 parameters based on an atactic, fully loaded polymer.[2] Each ruthenium complex unit was treated as a sphere of 2+ charge of 12 Å diameter. Two views of the polymer are illustrated, one side-on and one end-on. No solvent molecules were included in these calculations, and they are only elaborate cartoons of the real molecules. They do, however, give insight into polymer structure. As an example, the 2+ charges and large excluded molecular volumes of the added complexes force the polymers to adopt extended, rodlike structures. In these structures the average distance separating the peripheries of the complexes is 4 Å (18 Å, center-to-center).

The addition of the second $-CH_2-$ link in the homopolymer, compared to the single $-CH_2-$ link in the copolymers [*co*-PS-$CH_2NHCO(Ru^{II}{}_n)](PF_6)_{2n}$, was a design change intended to create sufficient extended volume along the backbone axis of the polymer to achieve complete loading. The second methylene link is sufficient for this purpose as shown by the ^1H NMR results, which are consistent with complete loading. For partly derivatized polymers, it was necessary to cap the unreacted amine groups because of their reactivity. This was achieved by reaction with acetic anhydride to give the corresponding acetyls, Scheme 1.

The visible absorption spectra of the polymers are dominated by metal-to-ligand charge transfer (MLCT) bands. These are broad bands with overlapping absorptions from both $Ru^{II} \rightarrow$ bpy and $Ru^{II} \rightarrow$ bpy-$CONHCH_2CH_2$ transitions.[32,33] On the basis of substituent effects and previous work on peptide-based assemblies, the lowest lying excited state is expected to be based on the amide ligand, $Ru^{III}(bpy^{\bullet-}CONHCH_2CH_2)$.[33] This prediction has been verified for [*co*-PS-$CH_2NHCO(Ru^{II}{}_n)](PF_6)_{2n}$ by direct excited-state resonance Raman measurements.[33] This is an important observation since it points to a lowest MLCT excited state of dipole orientation toward the polymeric backbone. Recent results have demonstrated that this can greatly enhance intrastrand site-to-site energy transfer hopping.[45a]

Properties. The polymers reported here and in an earlier communication[45a] are the second amide-linked cases we have reported, and the first homopolymer. The first was based on the 1:1 copolymer [*co*-PS-$CH_2NHCO(Ru^{II}{}_n)](PF_6)_{2n}$ formed by free radical polymerization.[1] The photophysical properties of the homopolymers, in gross detail, are nearly those of the amide-linked copolymers in terms of emission energy and average lifetime.[1] Comparison with $[Ru(bpy)_2(4\text{-}CONHCH_2CH_2C_6H_5\text{-}4'\text{-}CH_3\text{-}bpy)](PF_6)_2$, Table 1, reveals that the Ru^{II} sites on the polymers are not significantly perturbed, even at high loading levels.

There are structural and compositional nuances. The individual chromophoric sites are largely isolated electronically in the polymeric arrays. At low loading levels, decay of the MLCT excited states is essentially single-exponential, with average lifetimes approaching those of the model complexes, Table 1. For the fully loaded sample, the decays are nonexponential, Figures 4 and 5 and Table 1. The dynamics of excited-state decay are dependent upon the excitation irradiance but are essentially independent of monitoring wavelength.

Mathematically, all of these nuances are captured by the decay function in eq 5. This is the first derivative of the Williams–Watts equation, eq 4, which is a distribution function with β a measure of the width of the distribution and k an average rate constant.[3,4] For a pure exponential $\beta = 1$. There is no obvious connection between the form of eq 5 and the microscopic origin of the nonexponential decays, but the ability of the function to fit the data over the range of loadings and irradiances through the complete time course of decay is remarkable. This function is equally successful at fitting excited-state decays in the structurally analogous ether-linked polymers, [*co*-PS-CH_2OCH_2-$(Ru^{II}{}_n)](PF_6)_{2n}$.[45b]

In the most dilute sample, $[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_2Me_9)](PF_6)_4$, the decays are nearly exponential with $k = 7.4 \times 10^5$ s^{-1} in CH_3CN at 28 °C. The same is true for $[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_5Me_{13})](PF_6)_{10}$ at low light intensities. For the fully loaded polymer, $[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{18})](PF_6)_{36}$, the decay traces are nonexponential even at low irradiances, with the width of the distribution increasing (β decreasing) and k increasing slightly as irradiance increases. The highest irradiances in Table 2 correspond to the excitation of 1–2 chromophores/chain (approximately 1.6 for $[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{18})](PF_6)_{36}$) at an irradiance of 8.1 μJ/pulse·mm^2 at 457 nm. The decrease in β with increasing irradiance parallels an increase in the number of emitting sites per polymer strand. Related effects have been observed in other metal complex derivatized polymers.[1,3,4]

The available evidence points to a multichromophoric, multiphoton effect as the origin of the nonexponentiality. These effects are not important in $[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_2Me_9)](PF_6)_4$, where the individual sites are highly diluted, but they are of importance in $[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{18})](PF_6)_{36}$, where the probability of creating an excited state near a chromophore is unity.

The microscopic origin of the multichromophoric effect is not precisely definable with our data, but there are some reasonable explanations. A distribution of emitting sites is expected, given the local inhomogeneities in the backbone of the atactic polymer, which creates multiple local environments. Decay of MLCT excited states is known to be sensitive to the environment.[4,27] As discussed earlier for the polymers [*co*-PS-$CH_2NHCO(Ru^{II}{}_n)](PF_6)_{2n}$, one contribution to the multichromophore–multiphoton effect may come from polarization of the surrounding medium by the excited state. The lifetime of a second excited state created in the polarization field of a first would be affected. If intrastrand energy transfer is facile in these polymers, as it is in [*co*-PS-$CH_2NHCO(Ru^{II}{}_n)](PF_6)_{2n}$,[45a] a second contributing factor may be multiphoton excitation, energy migration, and excited-state–excited-state annihilation by electron or energy transfer.[46–52]

Acknowledgment. We wish to thank the DOE (Grant DE-FG02-96ER14607) and the Japan Synthetic Rubber Company (T.K.) for financial support of this research and NSERC for a postdoctoral fellowship (D.A.F.). The assistance of Dr. J. M. DeSimone, Mr. Michael O. Hunt, and Mrs. Dorian Canelas (discussions of polymer synthesis and GPC chromatograms) and Dr. S. Nakahama (information on the living anionic polymerization of the protected monomer) is also greatly appreciated.

IC9710420

---

(45) (a) Dupray, L. M.; Striplin, D.; Devenney, M.; Meyer, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 10243. (b) Danielson, E. Unpublished results.

(46) Furue, M.; Yoshidzumi, T.; Kinoshita, S.; Kushida, T.; Nozakura, S.; Kamachi, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1632.

(47) Furue, M.; Hirata, M.; Kinoshita, S.; Kushida, T.; Kamachi, M. *Chem. Lett.* **1990**, 2065.

(48) Watkins, D. M.; Fox, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 6441.

(49) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469.

(50) Guillet, J. E. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, 1985.

(51) Gratzel, M. *Heterogeneous Photochemical Electron Transfer*; CRC Press: Boca Raton, 1989.

(52) Sienicki, K. *Macromolecules* **1990**, *23*, 5023.