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Synthesis and Characterization of Soluble Polymers Containing Electron- and Energy-Transfer Reagents

Janet N. Younathan, Stephen F. McClanahan, and Thomas J. Meyer*

Department of Chemistry, University of North Carolina,
Chapel Hill, North Carolina 27599-3290.

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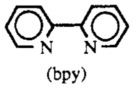
ABSTRACT: A series of monofunctional redox polymers containing a visible chromophore [tris(bipyridyl)ruthenium(II) derivatives] or an organic energy-transfer reagent (derivatized anthracenes) were synthesized by reaction of poly(*m*(*p*)-(chloromethyl)styrene-*stat*-styrene) with alkoxide or carboxylate nucleophiles. Bifunctional polymeric materials incorporating substituted anthracenes and a reductive organic electron-transfer quencher (phenothiazene) were prepared by analogous stepwise procedures. The degree of loading of the modified polystyrenes was controlled in a reproducible manner by variation of the ratio of the nucleophile to the starting copolymer as indicated by ^{1}H NMR, UV-visible spectroscopy, and elemental analysis. Results from cyclic voltammetry confirm the electroactivity of the pendant functionalities and are consistent with a hydrophobic environment surrounding the redox sites. Comparison of the steady-state emission spectra of the ruthenium(II) polymers with monomeric models indicates that the excited-state properties of the metal complex are maintained upon polymeric attachment.

Introduction

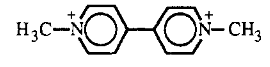
Soluble electroactive or photoactive polymers constitute unique excited-state redox reagents often enhancing energy migration[1] and attenuating charge recombination[2] of photoproduced transient intermediates. A number of homogeneous charge storage systems utilizing polymer-bound ruthenium(II) bipyridyl derivatives have been reported in aqueous[3-5] or organic[3b,6] media in response to their potential utility in the conversion and storage of solar energy. Our interests in this area include the assembly of mixed functional polymers containing a variety of chromophore-quencher combinations, with polymer-bound ruthenium(II) or osmium(II) tris(bipyridyl) derivatives serving as the primary chromophoric sites. One of our goals is to learn how to control intrapolymeric energy and electron-transfer events to effect efficient photochemically induced charge separation at the molecular level.

Typically, syntheses of polymeric ruthenium(II) bipyridyl complexes are based on vinylic derivatives of 2,2′-bipyridine (bpy) including 6-*p*-styryl-2,2′-bipyridine,[5a]

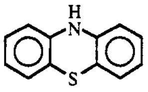


(bpy)

4-methyl-4′-vinyl-2,2′-bipyridine,[7,7a] and 6-vinyl-2,2′-bipyridine[7] as well as copolymeric combinations.[3b,3d,5b,6] Clearly, a more general synthetic approach is necessary for the attachment of a wide variety of potential photoredox reagents. We recently reported the preparation of soluble redox polymers containing controlled loadings of derivatives of a reductive quencher (phenothiazine, PTZ), an

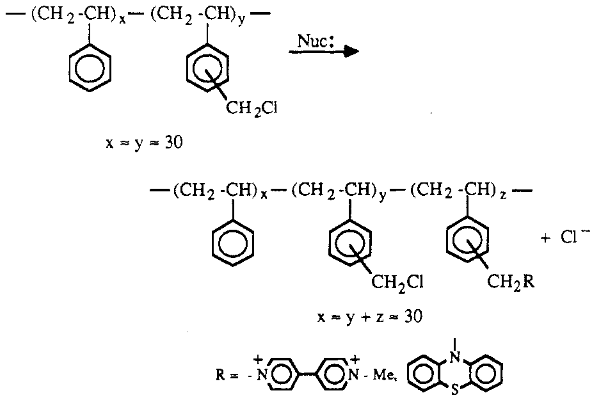


(PQ^{2+})



(PTZ)

oxidative quencher (paraquat, PQ^{2+}), and combinations of the two based on nucleophilic displacement of Cl$^-$ in a 1:1 statistical copolymer of styrene and *m*(*p*)-(chloromethyl)styrene (reaction 1).[8]



(1)

Current efforts have focused on the preparation of polymer-bound derivatives of tris(bipyridyl)ruthenium(II),

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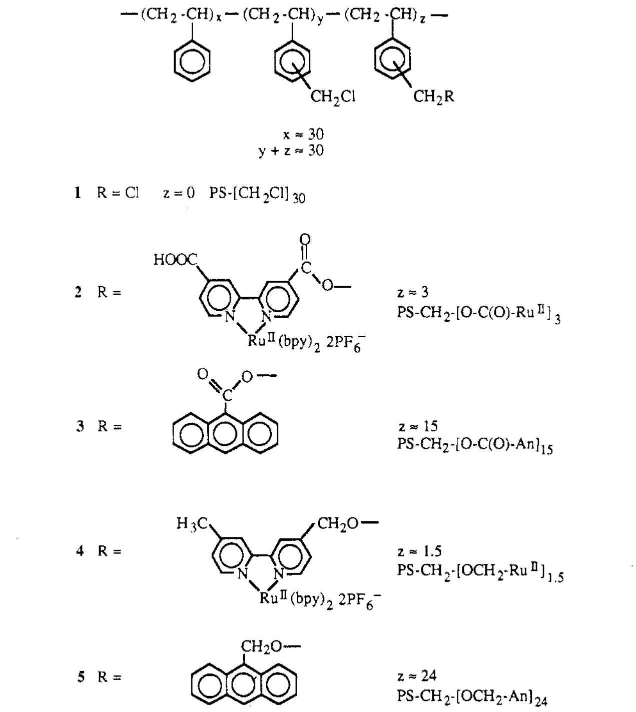
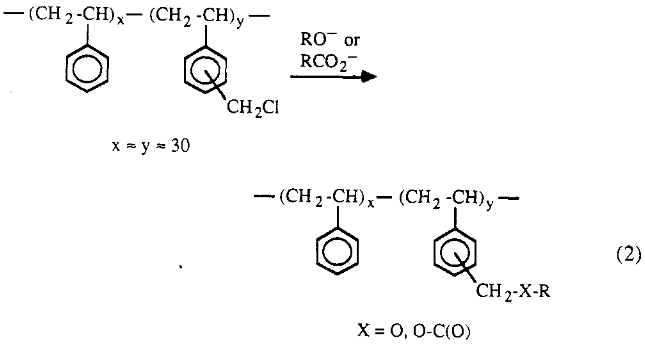


Figure 1. Structures of monofunctional polymers which contain chromophoric or redox sites.

a strong visible chromophore, and polymeric anthracenes, which act as energy-transfer acceptors and carriers in macromolecular assemblies.[9] These systems were designed to exploit the efficient triplet energy transfer from excited ruthenium(II) to anthracenyl derivatives known to occur between monomeric reagents in aqueous solution.[10] When polymer-bound ruthenium(II) is excited in the presence of monomeric 9-methylanthracene (9-MeAn) and separate polymers containing PTZ and PQ^{2+}, photoinduced charge separation of oxidative and reductive equivalents on isolated polymeric strands can be achieved.[11]

As a general synthetic strategy for the modification of chemically derivatized polystyrene, we have explored the nucleophilic displacement of Cl$^-$ from poly(*m*(*p*)-(chloromethyl)styrene-*stat*-styrene) with the concomitant formation of ester or ether linkages (eq 2). Similar approaches have been employed previously by Neckers[12] for the bonding of rose bengal to chloromethylated polystyrene beads and Cochet and co-workers for the attachment of aminophosphines to polystyrene supports.[13] These reactions occur under relatively mild alkaline conditions and, when combined with our synthetic procedures for bonding of PQ^{2+} or PTZ to modified polystyrene, are suitable for the stepwise attachment of two or more redox or chromophoric sites to the same polymeric chain.



The structures of the resulting polymers (1–7) are shown in Figures 1 and 2. The numerical subscripts following the abbreviated structures indicate the approximate number of modified sites in an average strand containing 30 chloromethyl units before substitution. As described below, these numbers are derived from analytical data (UV–visible, ^{1}H NMR, elemental analyses), which define the number of incorporated redox sites per total available chloromethyl groups.

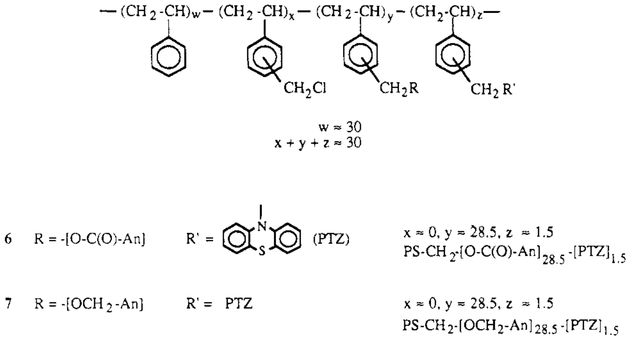


Figure 2. Structures of polymers which contain both chromophoric and redox sites.

Experimental Section

Materials. *N*,*N*-Dimethylformamide (DMF) was dried by distillation from BaO. Dimethyl sulfoxide (Me$_2$SO) was stirred over potassium hydroxide, distilled under reduced pressure, and stored under Ar. Tetrahydrofuran (THF) was heated at reflux over potassium metal and distilled immediately prior to use. Methylene chloride for electrochemical measurements was passed through a 1-in. plug of neutral activated alumina. Sephadex LH-20 (25–100-μm bead size) for column chromatography was supplied by Sigma Chemical Co. and was swollen in excess eluting solvent prior to separation.

N-Butyllithium in hexane was standardized by titration with 3 mL of a 0.3 M solution of diphenylacetic acid in THF until a yellow color persisted. 9-Anthracenemethanol and 9-anthracenecarboxylic acid were commercially available from Aldrich and were recrystallized twice from methanol. PTZ (Alfa) was recrystallized twice from toluene and stored in a desiccator protected from light. Polymer-bound phenothiazene (PS-CH$_2$-[PTZ]$_{1.5}$)[8] and *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) dihydrate[14] [Ru(bpy)$_2$Cl$_2$·2H$_2$O] were synthesized as previously described.

Instrumentation. ^{1}H NMR spectra were obtained at ambient probe temperature on a Bruker 200-MHz spectrometer with chemical shifts reported in parts per million downfield from tetramethylsilane as an internal standard. IR spectra were recorded on a Nicolet 20DX FTIR using KBr pellets. Emission spectra were obtained at right angle on a Spex Fluorolog spectrofluorimeter with double monochromators for excitation and emission. All samples were degassed with a minimum of four freeze–pump–thaw cycles. Emission quantum yields were calculated by using [Ru(bpy)$_3$](PF$_6$)$_2$ in acetonitrile as a standard. Gel permeation chromatography was performed in THF with an IBM LC/9560 solvent delivery system equipped with an LC/9525 differential refractometer detector and styrene–divinylbenzene column types A, C, and E (IBM) connected in order of decreasing pore size. Molecular weights were established by polystyrene standards.

Electrochemical measurements were conducted with an EG&G Princeton Applied Research (PAR) Model 173 potentiostat with a Model 179 digital coulometer. Excitation waveforms were programmed with a supercycle of local construction and design. Current–voltage curves were plotted on a Hewlett Packard 7015B X-Y recorder. A one-compartment cell was used. The methylene chloride solutions contained 0.1 M tetra-*n*-butylammonium perchlorate as the supporting electrolyte and were deaerated and kept under a positive pressure of Ar during each run. Potentials are referenced to the saturated sodium calomel electrode (SSCE). Teflon-shrouded platinum working electrodes of 0.1-cm^2 surface area were polished with 1.0-μm Buehler polishing paste prior to use. A Pt wire served as the counter electrode. Positive feedback for IR compensation was utilized in all runs to minimize the solution resistance between the working and reference electrodes.

The supporting electrolyte–methylene chloride solutions were scanned over the solvent window prior to the addition of substrate to ensure the absence of electroactive impurities.

The modified polystyrenes synthesized below were stored in a desiccator shielded from light. Unprotected samples exhibit changes in solubility properties presumably resulting from light-induced cross-linking of the chloromethylated polystyrene chains.

Diethyl 2,2′-Bipyridine-4,4′-dicarboxylate, 4,4′-$(COOEt)_2$bpy (8). Esterification of 2,2′-bipyridine-4,4′-dicarboxylic acid[15] (2 g, 8.2 mmol) according to the procedure of Maerker and Case[16] yielded 1.5 g (62%) of diester 8 as a white solid: mp 157–159 °C [lit.[16] mp 159–160.5 °C]; IR 1731 cm^{-1} (ester C=O).

(4,4′-Bis(ethoxycarbonyl)-2,2′-bipyridine)bis(2,2′-bipyridine)ruthenium(II) Hexafluorophosphate, $\{Ru^{II}[4,4'-(COOEt)_2bpy](bpy)_2\}(PF_6)_2$ (9). $Ru(bpy)_2Cl_2 \cdot H_2O$ (1 g, 1.9 mmol) was heated at reflux in 60 mL of 1:1 EtOH–H_2O for 1 h. The hot solution was filtered, and a suspension of diester 8 (0.58 g, 1 mmol) in 20 mL absolute EtOH was added dropwise with stirring. The reaction mixture was heated at 40 °C for 15 h under Ar and then concentrated to approximately 20 mL by rotary evaporation. The solution was cooled in ice and treated with excess NH_4PF_6. The resulting precipitate was filtered, washed with cold water, and dried under vacuum at room temperature, yielding 1.6 g (95%) of a red solid: IR 1729 cm^{-1} (C=O); ^1H NMR (CD_3COCD_3) δ 9.27 (d, 2 H, J = 2 Hz), 8.83 (d, 4 H, J = 8 Hz), 8.33 (d, 2 H, J = 6 Hz), 8.23 (ddd, 4 H, J = 8 Hz, J = 5 Hz, J = 1 Hz), 8.07 (t, 4 H, J = 5 Hz), 7.99 (dd, 2 H, J = 2 Hz, J = 6 Hz), 7.57 (m, 4 H), 4.47 (t, 4 H, J = 7 Hz), 1.39 (q, 6 H, J = 7 Hz).

(Tetraethylammonium 2,2′-bipyridine-4,4′-dicarboxylate)bis(2,2′-bipyridine)ruthenium(II) Hexafluorophosphate, $\{Ru^{II}[4,4'-(COONEt_4)_2bpy]bpy)_2\}(PF_6)_2$ (10). Salt 9 (1 g, 1.1 mmol) in 100 mL of THF was hydrolyzed to the dicarboxylate salt by heating at reflux for 6 h in the presence of 25 mL of 0.8 M aqueous NEt_4OH. The reaction mixture was concentrated to dryness on a rotary evaporator affording 10 in 95% yield: IR 1645, 1620, 1604 cm^{-1}; ^1H NMR (D_2O) δ 8.88 (s, 2 H), 8.55 (d, 4 H, J = 8 Hz), 8.02–8.10 (m, 4 H), 7.92 (d, 2 H, J = 4 Hz), 7.80 (t, 4 H, J = 6 Hz), 7.67 (dd, 2 H, J = 6 Hz, J = 2 Hz), 7.38 (ddd, 4 H, J = 2 Hz, J = 6 Hz, J = 8 Hz), 3.27 (q, 16 H, J = 8 Hz), 1.28 (m, 24 H).

[4-(Hydroxymethyl)-4′-methyl-2,2′-bipyridine]bis(2,2′-bipyridine)ruthenium(II) Hexafluorophosphate, $\{Ru^{II}(4-CH_2OH-4'-Mebpy)(bpy)_2\}(PF_6)_2$ (11). A stirred solution of $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (0.52 g, 1 mmol), 4-(hydroxymethyl)-4′-methyl-2,2′-bipyridine[17] (0.2 g, 1 mmol), and $NaHCO_3$ (0.28 g, 3.3 mmol) in 50 mL of 2:3 MeOH–H_2O was heated at reflux for 18 h. After the reaction mixture was cooled in ice, excess aqueous NH_4PF_6 was added. The precipitated product was filtered, washed with cold water, and dried under vacuum at 40 °C, providing 0.48 g (54%) of a red solid: ^1H NMR (CD_3CN) δ 8.39–8.50 (m, 6 H), 7.95–8.09 (m, 4 H), 7.69–7.75 (m, 4 H), 7.53 (d, 1 H, J = 6 Hz), 7.62 (d, 1 H, d, J = 6 Hz), 7.35–7.42 (m, 6 H), 4.78 (s, 2 H), 2.52 (s, 3 H); UV λ_{max} (CH_3CN) 456 nm (ϵ 13 400).

Poly[*m*(*p*)-(chloromethyl)styrene-*stat*-styrene], PS-$[CH_2Cl]_{30}$ (1). A 1:1 copolymer of styrene and (chloromethyl)styrene was prepared according to the method of Arshady et al.[18] by AIBN-initiated free-radical polymerization in chlorobenzene. The molecular weights of the resulting copolymer were M_w = 16 420, M_n = 6900, and M_w/M_n = 2.38 as determined by gel permeation chromatography using polystyrene standards. Anal. Calcd for 46 mol % chloromethylation: C, 80.35; H, 6.76; Cl, 12.90. Found: C, 80.23; H, 6.74; Cl, 12.75.

Preparation of PS-$CH_2[OC(O)Ru^{II}]_3$ (2). PS-$[CH_2Cl]_{30}$ (1; 1 g) and 10 (0.47 g, 0.48 mmol) were heated at 60 °C in 25 mL of DMF for 15 h. The solvent was removed by distillation leaving a dark red solid, which was purified by column chromatography (Sephadex LH-20, acetone). Elution resulted in two deep red bands: one moving essentially with the column void volume, the other retained at the top of the column. The eluted fraction was concentrated to 3–4 mL and added dropwise to rapidly stirred, excess Et_2O. The precipitate was collected by suction filtration and dried under vacuum at room temperature, yielding 0.6 g of 2: UV λ_{max} (CH_2Cl_2) 478 nm. Anal. Calcd for 3 mol % monoester and 7 mol % diester: C, 68.72; H, 5.55; N, 3.02; Cl, 7.13; F 7.81. Found: C, 69.02; H, 5.89; N, 2.65; Cl, 6.92; F, 7.94.

Preparation of PS-$CH_2[OC(O)An]_{15}$ (3). A solution of 1 (0.5 g), 9-anthracenecarboxylic acid (0.88 g, 4 mmol), and Na_2CO_3 (0.21 g, 2 mmol) in 20 mL of DMF was heated at 60 °C for 15 h under Ar. The reaction mixture was concentrated to 3–4 mL by vacuum distillation and added dropwise to rapidly stirred, excess methanol. The precipitate was isolated by suction filtration, washed with methanol, and dried at room temperature under vacuum, yielding 0.45 g of 3 as a yellow solid: IR 1722 cm^{-1} (C=O). Anal. Calcd for 50 mol % derivatized anthracene: C, 84.18; H, 6.16; Cl, 5.08. Found: C, 83.85; H, 6.37; Cl, 4.75.

Preparation of PS-$CH_2[OCH_2Ru^{II}]_{1.5}$ (4). Polystyrene modified with the ruthenium tris(bipyridyl) complex was prepared by alkylation of salt 11 in a procedure analogous to that of Johnstone and Rose.[19] A solution of PS-$[CH_2Cl]_{30}$ (1; 0.5 g) and 11 (0.17 g, 0.19 mmol) in 3 mL of Me_2SO containing powdered $CsOH \cdot H_2O$ (0.13 g, 0.77 mmol) was stirred at room temperature for 15 h. The crude reaction mixture was purified without further workup by column chromatography on Sephadex LH-20 (acetone) to yield 0.35 g of a deep brown solid (3): UV λ_{max} (CH_2Cl_2) 454 nm. Anal. Calcd for 5 mol % Ru(II): C, 77.44; H, 6.12; N, 1.40; Cl, 11.25. Found: C, 77.11; H, 6.55; N, 1.11; Cl, 10.38.

Preparation of PS-$CH_2[OCH_2An]_{24}$ (5). PS-$[CH_2Cl]_{30}$ (1; 0.75 g) and 9-anthracenemethanol (0.6 g, 2.9 mmol) were stirred at room temperature under Ar in 20 mL of Me_2SO containing 0.49 g of suspended, powdered $CsOH \cdot H_2O$. After reaction for 15 h, the mixture was quenched with 20 mL of water and the aqueous solution extracted with dichloromethane (3 × 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated to 3 mL. The polymer was purified by dropwise addition of the concentrated dichloromethane solution into rapidly stirred MeOH. The resulting precipitate was collected by suction filtration and dried under vacuum, yielding 0.7 g of a yellow solid (5): (IR 1277 cm^{-1} (C–O–C stretch). Anal. Calcd for 80 mol % derivatized anthracene: C, 86.42; H, 6.90; Cl, 0.73; O, 3.19. Found: C, 88.39; H, 6.55; Cl, 1.80; O, 3.25.

Preparation of PS-$CH_2[OC(O)An]_{28.5}[PTZ]_{1.5}$ (6). A polymeric material containing both PTZ and anthracenyl functionalities was synthesized in a stepwise manner. PS-$CH_2[PTZ]_{1.5}$[8] (0.30 g) was combined with 9-anthracenecarboxylic acid (0.50 g, 2.2 mmol) and Na_2CO_3 (0.12 g) in 15 mL of DMF under Ar in an apparatus shielded from light. The mixture was heated at 70 °C for 48 h and concentrated to 3–4 mL by distillation. The polymeric product was isolated by precipitation into rapidly stirred, excess methanol followed by suction filtration and vacuum drying at room temperature giving 0.37 g of a yellow powder (6): IR 1719 cm^{-1} (C=O). Anal. Calcd for 95 mol % substituted anthracene and 5 mol % bound PTZ: C, 86.88; H, 6.01; N, 0.15; Cl, 0.00. Found: C, 86.53; H, 6.01; N, 0.33; Cl, 0.17.

Preparation of PS-$CH_2[OCH_2An]_{28.5}[PTZ]_{1.5}$ (7). PS-$CH_2[PTZ]_{1.5}$ (0.5 g) and 9-anthracenemethanol (1.1 g, 5.4 mmol) were stirred at room temperature under Ar in the dark in 5 mL of Me_2SO containing 0.9 g of $CsOH \cdot H_2O$. After reaction for 15 h, the reaction mixture was added dropwise to rapidly stirred, excess methanol. The precipitate was filtered and dried to give 0.5 g of a yellow solid 7: UV λ_{max} (CH_2Cl) 334, 350, 368, 388 nm. Anal. Calcd for 95 mol % substituted anthracene and 5 mol % bound PTZ: C, 89.39; H, 6.51; Cl, 0.00; O, 3.56. Found: C, 89.23; H, 6.44; Cl, 0.05; O, 3.50.

Results and Discussion

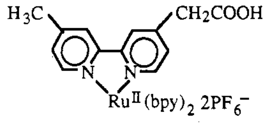
Synthesis and Purification. Both alkoxide and carboxylate anions function as sufficiently strong nucleophiles toward chloromethylated polystyrene in alkaline DMF or Me_2SO. The degree of substitution can be readily controlled by varying the stoichiometric ratio of the nucleophile to the starting copolymer. The choice of methods depends primarily on the availability of suitable starting materials, the stability of the reagents to prolonged heating, and the energetic and redox requirements of the pendant groups. The ether syntheses occur readily in stirred, room-temperature solution while the esterification procedures require temperatures of 60–70 °C for 22–48 h. Heat-sensitive carboxylic acids are unsuitable reactants

Table I
Spectroscopic Properties of Modified Polymers and Monomeric Models[a]

	λ_{max}(abs), nm (log ϵ, M^{-1} cm^{-1})	λ_{max}(lum), nm (Φ)
PS-CH_2[OC(O)Ru^{II}]$_3$ (**2**)	478	685 (0.076)
{Ru^{II}[4,4′-(COOEt)bpy](bpy)$_2$}(PF_6)$_2$ (**9**)	478 (4.20)	656 (0.080)
PS-CH_2[OCH_2Ru^{II}]$_{1.5}$ (**4**)	454	655 (0.053)[b]
{Ru^{II}(4-$HOCH_2$-4′-Mebpy)(bpy)$_2$}(PF_6)$_2$ (**11**)	454 (4.13)	650 (0.054)[c]
PS-CH_2[OC(O)An]$_{15}$ (**3**)	333, 348, 365, 385	
9-anthracenecarboxylic acid	330 (4.43), 346 (3.73), 362 (3.98), 382 (3.82)[c]	
PS-CH_2[OCH_2An]$_{24}$ (**5**)	334, 350, 368, 388	
9-anthracenemethanol	334 (3.45), 348 (3.75), 366 (3.91), 386 (3.89)	
PS-CH_2[OC(O)An]$_{28.5}$[PTZ]$_{1.5}$ (**6**)	333, 348, 365, 385	
PS-CH_2[OCH_2An]$_{28.5}$[PTZ]$_{1.5}$ (**7**)	334, 350, 368, 388	

[a] Data obtained at ambient temperature in methylene chloride unless otherwise noted. [b] In 2-methyltetrahydrofuran. [c] In methanol.

for the esterification procedure. For example, attempts to bind {Ru^{II}(4-CH_2COOH-4′-Mebpy)(bpy)$_2$}(PF_6)$_2$ (**12**) to chloromethylated polystyrene as depicted in eq 2 were unsuccessful, resulting in decarboxylation to give the 4,4′-dimethylbipyridine-containing complex. No polymer-bound ruthenium product was isolated.



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The positive counterion is critical in determining the reaction efficiency with both the alkoxy and carboalkoxy nucleophiles consistent with well-established data.[20] For the attachment of the anthracenecarboxylate anion to the soluble polymer, the Na^+ salt was formed in situ by the addition of base (Na_2CO_3) to DMF solutions of the acid and the copolymer. The reactions proceed smoothly and lead to the quantitative conversion of the chloromethyl sites in the presence of excess anthracenecarboxylic acid. In contrast, the sodium carboxylate salt of the metal complex, {Ru^{II}[4,4′-$(COONa)_2$bpy](bpy)$_2$}(PF_6)$_2$, is a much weaker nucleophile than sodium anthracenecarboxylate presumably because of the strong inductive influence of the nitrogen heteroatoms and the dicationic metal center. Attempts to bind the ruthenium bipyridyl derivative to the polymer by generating the sodium carboxylate salt in DMF were unsuccessful. However, the tetraethylammonium hydroxide salt successfully reacts with chloromethylated polystyrene, affording the ester-bound complex as shown by the appearance of the carbonyl ester group at 1732 cm^{-1} in the IR. The large ammonium counterion forms a looser ion pair with the carboxylate anion than the sodium cation, "freeing" the oxygen electrons and resulting in a stronger nucleophile.

The carboxylate complex is a "zwitterion" in the sense that the negatively charged carboxylate groups are located on the periphery of the complex at a single ligand with the ruthenium(II) ion at the center. Isolation of the complex in the solid state occurs with the coprecipitation of a salt as in {Ru^{II}[4,4′-$(COO^-)_2$bpy](bpy)$_2$}·2(NEt_4)(PF_6). This behavior suggests that in the crystal lattice the cations and anions are probably asymmetrically dispersed with the cations near the carboxylate groups and the anions on the opposite side of the complex as in $(NEt_4)_2$[4,4′-$(COO^-)_2$bpy]Ru^{II}(bpy)$_2$(PF_6)$_2$.

Similar counterionic effects were also noted in the etherification reactions. While both CsOH and KOH can be effectively utilized in the preparation of polymers **4**, **5**, and **7**, the size mismatch between the large cesium counterion and the alkoxide anion creates a poorly solvated, highly reactive nucleophile. Preparations employing CsOH resulted in higher loadings in shorter reaction times than syntheses using KOH as the base. Specifically, reaction of derivatized polystyrene and excess 9-anthracenemethanol in a Me_2SO suspension of powdered KOH for 20 h resulted in 53 mol % incorporation of anthracenyl groups. Preparation of an 80 mol % loaded anthracene-substituted polymer utilizing CsOH required a 15 h reaction period.

Purification of the derivatized polymers is straightforward. Polymers modified with neutral organic functionalities precipitate readily in excess methanol from methylene chloride solutions. The ruthenium(II)-containing polymers require chromatographic purification on Sephadex-LH 20 with acetone as the eluent. In this experiment, one fraction moved essentially with the void volume and one fraction was completely retained on the top of the column. The latter band, accounting for 10–20% of the total product weight, could be partially eluted with increasing quantities of water in the eluent; however, even with 1:1 aqueous acetone, only small amounts of this material were freed from the column. Interestingly, an infrared spectrum of this latter material was identical with that of the acetone eluted polymer except that bands characteristic of the PF_6^- anion at 837 and 559 cm^{-1} were absent. Finally, the chromatographic behavior described above is independent of the loading of the metal complex on the polymer; polymers containing 5–100 mol % Ru(II) chromatographed in an identical fashion.

Polymer Characterization. Ultraviolet–Visible Absorption Spectra. Electronic absorption spectral data for the modified polymers is summarized in Table I. The absorption spectra of the polymers can be used in quantitative analysis of polymer composition assuming that the extinction coefficient of the chromophore of interest is unchanged upon binding to the polymer.

In general, the properties of the UV–visible absorption bands parallel those of corresponding monomeric models. The strong, visible metal to ligand charge-transfer (MLCT)[21] transitions typical of ruthenium(II) tris(bipyridyl) complexes are present in both of the polymer-bound ruthenium samples **2** and **4**, confirming the presence of the complex on the polymeric chain. Furthermore, the energies of these transitions are unaffected by polymeric binding as evidenced by comparison with the electronic spectra of monomeric models **9** and **11**. Structured π–π^* absorptions of modest molar absorptivity ($\epsilon < 10000$) characterize the anthracenyl chromophore in polymers **3** and **5–7**. The model compounds, 9-anthracenecarboxylic acid and 9-anthracenemethanol, exhibit long-wavelength ultraviolet transitions at comparable energies.

^{1}H NMR. While the long relaxation times of polymeric samples cause peak broadening and loss of structural detail in the ^{1}H NMR spectra,[22] determination of peak areas is straightforward and provides a convenient method for analyzing the polymer compositions. Comparison of the

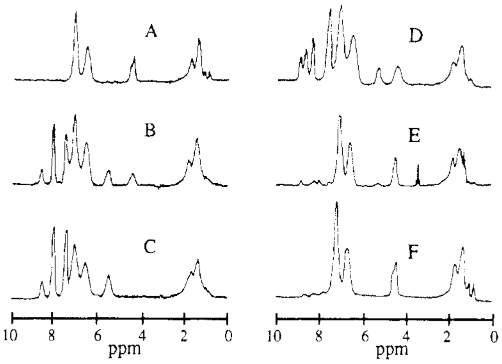


Figure 3. ^{1}H NMR spectra (200 MHz) of modified polymers in CDCl$_3$ vs TMS as internal standard: (a) PS-CH$_2$Cl (**1**), (b) PS-CH$_2$[OC(O)An]$_{15}$ (**3**), (c) PS-CH$_2$[OC(O)An]$_{30}$, (d) PS-CH$_2$[OCH$_2$An]$_{24}$ (**5**), (e) PS-CH$_2$[OC(O)Ru^{II}]$_3$ (**2**), (f) PS-CH$_2$[OCH$_2$Ru^{II}]$_{1.5}$ (**4**).

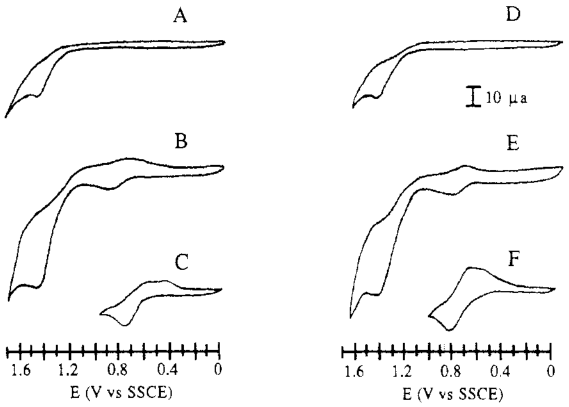


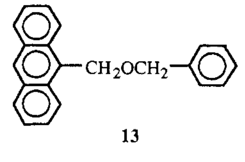
Figure 4. Cyclic voltammetric scans of modified polymers at a 0.1-cm^2 Pt disk electrode in methylene chloride–0.1 M Et$_4$NClO$_4$ at 100 mV/s. Solutions are 5 × 10^{-4} M in anthracene unless noted: (a) PS-CH$_2$[OC(O)An]$_{15}$ (**3**); (b) PS-CH$_2$[OC(O)An]$_{28.5}$[PTZ]$_{1.5}$ (**6**); (c) PS-CH$_2$[OC(O)An]$_{28.5}$[PTZ]$_{1.5}$ (**6**), 5 × 10^{-3} M in anthracene; (d) PS-CH$_2$[OCH$_2$An]$_{24}$ (**5**); (e) PS-CH$_2$[OCH$_2$AN]$_{28.5}$[PTZ]$_{1.5}$ (**7**); (f) PS-CH$_2$[OCH$_2$An]$_{28.5}$[PTZ]$_{1.5}$ (**7**), 5 × 10^{-3} M in anthracene.

signal areas arising from the benzylic protons of the chloromethyl group with those at derivatized sites leads to an estimate of the polymer loading. In addition, integration of appropriate peaks in the aromatic region (δ 7–9) often provides a second determination of sample composition.

The 200-MHz ^{1}H NMR spectra of polymers **1**–**5** are collected in Figure 3. Inspection of spectrum A of copolymer **1** reveals resonances in three distinct spectral regions consistent with the presence of aromatic (δ 7.1, 6.6), chloromethylene (δ 4.4), and aliphatic (δ 0.9–1.7) protons in the starting material. Comparison of the integrated intensity of the aromatic and chloromethylene signals shows a 1:1 ratio of styrene to chloromethylstyrene in agreement with that determined by elemental analysis.

The ^{1}H NMR spectrum of anthracene-modified polymer **3** is shown in Figure 3B. Binding of the anthracene carboxylate to the polymer backbone shifts the benzylic methylene protons to δ 5.4 while the chloromethylene proton signals at unreacted sites remain unchanged (δ 4.4). This assignment was confirmed by the preparation of a polymer in which every chloromethyl site was substituted with anthracene carboxylate. As depicted in Figure 3C, the signal at δ 4.4 is completely absent. In addition, the modified polymer exhibits three downfield resonances not present in the starting copolymer that arise from the anthryl functionality (δ 8.45, 7.93, 7.42). The signal of the proton in the 10-position is well-resolved from the other aromatic peaks and provides an alternate basis for quantitation of the polymer loading.

The ^{1}H NMR spectrum of polymer **5** prepared by etherification of anthracenemethanol is shown in Figure 3D. Four peaks (δ 8.39, 8.18, 7.93, 7.36) consistent with the presence of the anthracenyl moiety are present in the aromatic region in addition to those signals typical of the styrene rings. Both sets of benzylic methylene protons, $-\mathrm{C_5H_4C}H_2\mathrm{OR}$ and $-\mathrm{C_5H_4C}H_2\mathrm{Cl}$, are expected to show similar chemical shifts and are assigned to the peak centered at δ 4.39. The anthryl methylene protons show a resonance at δ 5.27. These assignments were confirmed by study of an appropriate model compound **13** prepared



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by reaction of benzyl bromide and anthracenemethanol according to the procedure of Johnstone and Rose.[19] The ^{1}H NMR spectrum of this compound exhibits two distinct resonances each of integration 2 protons at δ 5.48 and 4.71. The peak areas of the methylene resonances in the polymeric sample when corrected for proton number gave a loading of 80 mol % derivatized anthracene in agreement with elemental analysis data.

The ^{1}H NMR spectrum of the ruthenium-doped polymer **2** is depicted in Figure 3E. Examination of the spectrum reveals peaks in the δ 7.5–9.0 region indicative of the bipyridine group. The tetraethylammonium counterion of unbound carboxylate groups is evidenced by a quartet (δ 3.5) and a triplet (δ 1.4). The integrated peak areas of the two benzylic methylene proton signals in the δ 4–6 region can be used to calculate the fraction of substituted sites.[23] These calculations reveal that approximately 67 mol % of the bound ruthenium complex exists as the diester while 88 mol % is chemically bound at one site.

The polymer-bound bipyridyl complex (**4**) exhibits spectral characteristics similar to that of ruthenium polymer **2** (Figure 3F). Inspection of the aromatic region reveals broad resonances from δ 7.35–8.54 indicative of the bipyridine group. All of the aromatic methylene hydrogens (i.e., $\mathrm{C_6H_4C}H_2\mathrm{O}$–, $\mathrm{C_6H_4C}H_2\mathrm{Cl}$, $-\mathrm{OC}H_2\mathrm{C_{10}H_6N_2}$) appear superimposed at δ 4.4, and, thus, quantitative analysis using ^{1}H NMR is difficult. However, the visible absorption spectrum and elemental analysis proved successful for the determination of the polymer loading and were in agreement within resonable experimental limits.

Electrochemistry. The oxidative electroactivity of the polymer-bound redox sites was examined by cyclic voltammetry at scan rates of 100 mV/s in deaerated solutions of methylene chloride containing 0.1 M tetra-*n*-butylammonium perchlorate. All potentials reported are referenced to the sodium-saturated calomel electrode (SSCE). In the potential windows studied, the polymeric backbone **1** is electroinactive.

Anthracene-modified polymers **3** and **5** (parts A and D of Figure 4) exhibit irreversible oxidations at $E_{\mathrm{p,a}} = 1.45$ V and $E_{\mathrm{p,a}} = 1.42$ V, respectively, typical of anthracene and anthracenyl derivatives in which the reactive 9- and 10-positions are not blocked or stabilized by substitution.[24] One-electron oxidation of anthracene generates a short-lived cation radical, which undergoes rapid reaction with residual water coupled with further oxidative electron transfer to form a variety of products.[25] Only in very nonnucleophilic media (i.e., dichloromethane containing suspended alumina or a dichloromethane solution of trifluoroacetic acid and trifluoroacetic anhydride) has the reverse reduction of the anthracene cation radical been observed.[26] In addition, the oxidative peak potentials of the polymeric samples correspond within experimental error to those observed for appropriate monomeric models obtained under identical conditions. Methyl 9-anthracenecarboxylate and benzyl methyl-9-anthryl ether **13** exhibit irreversible oxidations at 1.44 and 1.42 V, respectively.

The electrochemical behavior of bifunctional polymers **6** and **7** each containing derivatized anthracene and phenothiazene is depicted in parts B–E of Figure 4. In solutions 5×10^{-4} M in anthracenyl groups, the cyclic voltammograms of polymers **6** and **7** show the characteristic irreversible oxidation of the anthracenyl sites (Figure 4B,E) at $E_{p,a} = 1.46$ and 1.43 V, respectively. The polymers are dilute in phenothiazene sites, and the oxidation of phenothiazene to its cation radical is more clearly visible at higher polymer concentrations (parts C and F of Figure 4, 5×10^{-3} M in anthracenyl sites). The observed oxidations are quasi-reversible and occur at more anodic potentials (**6**, $E_{p,a} = 0.93$ V; **7**, $E_{p,a} = 0.82$ V) than 10-methylphenothiazene (10-PTZ, $E_{1/2} = 0.73$ V). In addition, the reverse reductive peaks are broadened with no well-defined reductive peak potential.

While we have no definitive evidence to assign specific conformations of the bifunctional polymers, it is reasonable that a hydrophobic environment created by the high local concentration of anthracenyl molecules plays a significant role in the modified redox behavior of the PTZ sites. In this poorly solvated surrounding, oxidation of PTZ to its charged cation radical is more difficult relative to monomeric 10-MePTZ, and an anodic shift in the peak potential is observed. Differences in solvation of the electrochemically generated cation radicals may create nonhomogeneous sites along the polymeric chain, giving rise to the broadened return reductive waves observed in the voltammograms. Consistent with this interpretation, polymers that contain a lower concentration of anthracenyl sites ($PS\text{-}CH_2[OC(O)An]_{24}[PTZ]_6$) or no anthracenyl sites ($PS\text{-}CH_2[PTZ]_{1.5}$) show well-defined, reversible phenothiazine oxidations (PTZ/PTZ^+) with $E_{1/2} = 0.72$ V.

The ruthenium polymers **2** and **4** exhibit well-defined, reversible ($\Delta E_p = 60$ mV) oxidative waves corresponding to the $Ru^{II/III}$ couple at $E_{1/2} = 1.40$ and 1.30 V, respectively. These waves remain unchanged after multiple scans and are anodically shifted with respect to those measured for model compounds **9** ($E_{1/2} = 1.37$ V) and **11** ($E_{1/2} = 1.22$ V) in acetonitrile–0.1 M tetraethylammonium perchlorate consistent with a hydrophobic environment around the polymeric metal centers. Bipyridine-based reductions are observed in an initial cathodic scan to −1.8 V, but complete electroinactivity is observed in subsequent cycles because of absorption of the polymer onto the electrode surface. The anticipated electrochemistry is restored after removing the polymeric film by polishing the electrode.

Steady-State Emission. Emission from ruthenium polymers **2** and **4** was observed following excitation (λ 460 nm) into the MLCT absorption band of the ruthenium bipyridyl chromophore. Characteristics of the emission profiles are given in Table I. Polymer **2** contains two chemically distinct emitting chromophores because of the presence of both diester and monoester groups. Overlapping emissions from each of these different metal centers results in a very broad spectrum with a maximum 30 nm to the red of the monomeric complex **9**. In contrast, the pendent ruthenium complexes of polymer **4** are bound at a single site to the polymeric chain, and an emission profile which essentially duplicates that of monomeric complex **11** is observed. The emission quantum yields of the polymeric ruthenium complexes are the same within experimental error as those of the corresponding model compounds, indicating that self-quenching of the excited state is not an important process in these polymers which are dilute in ruthenium(II). Only at very high ruthenium loadings (95–100 mol %) can a significant (25%) reduction in the emission quantum yields be observed. The unusual photophysical properties of these heavily substituted materials are currently under investigation.

Conclusion

The synthetic methodology described here compliments that developed earlier[8] for the preparation of polymers containing bound paraquat and phenothiazene and allows for the stepwise preparation of multifunctional polymers. The procedures represent general methods for the chemical attachment of a variety of functional groups to modified polystyrene ranging from small, neutral organics to large organometallic salts. The modified polymers are readily characterized by UV–visible and ^1H NMR spectroscopies and can be prepared with controlled loadings by varying the stoichiometric ratio of the starting polymer to the nucleophile. Cyclic voltammetry and emission spectroscopy confirm that the excited-state and redox properties of the anthracenyl and the ruthenium sites are maintained upon polymeric attachment with only slight modifications induced by the hydrophobic character of the polymeric chain.

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Registry No. **1**, 54786-26-4; **8**, 1762-42-1; **9**, 83605-49-6; **10**, 117678-72-5; **11**, 117678-74-7; $Ru(bpy)_2Cl_2$, 19542-80-4; NEt_4OH, 77-98-5; 4-(hydroxymethyl)-4′-methyl-2,2′-bipyridine, 81998-04-1.

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Termination in Group Transfer Polymerization[†]

William J. Brittain*[,‡] and Ira B. Dicker

Central Research & Development Department, E. I. du Pont de Nemours & Company, Inc., Experimental Station, Wilmington, Delaware 19898. *Received May 6, 1988; Revised Manuscript Received July 29, 1988*

ABSTRACT: The major pathway for termination in group transfer polymerization (GTP) has been identified as a cyclization process analogous to backbiting in anionic polymerization. Rates of cyclization for oligomer mixtures prepared from methyl methacrylate (MMA) and [(1-methoxy-2-methyl-1-propenyl)oxy]trimethylsilane (P_1*) were determined by FT-IR spectroscopy. A stopped-flow FT-IR study of a discrete cyclization process involving an independently synthesized GTP oligomer P_3* (dp = 3) demonstrated that termination is much slower than propagation. As chain length of the living GTP oligomer increases, the rate of cyclization decreases by more than an order of magnitude. Detailed product analysis for the oligomer mixture prepared from 3:1 MMA:P_1* revealed that, for oligomers whose dp = 4–9, depolymerization of MMA can occur. Termination was more rapid for tris(piperidino)sulfonium bifluoride (TPSHF$_2$) than tetrabutylammonium bibenzoate (TBABB) catalyzed reactions, in accord with previously reported catalyst reactivity in GTP propagation.

Group transfer polymerization (GTP) of methacrylates affords polymers whose degree of polymerization is dictated by the stoichiometry of initiator and monomer.[1-3] GTP proceeds by transferring a reactive group to the incoming monomer, yielding a so-called "living end". GTP proceeds smoothly at room temperature and yields polymers with a narrow molecular weight distribution. We have now identified and characterized the major mode of termination in GTP. This paper details the study of oligomer mixtures by in situ FT-IR and product analysis of quenched aliquots. We have also studied the termination reaction as a single event by the independent synthesis of an intermediate oligomer.

Experimental Section

Materials. Tetrahydrofuran (THF) and pentane were distilled from sodium and benzophenone. Solvents were stored and handled in a drybox. Commercially available methyl methacrylate was passed through a short column of neutral alumina in the drybox to remove inhibitors and acidic impurities. [(1-Methoxy-2-methyl-1-propenyl)oxy]trimethylsilane (P_1*) was prepared according to a literature procedure[4] and was slowly distilled twice through a 24-in. spinning band column before use. Tris(piperidino)sulfonium bifluoride (TPSHF$_2$) was prepared according to a previously published procedure.[5] The synthesis of tetrabutylammonium bibenzoate has been described elsewhere.[6] The synthesis of dimethyl 2,4,4-trimethyl-2-[3-methoxy-2-methyl-3-(trimethylsiloxy)prop-2-en-1-yl]glutarate, P_3*, was described in a previous publication.[5] By that method, P_3* is obtained as a 87:13 mixture of *Z*:*E* geoisomers.

Methods. ^{1}H NMR spectra were recorded with either a Nicolet NT300/WB or GE QE300 spectrometer. ^{29}Si and ^{13}C NMR spectra were recorded with a Nicolet NT300/WB spectrometer. The stopped-flow apparatus has been described in a previous publication.[5] FT-IR spectra were recorded with either a Nicolet 170SX or 20SXB spectrometer.

Oligomer Characterization. For the 3:1 MMA:P_1* oligomer mixture, detailed product compositions were determined as a function of time. Aliquots were quenched in methanol, and the amounts of linear and cyclic oligomers were analyzed by gas and gel permeation chromatographies. Calibrated product distributions for oligomers up to dp = 6 were determined by using an internal standard (*n*-decane) in GC analysis. GC analyses were performed on a Hewlett-Packard 5890A chromatograph with a FID detector using a Macrobore DB1-30M (1.5-μm film) column. The identity of components was ascertained by comparison to elution times of authentic samples and by GC/MS identifications. Calibration of detector response was possible for MMA, P_1, P_2, P_3^c, P_3, P_4^c, and P_4; it was assumed that higher oligomers had a response similar to that of P_4^c and P_4. GC/MS data were obtained

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[†] Contribution no. 4726.

[‡] Present address: E. I. du Pont de Nemours & Co., B-22, P.O. Box 1217, Parkersburg, WV 26102.

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