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Surface Attachment of Well-Defined Redox-Active Polymers and Block Polymers via Terminal Functional Groups

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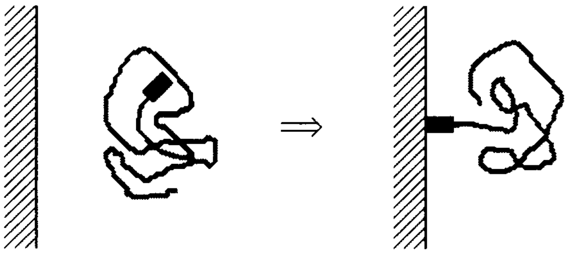
Abstract: Redox-active polymers and block polymers containing terminal groups for covalent attachment to surfaces have been prepared and characterized. Ferrocene- and phenothiazine-based redox-active polymers were prepared by ring-opening metathesis polymerization (ROMP) using Mo initiators of the type $Mo(CHR)(NAr)(O\text{-}t\text{-}Bu)_2$ (R = *tert*-butyl or ferrocenyl, Ar = 2,6-diisopropylphenyl). The functional end groups introduced for surface attachment chemistry were $Si(OEt)_3$, pyridyl, bromobenzyl, and pyrenyl derivatives. Polymers containing $Si(OEt)_3$ were successfully used to derivatize Pt, $In_2(Sn)O_3$, and n-Si electrodes, whereas analogues of those same polymers lacking $Si(OEt)_3$ groups do not bind to these surfaces. Polymers terminated with pyridyl or bromobenzyl groups, introduced in the capping reaction using the appropriate aldehydes, react with electrodes pretreated with benzyl chloride or pyridine groups, respectively, to give polymer-derivatized surfaces. Pyrene-capped polymers were made in an attempt to bind the polymers to carbon electrodes via selective pyrene adsorption. However, the polymer itself strongly adsorbs, precluding a specific role for the pyrene group. On the basis of the surface coverage found for the redox-active groups ($\sim 1 \times 10^{-10}$ mol cm^{-2}) and polymers ($\sim 8 \times 10^{-12}$ mol cm^{-2}) at the electrode surfaces, bound polymer chains hinder the access of unbound polymers to portions of the surface, thereby yielding a lower density of bound polymer than would be expected were the chain to extend away from the electrode surface.

We wish to report the preparation and characterization of redox-active polymers and block polymers that can be attached to electrode surfaces by chemistry associated with the end group of the polymer, Scheme I. Ring-opening metathesis polymerization (ROMP)[1,2] followed by a Wittig-like capping reaction with the appropriate aldehyde can be used to prepare such redox-active materials.[3] Attaching molecules to electrode surfaces in order to modify electrochemical properties is an area of wide interest,[4-7] and many methods for immobilizing reagents on surfaces to produce chemically modified electrodes have been developed.[8-10] Research in the areas of catalysis[11] and chromatography[12] has also led to the development of schemes for adsorbing or covalently bonding discrete molecules to surfaces. We are interested in applying ROMP techniques to prepare multifunctional polymers and capping such polymers with a terminal group, in order to attach them to electrode surfaces with a degree of orientation of the polymer with respect to the polymer/electrode interface.

Scheme I. Strategy for Linking Polymers to a Surface via a Terminal Functional Group



One of the more versatile methods of derivatizing a surface is to couple a silane derivative to a surface oxide via a siloxane bond.[13,14] This method is well-suited to electrode modification because of the presence of oxide surface layers on many electrode materials, such as Pt, $In_2(Sn)O_3$, Si, and C.[4] Films that are bound to a surface via siloxane linkages are also durable. Monofunctional silane reagents (e.g., $R(CH_3)_2SiCl$) can be used to form monolayers via single-point attachment of the molecule to the surface.[15] Similarly, typical organic[16,17] or inorganic[11,18,19] reactions can be carried out between a reactant that is surface-bound and a reactant in solution to produce a modified surface. The pyridyl group has been previously studied, in this regard, in reactions with small molecular reactants.[16,19] Another method for the surface attachment of molecules is the specific adsorption of aromatic hydrocarbons[18,20] and quinones[21] onto carbon surfaces. The adsorption process is usually fast and produces a relatively durable modified electrode.

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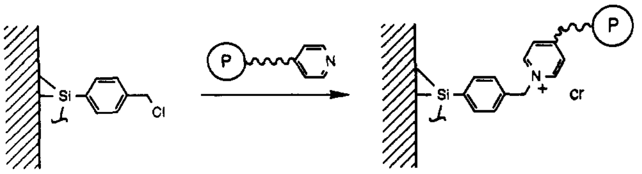
Scheme II. Attachment of a Polymer via Nucleophilic Attack of a Terminal Pyridine on a Surface-Confined Benzyl Chloride



The foregoing attachment schemes have been applied primarily to binding molecular reagents to electrode surfaces. Little analogous work has been done using redox-active polymers that contain some of the functional groups noted above. Typically, redox-active polymers (either preformed or ones prepared *in situ*) have been bound to electrodes by nonspecific adsorption.[22] They remain on the electrode because they are not soluble in the solvent/electrolyte medium. Recent work by McCarthy and co-workers[23] has demonstrated that polystyrene with S-containing or carboxylic acid end groups adsorbs onto appropriate surfaces, whereas polymers without the end group do not.

We report here results of investigations of the surface attachment of polymers via alkoxysilyl groups, organic nucleophiles, organic electrophiles, or polycyclic aromatic groups that have been introduced in the terminal position of polymers prepared by ROMP.[1,2] For example, the methodology for attachment of polymer chains using organic nucleophiles is illustrated in Scheme II. We have previously demonstrated the utility of ROMP by using initiators of the type $Mo(CH\text{-}t\text{-}R)(NAr)(O\text{-}t\text{-}Bu)_2$ (R = *tert*-butyl or ferrocenyl, Ar = 2,6-diisopropylphenyl) for preparing homopolymers and block polymers containing redox-active blocks and/or end groups.[3] Because this ROMP reaction is a living polymerization, the primary structure of the polymer, meaning the size and the nature of the blocks and the end groups, can be controlled as well as is possible for a polymerization reaction and the resulting polymers are nearly monodisperse. A key feature is the tolerance of the Mo catalyst toward a wide range of functional groups.[3,24] We have shown in an earlier paper that functional groups that can bind to electrode surfaces can be incorporated readily into well-defined redox polymers prepared by ROMP techniques.[25,26] In block polymers, the relative position of the surface linking group to the polymer blocks can be controlled according to the order in which the monomers are introduced in the polymerization. The terminal group used for surface binding is introduced last in a well-defined stoichiometric reaction. Therefore, the polymer chain can be attached to the surface through a single covalent bond between the surface and the polymer.

Experimental Section

General Procedures. All chemicals used were reagent grade. Tetrahydrofuran (THF) was distilled from CaH_2 or Na benzophenone ketyl under N_2 immediately prior to use. Pyridine was stored over 4-Å molecular sieves. Benzene was stirred with concentrated H_2SO_4, decanted, and distilled under N_2. Anhydrous Et_2O and the solvents used in chromatography were used as received. Silica gel (230–400 mesh) was used in chromatography. Octamethylferrocenecarboxaldehyde,[27] bis(2-phenothiazin-10-ylethyl) *trans*-5-norbornene-2,3-dicarboxylate (**2**),[3] *trans*-(*exo*,*endo*)-2-carbomethoxy-(*endo*,*exo*)-3-ferrocenyl-5-norbornene (**3**),[3] and $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$[28] and $Mo(CH\text{-ferrocenyl})(NAr)(O\text{-}t\text{-}Bu)_2$[3] (Ar = $2,6\text{-}i\text{-}Pr_2C_6H_3$) were prepared and purified as previously described. Other reagents were obtained from commercial sources. Norbornene (NBE) was distilled from molten sodium, and 5-norbornene-2-methanol was distilled under N_2. 4-Fluorobenzaldehyde, *N,N*-dimethyl-*p*-aminobenzaldehyde, and 4-pyridinecarboxaldehyde were purified by passage through a 5-cm column of activated alumina immediately prior to use. α-Bromo-*p*-tolualdehyde was recrystallized from Et_2O. $[n\text{-}Bu_4N]PF_6$ electrolyte was recrystallized from 95% ethanol and dried under vacuum.

^1H NMR spectra were recorded on either a Varian XL or Gemini 300-MHz FT spectrometer; ^{13}C NMR spectra were recorded on the same instruments at 75.4 MHz. Chemical shifts were measured by employing the residual protic solvent resonance relative to Me_4Si, δ 0.0. Electronic absorption spectra were obtained on a HP 8452A spectrophotometer using 1.00-cm path length quartz cuvettes. Mass spectrometry was done on a Finnigan MAT System 8200 with a double-focusing magnetic sector by electron impact (70 eV). Melting points were obtained with a Thomas capillary melting point apparatus and are uncorrected. Elemental analyses were done by Schwartzkopf Microanalytical Lab, Woodside, NY.

5-Norbornenyl-(*endo*,*exo*)-2-(methoxycarbonyl)ferrocene. The preparation of (chlorocarbonyl)ferrocene was adapted from the literature.[29] Ferrocenecarboxylic acid (2.1 g, 9.1 mmol) was added to 30 mL of benzene in which PCl_5 (2.2 g, 10.0 mmol) was suspended. The red solution was stirred for 2 h at room temperature. The reaction mixture was filtered, and the filtrate was concentrated under vacuum. The residue was taken up in hexane, washed with H_2O, dried over $MgSO_4$, and filtered, and the solvent was removed by rotary evaporation. The acid chloride was dissolved in THF and added to a three-necked, 100-mL flask fitted with a condenser, gas adapter, septa, and stir bar, which contained 30 mL of THF, pyridine (1.5 mL, 20 mmol), and 5-norbornene-2-methanol (1.2 mL, 10 mmol). The solution was stirred at reflux for 20 h and then worked up with $CHCl_3$ and H_2O. Chromatography (1:19 ethyl acetate:hexane) yielded 1.60 g (52%) of product, which was recrystallized from ether as orange prisms. The product was a 9:1 mixture of the *endo* and *exo* isomers, as determined by ^1H NMR: R_f (1:19 ethyl acetate:hexane) 0.34; mp 96–99 °C; ^1H NMR (C_6D_6) δ 0.45 (1H, m), 1.05 (1H, m), 1.42 (1H, m), 1.62 (1H, m), 2.38 (1H, m), 2.57 (1H, m), 2.87 (1H, m), 3.87 (1H, m), 4.04 (8H, m), 4.90 (2H, m), 5.95 (1H, m), 5.98 (1H, m); ^{13}C NMR (C_6D_6) δ 28.8, 38.2, 42.2, 44.1, 49.3, 67.4, 69.7, 70.3, 71.1, 80.2, 132.4, 137.7, 171.0; UV–vis (THF) λ_{max} nm (log ϵ) 304 (2.99), 340 (sh), 442 (2.35); MS (relative abundance) 336 (M^+, 96), 270 ($M - C_5H_6^+$, 100), 230 ($FeC_{10}H_9CO_2H^+$, 95), 185 ($FeC_{10}H_9^+$, 11), 121 ($FeC_5H_5^+$, 25). Anal. Calcd for $C_{19}H_{20}FeO_2$: C, 67.88; H, 6.00; Fe, 16.61. Found: C, 67.97; H, 6.10; Fe, 16.83.

Polymer Syntheses. Polymer syntheses were carried out under N_2 in a Vacuum Atmospheres drybox. The Mo initiator, $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ or $Mo(CH\text{-ferrocenyl})(NAr)(O\text{-}t\text{-}Bu)_2$ (Ar = $2,6\text{-}i\text{-}Pr_2C_6H_3$) (5–10 mg), was dissolved in THF (1 mL). The appropriate number of equivalents of a monomer was dissolved in THF (1 mL) and the solution injected into the well-stirred catalyst solution. After an appropriate reaction time, either a second monomer was added in a similar manner or the living polymer was terminated by adding 3–5 equiv of an aldehyde. When a series of related polymers was prepared, the solution of the living polymer was divided at the latest possible point. The polymers were purified by precipitating them twice in hexane, collecting them by centrifugation, and then drying them under vacuum. Polymers made using 5-(triethoxysilyl)norbornene (**1**) were handled exclusively in a drybox. Gel permeation chromatography (GPC) analyses of CH_2Cl_2 solutions (0.1–0.3 w/v %) were done using Shodex KF 802.5, 803, 804, 805, and 800P columns, a Knauer differential refractometer, and a Spectroflow 757 absorbance detector.

Representative preparations of these types of polymers have been described previously.[3] All polymers were characterized by ^1H and ^{13}C NMR. The ratio of end groups in all polymers was found to be 1:1. This was established by ^1H NMR, except in the case of polymers with redox-active groups at both ends,[3] where the end group ratio of 1:1 was determined via electrochemical measurements. Polymers containing **1** were not

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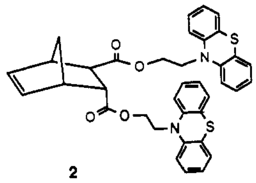
characterized by GPC or differential scanning calorimetry (DSC) due to the reactivity of the $Si(OEt)_3$ group. Instead, polymers made from the same living polymer but not containing **1** were characterized. The DSC and GPC characterization of Fc-$(\mathbf{2})_5$-$FcMe_8$, $(\mathbf{2})_{15}$, and $(\mathbf{2})_{30}$[3] and the GPC characterization of $(\mathbf{4})_{12}$-pyrene[25] are among those previously reported. The polydispersity of the other polymers used was $(\mathbf{2})_{15}$-pyrene, 1.23; $(\mathbf{2})_{10}$ and $(\mathbf{2})_{10}$-pyridine, 1.70; and $(\mathbf{3})_{15}$-BzBr, 1.22, as determined by GPC.

Electrochemical Measurements. Electrochemical experiments were done using conventional three-electrode cells, with a Pine Instruments RDE 4 bipotentiostat modified for low-current sensitivity. Cyclic voltammograms were recorded on a Kipp and Zonen BD 91 X-Y recorder. The solvent/electrolyte was purged with Ar before use. The Ag quasi-reference electrode was prepared by dipping a Ag wire in concentrated HNO_3, rinsing with H_2O and CH_3OH, and drying. The counter electrode was a large piece of Pt. Pt disk electrodes were prepared by sealing Pt wire in soft glass. The electrode was polished with 3- and 1-μm diamond paste (Buehler) to a mirrorlike finish. For derivatizations with a $Si(OEt)_3$ reagent the electrode was anodized to form an oxide layer on the surface by holding the potential at 1.30 V in 0.5 M H_2SO_4 until the current decayed to the background level and then removing it from potential control.[29] Indium(tin) oxide (ITO) electrodes were made from 50- × 7-mm slabs of ITO coated on glass (Delta Technologies, Stillwater, MN) that were cut in thirds. The ITO surface was scrubbed with warm, soapy H_2O, rinsed copiously with H_2O, and dried before use. n-Si electrodes were fabricated, pretreated, derivatized, and examined as previously described.[31] Glassy carbon electrodes, 3-mm disks inlaid in a Teflon mount, were obtained from BAS: Bioanalytical Systems, West Lafayette, IN. The electrodes were polished before each experiment using 1-μm diamond polish, then sonicated in CH_3OH for 10 min, and rinsed copiously with the electrochemical solvent.

Results and Discussion

In addition to norbornene (NBE), monomers **1**–**4** were used to prepare a variety of polymers that are shown in Chart I. Two strategies are employed for incorporating the active terminal groups. One strategy is to use a norbornenyl monomer that contains a functional group known to be useful for attaching molecular reagents to surfaces. For example, ROMP of a redox-active monomer such as **2** followed by the introduction of 2 equiv of **1** followed by capping with an aldehyde yields a polymer with a short sequence at the end of the polymer that contains the $Si(OEt)_3$ units, which are known to be useful for linking molecules to oxides. The second strategy is to terminate the living polymer with an aldehyde that contains a functional group (e.g., pyrene, pyridine, or benzyl bromide) of possible use in surface attachment. The following sections describe the results of studies directed toward establishing the viability of these strategies.

1



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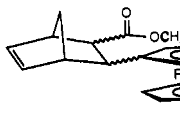

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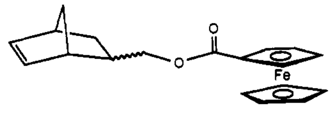

4

Use of (Triethoxysilyl)norbornene To Introduce a Surface Binding Group in Redox-Active ROMP Polymers. Triethoxysilyl groups, $Si(OEt)_3$, have been incorporated into two phenothiazine-containing polymers (Fc-$(\mathbf{2})_5(\mathbf{1})_2$-$FcMe_8$ and $(\mathbf{2})_{30}(\mathbf{1})_2$) and two ferrocene-containing block polymers ($(\mathbf{(3)}_m(\mathrm{NBE})_n(\mathbf{1})_p$ and $(\mathrm{NBE})_n(\mathbf{3})_m(\mathbf{1})_p$). Incorporating $Si(OEt)_3$ groups into a polymer employing **1** implies that the number of units of **1** per polymer chain will vary about an average. In order to maximize the number of separate polymer chains that may form bonds to the surface and yet minimize polymer cross-linking, only 1 or 2 equiv of **1** was employed. NMR data show that the $Si(OEt)_3$ groups were incorporated in the expected amount. However, some polymer chains may contain no **1** while others may contain several equivalents of **1** due to differences in the rate of block initiation and propagation and the statistical nature of chain growth.[32] However, only polymers containing **1** are expected to bind to the surface. Polymers lacking **1** were also synthesized in order to perform control experiments (cf. Chart I).

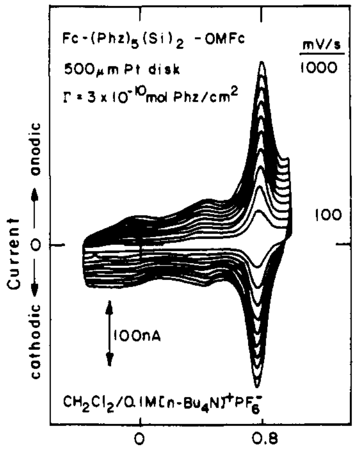

Figure 1. Scan-rate dependence of the cyclic voltammetry for a Pt electrode derivatized with Fc-$(\mathbf{2})_5(\mathbf{1})_2$-$FcMe_8$ in CH_2Cl_2/0.1 M $[n\text{-}Bu_4N]PF_6$ from 100 to 1000 mV s^{-1} in 100 mV s^{-1} increments. The coverage of phenothiazine groups is determined, from electrode area and integration of the current at slow scan rate, to be 3×10^{-10} mol cm^{-2}, and the coverage of the polymer is calculated to be 3×10^{-11} mol cm^{-2}.

Because more than one $Si(OEt)_3$ group may be present, derivatization of electrode surfaces was carried out under conditions designed to minimize silanol formation and condensation in the bulk solvent. The surface to be derivatized was immersed in a dry benzene solution of the polymer. The deliberate addition of H_2O is unnecessary since surface hydration and surface hydroxyl groups are sufficient for promoting siloxane bond formation at a surface.[33]

Treatment of a Pt electrode (pretreated to have an oxide layer)[30] by immersion in a benzene solution of Fc-$(\mathbf{2})_5(\mathbf{1})_2$-$FcMe_8$ for 14 h yields electrodes with persistently bound polymer. As shown in Figure 1, cyclic voltammograms of the derivatized electrode in CH_2Cl_2/0.1 M $[n\text{-}Bu_4N]PF_6$ reveal persistent redox waves for the octamethylferrocene (–0.05 V), ferrocene (0.40 V), and phenothiazine (0.80 V) units of the polymer. The position and relative areas of the waves are in accord with the polymer composition. The amount of material bound to the electrode surface is found by measuring the amount of charge associated with the oxidation of the redox centers. On the basis of the

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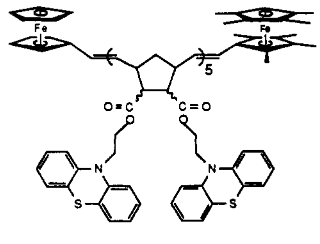
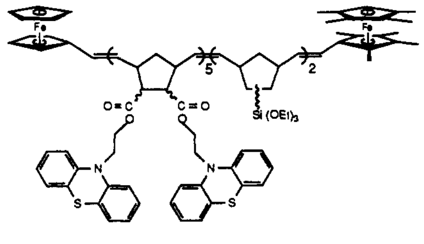
(34) Throughout this article, it is assumed that *all* redox-active centers in the polymer are being oxidized and reduced by the electrode when calculating the surface coverage of electroactive material. In the case of Fc-$(\mathbf{2})_5(\mathbf{1})_2$-$FcMe_8$, the observed cyclic voltammetric response supports this assumption since the charge associated with each of the redox couples is found to be in the same proportion as that of the polymer composition. Also, in solution electrochemical studies using similar redox polymers prepared by ROMP techniques, it has previously been shown that all redox-active sites in the polymer undergo redox reactions at the electrode (ref 3).

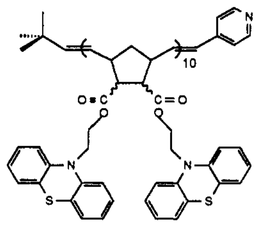
Chart I



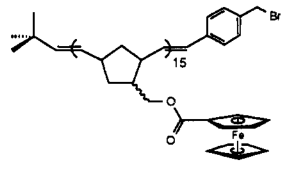
Fc-(**2**)$_5$-FcMe$_8$



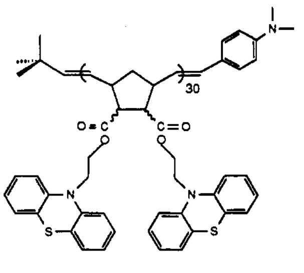
Fc-(**2**)$_5$(**1**)$_2$-FcMe$_8$



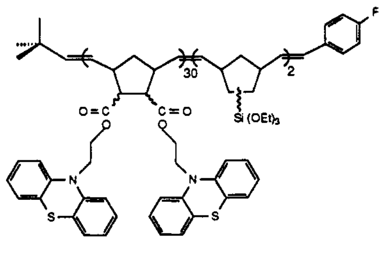
(**2**)$_{10}$-pyridine



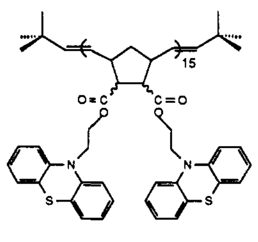
(**4**)$_{15}$-benzyl bromide



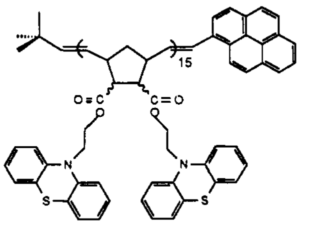
(**2**)$_{30}$



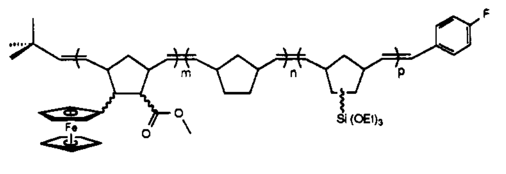
(**2**)$_{30}$(**1**)$_2$



(**2**)$_{15}$

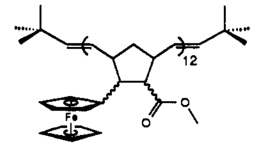


(**2**)$_{15}$-pyrene

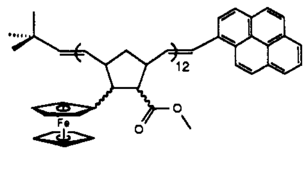


(**3**)$_m$(NBE)$_n$(**1**)$_p$

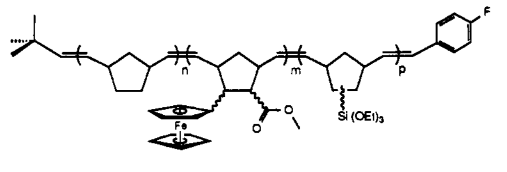
m=n=30, p=10 and m=15,n=60, p=2



(**3**)$_{12}$



(**3**)$_{12}$-pyrene



(NBE)$_n$(**3**)$_m$(**1**)$_p$

n=m=30, p=10 and n=60, m=15, p=2

phenothiazine wave, the coverage was found to be 3×10^{-10} mol cm^{-2} of **2**, or 3×10^{-11} mol cm^{-2} of polymer.[34] In the same electrolyte medium, the polymer containing no **1**, Fc-(**2**)$_5$-FcMe$_8$, does not persistently adhere to the surface, even after oxidative deposition, Figure 2. The electrode was poised at 0.95 V for 10, 20, and 30 s in consecutive sets of voltammograms at the same electrode. The stripping wave increased with the amount of charge passed in the oxidation, but subsequent scans showed that the cyclic voltammograms regained their original wave shape. Material does not accumulate on the electrode to result in either enhanced currents due to surface-confined material or loss of activity due to decomposition and fouling.

A set of longer polymers (30-mer vs 5-mer) of **2** was prepared. Again, the batch of the living 30-mer of **2** was divided in half; one half was terminated with *N,N*-dimethyl-*p*-aminobenzaldehyde, and the other half was treated with 2 equiv of **1** followed by termination with *p*-fluorobenzaldehyde. Pretreated Pt electrodes and In$_2$(Sn)O$_3$ (ITO) electrodes were immersed in separate solutions of (**2**)$_{30}$ and (**2**)$_{30}$(**1**)$_2$. A Pt electrode was soaked in the (**2**)$_{30}$ solution for 8 h and another for 1.5 h in (**2**)$_{30}$(**1**)$_2$. The ITO electrodes were soaked in the two solutions for 12 h. The cyclic voltammograms of these electrodes, after a thorough rinsing with solvent, are shown in Figure 3. Only the 30-mer of **2** containing **1** was found to bind to the electrode surface. The coverages calculated were 5×10^{-10} and 1×10^{-10} mol cm^{-2} of units of **2** for Pt and ITO, respectively. This corresponds to 8×10^{-12} and 2×10^{-12} mol cm^{-2} of polymer, respectively.

n-Si electrodes were also derivatized with (**2**)$_{30}$(**1**)$_2$. As shown in Figure 4, there was no current flow at a derivatized electrode in the dark. Upon illumination with photons of sufficient energy ($E >$ band gap = 1.1 eV), cyclic voltammograms characteristic of a redox couple whose redox potential lies between the valence and conduction band edges[35] were observed. The anodic peak was found at 0.38 V vs SCE, or ~0.4 V negative of the formal potential of phenothiazine at a Pt electrode. This negative shift of the anodic wave represents the photovoltage, or the extent to which light drives the oxidation of phenothiazine in a thermodynamically uphill sense. Turning off the light at the positive scan limit results in dark reduction of phenothiazine, after which no more charge passed upon further cycling. The observed coverage was 2.6×10^{-10} mol cm^{-2} of phenothiazine, or 4×10^{-12} mol cm^{-2} of polymer.

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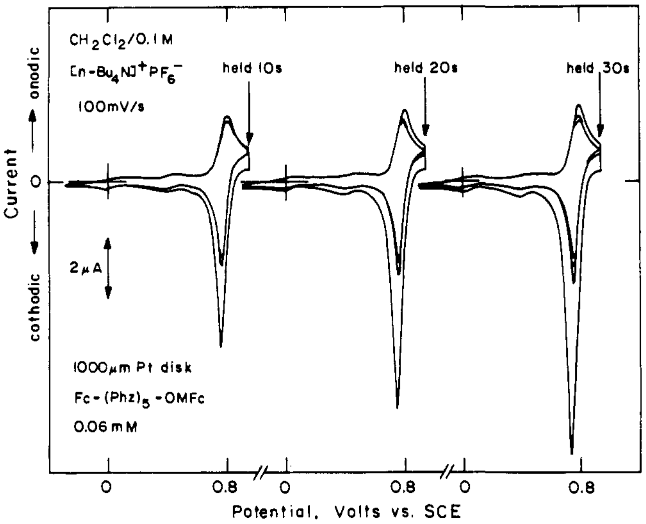

Figure 2. Solution electrochemistry of Fc-(**2**)$_5$-FcMe$_8$, 0.06 mM, in CH$_2$Cl$_2$/0.1 M [*n*-Bu$_4$N]PF$_6$. In this consecutive series of voltammograms using the same electrode, the electrode potential was held at the positive limit for the specified time, 10, 20, and 30 s, respectively, and then cycled 3 times at 100 mV s^{-1}.

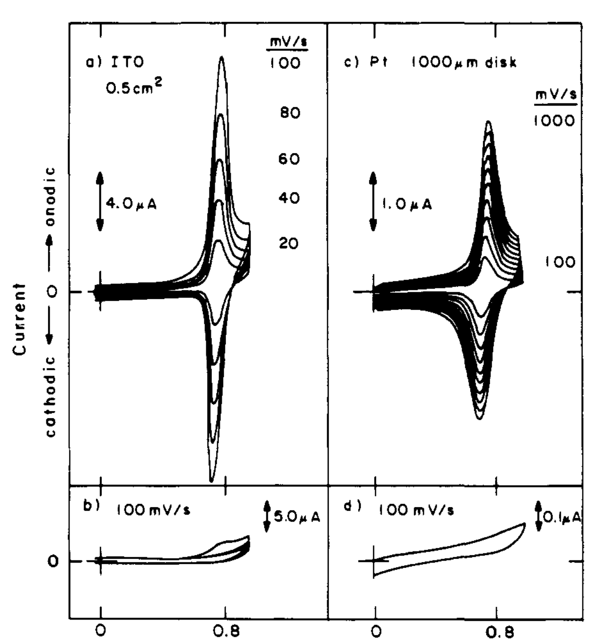

Figure 3. Cyclic voltammetry of (a) an ITO electrode that was soaked in a benzene solution of (**2**)$_{30}$(**1**)$_2$ for 12 h as a function of scan rate, (b) an ITO electrode that was soaked in a benzene solution of (**2**)$_{30}$ for 12 h at 100 mV s^{-1}, (c) a Pt electrode soaked in a benzene solution of (**2**)$_{30}$(**1**)$_2$ for 90 min as a function of scan rate, and (d) a Pt electrode that was soaked in a benzene solution of (**2**)$_{30}$ for 8 h at 100 mV s^{-1}. The coverage of phenothiazine on ITO in (a) was determined to be 1 × 10^{-10} mol cm^{-2} and on Pt in (c), 5 × 10^{-10} mol cm^{-2}, corresponding to a coverage of the polymer of 8 × 10^{-12} and 2 × 10^{-12} mol cm^{-2}, respectively.

Two sets of ferrocene-containing block polymers, (**3**)$_m$(NBE)$_n$(**1**)$_p$ and (NBE)$_n$(**3**)$_m$(**1**)$_p$, (cf. Chart I) were prepared in which the positions of the ferrocene-containing block and the block of NBE in relation to the Si(OEt)$_3$ groups are reversed. Pretreated Pt electrodes were immersed in benzene solutions of each of the polymers for 12 h. The electrodes were removed, rinsed with CH$_3$CN, and examined by cyclic voltammetry in CH$_3$CN/0.1 M [*n*-Bu$_4$N]PF$_6$. The results shown in Figure 5 for (**3**)$_m$(NBE)$_n$(**1**)$_p$ and (NBE)$_n$(**3**)$_m$(**1**)$_p$ ($n = m = 30$ and $p = 10$) are similar for all four polymers. The surface coverage was found to be in the range of 6–8 × 10^{-10} mol cm^{-2} (moles of redox sites per cm^2). Despite the different primary structures of the polymers, no significant differences in the electrochemical behavior were observed at scan rates from 5 mV/s to 1 V/s. This suggests that the polymer conformation at the surface (probably a random coil) is flexible enough for all ferrocene sites to communicate with the electrode. Pretreated Pt electrodes were also immersed for 12 h in solutions of (NBE)$_{15}$(**3**)$_{15}$ and (NBE)$_{60}$(**3**)$_{15}$, but no surface-bound redox-active material was observed by cyclic voltammetry for these polymers which do not contain any Si(OEt)$_3$ groups.

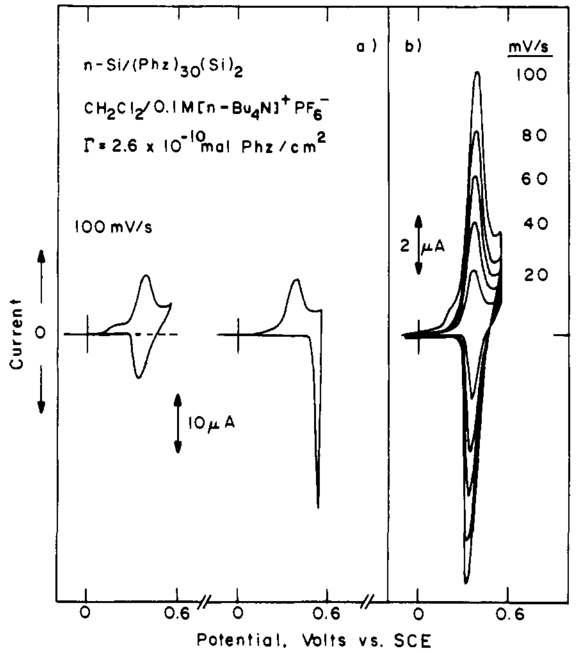

Figure 4. (a) Cyclic voltammetric behavior of an n-Si electrode derivatized with (**2**)$_{30}$(**1**)$_2$ in CH$_2$Cl$_2$/0.1 M [*n*-Bu$_4$N]PF$_6$ in the dark (– – –) and illuminated (—), on the left, and on the right, with light source turned off at the positive scan limit. (b) Scan-rate dependence of the cyclic voltammetry for the same electrode of n-Si derivatized with (**2**)$_{30}$(**1**)$_2$ under illumination. The coverage was determined to be 2.6 × 10^{-10} mol cm^{-2} of phenothiazine, corresponding to a coverage of 4 × 10^{-12} mol cm^{-2} of polymer.

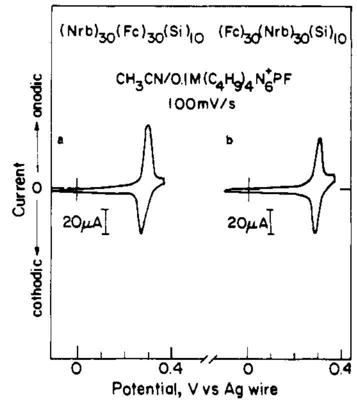

Figure 5. Cyclic voltammetry in CH$_3$CN/0.1 M [*n*-Bu$_4$N]PF$_6$ at 100 mV s^{-1} of Pt electrodes derivatized with (a) (NBE)$_{30}$(**3**)$_{30}$(**1**)$_{10}$ and (b) (**3**)$_{30}$(NBE)$_{30}$(**1**)$_{10}$, prepared by soaking pretreated Pt electrodes in a benzene solution of each polymer for 14 h. The coverage of ferrocene was determined to be 2.3 × 10^{-10} mol cm^{-2} and 1.8 × 10^{-10} mol cm^{-2}, respectively, corresponding to a coverage of the polymer of 7.7 × 10^{-12} mol cm^{-2} and 6.0 × 10^{-12} mol cm^{-2}, respectively.

As a terminal functional group of a polymer, the Si(OEt)$_3$ group is found to bind the polymer to an electrode surface. The control experiments comparing redox-active polymers with and without a short segment of Si(OEt)$_3$ groups clearly demonstrate the Si(OEt)$_3$ group to be useful in achieving persistent binding of the polymer to a surface.

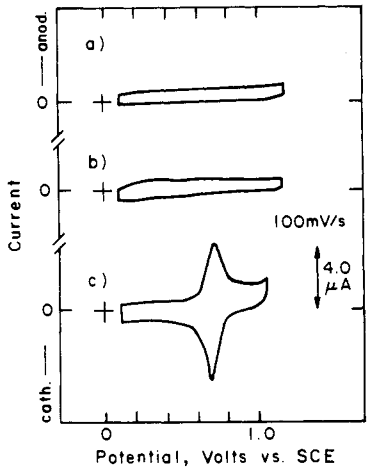

Figure 6. Cyclic voltammograms at 100 mV s^{-1} for (a) an untreated ITO electrode, (b) an ITO electrode treated with (*p*-(chloromethyl)phenyl-)trichlorosilane followed by a 24-h soak in a CH_2Cl_2 solution of $(\mathbf{2})_{10}$, and (c) an ITO electrode treated with (*p*-(chloromethyl)phenyl)trichlorosilane followed by a 24-h soak in a CH_2Cl_2 solution of $(\mathbf{2})_{10}$-pyridine. The coverage in (c) was determined to be 1.0×10^{-10} mol cm^{-2} of phenothiazine, corresponding to a coverage of 5×10^{-12} mol cm^{-2} of polymer.

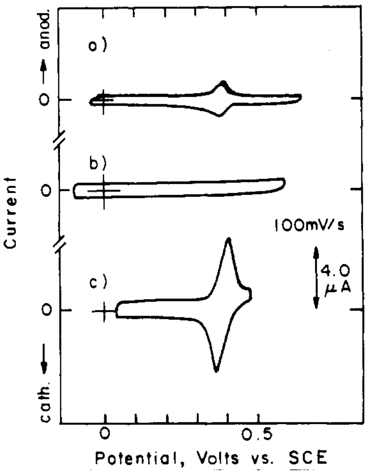

Figure 7. Cyclic voltammograms at 100 mV s^{-1} for (a) an untreated ITO electrode, (b) an ITO electrode treated with hexamethyldisilazane, and (c) an ITO electrode treated with 4-[2-(trichlorosilyl)ethyl]pyridine, which were immersed in separate solutions of $(\mathbf{4})_{15}$-benzyl bromide for 24 h. The coverage of ferrocene units is determined to be 6×10^{-12} mol cm^{-2} in (a) and 1.1×10^{-10} mol cm^{-2} in (c).

One must also consider the possibility of condensation reactions of $Si(OEt)_3$ groups of the polymers, producing larger aggregates that could bind to surfaces by nonspecific adsorption or precipitation. However, in all experiments performed, coverages on the order of 10^{-11} mol cm^{-2} of polymer were found without exception and the coverage was independent of the derivatization time up to 16 h. Moreover, derivatization solutions showed no signs of precipitate formation in this time. Since precipitation would, seemingly, yield time-dependent increases in coverage, we feel that the model of surface attachment via siloxane bonds between the polymer and the surface oxide is justified.

Use of Pyridine or Benzyl Bromide as a Terminal Group for Surface Attachment of ROMP Polymers. Reactions between a nucleophile at the terminus of a polymer and an electrophile bound to a surface can lead to covalently bound polymer molecules, as shown in Scheme II. The reverse situation, with regard to the reactants, is also possible. Both approaches were examined.

A polymer of **2** was terminated with 4-pyridinecarboxaldehyde to produce a polymer having a nucleophilic end group, $(\mathbf{2})_{10}$-pyridine. As a control, part of the same living polymer was terminated with pivaldehyde to give $(\mathbf{2})_{10}$. ITO electrodes were first treated with (*p*-(chloromethyl)phenyl)trichlorosilane and then soaked at room temperature in CH_2Cl_2 solutions containing $(\mathbf{2})_{10}$ or $(\mathbf{2})_{10}$-pyridine for 24 h. The cyclic voltammograms for electrodes recorded after this pretreatment are shown in Figure 6. In the cyclic voltammogram of the treated ITO electrode that was soaked in $(\mathbf{2})_{10}$ solution, Figure 6b, the capacitance of the electrode increased somewhat, but faradaic current associated with phenothiazine was not observed. However, cyclic voltammetry of the treated electrode soaked in $(\mathbf{2})_{10}$-pyridine, Figure 6c, showed a persistent redox wave for phenothiazine, corresponding to a surface coverage of 1×10^{-10} mol cm^{-2} of **2**, or 5×10^{-12} mol cm^{-2} of polymer. Thus, a pyridine-capped polymer

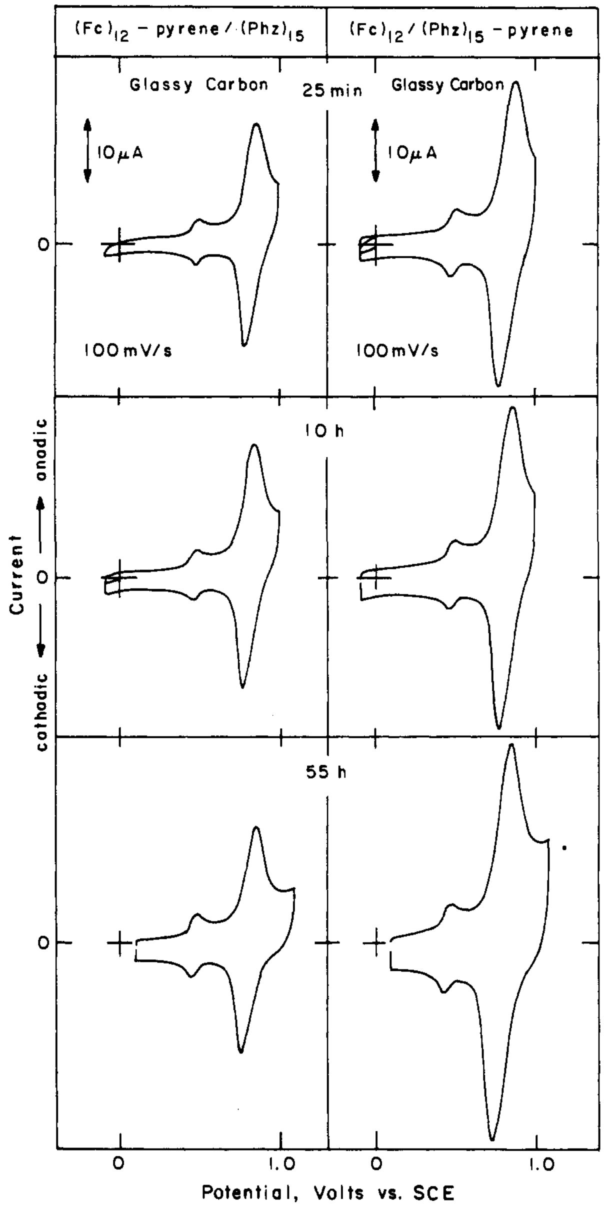

Figure 8. Competitive binding experiment between $(\mathbf{3})_{12}$-pyrene and $(\mathbf{2})_{15}$, and $(\mathbf{3})_{12}$ and $(\mathbf{2})_{15}$-pyrene. Each half of a freshly cleaved 3-mm glassy carbon rod was immersed into a benzene solution containing one of the pairs of polymers (2 mg/mL). The rods were periodically removed from the soaking solution, rinsed thoroughly with benzene, and then checked for their electrochemical response in CH_2Cl_2/0.1 M [*n*-Bu_4N]PF_6. The rods were then rinsed again and placed back into the soaking solution. The figure shows the electrochemical response after 25 min, 10 h, and 55 h of soaking time. The electrode area is estimated to be ~1.4 cm^2. Thus, the total coverage of polymer is determined to be 9×10^{-12} mol cm^{-2} and 1.3×10^{-11} mol cm^{-2}, respectively, with the phenothiazine-containing polymer accounting for 90% of the coverage.

can be linked to the surface via reaction of the pyridine terminus with the surface-confined benzyl chloride.

To illustrate that a terminal electrophile on the polymer can be used for surface attachment, a polymer of **4** was terminated with α-bromo-*p*-tolualdehyde to produce a polymer that was capped with an electrophile, $(\mathbf{4})_{15}$-benzyl bromide. The complementary nucleophilic reactant for this polymer, a surface-bound pyridine, was prepared by treating an ITO surface with 4-[2-(trichlorosilyl)ethyl]pyridine. Treated and untreated ITO surfaces (with and without a bound pyridine) and an ITO surface treated with hexamethyldisilazane (trimethylsilylated surface) were soaked in separate solutions of $(\mathbf{4})_{15}$-benzyl bromide for 24 h. The electrochemical responses of the resultant electrodes are shown in Figure 7. A much smaller amount ($\sim ^1/_{20}$) of surface-bound polymer was found on the untreated ITO electrode than on the electrode pretreated with the pyridine reagent. Soaking the pyridine-coated ITO surface in $(\mathbf{4})_{12}$-benzyl bromide solution produced a derivatized electrode with a coverage of 1.1×10^{-10} mol cm^{-2} of **4**, or 8×10^{-12} mol cm^{-2} of polymer, similar to the coverage obtained for $(\mathbf{2})_{10}$-pyridine that reacted with a surface-bound electrophile. The trimethylsilylated ITO surface does not show any bound polymer after attempted reaction with $(\mathbf{4})_{12}$-benzyl bromide. A reaction between the benzyl bromide end group and the hydroxylated surface could account for the small coverage of polymer observed on the untreated ITO electrode.

Attempted Use of Pyrene as an Anchoring Group for Polymers Prepared by ROMP. Pyrene has a strong affinity for carbon surfaces.[20] Addition of a pyrene group to a small molecule allows one to attach the small molecule to carbon surfaces under circumstances where the molecule otherwise would not adsorb. Soaking glassy carbon electrodes in benzene, THF, or CH_2Cl_2 solutions of polymers prepared here results in adsorption of the polymer independent of its composition, that is, polymers with and without the pyrene end group are found to adsorb to about the same extent. A competitive binding experiment was carried out in order to test whether a polymer with a pyrene end group could overcome the adsorption of another polymer and displace it from the surface. To 0.5 mL of benzene were added 1 mg each of $(\mathbf{3})_{12}$ and $(\mathbf{2})_{15}$-pyrene, and to another solution were added $(\mathbf{3})_{12}$-pyrene and $(\mathbf{2})_{15}$. A 3-mm glassy carbon rod was cleaved, and the freshly exposed surfaces were soaked in the two solutions. The electrochemical response of the carbon electrodes was checked periodically. The results after 25 min, 10 h, and 55 h of soaking are shown in Figure 8. There is essentially no change in the relative coverage of the $(\mathbf{3})_{12}$ and $(\mathbf{2})_{15}$ polymers.

As seen for $(\mathbf{3})_{12}$-pyrene vs $(\mathbf{2})_{15}$, the phenothiazine polymer shows a larger binding affinity than the pyrene end-capped polymer and occupies ~90% of the surface. $(\mathbf{3})_{12}$-pyrene did not displace the other polymer over time. On the other hand, $(\mathbf{2})_{15}$-pyrene does not completely occupy the surface to the exclusion of $(\mathbf{3})_{12}$. The invariance of the relative polymer coverage, independent of polymer composition, suggests that the adsorption is irreversible in the medium used and the surface coverage reflects the relative affinities of the ferrocene and phenothiazine polymers for the surface. Thus, we find little influence on the binding affinity of the polymer from introducing the pyrene end group.

Conclusion

Redox-active polymers prepared by ROMP have been attached successfully to electrode surfaces by siloxane bond formation or organic nucleophile/electrophile coupling chemistry. It has been demonstrated that for polymers up to MW ≈ 20 000, the $Si(OEt)_3$ groups in the few equivalents of **1** incorporated into the polymers were solely responsible for persistent binding to Pt, ITO, and n-Si electrode surfaces. Surface attachment was also achieved by a nucleophilic displacement reaction between a pyridine group and a benzyl halide group. Since the end group reactant in the polymer was introduced in the termination reaction, the polymer contains only one such group. Control experiments demonstrate that without the appropriate combination of reactants in the polymer and on the surface, the polymer does not bind to the surface. Adsorption of pyrene-capped polymers on carbon electrodes is dominated by nonspecific adsorption of the polymer itself, as demonstrated by competitive binding experiments with polymers without pyrene end groups. Thus, it is not possible to selectively control the derivatization of carbon surfaces using a pyrene end group in the systems studied.

None of the methods demonstrated to yield selective surface attachment via terminal groups has produced a complete "monolayer" of polymer chains (2×10^{-10} mol cm^{-2} of polymer) in which the polymer chains extend away from the surface. Limiting coverages in all cases were on the order of $\sim 8 \times 10^{-12}$ mol cm^{-2} of polymer chains. For comparison, the coverage of a close-packed monolayer of redox molecules adsorbed via an alkanethiol is $\sim 4 \times 10^{-10}$ mol cm^{-2}.[36] A simple calculation suggests that, on average, each polymer occupies 17 nm^2, or a circular region with a 23-Å radius. This correlates with the magnitude of estimates of the excluded volume for a variety of polymers comparable in size to the polymers studied here.[37] We tentatively conclude that the surface-attached polymers hinder reaction of more polymers with the surface groups. Under more forcing conditions, greater coverages might be obtained.

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