Oligo(ethylene glycol)-Spacered Siloxane Redox Polymers: Highly Diffusive Media for Electrochemical Redox Catalysis

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Abstract: Redox-modified oligosiloxanes were prepared from an Si_{60} oligo(hydrogen siloxane) and allyl-terminated oligo(ethyleneglycol) (OEG) esters of 3-carboxy-2,2,5,5-tetramethyl-Δ3-pyrroline-1-oxyl (PROXYL-COOH). Glassy carbon disk electrodes coated with the modified siloxane films were obtained by spin coating with film thicknesses between 10 nm and 15 μm and analyzed by cyclic voltammetry, chronoamperometry, and rotating disk voltammetry in acetonitrile and water. Due to the OEG content, the siloxane matrix offers a high diffusivity with respect to the mobility of redox centers and solute species. The PROXYL-mediated catalysis of the oxidation of 4-methoxybenzyl alcohol (PMBOH) to anisaldehyde was studied at spin-coated glassy carbon disk electrodes by cyclic voltammetry in acetonitrile with lutidine as a base and in buffered aqueous solution at pH = 7. The catalytic efficiency is 10-fold higher in the latter medium. In controlled potential microelectrolyses, current densities up to 15 mA/cm^2 and catalyst turnovers up to 30 000 were determined at ca. 0.1 mmol/cm^2 substrate conversion. Crucial factors of film performance are thickness and homogeneity, which are still difficult to control at larger area carbon felt electrodes.

The design and application of redox-modified electrodes[1] have been rapidly developing since the first reports of molecules covalently bound to electrode surfaces[2] and of polymer-modified electrodes.[3] Monolayered electrode coatings are available by surface derivatization[2] or, more recently, by direct adsorptive self-assembly.[1c] Polymers films containing redox centers can be attached to surfaces by film casting from solutions of preformed polymers to the electrode surface or, alternatively, by direct electrochemically initiated polymerization from the monomers.[1i]

Of particular interest is the mediation of electrochemical reactions by the redox centers located in the electrode coating.[1e,i,4,5] If the mediation process is specific for a single substrate or a group of related substrates, redox-modified electrodes can be used as sensors for trace level detections.[1h] On the other hand, such electrodes should be well suited for selective electrosynthesis at low overpotentials. This goal was attempted with some success in several laboratories, but in general, the current densities are low and the activity of the surface declines fairly rapidly.[1i,4,5]

Three main limiting factors for the performance of such processes have been identified:[6,7] (i) the rate of electron self-exchange of redox catalyst centers in the polymer layer; (ii) the rate of the catalysis step itself; and (iii) the diffusion rate of substrates, products, and supporting electrolyte ions within the polymer. Theory predicts that even for nonspecific or *outer sphere* redox catalysis, where the rate of catalysis is predominantly determined by the redox potential difference between the catalyst and substrate, overpotentials can be reduced by several hundred millivolts when a large part of the polymer layer is utilized as a reaction zone.[6,7] It should be possible to maintain practical current densities up to 10 mA/cm^2 when all three conditions are optimal.[7] Inner sphere mediators are supposed to be the choice catalysts because they can exchange electrons, possibly as pairs of two electrons, with the substrate within a defined reaction transition state. This would render the catalyst less sensitive to side reactions and thus would enhance selectivity and turnover numbers.[8] From previous experience, it appears *that the diffusion capability of the layer will be by far the most critical and important contribution.*[1i] Further requirements regarding the polymer matrix for practical purposes are a good stability of the polymer matrix with regard to the adherence to the surface and chemical and electrochemical inertness.

Organopolysiloxanes, the well-known "silicones", are among the most versatile polymers known.[9–11] In particular, oligosi-

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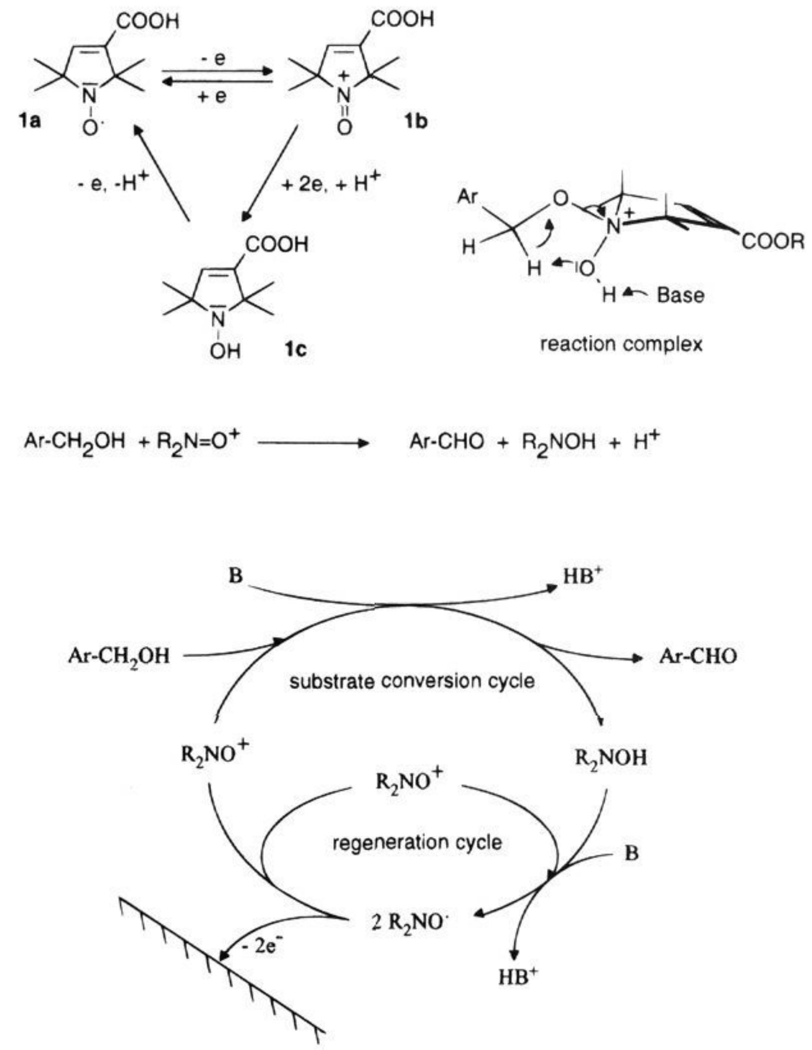
loxanes containing Si−H bonds, so-called hydrogen siloxanes, are easily modified by Pt-catalyzed polyhydrosilylation of vinylic substrates,[12] and controlled cross-linking by water with formation of Si−O−Si bridges is also facile. Since a variety of oligo(hydrogen siloxanes) are commercially available, tailor-made polymers are readily accessible via simple building block protocols. Polysiloxanes with medium to long pendant alkyl chains prepared in this way have been used for the surface modification of silica for reversed phase HPLC application,[13] but only recently have siloxane polymers been employed for modified electrodes. Whereas the group of Skotheim has demonstrated their use in biosensor techniques,[14] we have been concentrating on preparative electrochemistry at siloxane-modified electrodes.[15]

For the present study, the nitroixde-/nitrosodium-mediated oxidation of benzylic alcohols to the corresponding aldehydes with 2,2,5,5-tetramethylpyrroline-3-carboxylic acid (PROXYL-COOH,[16] **1a**) derivatives as catalysts was chosen as a typical inner sphere process. The oxidizing agent is the nitrosonium ion **1b** formed by one-electron oxidation of stable **1a**, and a large number of alcohols have been shown to be oxidized by chemically generated nitrosonium ions.[17,18] The reaction is thought to proceed *via* addition of the alcohol at the N=O double bond of **1b** to give a reactive complex in which two electrons are directly transferred with formation of the hydroxylamine **1c** (Scheme 1).[17] A base is essential for fast reaction with 2.6-lutidine being the best choice for nonaqueous solvents.

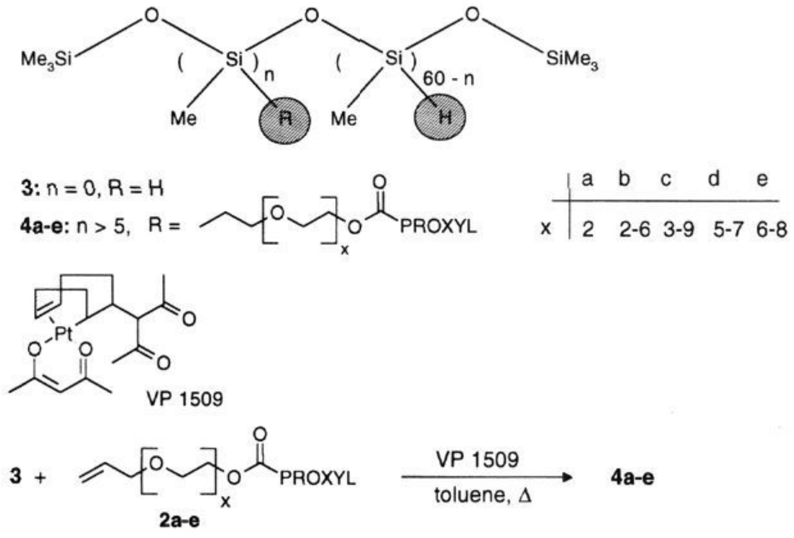
In the electrochemical redox catalysis cycle, the regeneration of the nitrosonium ion from the hydroxylamine is achieved by anodic oxidation. Probably, this partial cycle is also proceeding with catalytic assistance of the nitrosonium ion (Scheme 1).[19] THe catalytic model reaction has already been tested in homogeneous solution, and with polypyrrole[4,20] and acrylic[5] polymer supports, but the results of the present study demonstrate a diffusion behavior of tailor-made siloxane polymers superior to that of the previous polymers, with high current densities sometimes reaching 20 mA cm^{-2}.

At the beginning of our work with siloxane-modified electrodes, redox catalyst molecules were bound to the polymer backbone by short hydrocarbon chains.[15] Although these modified electrodes were effective with high catalyst turnover numbers, only very thin films ($d \approx 1$ nm) could be applied and thus only very modest current densities were observed. Thicker films of these polymers either were not homogeneous, forming lumps of rubber-like consistence, or behaved as an insulating layer on the electrodes, a phenomenon apparently due to the notorious nonpolar and hydrophobic nature of silicones.

Scheme 1



Scheme 2



As was shown by Bayer[21] for the Merrifield peptide synthesis, the separation of the growing peptide chain from the polystyrene surface by oligo(ethylene glycol) (OEG) spacers tremendously improved the efficiency of the polymer support. Obviously the OEG chains provide a solvent-like diffusion zone at the polymer−solution interface. Consequently, OEG spacers were included into the redox-modified siloxanes as given in Scheme 2. The esters **2a−e** of different OEG monoallyl ethers with PROXYL-COOH (**1a**) were coupled to the oligo(hydrogen siloxane) $Me_3Si-(SiHMe)_{60}-SiMe$ (**3**) with VP 1509 as a hydrosilylation catalyst in toluene solution with the desired stoichiometry to give random modified oligomers **4a−e** with various spacer lengths. In the course of this work, it turned out that siloxane oligomers with all Si−H bonds of **3a** substituted by redox chains were completely soluble. Oligomers **4b** with up to 40% substituted Si units were suitable, but a minimum of 5−10 redox spacers was sufficient in all cases. While it seemed appropriate to leave some of the Si−H bonds unreacted for anchoring siloxane oligomers to surface metal-

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OH or carbon-COOH or −Ar-OH groups and for controlled cross-linking of oligomer strands, excess Si−H bonds did not interfere with the electrochemical reactions.

For better readability, the oligomers **4a**−**e** are denoted in the following as $Si_{60}H_{60-n}SiR(x)_n$, where x indicates the spacer lengths, e.g. $Si_{60}H_{50}SiR(3-9)_{10}$ for an oligomer with 10 functionalized Si−H bonds with random mixed spacers varying between 3 and 9 OEG units (Scheme 2).

Experimental Section

Chemicals and Syntheses. The oligo(hydrogen siloxane) WACKER-H-Siloxane (**3**, $Me_3Si[(OSiHMe)]_{60}OSiMe_3$), the oligo(ethylene glycol) (OEG) monoallyl ethers Arylpon Al 6E and Al 10E (trade names of DuPont Co.) with averages of 6 and 10 OEG units, and the hydrosilylation catalyst WACKER-VP 1509 (1% stock solution in methyl isobutyl ketone) were supplied by WACKER GmbH, D-88489 Burghausen, Germany. From Arlypon Al 10E, narrower fractions of OEG monoallyl ethers with 5−7 and 6−8 OEG units were cut with a Leybold KD1 short-way molecular distilling set at 124 and 142 °C mantle temperatures and 10^{-5} hPa.

Bis(ethylene glycol) Monoallyl Ether. To bis(ethylene glycol) (13 g, 0.14 mol) in dry CH_2Cl_2 (100 mL) was added in portions potassium hydride (5.2 g, 0.14 mol) suspended in CH_2Cl_2 (30 mL). After gas evolution had ceased, allyl bromide (11.6 mL, 0.14 mol) was added and the mixture was stirred for 3 h. The KBr was removed by filtration, and the filtrate was extracted with water (5 × 40 mL). The aqueous phase was reextracted with CH_2Cl_2 (10 × 50 mL), and the organic phase was dried and concentrated to an oil (6.2 g, 30%). IR: 3450 (OH), 1640 (C=C), 1061−1140 (C−O). ^1H NMR (80 MHz): δ 3.38 (br. S, 1H, OH), 3.60 (m, 8 H, $=OCH_2CH_2O$), 4.00 (d, 2H, $=CH-CH2$), $J = 6.6$ Hz), 5.09−5.40 (m, 2H, $CH_2=$); 5.65−6.15 (m, 1H, $-CH=$).

2,2,5,5-Tetramethyl-3-carboxy-Δ3-pyrroline-1-oxyl (PROXYL-COOH, **1a**) was obtained from the corresponding carboxamide (Aldrich) by alkaline hydrolysis.[16] Esters **2a**−**e** of **1a** with the various OEG allyl ethers were prepared *via* the dicyclohexylcarbodiimide/(dimethylamino)pyridine method.[22]

For the oligohydrosilylation coupling of the oligo(hydrogen siloxane) **3** with the spacer-modified PROXYL derivatives **2a**−**e** (Scheme 2), the coupling components in the desired stoichiometry and VP 1509 stock solution (10 μL) were added to a 5 × 10^{-3} M solution of **3** in toluene (2 mL) under rigorous exclusion of moisture and the mixture was heated at 100 °C for 16 h. The completion of the reaction was verified by the absence of the $\nu_{C=C}$ band in the IR spectrum and in some samples by quantitative ESR analysis of the PROXYL content with respect to **1a** as a standard. The slightly yellow solutions of the oligomers **4a**−**e** were directly used for spin coating; they can be kept under argon for up to 4 weeks, whereafter they tend to form gallerteous precipitates.

Spin Coating. A 0.38 cm^2 PTFE sealed glassy carbon disk was dipped into 65% HNO_3 for 1 min, rinsed with water and ethanol, and dried in air. The electrode shaft was fixed face up in an ordinary laboratory stirring motor. A 5 μL volume of the polymer solution was applied to the surface and spinned off at 2000 rpm. After the electrode was dried in a nitrogen stream for 20 s, the process was repeated until the desired thickness was reached.

Electrochemical Methods. The electrochemical instrument was a Princeton Applied Research PAR Model 273 potentiostat/galvanostat controlled by a PC with PAR Model 270 software for parameter setup and data acquisition and processing. Cyclic voltammetry was done in small beakers equipped with PTFE stoppers with holes for the glassy carbon working electrode, a Pt wire as a counter electrode, the reference electrode, and an inert gas supply. An Ag/AgCl wire quasi-reference electrode ($E^\circ = -0.284$ V vs the ferrocene/ferrocenium couple) was used in acetonitrile and an SCE in aqueous solutions, both separated from the test solution by a vycor plug embedded in a PTFE shrinking tube. Rotating disk voltammetry was performed with a EG&G Rotel A motor and controller and a 0.28 cm^2 glassy carbon disk electrode. Acetonitrile (Merck HPLC quality) was used as received. Bu_4NClO_4 (Fluka purum) was recrystallized twice from 80% aqueous ethanol.

For micropreparative electrolysis experiments, glassy carbon plates (5 × 2.5 cm) with an integrated glassy carbon handle, or carbon felt strips (2.5 × 1.5 × 0.2 cm) with a Pt wire lead, both supplied by SIGRI GmbH, 96405 Meitingen, Germany, were used in a 50 mL undivided beaker cell. The plates were coated by application of stock solution which was distributed on the surface with a small paint brush. Carbon felt was either soaked with the polymer solution or sprayed with a hand-driven pumping device as used for TLC with diluted stock solution.

Results and Discussion

General Properties of PROXYL Siloxane Films on Analytical Glassy Carbon Disk Electrodes. Spin coating[23] was a reliable and well-reproducible means of preparing films on analytical electrodes as compared to dip coating or droplet evaporation techniques. Although the coupling of Si−H bonds to surface OH groups was not definitively proven, it turned out that carbon surfaces, after oxidative pretreatment with 65% nitric acid,[24] held 2−10 times more electroactivity than untreated electrodes. Accordingly, all experiments in this work were performed with pretreated electrodes.

Cyclic voltammetry was used as a tool for (i) determining the amount of redox activity on the surface by integration; (ii) studying the kinetic behavior of the reversible redox process; and (iii) studying the long-term behavior of the coating upon repeated cycling or standing in solution.

Freshly spin-coated films show striking differences depending on the substitution pattern of the siloxane chain. Polymers with a low loading of redox groups and/or short OEG spacers show distinct breaking-in phenomena which last up to 70 potential-controlled oxidation reduction cycles until the maximum peak current and the final narrow peak-to-peak separation is reached (Figure 1a), whereas films with higher loading ($n \geq 10$) give maximum responses instantaneously (Figure 1b). Upon repeated cycling, the maximum voltammetric peak currents of both types of films decline slowly and, over about 250 cycles, approach a constant level of 50 to 70% of the original maximum. Obviously, this latter effect is due to diffusion of loosely bound oligomer strands out of the film. The two types of films also differ in the microscopical surface. The more "silicone-like" films with swelling behavior have a rough surface with a dull, milky appearance whereas those with higher OEG content have a shiny and smooth surface and often show interference colors.

The amount of polymer electroactivity on the surface was determined from the integrated cyclovoltammetric curves at small scan rates ($\nu \leq 20$ mV/s) or by coulometry within a 5 mV/s voltammetric ramp across the redox peak. From the stoichiometry of the modified siloxane, assuming a polymer density of 1, the mass and volume of the film can be calculated. For an estimation of the real film thickness at the carbon/film/solution interface, the dry film volume was multiplied by swelling factors taken from the literature (CH_3CN, 3; H_2O, 2.5; CH_2Cl_2, 3; THF, 3.4).[21] Films from a few nanometers up to 15 μm thickness were studied.

Most of the initial studies were done with good results in acetonitrile/TBAP. Dichloromethane and acetone with TBAP supporting electrolyte gave similar results, but the electrode coatings were slowly degraded by dissolution, finally leaving only very thin stable films. In MeOH or EtOH, only sluggish redox responses are observed, and in THF, all films were quickly

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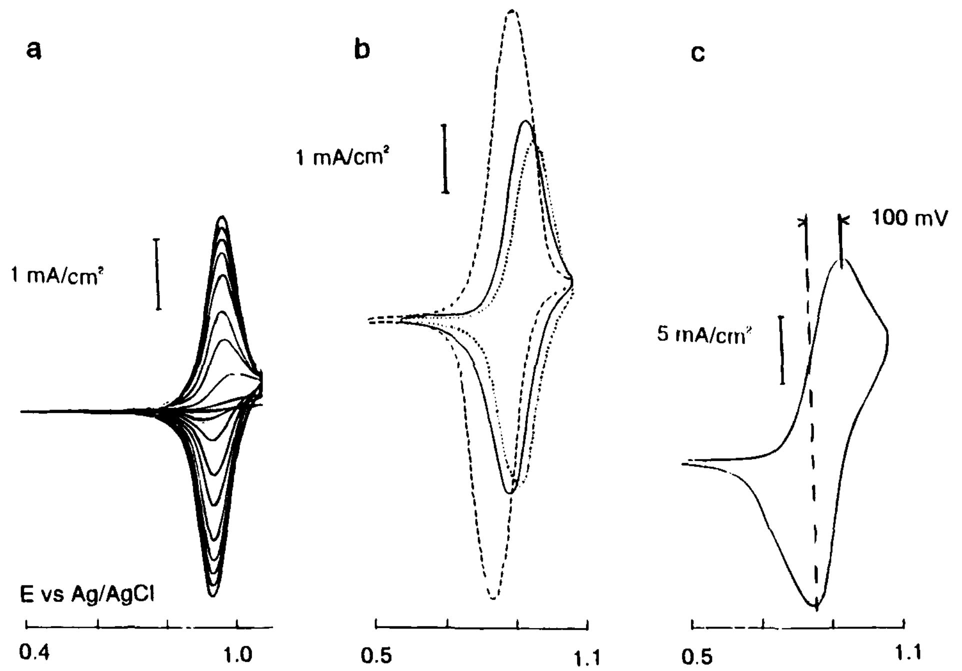

Figure 1. Representative cyclovoltammograms of PROXYL siloxane films in CH_3CN/0.1 M Bu_4ClO_4 at 50 mV scan rate: (a) breaking in a $Si_{60}H_{55}R(2)_5$ film, 60 μL stock solution spin coated in 5 μL portions on a 0.38 cm² glassy carbon disk, 21st–100th cycle; (b) redox potential dependence on film structure, 60 μL stock solution, (—) 2.8 μm $Si_{60}H_{55}R(3-9)_5$, after 5 cycles; (···) 2.2 μm $Si_{60}H_{55}R(2)_5$, after 70 cycles; (···) 2.7 μm $Si_{60}H_{50}R(2)_{10}$, 1st cycle; (c) high current density first cycle of a $Si_{60}H_{40}R(2)_{20}$ film, 60 μL stock solution, 13 μm thickness.

and completely dissolved from the surface. Surprisingly, a very stable redox behavior of the PROXYL siloxane films is seen in aqueous solution. In the following, only the electrochemistry in CH_3CN and in water will be discussed and all film data are given for films that have been broken in, if necessary, and redox cycled to a constant voltammetric behavior. Such films have a completely stable redox activity for several days as long as they are kept in CH_3CN solution. In water one observes a 20–30% decay over 24 h, after which time the films stabilize too. Standing in air for 24 h gives rise to a rubber-like appearance of the coatings, and voltammetric examination of such specimens reveals only broad voltammetric peaks which disappear on repeated cycling, leaving a disrupted film. The change of the siloxane films in (moist) air can be monitored by IR spectroscopy on a spin-coated NaCl plate: the Si–H absorption at 2160 cm^{-1} declines, and an Si–OH band at 3400 cm^{-1} grows. The rubber formation points to a gradual cross-linking.

The reversible redox potential of **1a** is 0.865 V vs Ag/AgCl in acetonitrile. In the films this potential depends on the film structure: the more or longer OEG units the film contains the less positive is E° due to better solvation of the cationic oxidation state, the nitrosonium ion **1b**, e.g. 0.961 V for $Si_{60}H_{55}R(2-5)_5$, 0.941 V for $Si_{60}H_{55}R(3-9)_5$ and 0.932 V for $Si_{60}H_{50}R(2-5)_{10}$ (Figure 1b). A similar trend is observed in aqueous solution.

Behavior in CH_3CN. The amount of redox polymer found electrochemically is proportional to the amount of coating solution for films up to 4.5 μm, for a chosen polymer structure. With thicker films, the available electroactivity becomes less. Nevertheless, at scan rates of ≤ 50 mV/s, remarkably narrow peak to peak separations between 50 and 100 mV are found even with peak currents up to 15 mA/cm² (Figure 1c). At higher scan rates, ΔE_p increases, but less than exponentially. At slow scan rates (1–20 mV/s), $i_p{}^a$ is proportional to the scan rate v, and at $200 \leq v \leq 1000$ mV/s, proportionality to the square root of v is observed which levels off at still higher scan rates. As long as the scan rate is in the region of v proportionality, the integrated electroactivity is equal to the coulometric value over a slow ramp, but at higher scan rates and particularly in thicker films, only part of the electroactivity is accessible.

Most likely, the rate-determining step is the electron self-exchange between the PROXYL centers, which is governed by a combination of the intrinsic rate constant and their mutual distance in the film.[25] From the thickness estimation of different solvent-swollen films, the concentration of redox centers ranges from 0.3 to 0.7 M and herefrom the mean center to center distance can be calculated as 12–20 Å. At low scan rates, the exchange reaction is rate determining, whereas with increasing scan rates, the mutual diffusion takes control. The charging of the film can be characterized by a charge transfer diffusion coefficient D_{ct}, which determines the rate of progression of the front of charged PROXYL groups through the film toward the solution site.

From Cottrell plots of short time potential step experiments in the time interval from 100 to 250 ms from the starting point,[1b,26] a linear portion can be identified from which an average apparent charge transfer diffusion constant D_{ct} [$(5.0 \pm 1.8) \times 10^{-8}$ cm²/s] at films of various thicknesses of $Si_{60}H_{50}R(2)_{10}$ is calculated.

This value compares very favorably with those for other polymer films, e.g. poly[Ru(4-vinyl-4′-methyl-2,2′-bipyridine)]$^{2+}$ with an apparent D_{ct} value of 2×10^{-10} cm²/s.[27] Thus a very good diffusivity in the OEG-modified siloxane structure is quantitatively confirmed. Further support is provided by measuring film diffusion constants D_f of solute species into the film from inverse Levich plots of rotating disk electrode (rde) measurements.[28] The rde voltammograms of a siloxane film in a 1 mM ferrocene solution consist of three regions (Figure

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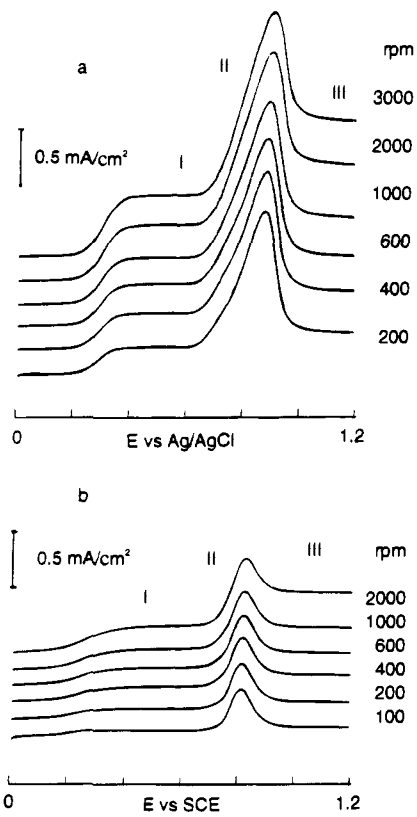

Figure 2. Rotating disk voltammograms of solute redox substrates at PROXYL siloxane-coated 0.38 cm^2 glassy carbon disks at different rotation speeds. (a) 1.4 mM ferrocene at 2.2 × 10^{-7} mol/cm^2 $\mathrm{Si_{60}H_{40}(R2)_{20}}$ in $\mathrm{CH_3CN}$/0.1 M $\mathrm{Bu_4ClO_4}$; (b) 0.8 mM 1,4-dihydroxybenzene at 4.3 × 10^{-8} mol/cm^2 $\mathrm{Si_{60}H_{50}R(6-8)_{10}}$ in 0.1 M phospahte buffer (pH = 7) + 0.1 M $\mathrm{NaClO_4}$.

2a). In region I ferrocene is oxidized at the electrode surface after diffusion from the homogeneous solution through the film, giving a rotation speed dependent limiting plateau current between 0.25 and 0.6 V. Region II, between 0.6 and 1.0 V, shows the peak-shaped oxidation of the entrapped PROXYL centers which is enhanced by film volume oxidation of ferrocene. In the absence of ferrocene, the PROXYL peak is independent of the rotation speed and essential the same as in a cyclic voltammogram at the same sweep rate. In region III, finally, above 1.0 V a new plateau level arises which is the sum of surface and steady state PROXYL-catalyzed ferrocene oxidations. It is seen from Figure 2 that not only a substantial flux of ferrocene (region I) is reaching the electrode surface but also additional redox catalysis occurs when the PROXYL catalyst is turned on (regions II and III).

From the intercept of the inverse Levich plot of the region I plateau, the current (i_s^{-1} vs $\omega^{1/2}$) at various ferrocene concentrations and film thicknesses D_f(ferrocene) is obtained as 2.5 ± 0.5·10^{-6} cm^2/s, a value only 10-fold less than D(ferrocene) in acetonitrile solution (2.4 × 10^{-5} cm^2/s).[29] In the notation of Savéant and Andrieux, this favors a situation where a large part of the redoxactive film is involved in catalysis, the SR case.[30]

Among several different polymer compositions that give satisfactory results, the $\mathrm{Si_{60}H_{50}(R2)_{10}}$ oligomer with 10 bis(ethylene glycol)-coupled redox groups is the simplest. This particular film material was therefore chosen for catalysis experiments in $\mathrm{CH_3CN}$.

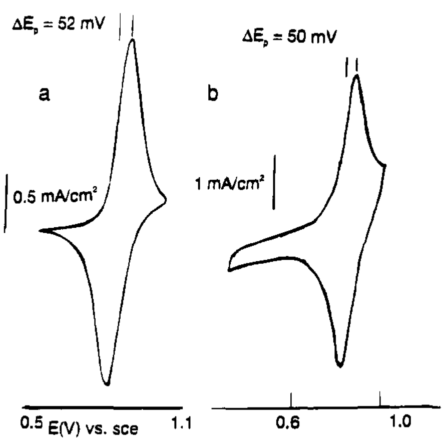

Figure 3. Cyclovoltammograms of $\mathrm{Si_{60}H_{50}R(5-7)_{10}}$ in 0.1 M phosphate buffer/0.1 M $\mathrm{NaClO_4}$ (pH = 7.0) at 50 mV scan rate. (a) 8 × 10^{-8} mol/cm^2 on a 0.38 cm^2 glassy carbon disk after 100 redox cycles; (b) 250 μL of 1 mM stock solution sprayed onto a 2 mm × 2.5 cm^2 carbon felt cloth.

Behavior in Water. PROXYL siloxane films in aqueous phosphate buffer show a behavior quite similar to that of $\mathrm{CH_3CN}$ *when perchlorate anions are present.* The latter turned out as essential for good swelling of the films. With respect to the catalysis experiments described below, an optimized supporting electrolyte consisting of 0.1 M phosphate buffer at pH = 7 plus 0.1 M $\mathrm{NaClO_4}$ was used throughout. The short spacered polymers like $\mathrm{Si_{60}H_{50}(R2)_{10}}$ that were adequate for the $\mathrm{CH_3CN}$ studies did not work well in aqueous solution due to complicated break-in phenomena that reappeared as soon as the potential cycling was interrupted for even short periods of time. The mixed random spacered polymers $\mathrm{Si_{60}H_{50}R(2-6)_{10}}$ and $\mathrm{Si_{60}H_{50}R(3-9)_{10}}$, and in particular, $\mathrm{Si_{60}H_{50}R(5-7)_{10}}$ and $\mathrm{Si_{60}H_{50}R(6-8)_{10}}$, gave even better dynamic responses than all polymers in acetonitrile. Very remarkable is the narrow peak-to-peak separation of a thick film (Figure 3). It appears that the hydrophobic/hydrophilic combination of $\mathrm{Si_{60}H_{50}R(5-7)_{10}}$ and $\mathrm{Si_{60}H_{50}R(6-8)_{10}}$ perfectly provides adherance of the siloxane at the electrode surface and, within the domains of solvated OEG clusters, a very good mobility of bound redox centers, supporting electrolyte anions and other solute species. This was again verified by potential step and rde experiments (Figure 2b) which yielded an apparent charge transfer diffusion constant D_{ct} of 2 × 10^{-8} cm^2/s and a film diffusion coefficient D_f (hydroquinone) = (3.7 ± 0.7) × 10^{-7} cm^2/s, about 20 times smaller than in aqueous 0.1 M $\mathrm{KNO_3}$ solution (7.4 × 10^{-6}).[31] In a $\mathrm{Si_{60}H_{50}R(2-6)_{10}}$ film, D_f(hydroquinone) was only ca. 0.6 cm^2/s.

Catalysis of the Oxidation of *p*-Methoxybenzyl Alcohol by PROXYL Silicone Films in Acetonitrile and Water. Benzyl alcohol (BOH), 4-methoxybenzyl alcohol (PMBOH), and 3,4-dimethoxybenzyl alcohol (3,4-DMBOH) were tested as substrates for the PROXYL-mediated oxidation to the corresponding aldehydes, and the catalysis phenomena were first studied by cyclic voltammetry at v = 50 mV/s. In nonaqueous solvents like $\mathrm{CH_3CN}$, the oxidation of alcohols requires the presence of a base, usually 2,6-lutidine (Scheme 1);[4,5,19] indeed, catalysis of the oxidation of the benzylic alcohols in $\mathrm{CH_3CN}$ is not observed at all in the absence of lutidine. Much to our surprise, efficient catalysis occurred in *neutral* aqueous phos-

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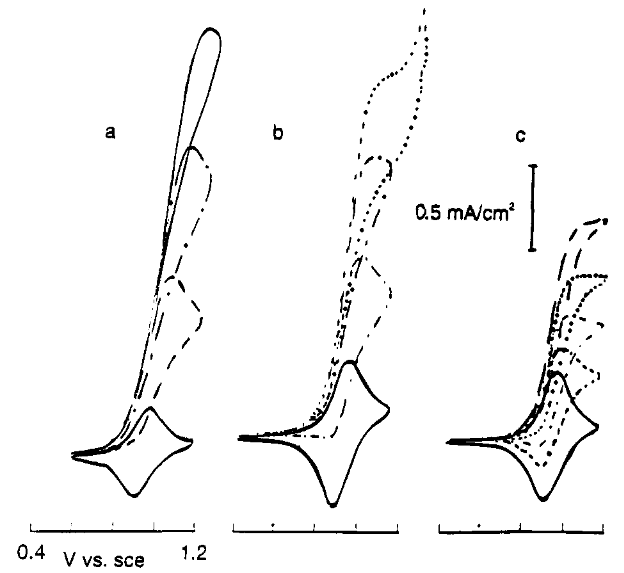

Figure 4. Catalysis of the oxidation of benzylic alcohols by PROXYL siloxane films at a 0.38 cm^2 glassy carbon disk in 0.1 M phosphate buffer/0.1 M $NaClO_4$ (pH = 7.0) at 50 mV scan rate: (a) 1.1 × 10^{-8} mol/cm^2 $Si_{60}H_{50}R(2-6)_{10}$ with addition of 0, 8, 16, and 24 mM PMBO; (b) 1.7 × 10^{-8} mol/cm^2 $Si_{60}H_{50}R(2-6)_{10}$ with addition of 0, 7, 14, and 21 mM DMBOH; (c) 1.4 × 10^{-8} mol/cm^2 $Si_{60}H_{50}R(2-6)_{10}$ with addition of 0, 9, 18, 27, and 36 mM BOH.

Table 1. Catalytic Efficiency of $Si_{60}H_{50}R(2-6)_{10}$ Films in the Oxidation of Various Benzylic Alcohols in Neutral Aqueous Phosphate Buffer[a]

	substrates								
parameters	3,4-dimethoxy-benzyl alcohol			4-methoxy-benzyl alcohol			benzyl alcohol		
$E_{p/2\ substr}$ (mV)[b]	1135			1300			1730		
Γ (10^{-8} mol/cm^2)[c]	1.7			1.1			1.4		
thickness (nm)[d]	130			85			110		
j_{med} (mA/cm^2)	0.60			0.40			0.57		
c_{substr} (mM)	7	14	21	8	16	24	9	18	27
j_{cat} (mA/cm^2)	1.46	2.29	2.96	1.49	2.56	3.56	0.77	1.04	1.37
CE (mM^{-1})	0.20	0.20	0.19	0.34	0.34	0.30	0.04	0.04	0.05

[a] 0.38 cm^2 glassy carbon disk. [b] Vs SCE; the $E_{p/2}$ of the PROXYL is 875 mV in this medium. [c] PROXYL centers in coating, coulometrically determined. [d] Estimated for solvent-swollen film.

phate buffer with no improvement at higher pH. For all three alcohols, in this medium, large catalytic waves were found (Figure 4) in the cyclovoltammograms. The catalytically effective current $j_{eff} = j_{cat} - j_{med}$ and the catalytic efficiency of the film normalized on the mediator current and substrate concentration CE = $[(j_{cat} - j_{med})/j_{med}]/c_{substr}$) for each experiment are given in Table 1, where results in CH_3CN are also given. As expected from the uncatalyzed oxidation potentials of the alcohols, the catalytic effect is smallest for BOH. On the other hand, with 3,4-DMBOH, the catalytic wave already merges with direct oxidation and therefore is not very comparable to the other two cases. PMBOH was best suited for a thorough analysis of the catalytic efficiency in dependence of the film thickness and the substitution pattern of the siloxanes and was used in the experiments below.

Generally, for a given film constitution, the normalized catalytic efficiency CE decreases with increasing film thickness, in particular for films with shorter spacers, although the absolute current density $j_{eff} = j_{cat} - j_{med}$ for substrate oxidation is usually higher for thicker films (Table 2). The best results are again obtained with the polymers $Si_{60}H_{50}R(2)_{10}$ in CH_3CN and $Si_{60}H_{50}R(5-7)_{10}$ and $Si_{60}H_{50}R(6-8)_{10}$ in water. With these polymers the catalytic efficiency is constant over a wide range of substrate concentrations until saturation is reached at $c \geq 0.2$ M.

Table 2. Catalytic Efficiencies of Various PROXYL Siloxane Films Differing in Composition and Thickness in the Oxidation of PMBOH[a]

polymer film	thickness (nm)	j_{med} (mA/cm^2)	j_{kat} (mA/cm^2)	CE (mM^{-1})
	CH_3CN Solution:[b]			
$Si_{60}H_{55}R(2)_5$	800	1.27	4.81	0.05
	2000	2.40	6.05	0.03
	2700	2.91	5.84	0.02
$Si_{60}H_{50}R(2)_{10}$	1300	2.75	10.8	0.05
$Si_{60}H_{45}R(2)_{15}$	2800	3.90	11.4	0.03
$Si_{60}H_{40}R(2)_{20}$	6500	9.45	16.9	0.01
	Aqueous Buffer:[c]			
$Si_{60}H_{50}R(2-6))_{10}$	200	0.39	4.39	0.26
	250	0.44	10.4	0.21
	600	1.14	4.44	0.07
$Si_{60}H_{50}R(5-7)_{10}$	85	0.17	9.30	0.90
	140	0.24	9.71	0.65
	220	0.40	11.9	0.47
$Si_{60}H_{50}R(3-9)_{10}$	600	0.90	4.23	0.06
	1600	3.51	15.4	0.05
$Si_{60}H_{50}R(6-8)_{10}$	2700	3.38	11.7	0.04

[a] Based on peak currents of cyclovoltammograms at a 0.38 cm^2 glassy carbon disk elektrode at 50 mV scan rate and 60 mM substrate concentration. [b] 0.1 M Bu_4NClO_4 as the supporting electrolyte. [c] 0.1 M phosphate buffer (pH 7) + 0.1 M $NaClO_4$.

The catalyses in the *aqueous* electrolyte are about 10-fold more effective than those in CH_3CN, e.g. almost the same activity is displayed by a 0.22 μm (10 nmol/cm^2) $Si_{60}H_{50}R(5-7)_{10}$ film in water as a 2.8 μm (120 nmol/cm^2) $SiH_{50}Si(R2)_{10}$ film in CH_3CN (Figure 5). The normalized catalytic efficiencies CE of the films are 0.36 and 0.03 mM^{-1}, respectively. The facile aqueous catalysis even at fairly thin films has the additional advantage that the film homogeneity in the spin-coating process is much better controlled because only few droplet applications are necessary. Furthermore, thicker films not only have lower efficiencies but also have a greater tendency to disintegrate at high current densities.

Controlled Potential Electrolyses. The high efficiency of the optimized siloxane electrodes allows for controlled potential electrolyses of sizable amounts of substrate even at the 0.38 cm^2 analytical glassy carbon electrode for a reliable determination of catalyst turnover numbers at reproducibility spin-coated films.

In these experiments the loading of the film was first determined by cyclic voltammetry. Ater addition of PMBOH to a desired concentration, the catalytic efficiency of each electrode at 50 mV/s was determined in the previously described manner, followed by controlled potential coulometry for 30–60 min. Finally, the remaining PROXYL activity of the film was checked in substrate-free solution. The electrolysis solution was analyzed for PMBOH and the aldehyde PMBA as well as the corresponding 4-methoxybenzoic acid which, however, was not detected in any experiment. The average turnover number per PROXYL center was calculated as the quotient of consumed Faradays by the initial charge of the catalyst.

The amount of PMBOH in the electrolyte was chosen such that the concentration of the substrate during the batch electrolysis at 5–12% conversion remained fairly constant. Actual conversions were between 10 and 50 μmol. The initial currents were between 4 and 11 mA/cm^2 depending on catalyst loading and substrate concentration. The current yield based on the analyzed substrate/product mixture was ≥90% in all cases,

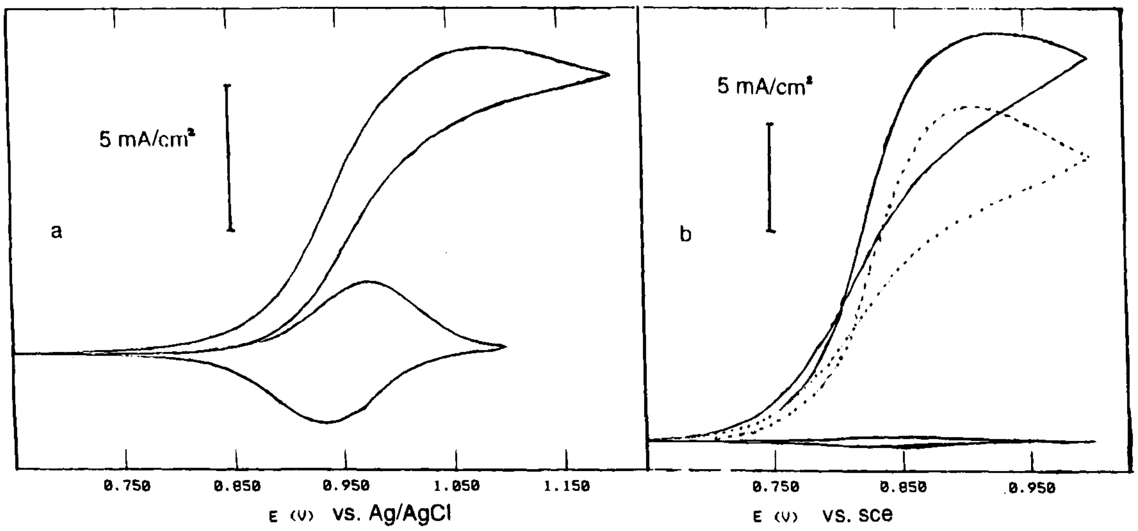

Figure 5. Catalytic efficiency of PROXYL siloxane films in acetonitrile and water: (a) 5.8 × 10^{-8} mol/cm² $Si_{60}H_{50}$ $R(2)_{10}$ at a 0.38 cm² glassy carbon disk in CH_3CN/0.1 M TBAP before and after addition of 140 mM PMBOH and 280 mM lutidine; (b) 5.6 × 10^{-9} mol/cm² $Si_{60}H_{50}R(5-7)_{10}$ at the same electrode in 0.1 M phosphate buffer + 0.1 M $NaClO_4$ before and after addition of 80 or 150 mM of PMBOH.

Table 3. Controlled Potential Electrolyses of PMBOH at PROXYL Siloxane Films at Various Carbon Surfaces

entry	polymer	film activity, initial/ final (10^{-8} mol/cm²)	c_{substr} (mM)/ n_{substr} (mmol)	total time (min)/ charge (μF)	current, initial/ final (mA/cm²)	chem yield/ current yield (%)	catalyst turnovers
			In CH_3CN				
	C-disk electrode:						
1	$Si_{60}H_{55}R(2)_5$	2.6/1.7	100/1,0	30/21.7	4.23/2.00	1/100	2200
2	$Si_{60}H_{55}R(2)_5$	8.3/6.5	120/1.2	30/32.1	5.12/3.84	1.3/100	1005
3	$Si_{60}H_{55}R(2)_5$	6.4/3.7	150/1.5	45/48.7	6.23/2.60	1.6/100	2000
			In Aqueous Solution				
	C-disk electrode:						
4	$Si_{60}H_{50}R(3-9)_{10}$	6.8/4.8	70/0.7	30/51.8	11.2/6.49	3.7/100	2000
5	$Si_{60}H_{50}R(3-9)_{10}$	10.8/9.37	80/0.8	30/26.9	7.01/2.68	1.7/100	650
6	$Si_{60}H_{50}R(2-6)_{10}$	1.1/0.9	50/0.5	60/50.1	5.92/1.32	5.0/100	12000
7	$Si_{60}H_{50}R(2-6)_{10}$	3.9/2.8	50/0.5	60/43.5	3.45/2.49	4.4/100	3000
8	$Si_{60}H_{50}R(5-7)_{10}$	0.65/0.36	60/0.6	60/76.7	10.1/2.94	6.3//100	31000
	C-plate:						
9	$Si_{60}H_{50}R(2-6)_{10}$	2.5/n.d.	12/0.48	60/266	3.4/0.4	23/83	1800
10	$Si_{60}H_{50}R(2-6)_{10}$	0.9/n.d.	12/0.48	60/269	3.0/0.3	25/87	7000
11	$Si_{60}H_{50}R(5-7)_{10}$	1.2/n.d.	12/0.48	60/412	5.4/0.6	33/77	5700
	soaked C felt:						
12	$Si_{60}H_{50}R(2-6)_{10}$	3.0/n.d.	12/0.48	60/130	3.5/0.8	12/85	2500
13	$Si_{60}H_{50}R(5-7)_{10}$	12.2/n.d.	12/0.48	345/817	6.8/0.8	63/74	2900
	sprayed C-felt:						
14	$Si_{60}H_{50}R(5-7)_{10}$	2.3/n.d.	12/0.48	60/183	7.3/0.4	19/100	3800
15	$Si_{60}H_{50}R(5-7)_{10}$	6.1/n.d.	12/0.48	60/319	14.7/0.6	33/100	1600

indicating the absence of major interfering side reactions (Table 3, entries 1−8).

Again, in the aqueous films, comparable initial current densities are observed in much thinner films than in the CH_3CN films and they give higher chemical yields in comparable electrolysis times. However, in both cases, the initial current densities declined substantially. In CH_3CN, the decline of current corresponds quite well to the decline of electroactivity at the interruption of the electrolysis; this is less well correlated in aqueous electrolyte. The highest reproducible turnover number of PROXYL units was 28 000 ± 3000 for a *thin* film of $Si_{60}H_{50}R(5-7)_{10}$ in aqueous solution (Table 3, entry 8).

The loss of redox activity during the electrolysis may be due to destructive side reactions of PROXYL moieties but also to abrasion of parts of the film. The presence of a coating after the experiments was evident from the surface appearance, especially interference rings, but we were not able to quantify the loss of activity to either or both phenomena. Whereas the initial catalytic currents were roughly proportional to the PMBOH concentration, not only higher currents declined more rapidly but in parallel also the average turnover numbers dropped. At least this latter observation points to film abrasion by frictional effects at rapid forced diffusion. In coincidence with the analytical experiments, the turnover numbers were higher for thinner films and much better in aqueous than in acetonitrile solution. In acetonitrile, the much smaller turnover numbers may be due to the action of the relatively strong base lutidine on the nitrosonium cations.[20,32]

Turnover numbers of several ten thousands and current densities up to 10 mA/cm² are remarkable, and such films should be suitable for catalytic conversions in the millimolar scale, provided materials with greater inner surfaces can be used. Macroscopic electrolyses in aqueous solution at smooth glassy carbon and carbon felt cloth were therefore performed. The plate electrodes were coated by paintbrushing 50−100 μL of the 5-fold-diluted oligomer stock solution onto the surface. This type of electrode was thought of as an extended version of the

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(32) Steckhan E. In *Electrochemistry I*; Steckhan, E., Ed.; Topics in Current Chemistry, Vol. 142; Springer-Verlag: Berlin, Heidelberg, New York, London, Paris, Tokyo, 1987; p 57.

analytical glassy carbon disk. At the felt material, soaking and spraying were examined for applying the surface films. In this case we expected higher current densities than those at the smooth electrode surface. It was also thought that the thickness of the films that was previously identified as crucial for the success of redox catalysis could be controlled by dilution of the standard polymer stock solution.

The sprayed electrodes showed surprisingly clear cyclovoltammograms even at 50 mV/s, with peak-to-peak separations as low as 50 mV (Figure 3b). Due to large capacitive currents, the initial loading levels at the plate and soaked felt electrodes were obtained from 2 mV/s coulometric scans. Some results of controlled potential electrolyses are included in Table 3 (entries 9−15). The catalysis experiments at the macroelectrodes clearly do not meet the expectations from the analytical experiments. Saturation of catalysis was approached at substrate concentrations as low as 20 mM, contrary to 200 mM at the analytical electrode. Therefore, catalysis experiments had to be performed as 0.5 mmol batch electrolyses at 12 mM concentration. While the current densities are initially comparable to those found at the spin-coated electrodes, they drop down to 1−10% within 60 min. The average chemical yield at the plate and soaked felt electrodes was 33% with a current yield of 80%. In the best case, 0.3 mmol of aldehyde could be generated with 63% chemical and 77% current yield. When the necessary charge of 920 mF for quantitative consumption of PMBO was applied by prolonged electrolysis, the chemical yield was not enhanced. The sprayed felt electrode gave generally quantitative current yields, but the current dropped to zero after ca. 30% alcohol conversion. Turnover numbers of PROXYL catalyst centers are in the range of 1000−1500; only in single cases do they approach 4000. Especially for the felt electrodes which should have an internal surface (0.7 m^3/gram) of 120 times of the exposed surface, these results are still quite unsatisfactory. This is a distinct indication that the homogeneity of the surface coatings is not nearly as good as that with spin-coated disk electrodes. If an efficient and easy to control coating procedure can be developed, it should be possible to extend the scope of redox catalysis further into the gram scale.

Conclusions. Nitroxide-modified polymers prepared from poly(hydrogen siloxanes) with oligo(ethylene glycol) spacers were examined electroanalytically. The oxidation of 4-methoxybenzyl alcohol to the corresponding benzaldehyde by inner sphere redox catalysis of 3-carboxy-Δ3-pyrroline-1-oxyl (**1a**, PROXYL-COOH) served as a model for electrochemical redox catalysis in acetonitrile and water. Cyclic and rotating disk voltammetry, chronoamperometry, and controlled potential electrolyses revealed a high mobility of the polymer constituents, the supporting electrolyte ions, and the substrate molecule in the film, and hence, a high fraction of catalyst centers actively engaged in the reaction zone within this medium. With longer chain ethylene glycol spacers, the catalytic efficiency in neutral aqueous solution is even better than in acetonitrile, where a strong base is needed. Turnover numbers of PROXYL catalyst molecules as large as 30 000 are reproducibly observed at spin-coated glassy carbon disks. Quantities in the 0.3 mmol range are produced at 6 cm^2 carbon plates or felt electrodes, but the threshold to preparative electrochemistry needs substantial amelioration of the coating techniques in this case. For small current applications like in analytical sensors, modified siloxane electrodes appear highly suitable due to their good chemical and electrochemical stability, their facile assembly as multicomponent systems from simple building blocks, and their applicability in aqueous solution.

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