Electron Transfer Reactions between Gels and Quinones

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Electron transfer reactions of quinone derivatives (QDs) with poly(4-vinylpyridine) gels in organic solvents were studied by means of ESR spectroscopy. Formation of radical anions from the QDs and cations from polymeric base was established. The QD^{2-} anions resulting from disproportionation of the QD$^{•-}$ radical anions produce additional cross-links in the gel, causing it to collapse. Sulfhydryl compounds complexed with the gel prevent formation of the ESR signals when the QDs are supplied into the solvent surrounding the gel under oxygen-free conditions. Oxidation of the sulfhydryl compound adsorbed onto the gel results in its desorption, enabling the gel to react with the QD, producing ESR signals. Gels modified with the sulfhydryl compounds collapse in response to the supply of oxygen into their liquid environment.

Introduction

Superior electromagnetic properties of conductive polymers, including doped gels, have generated much interest in the mechanistic understanding of the gel functioning in organic media.[1−5] Doped gels are commonly thought to comprise products of an electron transfer reaction, in which the polymer network is most usually an electron-donating agent, whereas low molecular weight dopants, such as iodine[3,4,6] or quinone derivatives,[2,7−13] serve as electron acceptors. Since quinone derivatives (QDs) tend to generate stable radicals readily observable by ESR spectrometry, in this study we employed QDs as a tool for elucidating possible mechanisms of the gel−dopant interactions. On the other hand, the inherent ability of the QDs to form donor−acceptor complexes with a variety of compounds including polymeric bases has made them a subject of liquid chromatography[14] as well as an emerging area of gels responsive to environmental stimuli.[8−13] In this study we employed ESR to reveal the nature of the products of the gel−QDs complexation, and to find how a gel "responds" to a QD that is added to the surrounding organic solvent. In doing so, we observed that QDs compete with other ligands for reacting with a gel; moreover, these ligands make the gel responsive to the presence of oxygen in the organic solvent.

Experimental Section

Materials. Tetrachloro-1,4-benzoquinone (TClBQ) (99%), 7,7,8,8,-tetracyanoquinodimethane (TCNQ) (98%), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DCBQ) (98%), 4-vinylpyridine (95%), divinylbenzene (80%, mixture of isomers), benzoyl peroxide (97%), and 1-dodecanethiol (98%) were all obtained from Aldrich and were used as received. 2,2′-Azobis(2-methylpropionitrile) (Kodak) was repeatedly crystallized from acetone. Bis(2-ethylhexyl)dithiophosphoric acid of 87% purity was obtained from Zeneca, Inc., and was purified by flash chromatography on silica gel. All other chemicals, gases, and dry organic solvents used were obtained from commercial sources and were of highest purity available.

To prepare gels, radical polymerization was carried out as follows. A mixture of 7.6 mL of 4-vinylpyridine, 220 μL of

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divinylbenzene, and 42 mL of toluene was deaerated by nitrogen bubbling overnight and, following addition of 200 μL of 2,2′-azobis(2-methylpropionitrile) in acetone (300 mg/mL), was kept in a temperature-controlled bath at 75 °C for 96 h, resulting in an opaque gel, which was washed with excess benzene and dried under vacuum. Alternatively, a mixture of 7.6 mL of 4-vinylpyridine, 220 μL of divinylbenzene, and 42 mL of *N,N*-dimethylformamide (DMF) was deaerated by nitrogen bubbling overnight and, following addition of 200 μL of benzoyl peroxide in DMF (300 mg/mL), was kept in a temperature-controlled bath at 75 °C for 96 h, resulting in an orange, transparent gel. A series of micropipets of various diameters had been inserted into the reactor prior to the liquid mixture addition.

Procedures. Gels recovered from micropipets[15] were cut into small cylinders and were kept in DMF. Volume transitions of cylindrical gels were monitored in a transparent, temperature-controlled cuvette under a microscope using a microscaler to fit to the boundaries of the gel on a video monitor. Volume transitions were characterized by d/d_0, where d and d_0 are the diameters of the gel at given and reference solvent composition, respectively.

X-band ESR spectra were recorded at 20 °C with a Bruker esp300E spectrometer in quartz capillaries (Bruker) of 4 mm internal diameter. Microwave power and amplitude of the high-frequency modulation (100 kHz) were adjusted in each experiment to result in the best possible combination of resolution of hyperfine splitting and signal-to-noise ratio. A concentration of electron acceptors equal to 1 mM was shown to provide the finest resolution and therefore was kept constant throughout the ESR study. The solution was purged with nitrogen flow where indicated, and the resulting sample was kept sealed. The unbound quinones and/or semiquinone radicals were removed from the gels, where indicated, by repeated washing with benzene.

Results and Discussion

An outline of the results of this study is presented in Table 1.

ESR spectra were measured for the complexes of QDs and PVP gels as well as QDs and ethylpyridine. The latter is a low molecular weight analog of poly(4-vinylpyridine), which has been extensively studied as a complexant for QDs,[2,7] and yet ethylpyridine is capable of dissolving QDs, thus making it possible to alleviate interference of any additional solvents. The

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TABLE 1: Outline of the Results

object of study	method	Figure
reaction between quinone derivatives and potassium	ESR	1 in Supporting Information
model reaction between quinone derivatives and ethyl pyridine	ESR	2 in Supporting Information
reaction between quinone derivatives and poly(4-vinylpyridine) gel	ESR	1−3
	electronic spectroscopy	4
	swelling	5
effect of oxygen on competitive reactions of quinone derivatives and sulfhydryl compounds with poly(4-vinylpyridine) gel	ESR	6
	swelling	7

QD−ethylpyridine reaction is quite evident due to bright products ranging in color from yellowish to black. The ESR spectra of TClBQ, TCNQ, and DCBQ reacting with ethylpyridine (see the Supporting Information) appeared to be similar to those produced by the corresponding QDs reduced by potassium in tetrahydrofuran:[16]

$$K + QD \rightarrow K^+QD^{\bullet-} \tag{1}$$
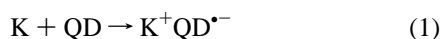
For instance, TCNQ reacting with potassium in the absence of oxygen produced a well-resolved spectrum with 27 lines, due to hyperfine interactions within four equivalent protons and four equivalent nitrogen nuclei (Figure 1A in the Supporting Information). In the presence of oxygen, the hyperfine structure drastically broadened, so that only a structureless singlet was observed. Both TCNQ and DCBQ produce stable free radical products with ethylpyridine, similar to those with potassium, although with a somewhat poorer resolution (TCNQ and TClBQ) or with a lower yield of stable radicals (DCBQ) (Figure 2 in the Supporting Information). Incomplete resolution of the spectrum of TCNQ in ethylpyridine was apparently due to the concentration broadening, since the resolution could be improved by dilution of the ethylpyridine with benzene. The dilution technique was not applicable to the TClBQ−ethylpyridine complex, which appeared to be insoluble in benzene. Differences in spectra of the QDs reacting with ethyl pyridine may be explained by the different solubility of the charge transfer complexes. Indeed, TCNQ and DCBQ formed homogeneous solutions in ethylpyridine, yielding isotropic ESR spectra, characteristic for fast molecular tumbling that completely averages the anisotropic contribution to the hyperfine interactions. TClBQ produced a paramagnetic precipitate with an unisotropic spectrum (Figure 2C in the Supporting Information). These observations correspond well to the reported solubilities of QD-based charge transfer complexes.[7]

The above results afford a conclusion that a QD reacts with the base (B) giving a stoichiometric complex:

$$QD^o + B \rightarrow [QD^{\bullet-}B^{\bullet+}] \tag{2}$$
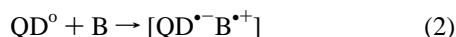
where the QD accepts an electron from ethylpyridine, acting as a π-acid. Existence of a stable cation radical is not supported by the ESR spectra. This is in accord with the reported formation of electron transfer complexes of TCNQ and aliphatic amines.[17] Complexes between TCNQ and amines are considered to involve transfer of a π-electron from TCNQ (strong acceptor) to the base (donor).[18] An ion−radical complex may exist in a diamagnetic singlet ground state with a corresponding paramagnetic triplet excited state or in a paramagnetic doublet state.[17,18] Paramagnetic salts of the TCNQ radical anion with onium cations of various bases, such as tertiary ammonium, pyridinium, quinolinium, and morpholinium, have been reported.[17,19−22] Notably, however, these salts usually contain a diamagnetic cation complexed with the TCNQ$^{\bullet-}$ anion radical as the only stable ESR-active species, even in the absence of a strong electron and/or proton donor. It may be hypothesized
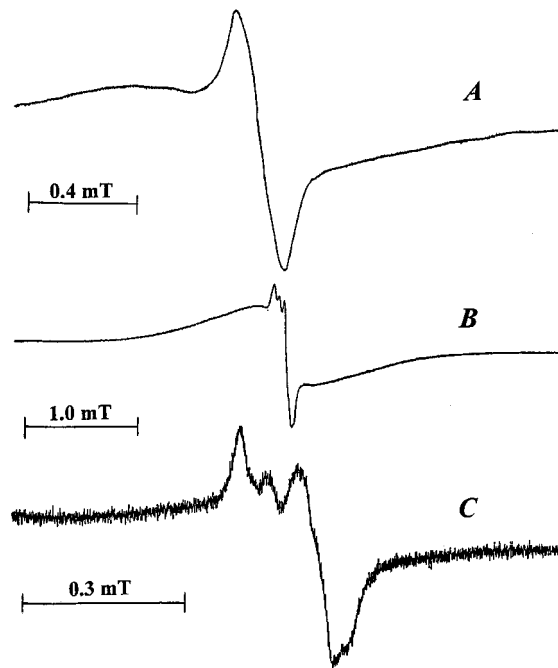
Figure 1. ESR spectra generated by TCNQ reacting with poly(4-vinylpyridine) (PVP) gel in benzene under oxygen-free conditions at different amplitudes of high-frequency modulation. Microwave power is 2.00 mW. Amplitudes are 540, 54, and 5.4 μT in A, B, and C, respectively. Gel was synthesized in toluene.

therefore that in a basic environment the cation-radical B$^{\bullet+}$ (reaction 2) disappears due to dimerization:

$$2B-H^{\bullet+} \rightarrow B-B + 2H^+ \tag{3}$$
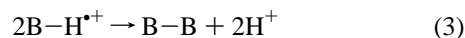
leaving the QD$^{\bullet-}$ to be the only free radical species stable in the presence of the abundant base.

Is the scheme (2) relevant for a QD−gel system? To address this question, we chose benzene to be a medium for the gel−QD reactions. Being a nonpolar solvent, it should cause no complications related to the strong absorption of microwave power, so that samples of substantial volume can be studied at room temperature. Also, the charge transfer complexes are unlikely to be dissociated in benzene, and moreover, formation of the complexes between QD and the solvent itself will be avoided. In contrast, Gong et al.[11] reported formation of charge transfer complexes between TCNQ and dimethylformamide in the form of DMF$^+$TCNQ$^{\bullet-}$.

Inspection of the ESR spectra shows that the QDs react with poly(4-vinylpyridine) (PVP) gels in benzene (Figures 1−3). This reaction results in stable paramagnetic products with characteristic ESR spectra. The somewhat poorer resolution than in the case of potassium or ethylpyridine can be explained by immobilization of the free radicals within the gel network.

Reaction of the PVP gel with TCNQ produced a bright yellow solution with at least two different ESR signals: one broad singlet line ($\Delta H = 0.6$ mT) clearly visible at higher modulation
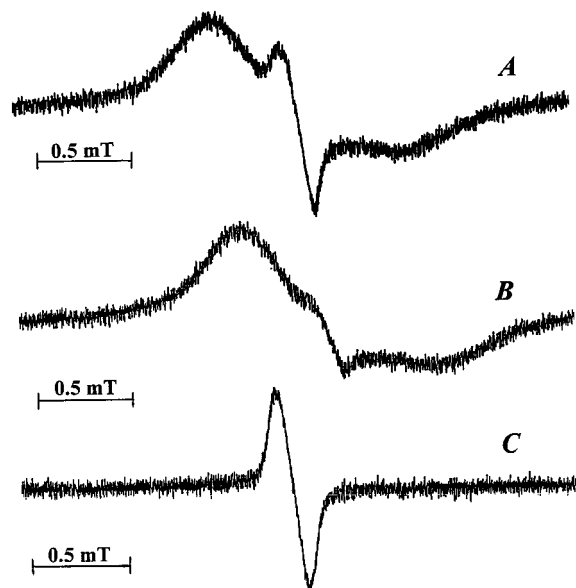
Figure 2. ESR spectra generated by TClBQ reacting with PVP gel in benzene: (A) the gel in contact with TClBQ-containing solution; (B) spectrum of the TClBQ complexed with gel that was removed from the solution and washed with excess benzene; (C) spectrum of the species removed from the gel by washing with benzene. Microwave power and amplitude of high-frequency modulation are 1.98 mW and 9.6 μT, respectively.
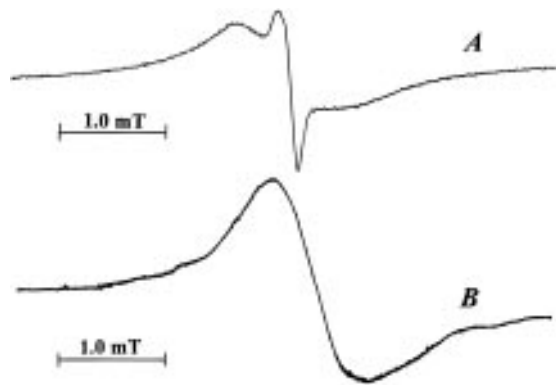
Figure 3. ESR spectra generated by DCBQ reacting with PVP gel in benzene: (A) the gel in contact with DCBQ-containing solution; (B) spectrum of the DCBQ−gel that was removed from the solution and washed with excess benzene. Microwave power is 2.00 mW. Amplitudes of high-frequency modulation are 96 and 54 μT in A and B, respectively.

level (Figure 1) and a set of four narrow lines better resolved at lower frequency modulation amplitude (Figure 1C). The multiplet signal was observed to be sensitive to electron- and proton-donating additives (see below). It is remarkable that when repeated washing of complexed TCNQ species off the gels was attempted by shaking with excess benzene and/or tetrahydrofuran, no ESR signal was detected in the concentrated washouts, while the ESR signal in the gel was persistent. These observations suggest that all the free radicals were bound to the polymer network.

Reaction of TClBQ with the PVP gel in benzene produced an ESR spectrum (Figure 2) that appeared to be a superposition of a broad singlet and narrow lines ($\Delta H_{1/2} = 0.10$ and 0.01 mT, respectively). The gel and the surrounding solution became yellow-green. The gel was filtered off, and both the gel and the supernatant were analyzed. The supernatant was observed to contain only the narrow ESR signal (Figure 2C), while gel possessed both narrow and broad lines. The narrow signal appeared to be removable from the gel phase by repeated
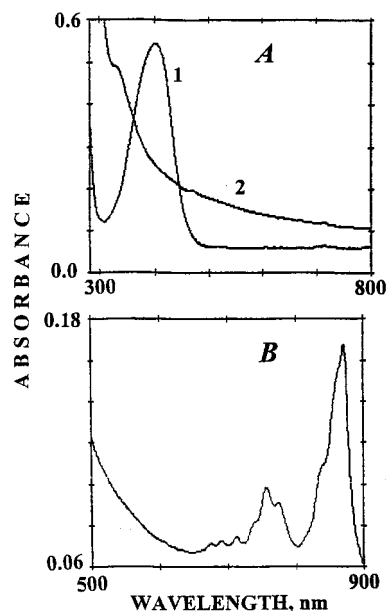

Figure 4. Electronic spectra of 1 mM TCNQ reacting with either PVP gel (A) or un-cross-linked poly(4-vinylpyridine) (M_r 10 000) (B) in benzene. $T = 20$ °C. In A: (1) solution of 1 mM TCNQ in benzene; (2) TCNQ-PVP gel equimolar mixture. To calculate molarity of the gel, cross-linking was disregarded.

washing with either benzene or acetone. The broad signal (Figure 2B) was exceptionally stable and did not change for at least 21 days despite the washing.

Similar results were observed with DCBQ−PVP gel complexes (Figure 3). Again, a narrow and a broad signal were observed, and the narrow signal that was produced by a loosely bound species could be washed from the gel by organic solvents. The broad signal belonging to the gel-immobilized species was persistent.

Electronic spectra of TCNQ reacting with PVP gel (Figure 4) support the proposed mechanism of formation of radical anions QD$^{\bullet -}$ following their immobilization in the gel. Indeed, addition of dry PVP resin into 1 mM TCNQ solution in benzene eliminated the peak at 402 nm characteristic for neutral TCNQ, thereby confirming that the QD was absorbed into the gel. Instead, a distinctive shoulder appeared at 330 nm, assignable to TCNQ.[2−11,23] The anion-radical complexed with the gel may further disproportionate, giving the observed anion:[11]

$$2TCNQ^{\bullet -} \rightarrow TCNQ^{o} + TCNQ^{2-} \qquad (4)$$
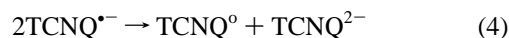
Absorbances at 871, 775, 757, 714, and 691 nm assignable to TCNQ$^{\bullet -}$ [11,17,23] due to the charge transfer reaction with PVP, although very minor in the solution outside the gel (Figure 4A), were clearly observable inside the gel, as modeled by the solution of un-cross-linked poly(4-vinylpyridine) in acetonitrile (Figure 4B).

It has been reported that the QD−gel reactions lead to volume phase transitions in organic solvents.[8−13] While the majority of these works were on the reaction of poly{N-(3-dimethylamino)propyl]acrylamide} with TCNQ in dimethylformamide,[8] Annaka et al.[9] reported TClBQ-induced discontinous phase transition (swelling above a certain concentration of TClBQ) of poly(4-vinylpyridine-co-styrene) gel in benzene. The discontinuity of the phase transition implies ionization of the gel (electron donor) at a certain, fairly narrow concentration range of TClBQ (electron acceptor).[9] However, complexation of the excess polymeric base and QD (reaction 2) is stoichiometric,[11] and the ensuing complex is very unlikely to dissociate in benzene. On the other hand, with the increasing concentration

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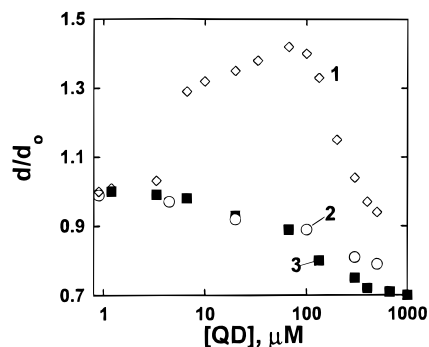
Figure 5. Effect of quinone derivatives on relative diameter of PVP gel. TCNQ (1,2) or TClBQ (3) were dissolved in either anhydrous *N,N*-dimethylformamide (1) or benzene (2, 3) in various concentrations. In 1, the gel was synthesized in *N,N*-dimethylformamide; in 2 and 3, in toluene. Oxygen was removed from the corresponding solvent by nitrogen bubbling for 16 h at 20 °C. For other experimental conditions, see the Experimental Section.

of the QD, the rate of radical anion disproportionation (reaction 2) increases, producing anion QD^{2-}. The latter should serve as an effective cross-linking agent for the gel, if its basic groups are not exhausted:

$$\sim B^+ + QD^{2-} + \sim B^+ \rightarrow \sim B^+ QD^{2-} B^+ \sim \quad (5)$$
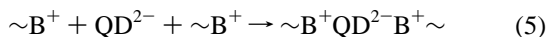
Appearance of additional cross-linking should drastically reduce the swelling of the gel, so that an almost 10-fold increase of swelling observed in the poly(4-vinylpyridine-*co*-styrene)[9] may be due to the presence of styrene in the polymer backbone of the gel. Since styrene moieties may adsorb TClBQ, although not as strongly as vinylpyridine,[24] TClBQ can continue to adsorb onto the copolymer even after all vinylpyridine groups have reacted with TClBQ (reaction 2). The excessive TClBQ will start to disproportionate (reaction 4), but at this point it will not become an additional cross-linker (reaction 5), because there will be no basic groups available for complexing with the $TCNQ^{2-}$. Appearance of the charged species adsorbed onto the gel will ionize the polymeric chains, which then repulse each other, causing the gel to swell. The discontinuity of the phase transition in this case is related to the increased chain stiffness.[9]

The above considerations suggest that in a PVP gel, devoid of QD-adsorptive moieties apart from vinylpyridine, the effect of the TClBQ addition should be opposite of that observed in copolymer-based gels.[9] Indeed, collapse of PVP gel in benzene was observed when TClBQ was added (Figure 5). This experiment is direct evidence of the TClBQ-induced additional cross-linking. The cross-linking can explain the insolubility in organic solvents of the complexes of TClBQ or DCBQ with initially un-cross-linked poly(4-vinylpyridine) reported in the early work by Hallensleben.[7] Interestingly, it was observed[7] that while products of the reaction of tetracyanoethylene (analog of TCNQ) and un-cross-linked PVP were insoluble in nonpolar methylene chloride, they dissolved in DMF. Thus we hypothesized that if a solvent can be found in which the QD–gel complexes would dissociate, the swelling behavior of the gel should be different from that in a dissociation-prohibiting solvent. Indeed, if the dissociation of the products (reaction 2) is allowed,

$$[QD^{\bullet -} B^{\bullet +}] \leftrightarrow QD^{\bullet -} + B^{\bullet +} \quad (6)$$
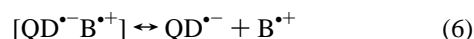
this would result in an ionization of the gel and therefore to its swelling. However, with the increased QD concentration, disproportionation of the $QD^{\bullet -}$ followed by the cross-linking
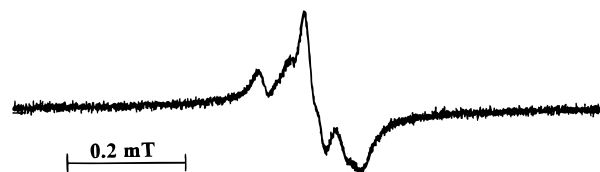

Figure 6. Effect of oxygen on ESR spectrum generated by TCNQ reacting with PVP gel in benzene in the presence of bis(2-ethylhexyl)-dithiophosphoric acid (DTPA). The spectrum in Figure 1C was inhibited by addition of 0.1 mM DTPA under oxygen-free conditions. Purging the system with oxygen restored the ESR signal (this figure). Microwave power and amplitude of high-frequency modulation are 2.00 mW and 5.4 μT, respectively.

(reaction 5) will override this tendency and the gel will collapse. Swelling of the PVP gel in DMF in the presence of TCNQ is in excellent agreement with this hypothesis (Figure 5).

Finally, we addressed the question of whether ligands other than QDs present in the gel environment would compete with the QDs for the binding with the gel. Since sulfhydryl compounds are known to act as proton-donating agents for PVP in organic solvents[15,25] and also can serve as electron donors for QDs and/or their radical anions,[25] we chose 1-dodecanethiol (DDT) and bis(2-ethylhexyl)dithiophosphoric acid (DTPA) as representative ligands. The narrow multiplet signal observed in the solutions of TCNQ complexed with PVP gel (Figure 1C) appeared to be inhibited by addition of DTPA (1 mM) under nitrogen atmosphere. Interestingly, the ESR signal in the DTPA-containing system could be restored under flow of oxygen. Relative intensities of spectral lines in the restored ESR spectrum were modified (Figure 6). It is thus plausible that several paramagnetic centers were formed in the TCNQ-doped PVP gel, rather than a single one. Alternating inhibition and appearance of the ESR spectrum in the DTPA–PVP–TCNQ system in benzene appeared to be reversible, depending on the concentration of oxygen in the system.

Addition of DCBQ into DDT (1 mM) solution in benzene containing PVP gel under oxygen-free conditions prevented the subsequent formation of the DCBQ semiquinone radical. No ESR signal was observed, although the red-brownish products formed. When the system was purged with oxygen, the ESR signal was restored within 2–3 hours. The sequence of the competitive reactions of either DDT or DCBQ was important, since the ESR signal of the already prepared DCBQ–PVP complex was insensitive to the presence of DDT. Hence, the QD-doped gels can act as ESR oxygen sensors in organic solvents. It is interesting to note that the QD species immobilized in the gel (Figures 2B and 3B) were insensitive to the addition of either DTPA or DDT, whereas radicals removed from the gel (see, for instance, Figure 2C) were inhibited by the sulfhydryl compounds.

We propose the following explanation of the above observations. In absence of oxygen, PVP gel complexes with the thiol (scheme (7)). This complexation competes with reaction 2, thus inhibiting the EPR spectra. On the other hand, oxygen prevents complexation 7 due to redox reactions 8.
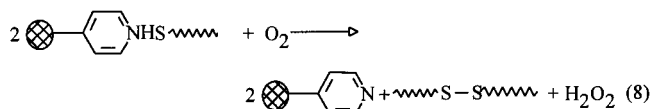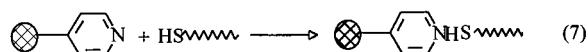
Removal of the thiol (reaction 8) restores the gel's ability to react with the QD, and thus the ESR signal is again observed
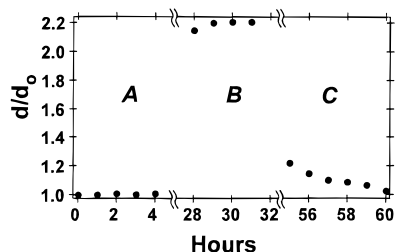
Figure 7. Effect of oxygen on relative diameter of PVP gel in benzene: (A) no 1-dodecanethiol added, oxygen-free conditions; (B) 1 mM 1-dodecanethiol added under constant flow of nitrogen; (C) system as in B, after supply of oxygen.

(spectrum 2 in Figure 4). Similarly, DTPA absorbed on PVP gels was shown[26] to oxidize to disulfide by TCNQ, which was reduced, taking up the electron to form the anion-radical TCNQ$^{\bullet-}$. Removal of the DTPA caused the gel to collapse in benzene.

Suggested complexation of the PVP with the thiol (reaction 7) called forth the subsequent set of experiments. Should reaction 7 take place, the thiol in turn is to make the gel more hydrophobic due to exposed dodecyl groups. These groups should readily absorb organic solvents (such as benzene, which is a poor solvent for PVP[27−29]), thereby causing the gel to swell.[15] Removal of the complexed thiol (scheme (8)) will then cause the gel to collapse. Indeed, high swelling of PVP gel was observed in 1 mM solution of 1-dodecanethiol in benzene in oxygen-free conditions, but when the solution was purged by oxygen bubbling for 16 h, the gel collapsed (Figure 7). To the best of our knowledge, this is the first encounter of a gas-sensitive nonaqueous gel system.

Conclusions

Electron transfer reactions of three quinone derivatives (QDs) with poly(4-vinylpyridine-*co*-divinylbenzene) gels and their low molecular weight analog, ethylpyridine, were studied by means of ESR spectroscopy with the goal of the mechanistic understanding of a design of a responsive gel system in organic solvents. It has been demonstrated that QDs react with polymeric base forming a polymer-bound radical anion QD$^{\bullet-}$. In benzene, anions QD^{2-} resulting from dismutation of semiquinone radical anions can serve as additional cross-links in the gel, causing it to collapse. However, in the polar solvent, such as *N,N*-dimethylformamide, dissociation of the QD−gel complex initially leads to an increase of the gel swelling due to its ionization. A rise in the QD concentration followed by generation of the QD$^{\bullet-}$ radical anions and QD^{2-} anions neutralizes the gels and adds cross-links, so that the gel collapses. Addition of the hydrophobic electron donors, such as 1-dodecanethiol or bis(2-ethylhexyl)dithiophosphoric acid into the gel environment, prevents formation of the ESR signals

when the QDs are then supplied into the system under oxygen-free conditions. Subsequent purging of the system with oxygen results in the removal of the thiol from the gel, which then reacts with the QD, producing ESR signals. Thus the system is an oxygen-sensitive ESR sensor. Redox reactions of the thiol interacting with the gel cause the gels to swell or collapse in response to the changes in the gas content in organic solvents.

Supporting Information Available: ESR spectra generated by 7,7,8,8-tetracyanoquinodimethane, tetrachloro-1,4-benzoquinone, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone reacting with potassium in anhydrous tetrahydrofuran or with ethylpyridine under oxygen-free conditions (2 pages). Ordering information is given on any current masthead page.

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