Interactions among Poly(4-vinylpyridine) Gels, Quinone Derivatives, and Sulfhydryl Compounds

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Competitive interactions of sulfhydryl compounds and quinone derivatives with poly(4-vinylpyridine) gels have been studied in organic solvents. 7,7,8,8-Tetracyanoquinodimethane (TCNQ) oxidizes a sulfhydryl compound to disulfide, while TCNQ is reduced to an anion radical that reacts with the gels. Adsorption of long-chain sulfhydryl compounds onto gels causes the gel swelling, whereas oxidation of the adsorbed sulfhydryl compound to disulfide by TCNQ, and therefore, its removal from the gel results in the gel shrinking. The larger the highest occupied molecular orbital energy of the sulfhydryl compound, the stronger its interaction with a quinone derivative and thus the faster the removal from the gels, as revealed by HPLC.

Introduction

Since their discovery by Benesi and Hildebrand,[1] charge-transfer reactions (CTRs) have become a subject of large amount of work[2,3] because of very pertinent interest in the mechanism of the CTRs, including molecular orbital considerations,[2] as well as the applications of the charge-transfer complexation, such as various types of chromatography.[4] CTRs are also utilized in an emerging area of conductive polymers, including doped gels, which are commonly thought to comprise products of a CTR, where a polymer network is most usually an electron-donating agent, whereas low molecular weight dopants, such as quinone derivatives (QDs), serve as electron acceptors.[5,6] Gels doped with QDs undergo discontinuous volume phase transitions due to ionization of the polymeric backbone in fully nonaqueous systems.[7] On the other hand, interaction of basic gels with surfactants bearing acidic sulfhydryl functionality causes large, continuous volume transitions of gels in neat organic solvents.[8] Applying the electron paramagnetic resonance (ESR) method, we have recently observed[9] formation of stable anion radicals from the QDs and cation radicals from poly(4-vinylpyridine) gels (polymeric base) upon complexation of the base and the QD. However, when a sulfhydryl compound was supplied into the nonaqueous gel environment, it prevented formation of the EPR signals when the QDs were then added into the system. Thus, quinone derivatives and sulfhydryl compounds compete for binding with polymeric bases in organic solvents. Consequently, in the present study we applied a poly(4-vinylpyridine)-modified stationary phase in HPLC to elucidate the competitive character of charge-transfer reactions among basic gels, quinone derivatives, and sulfhydryl compounds.

Experimental Section

Materials. 7,7,8,8-Tetracyanoquinodimethane (TCNQ) (98%, Aldrich) was recrystallized at 60 °C in acetonitrile. Phosphorus pentasulfide (99%), 4-vinylpyridine (95%), phenol (99+%), 1-nonanol (98%), ethylene glycol dimethacrylate (98%), divinylbenzene (DVB) (80%, mixture of isomers), styrene (99+%), ammonium persulfate (APS, 98+%), and 1-dodecanethiol (98%) were all obtained from Aldrich and were used as received. Ammonium diethyldithiocarbamate (99%) and potassium *O*-ethylxanthate (98%) were obtained from Aldrich and converted into their acidic forms by solvent extraction from the corresponding HCl aqueous solutions into carbon tetrachloride. The equilibrium extraction process was run in standard separation funnels and was followed by the acid purification by flash chromatography on silica gel.[10] Di(2,4,4-trimethylpentyl)-dithiophosphinic acid (82%) was obtained from Cytec Industries, Inc. and was purified by flash chromatography on silica gel. Diethyl-, di(*n*-propyl)-, di(2-ethylhexyl)-, di(1,3-dimethylbutyl)-, and di(isopropyl)phosphorodithioic acids of 83−95% purity were all obtained from Zeneca, Inc. and were purified by flash chromatography on silica gel. Dimethyl-, dibenzyl-, and dinonyldithiophosphates were synthesized by reacting methanol, phenol, and 1-nonanol, respectively, with phosphorus pentasulfide following purification as described previously.[10] 2,2′-Azobis(2-methylpropionitrile) (Kodak) was repeatedly crystallized from acetone. All other chemicals, gases, and dry organic solvents used were obtained from commercial sources and were of the 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 divinylbenzene, and 42 mL of toluene was deaerated by nitrogen bubbling overnight and after 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 that 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 after 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. Gels recovered from micropipets[8] were cut into small cylinders and were kept in an appropriate solvent.

Packing material for HPLC was synthesized from poly(4-vinylpyridine)-modified polystyrene latex beads by the following three-step procedure.[11] Emulsion of styrene in NaCl solution (effective concentrations of styrene and NaCl were 1 M and 15 mM, respectively) was deaerated by N_2 bubbling while stirring

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overnight at 20 °C. Then freshly prepared 0.5 mg/mL solution of APS in water was added, resulting in a 2.5 mM effective concentration of APS in the reaction mixture. The reactor was kept at 70 °C while the mixture was stirred for 24 h, and the resulting polystyrene latex particles (diameter of ca. 1 μm) were filtered off and washed extensively with water. Swelling of the suspension of polystyrene particles in water (0.1 g/mL) in an emulsion of dibutyl phthalate, benzoyl peroxide, and sodium dodecyl sulfate after equilibration with ethylene glycol dimethacrylate and toluene was carried out in a three-neck stirred 250 mL reactor at 20 °C as described previously.[11] Then the dispersion was allowed to stay at 80 °C under nitrogen atmosphere while being stirred for 4 h, and after addition of 4-vinylpyridine and APS (resulting in their 0.1 and 10 mM effective concentrations, respectively), it was kept at 80 °C under a nitrogen atmosphere and stirred for another 3 days. The reaction mixture was then poured into excess cold water, and the supernatant was discarded after sedimentation of the partciles. The polymer particles were washed with methanol, tetrahydrofuran, and acetone as described elsewhere[11] and dried at room temperature under vacuum. The slurry of the prepared round-shaped beads in a glycerol/water (5:1 v/v) mixture was packed[12] under pressure in a Hewlett-Packard stainless steel column (200 mm × 2.1 mm). After it was packed, the column was extensively washed with deionized distilled water and acetonitrile.

Procedures. NMR spectra were recorded on a Bruker AMX400 spectrometer using tetramethylsilane and H_3PO_4 as internal and external frequency locks for ^1H and ^{31}P NMR, respectively. Chromatography was run at 20 °C on a Shimadzu LC-10A Series HPLC system, which included an SPD-10AV UV−vis detector allowing for simultaneous dual-wavelength measurement, a LC-10AD solvent delivery unit, and a SCL-10A system controller. A solute in acetonitrile was loaded onto the column and then eluted with either acetontrile or solution of TCNQ in acetonitrile using a pump speed of 0.2 mL/min. Sharpest resolution was observed with 90 μM solution of TCNQ that was then used throughout. Detection at 195 nm ($\epsilon = 1400$, absorption of sulfhydryl group) was synchronized with detection at 260 nm where absorbance of the TCNQ was minimal and yet where most of the solutes absorbed strongly. Retention times with (RT_w) and without (RT_{wo}) TCNQ were determined three times for each solute, and less than 2% relative standard deviation was measured. Void volume of the column (RT_o) was determined using LiCl in acetonitrile (detection at 195 nm). Acceleration factors were defined as[13,14]

$$\phi = (RT_{wo} - RT_w)/(RT_{wo} - RT_o)$$

Volume transitions of cylindrical gels synthesized in micropipets were monitored at 20 °C in a transparent, temperature-controlled cuvette under a microscope using a microscaler to fit the boundaries of the gel on a video monitor. Kinetics of volume transitions was monitored, and only equilibrium data are further discussed. Volume transitions were characterized by d/d_o, where d and d_o are the diameters of the gel in a given and reference solvent, respectively.

To calculate the HOMO energy, dipole moment, *n*-octanol-to-water partition coefficient (log *P*), Hansen 3-D parameter (δ), and molecular weight (MW) of the solute, the Molecular Modeling Pro (version 2.0) program was used. Extended Huckel calculations[15] were applied to compute HOMO energies.

Results and Discussion

Electronic spectra of tetracyanoquinodimethane (TCNQ) reacting with PVP gel in acetonitrile are shown in Figure 1. It

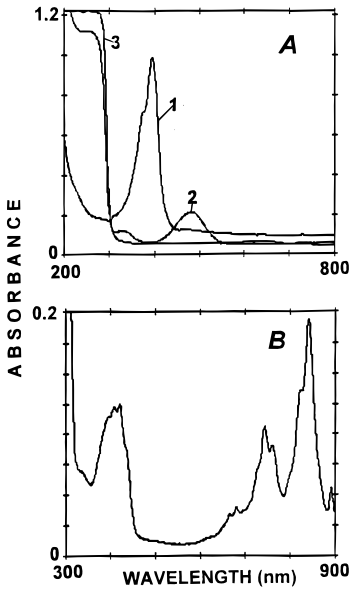
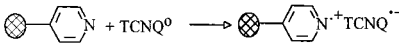


Figure 1. Electronic absorption spectra of TCNQ reacting with either poly(4-vinylpyridine-*co*-divinylbenzene) (PVP) gel (A) or uncross-linked poly(4-vinylpyridine) (B). All spectra were measured in acetonitrile. Part A shows 15 μM TCNQ (curve 1), extract from PVP gel (curve 2), and a solution of 15 μM TCNQ reacted with excess PVP gel (curve 3). In part B, a solution of 15 μM TCNQ reacted with 10 μM uncross-linked poly(4-vinylpyridine) ($M_r = 50\,000$).

can be seen that reaction of the TCNQ in solution contacting PVP gel results in a disapperance of the strong absorbance of neutral TCNQ at 394 nm,[5] whereas absorption bands at 330 (assigned to $TCNQ^{2-}$) and 482 nm (α,α-dicyano-*p*-toluoylcyanide anion, $DCTC^-$) appeared. Absorbances at 842, 761, 743, 680, and 420 nm assignable to $TCNQ^{\bullet -}$ [5,16] due to the charge-transfer reaction with PVP, although observable in the solution outside the gel (Figure 1A), were much stronger inside the gel, as modeled by the solution of uncross-linked poly(4-vinylpyridine) in acetonitrile (Figure 1B). Overall, the sequence of these reactions can be described by the following scheme:



(1)

$$2TCNQ^{\bullet -} \rightarrow TCNQ^0 + TCNQ^{2-} \quad (2)$$

$$TCNQ^{2-} + O_2 \rightarrow NCO^- + DCTC^- \quad (3)$$

We have recently shown the formation of radical anions from TCNQ and cations from the polymeric base (reaction 1) by ESR spectroscopy.[9] Salts of TCNQ and amines usually contain a diamagnetic cation complexed with the $TCNQ^{\bullet -}$ radical anion as the only stable ESR-active species.[16] ESR spectroscopy suggests that cation radicals of pyridine (reaction 1) may further form dimers.[9] Specificity of reaction 1 carried out with the gel (as opposed to the reaction with a low molecular weight gel analogue—ethyl pyridine) is in the immobilization of the free radicals within the gel network, as evidenced by ESR.[9] Thus, the reaction of the PVP gel with TCNQ produced a complex with at least two different ESR signals: one broad singlet line and a multiplet signal. When repeated washing of complexed TCNQ species off the gels was attempted with excess solvents, no ESR signals were detected in the concentrated wash-outs, while the ESR signal in the gel was persistent. These observations suggest that all the free radicals were bonded to the polymer network.[9]

Interestingly, addition of SH-containing compounds, such as di(2,4,4-trimethylpentyl)dithiophosphonate or di(2-ethylhexyl)-

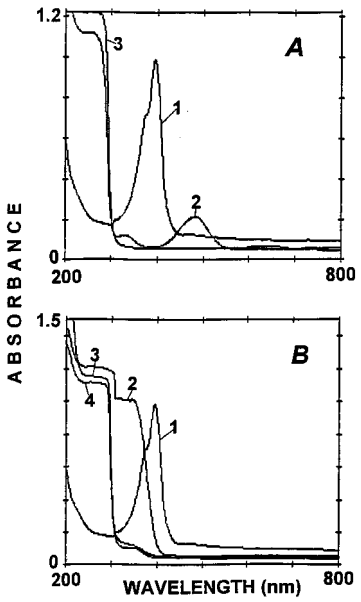
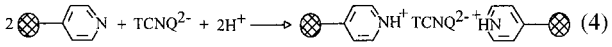


Figure 2. Electronic absorption spectra of TCNQ reacting with di(2,4,4-trimethylpentyl)dithiophosphonate (A) or di(2-ethylhexyl)dithiophosphate (B) in acetonitrile. PVP gel was synthesized in toluene (see Experimental Section). Part A shows 15 μM TCNQ (curve 1), 3 mM di(2,4,4-trimethylpentyl)dithiophosphonate reacted with 15 μM TCNQ (curve 2), and 3 mM di(2,4,4-trimethylpentyl)dithiophosphonate reacted with 15 μM TCNQ after addition of excess PVP gel (curve 3). Part B shows 15 μM TCNQ (curve 1), 3 mM di(2-ethylhexyl)dithiophosphate reacted with 15 μM TCNQ (curve 2), 3 mM di(2-ethylhexyl)-dithiophosphate (curve 3), and 3 mM di(2-ethylhexyl)dithiophosphate reacted with 15 μM TCNQ after addition of excess PVP gel (curve 4).

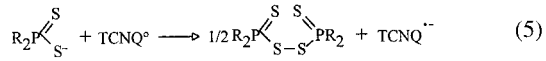
dithiophosphate, into the TCNQ solution caused a disappearance of the absorption at 394 nm and an appearance of a distinctive shoulder at 330 nm (parts A and B of Figure 2). Only minor absorption peaks in the charge-transfer area (798 and 730 nm) were observed, thus indicating that anion radicals $TCNQ^{\bullet-}$ disproportionated and anions $TCNQ^{2-}$ prevailed in the system (reaction 2). When PVP gel was further added into the solution, absorption at 300−330 nm either completely disappeared (Figure 2A) or substantially diminished (Figure 2B), suggesting that the $TCNQ^{2-}$ reacted with the polymeric base:



(4)

Here, the acidic[17] sulfhydryl group served as a proton source.

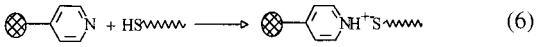
The possibility of the formation of ion radicals by reaction between sulfhydryl compounds and quinone derivatives has been demonstrated by ESR spectroscopy.[18] To verify the mechanism of the reaction between di(2-ethylhexyl)dithiophosphate (DTP) and TCNQ, the phosphorus-containing fraction of the products was separated after evaporation of acetonitrile and purified using flash chromatography on silica gel.[10] The oily residue was subjected to ^1H and ^{31}P NMR. In proton NMR spectrum, only minor resonances at around 4.3 ppm (S−H group of DTP[10]) were observed (below 2% total), whereas the ^{31}P spectrum featured the main peak at 86.83 ppm characteristic for disulfide DTP−S−S−DTP.[10] These data strongly indicate that DTP^- was oxidized to disulfide, while TCNQ was reduced by taking up the electron to form $TCNQ^{\bullet-}$:



(5)

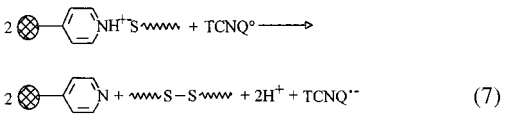
Almost complete disappearance of the peaks in the charge-transfer area (Figure 2B) suggests disproportionation (reaction 2) of the anion radicals formed in reaction 5. The anions were then consumed by the PVP gel (reaction 4).

The ability of TCNQ to react with both sulfhydryl compounds and PVP gels allows for the following hypothesis to be forwarded. PVP gels, with well-documented nucleophilicity of the 4-vinylpyridine nitrogen,[19] strongly associate with long-chain sulfhydryl compounds in organic solvents:



(6)

This makes the gels more hydrophobic because of the exposed alkyl group(s). It has recently been shown that the complexation of the gels with sulfhydryl-containing compounds causes the phenomenon of gel swelling in solvents that are usually poor for the PVP itself.[8] In the presence of TCNQ, thiol complexation (reaction 6) should compete with the charge-transfer reaction. Moreover, TCNQ should prevent complexation (reaction 6) due to redox reaction 5. Removal of the thiol (reaction 7) will then diminish the gels' ability to "superabsorb" solvents:



(7)

Gel swelling experiments were designed to verify the above hypothesis. Figure 3 shows effect of TCNQ on swelling of PVP gels in DTP-containing benzene (poor solvent for PVP[20]) where the gels had been equilibrium swollen. As predicted, this resulted in a significant decrease of the gel swelling, especially at higher DTP concentrations.

Existence of competitive reactions 1 and 4, 6 and 7 suggests that if TCNQ were added to modify the mobile phase in an HPLC experiment on a PVP-based stationary phase, this would lead to a certain decrease in the retention time of the thio compounds. To explore this possiblity, retention times for a number of representative sulfhydryl compounds were measured and corresponding acceleration factors in order of increasing ϕ

TABLE 1: Acceleration Factors (ϕ) and Properties of the Solutes

solute	ϕ	MW	HOMO energy (MeV)	log P	dipole moment (D)	δ (MPa$^{1/2}$)
O,*O*-dimethyldithiophosphate	0.52	158.2	−230.2	4.66	5.18	14.1
O,*O*-diethyldithiophosphate	0.56	186.2	−228.8	5.71	5.11	14.5
O,*O*-di(*n*-propyl)dithiophosphate	0.57	214.3	−228.6	6.77	5.05	15.4
1-dodecanethiol	0.62	202.4	−225.1	6.47	1.03	17.6
O-ethylxanthate	0.63	122.2	−219.5	1.92	1.86	22.9
O,*O*-dibenzyldithiophosphate	0.65	282.3	−218.8	6.73	5.15	19.3
O,*O*-dinonyldithiophosphate	0.68	382.6	−212.6	13.1	3.80	16.2
O,*O*-di(1,3-dimethylbutyl)dithiophosphate	0.71	298.5	−201.3	9.43	5.20	15.1
O,*O*-di(2,4,4-trimethylpentyl)dithiophosphonate	0.73	322.6	−195.4	8.27	2.10	16.3
O,*O*-di(isopropyl)dithiophosphate	0.75	214.3	−175.2	6.50	5.19	14.4
N,*N*-diethyldithiocarbamate	0.78	149.3	−152.8	2.90	0.594	21.9
O,*O*-di(2-ethylhexyl)dithiophosphate	0.81	354.6	−143.6	11.7	5.16	15.7

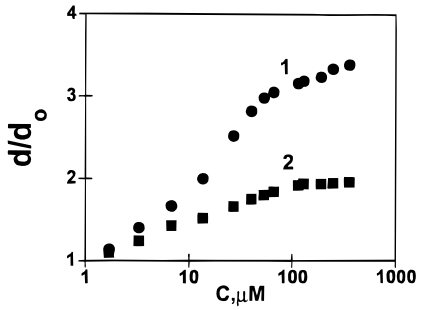


Figure 3. Effect of TCNQ on volume transition of PVP gel induced by di(2-ethylhexyl)dithiophosphate (DTP) in benzene. *C* is the micromolar concentration of DTP in benzene. Gels were synthesized in DMF (see Experimental Section). Curve 1 is the result with no TCNQ added. Curve 2 is the result with TCNQ added, resulting in 0.5 mM concentration in each benzene/DTP solvent composition.

were collected in Table 1. In an attempt to reveal the mechanism of acceleration, a number of parameters for each solute were calculated and also presented in Table 1. It can be seen that among the chosen parameters, the highest occupied molecular orbital (HOMO) energy strikingly correlates with the relative difference between retention times observed with and without the TCNQ in the mobile phase. No correlation was observed between ϕ and the solute hydrophobicity (log *P*) or in size (MW) or total Hansen solubility parameter (δ). These results can be understood in terms of charge-transfer complexation between the solutes (electron donors) and TCNQ (electron acceptor).[4,13,21] The difference between the ionization potential of the donor and the reduction potential of the acceptor is a measure of the interaction energy ΔE that reflects the stability of the charge-transfer complex. Within a certain approximation (i.e., only π-electrons are transferred from frontier orbitals of acceptor and donor), the equation of Klopman and Salem holds:[22]

$$-\Delta E = 2\sum c_{\mathrm{HOMO}}{}^2 c_{\mathrm{LUMO}}{}^2 \beta^2/(E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}}) \qquad (8)$$

where *c* and *E* are orbital coefficients and energies of frontier orbitals, respectively, and β is the resonance integral. Indexes HOMO and LUMO are related to highest occupied molecular orbital of the donor and lowest unoccupied molecular orbital of the acceptor, respectively.

In a series of structurally related compounds, the numerator in eq 8 can be approximated by a constant. Consequently, if only one acceptor is used (E_{LUMO} = constant), the higher the donating character of the solute (higher E_{HOMO}), the more stable the charge-transfer complex (larger ΔE) should be. Thus, the removal of the strongly donating solute from the stationary phase should occur relatively earlier than the weakly donating one, when the acceptor (TCNQ) is added to the mobile phase, which was indeed observed (see Table 1). Since the energy of the charge transfer (ΔE_{ct}) depends only on the difference between E_{HOMO} and E_{LUMO}, and not on electrostatic attractive forces,[4] there may be no correlation between ΔE_{ct} and individual donor or acceptor dipole moments or polarities and thus no correlation of these parameters with ϕ. This prediction is confirmed by the data in Table 1. Hence, it appears that the stronger the electron-donating character of the sulfhydryl compound (as reflected by its HOMO energy), the larger the retention decrease when the electron acceptor (TCNQ) is added to the mobile phase in the PVP-modified HPLC system.

Conclusions

Reaction of sulfhydryl compounds with 7,7,8,8-tetracyanoquinodimethane (TCNQ) causes oxidation of the sulfhydryl compound to disulfide, whereas TCNQ takes up an electron, producing anion radical $TCNQ^{\bullet -}$, which, in turn, reacts with poly(4-vinylpyridine) gels in organic solvents. Removal of long-chain sulfhydryl compounds absorbed onto gels by TCNQ leads to the gel shrinking in poor solvents. Addition of TCNQ into the mobile phase of an HPLC system based on a poly(4-vinylpyridine)-modified stationary phase results in a decrease of the retention times of sulfhydryl compounds. Correlation is found between the HOMO energy of the sulfhydryl compounds and the relative decrease of the corresponding retention time.

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