Macromolecules **1997,** *30,* 2657−2661

Electrochemical Properties of Poly(L-2-anthraquinonylalanine)

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Received November 7, 1996; Revised Manuscript Received March 4, 1997[⊗]

ABSTRACT: Electrochemical behavior of two block copolypeptides consisting of poly(L-2-anthraquinonylalanine) unit as a component was studied with voltammetric analyses and electrochemical spectroscopy. Cyclic voltammetry and differential pulse voltammetry indicated that the anthraquinonyl groups in the polypeptides show only the first redox wave at the potential that corresponds to the monoanion formation of monomeric compounds. Under the same conditions monomeric compounds showed both the first and second redox waves. Absorption spectra under constant electric potential indicated that anthraquinone dianions are formed in the polypeptides under potentials where monoanions are formed in the monomeric compounds. The result indicates that dianions are more stable than monoanions in the polypeptides. The mechanism of dianion formation was tentatively attributed to fast electron migrations among anthraquinonyl side groups of the polypeptides, followed by efficient disproportionations. CD spectroscopy indicated that no conformational change is associated with the redox processes. These unique properties suggest that poly(anthraquinonylalanine) is a promising candidate for a helical molecular wire that mediates electrons between electrodes and redox enzymes.

In the accompanying paper,[1] we reported the synthesis and conformation of novel redox polypeptides carrying anthraquinonyl side groups, poly(L-2-anthraquinonylalanine) ($n = 10$) [poly(anqAla)]. The polypeptide in the form of a diblock copolymer with poly(ethylene glycol) (pQE) was shown to take a left-handed α-helix, with possible fluctuations in the anthraquinonyl side groups. A triblock copolymer with poly(γ-benzyl L-glutamate) at both ends of poly(anqAla) was also prepared (pGQG). The CD profile of pGQG showed a typical pattern of the right-handed α-helix, but the conformation of a poly(anqAla) unit was more or less disordered, as suggested from a very small CD intensity at the anthraquinonyl absorption band.

Anthraquinonyl groups can receive and release electrons on electrodes reversibly, and the electrons may hop among the densely and regularly packed anthraquinonyl groups along the helical main chain. Therefore, poly(anqAla) may be expected to work as a molecular wire through which an electron travels from electrodes to redox enzymes, and *vice versa*. In this paper, we report electrochemical and spectroscopic data that suggest efficient electron migrations along a single poly(anqAla) chain in solution.

The synthesis of polymers carrying pendant anthraquinonyl groups has not been very successful.[2−4] Furthermore, due to the limited solubility of anthraquinonyl groups, experiments on the electrochemical behavior of those polymers *in solution* have not been reported.[2−6] The two types of block copolymers described in this paper are, therefore, unique examples of anthraquinonyl polymers that are soluble in organic solvents.

Peptides and polypeptides carrying redox-active groups, including an anthraquinonyl group, at specific sites have been reported recently.[7]

Experimental Section

Materials. Synthesis and characterization of the two polypeptides have been described in the accompanying paper.[1] *N*-Acetyl-DL-anthraquinonylalanine methyl ester (Ac-anqAla-OMe) was prepared by dissolving *N*-acetyl-DL-anqAla[1] in HCl-saturated methanol at room temperature. The amino acid was quickly converted to the methyl ester within 5 min. The methanol was evaporated, and the remaining solid was recrystallized from chloroform/ether. Mp: 201 °C. Anal. Calcd for $C_{20}H_{17}NO_5$: C, 68.36; H, 4.89; N, 3.99. Found: C, 67.91; H, 5.00; N, 4.05.

Measurement. Spectroscopic and electrochemical measurements were carried out in acetonitrile (AN), dimethylformamide (DMF), or trimethyl phosphate (TMP), each containing 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4). The solvents were distilled before use. Tetramethylammonium salt (Me_4NBF_4) was also used as the supporting electrolyte. Concentrations of polymers were determined from the absorbance of an anthraquinonyl group using $\epsilon_{328} = 6000$ in TMP, DMF, and AN. The concentration of an anthraquinone dianion was measured from $\epsilon_{384} = 9300$ in the three solvents.

Cyclic voltammograms and differential pulse voltammograms were measured on a BAS CV-50W instrument. A polished gold disk electrode was used as a working electrode and a platinum wire as a counter electrode. A silver wire immersed in 0.1 M Bu_4NBF_4 in AN containing 0.01 M $AgNO_3$ was used as a Ag/Ag^+ reference electrode. The electrolyte solution was degassed with argon gas for 20 min prior to each measurement. The potential values of CV and DPV diagrams were corrected to reproduce the oxidation potential of ferrocene (+0.08 V) measured under the same conditions.

Changes of the absorption spectrum during electrochemical reactions were followed on a Jasco 560 instrument with an electrooptical cell (optical path = 1.4 mm) equipped with a platinum minigrid of 8 mm × 6 mm as a working electrode, a platinum wire as a counter electrode, and a silver wire as a reference electrode. Constant electric potential was supplied from a BAS CV27 potentiostat. The cell was covered with a silicon rubber, and the sample solution was degassed with nitrogen gas for 15 min before each measurement. CD spectral changes were also followed on a Jasco J500 instrument using the same electrooptical cell as described above.

Results and Discussion

Electrochemical Behavior of Poly(L-2-anthraquinonylalanine)s. Electrochemical properties of the two polymers and Ac-anqAla-OMe as a monomer model compound were studied with cyclic voltammometry (CV) and differential pulse voltammetry (DPV). CV and DPV diagrams of the monomer model, pQE, and pGQG in 0.1 M Bu_4NBF_4/DMF are shown in Figures 1 and 2.

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[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

S0024-9297(96)01654-3 CCC: $14.00

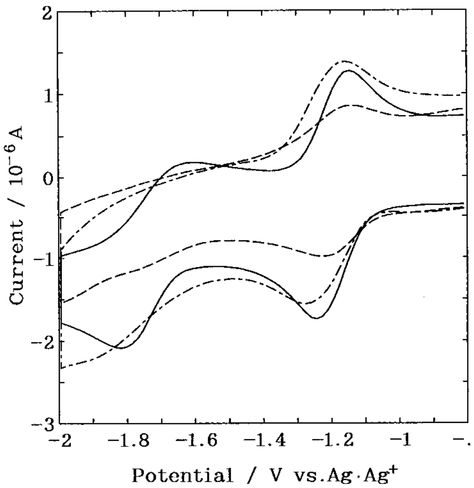

Figure 1. Cyclic voltammograms of Ac-anqAla-OMe (—), pQE (– –), and pGQG (—•—) in DMF containing 0.1 M Bu$_4$NBF$_4$ at room temperature. [anqAla] = 3.0×10^{-4} M for Ac-anqAla-OMe and pQE and 5.0×10^{-4} M for pGQG.

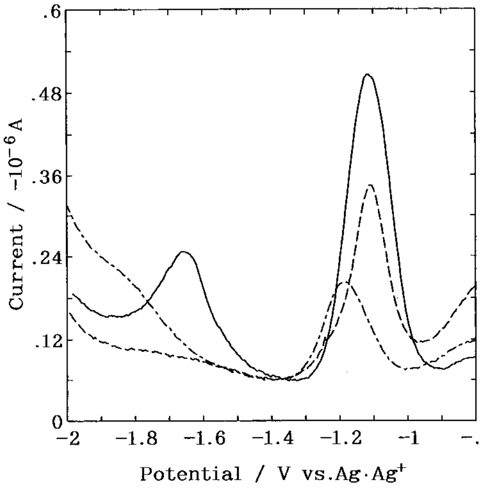

Figure 2. Differential pulse voltammograms of Ac-anqAla-OMe (—), pQE (– –), and pGQG (—•—) in DMF containing 0.1 M Bu$_4$NBF$_4$ at room temperature. [anqAla] = 5.0×10^{-5} M.

Ac-anqAla-OMe showed a two-step redox reaction with the first redox potential at −1.20 V (CV), −1.12 V (DPV) and the second potential at −1.71 V (CV), −1.65 V (DPV). Similar CV and DPV diagrams were also observed for anthraquinone and anthraquinonyl methanol, indicating that the peptide bond does not interfere with the redox property of the anthraquinonyl group.

The diblock copolymer pQE showed the first redox wave at −1.19 V (CV), −1.11 V (DPV). The peak position, the width of the DPV peak, and the peak separation of the CV diagram are not much different from the model compound. Generally, profiles of CV and DPV diagrams of polymeric redox groups are unchanged from those of the monomer model compound, if there is no interchromophore interaction in the polymer.[8] CV and DPV diagrams of pQE indicate that the anthraquinonyl groups in the polypeptide are electronically isolated from each other. The independence of the anthraquinonyl groups can be understood from the helix conformation of pQE predicted in the accompanying paper. The anthraquinonyl groups are stretched out from the helical main chain and are separated from each other (Figure 7 in the accompanying paper). The CV profile of pQE is symmetric, indicating that the electrochemical process is reversible.

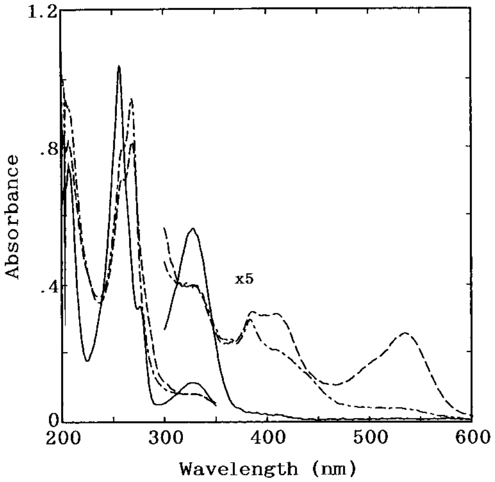

Figure 3. Electrochemical absorption spectra of Ac-anqAla-OMe in AN containing 0.1 M Bu$_4$NBF$_4$ at room temperature, under constant electric potentials of 0 V (—), −1.0 V after 20 min (– –), and −1.4 V after 45 min (—•—). [anqAla] = 1.4×10^{-4} M.

Contrary to the first redox wave, no clear wave is observed for the pQE polypeptide around the second redox wave of the monomer model in both the CV and DPV diagrams. This is a surprising result, since the anthraquinonyl groups behave independently during the first reduction.

In the case of pGQG, the first redox wave is slightly broadened and shifted toward more negative potentials: −1.21 V (CV), −1.18 V (DPV). Again, no clear peak is seen for pGQG around the second redox wave. The small shift and broadening of the first DPV peak of pGQG indicate some interactions between the anthraquinonyl groups in the polypeptides. It may be noted that the anthraquinonyl side groups in pGQG are more or less disordered, as indicated from small CD intensities.[1] The somewhat broadened CV and DPV profiles may be attributed to different electronic environments for each anthraquinonyl group in pGQG.

The marked weakening of the second redox waves of pQE and pGQG in both the CV and DPV experiments indicates some unusual electrochemical behavior that is occurring in the polymeric systems.

Spectral Changes during Electrochemical Reductions. In order to examine what is occurring during the redox processes in the polymeric systems, absorption spectra were measured under constant electric potentials. For this purpose, a thin optical cell equipped with electrodes as described in the Experimental Section was used. Figure 3 shows spectra of Ac-anqAla-OMe in AN under constant potentials that are corresponding to the first and second redox reactions. After keeping the potential at −1.0 V for 15 min, the spectrum of the anthraquinone group disappeared and a new band appeared at 540 nm. The latter is assignable to the anthraquinone monoanion.[9] When the voltage was set to −1.4 V, the spectrum of the monoanion appeared in the early stage (not shown in the figure), and after about 45 min the monoanion was converted to the dianion that shows a characteristic peak at 384 nm,[9] as indicated by the dash−dotted line in Figure 3. The observation of monoanions in the early stage has been interpreted in terms of intermolecular disproportionation between a dianion and a neutral anthraquinone to form two monoanions.[10] After prolonged application of the negative potential, virtually all the anthraquinonyl groups are converted to dianions. These spectral changes were

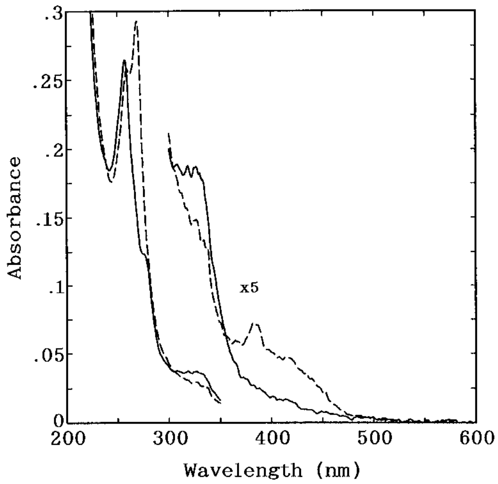

Figure 4. Electrochemical absorption spectra of pQE in AN containing 0.1 M Bu_4NBF_4 at room temperature, under constant electric potentials of 0 V (—) and −1.0 V (– –) after 20 min. [anqAla] = 4.4×10^{-5} M.

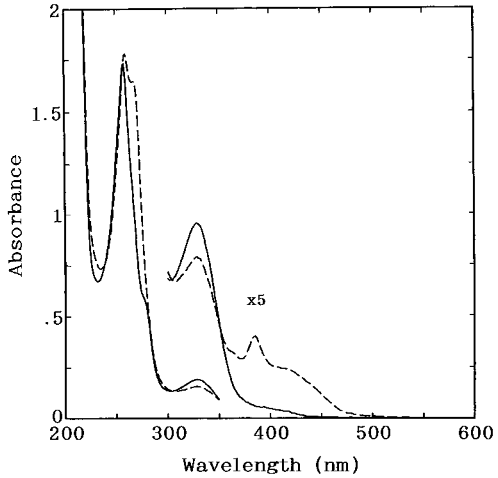

Figure 5. Electrochemical absorption spectra of pGQG in AN containing 0.1 M Bu_4NBF_4 at room temperature, under constant electric potentials of 0 V (—) and −1.0 V (– –). [anqAla] = 2.3×10^{-4} M.

reversible when the applied voltage was repeatedly switched between 0 and −1.4 V.

Spectral change was also followed for the pQE polypeptide (Figure 4). When the potential was set to the first reduction voltage (−1.0 V), no monoanion was observed and only dianions appeared even in the early stage of the reduction. The yield of dianion increased with time and saturated at 21% after 15 min. Similar spectral change was observed when the potential was set to −1.4 V. When the potential was set to 0 V, the original neutral anthraquinone was recovered after 10 min.

Again, only the dianion was formed under −1.0 V for the pGQG polypeptide as shown in Figure 5. The final yield of the dianion was about 33%. Similar behavior was observed when −1.4 V was applied to the polypeptide.

Discussion on the Stabilization of Dianions in the Polypeptides. The electrochemical spectroscopy indicates that the monoanions are not stable in the polypeptides and are rapidly converted to dianions. The relative stability of monoanions and dianions of monomeric anthraquinones has been discussed by Hayano and Fujihira.[10] In anhydrous DMF, monoanions are much more stable than dianions and the disproportionation equilibrium (1) is shifted exclusively to the left.

$$2AQ^{\bullet-} = AQ + AQ^{2-} \quad (1)$$

In the presence of hydrogen donors, such as water or alcohol, the dianions are stabilized by the hydrogen bonding and the disproportionation reaction from the left to the right becomes possible.[11] In the case of Ac-anqAla-OMe under −1.0 V in aprotic solvents such as TMP, DMF, and AN, the equilibrium favors monoanions (Figure 3).

When the potential was set to −1.4 V, the monoanion appeared during the early stage as a result of the disproportionation from the right to the left. After prolonged reduction at −1.4 V, however, all the anthraquinonyl groups became dianions (Figure 3).

In the case of polypeptides, only dianions were formed regardless of the potential value between −1.0 and −1.4 V, indicating that dianions are more stable than monoanions under conditions where monoanions are favored for model compounds. This is a noteworthy polymer effect. As described above, anthraquinone dianions may become stabilized by hydrogen bonding.[11] In poly(anqAla) hydrogen bonding is possible only between amide protons and anthraquinonyl carbonyl oxygens. In the case of pQE, however, the amide protons are already hydrogen bonded to carbonyl oxygens to support the left-handed α-helical conformation, as has been suggested in the accompanying paper.[1]

As will be discussed later, the supporting electrolyte is playing some important roles in the stabilization of dianions. The special side chain and the main-chain structure of the polypeptide that is conjugated with the supporting electrolytes may be the reason for the stabilization of the dianions in poly(anqAla).

Discussion on the Mechanism of Dianion Formation in the Polypeptides. There are three possible routes for the formation of dianions on the polypeptides under the potential for the first reduction step. First, an anthraquinonyl group would receive two electrons at once to form a dianion. This possibility may be ruled out, at least for pQE, since the CV and DPV profiles of pQE are not much different from those of the monomer models, except the peak intensities. It is known that the peak separation in the CV diagram, ΔE_p, is closely correlated with the number of electrons, *n*, that are transferred in a single-electron-transfer process.[12]

$$\Delta E_p = 60/n \text{ (mV)} \quad (2)$$

The observed ΔE_p was 80 mV for Ac-anqAla-OMe and 60 mV for pQE. These values indicate that the electron transfer in the first reduction step of pQE is a single-electron-transfer process that produces monoanions. The observed ΔE_p was 90 mV for pGQG.

The second possible mechanism for the dianion formation is that a monoanion formed on the polypeptide successively receives one more electron to form a dianion. For this process to occur, the electron on an anthraquinonyl group must stay on the same group and also the polypeptide molecule must keep the same position on the electrode until the next electron comes in. Both are unlikely unless the electron transfer from the electrode to the polypeptide occurs very frequently. The rate constants per unit surface of electrode for reversible electron transfers of organic molecules in DMF are usually on the order of 1 cm s^{-1} or lower.[13] If we roughly assume that the electron transfer will occur only when a redox molecule reached within 1 nm on the surface of electrode, the surface rate constant of 1 cm s^{-1} corresponds to a conventional rate constant of electron transfer, $k_{ET} = 10^7$ s^{-1}. The latter rate constant may be comparable to the rate constant of electron exchange (3).

$$AQ^{\bullet-} + AQ = AQ + AQ^{\bullet-} \qquad (3)$$

Although fast *inter*molecular electron exchange has been observed for concentrated anthraquinone solution in DMF,[10] the rate constant for *intra*molecular electron exchange has not been reported. The rate of intramolecular electron exchange for naphthyl or phthalimide groups that are separated by about 9 Å (center-to-center) has been reported to be on the order of 10^7 s^{-1} near room temperature.[14]

Since anthraquinonyl groups on the pQE polypeptide are separated by 7.9 Å (center-to-center distance of the 1−4 pair) or 4.1 Å (edge-to-edge distance of the 1−4 pair),[1] the frequency of electron exchange may be on the order of 10^7 s^{-1} or higher. Therefore, the rate of electron transfer from the electrode to an anthraquinonyl group may be comparable to or smaller than the frequency of electron migration on the polypeptide. In addition to this, local molecular motion may be frequent enough to move out a monoanion from the position where it received an electron from the electrode. From the above argument, we may rule out the second mechanism when the electron migrations are fast enough.

The third and most likely mechanism for the formation of dianion is a fast migration of an electron along the array of anthraquinonyl groups and the subsequent disproportionation with other monoanions on the same chain. As discussed above, the frequency of electron exchange may be on the order of 10^7 s^{-1} or higher. Therefore, there is enough time for monoanions to migrate among the helically arranged assembly of anthraquinonyl groups. Disproportionation from two monoanions to form a dianion and a neutral anthraquinonyl group has been reported for anthraquinone in water-containing DMF. We conclude tentatively that the dianions are formed from monoanions after frequent migrations on the polypeptide followed by the disproportionation.

Although it is unlikely that a monoanion may jump over a dianion on the same polypeptide, the electron migration will take place even after a few anthraquinonyl groups were reduced into dianions. The electron may migrate through a detour bypassing dianions on the same chain. This may be possible because of the helical arrangement of anthraquinonyl groups, as has been shown in the accompanying paper. But, after a considerable portion of the anthraquinonyl groups became dianions, the electron migration will be stopped and the yield of dianions will be saturated. From the absorption spectra of pQE (Figure 4) and pGQG (Figure 5), the final yields of dianions were 21% and 33%, respectively.

In order to evaluate the contribution of *inter*molecular electron transfers in the polypeptide systems, electrochemical spectra were measured for pGQG at two different concentrations of anthraquinonyl groups (2.3 × 10^{-4} and 0.48 × 10^{-4} M). Virtually no difference was observed, indicating the absence of intermolecular electron transfer when the concentration was lower than ~10^{-4} M.

Effect of Supporting Electrolytes on the Yields of Dianions. The yields of the dianions were saturated at 21% for pQE and at 33% for pGQG in 0.1 M Bu_4NBF_4/DMF. If the dianions were much more stabilized by effective supporting electrolytes, the other mechanism to form dianions will start to work. Electron repulsion between negative charges will be more effectively shielded by using supporting electrolytes that have a smaller cationic part, such as Me_4NBF_4.[15] The spectra of pQE under −1.0 V in the presence of Me_4NBF_4 are shown in Figure 6. The final yield of dianions is much larger for Me_4NBF_4 (70%) than for Bu_4NBF_4 (21%). The effect of supporting electrolytes was also examined for pGQG. Again, the yield of dianion is much larger in Me_4NBF_4 (66%) than in Bu_4NBF_4 (33%). Such a high yield of dianions cannot be interpreted in terms of the migration−disproportionation mechanism. Presumably, after a significant portion of anthraquinonyl groups became dianions, a monoanion cannot migrate on the polypeptide and receives one more electron from the electrode. This is the second mechanism discussed above.

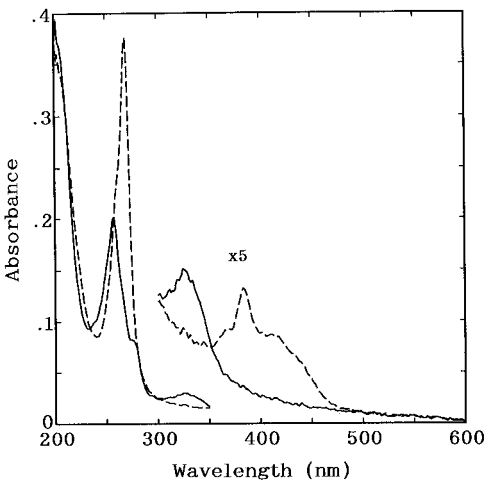

Figure 6. Electrochemical absorption spectra of pQE in AN containing 0.1 M Me_4NBF_4 at room temperature, under constant electric potentials of 0 V (—) and −1.0 V (– –). [anqAla] = 3.4 × 10^{-5} M.

Interestingly, the absorption profile in the presence of Me_4NBF_4 extended to longer wavelengths than 500 nm, indicating the presence of a small amount of monoanions. This may be interpreted in terms of the local stabilization of monoanions by an effective shielding with smaller tetramethylammonium cations.

Change of Circular Dichroism during the Electrochemical Reduction. In order to study conformations of the polypeptides during the redox processes, CD spectra before and after the electrochemical reduction were measured in AN containing 0.1 M Bu_4NBF_4. The electrochemical CD spectra of pQE are shown in Figure 7, and those of pGQG are shown in Figure 8. CD spectra of pQE show a minor change before and after the formation of monoanions under −1.0 V. The CD peak of the $\pi\pi^*$ band of the anthraquinonyl group at 271 nm slightly decreased with the formation of dianions and returned to the original intensity when neutral anthraquinonyl groups were recovered. A CD spectrum at shorter wavelengths showed no marked change during the electrochemical reaction, indicating no large conformational change is induced in the main chain of the pQE polypeptide. CD spectra of pQE in the presence of 0.1 M Me_4BF_4 as the supporting electrolyte also showed no conformational change even after about 70% conversion to dianions.

The CD spectrum of pGQG also shows no marked change in the amide absorption region, indicating a large conformational change is not accompanied with the dianion formation. The retention of the main-chain conformation during the reduction indicates that the

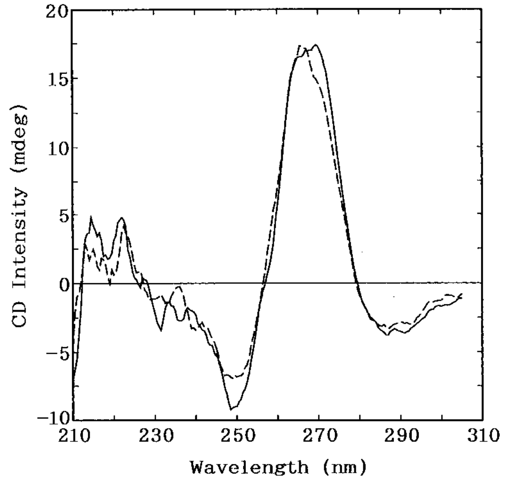

Figure 7. Electrochemical CD spectra of pQE in AN containing 0.1 M Bu_4NBF_4 at room temperature, under constant electric potentials of 0 V (—) and −1.0 V (– –). [anqAla] = 8.7 × 10^{-5} M.

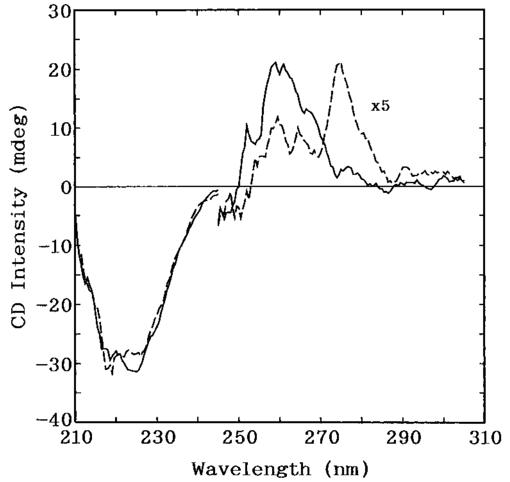

Figure 8. Electrochemical CD spectra of pGQG in AN containing 0.1 M Bu_4NBF_4 at room temperature, under constant electric potentials of 0 V (—) and −1.0 V (– –). [anqAla] = 8.6 × 10^{-5} M.

electronic shielding of the anionic charges by the supporting electrolytes is good enough to hold the helical conformations. A marked shift was observed in the anthraquinonyl absorption band of the pGQG polypeptide. This may be interpreted simply in terms of the shift of the absorption peak due to dianion formation.

Conclusions

Poly(anqAla) was found to produce dianions under the conditions where only monoanions are formed for monomeric anthraquinones. The reason for the stability of dianions is not clear at present. The most plausible mechanism for dianion formation is fast electron migrations among the side-chain anthraquinonyl groups, followed by efficient disproportionations. When strong supporting electrolytes are used, other mechanisms may begin to work and up to 70% of anthraquinonyl groups are converted to dianions. During the redox processes the helical main-chain conformations were retained. These unique properties of poly(anqAla)s make them promising candidates for polypeptide wires that transport electrons between electrodes and redox proteins.

Acknowledgment. M.S. is thankful for support from the Grant-in-Aid for Scientific Research on Priority Areas (No. 236) "New Development of Organic Electrochemistry" from the Ministry of Education, Science, Sports, and Culture.

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