Poly(anthraquinone)s Having a π-Conjugation System along the Main Chain. Synthesis by Organometallic Polycondensation, Redox Behavior, and Optical Properties

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Received October 28, 1994; Revised Manuscript Received February 23, 1995[⊗]

ABSTRACT: Polyquinones [poly(2-methylanthraquinone-1,4-diyl) [*P*(2Me-1,4-AQ)], poly(anthraquinone-1,4-diyl) [*P*(1,4-AQ)], etc.] having π-conjugation systems along their main chains have been prepared by an organometallic dehalogenation polycondensation of the corresponding dichloroquinones. P(2Me-1,4-AQ) is soluble in various organic solvents and has a molecular weight of 190 000 as determined by a light scattering method. Casting from solutions of P(2Me-1,4-AQ) gives films with good optical and mechanical quality. Chemical reductions of P(2Me-1,4-AQ) in *N*-methyl-2-pyrrolidone (NMP) with N_2H_4 and $Na_2S_2O_4$ lead to the formation of a dianion (Q^{2-}) and dihydrogenated species (QH_2) of the quinone unit (Q), respectively. On the other hand, chemical reduction of P(2Me-1,4-AQ) with a mixture of $Na_2S_2O_4$ and NaOH in NMP is interpreted by a stepwise mechanism involving formation of an intermediate radical-anion species ($Q^{\bullet-}$). Cyclic voltammogram of the P(2Me-1,4-AQ) film exhibits two redox cycles with $E_1°$ and $E_2°$ values of −1.38 and −1.69 V vs Ag/Ag^+ corresponding to quinone/radical anion ($Q/Q^{\bullet-}$) and radical anion/dianion ($Q^{\bullet-}/Q^{2-}$) redox couples, respectively. Reduction of P(2Me-1,4-AQ) and P(1,4-AQ) with sodium naphthalenide gives semiconducting materials.

Redox behavior of quinones has attracted the strong interest of chemists for many years, and a number of papers have been published on the synthesis and properties of quinones,[1] recently especially in relation to photosynthesis[1f-i] and functions in living systems.[2]

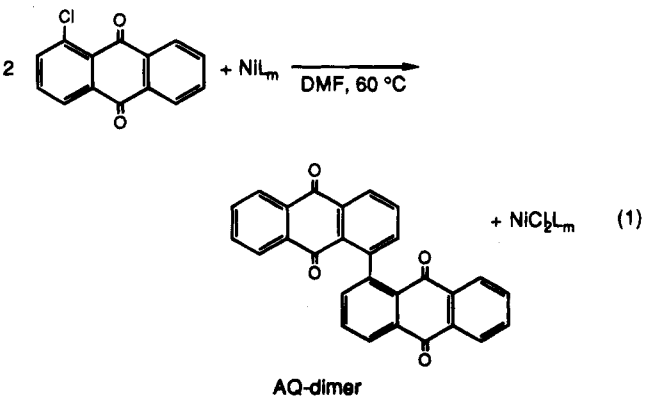
On the other hand, π-conjugated polymers have been the subject of recent interest because of their redox behavior as well as their conducting and optical properties.[3] However, in spite of the strong interest in both the quinones and π-conjugated polymers, polyquinones having π-conjugation systems along the polymer main chains have received much less attention[4] presumably due to difficulty in preparing such polyquinones by the usual methods.

Among reported preparative methods of π-conjugated polymers, organometallic dehalogenation polycondensation[5,6] (e.g., that using a zero-valent nickel complex NiL_m (nX−Ar−X + $n$$NiL_m$ → −(Ar)−$_n$ + $n$$NiX_2L_m$)[6]) has contributed to the preparation of various poly(arylene)s. We have applied the organometallic dehalogenation polycondensation to the preparation of π-conjugated polyquinones to find out that the method is also effective for the preparation of the polyquinones[4] and here report details of the preparation, characterization, and redox behavior of the polymers.

Results and Discussion

Preparation. A basic dehalogenation coupling reaction of 1-chloroanthraquinone using the zero-valent NiL_m complex yields the AQ dimer in a high yield (86%) under mild conditions. Obtaining the AQ dimer in high yield indicates that the Ni-promoted C−C coupling reaction is effective for the coupling of the chlorinated quinones.

Becuase of the effective C−C coupling between the chlorinated quinones (eq 1),application of the NiL_m-promoted C−C coupling to dichloroquinones gives the corresponding π-conjugated polyquinones in high yield (Table 1). The polycondensation seems to be energetically favored because of the formation of the π-conjugation system and is considered to proceed by a mechanism discussed previously.[6]



(1)

NiL_m: a mixture of bis(1,5-cyclooctadiene)nickel(0) $Ni(cod)_2$ and 2,2'-bipyridine (bpy)[6].

Use of the three kinds of dichloroquinones in eq 2 affords the corresponding polymers with negligible or only a low content of chlorine. On the other hand, employment of 2,6-dichloroanthraquinone (2,6-Cl_2-AQ) and 5,8-dichloro-1,4-naphthoquinone (1,4-Cl_2-NQ) leads to the formation of oligomeric products with empirical formulas of Cl(2,6-$C_{14}H_6O_2$)$_5$Cl (oligo(2,6-AQ)) and Cl(5,8-$C_{10}H_4O_2$)$_{10}$Cl (oligo(5,8-NQ)), respectively (cf. the Experimental Section).

IR spectra of P(2Me-1,4-AQ), P(1,4-AQ), and P(1,5-AQ) are reasonable for their structures. The spectra exhibit ν(C=O) bands at almost the same positions as the ν(C=O) bands of the starting monomers, whereas strong ν(C−Cl) bands[8] of the monomers near 1100 cm^{-1} (1075−1134 cm^{-1}) are not observable. Absorption pat-

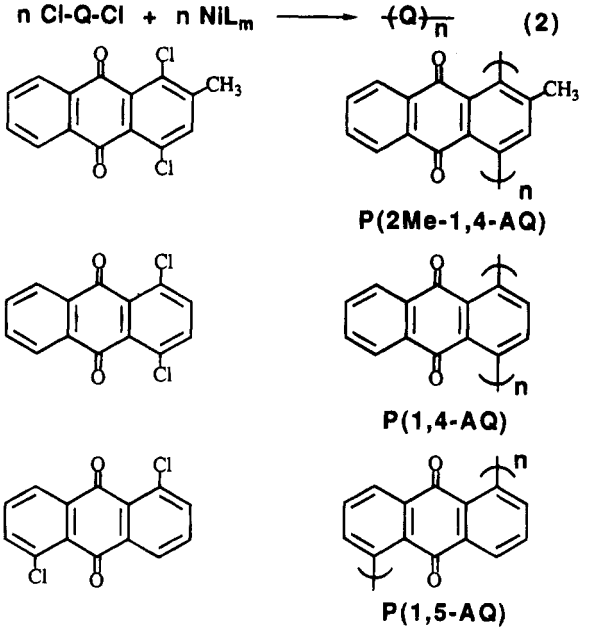
[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1995.

0024-9297/95/2228-3371$09.00/0

Table 1. Preparation of Polyquinones and Oligoquinones[a]

run	monomer, Cl-Q-Cl[b]	yield,[c]	color	λ_{max}, nm in $CHCl_3$	λ_{max}, nm in H_2SO_4[e]
1	Cl-2-Me-1,4-AQ-Cl	89	dark yellow	375, 385,[d] 268[d]	435,[d] 405
2	Cl-1,4-AQ-Cl	80	yellow	369, 282[d]	
3	Cl-1,5-AQ-Cl	90	yellow		404
4	Cl-2,6-AQ-Cl	95	cream yellow		540,[f] 440[f]
5	Cl-5,8-NQ-Cl	75	dark brown		

[a] Dehalogenation polycondensation according to eq 2. In *N,N*-dimethylformamide at 60 °C for 48 h. [b] Cl-2-Me-1,4-AQ-Cl = 2-methyl-1,4-dichloroanthraquinone. Cl-1,4-AQ-Cl = 1,4-dichloroanthraquinone. Cl-1,5-AQ-Cl = 1,5-dichloroanthraquinone. Cl-1,8-AQ-Cl = 1,8-dichloroanthraquinone. [c] Yield is calculated based on carbon recovered. [d] Shoulder. [e] In concentrated H_2SO_4. [f] Weak absorption band due to small solubility.



terns of the out-of-plane δ(CH) vibrations of the monomers are essentially unvaried after the polymerization.

P(2Me-1,4-AQ) is soluble in various solvents including $CHCl_3$, CH_2Cl_2, and *N*-methyl-2-pyrrolidone (NMP) (solubility = about 10 mg mL^{-1}), and its $CHCl_3$ solution has an intrinsic viscosity of 0.43 dL g^{-1} at 24 °C. Light scattering analysis[9,10] of the $CHCl_3$ solution of P(2Me-1,4-AQ) yields M_w = 190 000, a refractive index increment $\Delta n/\Delta c$ = 0.29 mL g^{-1}, and a small degree of depolarization of ϱ_v = 0.01.

In contrast to P(2Me-1,4-AQ), other polymers have poor solubility in $CHCl_3$, CH_2Cl_2, and NMP; P(1,4-AQ) exhibits a low solubility in $CHCl_3$, whereas P(1,5-AQ) is insoluble in organic solvents tested. P(1,5-AQ) has a slight solubility (about 2 mg mL^{-1}) in concentrated H_2SO_4, and light scattering analysis in concentrated H_2SO_4 yields M_w = 13 000 and a ϱ_v of 0.19, indicating that the polymer has a rather linear structure in concentrated H_2SO_4.[9,10]

The ^{1}H-NMR spectrum of P(2Me-1,4-AQ) (Figure 1) shows a complicated absorption pattern for the CH_3 protons presumably due to the presence of both head-to-tail and head-to-head microstructures.[5e,6a,b] The peak area ratio between the CH_3 signals and aromatic proton signals agrees well with the structure. ^{1}H-NMR as well as ^{13}C-NMR data of the polymers and oligomers are shown in the Experimental Section.

Thermogravimetric analysis of P(2Me-1,4-AQ), P(1,4-AQ), and P(1,5-AQ) reveals that their weight loss starts at about 310 °C and they have 65–70% residual weight at 900 °C under N_2.

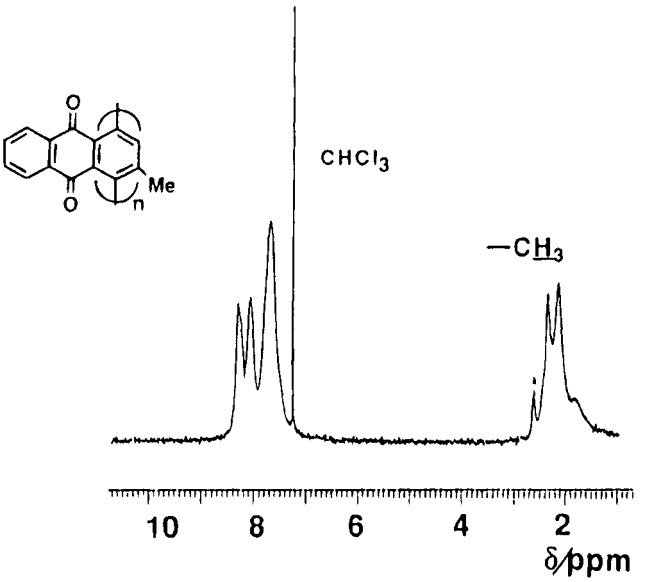
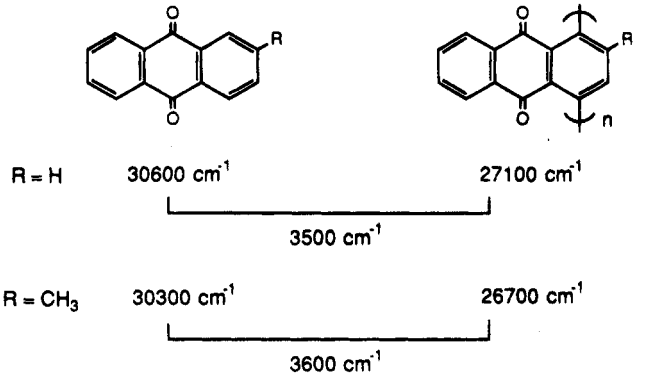


Figure 1. ^{1}H-NMR spectrum of P(2Me-1,4-AQ). In $CDCl_3$ at room temperature.

Chart 1. Absorption Peak Position and the Degree of Red Shift



Optical Properties. P(2Me-1,4-AQ) and P(1,4-AQ) have respective absorption bands at λ_{max} = 375 ± 1 and 369 ± 2 nm in organic solvents. The molar absorption coefficient of P(2Me-1,4-AQ) is 3600 M^{-1} cm^{-1} (molarity is based on the repeating monomer unit $C_{15}H_8O_2$). The peak positions are shifted to longer wavelength by 42–46 nm (or by 3500–3600 cm^{-1} (0.43–0.45 eV)) from the absorption bands of the corresponding monomeric quinones, as shown in Chart 1.

A cast film of P(Me-1,4-AQ) on a glass plate has an absorption band at the same position (λ_{max} = 376 nm).

Redox Behavior of P(2Me-1,4-AQ) and P(1,4-AQ). The polyquinones show interesting redox behavior due to the π-conjugation along the polymer chain. Although reducing reactions of anthraquinone under various

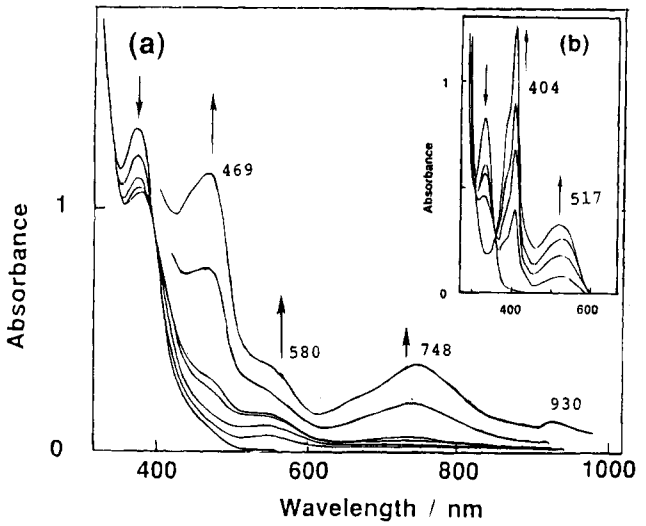
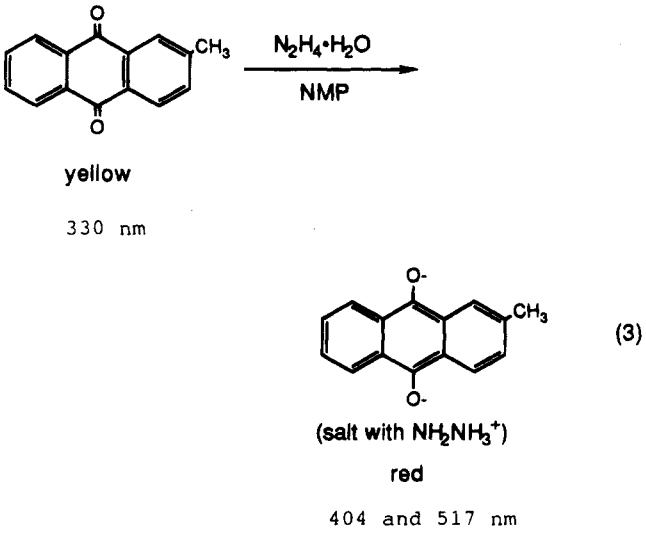


Figure 2. Change of UV–vis spectrum during the reduction of (a) P(2Me-1,4-AQ) and (b) 2-methylanthraquinone with $N_2H_4 \cdot H_2O$ (0.66 M) in NMP at room temperature (ca. 25 °C) under N_2. Times for a: 0, 60, 200, and 400 min and 10, 24, and 72 h. The direction of the change of the absorption peak with time is shown by an arrow. After 10 h, the clear isosbestic point at 390 nm is not observed. Times for b: 0, 10, 30, 60, and 90 min.

conditions have been reported, reduction of anthraquinone in NMP, which is suited as a solvent for the study of chemical reduction of P(2Me-1,4-AQ), has not been reported. Therefore, we first studied the chemical reduction of 2-methylanthraquinone in NMP and compared the results with the results of the chemical reduction of P(2Me-1,4-AQ) in NMP.

Chemical Reduction. Reduction with N_2H_4. Figure 2 compares the UV-visible changes observed during the reduction of (a) P(2Me-1,4-AQ) and (b) 2-methylanthraquinone (2-MeAQ) with hydrazine hydrate.[11] The reduction product of 2-MeAQ is assigned to a dianion of 2-methyl-9,10-dihydroxyanthracene, by comparing its UV–vis spectrum pattern (λ_{max} = 404 and 517 nm; Figure 2b) with a reported UV–vis spectrum pattern (λ_{max} = 417 and 508 nm) of a dianion of 9,10-dihydroxyanthracene.[12,13]



(3)

The reduction of P(2Me-1,4-AQ) with $N_2H_4 \cdot H_2O$ (Figure 2a) also gives the two absorption bands (λ_{max} = 469 and 580 nm) characteristic of the dianion, although the peak positions are red-shifted by about 65 nm from

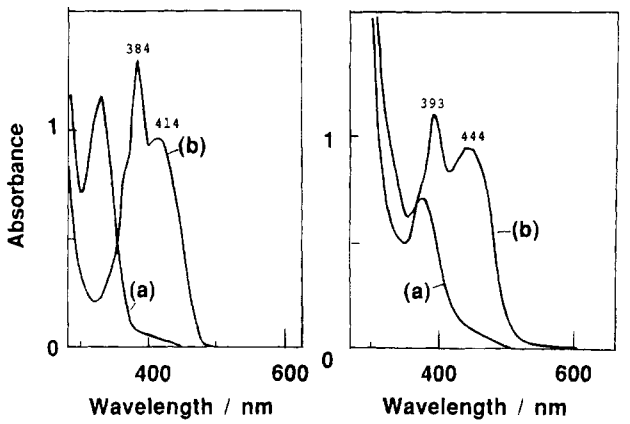
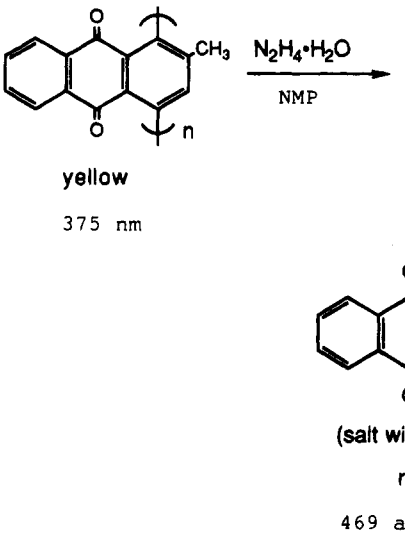


Figure 3. UV–vis changes in the reduction of 2-methylanthraquinone (left side) and P(2Me-1,4-AQ) (right side) with $Na_2S_2O_4$ (0.0019 M) in NMP: (a) quinone; (b) after reduction.

those of the monomeric dianion. The rate of the reduction is about 20 times slower.[14]

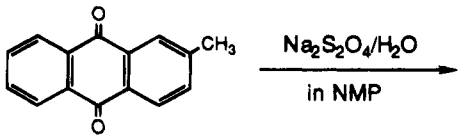


(4)

Further reduction (after 24 and 72 h; Figure 2a) causes the appearance of new additional absorption bands at 748 nm and at about 930 nm, which are not observed with 2-MeAQ. This strongly suggests the formation of special electronic state(s) along the π-conjugation system, e.g., polaron and/or bipolaron state(s). It is reported that various reduced and oxidized poly(arylene)s exhibit polaron and bipolaron absorption bands in the range of 700–1000 nm.[3]

In the early stages of the reduction of P(2Me-1,4-AQ) (60 min to 10 h; Figure 2), the concentration of the dianion species in the polymer chain is low and they are separated from each other to show an isosbestic point at 390 nm. On the other hand, a higher degree of reduction of P(2Me-1,4-AQ) leads to the formation of the special electronic state(s), and thus the isosbestic point disappears. However, the degree of the reduction of the quinone unit in P(2Me-1,4-AQ) achieved with $N_2H_4 \cdot H_2O$ seems not very high, since the degree of the change of the UV–vis spectrum in the region 300–600 nm is smaller than those observed with the monomeric 2-methylanthraquinone–$N_2H_4 \cdot H_2O$ system (Figure 2b) and with P(2Me-1,4-AQ) film at an extensive electrochemical reduction (*vide infra*). The relatively low reducing ability of hydrazine[11] seems to prevent an extensive reduction of the quinone unit in the polymer chain from proceeding.

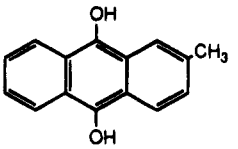
Reduction with $Na_2S_2O_4$. Reduction of 2-MeAQ in NMP with a stronger reducing reagent,[11] $Na_2S_2O_4$, gives a fluorescent yellow product, which is assigned to 2-methyl-9,10-dihydroxyanthracene (2-MeAQH_2) by comparing its UV–vis absorption pattern (Figure 3; λ_{max} = 384 and 414 nm with a shoulder absorption at about 365 nm) with the reported UV–vis absorption pattern (λ_{max} = ca. 382 415, and 365 nm) of 9,10-dihydroxyanthracene.[15]



2-MeAQ

yellow

330 nm



(5)

2-MeAQH_2

yellow and fluorescent[17]

384, 414, and 365 nm

In the reaction, $Na_2S_2O_4$ seems to be converted into neutral salt(s) and acid(s) (e.g., 2-methylanthraquinone (2-MeAQ) + $Na_2S_2O_4$ + $2H_2O$ → 2-methyl-9,10-dihydroxyanthracene (2-MeAQH_2) + Na_2SO_3 + H_2SO_3 or 2-MeAQ + $^1/_3Na_2S_2O_4$ + $^4/_3H_2O$ → 2-MeAQH_2 + $^1/_3Na_2SO_4$ + $^1/_3H_2SO_4$), and consequently the reaction system is considered to become rather acidic to give the nondissociated dihydroxy product.

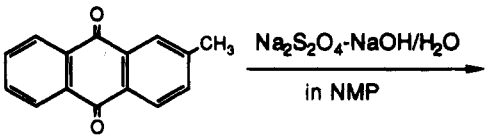
A similar reduction of P(2Me-1,4-AQ) in NMP with $Na_2S_2O_4$ gives a brown solution, which shows a UV–vis pattern (Figure 3; λ_{max} = 393 and 444 nm with a shoulder absorption at 374 nm)[16] similar to those of 2-MeAQH_2.

Treatment of a yellow powder of P(1,5-AQ) with an aqueous solution of $Na_2S_2O_4$ gives a brown powder, whose IR spectrum shows new strong absorption bands characteristic of *p*-hydroquinones at 3400 (ν(O–H)), 1100 (ν(C–O)), and 605 cm^{-1} (δ(C–H)). Similar treatment of powdery anthraquinone with the aqueous solution of $Na_2S_2O_4$ affords a yellow fluorescent powder which exhibits a similar IR change. On exposure to air, both the reduced P(1,5-AQ) and anthraquinone powders are converted into the original quinones as manifested by IR spectra.

In the case of the reduction product of P(2Me-1,4-AQ) with $Na_2S_2O_4$, no special absorption bands at the longer wavelength, such as those observed in the region of 700–1000 nm in Figure 2a, are observed. We believe that under the rather acidic reaction conditions the uncharged structure of the reduced polymer is obtained, which forms neither the polaron nor bipolaron states.

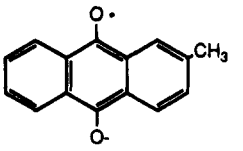
Reduction with $Na_2S_2O_4$ in the Presence of NaOH. $Na_2S_2O_4$ is a very strong reducing agent under alkaline conditions,[11] and the reduction of quinones with $Na_2S_2O_4$ in the presence of alkali (NaOH) gives considerably different and complicated results.

2-MeAQ. Figure 4a shows change of the UV–vis spectrum during the reaction of 2-MeAQ with $Na_2S_2O_4$ in the presence of NaOH. The two strong peaks at 400 and 539 nm as well as two weak broad characteristic peaks at 870 and 980 nm observed just after the addition of $Na_2S_2O_4$ (time = about 1 min) are assigned to the corresponding anion radical, based on reported UV–vis spectroscopic data of anion radicals of anthraquinone and its derivatives.[12,17,18]



2-MeAQ, yellow

330 nm

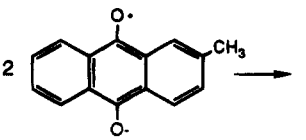


(6)

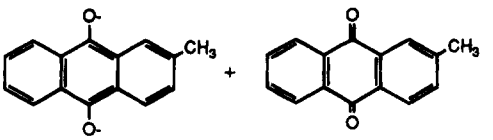
red

400, 539, 870, 980 nm

The anion radical, however, is not stable under the present reaction conditions, and the absorption spectrum rapidly changes to that shown by the broken line in Figure 3a. This absorption spectrum at t = 10 min exhibits a peak at about 385 nm which may be assigned to 2-methyl-9,10-dihydroxyanthracene (eq 5; Figure 3, left side (λ_{max} = 384 nm)) as well as two peaks at 404 and ca. 520 nm assignable to the dianion of 2-methyl-9,10-dihydroanthracene (eq 3; Figure 2b) (λ_{max} = 404 and 517 nm), indicating that the anion radical formed by eq 6 is unstable and undergoes the following disproportionation reaction (eq 7)[19] or further reduction by the strong reductant to give the dianion (eq 8).[20–22]

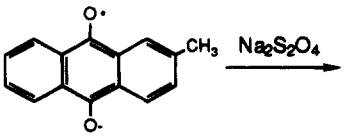


400, 539, 870, 980 nm

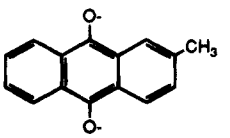


(7)

404 and 517 nm 330 nm



400, 539, 870, 980 nm

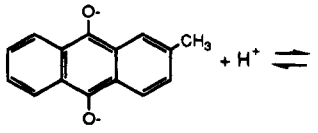


(8)

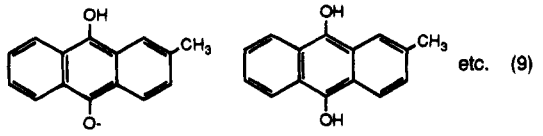
404 and 517 nm

The dianion thus formed seems to be in equilibrium with undissociated 2-methyl-9,10-dihydroxyanthracene

(2-MeAQH$_2$) and the monoanion of 2-methyl-9,10-dihydroxyanthracene, as suggested by the observation of the peak assigned to the undissociated dihydroxy species at about 385 nm.



404 and 517 nm

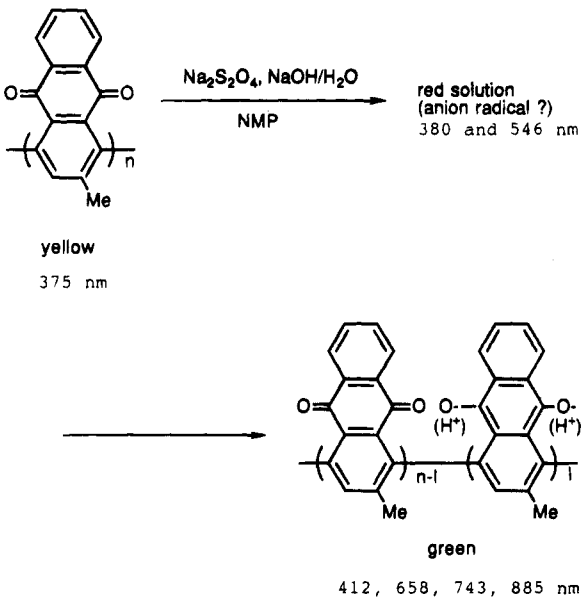


384 and 414 nm

(9)

Addition of excess NaOH will lead to a shift of the equilibrium to the left side, and in this case the reaction system will become simpler. However, limited solubility of NaOH in NMP prevents the reaction with $Na_2S_2O_4$ to be carried out at a higher concentration of NaOH.

P(2Me-1,4-AQ). Addition of the $Na_2S_2O_4$–NaOH mixture to a yellow NMP solution of P(2Me-1,4-AQ) causes an instant color change to red, and the reaction system shows two new absorption bands at 380 and 546 nm as shown in Figure 4b (t = ca. 1 min). The red solution, however, is rapidly changed to green, and the UV–vis spectrum exhibits four new absorption bands at 412, 658, 743, and 885 nm (Figure 4b, t = 5 and 20 min). These results characteristic of the polymer system strongly suggest a special electronic interaction between the anthraquinone unit and the dihydroxyanthracene unit or its anion in the polymer, e.g., eq 10.



yellow

375 nm

(10)

green

412, 658, 743, 885 nm

The presence of anionic unit(s) in the π-conjugated system will lead to the formation of the above discussed polaron and/or bipolaron, which will give absorption bands in the range 700–1000 nm (Figure 4). In addition, a specific interaction between the anthraquinone unit(s) and the reduced unit(s) may occur in the polymer chain to form a quinhydron type charge-transfer (CT) complex in the solution. Although formation of a quinhydron type CT complex has been considered to be difficult in the case of anthraquinone,[23] a special

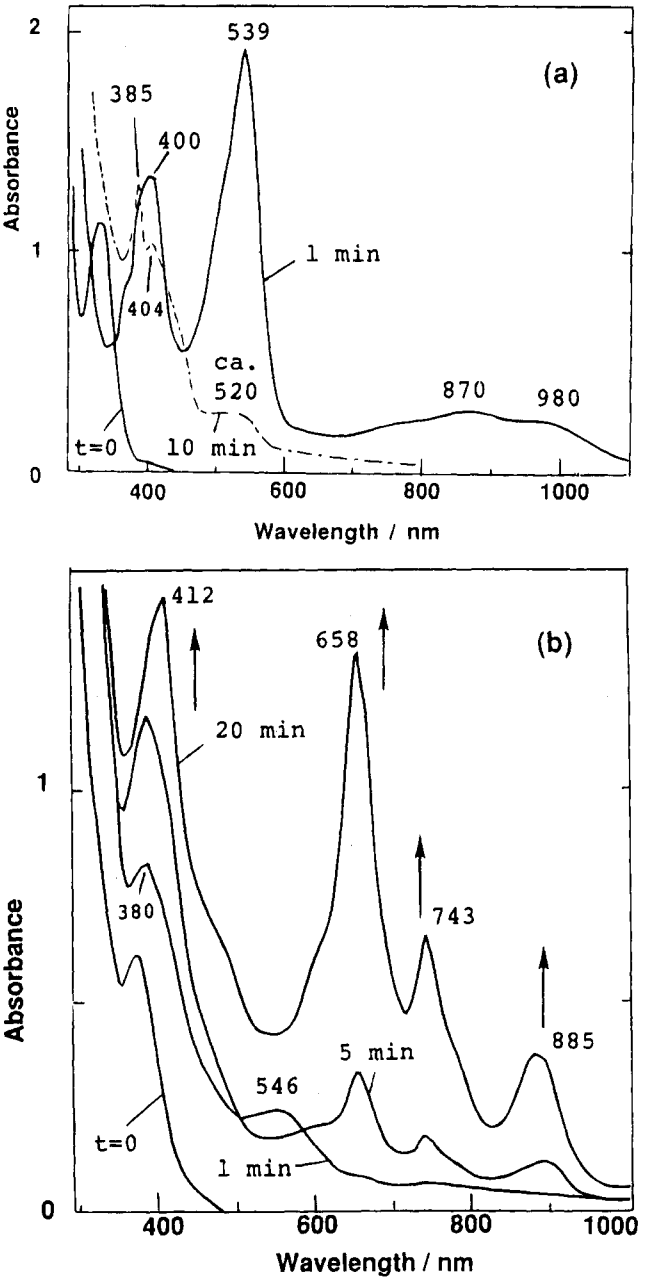


Figure 4. UV–vis changes in the reduction of (a) 2-methylanthraquinone and (b) P(2Me-1,4-AQ) with $Na_2S_2O_4$ (0.0019 M) in NMP under alkaline (NaOH, 0.016 M) conditions. Times for a: 0, about 1, and 10 min. Times for b: 0, about 1, 5, and 20 min. t = 0: before addition of $Na_2S_2O_4$ and NaOH. At room temperature (ca. 25 °C) under N_2.

interaction between the anthraquinone unit(s) and its reduced unit(s) in the polymer chain may lead to formation of the quinhydron type complex(es). Quinhydron is sometimes called "green hydroquinone", and the green color of the reaction product in eq 10 may be related to a partial formation of such CT adduct(s).

The ESR spectrum of the reaction mixture observed just after mixing the reactants gives rise to a strong absorption at g = 2.009 with a peak-to-peak width ΔH_{pp} of 0.205 mT. After 20 min (at room temperature), the intensity of the ESR signal decreases to 37% of the intensity observed just after the mixing.

Electrochemical Redox Reaction. Electrochemical reduction of a film of P(2Me-1,4-AQ) reveals characteristics of the redox behavior of the π-conjugated polyquinone more clearly.

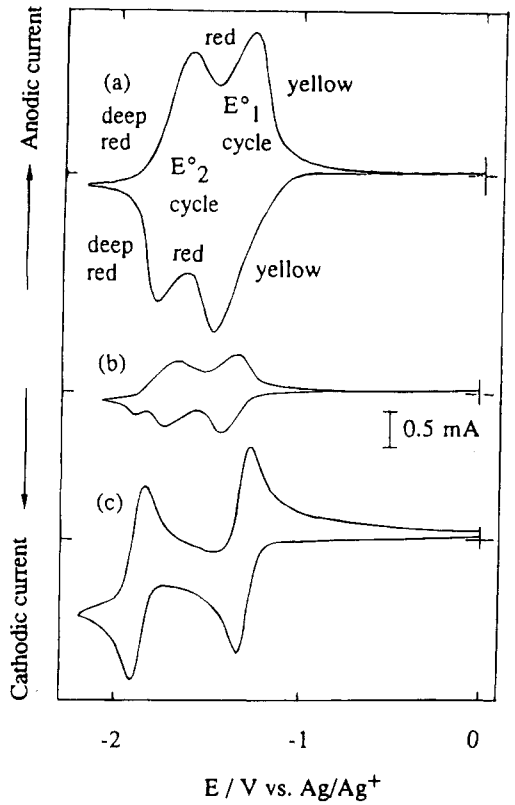
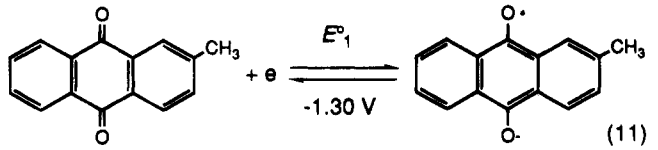
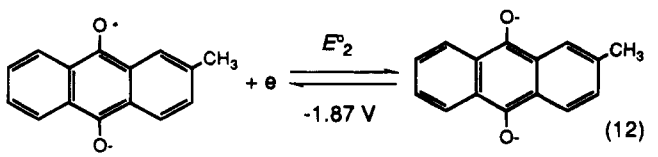


Figure 5. CV curves of P(2Me-1,4-AQ) laid on a Pt plate in a CH_3CN solution of 0.1 M $[Et_4N][ClO_4]$ at scanning rates of (a) 20 and (b) 10 mV s^{-1}, respectively. (c) CV curve of 2×10^{-3} M 2-methyl-9,10-anthraquinone in a CH_3CN solution of 0.1 M $[Et_4N][ClO_4]$ at a scanning rate of 100 mV s^{-1}.

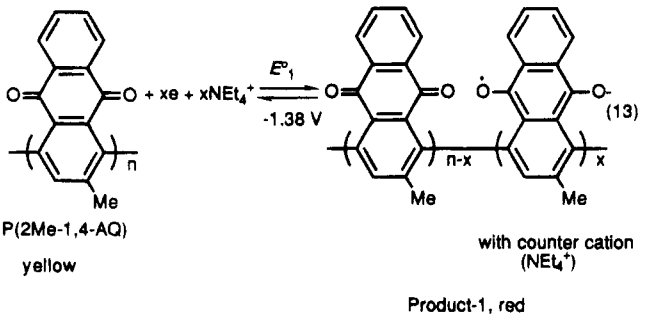
The redox behavior of P(2Me-1,4-AQ) has been investigated by cyclic voltammetry (CV) by using a cast film laid on a Pt plate, and the comparison of its CV curve with that of 2-MeAQ is shown in Figure 5. The CV curve of P(2Me-1,4-AQ) remains essentially constant in repeated scans, indicating that a P(2Me-1,4-AQ) film is stable in the redox reactions and that the redox reactions are reversible.

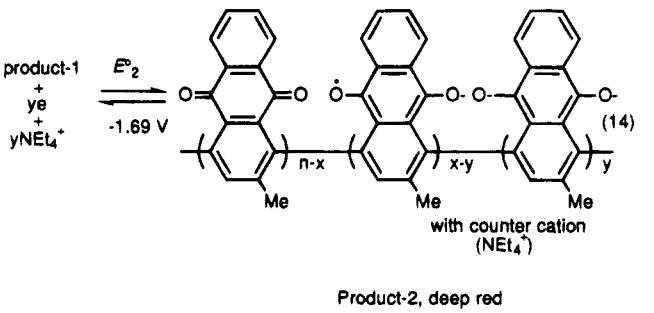
CV curves of quinones usually show two electrochemical redox cycles due to the Wurster-type two-step redox reactions[20,22] (quinone/radical anion couple and radical anion/dianion couple) as shown in Figure 5c and eqs 11 and 12.





In the case of P(2Me-1,4-AQ), the reduced molecules contain the neutral, radical anion, and dianion units (eqs 13 and 14) in the same molecule, and these units are considered to exchange electron(s) through the π-conjugated system.[1g-j,6a,24] Thus, in the reduced polymer film, electron(s) in the units shown above are considered to be delocalized along and/or between the





polymer chains. On these bases, broadening of the first ($E°_1$) and second ($E°_2$) CV cycles of P(2Me-1,4-AQ) (Figure 5a) compared with those of 2-MeAQ (Figure 5c) as well as a smaller potential difference (0.31 V; Figure 5a and eqs 13 and 14) between $E°_1$ and $E°_2$ compared with that (0.57 V; Figure 5c and eqs 11 and 12) of 2-MeAQ is ascribed to such electron exchange. Preparation of a non-π-conjugated poly(anthraquinone) having an anthraquinone unit as a pendant group and its CV data have been reported.[22] However, in the case of this polymer, such broadening of the CV cycles as described above does not take place; the CV curve of a film of a nonconjugated polymer with anthraquinone pendants shows two rather sharply separated redox cycles ($E°_1$ and $E°_2$ cycles) with the potential difference of about 0.57 V between $E°_1$ and $E°_2$.

Reducing levels x/n in eq 13 and y/n in eq 14 estimated from areas of the two redox cycles shown in Figure 5a are 0.62 and 0.48, respectively, and the smaller y/n value compared to the x/n value indicates that extensive electrochemical reduction to form the dianion unit in eq 14 is more difficult than the first reduction (eq 13), due to the presence of many negatively charged anion and dianion centers in the same π-conjugated polymer chain. However, in the case of monomeric anthraquinone, the second reduction (eq 12) occurs normally as revealed by equal areas of the two redox cycles (Figure 5c).

At a scanning rate of 20–100 mV s^{-1}, CV curves essentially with the same shape are observed. On the other hand, when the scanning rate is slowed from 20 mV s^{-1} (Figure 5a) to 10 mV s^{-1} (Figure 5b), a new reduction peak appears at about −1.88 V although its corresponding oxidation peak is not clearly observed presumably due to overlapping with the $E°_2$ cycle. The observation of the reduction at −1.88 V only at the slow scanning rate suggests that there is a slow electrochemical step for a further reduction of the anion-radical species in Product-2 formed in eq 14.

P(1,4-AQ) film laid on a Pt plate gives CV curves similar to that of P(2Me-1,4-AQ) at a sweep rate of 10–60 mV s^{-1} in a CH_3CN solution containing 0.1 M $[NEt_4][ClO_4]$. The $E°_1$ and $E°_2$ values of the two redox cycles of P(1,4-AQ) are −1.30 and −1.62 V vs Ag/Ag^+, and the

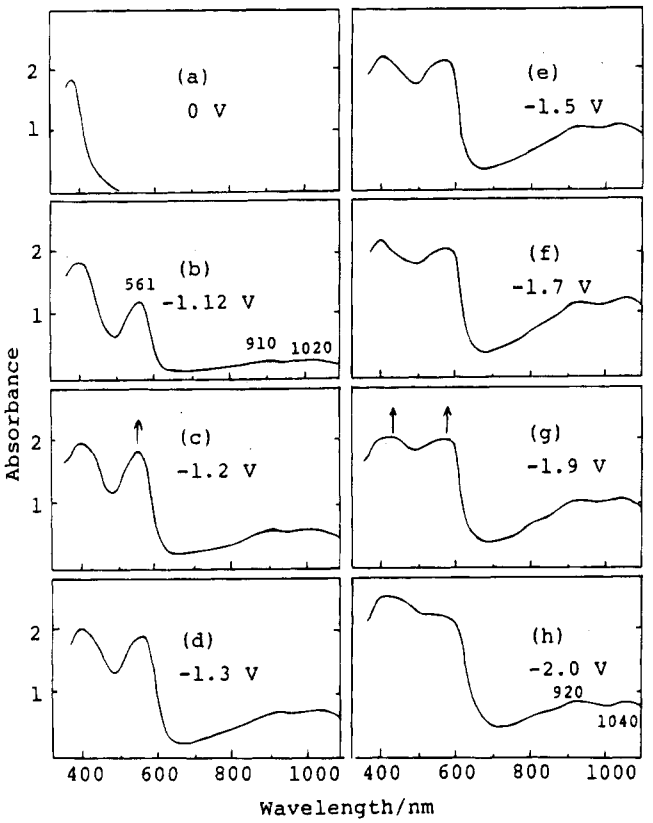


Figure 6. UV–vis spectra of the P(2Me-1,4-AQ) film on the ITO glass electrode at various applied potentials vs Ag/Ag^+: (a) 0, (b) −1.12, (c) −1.2, (d) −1.3, (e) −1.5, (f) −1.7, (g) −1.9, (h) −2.0 V. In a CH_3CN solution of 0.1 M $[NEt_4][ClO_4]$. Amount of P(2Me-1,4-AQ) = ca. 5×10^{-7} mol of monomer unit cm^{-2}.

potential difference between the two redox processes, $E^\circ_1 - E^\circ_2 = 0.32$ V, is also smaller than that observed with anthraquinone, $E^\circ_1 - E^\circ_2 = 0.57$ V.

As for the two redox cycles observed in each of the CV curves of P(2Me-1,4-AQ) and P(1,4-AQ) films, the peak electric current increases linearly with the sweep rate at sweep rates of 20–100 and 20–60 mV s^{-1} for the P(2Me-1,4-AQ) and P(1,4-AQ) films, respectively, indicating that all of the molecules in the films participated in the electrochemical redox reactions and the electric current is controlled by the mass of the polymer.

In the case of the P(2Me-1,4-AQ) film, the x/n and y/n values in eqs 13 and 14 are almost constant with P(2Me-1,4-AQ) from 5.5×10^{-8} to 58×10^{-8} mol of monomer unit/cm^2 corresponding to a film thickness between 1100 and 12 000 Å. This is in sharp contrast to reported results[22] that the degree (γ) of electrochemical reduction of anthraquinone pendant groups of the nonconjugated polymer strongly depends on the thickness of the film.

Figure 6 depicts the change of the UV–vis spectrum of the P(2Me-1,4-AQ) film on electrochemical reduction. The UV–vis spectrum of the P(2Me-1,4-AQ) film cast on an indium–tin oxide (ITO) glass substrate from $CHCl_3$ exhibits a relatively sharp π–π^* absorption band at 376 nm (Figure 6a), the same position where the absorption peak of P(2Me-1,4-AQ) in solutions (Figure 2) appears.

As shown in Figure 6b, application of a potential of −1.12 V vs Ag/Ag^+, where the radical anion is generated to some extent as judged from the CV curve (Figure 5a), leads to the appearance of new absorption bands at 395, 561, 910, and 1020 nm. The latter three absorption peaks are compared with those of the radical anion of 2-methylanthraquinone at 539, 870, and 980 nm (Figure 4a at 1 min), and the resemblance of the two absorption patterns supports the formation of the radical anion in the polymer. The broad absorption bands at 910 and 1020 nm may be overlapped with absorption bands of the polaron and/or bipolaron discussed above.

Application of negatively higher potentials of −1.2 through −1.5 V causes the increase in the intensity of these absorptions (Figure 6c–e). However, a further increase in the negatively applied potential (Figure 6f–h) leads to a change of the absorption pattern, due to the appearance of new absorption bands in the range 400–480 nm and at about 580 nm. On the application of the negatively higher potential, the peak positions of the two broad absorption bands in the region of 800–1100 nm are also shifted to 920 and 1040 nm, respectively.

From the CV data, these new absorption bands are associated with the formation of the dianion in the P(2Me-1,4-AQ) molecule which shows absorption bands at 469 and 580 nm in NMP (Figure 2a). On application of a reverse potential to P(2Me-1,4-AQ), the original UV–vis spectrum shown in Figure 6a reappears.

Employment of $LiClO_4$, instead of $[NEt_4][ClO_4]$, as the electrolyte gives CV results considerably different from those described above and complicated probably due to the known strong interaction of Li^+ with the reduced forms of quinones.[25] The CV curve of the P(2Me-1,4-AQ) film in a CH_3CN solution of $LiClO_4$ (0.1 M) exhibits one redox couple with E_{pc} at −1.22 and E_{pa} at −1.06 V vs Ag/Ag^+ as well as an irreversible cathodic peak at about −1.95 V vs Ag/Ag^+ in the first scanning. In repeated scanning in the range 0 to −2.2 V vs Ag/Ag^+, the CV currents are considerably weakened. These results indicate that Li^+ has a strong interaction with the dianion to form stable O–Li bonds, making reoxidation of the dianion difficult.

Reduction with Na. Treatment of P(2Me-1,4-AQ) having an electrical conductivity (σ) of 8×10^{-8} S cm^{-1} with excess sodium naphthalenide gives reduced P(2Me-1,4-AQ) with $\sigma = 2 \times 10^{-5}$ S cm^{-1} as measured with compressed powder. P(1,4-AQ) and P(1,5-AQ) also have the σ of an order of 10^{-8} S cm^{-1}, and the reduction with excess sodium naphthalenide affords semiconductors with σ of an order of 10^{-5} S cm^{-1}. The IR spectrum of the reduced P(2Me-1,4-AQ) is very different from that of the original P(2Me-1,4-AQ). The ν(C=O) absorption as well as other absorptions characteristic of the aromatic compounds (in-plane and out-of-plane δ(CH) vibrations) is profoundly weakened or absent in the IR spectrum of the reduced P(2Me-1,4-AQ), which exhibits a new broad strong absorption at 1430 cm^{-1}. Exposure of the reduced P(2Me-1,4-AQ) to air causes instant reoxidation to the original P(2Me-1,4-AQ) as judged from the color and the IR spectrum. Other polyquinones and oligoquinones give rise to similar IR changes on the reduction, and their reduced materials also exhibit high sensitivity to air.

In contrast to the reaction with sodium naphthalenide, exposure of the polyquinones and oligoquinones to the vapor of I_2 causes no apparent changes in their color and IR spectra, although various π-conjugated polymers like poly(thiophene-2,5-diyl) are easily oxidized with iodine.[3] These results are consistent with the electron-accepting nature of quinones.

Conclusion and Scope

Novel polyquinones having a π-conjugation system along the main chain have been synthesized by the

organometallic dehalogenation polycondensation. P(2Me-1,4-AQ) is soluble in various solvents, and casting from the solutions gives a film of P(2Me-1,4-AQ) with good optical and mechanical quality. The reduction of P(2Me-1,4-AQ) in solutions and films proceeds in a manner similar to that of its corresponding monomeric compound, 2-MeAQ. However, several interesting differences have been observed between the reductions of the polymeric and monomeric compounds (e.g., the difference in the $E°_1 - E°_2$ value observed in the electrochemical reduction) due to the presence of the π-conjugation system along the polymer main chain. These types of π-conjugated polyquinones are expected to provide new redox systems (e.g., modified electrodes) and electron-transfer systems.

Experimental Section

Materials. Solvents were dried, distilled, and stored under N_2. 1-Chloroanthraquinone, 2-methylanthraquinone, 2,2′-bipyridyl (bpy), 1,5-cyclooctadiene, 1,5-dichloroanthraquinone, and 1,8-dichloroanthraquinone were purchased from Tokyo Chemical Industry Co., Ltd. 2-Methyl-1,4-dichloroanthraquinone,[26] 1,4-dichloroanthraquinone,[27] 2,6-dichloroanthraquinone,[28] 5,8-dichloro-1,4-naphthoquinone,[29] and $Ni(cod)_2$[30] were prepared according to the literature.

Dimerization. An *N,N*-dimethylformamide (DMF, 14 mL) solution of 1-chloroanthraquinone (0.30 g, 1.2 mmol) was added to a DMF (14 mL) solution containing $Ni(cod)_2$ (0.41 g, 1.5 mmol), 1,5-cyclooctadiene (cod; 0.15 mL, 1.3 mmol), and bpy (0.23 g, 1.5 mmol) in a Schlenk type tube under N_2. After stirring for 24 h at 60 °C, the reaction mixture was poured into dilute hydrochloric acid to obtain a precipitate of yellow power. The yellow powder was washed with dilute hydrochloric acid (twice), a warm aqueous solution of disodium ethylenediaminetetraacetate (three times), warm water (once), and diethyl ether in this order and dried under vacuum to obtain a yellow powder (yield = 86%), which showed an IR spectrum identical with that of authentic 1,1′-dianthraquinone prepared according to the literature.[31]

Polymerization. A DMF (14 mL) solution of 2-methyl-1,4-dichloroanthraquinone (0.25 g, 0.85 mmol) was added to a DMF (14 mL) solution containing $Ni(cod)_2$ (0.303 g, 1.10 mmol), cod (0.104 mL, 0.85 mmol), and bpy (0.172 g, 1.10 mmol) in a Schlenk tube under N_2. After stirring for 48 h at 60 °C, the reaction mixture was poured into dilute hydrochloric acid to obtain a precipitate of yellow powder, which was washed with dilute hydrochloric acid (twice), methanol (once), a warm aqueous solution of disodium ethylenediaminetetraacetate (3 times), warm water, and methanol (once) in this order. The yellow powder thus obtained was dissolved in $CHCl_3$ and reprecipitated by adding to methanol. The yellow reprecipitated powder was collected by filtration and dried under vacuum to obtain P(2Me-1,4-AQ) (yield = 89%). Anal. Calcd for $(C_{15}H_8O_2)_n$: C, 81.8; H, 3.7. Found: C, 81.5; H, 3.8; Cl, 0. IR (KBr, cm^{-1}): 3050, 2950, 1665, 1590, 1526, 1303, 1247, 1158, 1120, 994, 796, 724, 628. ^1H NMR ($CDCl_3$, ppm): 2.1, 2.3, and 2.6 (3H, CH_3), 7.5–8.5 (5H, aromatic) (cf. Figure 1). ^{13}C NMR ($CDCl_3$, ppm): 20.9 (m, CH_3), 126.8, 127.5, 130.6, 131.3, 133.3, 133.9, 137 (br), 143.7, 144.2, 184.1 (m, C=O).

Other polymerizations and oligomerizations were carried out analogously except for the reprecipitation. P(1,4-AQ) for elemental analysis was obtained by the reprecipitation; however, the reprecipitation was not possible for other polymers and oligomers due to their low solubility. The dehalogenation polycondensation of 1,8-dichloroanthraquinone was carried out anaogously, and analytical and spectroscopic data of the product P(1,8-AQ) are also shown below.

P(1,4-AQ). Anal. Calcd for $(C_{14}H_6O_2)_n$: C, 81.5; H, 2.9. Calcd for $(C_{14}H_6O_2{\cdot}0.1H_2O)_n$: C, 80.8; H, 3.0. Found: C, 80.7; H, 3.8; Cl, 0. IR (KBr, cm^{-1}): 3400, 3060, 1667, 1590, 1375, 1323, 1304, 1247, 1175, 1117, 844, 801, 724, 587. ^1H NMR ($CDCl_3$, ppm): 7.6–8.6 (m, aromatic). CP-MAS ^{13}C NMR (ppm): 126.5, 133.8, 144.1, 183.9 (C=O).

P(1,5-AQ). Anal. Found: C, 80.4; H, 3.0; Cl, 0.87. IR (KBr, cm^{-1}): 3400, 3064, 1669, 1575, 1425, 1319, 1266, 1119, 814, 709, 624. CP-MAS ^{13}C NMR (ppm): 128.8, 133.0, 142.9, 182.9 (C=O). ^1H NMR (concentrated D_2SO_4, ppm from external $SiMe_4$): 8.2–9.6.

Oligo(2,6-AQ) and oligo(5,8-NQ) seem to contain H_2O as revealed in their analytical data and by the appearance of a strong absorption band at about 3400 cm^{-1}.

Oligo(2,6-AQ). Anal. Calcd for $Cl(C_{14}H_6O_2)_5Cl{\cdot}5H_2O$: C, 70.5; H, 3.4; Cl, 5.9. Found: C, 70.1; H, 3.5; Cl, 5.9. IR (KBr, cm^{-1}): 1666, 1592, 1410, 1288, 1040, 939, 847. CP-MAS ^{13}C NMR (ppm): 127.9, 146.2, 181.6 (C=O).

Oligo(5,8-NQ). Anal. Calcd for $Cl(C_{10}H_4O_2)_{10}Cl{\cdot}4H_2O$: C, 70.5; H, 2.8; Cl, 4.2. Found: C, 70.2, H, 2.7; Cl, 4.2. IR (KBr, cm^{-1}): 1654, 1372, 1320, 1243, 1090, 1058, 848. CP-MAS ^{13}C NMR (ppm): 136.5 (m), 185.1 (C=O).

P(1,8-AQ). Anal. Found: C, 79.1; H, 2.8; Cl, 0. IR (KBr, cm^{-1}): 3060, 1670, 1570, 1423, 1316, 1249, 1156, 1113, 800, 771, 736, 624. CP-MAS ^{13}C NMR (ppm): 126.7, 134.3, 143.4, 183.5 (C=O).

Reduction of Polyquinones. All of the chemical and electrochemical reductions as well as the spectroscopic measurements were carried out under N_2 by using standard Schlenk techniques. The reductants (hydrazine hydrate, an aqueous solution of $Na_2S_2O_4$ (0.058 M), and an aqueous solution containing $Na_2S_2O_4$ (0.058 M) and NaOH (0.50 M)) were added to the solutions of quinones. The CV measurements were carried out with films laid on Pt and ITO electrodes, which were obtained by casting from the chloroform solution of P(2Me-1,4-AQ).

A mixture of powdery P(2Me-1,4-AQ) (150 mg) and a THF solution (20 mL) of sodium naphthalenide, which was prepared by reaction of naphthalene (480 mg) and sodium (180 mg), was stirred for 3 h, and the obtained black powder was collected by filtration, dried under vacuum, and compressed at 200 kg cm^{-1} to make a disk, from which a bar was obtained by cutting for the measurement of the electrical conductivity.

Measurements. IR spectra were recorded on a Jasco IR-810 spectrometer. NMR spectra in solutions and solid-state NMR spectra were taken using JEOL JNM-GX-500, JNM-FX-100, or JNM-EX-90 and JEOL JNM-GX-270 spectrometers, respectively. TGA curves and UV–vis spectra were measured with a Shimadzu thermoanalyzer DT-30 and a Hitachi Model 200-20 spectrometer, respectively. Light scattering analysis was kindly carried out by Prof. K. Kubota of Gunma University[9] or by using an Otsuka Electronics DLS-700 dynamic light scattering spectrometer. $\chi^{(3)}$ was kindly measured by Mr. N. Ooba and Dr. A. Tomaru of NTT Opto-electronics Laboratories, Nippon Telegraph and Telephone Corp. Cyclic voltammetry was carried out with a Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko KB-104 function generator. The electrical conductivity was measured with a Takeda Riken TR-8651 electrometer. ESR spectra were recorded on a JEOL JES-RE3X spectrometer. Elemental analysis was carried out by Mrs. M. Tanaka of our laboratory with a Yanagimoto CHN Autocorder Type MT-2 (analysis of C, H, and N) and a Yazawa halogen and sulfur analyzer.

Acknowledgment. We are grateful to Prof. K. Kubota of Gunma University for the determination of the ϱ_v value of P(2Me-1,4-AQ) and light scattering analysis of P(1,4-AQ). Thanks are due to Dr. T. Kanbara of our laboratory for helpful discussion. This work was financially supported by a Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 06227222 from the Ministry of Education, Science and Culture, Japan.

References and Notes

(1) E.g.; (a) Willson, R. L. *Free Radical Res. Commun.* **1990**, *8*, 201. (b) Skancke, A.; Skancke, P. N. *Chem. Quinoid Compd.* **1988**, *2*, 1. (c) Evans, D. H. In *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Lund, H., Eds.; Marcel Dekker: New York, 1978; Vol. XII, p 1. (d) Patil, A. O.;

Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc.* **1984**, *106*, 348 and 4010. (e) O'Shea, K. E.; Fox, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 611. (f) Goulle, V.; Harriman, A.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 1034. (g) Johnson, D. G.; Niemczyk, M. P.; Minsek, D. W.; Wiederrecht, G. P.; Svec, W. A.; Gaines, G. L., III; Wasielewski, M. R. *J. Am. Chem. Soc.* **1993**, *115*, 5692. (h) Sessler, J. L.; Capuano, V. L.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 4618. (i) Hayashi, T.; Miyahara, T.; Hashizume, N.; Ogoshi, H. *J. Am. Chem. Soc.* **1993**, *115*, 2049.

(2) (a) Itoh, S.; Ogino, M.; Fukui, Y.; Murao, H.; Komatsu, M.; Ohshiro, Y.; Inoue, T.; Kai, Y.; Kasai, N. *J. Am. Chem. Soc.* **1993**, *115*, 9960. (b) Davidson, V. L., Ed. *Principles and Applications of Quinoproteins*; Marcel Dekker: New York, 1993. (c) Salisbury, S. A.; Forrest, H. S.; Cruse, W. B.; Kennard, O. *Nature* **1979**, *280*, 843.

(3) (a) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; Vols. I and II. (b) Salaneck, W. R.; Clark, D. L.; Samuelsen, E. J. E. *Science and Applications of Conducting Polymers*; Adam Hilger: New York, 1990. (c) MacDiarmid, A. G.; Heeger, A. J. NRL Memorandum Report, Proceedings of the Molecular Electron Devices Workshop, AD-A 05816,208, 1981. (d) Andre, J.-M.; Delhalle, J.; Bredas, J.-L. *Quantum Chemistry Aided Design of Organic Polymers*; World Scientific: London, 1991. (e) Bradley, D. D. C.; Mori, Y. *Electronic Properties of Conjugated Polymers III*, Kuzmany, H., Mehring, M., Roth, S., Eds.; Springer: Berlin, 1989. (f) Tour, J. M.; Lamba, J. J. S. *J. Am. Chem. Soc.* **1993**, *115*, 4935.

(4) Etori, H.; Kanbara, T.; Yamamoto, T. *Chem. Lett.* **1994**, 461.

(5) (a) Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1977**, 353. (b) Yamamoto, T. Hayashi, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091. (c) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 9. (d) Yamamoto, T.; Sanechika, K. *Chem. Ind. (London)* **1982**, (e) Yamamoto, T. *Prog. Polym. Sci.* **1992**, *17* 301. (f) Ueda, M.; Ichikawa, F. *Macromolecules* **1990**, *23*, 926. (g) Yamamoto, T. *Prog. Polym. Sci.* **1992**, *17*, 1153. (h) Schluter, A.-D.; Wegner, G. *Acta Polym.* **1993**, *44*, 59. (i) Child, A. D.; Reynolds, J. R. *Macromolecules* **1994**, *27*, 1975. (j) Bao, Z.; Chan, W.; Yu, L. *Chem. Mater.* **1993**, *5*, 2.

(6) (a) Yamamoto, T.; Maruyama, T.; Zhou, Z.-H.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832. (b) Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z.-H.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K. *Macromolecules* **1992**, *25*, 1214.

(7) (a) Schrauzer, G. N.; Thyret, H. *J. Am. Chem. Soc.* **1960**, *82*, 6420. (b) Uhlig, E.; Fischer, R.; Kirmse, R. *J. Organomet. Chem.* **1982**, *239*, 385. (c) Issleib, K. *Z. Chem.* **1984**, *24*, 386.

(8) Silverstein, R. M.; Bassler, C. G.; Morill, T. C. *Spectrometric Identification of Organic Compounds*, 3rd ed.; John Wiley: New York, 1974; p 115.

(9) Kubota, K.; Urabe, H.; Tominaga, Y.; Fujime, S. *Macromolecules* **1984**, *17*, 2096.

(10) Kubota, K.; Chu, B. *Biopolymers* **1983**, *22*, 1461.

(11) The half-wave potentials ($E_{1/2}$ vs SCE) obtained by polarographic measurements (against Hg pool) are −0.22 V for N_2H_4 (Karp, S.; Meites, L. *J. Am. Chem. Soc.* **1962**, *84*, 906), −0.38 V for $(C_6H_5CH_2)_2NOH$ (Iversen, P. E.; Lund, H. *Anal. Chem.* **1969**, *41*, 1322), and −0.48 V (in acidic media) or −1.21 V (in alkaline media) for $Na_2S_2O_4$ ((a) Cermak, V. *Collect. Czech. Commun.* **1958**, *23*, 1471. (b) Zhdanov, S. I. *Encyclopedia of the Elements*; Bard, A. J., Ed.; Marcel Dekker: New York, 1975; Vol. IV; p 288). Reduction of quinoide units in emeraldine base polyaniline (quinoid form of polyaniline) to give leucoemeraldine polyaniline proceeds by using these reductants, and a linear free energy relation holds between the rate of the reduction and the $E_{1/2}$ value (Moon, D.-K.; Ezuka, M.; Maruyama, T.; Oskada, K.; Yamamoto, T. *Makromol. Chem.* **1993**, *194*, 3149).

(12) Carlson, S. A.; Hercules, D. M. *Photochem. Photobiol.* **1973**, *17*, 123.

(13) H^+ formed by the reaction of anthraquinone with N_2H_4 (e.g., anthraquinone + $^1/_2N_2H_4$ → anthraquinone dianion + $2H^+$ + $^1/_2N_2$) seems to be exothermically trapped by N_2H_4 to form $NH_2NH_3^+$ (eq 3). This exothermic protonation reaction may give a driving force to promote the reaction (3), occurrence of which is not so favored from the viewpoint of the polarographic $E_{1/2}$ values.

(14) In the case of the AQ dimer (eq 1), the rate of reduction is about $^1/_3$ of that of 2-MeAQ.

(15) Foyle, V. P.; Takahashi, Y.; Guillet, J. E. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 257.

(16) The degree of red shift (600−1600 cm^{-1}) from 2-MeAQH_2 is smaller than that shown in Chart 1, presumably due to a larger steric repulsion between OH groups.

(17) Hayon, E.; Ibata, T.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 2072.

(18) The peak position of the longer wavelength absorption of the two strong absorptions (the absorption at 539 nm in Figure 4a) seems to shift depending on pH and the solvent.[12,17]

(19) Bridge, N. K.; Porter, G. *Proc. R. Soc. London, A* **1958**, *244*, 276.

(20) Hünig, S.; Erk, P. *Adv. Mater.* **1991**, *5*, 225.

(21) Degrand, C.; Miller, L. L. *J. Electroanal. Chem.* **1981**, *117*, 267.

(22) Hoang, P. M.; Holdcroft, S.; Funt, B. L. *J. Electrochem. Soc.* **1985**, *132*, 2129. Figure 4 in this reference reports CV and spectroscopic data of a film of a nonconjugated polymer with an anthraquinone pendant.

(23) Sandstede, G. *Z. Phys. Chem. (Frankfurt am Main)* **1975**, *98*, 389.

(24) (a) Johoulet, C.; Obeng, Y. S.; Kim, Y.-T.; Zhou, F. Bard, A. J. *J. Amer. Chem. Soc.* **1992**, *114*, 4237. (b) Helms, A.; Heiler, D.; McLendon, G. *Ibid.* **1991**, *113*, 4325. (c) Becker, B.; Bohnen, A.; Ehrenfreund, M.; Wohlfarth, W.; Sakata, Y.; Huber, W.; Mullen, K. *Ibid.* **1991**, *113*, 1121. (d) Powers, M.; Meyer, T. J. *Ibid.* **1978**, *100*, 4393. (e) Kramer, J. A.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 3330.

(25) (a) Peover, M. E.; Davies, J. D. *J. Electroanal. Chem.* **1963**, *6*, 46. (b) Audebert, P.; Bidan, G. *J. Electroanl. Chem.* **1987**, *238*, 183.

(26) Arient, J.; Slosar, J.; Sterba, V.; Obruba, K. *J. Chem. Soc. C* **1967**, 1331.

(27) Phillips, M. *J. Am. Chem. Soc.* **1926**, *48*, 3198.

(28) Fierz-David, H. E.; Krebser, A.; Anderau, W. *Helv. Chim. Acta* **1927**, *10*, 225.

(29) Torssel, K. *Acta Chem. Scand., Ser. B* **1976**, *30*, 353.

(30) Wilke, G. *Angew. Chem.* **1960**, *72*, 581.

(31) Ullmann, F.; Minajeff, W. *Chem. Ber.* **1912**, *45*, 687.

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