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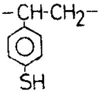
ABSTRACT

Polymers containing 1,4-dihydronicotinamide (P-NAH) alloxan (P-A), and viologen (P-V^{2+}) moieties were synthesized and characterized. P-NAH reduced various organic substances such as lipoic acid, alloxan, and viologens and also immobilized quinone mediated by alloxan. P-A was reduced to the polymer-bearing alloxan radical and the dialuric acid structure without crosslinks by one- and two-electron reduction, respectively, and P-A also mediated the redox reaction occurring between aqueous and organic (water-immiscible) layers. P-V^{2+} was converted to the stable viologen radical reversibly by one-electron reduction. Electric potentials and currents on photoreduction of P-V^{2+} and catalytic behavior of P-V^{2+} in the reduction of carbonyl compounds were examined.

INTRODUCTION

Oxidation-reduction polymers are well known [1-4] as one division of functional polymers. We have investigated, mainly from the viewpoint of polymeric reagents capable repeated use, synthesis and characterization of various types of polymers containing thiol (I-III) [5-7], ferrocene (IV) [8], positive halogens (V, VI) [9, 10], trivalent iodine (VII) [11], stable radicals (VIII) [12], and TTF (tetrathiofulvalene) type polymers (IX) which act as donors to some acceptor materials such as TCNQ (tetracyanoquinodimethane).



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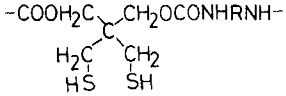

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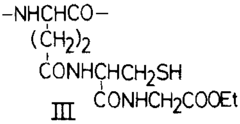

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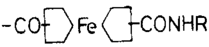

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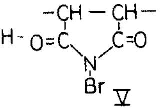

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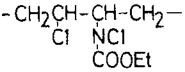

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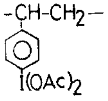

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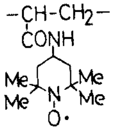

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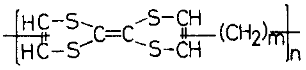


IX

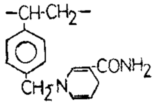
In this paper, we wish to summarize our recent research on the syntheses of new types of oxidation-reduction polymers and their behavior as biomimetic polymeric electron carriers.

POLYMERS CONTAINING THE NICOTINAMIDE STRUCTURE

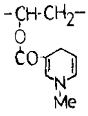
Recently, nicotinamide (NA) and dihydronicotinamide (NAH) have been receiving increased attention as the key structures in the active center of the most important coenzyme (NAD and NADH) in the biological oxidation-reduction system. The chemistry of 1-benzylnicotinamide (BNA) and its reduced form, 1-benzyl-1,4-dihydronicotinamide (BNAH), has been studied by several groups of workers in view of the model reaction of oxidation or reduction in vitro.

Synthesis

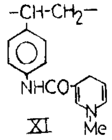
Synthetic P-NAH, X, or XI, polymers containing the BNAH moiety have been prepared by us previously [14]. Especially, the interesting reducing capability of P-NAH was examined independently by Lindsey [15] and by us [16]. However, the structure of P-NAH prepared by



P-NAH

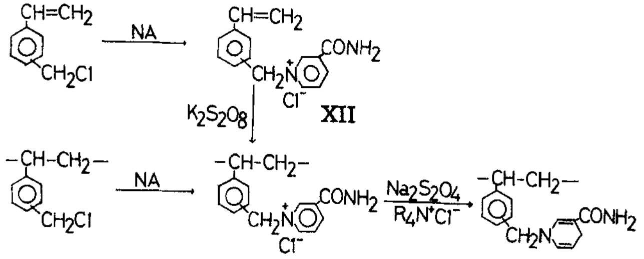


X



XI

the polymer reaction of chloromethylated polystyrene [15, 16] is not obvious, because a small quantity of chloromethyl group remains unaltered to the last, and also some sulfur-containing groups incorporated during the reduction of P-NA with dithionite are difficult to remove completely. So, alternative methods of synthesis and reduction of P-NA were reexamined.



P-NA P-NAH (1)

Commercial chloromethylstyrene (m-60%, p-40%, Seimi Kagaku Co.) was allowed to react with nicotinamide (room temperature, 24 hr in DMF) to give 1-styrylmethyl nicotinamide (XII, dec. 230°C) in 95% yield. P-NA was obtained as a hygroscopic white powder by the polymerization of XII in water with potassium persulfate as an initiator (70°C, 15 hr). P-NA was then reduced with sodium dithionite-sodium carbonate in the presence of benzyltriethylammonium chloride, precipitating P-NAH nearly quantitatively. The use of surfactant is essential to prevent the formation of stable salts between the adduct formed as an intermediate (probably 4-SO_2Na) and pyridinium cation. P-NAH thus obtained, initially soluble but insolubilized when dried, contains neither chlorine nor sulfur and shows 98% dihydro structure as determined by Tillman reagent (2,6-dichlorophenol indophenol). Although Tsuchida et al. [17] have examined the radical polymerization of dihydro monomer which was prepared by dithionite reduction of XII, only a polymer of rather low molecular weight ($\overline{M}_n \sim 1200$) was obtained, indicating the dehydrogenation of dihydropyridine with free radicals occurred during polymerization.

Redox Behavior

As expected from the low redox potential of BNA-BNAH [E_7 (NAD-NADH) = -0.32 V vs. NHE], P-NAH has fairly good ability to reduce the oxidized form of dyes such as Tillman regent and malachite green, and also the free radical, 1,1-diphenyl-2-picrylhydrazyl (DPPH). As for the activated carbonyl compounds, we already reported the reduction of chloranil with high redox potential by P-NAH under heating. In this report, the reaction of P-NAH with alloxan (A) or ninhydrin was examined in some detail. This is a cognate of "reductones" which play important roles in the biological oxidation-reduction system, and enhanced reactivity of the central carbonyl assisted by neighboring carbonyls has long been known [18]. While the central $>C = 0$ combines one mole of water in the gem-diol form, $>C(OH)_2$, it functions as a free carbonyl in the reaction by equilibrium.

On treating P-NAH with an equimolar amount of alloxan in methanol at room temperature, a yellow solid XIII with an electron spin resonance (ESR) spectrum as shown in Fig. 1 is obtained.

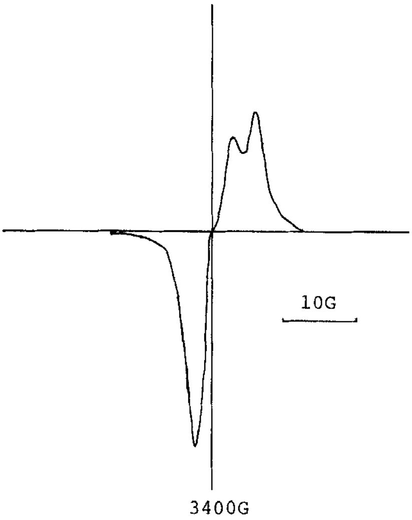
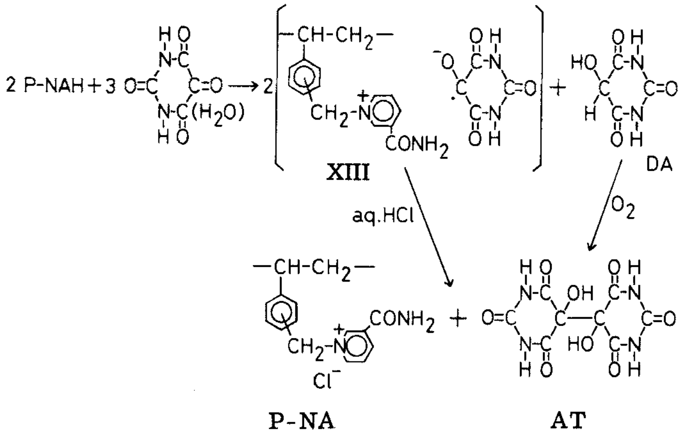


FIG. 1. ESR spectrum of XIII.

By bubbling oxygen into the filtrate, alloxantin (AT) was obtained, presumably due to the oxidation of the two-electron reduction product (dialuric acid, DA) of A. The hydrolysis of the solid product mentioned above afforded P-NA quantitatively; thus the structure was assumed as XIII, corresponding to the yellow powdery product (mp 195-196°C) [19] which was obtained by the reaction of BNAH and A.

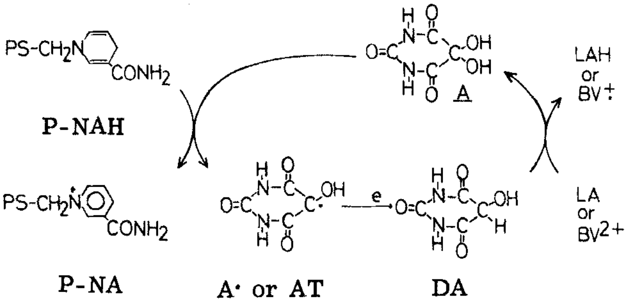


(2)

From the model reaction, it was confirmed that alloxan radical ($A^{\cdot}$), even its dimer (AT) under definite conditions, and DA are capable of reducing special oxidants such as oxygen, DPPH, Tillman reagent, malachite green, p-benzoquinone (Q), lipoic acid (LA), and benzyl viologen (BV^{2+}) at room temperature. Of these, LA and BV^{2+} are scarcely reduced in methanol with BNAH or P-NAH under similar conditions. However, addition of a catalytic amount of A induces the reduction effectively giving dihydro lipoic acid (LAH) or viologen radical cation ($BV^{+\cdot}$), respectively, in 40-70% yields, suggesting the reaction scheme (3).

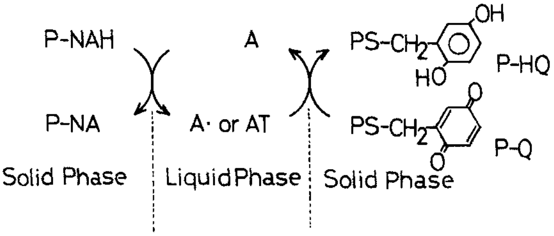
Special interest is the electron transfer between insoluble solids mediated with A. As has been suggested by Rebek [20], the reactions between the functional groups immobilized on the insoluble polymeric supports are hardly expected to proceed. Rebek has utilized the reactions to prove the existence of the intermediate, X ("triphase test") in which a reactive species (X) liberated from one solid support reacts, through the liquid (solution) phase, with a functional group immobilized on another solid support.

Insoluble, granular polystyrene (PS) as beads (DVB 2%, 200-400 mesh), was chloromethylated followed by quaternization with NA



(3)

and reduction, yielding completely insoluble P-NAH (NAH content, 23.7%). On the other hand, insoluble quinone polymer, P-Q (Q content, 92 mol%) was prepared by the reaction of chloromethylated PS (DVB 20%, 30-60 mesh) with hydroquinone (HQ) followed by oxidation according to Kun's procedure [21]. Whereas no reaction occurred on suspending the P-NAH and P-Q in alcohol-water, P-Q was reduced to P-HQ by addition of A. After the reaction, the two types of beads were separated by difference of densities, and the HQ content in the larger beads was determined by the DPPH method devised by us as summarized in Table 1. While the composition of solvent affected the reaction markedly, it was proved that the oxidation-reduction reaction between insoluble solids proceeded feasibly mediated with A as a carrier [Eq. (4)].



(4)

POLYMERS CONTAINING ALLOXAN STRUCTURE

As mentioned above, A could carry electron by way of A ⇌ A· (or AT) ⇌ DA. We therefore studied the immobilization of A to build up a new type of polymeric electron carrier.

TABLE 1. Electron Transfer from P-NAH to P-Q by use of A

No.	P-NAH (meq)[a]	P-Q (meq)[a]	A (mmole)	Solvent (EtOH/ H_2O)[c]	Temp (°C)	Time (hr)	P-HQ (meq/g)
1	0.4	0.4	0	50/50	50	12	0
2	0.5	0.5	0.5	50/50	r. t.	24	0.46
3	0.5	0.5	0.05	50/50	r. t.	48	0.11
4	1.0	0.5	0.5	50/50	50	8	0.58
5	1.0	0.5	0.05	50/50	50	12	0.50
6	1.0	0.5	0.05	20/80	50	12	0.64
7	1.0	0.5	0.05	20/80	50	12	0.71
8	1.0	0.5	0.05	95/5	50	48	0.01

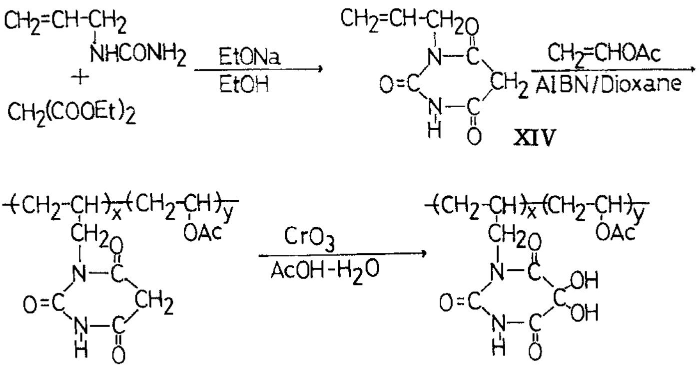
[a] DVB 2%, 200-400 mesh, 1.5 meq/g.
[b] DVB 20%, 30-60 mesh, 4.3 meq/g.
[c] 40 ml total.

Synthesis

The direct synthesis of vinyl monomer from A is unfavorable, because A is unstable in alkaline media and the central carbonyl group is too reactive for multistep synthesis. Therefore, a process via N-allylbarbituric acid was examined. P-A has been briefly reported by Kuhn [22] as a muscle model of redox type.

A typical example is as follows. N-Allylbarbituric acid was allowed to polymerize with a tenfold molar ratio of vinyl acetate in dioxane (70°C, 64 hr) in the presence of azobisisobutyronitrile (AIBN, 1 mole % relative to monomers). A white, powdery polymer (XV) was oxidized with chromium trioxide (40°C, 1 hr) in acetic acid-water, followed by repeated dissolution (methanol)-precipitation (H_2O) to give P-A with $[\eta] = 0.097$ (25°C, in dioxane) and $\overline{M}_n = 13600$ (vapor pressure osmometry) [Eq. (1)]. On changing the molar ratio of comonomer, a copolymer (P-A) with 8.6-45.2 mole % of A moiety was obtained in fairly good yield. To judge from infrared (IR) and NMR spectra, the barbituric acids in XV were converted to alloxan structure almost completely.

PVP-A (A content, 13 mole %) was prepared by the reaction of polyvinylpyridine and N-chloroethylbarbituric acid derivative,

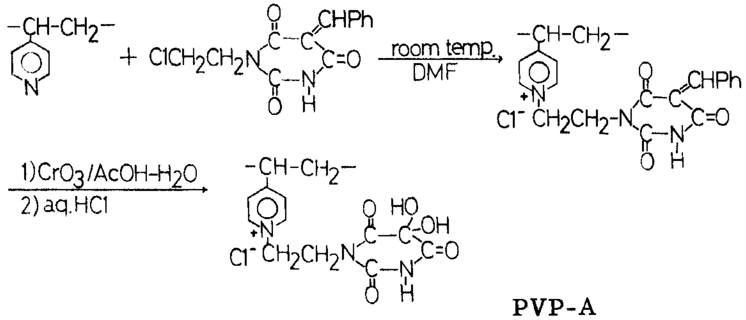


XIV

XV

P-A

(5)



PVP-A

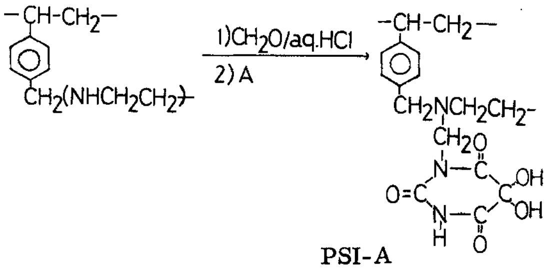
(6)

followed by simultaneous oxidation and removal of protective groups with chromium trioxide [Eq. (6)].

Further, commercial PS beads grafted with ethylenimine (XVI) (Mitsubishi Chem. Ind. Ltd., NH content, 6.3 mmole/g) were reacted with a large excess formalin in DMF and then with A in acidic media, giving PSI-A, for example, with content of 0.8 mmole A/g [Eq. (7)].

Redox Behavior

In the preliminary experiments, the reduction of A with hydrogen sulfide, sodium dithionite, or potassium cyanide gave alloxantin (AT) in good yield. Alloxan radical A· (one-electron reduction of A) seems



(7)

either to dimerize or react with DA (two-electron reduction product of A). Alternately, by the reduction of P-A with above reducing agents, soluble polymer (P-A) with intense reducing power but no ESR signal was produced. The formation of crosslinking (corresponded to AT) between P-A and P-DA would be prevented by steric hindrance of the polymeric main chain (polymer effect). From these results, the reaction of P-A with BNAH is expected to give noncrosslinked P-DA, probably via the P-A$^{\cdot}$ radical. For the cases of P-A or A with BNAH in dioxane, the reaction was followed (Fig. 2) from the decrease of absorbance at 360 nm of BNAH. From Fig. 2, second-order rate constants, k_2 in $v = k_2[\text{BNAH}][\text{A or PA}]$ were nearly equal, being 1.9×10^{-4} l/mole-sec for A or 2.2×10^{-4} l/mole-sec for P-A, respectively.

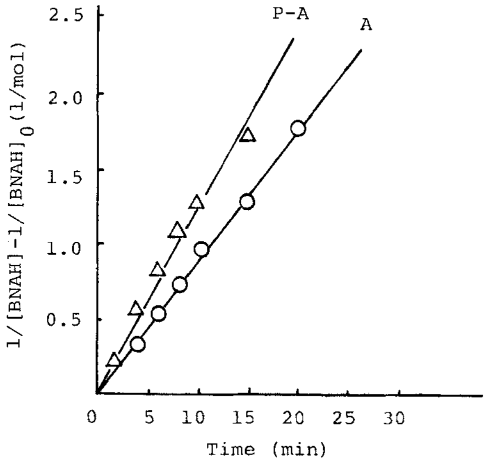


FIG. 2. Reactions of BNAH with A or P-A.

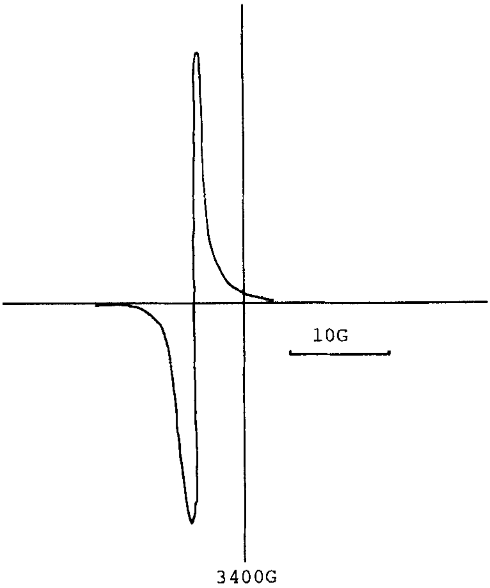


FIG. 3. ESR spectrum of P-A.

On the other hand, one-electron reduction proceeded homogeneously when P-A was irradiated in dioxane or methanol with a high-pressure immersion mercury lamp under nitrogen [23]. A white, powdery polymer (P-A·) obtained by pouring the reaction mixture into ether, showed a distinct ESR spectrum (Fig. 3) and the radicals persist so long as the product is kept at room temperature. Nevertheless, P-A thus obtained has the ability to reduce DPPH, Tillman reagent, malachite green, and triphenyl tetrazolium salt. Dependence of radical formation (estimated by DPPH method) on irradiation time is shown in Fig. 4. Even in the polymer (P-A) with high alloxan contents (A, 45 mmole %), no gelation was observed on prolonged irradiation. Since the model compound A gives AT in good yield under a similar condition [24], these facts indicate that P-A· does not dimerize due to the polymer effect as the case of chemical reduction described above [Eq. (8)]. However, the polymer obtained by the reaction of P-A with powdery P-NAH in methanol under nitrogen exhibited the same ESR spectrum as those of products from A and BNAH or A and P-NAH, indicating the formation of complex radical salt between both polymers.

On the other hand, as expected, P-A mediates the reduction of LA or BV^{2+} with BNAH in ethanol, and the corresponding reduced products were obtained in good yields [Eq. (9)].

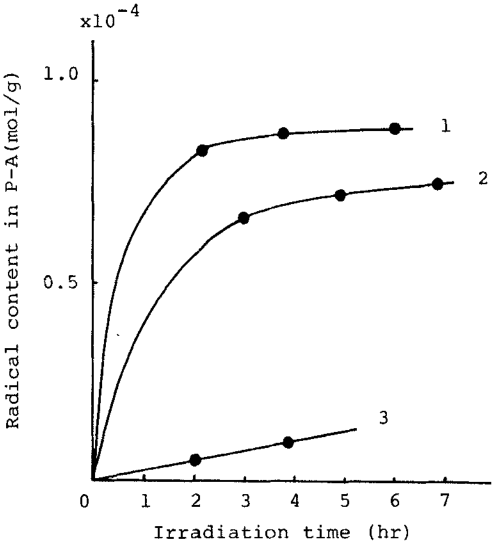
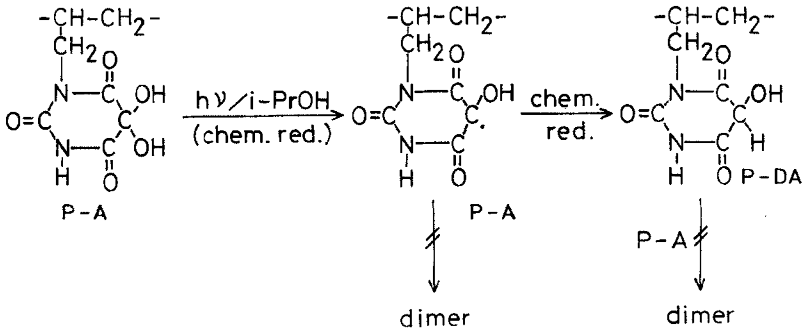


FIG. 4. UV irradiation of P-A: (1) i-PrOH-dioxane (1:1); (2) dioxane; (3) MeOH.



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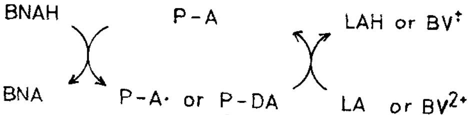
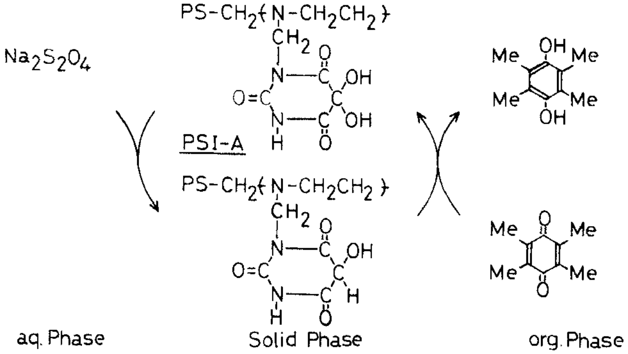


BNAH : P-A : LA or BV^{2+} = 10 : 1 : 15 (molar ratio)

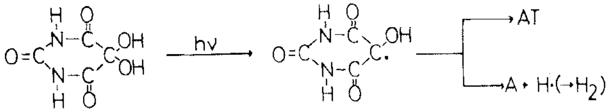
(9)

Further, it was confirmed that the usually impossible redox reaction between aqueous and immiscible organic (benzene) layers was performed by use of immobilized PSI-A [Eq. (10)].



(10)

Recently, Imoto et al. [25] observed that C–OH bond in A (hydrate) was cleaved on UV irradiation to produce hydrogen via the formation of H• and •OH [Eq. (11)].

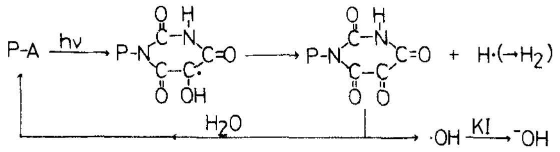


(11)

However, the efficiency of H_2 evolution was reduced by the formation of AT (dimerization of A•), and hydrogen was contaminated by the side reaction of •OH on A. Dimerization of A• would be expected to be minimized by immobilization of A on the polymeric support as mentioned before. In practice, using PVP-A together with potassium iodide to reduce •OH into OH^-, purity of hydrogen was improved up to 93%. The formation of insoluble (crosslinked) products during the irradiation (60 hr) was not observed as expected.

POLYMERS CONTAINING VIOLOGEN STRUCTURE

In analogy with 1-substituted nicotinamide, it is well known that the viologen (N,N'-dialkyl-4,4'-dipyridinium, $V^{2+}2X^-$) is subjected to one-electron reduction affording the blue radical cation ($V^{\dot{+}}X^-$), and in turn,



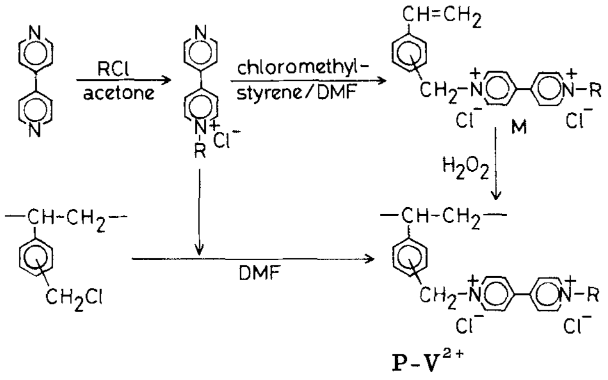
(12)

$\overset{+}{V}{\cdot}X^-$ is easily oxidized to regenerate $V^{2+}2X^-$. Thus, viologens attracted much attention, due to their low redox potentials, as herbicides which intercept the electron transfer in photosystem I in chlorplasts, or as candidates for the transducer in photoelectric recording systems.

While the polyaddition type of polymers (ionene form) containing viologen moieties in the main chain are known [26, 27], only a few examples of polyvinyl type are claimed in patents [28]. In this paper, synthesis of polymers with pendant V^{2+} moieties by polymerization of the corresponding monomer or by the polymer reaction and their redox behaviors are reported.

Synthesis

The synthetic scheme is shown in Eq. (13).



(13)

4,4'-Bipyridyl was first methylated with methyl iodide. After replacing the iodide counteranion with chloride by use of Amberlite IRA-400 (Cl^- form), N-methyl-4,4'-bipyridinium chloride (MBP) was reacted with chloromethylstyrene (m-60%, p-40%) to give the styryl monomer M (R = Me). Though both monomers (M, R = CH_3 or $C_6H_5CH_2$) gave satisfactory IR and NMR spectra, the chlorides were converted to the less hygroscopic tetraphenyl borates for elemental

TABLE 2. Viologen Polymer

Polymer no.	Monomer M	Comonomer M_{co}	M/M_{co} (mole/mole)	Conversion (%)	V^{2+} content (%)[a]	$[\eta]$ (dl/g)[b]
$P\text{-}V^{2+}1$	R = Me	-	-	50.0	100	0.08
$P\text{-}V^{2+}2$	Me	$CH_2{=}CHCONH_2$	1/1	42.3	41.3	0.37
$P\text{-}V^{2+}3$	Me	$CH_2{=}CHCONH_2$	1/5	65.8	16.4	0.65
$P\text{-}V^{2+}4$	Me	$CH_2{=}CHCOOH$	1/5	87.5	19.4	
$P\text{-}V^{2+}5$	CH_2Ph	$CH_2{=}CHCONH_2$	1/10	42.1	14.2	
$P\text{-}V^{2+}6$	$PS\text{-}CH_2Cl$ + MBP polymer/MBP = 3/2				51.3	insoluble

[a] From elemental analysis.
[b] In 1 N KCl at 30°C.

analysis. M was allowed to polymerize or copolymerize with another monomer in water at 50°C for 10 hr in the presence of hydrogen peroxide (3-4 mole % based on the monomer used). The precipitate obtained by pouring the reaction mixture into acetone was purified by dissolution in water and precipitation with 99% alcohol. The results are shown in Table 2. The copolymer of M with acrylamide was pale yellow in color and showed good film-forming properties. P-V^{2+}6 was prepared by the reaction of granular chloromethylated polystyrene (DVB 2%, 30 mesh, CH_2Cl 98 mole %) with MBP at 70°C for 18 hr in DMF; about half of the CH_2Cl reacts under these conditions.

Redox Behavior

All of the polymers obtained turned deep blue when reduced chemically (sodium dithionite, zinc etc.) or electrolytically, or when exposed to light. Figure 5 shows an example of the ESR spectrum for the reduced P-V^{2+}3. The blue color of the irradiated P-V^{2+}6 fades to pale yellow rapidly with moisture, and this coloration-discoloration was observed repeatedly.

The half-wave potentials of model viologens and polymers were measured at the dropping mercury electrode (Yanagimoto Digital Polarographs, PE-21) by use of a SCE as a reference electrode. Cyclic voltammetry of P-V^{2+}2 in phosphate buffer solution (pH 6.88) under nitrogen is illustrated in Fig. 6. The first half-wave potentials (E_1) measured are summarized in Table 3. The increase of E_1 in polymers compared with models was also observed for the case of ionene-type viologen polymer [27]. In our case, E_1 of the copolymer

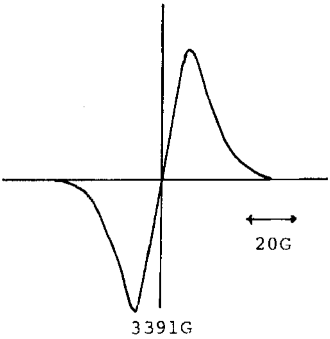


FIG. 5. ESR spectrum of reduced P-V^{2+}3.

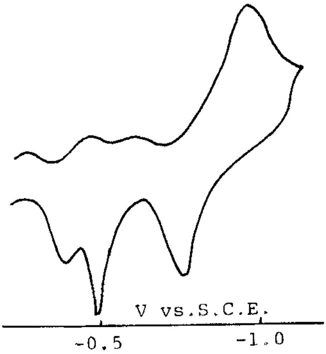


FIG. 6. Cyclic voltammogram of P-V^{2+}2.

TABLE 3. Half-wave Potentials E_1 of Viologens

Compound	E_1 vs. SCE, (mV)
Model compounds	
N-Me,N'-CH_2Ph	-460
N-Me,N1-$CH_2C_6H_4$–CH=CH_2	-413
Polymers	
P-V^{2+}1	-388
P-V^{2+}2	-403
P-V^{2+}3	-415

decreases and gradually approaches those of the models as the content of viologen decreases, as the mutual interaction between them is suppressed. Although the reason is not clear at present, similar phenomena were observed in the case of hydroquinone-formaldehyde redox polymer and its model compounds [29].

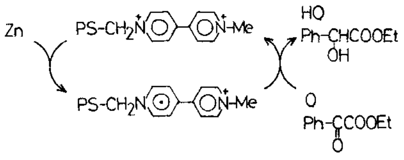
When the phosphate buffer solution of P-V^{2+}3 ([V^{2+}] = 4 × 10^{-3} mole/liter) was irradiated by a high-pressure mercury lamp (100W) in one compartment of the H-type glass cell (each compartment contains 20 ml of solution and a Pt electrode), the solution was polarized rapidly to show the maximum value of -550 mV (vs. SCE) within 10 min. The time required to attain the maximum value decreased on addition of p-carboxybenzophenone (triplet sensitizer) and increased on addition of Michler's ketone (triplet quencher). Further, the

TABLE 4. Photocurrent of Viologens

Compound	Concn (mmole/liter)	Photocurrent (μA/cm^2)
$MV^{2+}2Cl^-$	6.1	58.1
$BV^{2+}2Cl^-$	6.1	10.6
$P\text{-}V^{2+}3$	2.2	2.5

electric current, as shown in Table 4, was obtained by connection of the irradiated and unirradiated solution. The blue color faded by discharge and the coloration (charging)-discoloration (discharge) was held reversibly to some extent.

Viologens also mediate electron transfer, as expected. On standing for a month, a mixture of zinc powder (large excess) and p-benzoquinone or ethyl benzoylformate in water-acetonitrile (1:5) showed no appreciable reaction. On addition of a catalytic amount of P-V^{2+}3, hydroquinone or ethyl mandelate, respectively, was obtained almost quantitatively after 2 days at room temperature [Eq. (14)].



(14)

Finally glass beads coated with viologen polymer were prepared. By dipping glass beads (diameter 0.3 mm) into an aqueous 4% solution of P-V^{2+}3, wiping, and evaporating the excess water in vacuo, followed by treating with acidic formalin (prepared from paraformaldehyde, 38% formalin, hydrochloric acid, and ethanol) at 50°C for 5 hr, an insoluble viologen surface on glass was obtained. After reducing the beads with aqueous dithionite/sodium carbonate, the content of $V^{\dot{+}}$ was estimated to be 3×10^{-2} mmole/g by colorimetric determination of formazan (λ_{max} = 448 nm) resulting from the oxidation of beads with excess triphenyltetrazolium chloride.

In this study, three types of polymeric electron carriers, bearing nicotinamide, alloxan, and viologen structures, were prepared and characterized. It would be feasible to design metal or carbon electrodes modified with these functional groups and a functional membrane which could transfer electrons but not molecule. While each function was immobilized individually in the present study in a powdery, granular, or film state, further interest may be directed to more complex composites. For example, a blend of P-A and P-V^{2+} would form a biradical salt, $\text{P-A}^{\cdot -}\ \text{P-V}^{+\cdot}$ on reduction, which is expected to be a new type of electron-conducting material.

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