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Syntheses of Some Novel Polymers Containing the Viologen Structure and Their Application to Electron-Transfer Reactions in Heterophases

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ABSTRACT: Several new viologen polymers (P-V^{2+}) were synthesized through polymer reactions on poly(4-vinylpyridine), polystyrene, and silica gel. These insoluble polymers were used as electron-transfer catalysts for the reduction of azobenzene, either in a Zn–P-V^{2+} system (reductant: Zn, in CH_3CN–H_2O; solid (Zn)–solid (P-V^{2+})–liquid phase system) or in a $Na_2S_2O_4$–P-V^{2+} system (reductant: $Na_2S_2O_4$, in H_2O–CH_2Cl_2; liquid (H_2O)–solid (P-V^{2+})–liquid (CH_2Cl_2) phase system). The experiments showed that the electron-mediating activities varied with the nature of reducing agent (solid or liquid) and polymeric supports. It was observed that P-V^{2+} which had more hydrophobic residues were more effective as catalysts in the reduction of the hydrophobic substrate (azobenzene).

Introduction

Viologens (1,1′-dialkyl-4,4′-bipyridiniums) (V^{2+}) are known to be susceptible to one-electron reduction, producing cation radicals ($V^{+\cdot}$), which can be reoxidized to V^{2+}. Thus viologens have attracted much attention as electron-transfer catalysts[1-6] (Scheme I). Scheme I shows the mediation of electron transfer from a reductant to a substrate by viologens through their reversible redox reaction. In some instances, X may sensitize photoreduction of V^{2+}.[1-3]

Whereas many workers have studied methods to reduce V^{2+} and the substrates reduced by $V^{+\cdot}$, the photoproduction of hydrogen with $Ru(bpy)_3{}^{3+}$ as a sensitizer has attracted the most attention.[1-3] We, on the other hand, have been interested in the reaction using V^{2+} for the reduction of organic compounds to make good use of inexpensive and readily available reducing agents such as zinc and sodium dithionite. For instance, it was found that aromatic aldehydes and ketones,[5] quinones, and α-keto esters[6] could be easily reduced by using V^{2+} derivatives as electron-transfer catalysts. Further, we found that azobenzene and *vic*-dibromides could also be reduced by $V^{+\cdot}$.[7]

In this article, we describe the incorporation of viologens into poly(4-vinylpyridine), polystyrene, and silica gel and the mediation of electron transfer by these derivatives to a hydrophobic substrate, azobenzene, under two kinds of triphase conditions, namely, from zinc (solid) to azobenzene (solution) via P-V^{2+} (solid) or from $Na_2S_2O_4$ (aqueous solution) to azobenzene (organic solution) via P-V^{2+} (solid). This chemistry is compared with the two-phase electron-transfer reaction via the model compound propylviologen (1,1′-dipropyl-4,4′-bipyridinium) (PrV^{2+}).

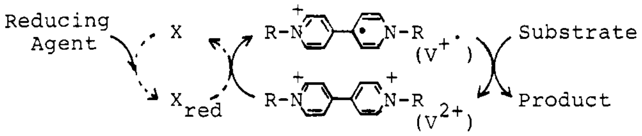
Results and Discussion

Preparation of Viologen Polymers. Procedures for the preparation of P-V^{2+} containing bipyridinium moieties in the main chain have previously appeared,[8,9] but only a few examples of the pendant type have been reported.[6,10]

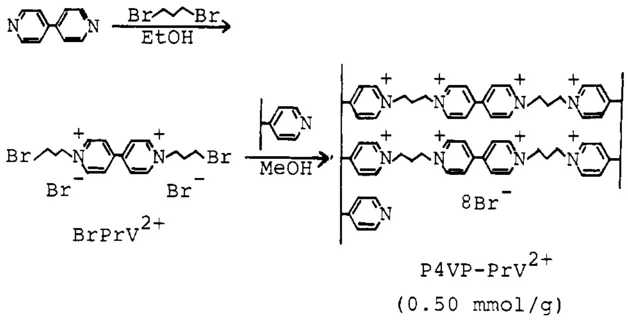
Incorporation of the viologen structure into poly(4-vinylpyridine) was achieved through the quaternization of the pyridine ring bound to the polymer main chain. $BrPrV^{2+}$, which has two reactive halogens, acts as not only a reactive viologen but a reagent to cross-link the polymer (Scheme II).

P4VP-PrV^{2+} was converted to $P4VP^{+}$-PrV^{2+} by the quaternization of the pyridine ring with 1-bromopropane. elemental analysis shows the presence of free pyridine moieties, even though an excess of 1-bromopropane was used in the quaternization (Scheme III).

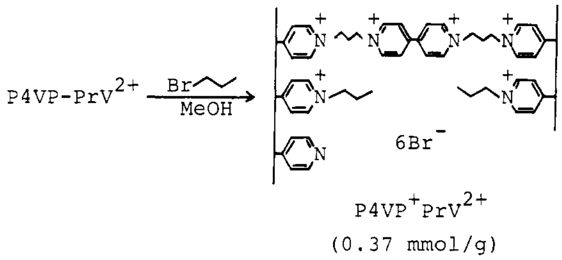
Scheme I



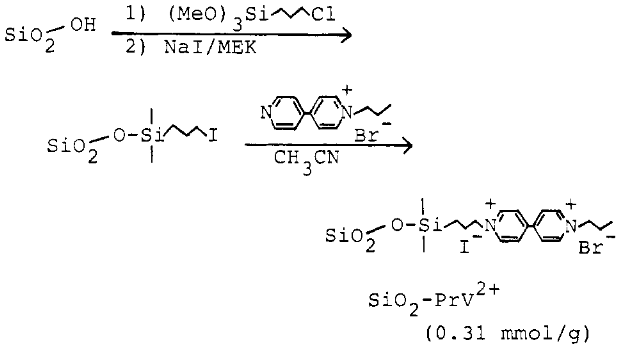
Scheme II



Scheme III



Scheme IV



We coupled the viologen structure to silica gel, which is well established as a polymeric support,[11] by using a silane coupler as shown in Scheme IV. In our series of experiments, 0.94–1.28 and 0.24–0.31 mmol/g of chloro-

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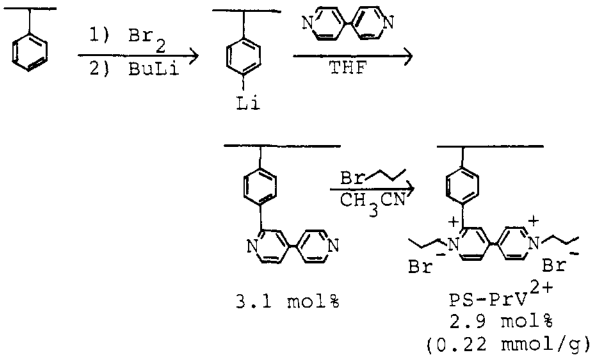
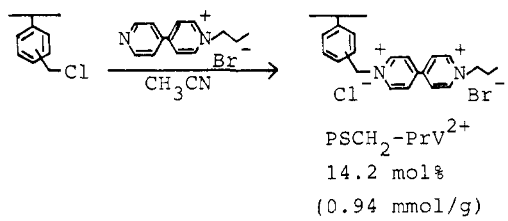
Scheme V



Scheme VI



Scheme VII

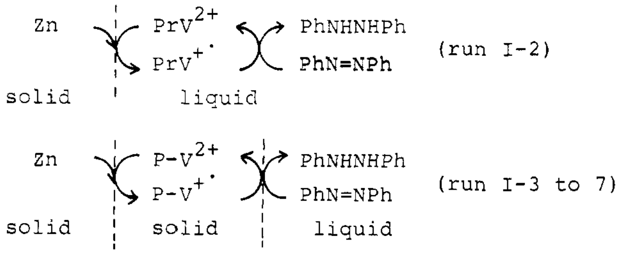


Table I
Reduction of Azobenzene in the Zn-V^{2+} System[a]

run	V^{2+}	phase[b]	yield,[c] %	cycle no. of V^{2+}
I-1	none	S-L	0	0
I-2	PrV^{2+}	S-L	100	40
I-3	P4VP-PrV^{2+}	S-S-L	80	32
I-4	$P4VP^+$-PrV^{2+}	S-S-L	27	10
I-5	Ps-PrV^{2+}	S-S-L	0	0
I-6	SiO_2-PrV^{2+}	S-S-L	29	11
I-7	$PsCH_2$-PrV^{2+}	S-S-L	51	20

[a] Zn, 3 mmol; PhN=NPh, 2.5 mmol; V^{2+}, 0.125 mmol. Room temperature, 24 h, under N_2, in 20 mL of MeCN-pH 4.0 buffer (9:1), with vigorous stirring. [b] S = solid; L = liquid. [c] ^1H NMR yield (see Experimental Section).

Table II
Reduction of Azobenzene in the $Na_2S_2O_4$-V^{2+} System[a]

run	V^{2+}	phase[b]	yield,[c] %	cycle no. of V^{2+}
II-1	none	L-L	0	0
II-2	PrV^{2+}	L-L	82	32
II-3	P4VP-PrV^{2+}	L-S-L	76	30
II-4	$P4VP^+$-PrV^{2+}	L-S-L	43	17
II-5	Ps-PrV^{2+}	L-S-L	75	30
II-6	SiO_2-PrV^{2+}	L-S-L	76	30
II-7	$PsCH_2$-PrV^{2+}	L-S-L	90	36
II-8	none (+$Bu_4N^+Br^-$)[d]	L-L	25	

[a] $Na_2S_2O_4$, 3.5 mmol; K_2CO_3, 3.5 mmol; PhN=NPh, 2.5 mmol; V^{2+}, 0.125 mmol. Room Temperature, 24 h, under N_2, in H_2O-CH_2Cl_2 (10 mL:10 mL), with vigorous stirring. [b,c] See footnotes of Table I. [d] 0.125 mmol.

propyl and viologen residues were introduced, respectively.

Following the procedure of Card and Neckers[12] for the preparation of the polymeric ligand from lithiated polystyrene and 2,2′-bipyridine, a polymeric viologen, PS-PrV^{2+}, was obtained (Scheme V).

Preparation of $PSCH_2$-PrV^{2+} was carried out as previously described[6] (Scheme VI).

Reduction of Azobenzene in the Zn-V^{2+} System. Although azobenzene is not reduced by zinc in acetonitrile–pH 4.0 phthalate buffer (9:1), reduction proceeds upon the addition of propylviologen (PrV^{2+}) or polymeric viologens (P-V^{2+}) to give hydrazobenzene in spite of the heterophase systems: solid (Zn)–liquid or solid (Zn)–solid (P-V^{2+})–liquid, respectively. The results are summarized in Table I.

In every run, hydrazobenzene and/or unreacted azobenzene was recovered, accounting for over 98% of the material balance.

In run I-2, hydrazobenzene was obtained quantitatively. PrV^{2+} and $PrV^{+\cdot}$ are soluble in the solvent, and thus the reaction with solid Zn is more facile than it is when insoluble polymer-bound viologens are used.

P4VP-PrV^{2+} (run I-3) was the most effective polymeric carrier, yielding 80% hydrazobenzene. Quaternized $P4VP^+$-PrV^{2+} (run I-4), having the same degree of cross-linking and substitution by the viologen as P4VP-PrV^{2+}, gave only a low yield. The difference in yields may be due to the more apolar environment of P4VP-PrV^{2+}, which enhanced the solubilization of azobenzene.

PS-PrV^{2+}, used in run I-5, was not reduced by zinc; accordingly azobenzene was completely recovered. The reduction of this polymer by zinc was tried in various solvents (CH_3CN, CH_3OH, H_2O, DMF, CH_2Cl_2, etc.), but coloration by viologen cation radical (deep blue) was not observed. We speculate that the viologen moieties cannot come into sufficient contact with zinc, because they are linked without a mobile spacer.

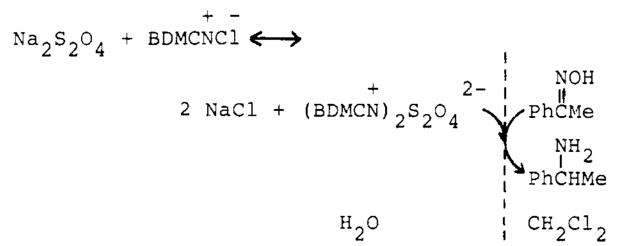
SiO_2-PrV^{2+} (run I-6), in which viologen was grafted onto the surface of SiO_2, also gave a low yield. Again, this seems to indicate that the spacer binding viologen to silica gel is too short to allow the viologen moiety to come in contact with the solid reductant (zinc).

Since zinc has no ability to reduce azobenzene without viologen, the reduction in the Zn-V^{2+} system must proceed through an electron-transfer scheme via viologen (see Scheme VII).

Reduction of Azobenzene in the $Na_2S_2O_4$-V^{2+} System. Our preliminary experiments showed that azobenzene was reduced in very low yield in an alkaline H_2O-CH_3OH (1:1) solution of sodium dithionite at room temperature. In addition, azobenzene was reduced to give hydrazobenzene in poor yield (24 h, 25%) in a H_2O–CH_2Cl_2 two-phase solution of sodium dithionite and potassium carbonate using tetrabutylammonium bromide as a phase-transfer catalyst. Addition of small amounts of viologens to a H_2O–CH_2Cl_2 solution of sodium dithionite, potassium carbonate, and azobenzene, however, induced smooth reduction and gave hydrazobenzene. In the case of propylviologen, the reduction proceeded in a two-phase system, whereas polymeric viologens were insoluble triphase catalysts. Yields of hydrazobenzene are shown in Table II. As in the Zn-V^{2+} system, only hydrazobenzene was obtained (i.e., without further reduction).

The oxidized form (PrV^{2+}) of propylviologen (run II-2) was soluble in water but not in dichloromethane; however, the deep blue coloration of the dichloromethane layer during the reaction indicates that the reduced form ($PrV^{+\cdot}$) is extracted into the dichloromethane layer from the

Scheme VIII



aqueous layer. Thus solubility change of propylviologen seems to accelerate electron transfer from the aqueous layer to the dichloromethane layer.

The insoluble viologen polymers used in runs II-3 to II-7 became deep blue during reaction. Comparison of run II-3 with run II-4 shows that the more hydrophobic P4VP-PrV^{2+} gave a higher yield than the more hydrophilic $P4VP^+$-PrV^{2+}. This result is similar to that for the Zn-V^{2+} system.

PS-PrV^{2+}, which could not mediate the reduction in the Zn-V^{2+} system, was used in run II-5, where the reductant was soluble, to give hydrazobenzene in good yield (75%). Similarly, the result of run II-6 (SiO_2-PrV^{2+}) is better than that of run I-6, which was carried out in the Zn-V^{2+} system using SiO_2-PrV^{2+}. It is estimated that a three-methylene spacer hanging the viologen structure from the silica gel is long enough to allow the reduction of viologen by sodium dithionite dissolved in the aqueous layer.

The superiority of the polymeric viologen to the monomeric one was observed in run II-7. As shown between P4VP-PrV^{2+} and $P4VP^+$-PrV^{2+} in the Zn-V^{2+} system, azobenzene might be attracted to hydrophobic units of the polymer (styrene parts) through hydrophobic interaction, to result in the smooth electron transfer from viologen cation radical units hanging from the main chain of the polymer.

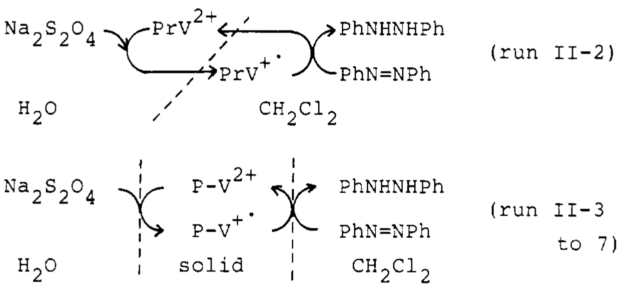
Viologens, which are a kind of ammonium salt, may accelerate the reaction as anion-transport catalysts, so-called phase-transfer catalysts. To determine whether dithionite ($S_2O_4^{2-}$) was transported or not, we examined the following two reactions. It is known that sodium dithionite can reduce oximes to give the corresponding amines; accordingly the reduction of acetophenone oxime was attempted under phase-transfer conditions ($Na_2S_2O_4$, K_2CO_3, benzylmethylcetylammonium chloride ($BDMCN^+C^-$), and acetophenone oxime in H_2O–CH_2Cl_2), to give (1-aminoethyl)benzene (see Scheme VIII). When viologens were used instead of $BDMCN^+Cl^-$, the corresponding amine was not obtained. These two experiments suggest that viologens do not transport dithionite dianion into the dichloromethane layer. Therefore, it is reasonable to assume that the viologens are acting as electron-transfer catalysts in this system as shown in Scheme IX.

Experimental Section

Materials. Pyridinium derivatives (propylviologen, 1-propyl-4-(4′-pyridyl)pyridinium bromide) were prepared by methods previously reported.[10,13] Organic chemicals and solvents used in this study were purified by recrystallization or distillation. Poly(4-vinylpyridine) was furnished from Koei Chemical Co., Ltd. Cross-linked polystyrene (2% DVB, granular gel form, 50–60 mesh) and polystyrene-*co*-(chloromethyl)styrene] (2% DVB, granular gel form, 50–60 mesh, 15.8 mol % chloromethyl residue) were kindly supplied by Mitsubishi Chemical Industries Ltd. Silica gel used as a polymeric support was Wakogel C-200 (70–149-Mm diameter, Wako Pure Chemical Industries).

1,1′-Bis(3-bromopropyl)-4,4′-bipyridinium Dibromide ($BrPrV^{2+}$). A solution of 4,4′-bipyridine dihydrate (2.0 g, 10.4 mmol) in 20 mL of ethanol was added dropwise to a refluxing ethanol (20 mL) solution of 1,3-dibromopropane (21.0 g, 104 mmol) for 4 h with stirring. After continuous reflux for 2 h, the reaction mixture was allowed to stir overnight at room temperature and then cooled in an ice bath. The yellow precipitate was collected on a glass filter. $BrPrV^{2+}$ was obtained in 56% yield (3.26 g) after two recrystallizations from methanol–ethanol: mp >300 °C; ^1H NMR (D_2O) δ 2.80 (m, 4 H), 3.70 (t, 4 H), 5.07 (t, 4 H), 8.75 (d, 4 H), 9.33 (d, 4 H). Anal. Calcd for $C_{16}H_{20}N_2Br_4$: C, 34.32; H, 3.60; N, 5.00. Found: C, 34.69; H, 3.62; N, 5.24.

Scheme IX



P4VP-PrV^{2+}. Poly(4-vinylpyridine) (2.0 g, 19.0 mmol) and $BrPrV^{2+}$ (1 g, 1.79 mmol) were dissolved in 135 mL of methanol, and the mixture was refluxed for 52 h. After evaporation of 75% of the solvent, the yellow precipitate was filtered through a glass filter and thoroughly washed with water and methanol. The cross-linked polymer (P4VP-PrV^{2+}) (1.8 g), which had 0.50 mmol/g of viologen structure, was obtained (N, 11.01; Br, 15.78); IR (KBr) 1640 (ν(C=N$^+$)), 1595 (ν(C=N)).

$P4VP^+$-PrV^{2+}. P4VP-PrV^{2+} (1.4 g) and 1-bromopropane (1.0 g, 8.0 mmol) were added to 50 mL of methanol, and the mixture was refluxed for 48 h. After cooling, the resulting methanol dispersion was filtered through a glass filter. The polymer ($P4VP^+$-PrV^{2+}) was extensively washed with water and methanol and dried in vacuo. From elemental analysis (N, 7.89; Br, 27.19), 40.7 mol % of the pyridine ring, bound to the polymer main chain, was found to be quaternized with 1-bromopropane, and viologen structure content was 0.37 mmol/g of polymer.

PS-PrV^{2+}. Styrene–2% divinylbenzene granular copolymer (gel form, 50–60 mesh) was brominated according to the method of Card and Neckers;[12] degree of bromination, 23.8 mol % (Br, 15.29). The brominated polymer was lithiated[12] and then reacted with anhydrous 4,4′-bipyridine.[14] The resultant polymer was washed with tetrahydrofuran, benzene, ethyl acetate, and ether and dried in vacuo at 40 °C for 10 h. A pale yellow powdery polymer (10.8 g) containing 3.1 mol % of 4,4′-bipyridine (N, 1.09; Br, 20.94) was obtained from 11 g of the brominated polymer, 18 mL of 1.45 N butyllithium, and 4.7 g of 4,4′-bipyridine. This bipyridine-bound polymer (5 g) and 1-bromopropane (10 g, 40 mmol) were added to dry acetonitrile (35 mL) and refluxed for 48 h. After extensive washing with acetonitrile, methanol, benzene, and ether, a quaterized brown polymer (PS-PrV^{2+}) that had 2.9 mol % of viologen structure was obtained (N, 0.83; Br, 20.19).

SiO_2-PrV^{2+}. Silica gel (Wakogel C-200) was dried in a vacuum oven at 120 °C for 10 h. To dry *o*-xylene were added 10 g of silica gel and 10 g (50.4 mmol) of 1-chloro-3-(trimethylsilyl)propane. After the reaction mixture was refluxed for 24 h, chloropropylated silica gel was filtered and washed with methanol, acetone, chloroform, and benzene. The resultant gel was reacted with NaI (4.5 g, 30 mmol) in refluxing ethyl methyl ketone (45 mL) for 12 h, to yield iodopropylated silica gel. This gel and 4.2 g (15 mmol) of 1-propyl-4-(4′-pyridyl)pyridinium bromide were added to 30 mL of dry acetonitrile and refluxed for 10 h. The resulting brown solid was filtered, washed with hot acetonitrile, methanol, chloroform, and benzene, and dried in a vacuum oven at 50 °C for 10 h. SiO_2-PrV^{2+} (4.26 g) carrying 0.31 mmol/g of V^{2+} residue was obtained (N, 0.87).

$PSCH_2$-PrV^{2+}. To a 50 mL of dry acetonitrile solution of 1-propyl-4-(4′-pyridyl)pyridinium bromide (2.79 g, 10.0 mmol) was added 5 g (7.05 mmol) of granular poly[styrene-*co*-(chloromethyl)styrene] cross-linked with 2% divinylbenzene (gel form, 50–60 mesh). The reaction mixture was refluxed for 48 h and filtered through a glass filter. The resulting brown polymer ($PSCH_2$-PrV^{2+}) was thoroughly washed with *N*,*N*-dimethylformamide, methanol, and ether. From elemental analysis (N, 3.30;

Br + I, 14.07), the degree of substitution was estimated as 14.2 mol % (0.94 mmol of V^{2+} in 1 g of polymer).

Reduction of Azobenzene in the Zn-V^{2+} System. To an acetonitrile–pH 4.0 phthalate buffer (9:1) in a three-necked flask equipped with a nitrogen inlet and outlet were added Zn powder (0.916 g, 3 mmol), azobenzene (0.455 g, 2.5 mmol), and viologen (0.125 mmol). The reaction mixture was stirred vigorously with a Teflon-coated magnetic bar (1 cm) at room temperature. After 24 h, insoluble parts were filtered with suction, and to the filtrate was added 10 mL of pH 4.0 buffer. The solution was evaporated under reduced pressure before being extracted with dichloromethane (3 20-mL portions). The extract was washed with 20 mL of water, dried over $MgSO_4$, and evaporated in vacuo. The resulting residue was weighed and a yield of hydrazobenzene was determined by ^1H NMR in CD_3CN; δ 6.60–7.35 (aryl protons of hydrazobenzene), 7.40–8.10 (aryl protons of azobenzene).

Reduction of Azobenzene in the $Na_2S_2O_4$ System. To a 10-mL aqueous solution of sodium dithionite (0.609 g, 3.5 mmol), potassium carbonate (0.483 g, 3.5 mmol), and viologen (0.125 mmol) in a three-necked flask was added a 10-mL solution of azobenzene (0.455 g, 2.5 mmol) in dichloromethane under nitrogen pressure. The reaction mixture was stirred vigorously with a Teflon-coated magnetic bar (1 cm) at room temperature. After 24 h, the dichloromethane layer was separated and the aqueous layer was extracted with 20 mL of the dichloromethane. Two dichloromethane solutions were combined and treated in manner similar to that described above.

Registry No. Zn, 7440-66-6; $Na_2S_2O_4$, 7775-14-6; $BrPrV^{2+}$, 85681-39-6; P4VP, 25232-41-1; azobenzene, 103-33-3.

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(14) 4,4′-Bipyridine was dehydrated refluxing benzene in a flask equipped with a Dean–Stark trap; mp 114 °C.

Electron Transport across Polymeric Membranes Containing the Viologen Structure

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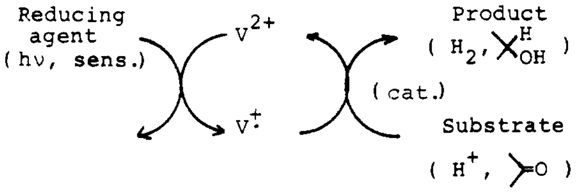
ABSTRACT: Cross-linked membranes containing viologen units were prepared by the reaction of copoly[acrylonitrile–(chloromethyl)styrene] with 4,4′-bipyridyl as a cross-linking agent. Electron transport from $S_2O_4^{2-}$ to $Fe(CN)_6^{3-}$ was achieved with the resultant membranes. Electron transport in the membranes proceeded smoothly by electron diffusion between the viologen units. The rates of diffusion depend on the thickness and degree of cross-linking of the membranes and the concentration and location of the viologen units.

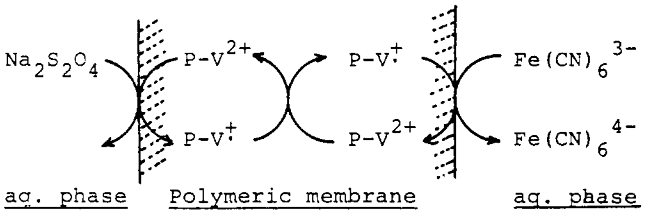
Introduction

Viologen (1,1′-dialkyl-4,4′-bipyridinium, V^{2+}) is known to undergo one-electron reduction to produce the cation radical ($V^{+}\cdot$), which is easily reoxidized to V^{2+}. Recently, viologens have received much attention as an electron-transfer catalyst (ETC) in oxidation–reduction systems,[1-5] especially in hydrogen production by photoreduction of proton (Scheme I). In the oxidation–reduction system containing ETC, the device for charge separation to suppress the back-electron-transfer process must also be effective for electron transport. For this purpose, several redox reactions mediated by liquid membrane,[6-9] micelle,[10-14] bilayer membrane,[15-17] and polymeric membrane[18-23] have been reported. Tabushi et al.[9] have succeeded in this charge separation by the combination of liquid membrane (CH_2Cl_2), and Matsuo et al.[24] have achieved charge separation between Ru^{2+} complex (sensitizer) and $V^{+}\cdot$ for the photoreduction system including viologen–micelle or polysoap. However, the redox reaction using polymeric membrane linked viologen units for charge separation and electron transport has not been reported.

Scheme I



In this article, we describe the preparation of a polymeric membrane with covalently bound viologen units (P-V^{2+}) and the reduction of Fe^{3+} by $S_2O_4^{2-}$ across the solid polymeric membrane.



Experimental Section

Materials. 1-Propyl-4-(4-pyridyl)pyridinium bromide was prepared according to the method previously reported.[25] Other