Pergamon

Eur. Polym. J. Vol. 30, No. 3, pp. 289–294, 1994
Elsevier Science Ltd
Printed in Great Britain.
0014-3057/94 \$6.00 + 0.00

PREPARATION OF POLYMERS WITH PENDANT VIOLOGEN GROUPS AND THEIR APPLICATION TO ELECTRON TRANSFER REACTIONS IN HETEROPHASES

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(Received 11 January 1993; accepted 9 June 1993)

Abstract—Polymers with pendant viologen groups were prepared by the reaction of tosylated polyvinyl alcohol (Ts–PVA) with 4,4′-bipyridine or with 1-propyl-4-(4′-pyridyl) pyridinium bromide (B–Py). The polymers were used as electron-transfer catalysts (ETC) for the reduction of azobenzene either in a Zn–PV^{2+} system (reductant: Zn in CH_3CN–H_2O) or in a $Na_2S_2O_4$–PV^{2+} system (reductant: $Na_2S_2O_4$ in H_2O–CH_2Cl_2). The experiments showed that more viologen moieties can be incorporated into the PVA chain by the reaction of Ts–PVA with 4,4′-bipyridine, and the polymers show good electron-transfer mediating abilities for the reduction of azobenzene.

INTRODUCTION

It is well known that viologen (*N,N*′-dialkyl-4,4′-dipyridinium salts, $V^{2+}2X^-$) is subjected to a one-electron reduction which produces the blue radical cation ($V^{+\bullet}X^-$); in turn, $V^{+\bullet}X^-$ is easily oxidized to regenerate $V^{2+}2X^-$ (Scheme 1).

Because of the special electrochemistry property of viologen, it has been introduced into polymer chains, and has been used as photochromic and electronchromic films [1, 2], modified electrodes [3, 4], polymer electron transport membranes [5, 6].

Another important aspect of viologen is as an electron-transfer catalyst (ETC). Viologen as an electron relay in the photoproduction of hydrogen with $Ru(bpy)_3^{2+}$ as a sensitizer has attracted the most attention [7–9]. Furthermore, viologen as ETC for the reduction of organic compounds is very interesting. It was found that aromatic aldehydes [10], α-keto esters [11], azobenzene [12], acrylonitrile [13], and vicinal-dibromides [14] could be reduced easily in the presence of viologen.

This article describes the incorporation of viologen into polyvinyl alcohol, and the mediation of electron transfer by the product to a hydrophobic substrate, azobenzene, under two kinds of heterophases, namely from zinc (solid) to azobenzene (solution) via PV^{2+} or from $Na_2S_2O_4$ (aqueous solution) to azobenzene (organic solution) via PV^{2+}. The electron mediating abilities were compared with a two-phase electron transfer reaction via a model compound polypropyl viologen ($PPrV^{2+}$)

EXPERIMENTAL PROCEDURES

Materials

4,4′-Bipyridine was purified by two recrystallizations in benzene–petroleum (1:1). PVA (with 12% residual acetyl content) was dried over phosphorus pentoxide (P_2O_5). Tosyl chloride (TsCl), 1-bromopropane and azobenzene were available without further purification. The other reagents and solvents were purified according to the usual methods.

Tosylation of PVA (Ts–PVA)

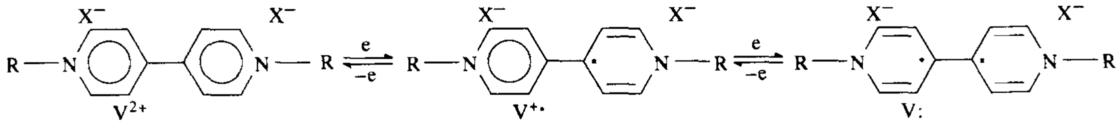
A pendant hydroxyl group of PVA was tosylated with TsCl in anhydrous pyridine as follows: 6.6 g PVA was first swollen in 90 ml pyridine at refluxing temperature for 12 hr, and the mixture was cooled at 0°. The 200 ml pyridine solution containing 42.8 g TsCl was added dropwise to the mixture containing swollen PVA. A homogeneous solution was obtained after the mixture stirred at room temperature for 36 hr. The solution was mixed with an equal volume of acetone and a white fibrous polymer was isolated by pouring the mixture into distilled water. The polymer was filtered, purified in acetone-water and thoroughly dried over P_2O_5 at 50° in vacuum, yield 20.5 g.

i.r. (film): 1359.9 and 1190 ($\underline{OSO_2}C_6H_4CH_3$) cm^{-1},
1738.0 cm^{-1} (residual acetyl group)

NMR($CDCl_3$): δ 7.2, 7.6 (m, $CH_3C_6\underline{H_4}SO_2O$—) ppm
δ 2.01 (s, $\underline{CH_3}COO$—) ppm,
δ 2.3 (s, $\underline{CH_3}C_6H_4SO_2O$—) ppm

Anal.: C, 53.4%; H, 5.2%; S, 13.7%.

This indicates that the polymer contained 63.1 mol% vinyl *p*-toluenesulfonate units and 24.9 mol% vinyl alcohol units.



Scheme 1

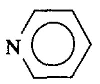
Synthesis of Polymer with Pendant Viologen Structure

1. Synthesis of 1-propyl-4-(4′-pyridyl) pyridinium bromide (B–Py)

The pyridinium derivative (B–Py) was prepared by the method previously reported [15]. Pale yellow hygroscopic crystals were obtained in 50% yield after recrystallization from anhydrous acetonitrile.

Anal. cald. for $C_{13}H_{15}N_2Br$: C, 55.9%; H, 5.4%; N, 10.1%.
found: C, 55.7%; H, 5.3%; N, 9.8%

i.r. (KBr): 2880–2970 (alkyl), 3030, 2600 (aromatic) cm^{-1}.

NMR(D_2O): δ 1.1 (t, 3H, $C\underline{H_3}$),
2.2 (m, 2H, $—C\underline{H_2}CH_3$), 4.7 ($\rangle\overset{+}{N}—C\underline{H_2}—$),
7.7–9.3 (m, 8H, ) ppm

2. Synthesis of polymer with pendant viologen groups (PV^{2+})

Two methods were employed in the preparation of PV^{2+}.

(1) The reaction of Ts–PVA with B–PY. A mixture of Ts–PVA (0.5 g) and B–Py (0.5 g) was heated at the desired temperature in *N,N*-dimethyl formamide (DMF). The product was isolated by pouring it into distilled water, washed thoroughly with water and dried in vacuum at 50°.

(2) The reaction of Ts–PVA with 4,4′-bipyridine. A mixture of Ts–PVA (1.0 g), 4,4′-bipyridine (1.5 g) and 20 ml DMF was heated at 65° for 72 hr. A slight yellow precipitate was collected by pouring the mixture into distilled water. The precipitate was purified by precipitation from dichloromethane-petroleum ether three times. The purified polymer was dried and weighed 1.2 g.

0.5 g of above polymer, 1-bromopropane (benzyl chloride or methyl iodide) (15 mmol), and 20 ml DMF were mixed, and reacted at 65° for 30 hr. The precipitate was collected by pouring the mixture into KBr saturated solution. 0.40 g product was obtained after dried.

3. Reduction of azobenzene in the Zn–PV^{2+} system

Zinc powder (14 mmol), azobenzene (2.9 mmol) and viologen (0.04 mmol) were added to a glass tube with acetonitrile-pH 4.0 potassium phthalate buffer (9:1).The mixture was deoxygenated by freezing and thawing technique before nitrogen was introduced, and stirred vigorously with a magnetic bar (1 cm) at room temperature. After 24 hr, the insoluble part was filtered. The filtrate was evaporated under reduced pressure before extracting with dichloromethane (3, 20 ml portions). The extract was washed with 20 ml distilled water, dried over $MgSO_4$ and evaporated. The resulting residue was weighed and the yield of hydrazobenzene was determined by ^1H-NMR in CD_3CN; δ 6.60–7.35 (aryl protons of hydrazbenzene), 7.40–8.10 (aryl protons of azobenzene).

4. Reduction of azobenzene in the $Na_2S_2O_4$–PV^{2+} system

Viologen (0.04 mmol) and 10 ml dichloromethane solution of azobenzene were added to a glass tube containing 10 ml aqueous solution of sodium dithionite (4 mmol) and potassium carbonate (3.5 mmol). The mixture was then deoxygenated and stirred vigorously with a magnetic bar (1 cm) at room temperature for 24 hr. The insoluble part was filtered. The dichloromethane layer was separated, and the aqueous layer was extracted twice with dichloromethane. The combined dichloromethane layer was dried over $MgSO_4$ and evaporated at reduced pressure. The resulting residue was weighed and hydrazobenzene was determined by ^1H-NMR as described above.

RESULTS AND DISCUSSION

1. Synthesis and properties of polymers bound with viologen

Two methods were applied to introduce viologen into a polymer chain (Scheme 2): the reaction of Ts–PVA with 4,4′-bipyridine or with 1-propyl-4-(4′-pyridyl) pyridinium bromide (B–Py). The results are listed in Table 1.

In run 1–1 to 1–3, the introduced viologen content was comparatively lower than that of run 2–1, but the sulfur content changed greatly.

Three reactions may occur [16] in the reaction:

(1) quaternization of Ts–PVA with B–Py;
(2) an intramolecular condensation of a toluenesulfonate group with a hydroxyl group; and
(3) intermolecular reaction of a toluenesulfonate group with a hydroxyl to form a cross-linked polymer.

Since the obtained polymer was soluble, the intermolecular cross-linking reaction of toluenesulfonate with hydroxyl could be ruled out. Thus, the two reactions existed and competed, since B–Py is the monosubstituted 4,4′-bipyridine, the nucleophility became weakened. Decreasing sulfur content shows that intramolecular condensation resulted in the loss of sulfur.

Figure 1 is the i.r. spectra obtained by method 1 with different reaction conditions. Compared with Ts–PVA, a new absorption was found at 1664 cm^{-1}; moreover, when the reaction was at 90° for 45 hr, the vibration of the toluenesulfonate group largely disappeared. The NMR spectrum (Fig. 2) confirmed the existence of viologen groups (δ, m, 8.0–9.3 ppm).

In contrast to method 1, the quaternization of Ts–PVA with 4,4′-bipyridine showed that more viologen group was introduced into a polymer chain indicating the stronger nucleophility of bipyridine. This polymer was difficult to precipitate in water, but a brown precipitate was obtained rapidly when KBr was added, which showed that anion exchange of Br^- with toluenesulfonate occurred. This fact can also be proved by adding 1 N $AgNO_3$ when a pale yellow precipitate could be observed on the surface of polymer.

All polymers obtained by method 1 did not show the color change when reacting with sodium

Table 1. Results of polymer obtained by the reduction of Ts–PVA with 4,4′-bipyridine or with B–Py

Run	Amine	*S*%	*N*%	Time (hr)	Viologen content (mmol/g)
1-1	B–Py	8.33	0.26	30	0.09
1-2	B–Py	5.49	0.39	65	0.14
1-3	B–Py	5.30	0.40	72	0.14
1-4*	B–Py	0.86	0.50	45	0.18
2-1	Bipyridine	4.85	0.78	72	0.28

*The result was obtained at 90°. The others were obtained at 65°.

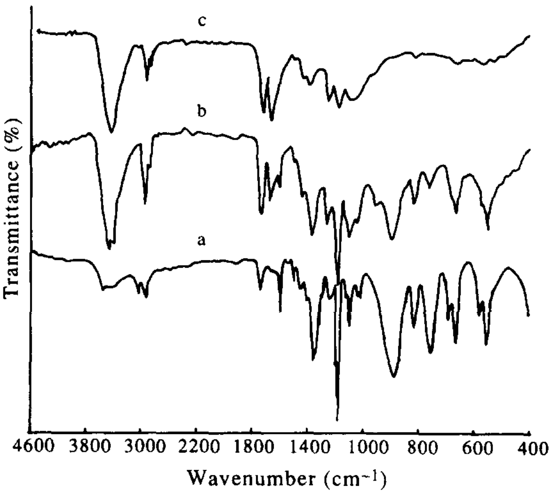


Fig. 1. Infrared spectra of polymers obtained by method 1 with different conditions: (a) tosylated PVA(Ts–PVA); (b) obtained at 65° for 45 hr; (c) obtained at 90° for 45 hr.

dithionite. But the polymer obtained by method 2 turned a deep blue when reduced chemically by sodium dithionite. The color of the reduced polymer changed to brown when exposed to air for several hours, and this colouration–discolouration was observed repeatedly when reduced chemically again. An example of an ESR spectrum for this polymer is shown in Fig. 3. The ESR signal confirmed the existence of a free radical within the reduced viologen group ($PV^{+\bullet}$).

Table 2. Results of the reduction of azobenzene in Zn–PV^{2+} system*

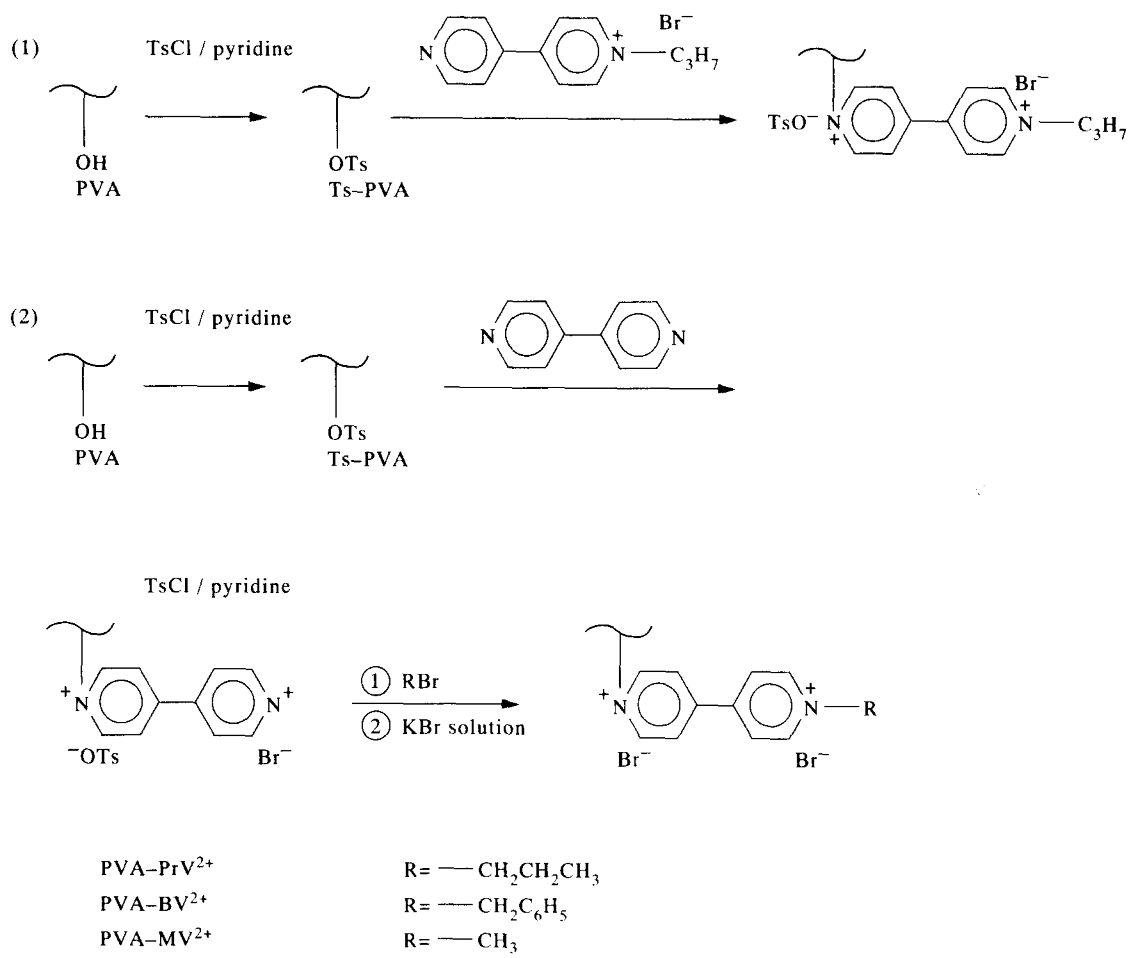
Run	V^{2+}	Phase†	Yield (%)‡	Cycle no. of V^{2+}
1-1	None	S–L	0	0
1-2	PVA–PrV^{2+}§	S–L	0	0
1-3	$PPrV^{2+}$	S–L	100	34.5
1-4	PVA–PrV^{2+}	S–S–L	85	29.3
1-5	PVA–BV^{2+}	S–S–L	87.8	30.3
1-6	PVA–MV^{2+}	S–S–L	94.7	32.7

*Zn, 14 mmol; PhN=NPh, 2.9 mmol; V^{2+}, 0.04 mmol; room temperature for 24 hr under N_2.
†S, solid; L, liquid.
‡^{1}H-NMR yield.
§The polymer was obtained by the reaction of Ts–PVA with B–Py.

2. *Reduction of azobenzene in the Zn–PV^{2+} system*

Results of the reduction of azobenzene using PV^{2+} as ETC are shown in Table 2. In every run, hydrazobenzene and/or azobenzene was recovered, accounting for over 98% material balance.

As seen from Table 2, hydrazobenzene was not reduced by zinc in the absence of PV^{2+} (run 1-1). Addition of a small amount of PV^{2+} (run 1-2)



Scheme 2

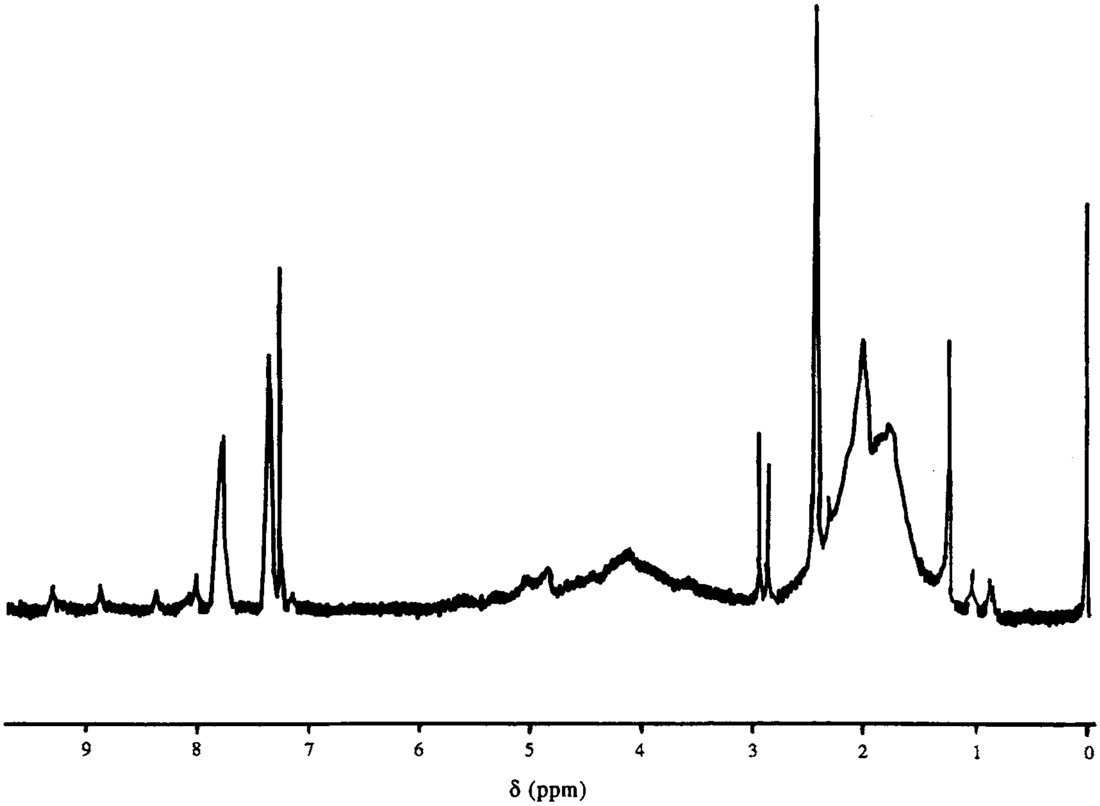


Fig. 2. ^{1}H-NMR spectrum of polymer obtained by method 1 at 65° (Recorded with Brucker AM-400 spectrometer).

obtained by method 1 also didn't mediate the reduction which conformed to the above property test. But addition of a small amount of PV^{2+} obtained by method 2 could facilitate the reduction smoothly.

Since the reactions proceeded in heterophases, two factors might affect the reduction of azobenzene: 1, the contact of viologen with zinc; 2, the solubility of viologen with azobenzene.

In runs 1-3, hydrazobenzene was obtained quantitatively. $PPrV^{2+}$ and $PPrV^{+\cdot}$ were soluble in the solvent from the fact that the whole solution became deep blue. Thus, the reduction of azobenzene with solid zinc is more facile than the insoluble PVA–RV^{2+} used.

PVA was an effective polymeric carrier which could make good contact of viologen with zinc. But the different substituted group of viologen also effect the reduction of azobenzene. Different yields of hydrazobenzene were obtained: 85% for PVA–PrV^{2+} (run 1-4); 87.8% for PVA–BV^{2+} (run 1-5); and 94.7% for PVA–MV^{2+} (run 1-6).

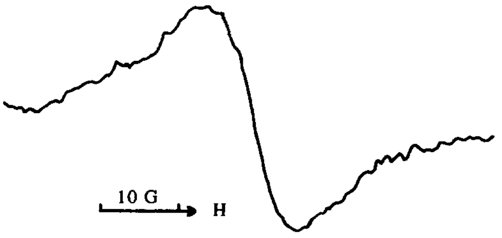


Fig. 3. ESR spectrum of polymer obtained by method 2 (reduced by sodium dithionite).

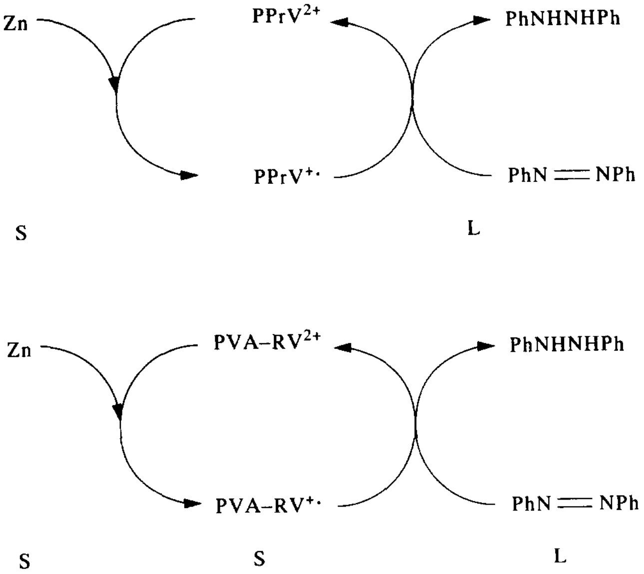
Two factors for a different substituent might affect the reaction: 1, the contact of RV^{2+} with zinc and; 2, the compatibility of RV^{2+} with azobenzene. A more polar group was easier to contact with zinc but not very compatible with azobenzene, and the more apolar one was not easy to contact with zinc but easily compatible with azobenzene. Thus, the factors resulted in the mediating order of PVA–RV^{2+}: PVA–MV^{2+} > PVA–BV^{2+} > PVA–PrV^{2+}.

Since azobenzene was not reduced by zinc without the presence of viologen, the effect of PV^{2+} are thought to act as an ETC in this system as shown in Scheme 3.

3. Reduction of azobenzene in a $Na_2S_2O_4$–PV^{2+} system

Results of the reduction of azobenzene in $Na_2S_2O_4$–PV^{2+} system are listed in Table 3. The preliminary test (run 2-1) showed that azobenzene was not reduced in the absence of PV^{2+}. Addition of PVA–PrV^{2+} obtained by method 1 (run 2-2) could not induce the reduction either. However, addition of a small amount of PVA–RV^{2+} obtained by way 2 could induce the reduction of azobenzene smoothly.

In runs 2-3, $PPrV^{2+}$ was less effective (38% yield of hydrazobenzene) than it was in run 1-3 (100%



Scheme 3

hydrazobenzene). Earlier work [17] reported that the reduced form of $PPrV^{2+}$ was easy to form radical dimers even in very low concentration. The low effect of $PPrV^{2+}$ in this system is due to the formation of $V^{+\bullet}$ dimer. But in a low dielectric constant solvent such as acetonitrile, viologen anions exist in the ion bonding state [18]; the viologen radical dimer can be prevented effectively.

Table 3. Results of the reduction of azobenzene in $Na_2S_2O_4$–PV^{2+} system*

Run	V^{2+}	Phase†	Yield (%)‡	Cycle. no. of V^{2+}
2-1	None	L–L	0	0
2-2	PVA-PrV^{2+}§	L–L	0	0
2-3	$PPrV^{2+}$	L–L	38	13.1
2-4	PVA-PrV^{2+}	L–S–L	60	20.7
2-5	PVA-BV^{2+}	L–S–L	65	22.4
2-6	PVA-MV^{2+}	L–S–L	50	17.2

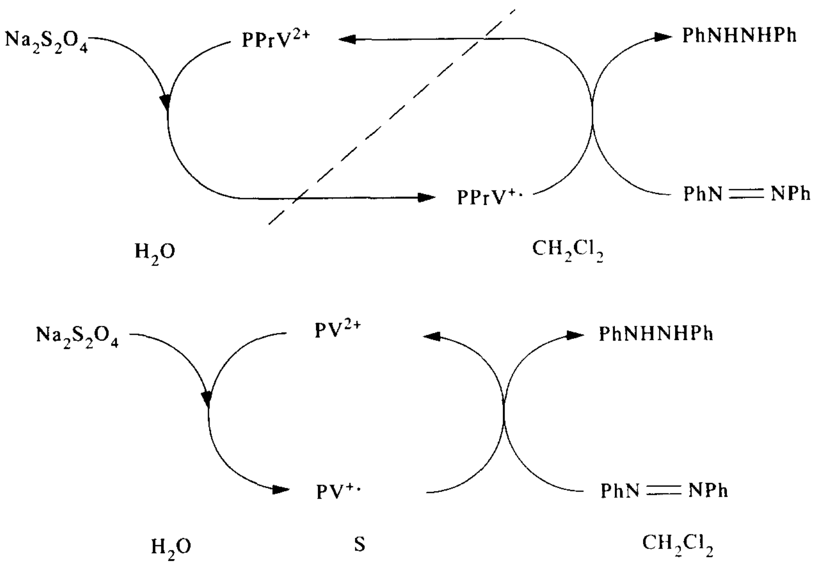
*$Na_2S_2O_4$, 4 mmol; PhNHNHPh, 2.9 mmol; V^{2+}, 0.04 mmol; room temperature for 24 hr under N_2.

†S, solid; L, liquid.

‡^{1}H-NMR yield.

§The polymer was obtained by the reaction with B–Py.

In runs 2-4 to 2-6, PVA–RV^{2+} is more effective [60% hydrazobenzene for PVA–PrV^{2+} (runs 2-4); 65% for PVA–BV^{2+} (run 2-5); and 50% for PVA–MV^{2+} (run 2-6)]. Since PVA–RV^{2+} has a low content of viologen (0.28 mmol/g), together with their insolubilities, the $V^{+\bullet}$ dimer can be retarded. In this system, the factor that affects the reduction is the solubility of viologen with azobenzene. Since the order of PVA–RV^{2+} solvating azobenzene is: PVA–BV^{2+} > PVA–PrV^{2+} > PVA–MV^{2+}, the mediating ability for the reduction of azobenzene has the same order too. Since $Na_2S_2O_4$ was insoluble in CH_2Cl_2, the effect of PV^{2+} is thought to act as ETC as shown in Scheme 4.



Scheme 4

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