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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Fu-Tian Liu^a; Hong Li^a; Bing-Lin He^a; Alain Deffieux^b

^a Institute of Polymer Chemistry The State Key Laboratory of Functional Polymeric Materials for Adsorption and Separation Nankai University, Tianjin, People's Republic of China ^b Laboratoire de Chimie des Polymeres, Organiques CNRS-ENCPB Université Bordeaux I, Talence-Cedex, France

To cite this Article Liu, Fu-Tian , Li, Hong , He, Bing-Lin and Deffieux, Alain(1996) 'Preparation of Polymers with Viologen Moieties and Their Application to the Selective Reduction of Substituted Nitroarenes', Journal of Macromolecular Science, Part A, 33: 9, 1317 – 1330

To link to this Article: DOI: 10.1080/10601329608010924

URL: <http://dx.doi.org/10.1080/10601329608010924>

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PREPARATION OF POLYMERS WITH VIOLOGEN MOIETIES AND THEIR APPLICATION TO THE SELECTIVE REDUCTION OF SUBSTITUTED NITROARENES

FU-TIAN LIU, HONG LI,* and BING-LIN HE

Institute of Polymer Chemistry
The State Key Laboratory of Functional Polymeric Materials for
Adsorption and Separation
Nankai University
Tianjin 300071, People's Republic of China

ALAIN DEFFIEUX

Laboratoire de Chimie des Polymeres, Organiques
CNRS-ENCPB
Université Bordeaux I
BP 108, 33402 Talence-Cedex, France

Key Words: Polymeric viologens; Selective reduction; Substituted nitroarenes; Electron-transfer catalyst

ABSTRACT

Polymers with viologen moieties were synthesized by using polychlorethyl vinyl ether (PCEVE) as mother supports. These polymers were used as electron-transfer catalysts (ETC) for the reduction of substituted nitroarenes under heterophase conditions (reductant: $\text{Na}_2\text{S}_2\text{O}_4$ in $\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$). The experimental results show that the substituted nitroarenes were reduced selectively and efficiently to the corresponding aniline derivatives in the presence of viologen polymers. The catalytic active species of viologen were detected by ESR and electrochemical methods.

It was found that the viologen cation radical ($V^{+\cdot}$) acts as the active species during the viologen-mediated reduction of substituted nitroarenes.

INTRODUCTION

Viologens (1,1'-dialkyl-4,4'-bipyridinium salts, V^{2+}) are well known to undergo one-electron reduction to form the stable but air-sensitive cation radical ($V^{+\cdot}$) and afford the neutral reduced form ($V:$) by two subsequent one-electron transfer steps as shown in Scheme 1.

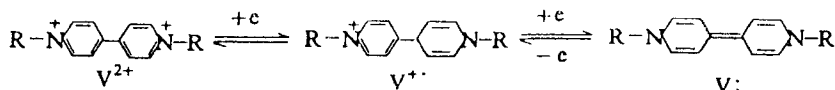
There have been many studies on the synthesis of polymers with viologen structure in the main chain or as a pendant group [1-4], and the applications of viologen polymers to photochromic films [1], modified electrodes [2, 3], and polymeric electron-transport membranes [4, 5] have been studied. Recently, viologens have received much attention as electron-transfer catalysts (ETC) in oxidation-reduction systems [6, 7], particularly in hydrogen production by photoreduction of protons. We have been interested in the reaction using viologens as ETC for the reduction of organic compounds to make good use of inexpensive and easily available reductant such as Zn or $\text{Na}_2\text{S}_2\text{O}_4$ under mild conditions. It was found that azobenzene [8], vic-dibromides [9], diphenyl methane bromide [10], aromatic aldehydes and ketones [11], quinone and α -keto esters [12], and α -halogeno-ketones [13] could be easily reduced by using viologen derivatives as ETC.

The incorporation of viologen moieties into polymers not only makes viologens be easily separated and reused, but also retards association of the viologen cation radical.

In this paper we describe the incorporation of viologen moieties into polychloroethyl vinyl ether (PCEVE) and the mediation of electron-transfer via the formed polymeric viologens to hydrophobic-substituted nitroarenes under heterophase conditions from $\text{Na}_2\text{S}_2\text{O}_4$ (aqueous phase) to nitroarenes (organic phase) via polymeric viologens (organic phase). This reaction is compared with the two-phase electron-transfer reaction via the model compound, ethyl viologen (1,1'-diethyl-4,4'-bipyridinium, EV^{2+}).

EXPERIMENTAL

The elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer. $^1\text{H-NMR}$, IR, and ESR spectra were recorded on a Bruker AC-P 200 spectrometer, Nicolet FT-IR 50DX infrared spectrometer, and JES-FEIXG spectrometer, respectively. Cyclic voltammograms were recorded on BAS-100B electron chemical analyzer.



SCHEME 1.

Reagents and Materials

PCEVE ($\bar{M}_n = 8000$) was prepared by procedures described previously [14, 15]. 4,4'-Bipyridine, ethyl bromide, $\text{Na}_2\text{S}_2\text{O}_4$, Na_2CO_3 , and substituted nitroarenes were all chemical pure reagents used as received without further purification. General organic chemicals and solvents used in this study were purified by routine methods.

EV^{2+} was prepared by reacting 4,4'-bipyridine with ethyl bromide in DMF at 70°C for 7 hours. Then the yellow precipitate was filtered off, washed with ether, and dried. Elemental analysis, IR, and $^1\text{H-NMR}$ spectrum were all in agreement with its structure.

Synthesis of Polymers with Pendant Viologen Groups (PV^{2+})

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

Reaction of PCEVE with 4,4'-Bipyridine

A mixture of PCEVE (0.43 g, 4 mmol, CH_2Cl) and 4,4'-bipyridine dihydrate (0.58 g, 3 mmol) was heated at 100°C in DMF for 16 hours. The brown precipitate was isolated by pouring the reaction mixture into a large amount of ether, and it was purified by reprecipitation from CH_2Cl_2 -ether twice. The content of bipyridinium moieties in the PCEVE chain was estimated by $^1\text{H-NMR}$ analysis, $\delta 1.5\text{--}1.8$ ppm [$-\text{CH}_2-\text{CH}(-\text{O}-)$], 3.62 [m, $-\text{CH}_2-\text{CH}(-\text{O}-\text{CH}_2-)$], 5.1 ($-\text{CH}_2\text{N}^+$), 7.8–9.8 (m, $-\text{N}^+ - \text{N}$). 0.7 g of product (65.8% yield) was obtained.

0.5 g of the above product (0.2 mmol $-\text{N}^+ - \text{N}$), 5 ml PhCH_2Cl (43 mmol) (or $\text{C}_2\text{H}_5\text{Br}$), and 15 mL DMF were mixed and reacted at 70°C for 24 hours. The final product was collected by pouring the mixture into ether, and it was purified by reprecipitation from CH_2Cl_2 -ether. 0.6 g of a brown polymer was obtained after drying (yield, 82.7%). The polymers were abbreviated as PCEVE- BV^{2+} (or PCEVE- EV^{2+}).

PCEVE First Iodinated, Then Reacted with 4,4'-Bipyridine

PCEVE (0.85 g, 8 mmol) and NaI (1.8 g, 12 mmol) were mixed in DMF (15 mL) and kept at 80°C for 16 hours. A yellow precipitate was obtained by pouring the reaction mixture into water. The precipitate was thoroughly washed with water and dried in vacuum. 1.0 g yellow product was obtained (yield, 63.3%) and the degree of iodination of PCEVE was determined by $^1\text{H-NMR}$ analysis.

0.8 g of the above iodinated PCEVE (PCEVE-I) (4 mmol, $-\text{CH}_2\text{I}$) and 1.2 g of 4,4'-bipyridine dihydrate (6.9 mmol) were reacted in 15 mL DMF at 70°C for 18 hours. The swollen gel was washed with methanol-water (1:3, 20 mL) and ether (30 mL), and then dried. 1.0 g of a brown product was obtained (yield, 66.5%).

0.8 g (2.1 mmol, $-\text{N}^+ - \text{N}$) of the above product and 5 mL PhCH_2Cl (43 mmol) were further reacted in 35 mL DMF at 70°C for 12 hours. The insoluble part was isolated by filtration and washed thoroughly with ether. 0.8 g of product (74.6% yield) was obtained after drying (PCEVE- V^{2+}).

Electrochemistry Analysis

Cyclic voltammograms were measured using C-Pd as a working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Measurements were carried out under an argon atmosphere in a phosphorous buffer (pH 6.98)–methanol mixture (volume ratio, H₂O/MeOH = 3:1). The cyclic voltammograms of 1 mM EV²⁺, 5 mM *o*-chloronitrobenzene, and 20 mL of 1 mM EV²⁺ solution containing 0.125 mmol *o*-chloronitrobenzene were each measured. Their cyclic voltammograms were compared.

ESR Spectra of the Reaction

The EV²⁺ solution (5 mM) was first reduced to a deep blue color by Na₂S₂O₄ under the protection of highly pure nitrogen. The colored solution was placed into a capillary (1 × 70 mm), sealed, and introduced into the ESR sampling tube (5 mm). The ESR spectra were measured at room temperature with a JES-FE1XG ESR spectrometer equipped with a 100 kHz field modulation unit. Mn²⁺ (MgO) was used as the standard field marker.



Typical Procedures of the Reduction of Nitroarenes

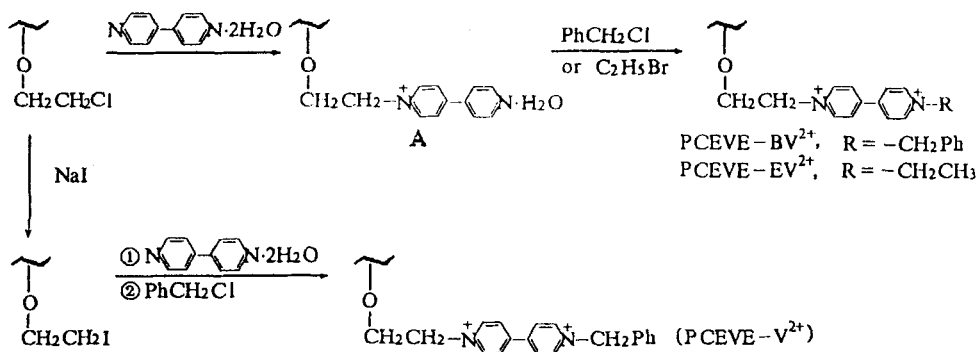
Ethyl viologen (or polymeric viologen) and a 15 mL CH₂Cl₂ solution of nitroarenes (3.4 mmol) were added to a glass tube (40 × 80 mm) containing 15 mL aqueous solution of Na₂S₂O₄ (15 mmol) and Na₂CO₃ (15 mmol). The mixture was then deoxygenated and stirred vigorously with a magnetic bar (1 cm) at room temperature for 12 hours. The insolubles were removed by filtration, the CH₂Cl₂ layer was separated, and the aqueous layer was extracted twice with CH₂Cl₂. Combined CH₂Cl₂ fractions were dried over anhydrous MgSO₄ and evaporated to give a mixture of starting material and product. The products were separated by column chromatography on silica gel [benzene: ether = 4:1 (volume ratio)]. Finally, yields were calculated by weighing the product. A similar procedure was applied with other mixed solvents.

RESULTS AND DISCUSSION

Synthesis and Properties of Viologen Polymers

The preparation of polymeric viologens was carried out by direct quaterization of 4,4'-bipyridine with PCEVE, or quaternization of 4,4'-bipyridine with iodinated PCEVE (Scheme 2).

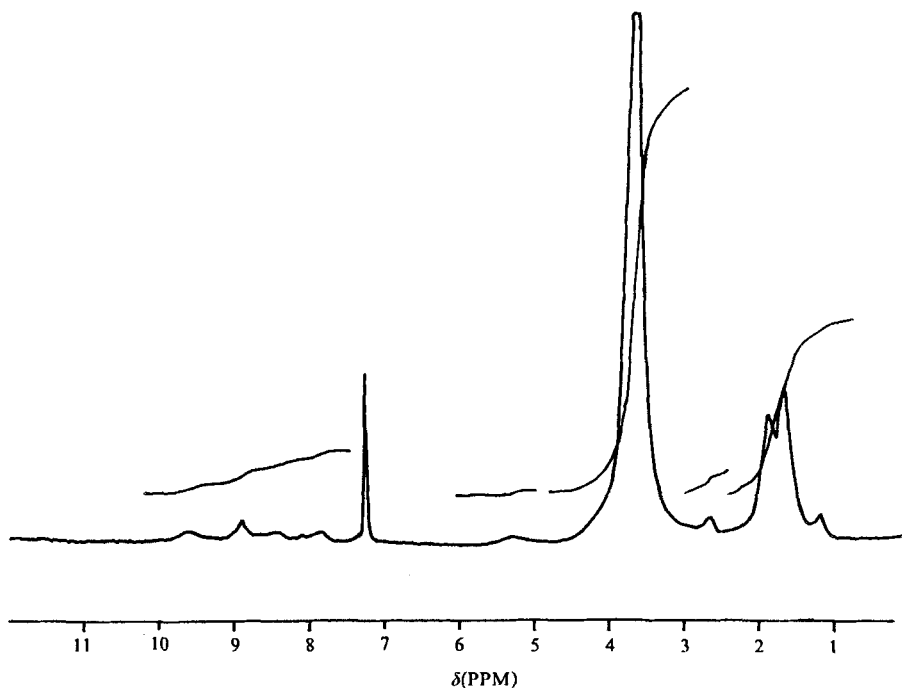
The product (A) obtained by the reaction of the chloroethyl pendant groups on PCEVE chain with 4,4'-bipyridine was soluble in CH₂Cl₂, benzene, and DMF, indicating that no crosslinking of the PCEVE chain by further reaction with the anchored 4,4'-bipyridyl moieties takes place. IR (thin film) at 1640 cm⁻¹ and ¹H-NMR spectra (Fig. 1) show clearly that the bipyridine structure has been incorporated into the PCEVE chain. The content of quaternization (19%) of PCEVE was thus estimated from the integral value of bipyridine protons 7.8–9.8 (8H,  — ) and 1.6–1.8 [—CH₂—CH(—O—), 2H].



SCHEME 2.

When polymer A was further reacted with PhCH_2Cl (or $\text{C}_2\text{H}_5\text{Br}$), it afforded the polymer with viologen structure, PCEVE-BV^{2+} (or PCEVE-EV^{2+}). The cyclic voltammogram of PCEVE-BV^{2+} is shown in Fig. 2, whereas the redox potential [$E_{1/2} = (E_{pc} + E_{pa})/2$, the average potential of cathodic and anodic peaks] is 0.39 V vs SCE.

The chlorine atom of the pendant chloroethyl group of PCEVE can be substituted by iodide using NaI in DMF. The $^1\text{H-NMR}$ spectra of PCEVE and PCEVE-I are respectively shown in Figs. 3 and 4. By comparison, a new chemical shift of

FIG. 1. $^1\text{H-NMR}$ spectrum of PCEVE quaternized by 4,4'-bipyridine (CDCl_3).

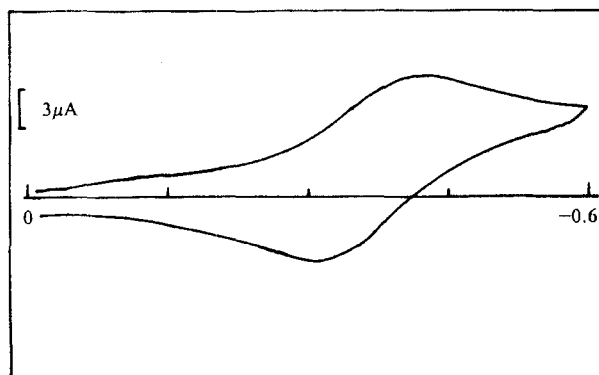


FIG. 2. Cyclic voltammogram of PCEVE-BV²⁺ in pH 6.98 buffer/MeOH (volume ratio = 3/1).

proton at 3.24 ppm is observed for PCEVE-I, which is attributed to protons linked by iodine ($-CH_2I$). Based on the integral value of PCEVE-I at 3.24 ppm ($-CH_2I$) and that at 1.6–1.8 ppm [$-CH_2-CH(-O-)-$], about 46% of the chloroethyl groups have been replaced by the iodoethyl group.

PCEVE-I was used as a precursor for the preparation of viologen polymers. The reaction of PCEVE-I with 4,4'-bipyridine afforded insoluble brown products, indicating the existence of crosslinking reactions between PCEVE chains, likely by

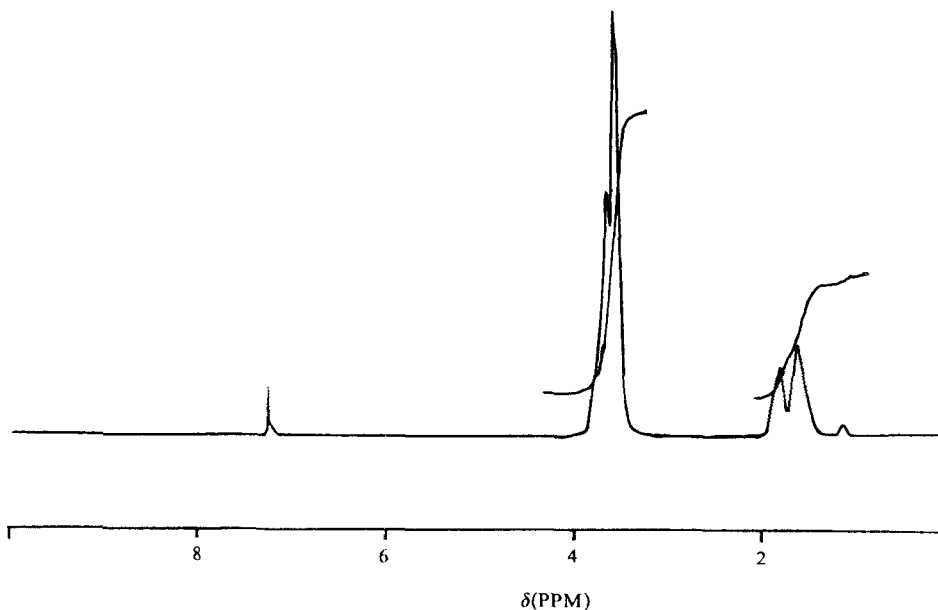


FIG. 3. ¹H-NMR spectrum of PCEVE (CDCl₃).

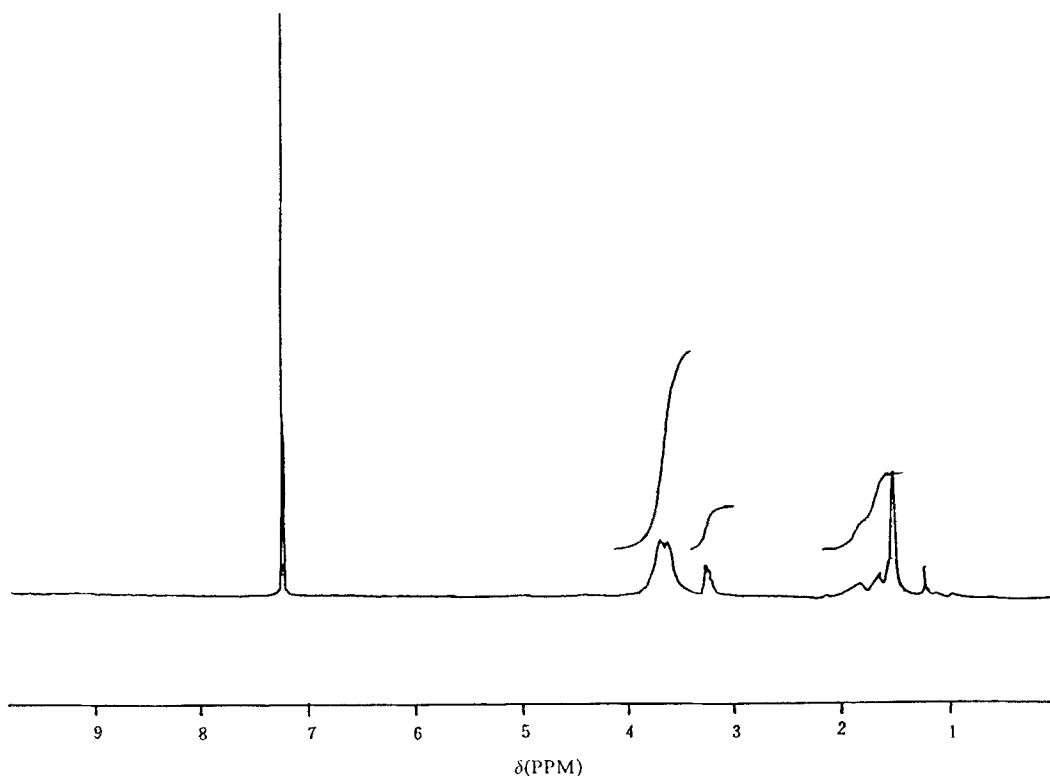


FIG. 4. ^1H -NMR spectrum of PCEVE-I (CDCl_3).

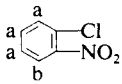
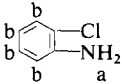
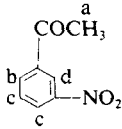
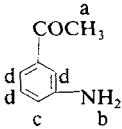
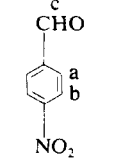
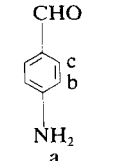
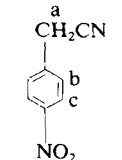
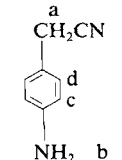
coupling through 4,4'-bipyridyl moieties. This suggests that PCEVE-I is more reactive than PCEVE.

The insoluble polymers were further quaternized by PhCH_2Cl . The presence of the viologen moiety was ascertained by the observation of IR absorption at 1640 cm^{-1} ($\text{>C}=\text{N}^+$). It turned deep blue when dipped in aqueous $\text{Na}_2\text{S}_2\text{O}_4$, in agreement with the formation of the viologen cation radical ($\text{V}^{+\cdot}$). The amount of viologen moieties (1.64 mmol/g) in the polymer was determined by elemental analysis ($\text{N} = 4.59\%$). This corresponds to a mole unit fraction of 15.6% viologen groups in the polymer chain.

Reduction of Substituted Nitroarenes Mediated by Viologen Polymers

$\text{Na}_2\text{S}_2\text{O}_4$, an inexpensive catalyst and easily available reductant, could not reduce nitroarenes in the absence of viologen (EV^{2+}) or viologen polymers. However, the reaction proceeds smoothly in the presence of the latter. The products obtained were isolated by column chromatography and characterized by ^1H NMR. Data are shown in Table 1. Compared with their authentic compounds, the nitro group was reduced selectively to an amino group without affecting other unsatu-

TABLE 1. H-NMR Data of Substituted Nitroarenes and Their Reduction Products

Substrate	¹ H-NMR data ^a	Product	¹ H-NMR data ^b
	a. 7.19–7.59 b. 7.79		a. 4.0 (–NH ₂) b. 6.67–7.40
	a. 2.76 (–COCH ₃) b. 7.8 c. 8.48 d. 8.87		a. 2.57 (–COCH ₃) b. 3.90 (–NH ₂) c. 6.71–6.95 d. 7.63
	a. 8.09 b. 8.39 c. 10.18 (–CHO)		a. 4.26 (–NH ₂) b. 6.70 c. 7.71 d. 9.77 (–CHO)
	a. 3.89 (–CH ₂ CN) b. 7.48 c. 8.18		a. 3.60 (–CH ₂ CN) b. 3.70 (–NH ₂) c. 6.71 d. 7.22

^aCited from Sadtler NMR standard spectra.^bExperimental data.

rated groups (–CO–, –CHO, –CH₂CN). This shows that viologen polymers have the ability to mediate selectively the reduction of substituted nitroarenes.

Numerous procedures have been developed to accomplish the reduction of aromatic nitrocompounds [16]. Most of them require relatively expensive catalysts and/or harsh conditions. Selective reduction of nitrobenzene by Fe/HCl [17] or Fe²⁺ + /NH₃OH [16] requires severe conditions of temperature and pH. Reduction by Fe₃(CO)₁₂-MeOH [18] or phthalocyanine cobalt(I) [19] gives good results in mild conditions, but the former complex is somewhat hazardous and the latter has less reactivity and is not easy to handle. Therefore, the viologen-mediated reduction method can be considered as a mild and inexpensive alternative route for reduction.

Table 2 shows the reduction data of substituted nitroarenes mediated by EV²⁺ or viologen polymers. The conversion of *o*-chloronitrobenzene first increases and then decreases with an increasing amount of EV²⁺, which most likely is due to dimer formation of the viologen radical [20]. The polymeric viologens PCEVE-BV²⁺, PCEVE-EV²⁺, and PCEVE-V²⁺, on the other hand, remain very effective electron-transfer catalysts in the whole concentration range examined. In the last case the dimerization of viologen radicals could be interrupted by steric hindrance of the polymer chain.

TABLE 2. Reduction of Nitroarenes with $\text{Na}_2\text{S}_2\text{O}_4$ Using EV^{2+} or Viologen Polymers as ETC^a

Substrate	Product	Viologen	V^{2+} / substrate (mol ratio)	Conversion, % ^b
<i>o</i> -Chloro- nitrobenzene	<i>o</i> -Chloroaniline	None	0	0
		EV^{2+}	0.01	90
			0.02	95
			0.05	72
		PCEVE-BV ²⁺	0.02	95
			0.05	94
		PCEVE-EV ²⁺	0.02	96
		PCEVE-V ²⁺	0.02	96
		0.05	95	
<i>m</i> -Nitroace- tophenone	<i>m</i> -Aminoace- tophenone	None	0	0
		EV^{2+}	0.02	96
		PCEVE-BV ²⁺	0.02	95
		PCEVE-EV ²⁺	0.02	96
		PCEVE-V ²⁺	0.02	98
<i>p</i> -Nitrobenz- aldehyde	<i>p</i> -Aminobenz- aldehyde	None	0	0
		EV^{2+}	0.02	93
		PCEVE-BV ²⁺	0.02	92
		PCEVE-EV ²⁺	0.02	92
		PCEVE-V ²⁺	0.02	95
<i>p</i> -Nitrophenyl- acetonitrile	<i>p</i> -Aminophenyl- acetonitrile	None	0	0
		EV^{2+}	0.02	96
		PCEVE-BV ²⁺	0.02	97
		PCEVE-EV ²⁺	0.02	98
		PCEVE-V ²⁺	0.02	98

^aReaction conditions: 15 mmol $\text{Na}_2\text{S}_2\text{O}_4$, 15 mmol Na_2CO_3 , 3.4 mmol substrate, room temperature for 13 hours under N_2 in CH_2Cl_2 - H_2O (30 mL, 1:1).

^bIsolated yields.

The reduction reaction of *m*-nitroacetophenone by $\text{Na}_2\text{S}_2\text{O}_4$ with EV^{2+} as ETC was further examined in diethyl ether-water, ethyl acetate-water, and dichloromethane-water two-phase systems, as well as in a homogeneous methanol-water (3:1) medium. The results are shown in Table 3. A difference in the organic layer in the two-phase systems did not afford a significant change in the reduction yield. No further reduction of the carbonyl group was found when the reaction proceeded in homogeneous methanol-water (3:1), under alkaline condition, for 72 hours. This shows that EV^{2+} possesses good ability to induce the reduction of substituted nitroarenes.

TABLE 3. Effect of Mixed Solvents on the Reduction of *m*-Nitroacetophenone^a

EV ²⁺ / <i>m</i> -nitroacetophenone	Reaction medium	Isolated yield, % ^b
0.02	Diethylether-H ₂ O	98
0.02	CH ₂ Cl ₂ -H ₂ O	96
0.02	CH ₃ COOC ₂ H ₅ -H ₂ O	95
0.02 ^c	CH ₃ OH-H ₂ O	97

^aReaction conditions: see Table 2.

^bThe conversion is quantitative.

^cReaction conditions: Na₂S₂O₄, 15 mmol; Na₂CO₃, 65 mmol, reaction time, 72 hours.

The active species involved in the reduction of nitroarenes could be either the radical cation ($V^{\cdot+}$) or the product resulting from the two subsequent one-electron transfer reduction ($V:$) which is formed by the disproportionation reaction of $V^{\cdot+}$ ($2V^{\cdot+} \rightarrow V: + V^{2+}$) in the organic layer [21]. In this case, spectroscopic studies [21] have shown that the disproportionation constant (k_d) depends strongly on the nature of the organic phases. The weak dependence of the reduction yield of *m*-nitroacetophenone on the organic phase, observed in this study, suggests that the active species for the hydrogenation of *m*-nitroacetophenone might be the radical cation ($V^{\cdot+}$).

Cyclic Voltammogram Study of the Reaction

The cyclic voltammogram of EV²⁺ in a water/methanol mixture (volume ratio 3:1) containing 1 mM EV²⁺ and the phosphorous buffer (pH 6.98) is shown in Fig. 5. The two redox waves at $E_{1/2} = -0.66$ and -1.03 V correspond to the formation of the viologen cation radical (EV^{•+}, one-electron reduction) and its quinonoid form (EV:, two subsequent one-electron transfer reductions), respectively. The un-

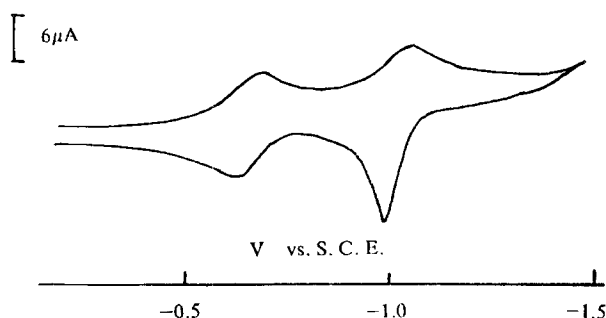


FIG. 5. Cyclic voltammogram of EV²⁺ in pH 6.98 buffer/MeOH (volume ratio = 3/1) under an argon atmosphere.

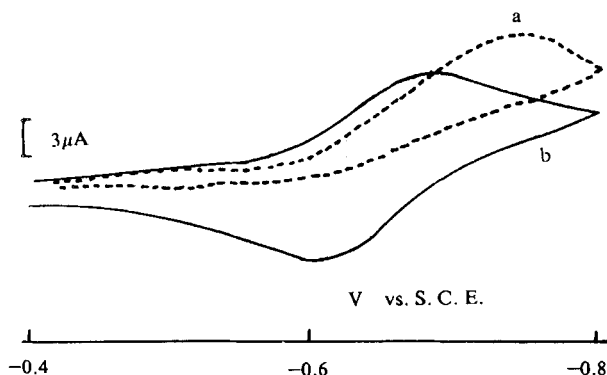


FIG. 6. Cyclic voltammograms of solutions. a: 20 mL of 1 mM EV^{2+} containing 0.125 mmol *o*-chloronitrobenzene. b: 1 mM EV^{2+} .

symmetrical second redox wave indicates precipitation of the reduction product on the electrode. Under controlled potential conditions, the first reversible redox wave is observed as shown in Fig. 6, Curve b. Addition of benzaldehyde to the system did not alter the reversibility of the redox wave of EV^{+} ; however, a change of the reversibility could be observed when 0.125 mmol of *o*-chloronitrobenzene was added (Fig. 6, Curve a) to the system. The redox wave of *o*-chloronitrobenzene under fixed potential conditions is shown in Fig. 7. The redox potential is -0.83 V, a value which is more negative than the first redox potential of EV^{2+} . The change of reversibility of EV^{2+} upon the addition of *o*-chloronitrobenzene to EV^{+} shows that an electron-transfer reaction occurred from EV^{+} to *o*-chloronitrobenzene. Therefore, we can consider it is EV^{+} which acts as the active species during the reduction reaction of nitroarenes.

ESR Study of the Reactions

The reduction of EV^{2+} with $Na_2S_2O_4$ in a CH_2Cl_2 - H_2O mixture under stirring results in a blue color in the CH_2Cl_2 phase which is characteristic of viologen radicals. The ESR spectra is shown in Fig. 8(a). After the addition of a substrate

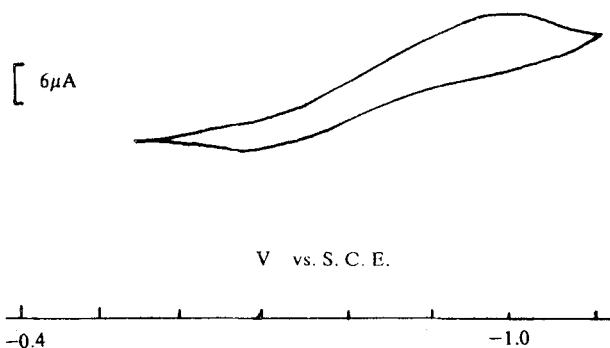


FIG. 7. Cyclic voltammogram of *o*-chloronitrobenzene (5 mM).

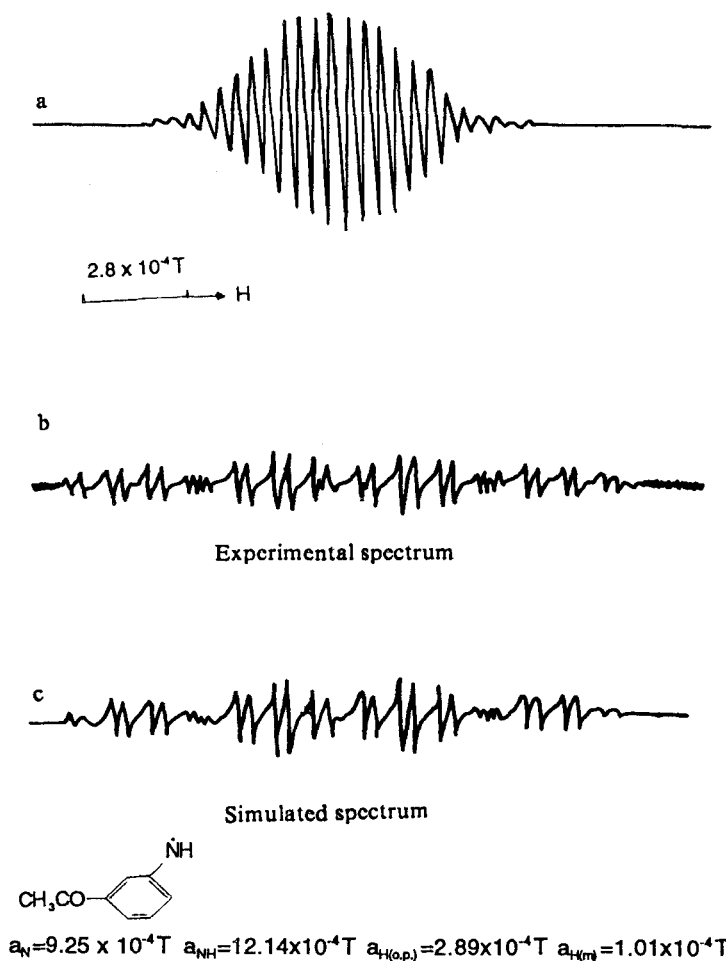
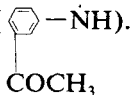


FIG. 8. ESR spectra of $\text{EV}^{+\bullet}$ (a) and intermediate produced in viologen-mediated reduction of *m*-nitroacetophenone (b and c). b: Experimental spectrum. c: Simulated spectrum.

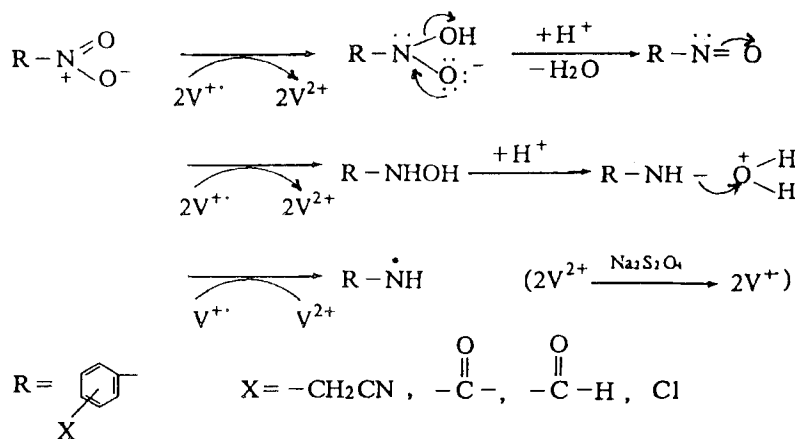
such as 3-nitroacetophenone, however, the CH_2Cl_2 blue color phase faded gradually and no $\text{EV}^{+\bullet}$ signal could be detected but a new signal appeared. The actual ESR spectrum and a computer simulated spectrum are shown in Figs. 8(b) and 8(c), respectively. Based on its splitting constants, the new signal was attributed to the intermediate, produced during the reduction of *m*-nitroacetophenone ($\text{C}_6\text{H}_4(\text{NH})\text{COCH}_3$).



Discussion about the Reaction Mechanism

As a family of organic substrates, the aromatic nitroarenes can be easily hydrogenated by various means, producing corresponding amines as the final products. At different reduction stages, however, nitrosobenzene and phenyl hydroxyl-

amine might be produced as by-products. Azoxyl or hydrazobenzene may also form due to a coupling reaction between radical intermediates. Viologens can mediate the reduction of azobenzene, giving hydroazobenzene without further reduction [8] whereas the reduction of substituted nitroarenes mediated by viologens or polymeric viologens under mild conditions gives corresponding aniline derivatives. No azobenzenes by-products are produced. Since the viologen active species are proved to be viologen cation radicals and the aniline radical was detected as the intermediate, the reaction may proceed as follows:



CONCLUSIONS

Polymers with viologen moieties could be prepared through polymer reactions on polychloroethyl vinyl ether (PCEVE). These polymers act as effective electron-transfer catalysts (ETC) to mediate the reductions of substituted nitro arenes, affording the corresponding aniline derivatives. Viologen radicals ($\text{V}^{+\cdot}$) act as the active species during the viologen-mediated reductions. Further studies on the reduction of other organic substrates using polymeric viologens as ETC are in progress.

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Received July 28, 1995

Revision received December 10, 1995