Polymer Effect in Electrochromic Behavior of Oligomeric Viologens
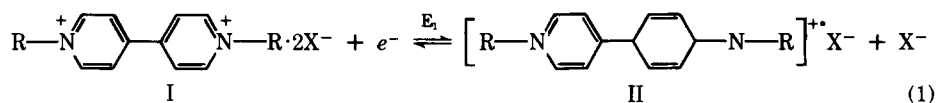
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Synopsis

A series of oligomeric viologens were synthesized in order to investigate the polymer effect in electrochromic behavior of viologen compounds. These materials have a lower first-step reduction potential and a higher second-step reduction potential compared with monomeric viologens. As a result, they have wider potential separation, where stable viologene radical salts are produced. Spectroscopic analysis suggests that stable monomeric viologen radical salts do not exist in water, but there is some intramolecular interaction between viologen radicals of the oligomers. This intramolecular interaction is responsible for the reduction behavior and the stability of radical films of oligomeric viologens.

INTRODUCTION

Viologens (4,4′-dipyridinium salts) (I) are easily reduced on the electrode surface electrochemically at applied potential E_1 to produce dark-purple radical cation salts (II)[1]:

$$R-\overset{+}{N}\langle\rangle-\langle\rangle-\overset{+}{N}-R\cdot2X^- + e^- \underset{\rightleftharpoons}{\overset{E_1}{}} \left[R-\overset{+}{N}\langle\rangle-\langle\rangle-N-R\right]^{+\bullet}X^- + X^-$$

<p style="text-align:center">I   II   (1)</p>

Schoot et al. reported that by using suitable alkyl groups (R), the radical salts are insoluble with solvent and the electrode is covered with persistent colored film.[2] This phenomenon can be applied to display a memory effect.[2] These electrochromic materials are heptylviologen dibromide (DpHpBr), benzylviologen dibromide (DpBzBr), *p*-cyanophenylviologen dichloride (DpCyPheCl), etc. Reduction potentials of these materials are shown in Table I. Polymeric materials (III) have lower E_1 than monomeric viologens,[3] and the electrochromic device containing the material can be driven at lower potential[4]:

$$\left(R-\overset{+}{N}\langle\rangle-\langle\rangle-\overset{+}{N}\right)_n$$
<p style="text-align:center">X⁻   X⁻</p>
<p style="text-align:center">III</p>
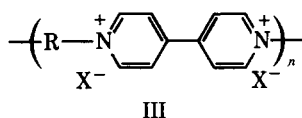
Viologen radical cation salts are reduced at higher potential E_2 to produce quinoid-type products (IV)[5,6]:

$$\left(R-\overset{+}{N}\langle\rangle-\langle\rangle-N-R\right)^{+\bullet}X^- + e^- \underset{\rightleftharpoons}{\overset{E_2}{}} R-N\langle\rangle-\langle\rangle-N-R + X^- \quad (2)$$

<p style="text-align:center">II   IV</p>

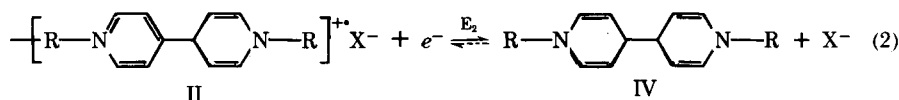0021-8995/79/0024-2075$01.00

TABLE I
Reduction Potentials of Monomeric Viologens and Ionene Polymer

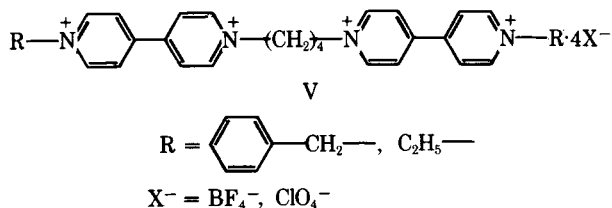| Material	E_1 vs. SCE,[d] V	E_2 vs. SCE, V	$\Delta E = E_1 - E_2$, V
DpHpBr[a]	−0.54	−0.84	0.30
DpBzBr[a]	−0.51	−0.80	0.29
DpCyPheCl[b]	—	—	0.2
Ionene polymer[c]	−0.436	−0.854	0.418

[a] Measured in $2.5 \times 10^{-3} M$ viologen and $0.2 M$ KBr solution.
[b] Adapted from reference 7.
[c] Adapted from reference 3.
[d] Saturated calomel electrode.

The second-step reduction is not reversible and causes poor diplay performance.[7] The reduction potential separation, where stable viologen radicals are produced, is not wide (Table I). Impedence of electrochromic devices is quite low (below a few ohms), as it contains electrolyte solution. More than several milliamperes of current flows when the voltage is applied to the device. A transparent electrode, such as SnO_2 has a relatively high resistance ($\sim$10 $\Omega/\square$); therefore, the ohmic drop comparable to ΔE occurs within the electrode. Higher potential is needed to overcome the ohmic drop. Then the second-step reduction is apt to occur. Electrochromic materials that have wider separation of the two reduction steps are desirable.[8] Ionene-type polymers (III) have higher E_2 values, compared to those of monomeric materials (Table I). Radical films of DpHpBr deteriorate during memory period,[9] resulting in poor display performance. Recently, Bruinink, Kregting, and Ponjee reported that the viologen dimer V is more stable against deterioration than DpHpBr[10]:

$$R-\overset{+}{N}\overset{}{\underset{}{\bigcirc}}\overset{}{\underset{}{\bigcirc}}\overset{+}{N}-(CH_2)_4-\overset{+}{N}\overset{}{\underset{}{\bigcirc}}\overset{}{\underset{}{\bigcirc}}\overset{+}{N}-R\cdot 4X^-$$

V

$$R = \overset{}{\underset{}{\bigcirc}}-CH_2-,\ C_2H_5-$$
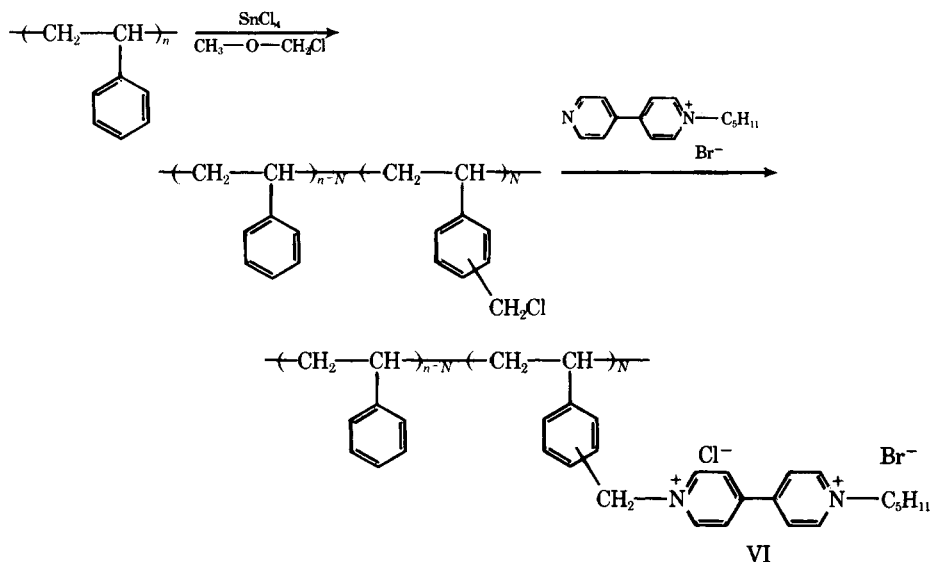
$$X^- = BF_4^-,\ ClO_4^-$$

It is not clear whether the stability of the dimer comes from the dimerization effect or from the size effect of the counteranion.

The ionene-type polyviologens mentioned above have wide molecular weight distributions, low degrees of polymerization,[4] and lower water solubilities. Noguchi synthesized the "polyviologens" which have viologen groups in the side chain from poly(chloromethylstyrene) and dipyridylmonoalkyl halide.[11] However, these materials also have wide molecular weight distributions and are not suitable for investigating the polymer effect in electrochromism. In this report, we synthesized a series of new oligomeric viologens whose molecular weight distribution is quite narrow[12] and investigated the polymer effect in electrochromic behavior of the materials.

EXPERIMENTAL

### Synthesis of Polystyrene-Type Polyviologens

In order to minimize the molecular weight distribution of the materials, we used anionic styrene oligomer as a matrix polymer. The synthetic route is as follows:

$$\text{--(CH}_2\text{---CH)}_n\text{--} \xrightarrow[\text{CH}_3\text{---O---CH}_2\text{Cl}]{\text{SnCl}_4}$$

(with phenyl substituent)

$$\text{--(CH}_2\text{---CH)}_{n-N}\text{--(CH}_2\text{---CH)}_N\text{--}$$

(phenyl; CH$_2$Cl substituted ring)

reacting with

N$\equiv$ $\equiv$N$^+$---C$_5$H$_{11}$ Br$^-$ (dipyridyl monoamyl bromide)

$$\text{--(CH}_2\text{---CH)}_{n-N}\text{--(CH}_2\text{---CH)}_N\text{--}$$

CH$_2$---N$^+$ $\equiv$ $\equiv$N$^+$---C$_5$H$_{11}$ Cl$^-$ Br$^-$

VI

where n represents the degree of polymerization of styrene oligomers, which has a value of 5, 9, 28, and 97; and N is the number of styrene units functionalized with chloromethyl groups or viologen groups. Care was taken in the reaction conditions for chloromethylation to avoid variation in molecular weight distribution and gelation.[13] The chloromethylated styrene oligomers were characterized by infrared spectrum, elemental analysis, and gel permeation chromatography. The polydispersity (M_w/M_n) and the degree of chloromethylation (X) of the chloromethylated styrene oligomers are tabulated in Table II. They were allowed to react with dipyridylmonoamyl bromide in dimethyl sulfoxide at 90–110°C for 1–3 hr. The reaction mixtures were poured into tetrahydrofuran. The precipitate was purified four times by reprecipitation and identified by its infrared spectrum.

Synthesis of Xylyl- and Mesityl-Type Viologen Oligomers

As another type of viologen oligomers, we synthesized α,α'-diviologen-yl-m-xylene (viologen dimer VII) and α,α',α''-triviologenylmesitylene (viologen trimer IX). The synthetic routes are as follows:
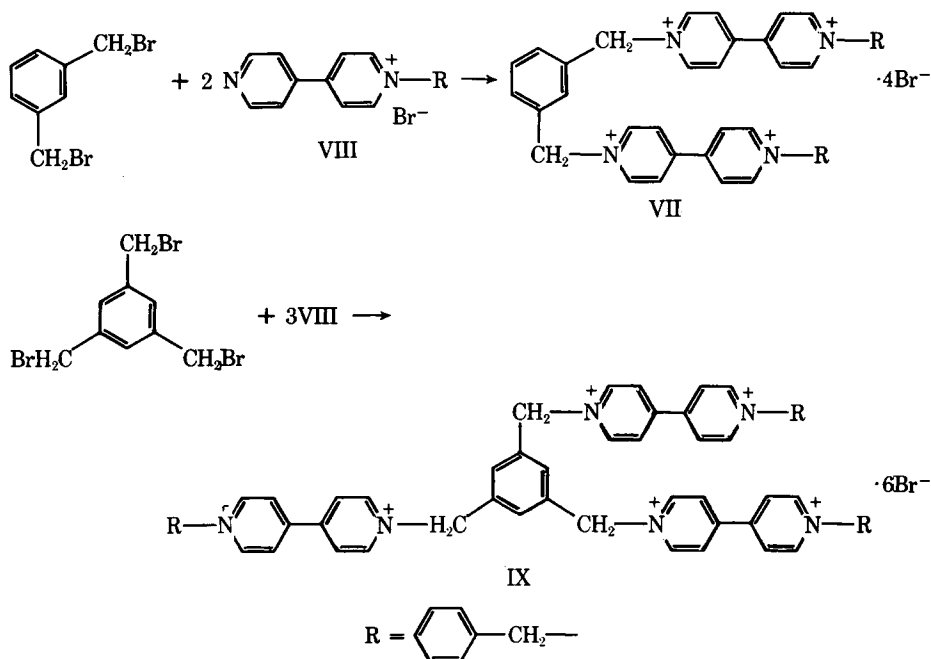
As a starting material for the trimer α,α',α'',-tribromomesitylene was prepared from mesitylene.[14]

Synthesis of Monomeric Viologens

Heptylviologen dibromide and benzylviologen dibromide were synthesized as monomeric viologens.

Polarography

A Yanagimoto polarograph Model P-3C was used for the polarographic measurements. A saturated calomel electrode (SCE) was used as a reference electrode. Water was distilled twice from the quartz distillation column and degassed with oxygen-free nitrogen before use. The viologen concentration was $2.5 \times 10^{-3}M$, and that of the supporting electrolyte potassium bromide was $0.2M$. All the measurements were performed at room temperature.

TABLE II
Characterization of Chloromethylated Styrene Oligomers

n	M_w/M_n [a]	$x = N/n$, % [b]
5	1.17	62.8
9	1.14	77.1
28	1.15	66.6
97	1.15	71.5

[a] Determined by gel permeation chromatography (GPC) in methyl ethyl ketone at room temperature.

[b] Determined by elemental analysis.

Electrospectroscopy

A Nihonbunko spectrometer Model UVIDEC-505 was used to measure the visible and ultraviolet spectra. Near-infrared spectra were measured using a Hitachi spectrometer Model EPS-3T. Radical salt films were prepared electrochemically on transparent SnO_2 electrodes ($10\Omega/\square$, 1 cm^2). The applied charge density was 8–10 mC/cm^2. Viologen radical solution was produced by adding $0.5N$ KOH solution into the 10^{-4}–$10^{-2}M$ viologen solution.[15] The solvents (water and methanol) were degassed with oxygen-free nitrogen before use. A sealed quartz cell was used to measure the spectra. All the measurements were performed at room temperature.

RESULTS AND DISCUSSION

Synthesis

The infrared spectra of chloromethylated styrene oligomer ($n = 9$) and the viologen oligomer synthesized from it are shown in Figure 1. After the amination, the absorption for the chloromethyl (1260 cm^{-1}) disappeared completely and the absorption for the quarternized pyridinium salt (1640 cm^{-1}) appeared, confirming that the chlorine is substituted quantitatively with viologens. Viologens are contained in the material in the ratio of 63–77%, as shown in Table II. The results of elemental analysis and melting points of viologen dimer and trimer are shown in Table III together with those of α,α',α''-tribromomesitylene.
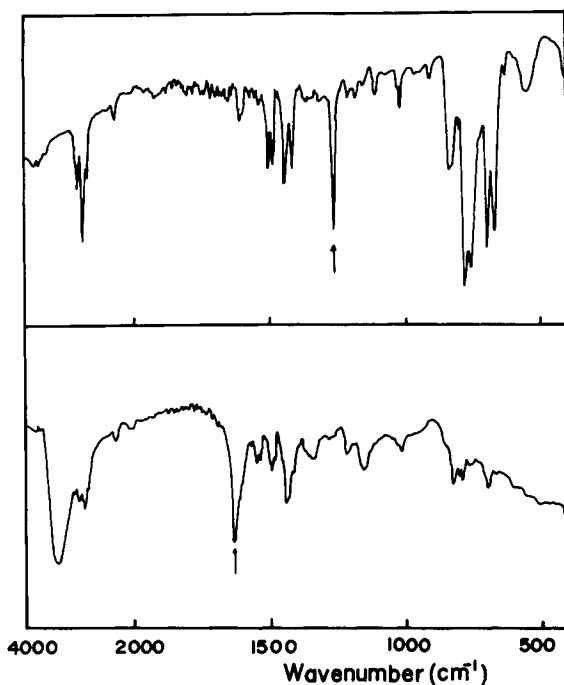

Fig. 1. Infrared spectra of chloromethylated styrene oligomer ($n = 9$, upper spectrum) and viologen oligomer synthesized from it (lower spectrum).

TABLE III
Analysis of Viologen Dimer and Trimer

	Elemental analysis				Melting point,[a] °C	Recrystallization solvent
	C, %	H, %	N, %	Br, %		
Viologen dimer ($C_{42}H_{38}N_4Br_4$)						
Analytical	54.7_4	4.4_2	6.3_5	33.9_6	281	methanol
Calculated	54.93	4.17	6.10	34.80		
Viologen trimer ($C_{60}H_{54}N_6Br_6$)						
Analytical	53.1_2	4.2_5	6.3_1	34.9_8	299	ethanol (2)[b]
Calculated	53.83	4.08	6.28	35.81		methanol (1)[b]
α,α',α''-Tribromomesitylene ($C_9H_9Br_3$)						
Analytical	30.3_5	2.5_4		67.1_0	95.5	cyclohexane
Calculated	30.25	2.52		67.27		

[a] Measured by DSC; rate 20°C/min.
[b] Volume ratio.

Polarography

The results of polarographic analysis for the synthesized materials are shown in Figure 2. The first and second half-wave potentials E_1 and E_2 and the potential separation ΔE are plotted versus log N. The absolute E_1 of oligomers is lower, and the absolute E_2 is higher than those of the monomers. The ΔE of oligomers is about twice as large as that of the monomers. Even at a low value of N, such as 2 or 3, the polymer effect is observable. It is interesting that for $N > 1$, the reduction potential is not as dependent on N. These features differ from that of the so-called polymer deffect. Hence, the electronic state of the oligomeric radical is more stable than that of the monomeric radical.

Electrospectroscopy

In order to investigate the electronic state of the viologen radicals, the ultraviolet, visible, and near-infrared spectra were measured. The spectra of the monomeric viologen radical films are shown in Figure 3. There is not much difference between DpHpBr and DpBzBr. The spectra of the oligomers are shown in Figures 4 and 5, which have main absorption peaks at 525–540 nm and broad absorption peaks at 900–980 nm. The differences between the absorption spectra of oligomers and those of monomers include a shift in the visible absorption to shorter wavelengths and a shift in the near-infrared absorption to longer wavelengths. The resulting color changes from reddish purple for monomeric to bluish purple for oligomeric viologens. In the study of aqueous
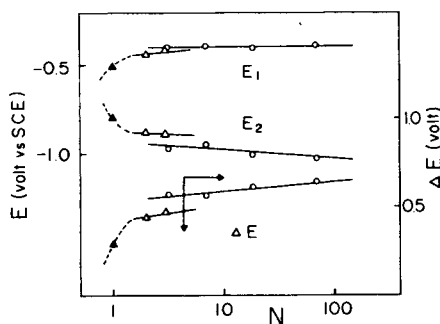

Fig. 2. Dependence of reduction potentials on viologen numbers contained in the material: (▲) DpBzBr; (△) dimer and trimer; (○) styrene-type oligomers.
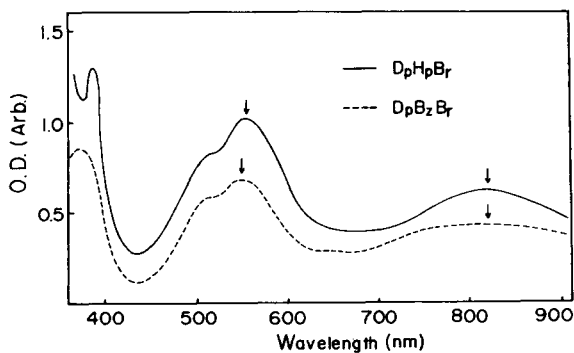

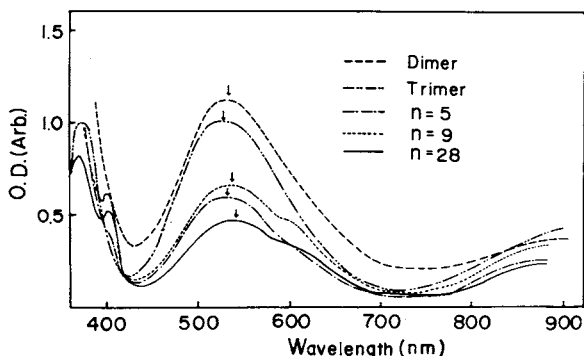Fig. 3. Absorption spectra of monomeric viologen radical films.

Fig. 4. Absorption spectra of oligomeric viologen radical films.

methylviologen radicals, Kosower and Cotter reported that a new ban at 870 nm appeared depending on concentration.[1] They explained the new absorption in terms of dimer formation. The absorption at 820 nm for DpHpBr radical film is not observed if the applied charge density is low.[16]

These results suggest that there is some intermolecular interaction between viologen radicals, whether it is a dimer formation or not. It is asserted that the interaction is responsible for the near-infrared absorption. To obtain further information concerning the interaction, the spectra of viologen radical solutions were measured. The spectra of aqueous oligomeric radicals are shown in Figure 6. They resemble the spectra of radical films. The concentration of the oligomers is 10^{-5}–$10^{-6}M$; the intermolecular interaction between radicals can be neglected.[17] Absorption in the near-infrared region of oligomers is attributed to the intramolecular interaction of viologen radicals.

The spectrum of the aqueous DpHpBr radical is shown in Figure 7, which shows the main absorption peak at 600 nm and does not have near-infrared absorption. It is quite different from the spectra shown in Figure 3. The spectra of the methanol solution of some oligomeric viologen radicals are shown in Figure 8, together with that of DpHpBr. They have a main absorption peak at 600 nm but no near-infrared absorption. They resemble the spectrum shown in Figure 7, except for a slight broadening of the latter. They also yield quite similar results to that of DpEtCl and DpHpClO4 radical solutions, which are produced electrochemically in water, in acetonitrile, respectively.[18] The methanol solution
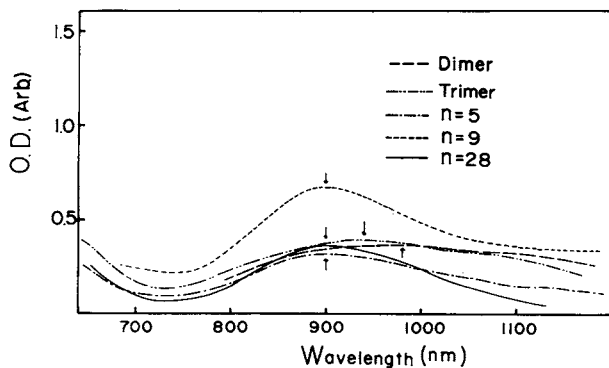

Fig. 5. Near-infrared spectra of oligomeric viologen radical films.
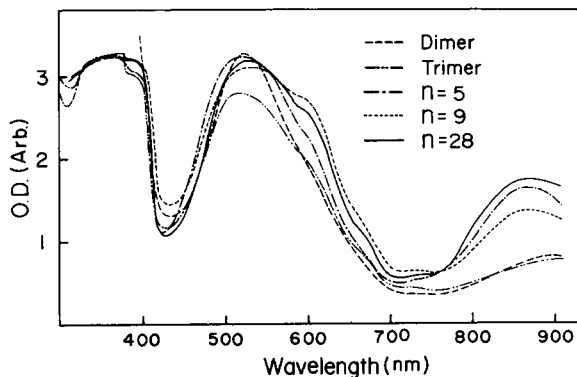
Fig. 6. Absorption spectra of aqueous viologen radical solution of oligomers.

of monomeric and oligomeric radicals showed the same blue color as that of the aqueous DpHpBr radical solution. From conductance measurements, viologens are completely dissociated in water; in methanol, the dissociation of the second anion is not complete with a dissociation constant[19] $K = 5.5 \times 10^2$. This means that viologens X exist in methanol:
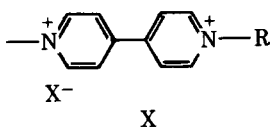
As mentioned by van Dam and Ponjee, viologen radicals in low dielectric constant solvents such as methanol and acetonitrile are in the state of XI instead of the radical cation salt XII.[18] In the former case, viologen counteranions exist in the ion bonding state, and in the latter case, in the ion pair state:
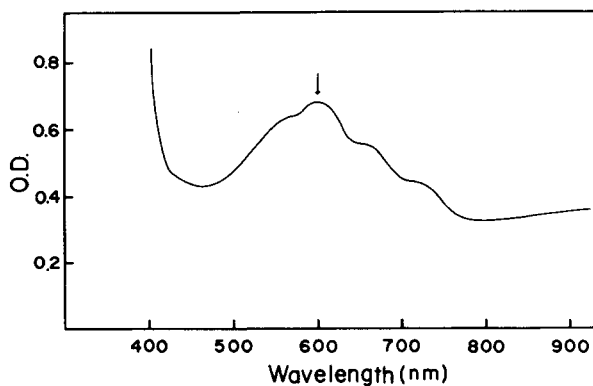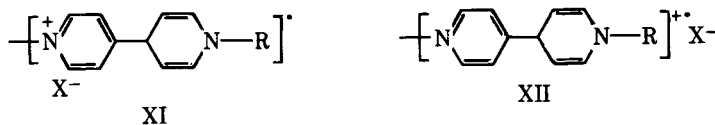

Fig. 7. Absorption spectrum of aqueous viologen radical solution of DpHpBr.
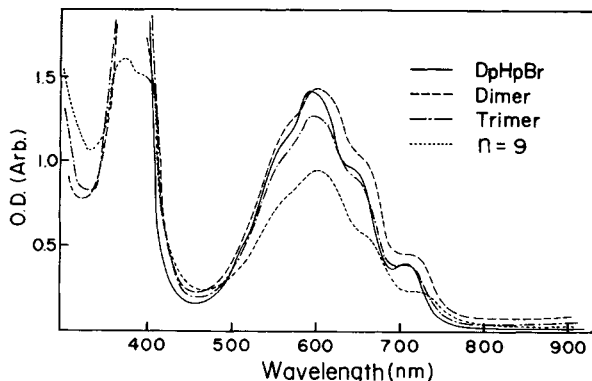
Fig. 8. Absorption spectra of methanol solution of viologen radicals.

The spectra shown in Figure 8 correspond to the state, XI. The similarity of the spectrum of the aqueous DpHpBr radical solution to that of the viologen radical methanol solution suggests that the DpHpBr radical shown in Figure 7 is in the state of XI. Furthermore, it appears that monomeric viologen radicals do not exist in the stable state as an ion pair [XII] in water. The state shown in Figure 3 cannot be identified. It might be a viologen radical dimer, as mentioned by Kosower and Cotter, or a small cluster of viologen radicals, as mentioned by van Dam and Ponjee.[18] The size effect of the counteranion on the reduction behavior of viologens appeared only in the radical film XII.[18] The polymer effect is not observed in the state of XI (Fig. 8).

The interaction between viologen radicals comes from the intermolecular interaction for the monomeric viologens and the intramolecular interaction for the oligomeric viologens. The intramolecular interaction is responsible for the behavior of the reduction potential of oligomers. The deterioration of monomeric viologen radical films is ascribable to the intermolecular interaction between viologen radicals and to the structural change of viologen radicals from XII to XI.

CONCLUSIONS

The new oligomeric viologens have a lower E_1 and a wider ΔE than monomeric materials. The radical films of oligomers are more stable in water than are the monomers. These results are due to the intramolecular interaction between viologen radicals of oligomers. An electrochromic device using these oligomers can be driven at lower potential and have a wider potential margin than the device using monomers. Furthermore, the device has a longer memory period because of the radical film stability. Thus, the oligomeric viologens are more promising materials for electrochromic devices than the monomeric viologens.

References

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