

Odd-Even Effect on Absorption Spectra of Reduced Viologen Ionene Polymers complexed with Anionic Bilayer Membranes

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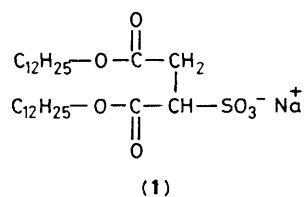
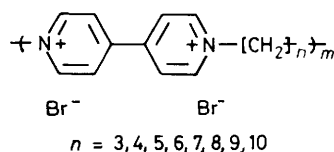
An odd-even effect was observed for reduction of viologen ionene polymers in cast films complexed with anionic bilayer membranes.

The redox behaviour of viologens and their polymeric derivatives has attractive prospects for photoenergy conversion and electrochromism. Regulation of the molecular orientation of viologen polymers may be essential for their redox properties, *e.g.* efficient electron migration along the polymer chain.¹

Kunitake and co-workers found that J-aggregates (an unusual molecular orientation) of anionic cyanine dyes were formed at the charged surface of cationic bilayer membranes.² It seems that the well defined charged surface of bilayer membranes is a suitable tool for the regulation of the molecular orientation of a polymer having an opposite charge.

In this communication, we describe the unusual redox behaviour of immobilized viologen ionene polymers complexed with an anionic bilayer membrane (1).³ The ionene polymers were prepared by Menshutkin reaction of 4,4'-bipyridyl and the corresponding dibromide in dimethylformamide. According to Kunitake's method,⁴ a poly-ion complex

of the anionic bilayer membrane and the viologen polymer was prepared. The precipitate formed on mixing the aqueous solutions was extracted with chloroform and washed with



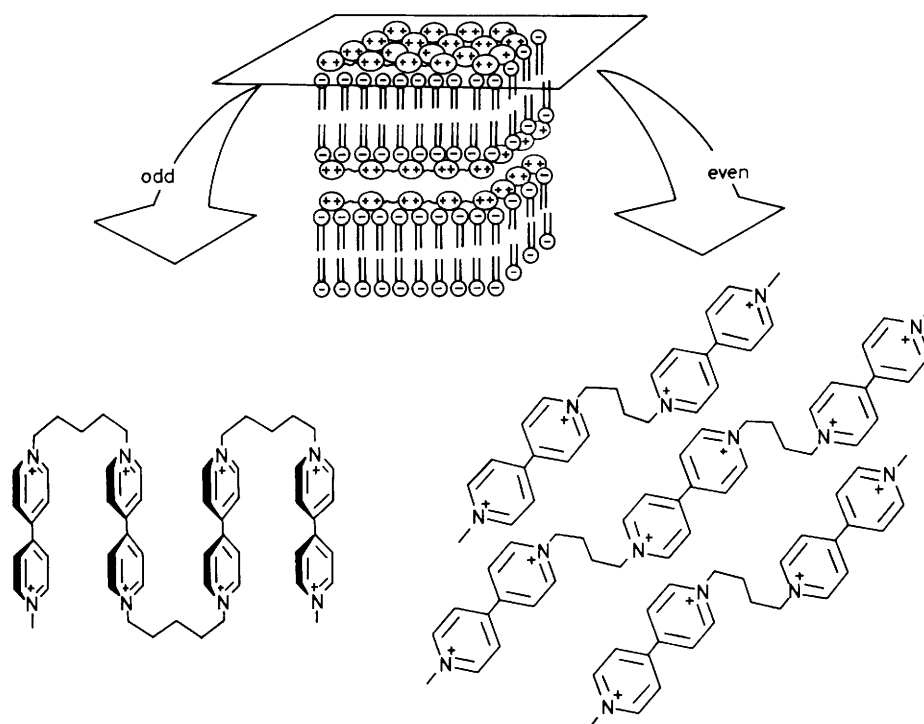


Figure 1. Probable molecular orientation of the viologen polymer fixed on the membrane surface. Face-to-face orientation of viologen groups for the odd- n polymers and head-to-tail orientation for the even- n polymers.

water several times to remove water-soluble species. Transparent and self-supporting complex films were cast from chloroform solution.

The ratio of anion to cation calculated from sulphur and nitrogen elemental analyses is 0.93 ± 0.15 for all the complex films prepared. X-Ray diffraction studies of the complex films suggest that a layered structure is maintained (as in another complex film prepared from cationic viologen bilayers and anionic polymers⁵), because clear Debye-Scherrer rings, whose spacing (3.5–3.9 nm, depending on polymer) corresponds to the bilayer thickness, were observed. As shown in Figure 1, intercalation of the cationic viologen polymers into the charged layers of the anionic membranes is the most plausible structure for the complex film.

The poly-ion complex films were reduced both chemically and electrochemically.⁶ Strongly coloured radical cations were formed when the complex films were immersed in an aqueous solution containing excess of $\text{Na}_2\text{S}_2\text{O}_4$. As shown in Figure 2, an apparent odd-even effect was observed in the u.v.-visible absorption spectra of the reduced complex films. When the number of methylene groups, n , is even, the absorption maximum of the film is located at around 610 nm, characteristic of a monomeric viologen radical. However, films in which n is odd show a hypsochromic shift to around 560 nm, attributable to dimer radical formation.⁷ Moreover, a broad absorption at around 880 nm, characteristic of a dimer radical, was also observed for the odd- n polymer, even in a dilute solution of $\text{Na}_2\text{S}_2\text{O}_4$. This suggests that the favoured orientation for dimer radical formation is already fixed in the complex films. No odd-even effect was observed in the absorption spectra of aqueous solutions of the viologen polymer itself, which formed the dimer radical in the presence of excess of $\text{Na}_2\text{S}_2\text{O}_4$ (Figure 2).

If the all-*trans* conformation of the alkyl chain between two viologen groups is fixed at the charged membrane surface,⁸

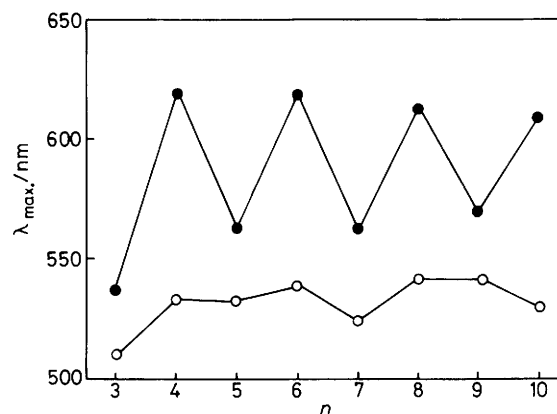


Figure 2. U.v.-visible absorption maxima of reduced viologen polymers. Complex films were immersed in a $10^{-1} \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_4$ aqueous solution (●). Aqueous polymers (*ca.* $10^{-5} \text{ unit mol dm}^{-3}$) without bilayer membranes were reduced by a large excess of $\text{Na}_2\text{S}_2\text{O}_4$ ($10^{-3} \text{ mol dm}^{-3}$) (○).

the neighbouring viologens may be located on the same side of the alkyl chain in the odd- n polymers, but on opposite sides in the even- n polymers. A face-to-face orientation of the viologen groups is probable for the odd- n polymers and a head-to-tail orientation is probable for the even- n polymers. Proposed models of the fixed conformation are shown in Figure 1. Interlayer interaction may be negligible, because the dimer radicals were not observed in the even- n polymers.

This is the first example of the regulation of the molecular arrangement of viologen polymers by taking advantage of the organization of bilayer membranes. Fixation of polymers on the well defined charged surface of bilayer membranes could

become a useful technique for the design of ordered molecular assemblies.

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References

- 1 T. Nishijima, T. Nagamura, and T. Matsuo, *J. Polym. Sci., Polym. Lett. Ed.*, 1981, **19**, 65.
 - 2 N. Nakashima and T. Kunitake, *J. Am. Chem. Soc.*, 1982, **104**, 4261.
 - 3 T. Kunitake and Y. Okahata, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1877.
 - 4 T. Kunitake, A. Tsuge, and N. Nakashima, *Chem. Lett.*, 1984, 1783.
 - 5 Y. Okahata, G. Enna, K. Taguchi, and T. Seki, *J. Am. Chem. Soc.*, 1985, **107**, 5300.
 - 6 K. Utsugi, unpublished results.
 - 7 E. Kosower and J. Cotter, *J. Am. Chem. Soc.*, 1964, **86**, 5524.
 - 8 D. Tirrell, A. Turek, D. A. Wilkinson, and T. McIntosh, *Macromolecules*, 1985, **18**, 1513.
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