Functional Capsule Membranes. Part 28.[1] A Capsule Membrane grafted with Viologen-containing Polymers as a Reactor of Electron-transfer Catalysis in Heterophases

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Large, ultrathin nylon capsule membranes surface-grafted with viologen-containing polymers [poly-(C_nV^{2+}); n = 3, 6, and 10] were prepared. The viologen polymers acted as an effective electron-transfer catalyst in heterophases: the debromination of *meso*-1,2-dibromo-1,2-diphenylethane and the reduction of azobenzene in the inner organic solution of the capsule with excess of sodium dithionite in the outer aqueous solution was largely accelerated by the poly(C_nV^{2+}) polymers grafted on the capsule membrane. The reaction rates increased with increasing spacer chain length (C_n) of the grafted poly(C_nV^{2+}). The efficiency of electron-transfer catalysis was also influenced by the graft amount of poly(C_nV^{2+}) on the capsule surface and by the ionic strength of the outer aqueous phase.

Microcapsules have been widely used for encapsulation of solids, liquids, or gases in order to protect, separate, and aid in storage and for sustained release of medicaments.[2] Therefore, permeation or release behaviours across the capsule membrane have been extensively investigated.[3] We have developed a nylon capsule whose porous membrane was corked with lipid bilayers[4,5] or surface-grafted with functional polymers,[6–8] and have controlled the permeability by outside effects such as temperature change, photoirradiation, pH change, and electric field. Their signal-receptive permeability control would be explained by changes in the orientation of corking bilayers or the conformation of graft-polymers, which acts as a permeation valve.[4–8]

In this paper, we report that large nylon capsule membranes grafted with viologen-containing polymers [poly(C_nV^{2+}); n = 3, 6, and 10] can be used as a reactor for electron-transfer catalysis. *meso*-1,2-Dibromo-1,2-diphenylethane or azobenzene in the inner chloroform solution of the poly(C_nV^{2+})-grafted capsule membrane can be reduced to *trans*-stilbene or hydrazobenzene, respectively, when the capsule was soaked in an aqueous solution of an excess of sodium dithionite ($Na_2S_2O_4$), in which the surface-grafted viologens acted as an electron-transfer catalyst. A schematic illustration of the reaction is shown in Figure 1.

It is known that organic substrates such as aromatic aldehydes and ketones,[9] α-keto esters,[10] azobenzene,[11] and 1,2-dibromostilbene[12,13] can be reduced in the presence of viologens (*NN'*-dialkyl-4,4'-bipyridinium) as an electron-transfer catalyst in liquid–liquid or liquid–solid phases.

Experimental

Materials.—Viologen-containing methacrylamide monomers (C_nV^{2+}; n = 3, 6, and 10) were prepared as follows.[8] *N*-(ω-Bromoalkyl)methacrylamide was synthesized from ω-bromoalkylamine and methacryloyl chloride at 0 °C in chloroform for 10 h in the presence of triethylamine. *N*-(ω-Bromoalkyl)-methacrylamide was treated with 4,4'-bipyridyl in ethanol for 24 h at 40—50 °C and the *N*-mono(alkylated)bipyridyl was

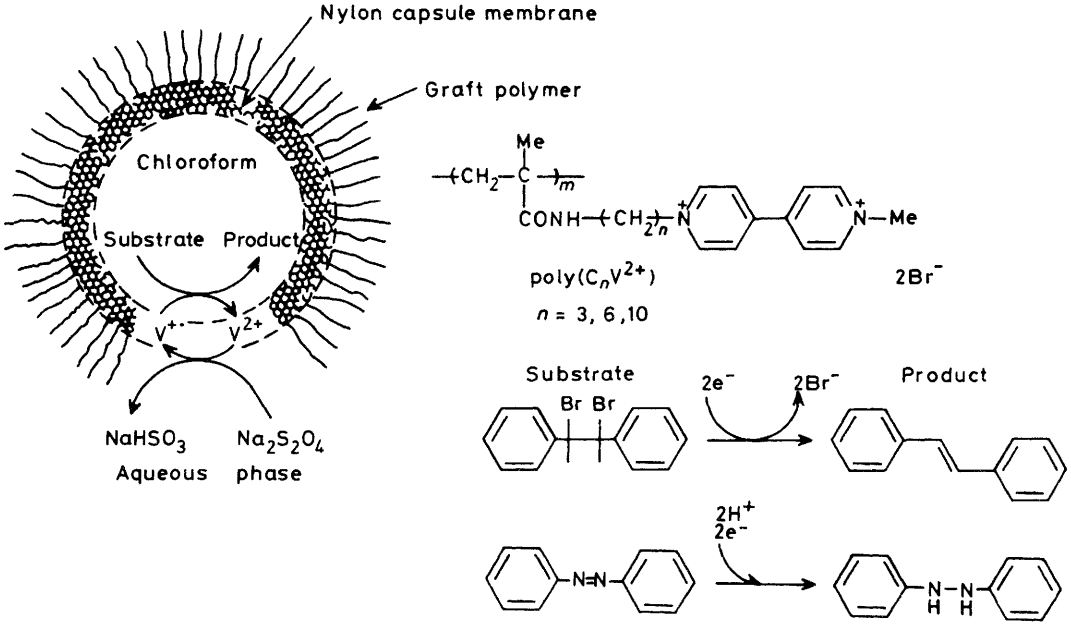


Figure 1. A capsule membrane grafted with viologen-containing polymer [poly(C_nV^{2+}); n = 3, 6, 10] as a reactor for electron-transfer catalysis

obtained by recrystallization from benzene. *NN'*-Bis(alkylated)-bipyridyl was not obtained under these reaction conditions. The *N*-mono(alkylated)bipyridyl was then quaternized with an excess of methyl bromide in methanol at 50 °C for 3 days in a sealed bottle; C_nV^{2+}, m.p. 210—230 °C for *n* 3, 215—217 °C for *n* 6, and 240 °C for *n* 10. Structures were confirmed by t.l.c. with flame ionization detection, n.m.r. spectroscopy, and elemental analysis.

Sodium dithionite, *meso*-1,2-dibromo-1,2-diphenylethane, and azobenzene were commercially available (Tokyo Kasei Co. Ltd., Tokyo).

Capsule Membranes Grafted with Poly(C_nV^{2+}).—Large, porous nylon-2,12 capsule membranes were prepared from ethylenediamine and 1,10-bis(chlorocarbonyl)decane by interfacial polycondensation. The details were described in previous papers.[4,5,14] The capsule diameter and membrane thickness was 2.5 mm and 5 μm, respectively. The dry weight of a capsule was 25 ± 2 μg.

Viologen-containing monomers (C_nV^{2+}) were grafted onto the nylon capsule membrane as follows.[8] In order to introduce vinyl groups onto the capsule membrane, capsules were soaked in a tetrahydrofuran (THF) solution (25 ml) of cerium(IV) ammonium nitrate (0.5 g) and ethylene glycol dimethacrylate (EDM) (1.0 g) for 30 min at room temperature. The capsules were washed with THF and methanol to remove a small amount of non-grafted, cross-linked gel and a large amount of ungrafted monomer. EDM was estimated to be introduced to the extent of 5—10 μg per capsule. The obtained capsules were graft-polymerized in a degassed aqueous solution (15 ml) of the C_nV^{2+} monomers (0.2—2.0 g) with the radical initiator potassium persulphate (50 mg) at 70 °C for 4 h under nitrogen. The capsules were washed and dialysed against an excess of water, methanol, and then isopropyl alcohol to remove non-grafted polymers and unchanged monomer.

The amount of polymers grafted (10—60 μg per capsule) could be controlled by changing the monomer concentration and determined from the weight of crushed, dried capsule membranes before and after polymerization. The molecular weight of the grafted poly(C_nV^{2+}) was determined after complete hydrolysis of nylon capsule membranes under strong acidic conditions at 60 °C for 1 day. The residual graft-polymer, poly(methacrylic acid), was analysed by gel-permeation chromatography [column: TSK-GEL G-6000PW, Toyo Soda Co. Ltd., Tokyo; eluant: 0.2M-phosphate buffer (pH 6.8) + 20% CH_3CN]. The average degree of polymerization of the grafted poly(C_nV^{2+}) was estimated to be 300—800 as standards of poly(ethylene oxide).

Rate Measurements.—Poly(C_nV^{2+})-grafted capsules containing isopropyl alcohol in the inner core were dialysed against a chloroform solution of *meso*-1,2-dibromo-1,2-diphenylethane or azobenzene for 2 days to obtain capsules containing 1.0×10^{-7} or 1.0×10^{-6} mol of substrates in the inner organic core (10 μl), respectively. Reactions were started under stirring at 30 °C in deaerated, aqueous alkaline solution (5 ml; 10^{-3}M-Na_2CO_3) with a large excess of sodium dithionite (5.0×10^{-3} mol) after dropping a capsule containing substrate in the inner organic core. Within the prescribed time interval, the capsule was picked up from the aqueous solution, crushed in chloroform (0.5 ml), and both the reduction of substrates and the production of *trans*-stilbene or hydrazobenzene in the inner phase were monitored by h.p.l.c. (instrument, Toyo Soda HLC-803C with u.v. detector; column, TSK gel ODS-120T; eluant, methanol–water 8:2; flow rate, 1.0 ml min^{-1}). Identification of products was made by comparison of the h.p.l.c. retention time, and the i.r. and n.m.r. spectra with that of the authentic sample.

Results and Discussion

Electron-transfer Catalysis.—The debromination of *meso*-1,2-dibromo-1,2-diphenylethane or the reduction of azobenzene in the inner chloroform solution was catalysed by poly(C_nV^{2+}) grafted on the capsule membrane which was soaked in an aqueous solution of $Na_2S_2O_4$. The surface of the capsule membrane immediately turned from pale yellow to deep blue, which shows the formation of the radical cationic poly($C_nV^{+\bullet}$) polymers on the capsule membrane.

Figure 2 shows typical examples of semilogarithmic plots for the decrease of 1,2-dibromo-1,2-diphenylethane in the inner oganic phase of the capsule as a function of time. The reaction followed pseudo-first-order kinetics up to 90% conversion of substrate. An induction period for the reaction was not observed. The $k_{obs.}$ values of debromination obtained from the slope of Figure 2 are summarized in Table 1. The reduction of azobenzene was also obeyed first-order kinetics and the reaction rates are summarized in Table 2. The concentration of the viologen unit of the graft polymer on the capsule membrane was calculated as (5—6) × 10^{-8} mol (26—28 μg) per capsule.

The effect of the concentration of sodium dithionite in the outer aqueous phase on the $k_{obs.}$ value is shown in Figure 3. In the case of the ungrafted capsule, the $k_{obs.}$ value was very small and linearly increased with increasing $Na_2S_2O_4$ concentration. When a capsule grafted with poly($C_{10}V^{2+}$) or poly(C_6V^{2+}) was employed, the $k_{obs.}$ value increased steeply with increasing concentration of $Na_2S_2O_4$ and reached a plateau above 2×10^{-3} mol $Na_2S_2O_4$ in aqueous solution (5 ml). This indicates that the reduction of poly(C_nV^{2+}) to poly($C_nV^{+\bullet}$) in the aqueous phase is very fast and has no effect on reaction rates for $Na_2S_2O_4$ >0.4M (2×10^{-3} mol in 5 ml) in the outer aqueous phase. The concentration of a viologen unit on the capsule is estimated to be 0.8M per capsule when 5×10^{-8} mol (28 μg) of poly(C_nV^{2+}) is grafted onto 6×10^{-11} m^3 of capsule membrane (capsule diameter, 2.5 mm; membrane thickness, 5

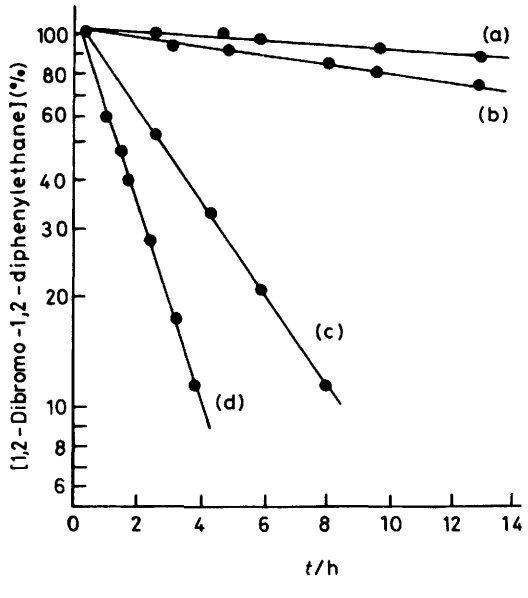


Figure 2. Plots of percentage 1,2-dibromo-1,2-diphenylethane in the inner chloroform solution as a function of time at 30 °C. [1,2-Dibromo-1,2-diphenylethane] 1.0×10^{-7} mol in 10 μl of the inner chloroform solution, [$Na_2S_2O_4$] 5.0×10^{-3} mol in 5 ml of the outer aqueous solution (pH 10), [viologen] (5—6) × 10^{-8} mol [26—28 μg of poly(C_nV^{2+})] per capsule. (a) Non-grafted capsule, (b) poly(C_3V^{2+})-grafted capsule, (c) poly(C_6V^{2+})-grafted capsule, (d) poly($C_{10}V^{2+}$)-grafted capsule

Table 1. Rates of debromination of *meso*-1,2-dibromo-1,2-diphenylethane catalysed by viologen-polymers on or in the capsule membrane at 30 °C[a]

Catalyst	Graft amount per capsule (μg)[b]	$10^6 k_{obs.}/s^{-1}$	Rate enhancement
Non-grafted capsule	—	7.91	1
Ammonium salt-grafted[c]	22	8.51	1
Phosphonium salt-grafted[d]	27	9.01	1.1
Poly(C_3V^{2+})-grafted	26	19.7	2.5
Poly(C_6V^{2+})-grafted	27	57.2	7.2
Poly($C_{10}V^{2+}$)-grafted	28	115	15
Poly(C_3V^{2+}) in capsule[e]	(27)	16.7	2.1
Poly(C_6V^{2+}) in capsule[e]	(27)	27.8	3.5
Poly($C_{10}V^{2+}$) in capsule[e]	(28)	45.4	5.7

[a] [1,2-Dibromo-1,2-diphenylethane] 1.0×10^{-7} mol in the inner chloroform solution (10 μl), [$Na_2S_2O_4$] 5.0×10^{-3} mol in the outer aqueous phase (5 ml). [b] Concentration of viologen unit was calculated to be (5—6) $\times 10^{-8}$ mol per capsule. [c] Capsule membrane grafted with polymer (**1**) was employed. [d] Capsule membrane grafted with polymer (**2**) was employed. [e] Homopolymers of poly(C_nV^{2+}) were dissolved in the inner chloroform solution of the non-grafted capsule.

Table 2. Rates of reduction of azobenzene catalysed by capsule membrane grafted with viologen-polymers at 30 °C[a]

Catalyst	Graft amount per capsule (μg)[b]	$10^6 k_{obs.}/s^{-1}$	Rate enhancement
Non-grafted capsule		1.16	1
Ammonium salt-grafted[c]	22	1.20	1
Poly(C_3V^{2+})-grafted	26	4.8	4.1
Poly(C_6V^{2+})-grafted	27	24.9	21
Poly($C_{10}V^{2+}$)-grafted	28	30.3	26

[a] [Azobenzene] 1.0×10^{-6} mol in the inner aqueous solution (10 μl), [$Na_2S_2O_4$] 5.0×10^{-3} mol in the outer aqueous solution (5 ml). [b] Concentration of viologen unit was calculated at (5—6) $\times 10^{-8}$ mol per capsule. [c] Capsule membrane grafted with polymer (**1**) was employed.

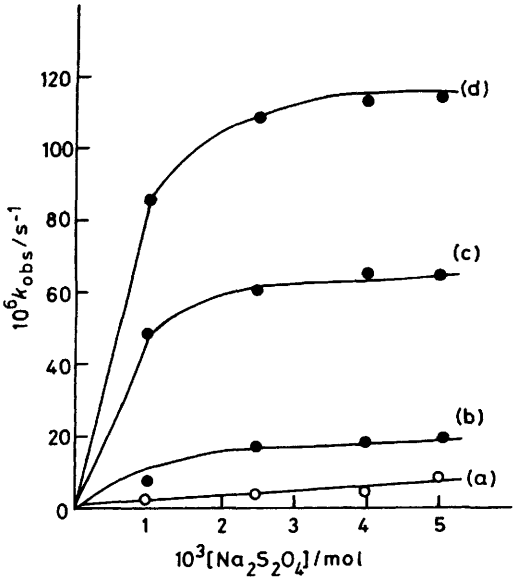
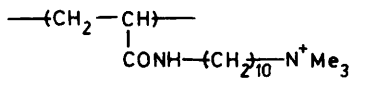


Figure 3. Effect of concentration of $Na_2S_2O_4$ in 5 ml of the outer aqueous phase on $k_{obs.}$ values for debromination of 1,2-dibromo-1,2-diphenylethane at 30 °C. [1,2-Dibromo-1,2-diphenylethane] 1.0×10^{-7} mol in 10 μl of the inner chloroform solution, [viologen] (5—6) $\times 10^{-8}$ mol [(26—28) μg of poly(C_nV^{2+})] per capsule. (a) Non-grafted capsule, (b) poly(C_3V^{2+})-grafted capsule, (c) poly(C_6V^{2+})-grafted capsule, (d) poly($C_{10}V^{2+}$)-grafted capsule

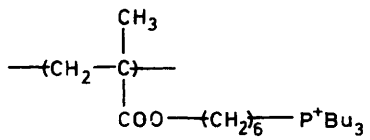
μm), which is nearly consistent with the saturated value of Figure 3 ([$Na_2S_2O_4$] 0.4M, 2×10^{-3} mol in 5 ml).

Structures of Viologen Polymers.—The $k_{obs.}$ values of reductions of 1,2-dibromo-1,2-diphenylethane and azobenzene in capsule membranes are summarized in Tables 1 and 2, respectively. When the non-grafted capsule was employed, the debromination of 1,2-dibromo-1,2-diphenylethane was very slow at 30 °C ($k_{obs.}$ 7.91×10^{-6} s^{-1}, $t_{1/2}$ 24 h) (Table 1). In the case of the capsule grafted with viologen-polymers [poly(C_nV^{2+}); n = 3, 6, and 10], the $k_{obs.}$ value increased by a factor of 2.5—15 compared with that in the case of the non-grafted capsule. The extent of rate acceleration depended on the spacer chain length between the viologen groups and graft-polymer chains. Thus, the reactivity increased with increasing spacer chain length in the order $C_{10} > C_6 > C_3$. A similar trend was observed in the reduction of azobenzene: the reduction catalysed by poly($C_{10}V^{2+}$)-grafted capsule proceeded 26 times faster than that of the non-grafted capsule (see Table 2).

The grafted poly(C_nV^{2+}) may act as either a true electron-transfer catalyst or as a phase-transfer catalyst (p.t.c) carrying $S_2O_4^{2-}$ anions from the outer aqueous to the inner organic phase and the substrate is reduced directly by $S_2O_4^{2-}$ anions. In order to investigate this, we prepared[15] a capsule grafted with polymers having ammonium salts (**1**) or phosphonium salts (**2**) in side chains instead of viologens.



(**1**)

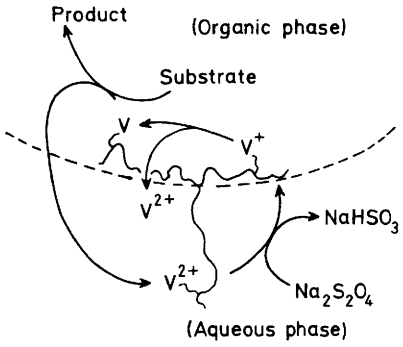


(**2**)

In the case of a capsule grafted with 'onium salt-containing polymers (**1**) or (**2**), reductions of dibromostilbene and azobenzene were not accelerated and the $k_{obs.}$ values were consistent with that of the ungrafted capsule (Tables 1 and 2). The surface of the poly(C_nV^{2+})-grafted capsule changed immediately from pale yellow to deep blue when the capsule was soaked in an aqueous solution of $Na_2S_2O_4$, which shows the production of radical cationic poly($C_nV^{+\bullet}$) on the capsule membrane. These two results indicate that the poly(C_nV^{2+}) does not act as a p.t.c. carrying $S_2O_4^{2-}$ but as an electron-transfer catalyst across the capsule membrane.

When a homopolymer of poly(C_nV^{2+}) dissolved in the inner organic phase of the non-grafted capsule was employed, the $k_{obs.}$ value decreased to one-half or one-third compared with that of the poly(C_nV^{2+})-grafted capsule. This means that the graft-polymers always exist near the interface between the inner organic and the outer aqueous phases and act as more effective catalysts than the polymer dissolved in the organic phase.

Reaction Mechanism.—There are three steps in the reduction of substrates in the inner organic phase of the capsule membrane grafted with poly(C_nV^{2+}), as shown in the Scheme.

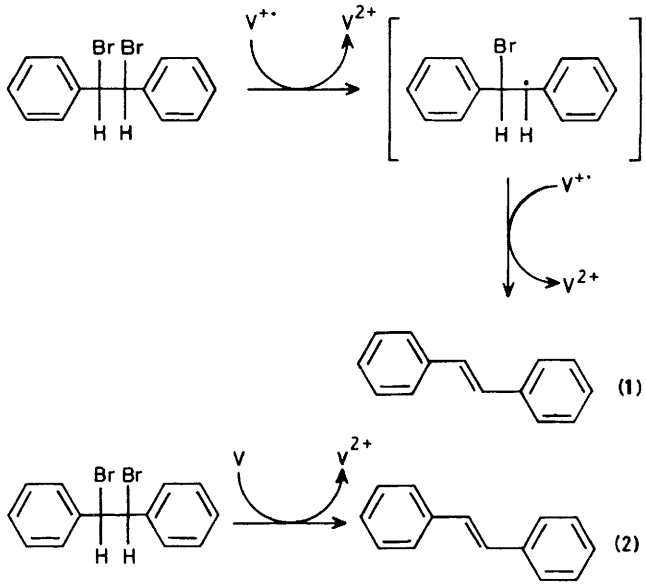


Scheme.

The first step is the reduction of poly(C_nV^{2+}) by $S_2O_4^{2-}$ anions in the outer aqueous phase. The second is the extraction of the reduced poly($C_nV^{+\bullet}$) from the outer aqueous to the inner organic phase across the capsule membrane. The third is the two-electron reduction of substrates by poly($C_nV^{+\bullet}$) in the inner organic phase. The first step may be fast, and it has no effect on the reaction rate, when $S_2O_4^{2-}$ is present in more than 2×10^{-3} mol in the outer aqueous phase (5 ml) (0.4M) (see Figure 3).

The second step, the extraction of the radical cationic poly($C_nV^{+\bullet}$) into the inner organic phase, would be affected by the structure of graft-polymers. The partition coefficient of homopolymers of poly(C_nV^{2+}) and poly($C_nV^{+\bullet}$) between chloroform and water was studied. The oxidized poly(C_nV^{2+}) (n = 3, 6, and 10) was very soluble in the water phase and only 1—6% of polymers could be extracted into the chloroform solution, independent of the spacer chain length. On the other hand, the reduced, radical cationic homopolymer of poly($C_nV^{+\bullet}$) could be extracted into the chloroform phase in 92, 63, and 3% for poly($C_{10}V^{2+}$), poly(C_6V^{2+}), and poly(C_3V^{2+}), respectively. This means that the grafted poly(C_nV^{2+}) having the longer spacer chain can be extracted into the organic phase by reduction with $S_2O_4^{2-}$ in the aqueous phase, and hence show higher reactivity in the reduction of substrates (see Tables 1 and 2).

In the third step, it is not clear whether the radical cation poly($C_nV^{+\bullet}$) can directly reduce the substrate in the inner organic phase or not. Endo *et al.* have reported that 1,2-dibromo-1,2-diphenylethane can be reduced by the radical cationic $V^{+\bullet}$ in two steps: the carbon radical intermediate is formed by reduction of a carbon–bromide bond with $V^{+\bullet}$ [equation (1)].[13] Willner and his co-workers have demonstrated that the active species is the two-electron reductant V rather than the one-electron reductant $V^{+\bullet}$ in the photochemical or chemical debromination of 1,2-dibromo-1,2-diarylethane in heterophases.[12] The reduction potential of sodium dithionite in aqueous solution (E^{o} = −0.386 V *versus* s.c.e.) is only adequate for generating the one-electron reductant $V^{+\bullet}$. The radical cation undergoes an induced disproportionation to V and V^{2+} since V^{2+} is re-extracted into the aqueous solution. As a result, the doubly reduced V can reduce the substrate in one-electron transfer reaction as a concerted or consecutive process



[equation (2)]. In this study, the reduction of substrates is carried out in heterophases across the capsule membrane and the doubly reduced poly(C_nV) seems to be easily formed by disproportionation because the other disproportionation product, poly(C_nV^{2+}), is easily re-extracted into the outer aqueous phase, as shown in the Scheme. However, we cannot decide whether the true active species of the reduction of 1,2-dibromostilbene is either poly($C_nV^{+\bullet}$) or poly(C_nV).

Graft Amount of Viologen Polymers.—Figure 4 shows the effect of the graft amount of poly($C_{10}V^{2+}$) per capsule on the $k_{obs.}$ value for reductions of 1,2-dibromo-1,2-diphenylethane and azobenzene. In both cases, the $k_{obs.}$ value increased, reached a plateau at (5—6) $\times 10^{-8}$ mol, and decreased with increasing graft amount. This is explained by the fact that there is a limited surface area of the capsule membrane for the grafted poly(C_nV^{2+}) to act as an effective electron-transfer catalyst at the interface, so that the reaction rate reaches a plateau when (5—6) $\times 10^{-8}$ mol [28 μg of poly($C_{10}V^{2+}$)] is grafted per capsule. This value roughly corresponds to 6×10^{13} polymer chains having 5×10^{2} viologen units per chain grafted onto a 2×10^{-5} m^2 surface area of a capsule membrane. Thus, one polymer chain is calculated to be grafted per 0.33 nm^2 of membrane surface. When the capsule membrane is grafted with a large excess of polymers (> 6×10^{-8} mol per capsule), the membrane surface may swell due to the hydrophilic properties of poly($C_{10}V^{2+}$) and the viologen polymer becomes an ineffective catalyst at the interface.

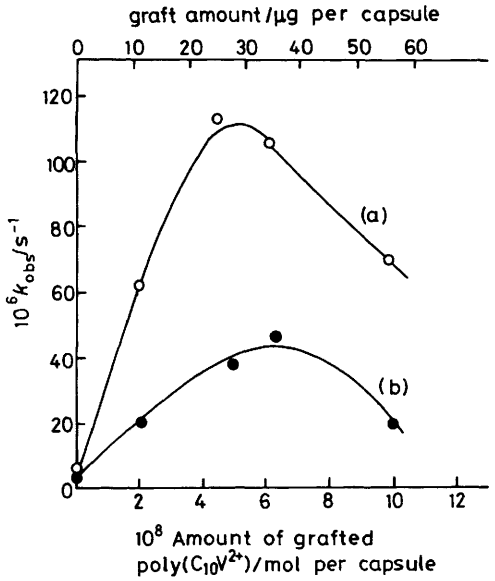


Figure 4. Effect of graft amount of poly($C_{10}V^{2+}$) per capsule on $k_{obs.}$ values at 30 °C. [$Na_2S_2O_4$] 5.0 × 10^{-3} mol in 5 ml of the outer aqueous phase (pH 10). (a) Debromination of 1,2-dibromo-1,2-diphenylethane (1.0 × 10^{-7} mol), (b) reduction of azobenzene (1.0 × 10^{-6} mol)

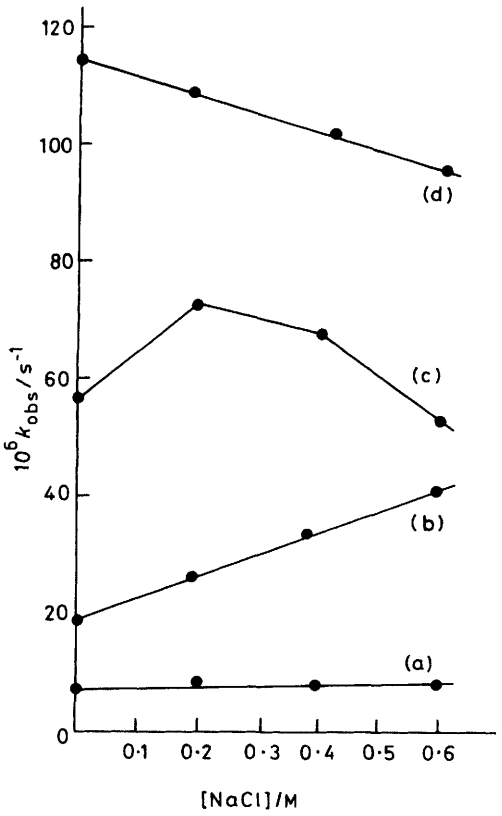


Figure 5. Effect of ionic strength on $k_{obs.}$ values of debromination of 1,2-dibromo-1,2-diphenylethane at 30 °C. [1,2-Dibromo-1,2-diphenylethane] 1.0 × 10^{-7} mol in 10 μl of the inner chloroform solution, [$Na_2S_2O_4$] 5.0 × 10^{-3} mol in 5 ml of the outer aqueous solution (pH 10), [viologen] (5—6) × 10^{-8} mol [(26—28) μg of poly(C_nV^{2+})] per capsule. (a) Non-grafted capsule, (b) poly(C_3V^{2+})-grafted capsule, (c) poly(C_6V^{2+})-grafted capsule, (d) poly($C_{10}V^{2+}$)-grafted capsule

Effect of Ionic Strength.—It is well known that the conformation of polyelectrolytes is much affected by the ionic strength of the medium. The catalytic efficiency of grafted poly(C_nV^{2+}) on the capsule membrane is expected to be affected by the ionic strength of the outer aqueous phase. Figure 5 shows the effect of the ionic strength of the outer aqueous phase on the $k_{obs.}$ value. The ionic strength was maintained by the addition of NaCl to the aqueous phase of sodium dithionite. The $k_{obs.}$ value of poly(C_nV^{2+})-grafted capsule was influenced by the ionic strength of the outer aqueous phase depending on the spacer alkyl chain length of the graft-polymer. When the capsule grafted with relatively hydrophobic poly($C_{10}V^{2+}$) was employed, the reaction rate decreased with increasing ionic strength. This means that the partition of poly($C_{10}V^{2+}$) into the aqueous phase decreased with increasing ionic strength due to the salting-out effect and the poly($C_{10}V^{2+}$) is difficult to reduce with $S_2O_4^{2-}$ anions in the outer aqueous phase. When the graft-polymer was the hydrophilic poly(C_3V^{2+}), the $k_{obs.}$ value increased linearly with increasing NaCl concentration. This is because the extraction of the reduced poly($C_3V^{+\bullet}$) into the organic phase becomes large with increasing ionic strength due to the salting-out effect. In the case of the poly(C_6V^{2+}) graft-polymers, the $k_{obs.}$ value rapidly increased and then decreased with increasing ionic strength. This is explained by a combination of the above two factors: the extraction of the reduced poly($C_6V^{+\bullet}$) into the organic phase increased at first and then the partition of the oxidized poly(C_6V^{2+}) into the aqueous phase decreased with increasing ionic strength.

Conclusions.—The capsule membrane surface-grafted with viologen-containing polymers [poly(C_nV^{2+}); n = 3, 6, and 10] can be used as a new type of reactor which catalyses reduction of 1,2-dibromostilbene and azobenzene in the inner organic phase by electron-transfer catalysis in heterophases. The viologen-polymers grafted onto the capsule membrane showed high reactivity compared with the viologen analogue dissolved in the inner organic phase, because the viologen attached to long graft-polymer chains can always exist at the interface and can move freely across two phases. Recently, we observed that a capsule membrane grafted with the 'onium salt-containing polymers (**1**) or (**2**) could much accelerate the nucleophilic substitution of substrates in the inner organic phase with nucleophilic anions in the outer aqueous phase: the 'onium salts on the graft-polymer act as a phase-transfer catalyst carrying anions across the capsule membrane.[15] When the capsule surface was immobilized with a natural enzyme (thermolysin) containing a buffer solution in the inner core, the capsule can efficiently produce dipeptides from amino acids in the outer chloroform solution.[16] These capsule membranes have the following features as a new type of reactor in liquid–liquid phases, compared with other catalyst(enzyme)-immobilized polymer-gels or membranes: (1) high reactivity due to catalysts attached to long graft-polymer chains; (2) no induction period for the reaction caused by swelling of supports, which has frequently been observed for insoluble gel-supported catalysts; and (3) the inner organic phase can be easily separated from the catalyst and the outer aqueous phase by picking up and crushing the capsule.

References

1 For Part 27, see ref. 15.
2 For a review see, T. Kondo, 'Microencapsulation, New Techniques and Applications,' Techno, Tokyo, 1979.
3 For a review see T. M. S. Chang, 'Artificial Cells,' Charles C. Thomas, Springfield, 1972.
4 For a review see Y. Okahata, *Acc. Chem. Res.*, 1986, **19**, 57.

5 Y. Okahata, S. Hachiya, K. Ariga, and T. Seki, *J. Am. Chem. Soc.*, 1986, **108**, 2863.
6 Y. Okahata, K. Ozaki, and T. Seki, *J. Chem. Soc., Chem. Commun.*, 1984, 519; Y. Okahata, H. Noguchi, and T. Seki, *Macromolecules*, 1987, **20**, 15.
7 Y. Okahata, H. Noguchi, and T. Seki, *Macromolecules*, 1986, **19**, 493.
8 Y. Okahata, K. Ariga, and T. Seki, *J. Chem. Soc., Chem. Commun.*, 1986, 73.
9 K. Ageishi, T. Endo, and M. Okawara, *J. Polym. Sci., Polym. Chem. Ed.*, 1983, **21**, 175.
10 M. Okawara, T. Hirose, and N. Kamiya, *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17**, 927.
11 Y. Saotome, T. Endo, and M. Okawara, *Macromolecules*, 1983, **16**, 881.
12 R. Maidan, Z. Goren, Y. Becker, and I. Willner, *J. Am. Chem. Soc.*, 1984, **106**, 6217; Z. Goren and I. Willner, *ibid.*, 1983, **105**, 7764; D. Mandler, Y. Degani, and I. Willner, *J. Phys. Chem.*, 1984, **88**, 4366; R. Maidan and I. Willner, *J. Am. Chem. Soc.*, 1986, **108**, 1080.
13 T. Endo, Y. Saotome, and M. Okawara, *J. Am. Chem. Soc.*, 1984, **106**, 1124.
14 T. Seki and Y. Okahata, *J. Polym. Sci., Polym. Chem. Ed.*, 1986, **24**, 61.
15 Y. Okahata, K. Ariga, and T. Seki, *J. Chem. Soc., Chem. Commun.*, 1985, 921; *J. Org. Chem.*, 1986, **51**, 5064.
16 Y. Okahata and K. Ijiro, *J. Chem. Soc., Perkin Trans. 2*, in the press.

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