POLYVIOLOGENS

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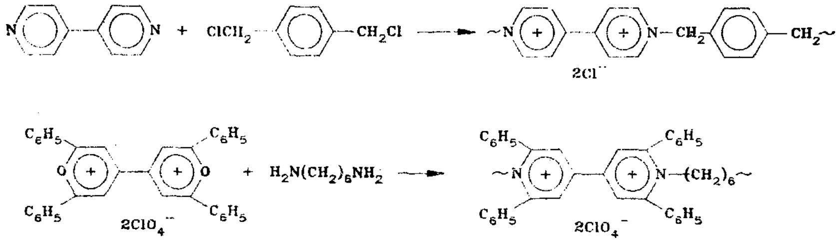
UDC 547.828:541.64:542.952.6

Polymers that contain γ,γ'-dipyridinium "viologenic" groupings are of interest as electron-exchange membranes [1], and their study is also extremely promising in connection with possible semiconductor and photoinitiating properties. In addition, such polymers can be used for the preparation of electron-exchange resins.

We have obtained two polymers with viologenic links in the main chain. Poly(N,N'-p-xylylene-4,4-dipyridinium dichloride) (I) is formed by fusing 4,4-dipyridyl with p-xylylene dibromide [sic], and poly(N,N'-hexamethylene-2,2,6,6-tetraphenyl-4,4-dipyridinium dichloride) (II) is formed by an exchange reaction of 2,2,6,6-tetraphenyl-4,4-bispyrylium diperchlorate with hexamethylenediamine (by heating in methanol for 2 h).



After reprecipitation from methanol by means of acetonitrile, both substances were almost colorless amorphous powders that decomposed at 230-240°C (I) and 130-135°C (II) and were insoluble in acetonitrile but soluble in DMF, acetic acid, and water. The molecular masses (by the Rast method) were 1340 (I) and 2200 (II). Both compounds undergo redox reactions that are characteristic for viologens and lead to stable viologenic poly(cation radicals); in particular, they are reduced by the I^- anion, alkali, and zinc and dehydrogenate triethoxysilane. Under UV irradiation the rates of these reactions increase sharply, and polyviologens I and II rapidly dehydrogenate the leuco base of Malachite Green, hydrazobenzene, and methanol.

The EPR spectra of the poly(cation radicals) have well-resolved hyperfine structures that are peculiar to monomeric analogs ($a_N = 4.2$, $a_H = 1.4$, and $a_H = 4.8$ Oe) in which the form of the spectra depends very little on the nature of the substituents attached to the nitrogen atom [2]. The absence of broadening of the lines in the spectra constitutes evidence for the absence of appreciable spin-spin coupling between the individual paramagnetic links that enter into the main chain.

The electrochemical properties of polyviologens I and II were studied by means of cyclical voltammetry (E_{pK} of I = −0.43 V, −0.86 V; E_{pK} of II = −0.82 V, −1.27 V; DMF, 0.1 mole/liter $NaClO_4$ relative to a saturated calomel electrode, on platinum electrodes).

The absence of a substantial difference in the reduction potentials (E_{pK}) of polyviologen I and the model N,N'-dibenzyl-4,4-dipyridinium compound (E_{pK} = −0.40 V, −0.80 V) indicates the autonomous character of the reduction of the dicationic groupings in the main chain. It follows from the cyclical voltammetric curves that the reduction of polycations I and II proceeds in two reversible one-electron (with respect to each link) waves corresponding to stable poly(cation radicals) and then to completely reduced "quinoid" structures. Polymers of the latter type have the properties of active electron donors: they reduce triphenylpyrylium cations to pyranyl free radicals and also reduce diazonium

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0009-3122/85/2109-1060$09.50

and triarylmethyl cations and sterically hindered o-quinones.

LITERATURE CITED

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