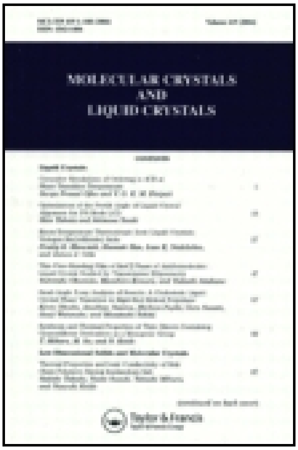

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Organizational Characteristics of Some Ionene Oligomers Bearing the Viologen Mesogenic Moiety

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ORGANIZATIONAL CHARACTERISTICS OF SOME IONENE OLIGOMERS BEARING THE VIOLOGEN MESOGENIC MOIETY

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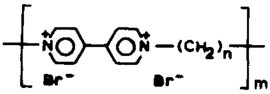
Abstract The synthesis and characterization of some ionene oligomers bearing the viologen moiety and separated by methylenic spacers of varying length is reported. The organization of these oligomers, which was the main subject of the characterization was studied by various methods including X-ray powder diffraction patterns, differential scanning calorimetry and electron microscopy. For these oligomers, both in the bulk and the solution a **lamellar** structure was proposed consisting of alternate polar layers, formed through the electrostatic interaction of quaternary nitrogens with bromides, and of the lipophilic layers of the methylenic spacers.

INTRODUCTION

We report in this paper the synthesis and characterization of a class of ionene polymers[1], or rather oligomers, bearing the viologen mesogenic moiety[2] separated by methylenic spacers of the varying length i.e.



Scheme where n = 4,10,12

The main objective of this work was to investigate the effect of viologen mesogenic moiety, coupled with the various spacers, on the organizational characteristics of the above oligomers in the bulk and the aqueous phase. A second

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incentive will be to investigate whether the incorporation of viologen **groups** in the main chain of the polymers or oligomers affects the well-known property of one electron reduction of the monomeric counterpart i.e., of methyl viologen which is used extensively as a relay in photochemical solar conversion[3] and also as **an electron-transfer catalyst** (ETC) in oxidation-reduction systems[4]. In this paper however the investigation is limited to the first objective i.e.,to the structural organization of the oligomeric chains.

EXPERIMENTAL

Polymer Synthesis

Equimolar quantities of 4,4 bipyridine are reacted in acetonitrile with certain unbranced dibromides i.e. with 1,4 dibromobutane, 1,10 dibromodecane and 1,12 dibromododecane resulting in the synthesis of $PV^{2+}C_4$, $PV^{2+}C_{10}$ and $PV^{2+}C_{12}$ ionene polymers respectively. Polyquaternization was performed at room temperature and the polymers precipitating from the reaction mixture were separated and dried in vacuum over phosphorous pentoxide. Oligomer formation and its subsequent precipitation is relatively fast for $PV^{2+}C_4$, while several days were required for the quantitative precipitation of $PV^{2+}C_{10}$ and primarily of $PV^{2+}C_{12}$.

Analysis Calcd for $PV^{2+}C_4$ ($C_{14}H_{16}N_2Br_2$):C,45.20%, H,4.30%; N, 7.52%. Found: C, 44.79%; H, 4.18%; N, 7.26%.

Analysis Calcd for $PV^{2+}C_{10}$ ($C_{20}H_{28}N_2Br_2$): C, 52.67%;H,6.14%; N, 6.14%. Found: C, 52.35%; H, 6.07%; N, 6.39%.

Analysis Calcd for $PV^{2+}C_{12}$ ($C_{22}H_{32}Br_2N_2$): C,54.58%;H,6.66%; N, 5.78%. Found: C, 54.79%; H, 6.56%; N, 5.89%.

The thermal behavior of the polymers was studied with a Du Pont R90 thermal analyzer in conjunction with 910 differential scanning calorimeter operating at 10°C/min.

Proton NMR spectra were recorded on a Varian spectrometer operating at 80M Hz. For $PV^{2+}C_4$ D_2O was used as solvent while DMSO-d_6 was used as solvent for $PV^{2+}C_{10}$ and $PV^{2+}C_{12}$.

X-ray powder diffraction patterns were obtained with a Phillips 1130 diffractometer, using CoKα radiation.

Electron microscopy experiments were performed with a Siemens Elmiscope electron microscope operating at 75 kV. **An aliquot of 0.01 M aqueous $PV^{2+}C_4$ solution was applied** on carbon-coated electron microscope grids and the material adhering on the grids was stained by a 2% uranyl acetate solution by washing it several times with this solution. The dissolution of $PV^{2+}C_{10}$ and $PV^{2+}C_{12}$ was facilitated by sonicating their aqueous dispersions with a MSE sonicator. However these oligomers were not completely dissolved at room temperature.

RESULTS AND DISCUSSION

The "oligoquaternization" was preferentially performed at room temperature in order to avoid possible decomposition of the oligomers. Acetonitrile was used as solvent since the reaction proceeds faster in it[5] as compared to several other solvents. For the characterization experiments the materials were used as obtained from precipitation from acetonitrile without any after treatment.

Proton NMR spectra were consistent with the ionene structure formation. Thus, for $PV^{2+}C_4$ (Fig. 1) the peak at 4.74 ppm is attributed to $\gtrdot N^+ - CH_2 -$ while the peak at 2.30 ppm to $\gtrdot N^+ - CH_2 - CH_2 -$. The peak at 3.60 ppm is assigned to $BrCH_2-$. i.e. to unreacted terminal group of the dibromide and the peaks between 9-7.5 ppm to the heterocyclic protons. $PV^{2+}C_{10}$ and $PV^{2+}C_{12}$, bearing long spacers have, as expected similar spectra, Fig. 2 and Fig. 3, showing in addition to the above assignments, a peak at 1.25 ppm of

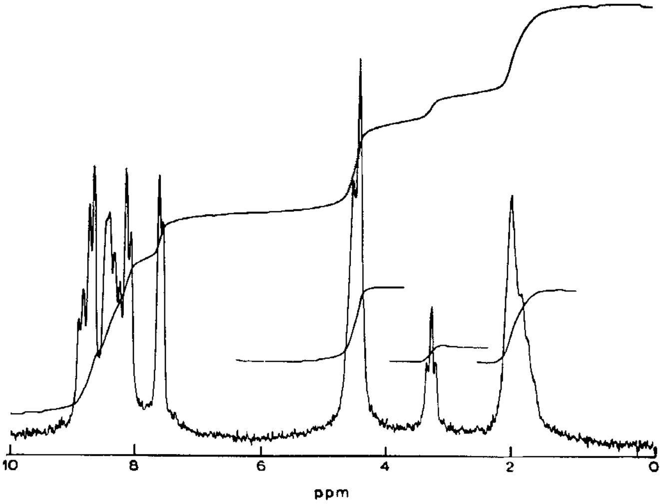

FIGURE 1. Proton NMR spectrum of $PV^{2+}C_4$ in D_2O

central methylenes $-(CH_2)_n-$ while the peak of $>N^+-CH_2\underline{CH_2}-$ was shifted at about 1.90 ppm. NMR spectra were employed

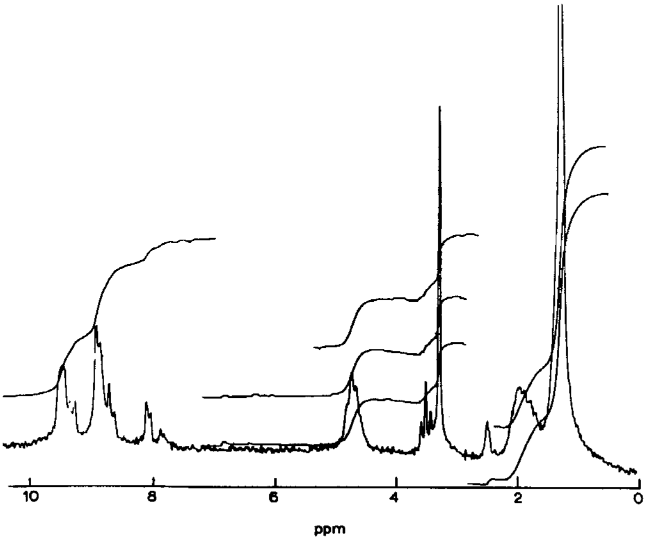

FIGURE 2. Proton NMR spectrum of $PV^{2+}C_{10}$ in DMSO-d_6.

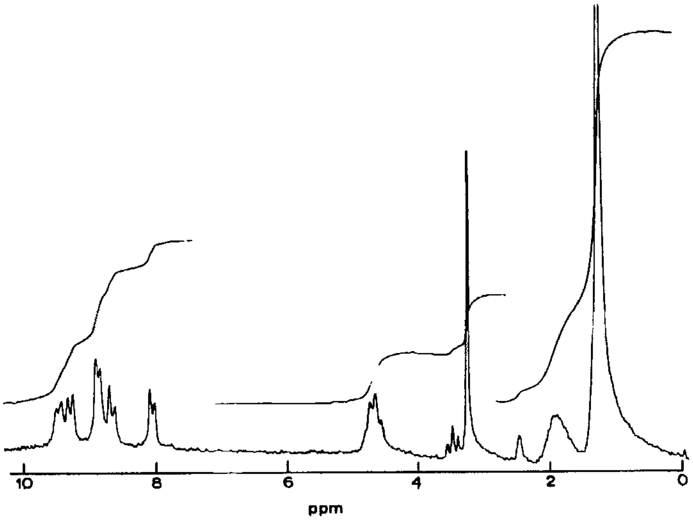

FIGURE 3. Proton NMR spectrum of $PV^{2+}C_{12}$ in DMSO-d_6.

for the determination of the degree of polymerization ($\overline{DP}$) by the end group method. Thus the intergrated values of $BrCH_2$- protons absorption were compared to heterocyclic or central methylenes, $-(CH_2)_n-$, values and the $\overline{DP}$ for the three oligomers were determined to be equal to 3-4.

According to the structural characteristics[6] for the formation of main-chain liquid crystalline polymers which requires the existence of rigid rod groups connected by flexible spacers, it may be assumed that the introduction of the rigid viologen mesogenic-like moiety in the main chain of the oligomers coupled with the flexible methylenic spacers would result, in principle, in the exhibition of mesomorphic character. The first member of the series, with n = 4, which was examined on the hot stage of a polarizing microscope, decomposed before melting. This is attributed to the predominance of the "salt-like" character of the quaternary nitrogens over the lipophilic character of the short spacer. It was also shown, though not expected, that the two other oligomers with spacers $-(CH_2)_{10}-$ and $-(CH_2)_{12}-$ also decompose before melting, this behavior again attributed to the same reason as before. Oligomer blends, did not also show significant melting point depression. It is however possible that the introduction of a longer spacer, i.e., C_{18} or C_{20} could lower the melting point allowing the appearance of a mesophase.

However, the suspected subtle modifications, in the oligomer structure during heating were revealed by differential scanning calorimetry. Thus $PV^{2+}C_4$ (Curve I), Fig. 4. due to its short spacer and very possibly to the lack of conformational transformations, decomposes at about 131°C without any intermediate phase transition, whereas $PV^{2+}C_{10}$ (Curve II) and $PV^{2+}C_{12}$ (Curve III) show multiple melting behavior. Specifically $PV^{2+}C_{10}$ exhibits two phase transitions before decomposing at about 120°C while $PV^{2+}C_{12}$ shows analogous transitions before its decomposition at about 126°C. These solid-solid phase transitions, which were not observable during the heating on the hot stage of the polarizing microscope are certainly attributed to the conformational melting of the long spacers of $PV^{2+}C_{10}$ and $PV^{2+}C_{12}$. In this connection it is interesting to notice that analogous polymers[7], $-\!\!(H_2N\,(CH_2)_m\,NH_2ZnX_2)\!\!-_n$, containing polymethylenic groups alternating with polar $-NH_2ZnX_2-$ moieties are crystalline and specifically that member with a C_{12} spacer and X=Cl also shows smectic mesophase with long range layer stacking. As seen by x-ray powder diffraction patterns, Figs. 5-7, the oligomers used in this study without any attempt to crystallize them showed peaks characteristic of crystalline structure

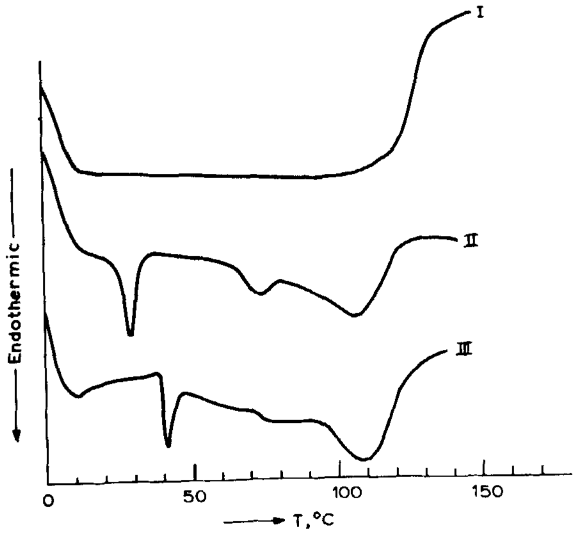

FIGURE 4. DSC traces of the oligomers.

superimposed on wide angle bands characteristic of amorphous materials. It is clear that $PV^{2+}C_4$ possesses higher degree of crystallinity, as compared to $PV^{2+}C_{10}$ or $PV^{2+}C_{12}$ due to its shorter spacer contributing to a more efficient packing of the oligomers. By analogy with the previously mentioned polymers and the structural hypothesis that ionic or

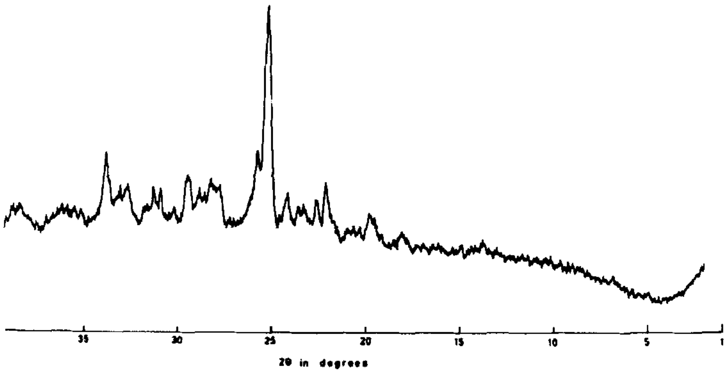

FIGURE 5. X-ray diffraction pattern of $PV^{2+}C_4$.

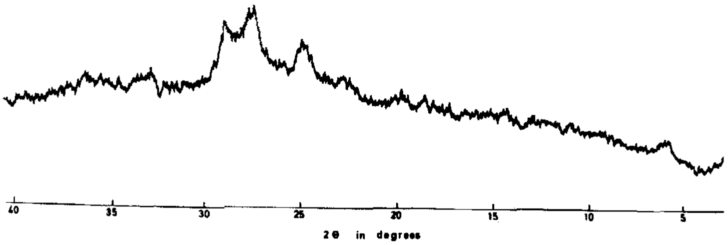

FIGURE 6. X-ray diffraction pattern of $PV^{2+}C_{10}$.

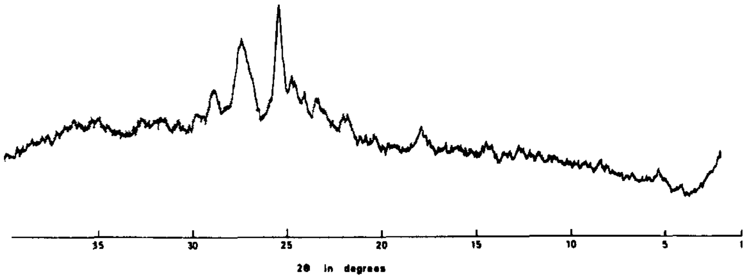

FIGURE 7. X-ray diffraction pattern of $PV^{2+}C_{12}$.

strongly polar groups included in hydrocarbon portions tend to segregate in layers for electrostatic reasons[7,8], we may envisage that the viologen oligomers run parallel in such a way that bidimensional polar layers consisting of the quarternary nitrogens and bromides are formed which are sandwiched between the lipophilic layers formed by the methylenic spacers. In ionic layers ionic-type bonding is involved while van der Waals forces are acting between the hydrocarbon spacers of the lipophilic layers. Thus the weak peaks in the region of higher angles than $2\theta=30^\circ$ are assigned to the frozen hydrocarbon[9,10] spacers while those in the low angle region to the ionic layers[9]. Layered structures are also formed by long-chain ammonium[11] and quaternary ammonium salts[9,12] which upon heating are transformed through conformational melting (solid-solid phase transition) to a smectic-like phase in which ionic bonding inside the polar layers remains practically intact. By further heating certain of these functionalized monomeric quaternaries are transformed to isotropic melts. This was not however the case with the viologen oligomers, apparently because of the incorporation of the quaternary nitrogen within the oligomeric backbone.

Electron microscopy of the aqueous solution of the oligomers showed the formation of lamellar structures (Fig.8-10). As shown in the electron microscope photographs folding or overlapping of lamellae usually occurs. The formation of these structures may be attributed to a parallel placement of the oligomers held together by ionic and van der Waals forces forming the lamellar structure. A similar structure, without however the involvement of water, was proposed before for the same oligomers in the bulk. In

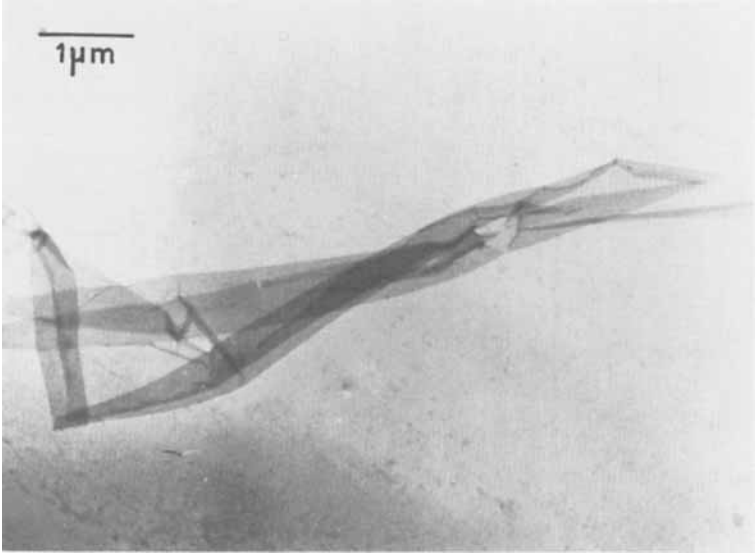

FIGURE 8. Electron micrograph of $PV^{2+}C_4$.

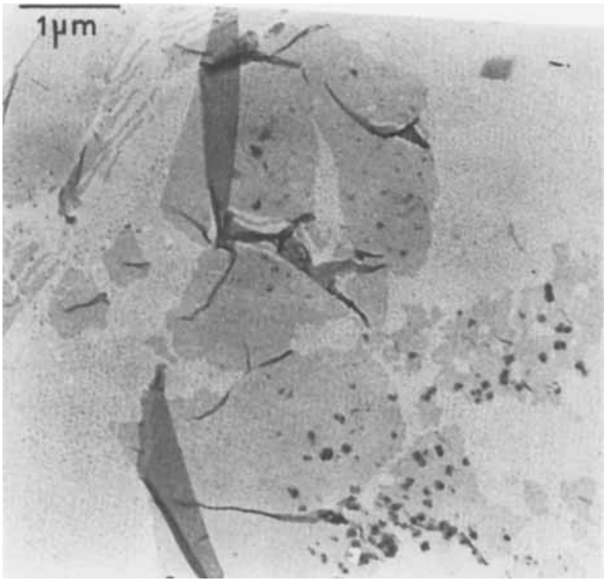

FIGURE 9. Electron micrograph of $PV^{2+}C_{10}$.

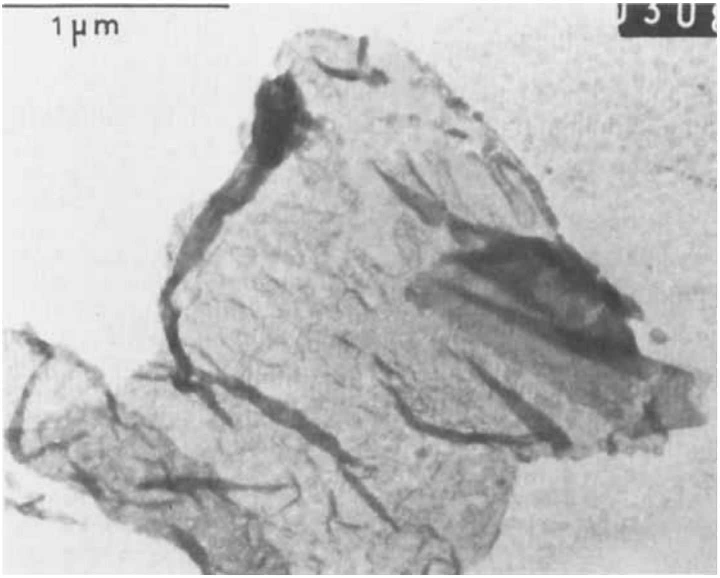

FIGURE 10. Electron micrograph of $PV^{2+}C_{12}$.

Figure 11 is shown the organization of the oligomers in the

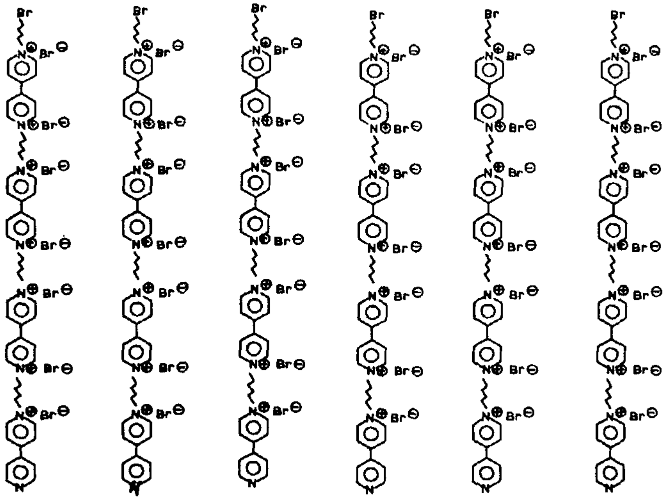

FIGURE 11. Parallel organization of oligomers resulting in the formation the lamellar structure.

lamella the thickness of which corresponds to the length of the oligomer i.e. 3-4 monomer units. In the diagram only one site of the lamella is seen to be quaternized which however is irrelevant to the actual situation. To our knowledge this is the first time that monolayers are formed by ionene oligomers, in which alternate polar and hydrophobic moieties are bound by covalent bonding. Solubilizing water molecules are placed at the surface and the interior of the lamella in the vicinity of quaternary nitrogen. Also, certain a,ω Bis (paraquat) amphiphiles[13] form, among other organized assemblies monolayer organic crystals which were observed by electron microscopy. These crystals result from an organization of the amphiphiles analogous to the ionene oligomers, Fig. 11. As far as the accomodation of the long-chain end groups of $PV^{2+}C_{10}$ and $PV^{2+}C_{12}$ in the aqueous environment of the quarternary nitrogens is concerned, it, may be assumed that such a placement can occur in view of the recent findings on the aggregation of surfactants in micelles. According to these new ideas of micellar structure [14] hydrophobic portions including chain termini can coexist with polar heads and water molecules forming the unique environment of Stern region.

Further work will be done in order to extend the series to these ionene oligomers by the use of various dibromides and to investigate to what extent the conditions of quaternization affect molecular weights and consequently their organizational behavior as well as their one-electron reduction property.

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