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ELECTRO-OPTICAL STUDIES ON SYNTHETIC POLYELECTROLYTES.

I. Ultraviolet electric dichroism of poly-N-alkylvinylpyridinium bromides in aqueous solution

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The electric dichroism of aqueous solutions of poly-2- and 4-vinylpyridinium bromides has been measured in the 220 to 300 nm region. From the knowledge of the assignments of the absorption bands, the orientation of the pyridinium ring with respect to the macromolecular axis was determined for the poly-N-butyl-4-vinylpyridium bromide.

An estimation of the birefringence contribution in the visible region originating from these ultraviolet dichroic bands revealed that the negative birefringence observed mainly arose from electronic transitions at shorter wavelengths.

1. Introduction

The dynamo-optical properties of the polyvinylpyridinium salts have been extensively studied by several authors [1–3]. This kind of vinylic polyelectrolyte reaches a very extended conformation at high dilution and low salt concentration as a result of the electrostatic repulsion between the charged side groups.

We have studied the conformation and the electro-optical properties of the polyvinylpyridinium salts and of related polyelectrolytes [4]. We have also previously reported in a preliminary note that the poly-N-alkylvinylpyridinium salts gave high negative values of the birefringence in aqueous solution [5], in good agreement with an orientation of the pyridinium ring perpendicular to the main axis of the chain.

We describe in the present paper the results of linear electric dichroism and of electronic absorption spectra measurements on polyalkylvinylpyridinium salts in order to obtain more accurate information on the orientation of the pyridinium ring with respect to the main axis of the particle.

If a pulsed electric field is applied to a solution of such macromolecules, the reduced dichroism at infinite field strength

$$\left(\frac{\Delta A}{A}\right)_s = \left(\frac{A_\parallel - A_\perp}{A}\right)_s \tag{1}$$

(where $A_\parallel$ and $A_\perp$ are the absorbances in the polarisation directions respectively parallel and perpendicular to the field) is related to the angle α between the orientation axis of the particle and the transition moment direction of the corresponding absorption band by the relation

$$\left(\frac{\Delta A}{A}\right)_s = \tfrac{3}{2}(3\cos^2\alpha - 1). \tag{2}$$

The determination of $(\Delta A/A)_s$ allows thus to obtain information about the orientation of a chromophore provided that the angles α of two transitions polarized in different directions in the pyridinium ring can be obtained.

2. Experimental

The polyvinylpyridinium salts were obtained by a direct quaternisation of the fractionated samples of the poly-2- and 4-vinylpyridines in nitromethane solution. The average viscometric molecular weights of the poly-N-butyl-4-vinylpyridinium bromide (4 PVP. BuBr C) and of the poly-N-methyl-2-vinylpyridinium bromide (2 PVP.MeBr D) are equal to 557000 and 437000 respectively. The quaternization degrees determined by potentiometric titration of the bromide counterions are found around 91% for 4 PVP. BuBr and 71% for 2 PVP. MeBr. The preparation and the characterization of the polyvinylpyridinium salts will be further described in a subsequent paper.

Monomeric model compounds of our polyelectrolytes have been prepared by a direct addition of alkylbromides to the 2- and 4-ethylpyridines in the absence of solvent; these very hygroscopic salts (4 EtPy. MeBr, 4 EtPy. BuBr and 2 EtPy. MeBr) were washed with anhydrous diethylether and stored in the presence of phosphorous pentoxyde.

The measurement and the calculation of the electric dichroism were made as reported in previous papers [6,7]. All the experiments are performed in the absence of any added salt.

3. Results and discussion

The electronic absorption spectra of the 4-ethyl-N-alkylpyridinium bromides in a polar solvent (water/methanol 50/50% vol.) are represented in fig. 1; two main absorption bands are observed, one near 255–260 nm and another at around 225 nm. The absorption spectrum of the 2-ethyl derivative is quite different and characterized by a main absorption band around 265 nm. The absorption spectra of the 2 PVP. MeBr and 4 PVP.BuBr in aqueous solution are shown in figs. 2 and 3.

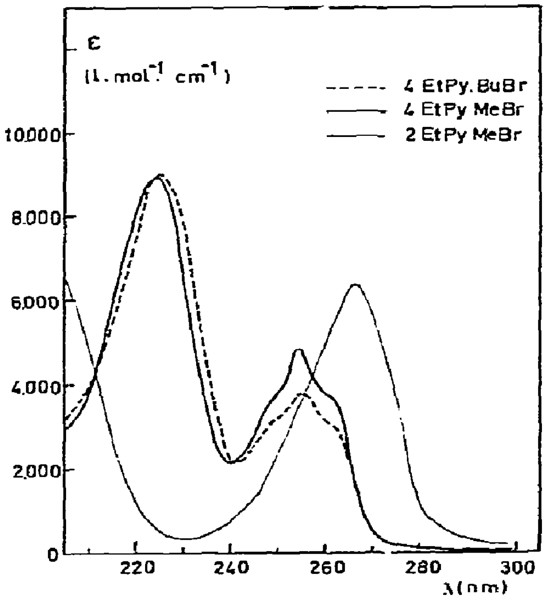

Fig. 1. Electronic absorption spectra of some ethyl-N-alkylpyridinium bromides.

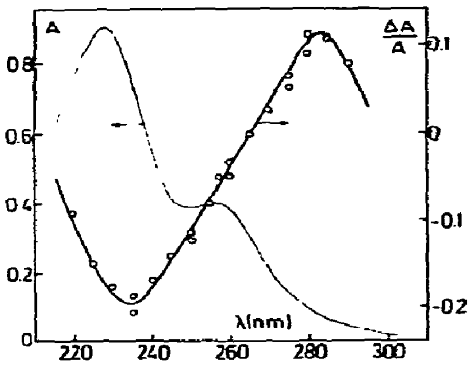

Fig. 2. Absorption and dichroism spectra of polybutyl-4-vinylpyridinium bromide in aqueous solution ($C = 0.075$ mg/cm^3).

The reduced electric dichroism spectra, measured at an electric field strength of 13 kV/cm, are shown in the same figures. The reduced dichroism values appear to vary in the spectral range investigated, so that we shall have to consider the respective influence of several transition moments. The change of sign of the dichroism for the 4 PVP.BuBr sample occurs at about 270 nm.

Fig. 4 shows the field strength dependence of the

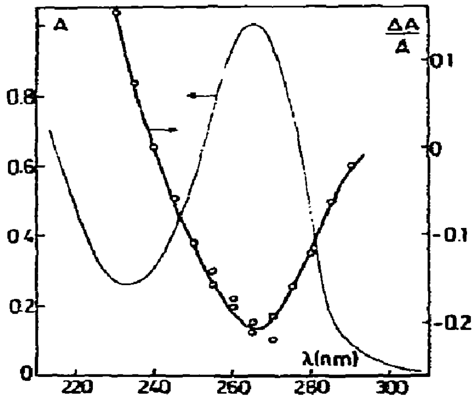

Fig. 3. Absorption and dichroism spectra of polymethyl-2-vinylpyridinium bromide in aqueous solution ($C = 0.075$ mg/cm^3).

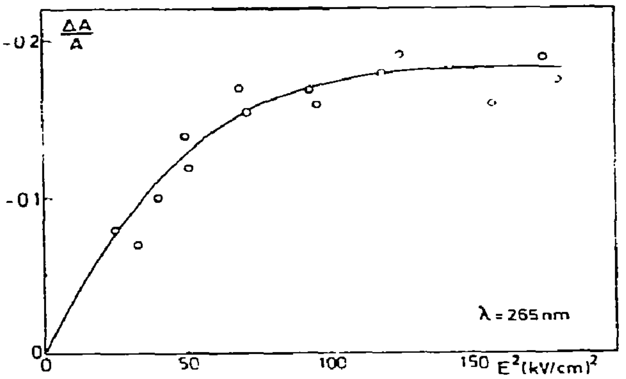

Fig. 4. Electric field dependence of the reduced dichroism for 4 PVP.BuBr sample at 0.075 mg/cm^3.

dichroism of 4 PVP.BuBr (C = 0.075 mg/cm^3) at 255 nm. Despite the scatter of the experimental points, it seems that the ΔA values are practically constant at field strengths higher than 11 kV/cm, so that we could consider that the dichroism measured at $E \approx 13$ kV/cm is close to the saturation value. However, the analysis of the electric birefringence results [4] allows us to determine a more precise value of the orientation function $\Phi(\beta,\gamma)$:

$$\Phi(\beta,\gamma) = \frac{\Delta n}{\Delta n_s} = \frac{\Delta A}{\Delta A_s}\,, \tag{3}$$

which at the same polyelectrolyte concentration and at 13 kV/cm approaches a value 0.8. The reduced dichroism values at saturation obtained in this way are given in table 1. The application of relation 2 gives the average values of the angle α mentioned in the same table. We recall that the reduced dichroism values vanish for an angle α equal to 54°45′.

It is known that the main $\pi \rightarrow \pi^*$ transitions of the chromophores like those investigated here are polarized in the plane of the heterocyclic rings, whereas the $n \rightarrow \pi^*$ transitions at longer wavelength (≈ 280 nm) have a polarization direction perpendicular to this plane (fig. 5); the latter transitions are not expected to be found in the quaternized derivatives. Recently, Ferré et al. have examined by a theoretical treatment the repartition of the positive charge of the quaternary nitrogen on the carbon atoms of the ring for some heterocyclammonium derivatives [8]. Taking into account the change in the molecular orbitals due to the presence of the positive charge, these authors estimated not only the intensities and the directions of the transition moments but also the transition energies, which are in good agreement with the experimental observations; this is mainly due to the fact that these authors have considered the polarization of the σ-bounds, particularly important for these ionic compounds [8,9]. Table 2 summarizes the transition energies for the 1-4 dimethylpyridinium ring together with the values we have observed for the 4 EtPy.MeBr; the transitions of lower (λ ~ 255 nm) and of higher energy (λ ~ 225 nm) are respectively polarized along the x and y axis (fig. 5). The latter transition is of particular interest since it allows to explain the negative sign of the dichroism at wavelength lower than 270 nm in the case of the 4 PVP.BuBr sample; the corresponding transition is in first approximation perpendicular to the axis of the macromolecule (fig. 5).

Table 1
Reduced electric dichroism values and orientation angles of the transition moments for the polyalkylvinylpyridinium bromides

Sample	λ(nm)	$\Delta A/A$ (13 kV/cm)	$(\Delta A/A)_s$	α
4 PVP.BuBr C	230	−0.2	−0.25	58°
	280	+0.1	+0.125	53°
2 PVP.MeBr D	265	−0.2	−0.25	58°

On the contrary, the positive sign of the dichroic band at longer wavelength for the 4 PVP.BuBr is more difficult to justify. It cannot be attributed to the

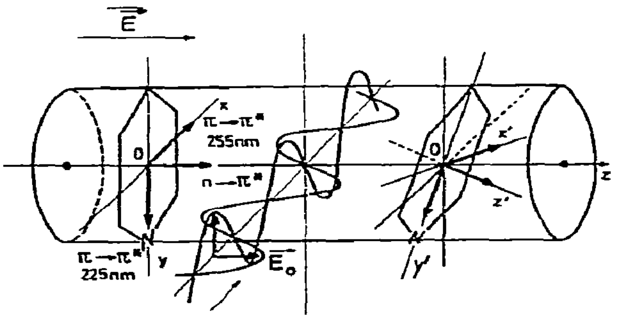

Fig. 5. Schematic representation of the orientation of the pyridinium ring and of its principal transition moments in the polyelectrolytic particles.

Table 2
Transition energies and orientation of the transition moments in the pyridinium rings

Calculated values			Experimental values		
1-4 dimethylpyridinium			1-4 dimethylpyridinium [b]		4-ethyl-N-methylpyridinium [c]
ΔE (eV) [a]	λ (nm)	transition moment	E (eV) [a]	λ (nm)	λ (nm)
4.71	263.2	x	4.73	262.1	262
			4.86	255	255
5.36	231.3	y			224
6.46	192	x			
6.68	185.6	y			

[a] These values are given in ref. [8]; [b] values measured in water; [c] values measured in water–methanol 50/50 vol.%.

$n \rightarrow \pi^*$ transition polarized in the direction perpendicular to the pyridinium plane [10] because no corresponding absorption band is observed in this region and also because these transitions should be shifted to shorter wavelengths in polar solvents. Furthermore the $n \rightarrow \pi^*$ transitions could only arise from the non-quaternized pyridine units which are present in the polybutyl-4-vinylpyridinium bromide only in small amounts (5 to 10%) Although these $n \rightarrow \pi^*$ transitions could contribute to a small extent to the positive dichroism observed, we must admit that they could not be the only factor responsible for such an intense dichroic band.

The only possible interpretation we see at the moment is to assume that the pyridinium ring is not rigorously perpendicular to the main axis of the particle. From the simple observation of molecular models, it appears that the pyridium rings cannot be stacked at an angle of about 55–60° with respect to the z axis of the particle, because of steric hindrance. If we consider that the $\pi \rightarrow \pi^*$ transition at 225 nm is practically perpendicular to the z axis, we can explain the low corresponding dichroism value (–0.2) by taking into account the kinked aspect of the chain. Owing to the flexibility of the vinylic chain, the polyvinylpyridinium salts cannot be expected to exist in a fully extended conformation, even at the very high dilutions used. From the decay curves of the electric birefringence, we have determined the mean value of the relaxation time $\bar{\tau}$ and estimated the chain length on the basis of an ellipsoidal model [4]. We shall not report these results in detail here, but we only indicate that the $\bar{\tau}$ value for the 4 PVP.BuBr C sample is around 60 μs at a concentration of 0.072 mg/cm^3. The $\bar{\tau}$ values extrapolated to zero concentration amount to 90 μs. The corresponding chain lengths are 1900 Å and 2400 Å respectively. These values differ significantly from the length of the fully stretched chain $L_T \approx 4600$ Å calculated with the aid of the polymerization degree and of the length of the monomeric unit, even if we take for the latter parameter the effective contribution of a vinylic unit to a polyelectrolytic chain, i.e., 1.9 Å [11]. The discrepancy observed between the experimental and the calculated lengths is indicative of the presence of flexible joints along the backbone.

The shape of the dichroism spectrum can be explained easily after decomposition of the absorption spectrum in two components (fig. 6), one centered at 227 nm and the other, about four times less intense, centered at 262 nm. Taking values of –0.2 and 0.1 for the reduced dichroisms of the y (227 nm) and x (262 nm) transitions respectively, we obtain the calculated reduced dichroism spectrum shown in fig. 6, whose shape agrees with the experimental spectrum (fig. 2).

In the case of the 2 PVP.MrBr, the decrease of the reduced dichroism above 270 nm can be similarly attributed to the presence of a transition with positive dichroism revealed by a slight shoulder in the absorption spectrum in the region of 275 nm. The more important overlapping between the two transitions as compared to the 4 PVP.BuBr, results in a decrease of the reduced dichroism rather than a change in its sign. No experimental data are, however, available for the exact assignment of the transitions for the 2 PVP.MeBr

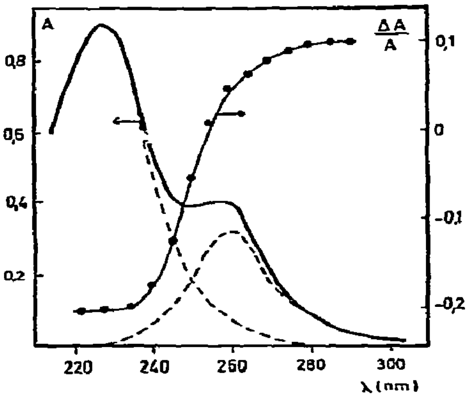

Fig. 6. Decomposition of the experimental absorption spectrum of 4 PVP.BuBr into two components. The reduced dichroism spectrum was calculated making use of the relation

$$\left(\frac{\Delta A}{A}\right)_{\text{total}} = \left(\frac{\Delta A_1}{A_1}\right)\frac{A_1}{A} + \left(\frac{\Delta A_2}{A_2}\right)\frac{A_2}{A},$$

where A_1 and A_2 are the absorptions for the transitions centered at 227 and 260 nm respectively. The values of $\Delta A_1/A_1$ and $\Delta A_2/A_2$ were taken equal to -0.2 and 0.1 respectively.

and we were unable to measure the dichroism below 230 nm, so that it is impossible to calculate the orientation of the pyridinium ring in this case.

Another possible explanation for the wavelength dependence of the reduced dichroism would be to consider that exciton interactions between the pyridine ring would result in parallely and perpendicularly polarized components of the absorption band as it is observed in the case of proteins and polypeptides [12].

This could explain the variation of $\Delta A/A$ with the wavelength in the 225 nm band of 4 PVP.BuBr and in 275 nm band of 2 PVP.MeBr. In the case of the 4 PVP derivative, we believe that the low values of the electric dichroism mainly arise from the kinked aspect of the chain of the polyelectrolyte chain. This results in a slight tilting of the y axis of the pyridinium side group with respect to the orientation axis. This pyridinium group has also its x axis turned through a certain angle around the y axis.

An estimation of the birefringence which should be observed in the visible region ($\lambda = 550$ nm) if it originated solely from the ultra-violet band investigated, can be made using the correlation between the birefringence dispersion curve [$\Delta n(\hat{\nu})$ versus $\hat{\nu}$] and the dichroism spectrum [7,13]. Assuming a gaussian shape of the dichroism spectrum, the birefringence at a wave number $\hat{\nu}$ is found to be given by the relation:

$$\Delta n(\hat{\nu}) = \sum_i \left(2.303\, \Delta A_{0,i} \sqrt{\pi}/2\pi^2 l \hat{\nu}\right) \times \left(\exp(-q_i^2)\int_0^{q_i} \exp(u^2)\,\mathrm{d}u - \Delta\hat{\nu}_{1/2,i}/3.33(\hat{\nu}_{0,i}+\hat{\nu})\right), \tag{4}$$

where $\Delta A_{0,i}$ is the dichroism at the maximum of the i-band, l the optical path length, $\hat{\nu}_{0,i}$ the wave number corresponding to the maximum of the dichroism band; q is equal to $1.6651\,(\hat{\nu}_{0,i} - \hat{\nu})/\Delta\hat{\nu}_{1/2,i}$ where $\Delta\hat{\nu}_{1/2,i}$ represents the band width at half maximum.

The integral term $\exp(-q^2)\int_0^q \exp(u^2)\,\mathrm{d}u$ becomes approximately equal to $1/2q$ for the values of q greater than 4 [14]. Taking $\hat{\nu} = 18180\ \text{cm}^{-1}$ ($\lambda = 550$ nm) and $l = 1$ cm, we found, respectively, for 2 PVP.MeBr:

$\hat{\nu}_0 = 37740\ \text{cm}^{-1}$ ($\lambda = 265$ nm), $q = 8.6$,

$\Delta\hat{\nu}_{1/2} \approx 3800\ \text{cm}^{-1}$, and $\Delta n(\hat{\nu}) = -0.85 \times 10^{-7}$,

for 4 PVP.BuBr:

$\hat{\nu}_0 = 44050\ \text{cm}^{-1}$ ($\lambda = 227$ nm), $q = 22$,

$\Delta\hat{\nu}_{1/2} \approx 1950\ \text{cm}^{-1}$ and $\Delta n(\hat{\nu}) = -0.28 \times 10^{-7}$.

The experimental Δn values at the same concentration are equal to -5×10^{-7} and -3.5×10^{-7} for 2 PVP.MeBr and 4 PVP.BuBr respectively, i.e., six to ten times higher than the calculated values. It thus appears that the negative birefringence in the visible region does not mainly arise from the $\pi \to \pi^*$ transitions of the pyridinium ring (225–265 nm), but from other electronic transitions at shorter wavelengths.

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