Hydrodynamic properties of poly-1, 2,5-trimethyl- and 2,5-dimethyl-4-ethynilpyperidol-4 hydrochlorides in solution

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Poly-1,2,5-trimethyl- and 2,5-dimethyl-4-vinylethynyl-pyperidol-4 hydrochlorides with strong polyelectrolyte properties have been investigated in water–salt and water–alcohol mixtures. The parameters K_η and a, K_s and b in the Mark–Houwink equation, the unpertubed dimensions K_0 and flexibility factor of polymer chain σ were determined in these solvents. We also studied the influence of ionic strength, the values of counterion charges and temperature on the size of polyelectrolyte molecules. The formation of interchain 'bridges' in the case of multivalent anions were found, resulting in a strong decrease of the chain dimensions. The addition of organic solvent gives a 2–3-fold in intrinsic viscosity, whereas the conformational parameters change little.

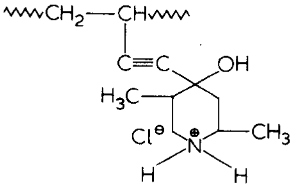
INTRODUCTION

Polyelectrolyte effects due to the electrostatic repulsion of fixed charges in the polymer chain disappear when simple electrolytes are added[1–3]. Under the influence of high ionic strength, the polyelectrolyte molecules act as uncharged polymers[4]. Consequently, the behaviour of polyelectrolyte molecules in mixed solvents, in the presence of multivalent ions at different temperatures, are of interest.

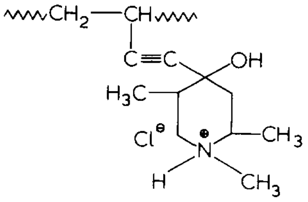
This paper relates a study of hydrodynamic properties of poly-1,2,5-trimethyl- and 2,5-dimethyl-4-vinyl-ethynilpyperidol-4 hydrochlorides in water–salt and water–alcohol mixtures.

EXPERIMENTAL

Polymer samples were synthesized by radical polymerization in the presence of dinitrylazoisobutyric acid as initiator at 60°C[5–6]. Poly-1,2,5-trimethyl- and 2,5-dimethyl-4-vinylethynilpyperidol-4 hydrochlorides have a linear structure of the following type:



I



II

The conservation of triple bonds during free radical polymerization of monomers was detected by i.r. spectroscopy and by catalytic hydrogenation[6].

Fractionation of polymers was done by precipitation from 1% methanol solution by diethyl ether at 25°C. Viscosities of the fraction were measured at 25°C by Ubbelhode viscometer. The determination of molecular weights M_w was by the Archibald[7] method. The sedimentation constants were measured by ultracentrifuge (3170/b, MOM, Hungary). The molecular weight $M_{s\eta}$ was calculated from intrinsic viscosity and sedimentation constants via the Flory–Mandelkern[8] equation. Potassium chloride and potassium bromide were used as simple electrolytes. The Arhimed multiplier $(1-\bar{v}\rho)$ of polymers were determined by the method of Rafikov *et al.*[9], where $\bar{v}$ = partial specific volume and ρ = solvent density.

RESULTS AND DISCUSSIONS

Values of intrinsic viscosities $[\eta]$, sedimentation constants S_0 and molecular weight fractions M_w and $M_{s\eta}$ of polymers I and II are listed in *Tables 1* and *2*. The parameters K_η and a, K_s and b were calculated from the logarithmic plots of $[\eta]$ and S_0 *versus* M_w of the Mark–Houwink equation (*Tables 3* and *4*). The data of *Tables 3* and *4* show that the exponents a for both polymers decreased with increasing ionic strength. The lesser values of exponent a for polymer II are probably due to its higher hydrophobity—it has an extra methyl group.

The K_0 values have been calculated by extrapolation of $[\eta]/M^{1/2}$ *versus* $M^{1/2}$ (*Figure 1*) according to the Stockmayer–Fixman[10] equation. The flexibility factors σ at different ionic strength were found from the equation:

$$\sigma = \frac{(\bar{r}_0^2)^{1/2}}{(\bar{r}_f^2)^{1/2}}$$

where $(\bar{r}_0^2)^{1/2}$ is the mean square unperturned end-to-end distance calculated from K_0 values; $(\bar{r}_f^2)^{1/2}$ is the same quantity for a 'freely' jointed chain. K_0 and σ for polymer II decrease with increasing concentration of simple electrolytes

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Table 1 Hydrodynamic characteristics of poly-1,2,5-trimethyl-4-vinylethynilpyperidol-4 hydrochlorides in water–salt solutions

	$[\eta]$ (dlg^{-1})						$\bar{M}_w \times 10^{-3}$	$\bar{M}_{s\eta} \times 10^{-3}$	$S_0 \times 10^{13}$ (s)
	[KCl] (M)								
Experiment	0.005	0.01	0.1	1.0	0.02 M K_2SO_4	0.0165 M Na_3PO_4		0.01 M	KCl
1	–	1.75	0.80	0.40	0.33	0.15	450	–	–
2	1.58	1.10	0.49	0.24	0.23	0.10	250	215	3.13
3	–	0.99	0.46	0.23	0.18	0.09	210	160	2.86
4	1.45	0.91	0.44	0.22	–	0.10	200	126	2.50
5	–	0.86	0.43	0.21	0.16	0.05	180	–	–
6	1.04	0.78	0.40	0.18	0.15	0.09	150	82	2.00
7	–	0.75	0.36	–	0.14	0.06	140	82	2.00
8	0.75	0.57	0.29	0.13	0.11	0.04	91	–	–
9	0.66	0.47	0.24	0.11	0.09	0.05	71	50	1.67
10	–	0.40	0.17	0.08	0.08	0.03	52	–	–

Table 2 Hydrodynamic properties of poly-2,5-dimethyl-4-vinylethynilpyperidol-4 hydrochloride in water–salt solutions

	$[\eta]$ (dl g^{-1})				$\bar{M}_w \times 10^{-3}$	$\bar{M}_{s\eta} \times 10^{-3}$	$S_0 \times 10^{13}$ (s)
	[KBr] (M)						
Experiment	0.01	0.1	0.5	0.02 M K_2SO_4		0.01 M KBr	
1	1.48	0.65	0.40	0.40	426	372	4.54
2	1.34	0.58	0.34	0.33	366	311	4.20
3	0.76	0.29	0.23	0.20	212	172	3.57
4	0.43	0.23	0.10	0.10	142	139	3.33
5	0.25	0.10	0.05	0.08	62	60	2.78
6	0.10	0.05	0.03	–	22	–	–

Table 3 Molecular characteristics of poly-1,2,5-trimethyl-4-vinylethynilpyperidol-4 hydrochloride in water–salt solutions

Solvent	$K_\eta \times 10^{-4}$	a	$K_s \times 10^{15}$	b	$K_0 \times 10^{-4}$	σ
0.01 M KCl	2.53	0.67	3.4	0.58	13.5	3.40
0.10 M KCl	2.02	0.63	–	–	8.0	2.86
1.00 M KCl	1.24	0.61	–	–	3.5	2.15
0.02 M K_2SO_4	1.51	0.60	–	–	3.0	2.07

Table 4 Molecular characteristics of poly-2,5-dimethyl-4-vinylethynilpyperidol-4 hydrochloride in water–salt solutions

Solvent	$K_\eta \times 10^{-6}$	a	$K_s \times 10^{15}$	b
0.01 M KBr	3.98	1.00	–	–
0.10 M KBr	5.75	0.90	0.135	0.75
1.00 M KBr	39.80	0.71	–	–

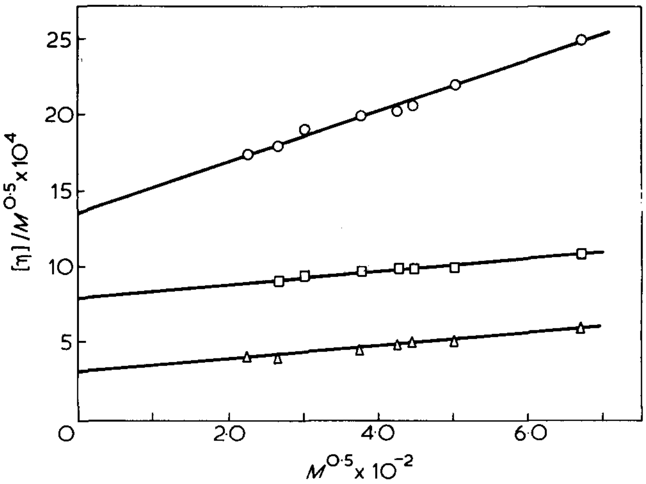

Figure 1 Stockmayer–Fixman plots for polymer II in water at different ionic strength. ○, 0.01; □, 0.1; △, 1.0 M KCl

and are of the same order as for unchanged macromolecules (*Table 3*).

Figure 2 shows the dependence of intrinsic viscosity of several fractions of polymer II on the composition of mixtures (0.005M KCl–C_2H_5OH). At the beginning, values of $[\eta]$ are little changed. This effect can be explained by the association of polyions and simple ions in the medium with low dielectric constant. The addition of ethanol will improve the ability of the solvent to solvate hydrophobic groups of the polyelectrolyte. The further fall in intrinsic viscosity is due to the preferential interaction of hydrophylic parts of the polymer chain one with other in organic solvents (*Table 5*).

Figure 3 shows plots of reduced viscosity fractions of polymer II *versus* concentration in the presence of 0.0165M Na_3PO_4. The low values of viscosity ($[\eta] = 0.1 \pm 0.05$) (*Table I*) show the compact conformation of macromolecular coils. This is probably because of the formation of intrachain 'bridges' which lead to the 'folding' of polyelectrolyte coils. At the same time, one can suggest that both the formation of intrachain 'bridges' and hydrophobic interactions of side groups will stabilize the compact structure of polymer molecules in

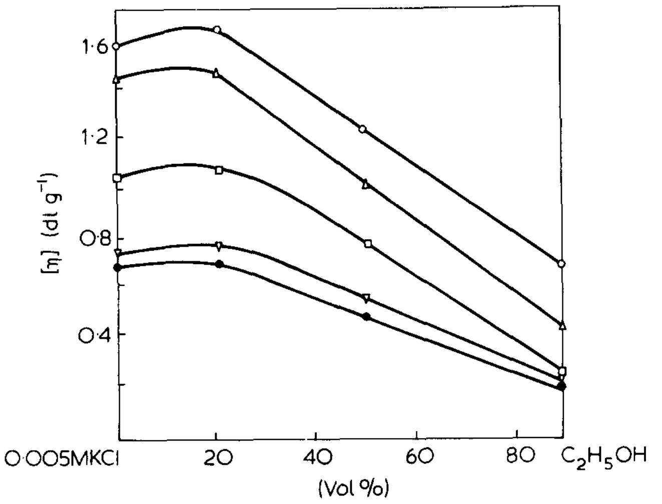

Figure 2 Variation of intrinsic viscosity of polymer II as a function of mixture composition (0.005 M KCl–C_2H_5OH). ○, 2; △, 4; □, 6; △, 8; ●, 9 fractions

Table 5 Molecular characteristics of poly-1,2,5-trimethyl-4-vinylethynilpyperidol-4 hydrochloride in water–alcohol solutions

0.005M KCl; C_2H_5OH (vol %)	$K_\eta \times 10^{-4}$	a	$K_0 \times 10^{-4}$	σ
100:0	1.20	0.77	17.0	3.70
80:20	1.34	0.76	19.0	3.80
50:50	1.66	0.75	14.0	3.50
10:90	0.35	0.76	7.0	2.80

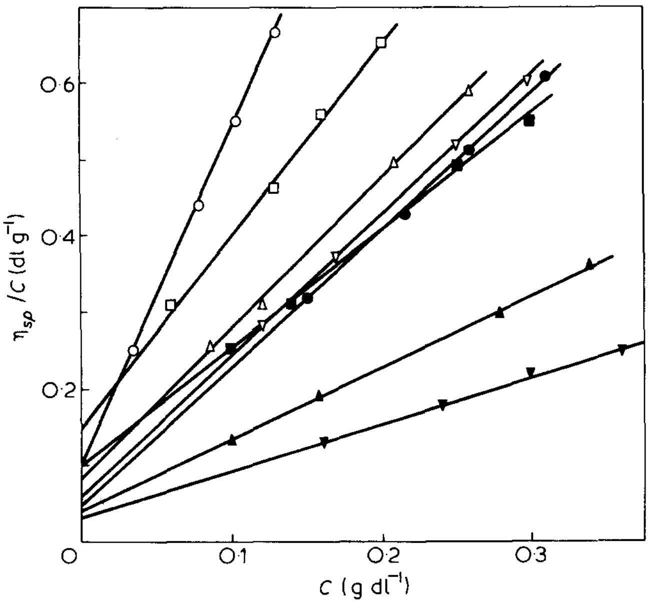

Figure 3 Plots of reduced viscosity *versus* concentration of polymer II in water in presence of Na_3PO_4. □, 1; △, 3; ○, 4; ■, 6; △, 7; ▲, 8; ●, 9; ▲, 10 fractions

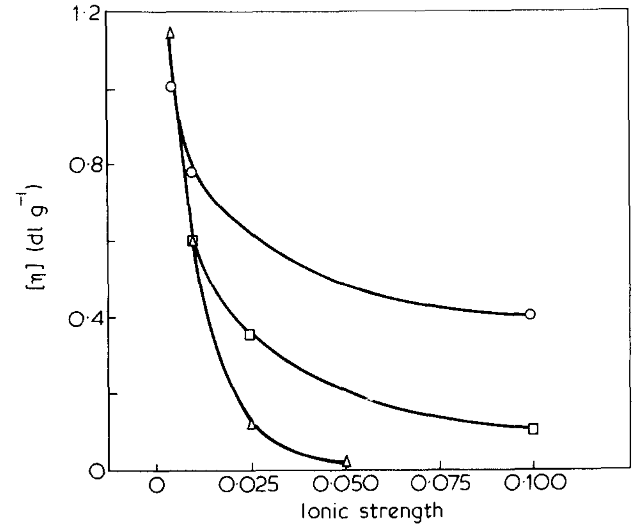

Figure 4 Variation of intrinsic viscosity of polymer II in water with ionic strength in presence of different salts. ○, KCl; □, K_2SO_4; △, Na_3PO_4

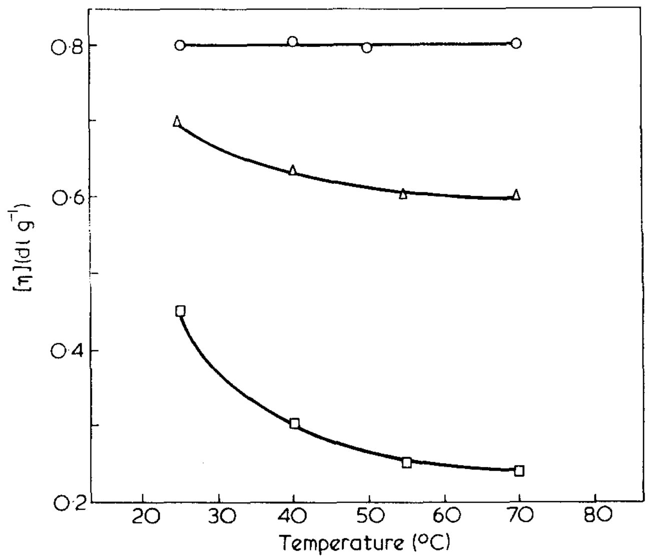

Figure 5 Variation of intrinsic viscosity of polymer II with temperature at different ionic strengths. ○, 0.005; △, 0.01; □, 0.1 M KCl

the aqueous medium. As seen from *Figure 4*, the values of intrinsic viscosity sharply decrease with concentration for divalent anions, more so for trivalent anions, and rather less for univalent ones.

The influence of temperature on the conformation of polyelectrolyte molecules is shown in *Figure 5*. In the presence of 0.005M KCl, the rise in temperature does not modify intrinsic viscosity. This is the result of the compensation of two factors: hyfrophobic interactions and electrostatic repulsions. When the concentration of added salts increases (0.01 and 0.1 M KCl), the charges of macromolecules are strongly screened and will intensify hydrophobic interactions.

Thus, the obtained data show that both increase in ionic strength and addition of organic solvent lead to a decrease in size of polyelectrolyte molecules; but, in the presence of multivalent ions, the macromolecular chains assume globular conformation.

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