Eur. Polym. J. Vol. 22, No. 5, pp. 413–415, 1986
Printed in Great Britain

0014-3057/86 \$3.00 + 0.00
Pergamon Press Ltd

SOLUTION PROPERTIES OF COPOLY(4-VINYLPYRIDINE-4-VINYLPYRIDINE ACETIC ACID)

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(*Received* 1 *July* 1985; *in revised form* 24 *October* 1985)

Abstract—The solution properties of copoly(4-vinylpyridine-4-vinylpyridine acetic acid) have been investigated by u.v., i.r. spectroscopy and viscometry. The molecular characteristics of copolymer at various ionic strengths were determined from the relations of Mark-Houwink-Kuhn and Stockmayer-Fixman. There is a strong influence of ionic strength on the hydrodynamic dimensions of the polymer coils. It is assumed that the conformation of macromolecule in the presence of low-molecular-weight ions is controlled by a balance of intramolecular forces.

INTRODUCTION

Some publications [1, 2] have been concerned with the properties of solutions of polyelectrolytes, the oppositely charged groups of which are situated on different units. However, until now the behaviour of macromolecules consisting of a base and zwitterion units, has not been studied. In the present work, the hydrodynamic properties of an amphoteric polyelectrolyte with betaine units in the chain, viz. copoly(4-vinylpyridine-4-vinylpyridine acetic acid), are considered.

EXPERIMENTAL

Poly(4-vinylpyridine) P4VP was synthesized by radical polymerization [3] using toluene as solvent and dibenzoyl peroxide as initiator. Samples with various molecular weights were synthesized. The conversion degree for high molecular fractions did not exceed 10 wt%, and for low molecular about 60 wt%. Fractionation of P4VP was carried out by the precipitation method at 25° in the solvent/non-solvent system methanol/ethyl acetate. Alkylation of the fractions of P4VP by chloracetic acid was carried out in dimethylformamide at 50°. The alkylation degree of P4VP relative to active nitrogen was about 50 mol% (Table 1; the results of elemental analysis for N and Cl).

The viscosities of the fractions were measured at 25° in an Ubbelohde viscometer.

RESULTS

The presence of the alkylated units and the composition of the copolymer were determined by elemental analysis (Table 1), conductometry, u.v. and i.r. spectroscopy. In u.v. spectra of the copolymers, an absorption band appears in 230 nm region, characteristic of the quaternary nitrogen atom [4]. The valency vibrations of ester groups are observed in the i.r. spectra in the region of 1725 cm^{-1}. The intrinsic viscosities of P4VP fractions were measured in ethanol and values of viscometric-average molecular weight $\bar{M}_v$ were calculated by means of $[\eta] = 1.51 \times 10^{-3} M^{0.52}$ [3]. These values of $\bar{M}_v$ were found taking into consideration the degree of alkylation (Table 1). At low salt concentration, the values of η_{sp}/C monotonously fall with decrease of polymer concentration and the values of the intrinsic viscosity have been determined by the usual Huggins method by extrapolation of η_{sp}/C values to zero polymer concentration. The intrinsic viscosities of the copolymer fractions were measured in 0.005, 0.01, 0.025, 0.05, 0.1, 0.5. 1.0 and 3.0 M KCl (Fig. 1). The unperturbed dimensions of K_0 have been calculated by $[\eta]/M^{0.5} = K_0 + 0.51\,\phi B \cdot M^{0.5}$ of Stockmayer–Fixman [5] and the coiling degree of the polymeric chain $\sigma = (\bar{h}^2_\Theta)^{0.5}/(\bar{h}^2_0)^{0.5}$, where $(\bar{h}^2_\Theta)^{0.5}$ is the unperturbed end-to-end dimensions of the

Table 1. Intrinsic viscosities of the copolymer fractions at various ionic strengths

Cl (wt%)	N (wt%)	$M_v \times 10^{-3}$	Ionic strength, C_s, M KCl							
			0.005	0.01	0.025	0.05	0.10	0.5	1.0	3.0
10.76	10.64	8358	8.20	6.98	2.80	0.99	—	—	2.13	2.25
11.11	9.81	4530	4.80	4.22	1.83	0.82	—	–	1.30	1.47
10.92	10.34	2420	4.40	3.70	1.50	0.75	—	—	1.28	1.32
10.83	9.65	1606	3.10	2.54	1.15	0.68	0.35	—	0.80	0.93
11.19	9.57	639	1.70	1.34	0.96	0.50	0.26	–	0.38	0.48
11.20	9.38	282	1.06	0.80	0.45	0.31	0.18	0.15	0.25	0.37
10.75	9.31	194	0.55	0.54	0.29	0.25	0.15	0.12	0.32	0.36
11.28	9.40	83	0.42	0.35	0.21	0.14	0.10	0.09	0.20	0.25
11.36	9.29	48	0.34	0.26	0.19	0.14	0.09	0.08	0.15	0.15

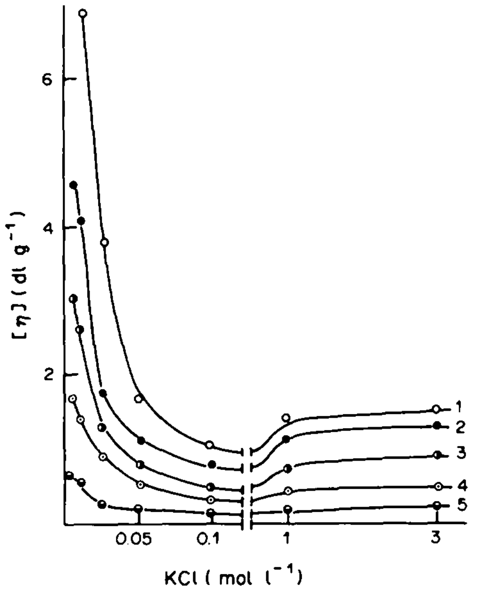
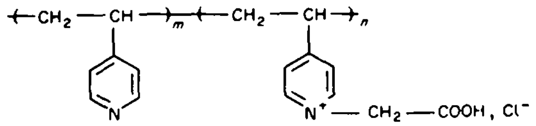


Fig. 1. Dependence of the intrinsic viscosity of the fractions on the ionic strength of the solution: curve 1, fraction 2; 2, 4; 3, 5; 4, 6; 5, 8.

macromolecule and $(\bar{h}_0^2)^{0.5}$ is the end-to-end dimensions calculated for the free-rotation model, are given in Table 2.

DISCUSSION

From the results of the analysis and absorption spectra, the structure of the statistical copolymer can be represented as:



It is stated that, in aqueous-salt solutions, the hydrodynamic volume of poly(vinylpyridine) decreases with increasing ionic strength [6, 7]. On the other hand, with increasing C_s there is a monotonic increase of the dimensions of macromolecules composed of zwitterion units only [2].

Table 2. Molecular characteristics of copoly(4-vinylpyridine-4-vinylpyridine acetic acid) at various ionic strengths

C_s (mol/l KCl)	a	$K_\eta \times 10^4$ (dl/g)	σ	$K_0 \times 10^4$ (dl/g)
0.005	0.65	2.8	2.98	1.18
0.01	0.63	2.9	2.84	1.02
0.025	0.53	6.0	2.69	0.87
0.05	0.49	6.8	2.46	0.67
0.1	0.45	7.1	2.12	0.42
0.5	0.35	9.1	2.05	0.28
1.0	0.49	7.7	2.48	0.68
3.0	0.52	2.7	2.60	0.79

C_s—concentration of low molecular salt, mol/l; K_η and a—constants of the relation of Mark–Houwink–Kuhn; σ—the flexibility parameter of polymeric chain; K_0—the unperturbed dimension of macromolecules, determined from the relation of Stockmayer–Fixman.

As is seen from Fig. 1, the behaviour of the copolymer at $C_s = 0.5$ M KCl is analogous to that of the homopolyelectrolytes. The value of the intrinsic viscosity decreases with increase of the ionic strength. Upon further increasing the concentration of the low-molecular-weight electrolyte, a significant increase in the intrinsic viscosity is observed.

At $C_s = 0.005$ M KCl, the exponent a is 0.65. The polyion is in the form of the statistic coil in spite of the high density of charge along the chain. This conformation of the macromolecule at low ionic strength is stabilized by the intrasalt bonds between different units. Indeed, in the i.r. spectrum of the copolymer precipitated from aqueous solution, there is no absorption band in the region 1420 cm^{-1}, characteristic for molecular 4-vinylpyridine. All pyridine units are thus in the protonated state. So, the oppositely charged COO$^-$ and $>\mathrm{N^+H}$ or $>\mathrm{N^+}$-groups in aqueous solution form zwitterions [6].

With increasing C_s, the value of a gradually drops and at $C_s = 0.5$ M KCl it is 0.35. The coiling of the macromolecule at intermediate ionic strength is caused by screening of $>\mathrm{N^+H}$ and $>\mathrm{N^+}$-groups by low-molecular-weight ions. The coiled conformation may be additionally stabilized by hydrophobic interactions.

The increase of $[\eta]$ and a with increasing KCl concentration shows the uncoiling of the macromolecules due to weakening of electrostatic interactions. Increase of polyion dimensions at high ionic strength is caused by the destruction of the zwitterions between units, as the high salt concentration screens all types of electrostatic interaction along the chain. For $C_s = 0.5$ to 3.0 M KCl, the coulombic repulsion forces between $>\mathrm{N^+H}$ and $>\mathrm{N^+}$-groups is almost completely suppressed. Therefore, the destruction of the zwitterions leads to uncoiling of the macromolecules.

The influence of temperature on the polyion conformation was studied at $C_s = 0.005$ and 0.1 M KCl. As can be seen from Fig. 2, at low ionic strength dimensions are not significantly influenced. At

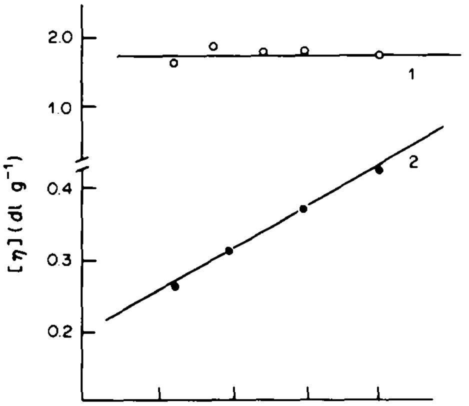


Fig. 2. Dependence of the intrinsic viscosity of fraction 6 of the copolymer on temperature at ionic strength 0.005 M (1) and 0.1 M (2) KCl.

$C_s = 0.1$ M KCl the value of $[\eta]$ monotonously increases with rise in temperature. The increase of polyion dimension in this case is probably caused by destruction of the intersalt contacts, partially screened by the low-molecular-weight ions.

Thus, the behaviour of the polyelectrolyte in water salt solutions differs from that of homopolyelectrolytes. The presence of different units in one chain leads to a complex equilibrium of intramolecular forces. At ionic strengths below that of 0.5 M KCl, the properties of the copolymer are similar to those of homopolymers of vinylpyridine. Above $C_s = 0.5$ M KCl, the behaviour of the copolymer is the same as that of amphoteric macromolecules consisting of betaine units only.

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