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Physico-Chemical Studies of Polymeric Carriers:

2. Molecular Mass Determination of Poly(N-Vinylpyrrolidone-co-maleic acid) Fractions

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SUMMARY

Critical interpretation of the various conceptions concerning the problems in characterization of linear polyelectrolyte type polymers containing maleic acid as a comonomer is given. Proper conditions to avoid the fundamental experimental difficulties are proposed. Our conception is supported by molecular light scattering measurements of hydrolysed, fractionated poly(N-vinylpyrrolidone-co-maleic anhydride) samples. It was found that the problems were eliminated by the reduction of the degree of dissociation of carboxyl groups to a minimum value.

INTRODUCTION

Among various characteristics of copolymers containing maleic acid, molecular mass and intrinsic viscosity may be regarded as the most important data, but their determination encounters difficulties.

In spite of a vast number of publications on the characterization of linear polyelectrolytes and the necessity of the expression of real molecular mass figures, the most prominent features of weak polyelectrolytes in solution have still remained obscure. Problems arise from the high charge density on the macromolecular polyion. Interesting attempts have been made to overcome these difficulties. Several characteristics of polyelectrolytes were studied in the presence of added salt e.g. conformation (TAKAHASHI et al., 1967, SAKURADA et al., 1970, HEALY et al., 1972, OHNO et al., 1973 and KITANO et al., 1980), viscosity (NODA et al., 1970, DUBIN and STRAUSS, 1970), electrochemical behaviour (OTH and DOTY, 1952 and others). The results obtained were generally explained adopting different conceptions. Unfortunately the ideas have not yet been proved completely. The application of the theories of (i) excluded volume effect, (ii) ion binding (KOTIN and NAGASAWA, 1962), (iii) counterion distribution of partially neutralized polymeric acids (ALFREY et al., 1952, MUTO et al., 1973), (iv) apparent dissociation constant of the degree of dissociation of the primary carboxyl group of maleic acid in copolymers (OHNO et al., 1973), (v) interaction of neighbouring groups in maleic acid copolymers (SCHULTZ and STRAUSS, 1972), etc., clearly shows the variety of the different conceptions in this field.

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The aim of our present work is to report our results in characterization of fractionated poly(N-vinylpyrrolidone-co-maleic acid), later P(NVP-co-MA). Hydrolysis and fractionation procedures are described in the previous paper of the series.

PROPER CONDITIONS FOR MOLECULAR MASS DETERMINATION OF THE COPOLYMER P(NVP-co-MA)

Since maleic acid (MA) becomes saturated being built into a polymer chain, it can be expected, that the values of the dissociation constants of the dibasic acid are closer to those of succinic acid (SA).

It is known, that one of the two carboxyl groups of a dibasic acid can only be titrated on condition that:

$$pK_2 - pK_1 = 4.$$

This condition is perfected in the case of MA, as $pK_1 = 2.00$ and $pK_2 = 6.26$, and the pH of the first dissociation step is:

$$pH = \frac{pK_2 - pK_1}{2} = 4.13$$

while the corresponding values for SA are $pK_1 = 4.19$ and $pK_2 =$ $= 5.57$. The fact that the difference between the two pK values for succinic acid is too small, makes evident that the two dissociation steps can not be distinguished.

It has to be pointed out in contrast with the earlier conceptions that (i) there is no anomaly in the titration behaviour of maleic acid copolymers, as it was supposed (e.g. SCHULTZ and STRAUSS, 1972), (ii) the determination of the degree of the dissociation of the primary carboxyl group of MA in polymers (e.g. OHNO et al., 1973) is impossible, (iii) the composition of copolymers can not be determined by the MA titration (e.g. CONIX and SMETS, 1955, KOTENKO et al., 1972, NYKOLAEV et al., 1973, GEORGIEV et al., 1979).

In order to avoid these problems it seemd to be promising to suppress the dissociation of the dibasic acid. This can be attained at $pH = 2.1$ in the case of P(NVP-co-MA). By this means proper conditions are ensured for molecular light scattering and for viscometry. The polymer behaves as a coil, because there is no electrostatic repulsion between the segments and the chains. The measure of polymer-polymer and polymer-solvent interaction is negligible. Besides, as P(NVP-co-MA) is supposed to be an alternating copolymer, it may be regarded as a homopolymer in which the repeated unit is $\mathrm{+}$NVP-MA$\mathrm{+}$. Thus the refractive index and the angular distribution of the scattered light do not depend on the chemical composition of the polymer, that makes it possible to use a single colvent.

EXPERIMENTAL

Brice Phoenix Series 2000 light scattering photometer and Phoenix Precision Instrument 60 differential refractometer were applied. Hydrochloric acid solution $pH = 2.07$ was used as a solvent. The polymer solutions were prepared in the range of concentration $1.0\cdot10^{-3}$ - $4.0\cdot10^{-3}$ gcm^{-3} for light scattering and $1.0\cdot10^{-2}$ - $5.0\cdot10^{-2}$ gcm^{-3} for the measurements of the refractive index increment. Unpolarized and polarized light of 546 nm from a mercury lamp was used. Temperature of the cell was maintained at 25 ± 0.1 °C, the room was air-conditioned. The calibration of the photometer was carried out using dried benzene ($R_{90}^{546} = 17.1$). The solvent and the solutions were filtered directly into the cell through G_5 and G_4 glass-sinters respectively. The calibration of the differential refractometer was carried out using NaCl solutions.

RESULTS AND DISCUSSION

It was found that the value of the refractive index increment is the same for each fraction, i.e. independent of molecular mass ($dn/dc = 0.146$).

In the interpretation of light scattering data the classical dissimmetry method (DOTY and STEINER, 1950) was applicable, and the optical anisotropy of the segments had to be also taken into account. The following equation was applied:

$$M = P^{-1}(90)\cdot[Kc/R_{90}]^{-1}_{c=0}$$

where P(90) is the particle scattering factor determined from the experimentally obtained intrinsic dissimmetry $[Z]_d$ presuming coil shape according to the considerations on proper conditions. $\underline{K}$ is the optical constant; $\underline{c}$ is the concentration of the solution; R_{90} is the Rayleigh factor at $\theta = 90°$. Cabannes factor was used as a correction for optical anisotropy (STACEY, 1956): $(6+6\rho_u / 6-7\rho_u)$; where $\rho_u = H_u/V_u$; H_u and V_u are the horizontally and vertically polarized components of the scattered unpolarized incident light respectively.

Straight lines were obtained plotting the corrected values of Kc/R_{90} against concentrations of the polymer solutions. Three data-pair sets $\underline{c}$ and Kc/R_{90} from the seven fractions studied are listed in Table I. A further set is shown in Figure 1 to

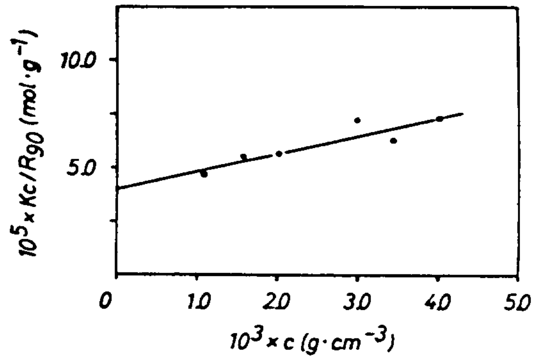

Figure 1.

Dependence of Kc/R_{90} on the concentration of poly(N-vinylpyrrolidone-co-maleic acid), in the case of Fraction I.3.

Table I

Fraction I.1.		Fraction III.2.		Unfractionated sample	
$10^3 \cdot c$ $(g \cdot cm^{-3})$	$10^5 \cdot Kc/R_{90}$ $(mol \cdot g^{-1})$	$10^3 \cdot c$ $(g \cdot cm^{-3})$	$10^5 \cdot Kc/R_{90}$ $(mol \cdot g^{-1})$	$10^3 \cdot c$ $(g \cdot cm^{-3})$	$10^5 \cdot Kc/R_{90}$ $(mol \cdot g^{-1})$
1.06	3.38	0.96	10.65	0.98	5.87
1.52	3.72	1.53	11.71	1.46	5.83
2.11	3.67	2.55	11.12	2.02	5.60
2.47	3.89	2.99	11.95	2.54	5.98
2.99	4.13	3.50	13.44	3.06	6.38
3.53	4.61	4.01	13.42	4.07	6.50
4.08	4.76				
$\left(\frac{Kc}{R_{90}}\right)_{c=0} = 2.86 \cdot 10^{-5}$		$\left(\frac{Kc}{R_{90}}\right)_{c=0} = 9.82 \cdot 10^{-5}$		$\left(\frac{Kc}{R_{90}}\right)_{c=0} = 5.43 \cdot 10^{-5}$	
$M_w = 35\ 000 \pm 5\%$		$M_w = 10\ 000 \pm 10\%$		$M_w = 18\ 400 \pm 10\%$	

illustrate the linear dependence. Molecular mass values* were calculated using the least square method.

On the basis of the measurements it can be concluded that the values of molecular mass, intrinsic viscosity and the constants of the Mark-Houwink equation** (K,α) can be correctly and conveniently determined when the dissociation of the carboxyl groups is suppressed to a minimum value. Under these conditions the polymer does not exhibit polyelectrolyte character. Finally, the hypothesis of an alternating copolymer structure is supported by the results obtained.

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*given in Table I in the previous paper of the series
**reported in the previous paper

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