



## BEHAVIOUR OF MAn-BASED POLYELECTROLYTES IN WATER SOLUTIONS: INFLUENCE OF pH AND IONIC STRENGTH

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**Abstract**—By heterogeneous copolymerization in benzene, maleic anhydride (MAn) copolymers differing in the ratio of hydrophilic/hydrophobic units were synthesized in order to study their behaviour in water solution. The conformational behaviour of the MAn copolymers arising from variations of pH and ionic strength was followed by viscometric measurements. The MAn copolymers in water solution exhibit relatively sophisticated conformational changes partially resulting from the different character of carboxyl groups generated during hydrolysis of anhydride rings. It has been found that the conformational changes not only depend on anhydride units themselves but are also considerably affected by the polarity of a monomer unit located in the neighbourhood of an anhydride residue.

### INTRODUCTION

Water-soluble polymers carrying a large number of ionizable groups along a polymer chain are of interest from industrial and academic points of view [1]. In the academic sphere, the interest is mainly focused on the relationship between structure/charge density and solution conformation [2]. Although the behaviour of polyelectrolyte homopolymers has been studied in detail, there is still much to be resolved in understanding the structure–property relationship of polyelectrolyte copolymers and terpolymers [3].

Maleic anhydride (MAn) copolymers and terpolymers belong to a large family of anionic polyelectrolytes. Through hydrolysis of the anhydride rings in an alkaline medium, segments containing ionic groups are formed. The concentration of these ionic groups significantly affects polyelectrolyte properties. The ionization of carboxylic groups, and thus the net charge in hydrolyzed MAn copolymers mainly depends on the pH. However, the effect of ionic strength, as determined by simple salt concentration, is not negligible. Both these parameters are reflected in the conformation changes of a polymer chain. The expansion of the polymer coil occurs due to electrostatic repulsion of the dissociated carboxylic groups. The addition of simple electrolyte leads to chain folding and subsequently to coil compression.

Whilst our previous papers [4–6] dealt with the preparation and characterization of MAn copolymers and terpolymers, the aim of this work was to investigate the behaviour of MAn copolymers differ-

ing in the ratio of hydrophilic:hydrophobic units in aqueous medium.

### EXPERIMENTAL PROCEDURES

#### Materials

Maleic anhydride of analytical grade was purified by sublimation. Other monomers used for the copolymerization were purified by conventional methods.  $\alpha,\alpha'$ -Azoisobutyronitrile (AIBN) was recrystallized twice from ethanol. All other chemicals used in this study were of analytical grade.

#### Polymerization procedure

The copolymers and terpolymers of MAn with various vinyl monomers such as styrene (St), vinyl acetate (VAc), and methyl methacrylate (MMA), 2-ethylhexyl acrylate (2-EHA) were prepared by heterogeneous polymerization in benzene at 70°C under a nitrogen atmosphere in the presence of AIBN as the initiator of the polymerization. The compositions of monomer feeds used for the synthesis of MAn copolymers and terpolymers are listed in Table 1. In the course of the polymerization the copolymer precipitated in the form of a white powder. The polymerization was allowed to go to high conversion. The product was filtered off and washed with benzene. In the case of the MAn/VAc copolymer petroleum ether was used to facilitate product isolation.

#### Infrared spectrophotometry

Infrared spectrophotometry was performed using a Philips model PU 9152 i.r. spectrophotometer. The composition of St-containing copolymers was determined on the basis of i.r. spectra recorded by means of the KBr technique as described elsewhere [6].

#### <sup>13</sup>C-NMR spectrometry

<sup>13</sup>C-NMR spectrometry was used to determine the composition of the MAn/VAc copolymer and MAn/2-EHA/St terpolymer. The measurements were performed by means of a NMR spectrometer JEOL FX-100 at a field modulation

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Table 1. Monomer feed compositions used for preparation of the MAn copolymers and terpolymers expressed in mole ratios

	Monomer feed composition				$10^3 \cdot [I]^a$ (mol·kg <sup>-1</sup> )	$[M]^b$ (mol·dm <sup>-3</sup> )
	$f_{\text{MAn}}$	$f_{\text{St}}$	$f_{\text{VAc}}$	$f_{2\text{-EHA}}$		
1	0.5	0.5	—	—	2.14	0.666
2	0.5	—	0.5	—	2.16	0.666
3	0.4	0.4	—	0.2	2.14	0.921

<sup>a</sup>Initiator concentration with respect to overall amount of polymerization feed.

<sup>b</sup>Overall monomer concentration with respect to volume of solvent.

20.047 MHz, magnetic field induction 2.3 T and 5000 accumulations. The polymer content in CD<sub>3</sub>COCD<sub>3</sub> was 10 wt% and the temperature 50°C. The composition of MAn/VAc copolymer was determined from the integral intensities of carbon signals of the following groups: —CH<sub>2</sub>—CH(O)—CH<sub>2</sub>— (67.057–72.759 ppm), —CH(COO)— (47.721–53.488 ppm). The <sup>13</sup>C-NMR spectrum of the MAn/VAc copolymer is shown in Fig. 1. For the estimation of the MAn/2-EHA/St terpolymer composition the following groups were used: C<sub>6</sub>H<sub>5</sub>— (125.385–133.270 ppm), —CH(COO)— (49.016–55.205 ppm) and CH<sub>3</sub>— (18.089–20.432 ppm).

#### Electrical conductivity measurements

The content of units from MAn in the copolymers was also assayed by conductometric titration. The electrical conductivity was measured with a Radelkis conductivity meter OK-104 connected with a conductivity cell OK-0902P under a nitrogen atmosphere. All the measurements were carried out in slowly stirred solutions at 25°C. The copolymer was dissolved in 0.1 M NaOH and titrated by 0.5 M H<sub>2</sub>SO<sub>4</sub> (mass concentration of polymer  $c_p = 4.44 \text{ g} \cdot \text{l}^{-1}$ ). The conductometric titration curve of the MAn/St copolymer is depicted in Fig. 2.

#### Molecular weight determination

The number-average molecular weight of MAn copolymers was measured by means of size-exclusion chromatography with a high-performance liquid chromatograph [7].

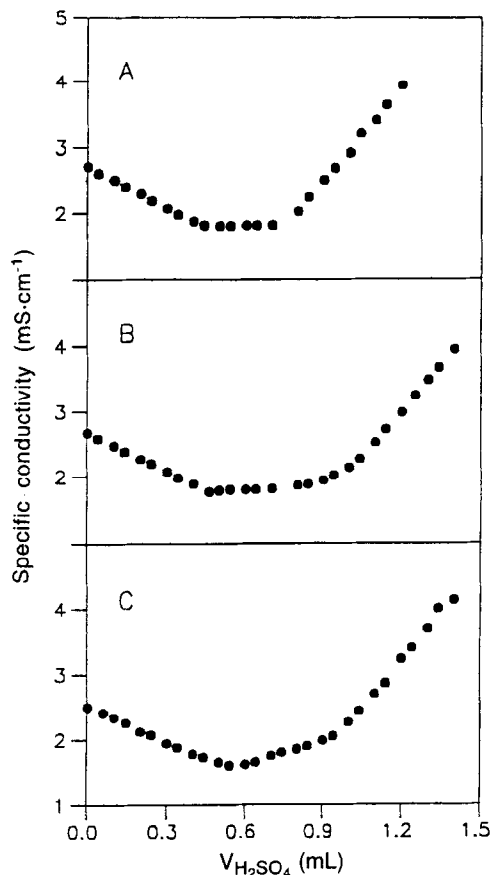


Fig. 2. Conductometric titration curves of MAn (A), succinic anhydride (SA) (B), and MAn/St copolymer (C) in 0.1 M NaOH. (A)  $c(\text{MAn}) = 2.5 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ ; (B)  $c(\text{SA}) = 2.5 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ ; (C)  $c_p = 4.44 \text{ g} \cdot \text{dm}^{-3}$ .

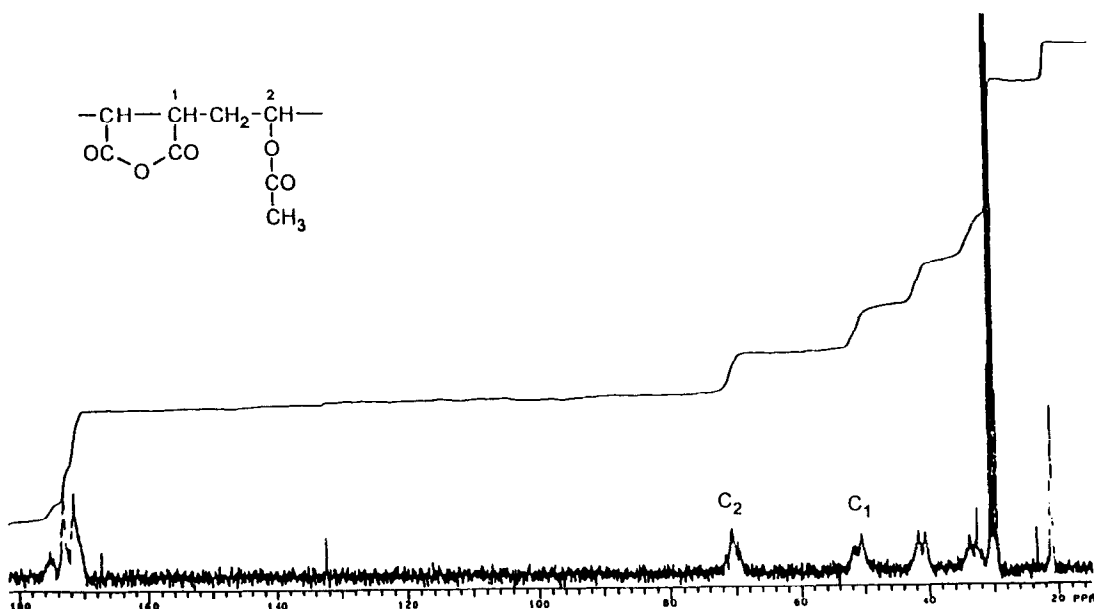


Fig. 1. <sup>13</sup>C-NMR spectrum of MAn/VAc copolymer.

Table 2. Composition of MAN copolymers expressed in mole ratios

Polymer	Copolymer composition				$10^{-5} \cdot \bar{M}_n$
	$F_{\text{MAN}}$	$F_{\text{St}}$	$F_{\text{VAc}}$	$F_{2\text{-EHA}}$	
1 MAN/St	0.47 <sup>a</sup>	0.53 <sup>a</sup>	—	—	2.5
2 MAN/VAc	0.46 <sup>b</sup>	0.54 <sup>b</sup>	—	—	1.4
3 MAN/2-EHA/St	0.50 <sup>bc</sup>	—	0.50 <sup>bc</sup>	—	2.8
	0.43 <sup>c</sup>	0.45 <sup>c</sup>	—	0.12 <sup>c</sup>	

<sup>a</sup> Determined by i.r. spectrophotometry.<sup>b</sup> Determined by conductometric titration.<sup>c</sup> Determined by <sup>13</sup>C-NMR spectrometry.

The characteristics of prepared copolymers regarding composition and molecular weight are summarized in Table 2.

#### Potentiometric titration

Potentiometric titration was performed by means of a Radelkis digital pH meter OP-211/1 equipped with a combined glass electrode. The polymer samples were dissolved in 0.1 M NaOH (1 wt% solution). Then 10 ml of the alkaline polymer solution were charged in a 50 ml beaker and diluted with 20 ml of deionized water. The titration was carried out under stirring using 0.1 M H<sub>2</sub>SO<sub>4</sub> as a titrant.

#### Viscometric measurements

The viscosities of 0.5 wt% water solutions of the MAN copolymers were determined with a Ubbelohde viscometer at 25°C, constant pH and varying ionic strength. Corrections for kinetic energy were found to be negligible. A desired pH value for a 1 wt% polymer solution in 0.1 M NaOH was adjusted on the basis of a potentiometric titration curve adding the volume aliquot of 0.1 M H<sub>2</sub>SO<sub>4</sub>. The ionic strength of a polymer solution was controlled by the addition of 1 M NaCl. Finally, twice-distilled water was added to reach the overall polymer concentration 0.5 wt%. The ionic strength of studied polymer solutions was estimated according to the following relationship:

$$I = \frac{1}{2} [2c(\text{NaOH}) + 6c(\text{H}_2\text{SO}_4) + 2c(\text{NaCl})] \text{ mol} \cdot \text{dm}^{-3}.$$

### RESULTS AND DISCUSSION

From the previous detailed studies performed on the dissociation behaviour of polyacids such as poly-

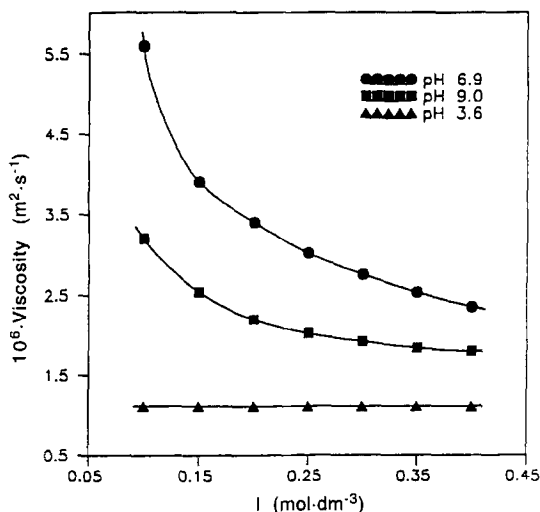


Fig. 3. Effect of ionic strength on viscosity of 0.5% water solutions of MAN/St at 25°C and constant pH.

acrylic [8, 9], polymethacrylic [10, 11], polymaleic, polyfumaric [12, 13] and polyitaconic [14] acid it is well known that the dissociation of dibasic polyacids undergoes two steps attributed to the different features of carboxylic groups bound to the main polymer chain. Moreover, the two-step dissociation is also exhibited by alternating copolymers of maleic anhydride and maleic acid [15–17], respectively, although they possess the same charge density as the common vinylic polyacids.

In the case of the alternating copolymers of MAN with St and VAc, respectively, hydrophilic anhydride segments are regularly followed by the comonomer unit. The composition of the MAN/2-EHA/St terpolymer is statistical; therefore, the MAN segments are likely to be followed by at least two St and/or 2-EHA units.

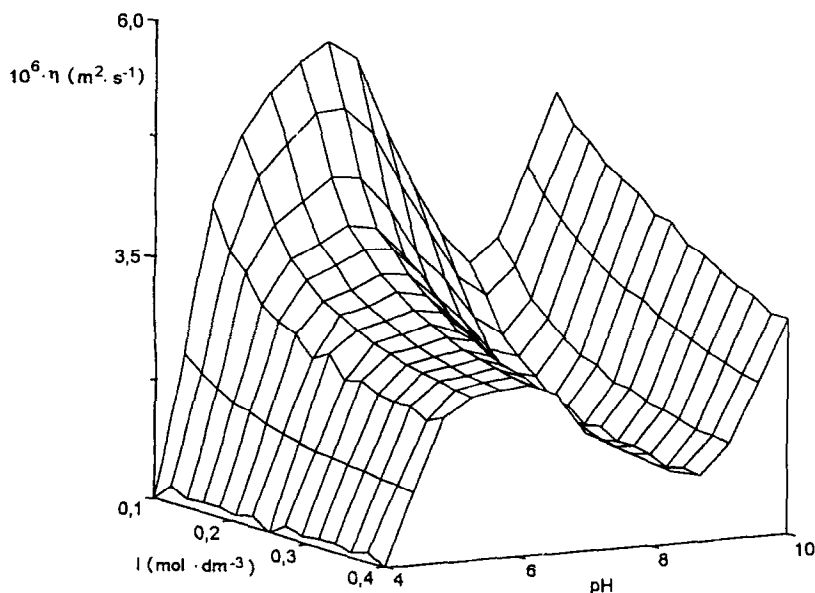


Fig. 4. Effect of pH and ionic strength on viscosity of 0.5% water solutions of MAN/St copolymer at 25°C.

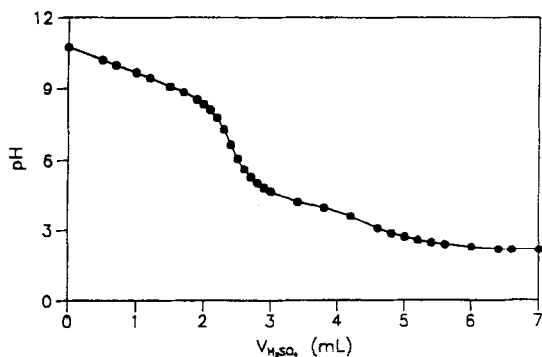


Fig. 5. Potentiometric titration curve of 1% solution of MAn/St copolymer in 0.1 M NaOH.

The conformational changes of the MAn copolymers resulting from variations of pH and ionic strength  $I$  were examined by viscometric measurements described in the Experimental Procedures. The significance of these two parameters is suggested by Fig. 3 and can be seen more clearly in Fig. 4. A rather sophisticated dependence of  $\eta$  on pH and  $I$  can be mainly ascribed to the above-mentioned presence of the two different types of COOHs; however, there are some additional factors (e.g. hydrophobicity of comonomer unit, regularity of polymer chain) that will be discussed later.

Maleic anhydride, once incorporated in a polymer chain, turns into a succinic anhydride residue, as confirmed by conductometric titration curves, depicted in Fig. 2. The hydrolysis of MAN itself results in maleic acid with considerably different values of  $pK_1$  and  $pK_2$  ( $pK_1 = 1.83$  and  $pK_2 = 6.07$ ). As a consequence, only one COOH takes place in titration while another one is stabilized by a hydrogen bond with the already ionized neighbour  $\text{COO}^-$ . For succinic acid ( $pK_1 = 4.21$  and  $pK_2 = 5.64$ ) as well as the MAn

copolymers the values of  $pK_1$  and  $pK_2$  are much closer; thus, the carboxylic groups are less susceptible to intramolecular hydrogen bonding and they both are titrated (the consumption of  $\text{H}_2\text{SO}_4$  in the course of titration is 2-fold larger than for MAn, see Fig. 2).

As shown in the plots of  $\eta$  vs pH (Fig. 4), the viscosity of the MAn/St copolymer declines within the pH range of 9.0–10.0, which is connected with suppressed dissociation of COOH. At the same time, the electrostatic repulsion between ionic groups decreases and the polymer chain begins to fold. We assume that the abrupt increase in  $\eta$  at pH 6.0–9.0 is caused by intermolecular associates of macromolecules formed via dissociated and non-dissociated carboxylic groups in a manner similar to that of low molecular weight compounds. At nearly pH 6.0,  $\eta$  attains a maximum closely corresponding to the inflection point on a potentiometric back-titration curve of the MAn/St copolymer (Fig. 5). It is noteworthy that Kawaguchi *et al.* [18] successfully confirmed the existence of hydrogen bonding in an alternating copolymer of maleic acid and isobutylene by u.v. spectrophotometry. However, they were not able to distinguish hydrogen-bonded pairs of COOH and  $\text{COO}^-$  between adjacent pairs of the unit of maleic acid, between intramolecular pairs separated far along the same polymer chain, or between intermolecular pairs of two different chains.

Our assumption regarding intermolecular association as a phenomenon responsible for a viscosity increase (pH 6.0–9.0) also supports the fact that the plots of  $[\eta]$  vs degree of dissociation for dibasic polyacids studied so far [12–14] and the alternating copolymers of MAn or maleic acid [15–17] showed the maximum around a dissociation degree  $\alpha = 0.5$  and at  $\alpha < 0.5$  decreased steeply. At first sight, the dependence of  $[\eta]$  on  $\alpha$  may look strange because if the electrostatic long-range interaction plays a dominant role in  $[\eta]$  of a flexible polyelectrolyte chain then

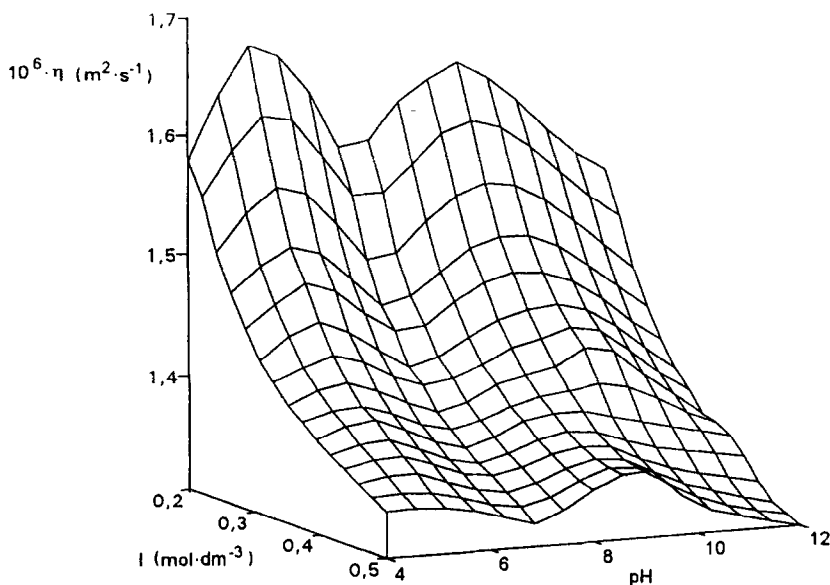


Fig. 6. Effect of pH and ionic strength on viscosity of 0.5% water solutions of MAn/VAc copolymer at 25°C.

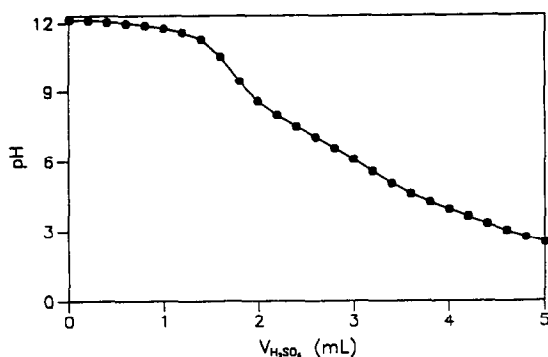


Fig. 7. Potentiometric titration curve of 1% solution of MAN/VAc copolymer in 0.2 M NaOH.

$[\eta]$  is supposed to decrease monotonically with decreasing  $\alpha$  in the same way as that of polyacrylic acid [19]. Therefore, we feel it is reasonable to presume that besides long-range electrostatic interactions the  $[\eta]$  dependence on  $\alpha$  (pH) for MAN homopolymers and copolymers is to a large extent affected by hydrogen bonds formed between the COOH and COO<sup>-</sup> groups of two different polymer chains folding upon lowering the pH. Once the pH is shifted further towards the acidic region, hydrogen bonds are disrupted and the viscosity again declines gradually.

In spite of the structural irregularity of the MAN/2-EHA/St terpolymer, the dependence of  $\eta$  on pH and  $I$  for the terpolymer exhibited the same tendency as in the case of the structurally regular MAN/St copolymer. However, the MAN/VAc copolymer has been found to behave differently from both styrene-containing MAN copolymers (Fig. 6), since on the plot of  $\eta$  vs pH two maxima were observed, although the viscosity difference between the local maximum and local minimum was less significant than that for the former two polymers. It should be noted here that the anomaly observed in the behaviour of the MAN/VAc copolymer reflects in a certain sense its different nature in comparison with the St-containing copolymers. The polar ester group of the MAN/VAc copolymer enhances its water-solubility and due to the inductive effect lowers the  $pK$  value of a neighbouring carboxylic group as well (Fig. 7). Likewise for the MAN/VAc copolymer, the maxima of  $\eta$  appear at the same value of pH as the inflection points on a potentiometric back-titration curve (Fig. 7). Along with the carboxylic groups themselves, the ester group of the vinyl acetate unit is also considered to participate in the intermolecular associ-

ation of macromolecules and its presence presumably contributes to the viscosity increase at pH 9.0.

This study on the behaviour of the MAN copolymers in water systems under different pH and  $I$  supports the fact that their relatively sophisticated conformational changes arise not only from the different character of carboxylic groups formed by hydrolysis of anhydride rings but also from the polarity of a monomer unit located in the neighbourhood of an anhydride residue. The information obtained on the behaviour of the water-soluble MAN copolymers was subsequently explored for a protein modification performed in aqueous medium [7, 20].

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