

## Polymethacrylic Acid Derivatives

### 6. Hydrodynamic Behavior of Poly(N Methacryloyl-L-Alanine-Co-n-Phenyl-Methacrylamide)

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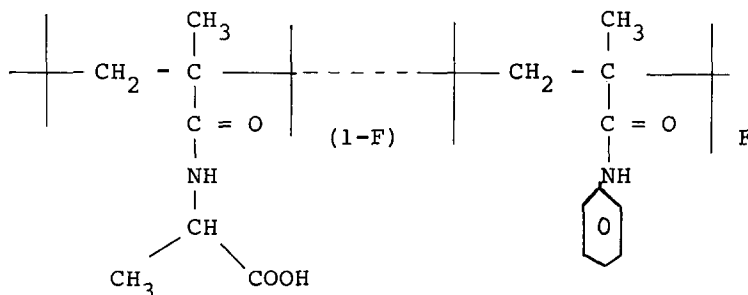
#### Summary

The viscosimetric titrations of poly(N methacryloyl-L-alanine) and of a series of poly(N methacryloyl-L-alanine-co-N phenylmethacrylamide) have been studied. The stability of the compact conformation at low degree of neutralization  $\alpha$  depends on the hydrophobic nature of the copolymer. When titrating with tetraalkylammonium hydroxides instead of sodium hydroxyde, the tetraalkylammonium ion has been found to increase the molecular dimensions of PNMA and in opposite, to decrease those of the copolymers. This has been explained by the existence of intermolecular hydrophobic interactions.

The titration of one of the copolymers in the presence of calcium ions, has shown that this divalent cation strongly depresses the electrostatic repulsions, giving to the copolymer a marked hydrophobic character.

#### Introduction

For polyelectrolytes undergoing a conformational transition upon increasing the degree of dissociation  $\alpha$  of the ionizable groups, viscosimetric measurements have become a classical way for studying the changes in their hydrodynamic behaviour. We report in this paper the viscosimetric titrations of a series of hydrophilic - hydrophobic copolymers of N-methacryloyl-L-alanine and N phenylmethacrylamide :



It has been shown in a previous paper (MORCELLET-SAUVAGE et al, 1981) that such copolymers take in water a compact conformation stabilized by hydrophobic interactions, when the mole fraction F of hydrophobic residues is higher than 15 %. Thus,

two kinds of conformational behaviour are observed in this series of copolymers depending on the value of F. First, for  $F < 0.15$ , ionization results in a normal polyelectrolyte behaviour. Second, for  $F > 0.15$  the compact conformation is retained until a critical value of  $\bar{\alpha}$ , which depends on the strength of the cohesive intramolecular hydrophobic interactions. Beyond this value, the molecular expansion results from the balance between the cohesive hydrophobic interactions and the repulsive electrostatic interactions and thus should depend among other factors on :

- . the composition of the copolymer
- . the average distance between the carboxylate groups
- . the strength of the association of the carboxylate groups with the counter-ions.

### Experimental

The synthesis and characterization of the copolymers has been described earlier (MORCELLET-SAUVAGE et al, 1981). Copolymers are referred to as  $P_F$ , F being the mole fraction of hydrophobic residues. The poly(N methacryloyl-L-alanine) homopolymer is referred to as PNMA. Aqueous solutions were prepared either by direct dissolution in water (PNMA and copolymers with  $F < 0.15$ ) or by percolation through a cationic exchange column. Potentiometric titrations were carried out at 5°, 25° and 45°C with a Radiometer pHm 62 pHmeter.

Viscosimetric measurements were made with a Fica "Viscomatic" apparatus equipped with a Ubbelohde viscosimeter at  $25 \pm 0.02^\circ\text{C}$ .

### Results and discussion

#### . Titration of the copolymers with sodium hydroxide

Potentiometric titrations were carried out at different temperatures for PNMA, P20, P24, P38 and P50. Results were plotted according to the modified Henderson-Hasselbach equation :

$$\text{pH} = \text{pK}_{1/2} - n \log \frac{\bar{\alpha}}{1-\bar{\alpha}} \quad (1)$$

which holds for  $0.05 < \bar{\alpha} < 0.7$  ( $\bar{\alpha}$  is the degree of neutralization of the copolymer).

The values of  $\text{pK}_{1/2}$  and n, obtained in this way, are given in Table I.

TABLE I

n and  $\text{pK}_{1/2}$  values for PNMA and the copolymers titrated by NaOH in pure water at different temperatures

		PNMA	P 20	P 24	P 38	P 50
n	5°	2.14	1.83	1.73	1.70	1.40
	25°	2.02	2.27	2.01	1.85	1.66
	45°	1.80	2.01	2.03	1.74	1.60
$\text{pK}_{1/2}$	5°	5.72	5.60	5.60	5.48	5.20
	25°	5.78	5.53	5.53	5.53	4.90
	45°	5.40	5.66	5.78	5.60	5.10

It is well known that  $n$  and  $pK_{1/2}$  both increase when the electrostatic repulsions between the carboxyl groups increase ( $n=1$  for a monoacid). Table I shows that the introduction of non ionizable side chains in the copolymer decreases the  $n$  and  $pK_{1/2}$  values. This may be explained by the decrease of the average distance between the ionized groups \*.

The value of  $n$  and  $pK_{1/2}$  for PNMA at  $25^\circ$  are lower than those of polyacrylic acid (GREGOR et al, 1957) which is related with the greater length of the side chain of PNMA (lower electrostatic interactions).

Fig. 1 shows the variation of the reduced viscosity  $\eta_{sp}/C$  as a function of  $\bar{\alpha}$  for PNMA, P38, P50 and P63. At  $\bar{\alpha} = 0$  the reduced viscosity of PNMA is rather high compared to the copolymers which take a compact conformation. Upon increasing  $\bar{\alpha}$ , PNMA behaves like a normal polyelectrolyte with a progressive expansion of the macromolecular chain. For P38 the viscosity at  $\bar{\alpha} = 0$  is low, but it increases rapidly upon ionization even before the beginning of the conformational transition as determined by potentiometric titrations (arrows in Fig. 1) (MORCELLET-SAUVAGE et al, 1981). In this case electrostatic interactions are predominant. For P50, the reduced viscosity remains low up to  $\bar{\alpha} = 0.2$  then increases. For the more hydrophobic copolymer in this series (P63) the initial plateau is

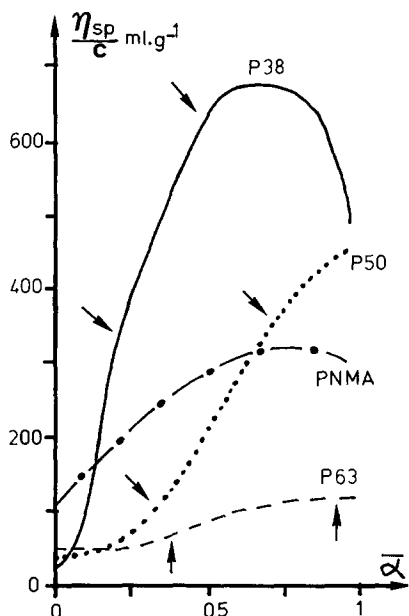


Figure 1. Variation of  $\eta_{sp}/C$  with  $\bar{\alpha}$  for PNMA, P38, P50, and P63 ( $C = 4.7 \cdot 10^{-3} \text{ eq.l}^{-1}$  except for P63 :  $1.5 \cdot 10^{-3} \text{ eq.l}^{-1}$ )

\* Similar results have been obtained for other hydrophilic hydrophobic copolymers (MILLER and RAHUT, 1959, BRAUD, 1975).

more pronounced and ionization results only in a slight increase of  $\eta_{sp}/C$ , even after the completion of the transition. In this case, hydrophobic interactions are very strong and the macromolecule retains a tightly coiled conformation. The overall trend when going from PNMA to P63 is very close to the behaviour reported by DUBIN and STRAUSS (1975) and VILLIERS and BRAUD (1978) for a series of maleic acid - alkylvinylethers copolymers with increasing hydrophobic character.

. Titration of the copolymers with tetrapropyl- and tetrabutyl ammonium hydroxides

It is well known that the association of a carboxylate group with its counter-ion decreases in the following order :  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , tetra methyl-, ethyl-, propyl-, and butyl ammonium ion. This correlated with an increase in the value of  $n$ , (increase of the electrostatic repulsions) as shown for acrylic acid - N butyl, N methylacrylamide copolymers (BRAUD, 1975). The potentiometric titration of PNMA with tetrabutyl-ammonium hydroxide gives  $n = 2,10$  value which is only slightly higher than for the titration with NaOH. Nevertheless, the viscosimetric titration (Fig. 2) shows that the electrostatic repulsions are more intense when using tetrabutylammonium hydroxide, indicating a lower ion-counterion compensation. Fig. 3 shows the effects of tetraalkylammonium ions on the viscosimetric titrations of P38 and P50.

In the fully ionized state  $\eta_{sp}/C$  decreases from NaOH to tetrapropyl and tetrabutyl ammonium hydroxide. Such an effect has already been reported for an other hydrophilic hydrophobic copolymer in water (FENYO et al, 1974, MÜLLER et al, 1974). This result, which can be considered as abnormal when compared to what is observed with hydrophilic polyelectrolytes (polyacrylic acid, polymethacrylic acid, or PNMA, Fig. 2) is not only due to a screening effect and indicates that there is a specific effect of the tetraalkylammonium cations on the molecular dimensions of P38 or P50, involving hydrophobic interactions between the hydrophobic part of the cation and the hydrophobic residues of the copolymers, through changes in the structure of water (MÜLLER et al, 1974).

The nature of the counterion has no important effect on the stability of the compact conformation. This is not surprising since, in the compact conformation, hydrophobic groups are screened from contact with the surrounding solvent. Thus, intermolecular interactions with the tetraalkylammonium ions, are not allowed. Nevertheless for an other hydrophobic - hydrophilic polymer (FENYO et al, 1974) tetraalkylammonium ions have been shown to stabilize the compact conformation, through changes in the structure of surrounding water.

. Effect of a divalent cation

In Fig. 3 is also reported the viscosimetric titration of P50 with NaOH in the presence of  $\text{CaCl}_2$  ( $R = \text{meq. Ca}^{2+}/\text{meq. COOH} = 0.86$ ). The addition of the calcium ion has two effects : at low degree of neutralization  $\alpha$ , when P50 is still in the compact conformation, it combines with two carboxylate groups, decreases the electrostatic repulsions and thus stabilizes the compact conformation. At high degree of neutralization, the calcium ion has a screening effect as monovalent cations but it also condense with the carboxylate ions (MANDEL et al, 1964 and 1967, BARONE et al, 1965). In this case the hydrophobic interactions become predominant.

Conclusion

The above results show that for PNMA and the series of copolymers the hydrodynamic behaviour is very dependent on the

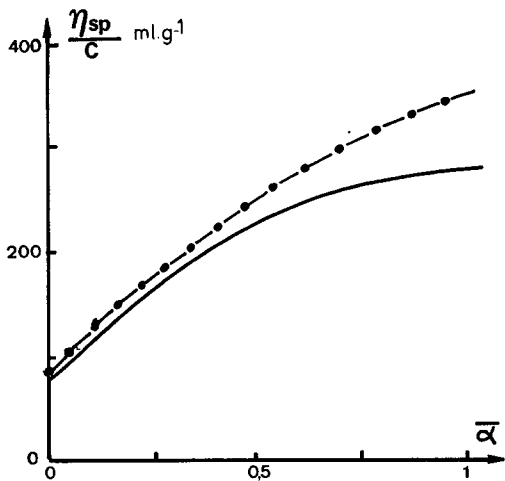


Figure 2. Viscosimetric titration of PNMA with NaOH (—) and tetrabutylammonium hydroxide (---•---)

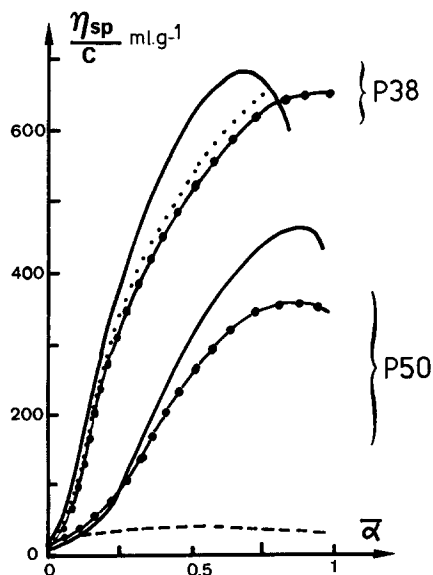


Figure 3. Effect of sodium (—), tetra propyl ammonium (.....), tetrabutyl ammonium (---•---) and calcium ion (----) on the viscosimetric titration of P38 and P50.

balance between the hydrophobic cohesive interactions and the electrostatic repulsive forces. Tetraalkylammonium ions have opposite effects on the repulsive and cohesive forces which lead to an increase of the viscosity for the more hydrophobic copolymers. Divalent cations such as the calcium ion strongly weakens the electrostatic repulsions and increases the hydrophobic character of the copolymers.

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