EFFECT OF THE NET CHARGE DISTRIBUTION ON THE AQUEOUS SOLUTION PROPERTIES OF POLYAMPHOLYTES

F. CANDAU and A. OHLEMACHER

Institut Charles Sadron[1]

J.P. MUNCH and S.J. CANDAU

Université Louis Pasteur[2]

EFFET DE LA RÉPARTITION DE LA CHARGE NETTE SUR LES PROPRIÉTÉS DES SOLUTIONS AQUEUSES DE POLYAMPHOLYTES

La nature « zwitterionique » des polymères ampholytes présente des caractéristiques qui sont utiles dans les applications environnementales et industrielles, comme les membranes d'échange ionique, les floculants dans le traitement des eaux usées et dans les procédés de récupération de pétrole. Dans ce dernier cas, l'augmentation de viscosité qui est observée en présence de saumure (comportement antipolyélectrolyte) en fait des candidats idéaux pour des milieux de salinité élevée. Les propriétés de la solution aqueuse d'une série de terpolymères ampholytes à base de 2-acrylamido-méthylpropanesulfate de sodium (NaAMPS), le chlorure de méthacryloyloxyéthyltriméthylammonium (MADQUAT) et l'acrylamide (AM), préparés en microémulsions inverses ont été étudiées par viscométrie et diffusion de lumière. La répartition des charges le long des chaînes a été modifiée en ajustant la composition en monomères initiale et le degré de conversion. L'effet de cette répartition sur la solubilité des échantillons et sur la conformation de la chaîne a été étudié. On a constaté que des échantillons avec une répartition étroite de charge nette étaient solubles dans l'eau même si la charge moyenne nette est faible. L'addition de sel produit une transition entre une conformation étirée et une conformation plus compacte en accord qualitatif avec les prédictions théoriques. Un copolymère NaAMPS-MADQUAT pratiquement alterné préparé en solution homogène et avec une faible charge moyenne nette présente un comportement assez similaire à celui des terpolymères.

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The zwitterion nature of ampholytic polymers provides features that are useful in environmental and industrial applications, e.g. ion-exchange membrane, as flocculants in sewage treatment and in oil recovery processes. In the latter case, the increase in viscosity which is observed in the presence of brine (anti-polyelectrolyte behavior) make them ideal candidates for high salinity media. The aqueous solution properties of a series of ampholytic terpolymers based on sodium-2-acrylamido-2-methylpropanesulfonate

(1) 6, rue Boussingault,
67083 Strasbourg Cedex - France

(2) Laboratoire d'Ultrasons et de dynamique des fluides complexes,
Unité de Recherche Associée au CNRS,
4, rue Blaise Pascal,
67070 Strasbourg Cedex - France

(NaAMPS), methacryloyloxyethyltrimethylammonium chloride (MADQUAT) and acrylamide (AM), prepared in inverse microemulsions have been investigated by viscometry and light scattering experiments. The distribution of the net charge among the chains was varied by adjusting the initial monomer composition and the degree of conversion. The effect of this distribution on the solubility of the samples and on the chain conformation was studied. It was found that samples with a narrow distribution of net charges were soluble in water even if the average net charge is small. Addition of salt produces a transition from an extended conformation to a more compact one in qualitative agreement with theoretical predictions. A practically alternated NaAMPS-MADQUAT copolymer prepared in homogeneous solution and with a small average net charge shows a behaviour quite similar to that of the terpolymers.

EFECTO DE LA DISTRIBUCIÓN DE LA CARGA NETA SOBRE LAS PROPIEDADES DE LAS SOLUCIONES ACUOSAS DE POLIANFOLITOS

La naturaleza zwitteriónica de los polímeros anfolitos tiene características que son útiles para las aplicaciones medioambientales e industriales, como por ejemplo, las membranas de intercambio iónico, los floculantes en el tratamiento de los productos de saneamiento (alcantarillas) y en los procedimientos de recuperación del petróleo. En este último caso, el aumento de la viscosidad observado en presencia de salmuera (comportamiento antipolielectrolítico) hace que estos elementos constituyan los candidatos ideales para los medios de salinidad elevada. Las propiedades de la solución acuosa de una serie de terpolímeros anfolitos fundados en el 2-acrilaminodo-metilpropanosulfato de sodio (NaAMPS), el cloruro de metacriloioxiletiltrimetilamonio (MADQUAT) y el acrilamido (AM), preparados en microemulsiones inversas, se han estudiado por viscometría y difusión de luz. La distribución de las cargas a lo largo de las cadenas se ha modificado ajustando la composición en monómeros inicial y el grado de conversión. También se ha estudiado el efecto de esta distribución sobre la solubilidad de las muestras y sobre la conformación de la cadena. Se ha comprobado que las muestras con una distribución estrecha de carga neta eran solubles en el agua, incluso si la carga de promedio neto es reducida. La adición de sal produce una transición a partir de una conformación extendida hacia una conformación más compacta, que vienen a confirmar la conformidad cualitativa con las predicciones teóricas. Un copolímero NaAMPS-MADQUAT prácticamente alternado, preparado en solución homogénea y con una carga reducida de promedio neto, presenta un comportamiento bastante similar de aquel de los terpolímeros.

INTRODUCTION

Polyampholytes (PA) are copolymers containing both positive and negative charged units on the same polymer chain. The number of charged monomers, either positive (f^+) or negative (f^-), can be varied at will over a large range from almost zero up to 100 % [1].

One can roughly distinguish two classes of polyampholytes :

- Annealed PA obtained by copolymerization of weak acidic or basic monomers, as for example methacrylic acid and vinylpyridine. In this case, by varying the pH, one can tune the charge distribution and the net charge δf ($\delta f = f^+ - f^-$). In particular, at the isoelectrical point (IP), the polyampholyte is electroneutral.
- The second class corresponds to quenched PA. This is the case of strong PA as for instance those prepared by copolymerization of sodium-2-acrylamido-2-methylpropane sulfonate (NaAMPS) and 2-(methacryloyloxy)-ethyltrimethylammonium chloride (MADQUAT). Here the charge distribution and the net charge are imposed by the chemistry. They only depend on the initial monomer feed composition and are pH insensitive.

What can we intuitively expect for the conformational behavior of PA when dissolved in aqueous solution? The introduction of ionic groups of opposite sign onto the polymer chain should result in a behavior essentially controlled by electrostatic interactions. If the polyampholyte is very unbalanced in charge, for example with a large excess of positive units with respect to the negative ones, then the behavior will be that of a classical polyelectrolyte, with an extended conformation in pure water and a contraction of the coil upon addition of salt. On the other hand, a polyampholyte with a balanced stoichiometry, that-is globally neutral, will tend to collapse in pure water due to the attractions between charges of opposite sign. These attractions are screened upon adding salt, resulting in an expanded configuration. These general trends have been observed experimentally and are also described in the current theories [2] and [5]. However, there are more subtle effects which have been recently observed experimentally [6] and are generally not taken into account by the theory. These effects are the following:

- the way the charges are distributed along the polymer backbone (random, alternated, blocky, etc.);

– the effect of charge fluctuations from one chain to another one. These fluctuations can be simply statistical, but in this case, the effect should vanish in the limit of infinite molecular weight [5]. More important is the difference in the reactivity of the monomers involved in the free radical copolymerization reaction. This results in a more rapid consumption of one monomer with respect to the other one in the course of the reaction. As a result, the copolymer obtained at full conversion is a mixture of polymer chains exhibiting a large distribution of the net charge. This is this issue which is addressed in the present paper.

RESULTS AND DISCUSSION

Polyampholytes of low charge density have been prepared by incorporating a large amount of a neutral monomer which was acrylamide (AM) along with the two charged monomers of opposite sign which were MADQUAT and NaAMPS (Table 1). The resulting terpolymer belongs to the class of quenched PA mentioned above. The samples were prepared using a microemulsion polymerization process in which the monomers are confined within the aqueous domains of a bicontinuous microemulsion. This process leads to very high molecular weights around 10^7. Details on the polymerization procedure can be found in refs. 7 and 8.

In Figure 1 are reported the incorporation curves of each monomer in a terpolymer, as a function of conversion from monomer to polymer. The monomer feed contained NaAMPS/AM/MADQUAT in a molar ratio 3.75/92.5/3.75. It can be seen that MADQUAT is consumed at a faster rate than AM or NaAMPS as the reaction proceeds. This means that mainly positively charged chains are formed at the early stages of the reaction whereas mainly negatively charged chains are obtained at higher conversion. Eventually, the overall terpolymer composition is that on the initial monomer feed with an average net charge close to zero.

This is illustrated by the schematic plot of Figure 2 which represents the distribution of the number of chains n(δf) as a function of the net charge. The diagram was simulated from the monomer-conversion curves of Figure 1. At low conversion, one has a rather narrow distribution of positively charged chains. As the conversion increases, the distribution is broadened and eventually at complete conversion the average net charge is zero with a very large distribution of both positive and negative charged chains.

Two series of terpolymers have been prepared.

The first series (A) corresponds to samples obtained from the same initial mixture of monomers with balanced stoichiometry, but at different degrees of conversion (10% < P < 90%). These samples are characterized by an average net charge decreasing upon increasing the degree of conversion with a simultaneous broadening of the distribution of the net charge among the chains.

In the second series (B), the polymerization was stopped at a very low degree of conversion (< 3%) and

TABLE 1

Compositions of the initial monomer feeds and characteristics of the polyampholytes

Monomer composition (mol %)			Degree of conversion %	Terpolymer Composition (mol %)			10^2 δf	Solubility in water
AM	NaAMPS	MADQUAT		AM	NaAMPS	MADQUAT		
			Series A					
92.5	3.75	3.75	14.8	82.66	5.44	11.89	6.45	S*
92.5	3.75	3.75	26.8	87.07	4.73	8.20	3.47	S
92.5	3.75	3.75	47.8	88.45	5.06	6.49	1.43	I**
92.5	3.75	3.75	84.8	91.55	4.00	4.45	0.45	I
			Series B					
95.97	2.82	1.21	4.43	91.00	3.93	5.07	1.14	S
96.50	2.50	1.00	2.31	92.68	3.35	3.97	0.62	S

S* soluble; I** insoluble.

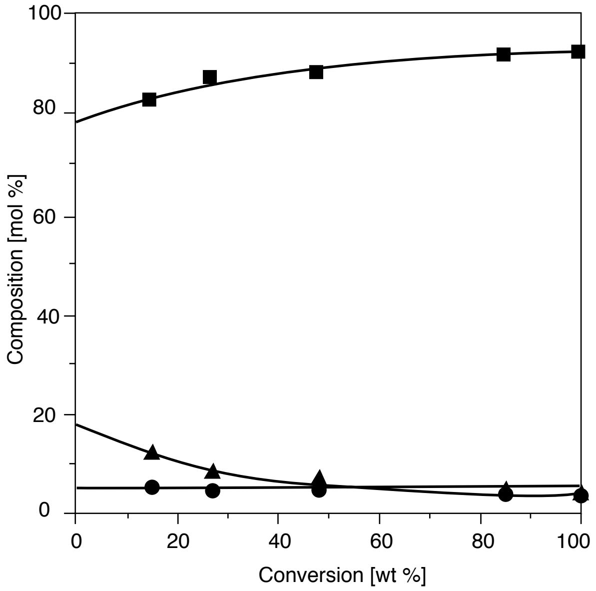

Figure 1

Monomer incorporation as a function of the degree of conversion : (■) AM, (●) NaAMPS, (▲) MADQUAT.

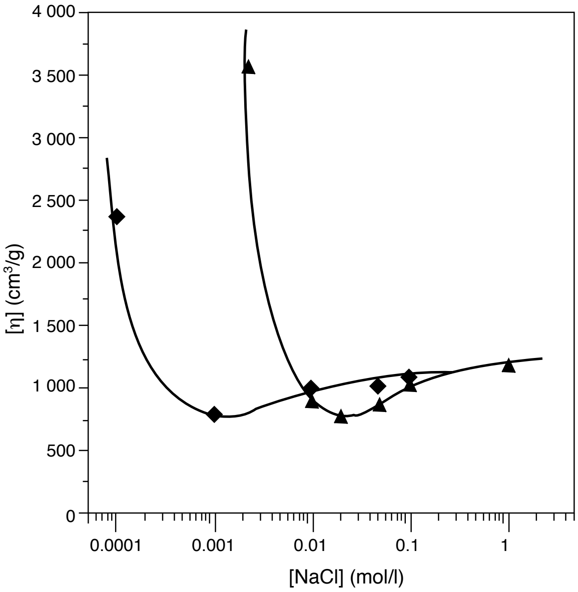

Figure 2

Intrinsic viscosity versus NaCl concentration (T = 25°C) for samples of series B (♦) : P = 2.31 % ; ▲ : P = 4.43 %.

the initial mixtures of monomers had an unbalanced stoichiometry designed in such a way that the difference in reactivity ratios of NaAMPS and MADQUAT was partially compensated. As a result, both the net charge of the samples and its distribution are small.

The solubility of the samples was determined in pure water by turbidimetry experiments. The two samples of series B are soluble in water even though they possess a very small net charge (~ 1 %). As for the other B series, the two samples obtained at the lowest degrees of conversion and which possess a relatively high net charge are fully soluble. On the other hand, those two prepared at higher degrees and with a smaller net charge and higher compositional heterogeneity are insoluble likely due to the formation of complexes between chains of opposite net charge. The comparison between the solubility behavior of these different samples emphasizes the strong effect of the sample homogeneity.

The above features are qualitatively predicted by a recent theoretical model meant for systems with a large amount of neutral termonomer [2]. In pure water, the behaviour of a charged polyampholyte is expected to be that of a polyelectrolyte if the excess of charge is large enough. This occurs when the polyampholyte attraction is dominated by the coulombic repulsion at all length scales. For a random distribution of charges, this corresponds to the condition :

$$\delta f = f^+ - f^- > \delta f_1 = f^{3/2}\,(l_B/a) \qquad (1)$$

where l_B is the Bjerrum length, a is the length of the monomeric unit, f^+ and f^- are the fractions of the monomers carrying a positive and a negative charge respectively and $f = f^+ + f^-$ is the fraction of charged monomers.

When $\delta f < \delta f_1$ the polyampholyte attractions are dominant at small length scales and the polyampholyte collapses locally.

In Table 2 are compared the experimental net charge df for the two samples of series B with the theoretical net charge δf_1, above which the polyampholyte is soluble. In both cases, the values of δf are of the same order of magnitude as δf_1, although slightly smaller. In fact, δf_1 has been calculated by assuming that there was no excluded volume for the neutral polymer. Water is indeed a good solvent at 25°C for polyacrylamide. This extra-excluded volume complements the coulombic repulsions to make the polymer soluble in water at a lower net charge.

The effect of the ionic strength on the conformational behavior of PA has been investigated by viscometry experiments. In Figure 3, is plotted the intrinsic viscosity [η] as a function of sodium chloride concentration for the two homogeneous samples of series B. In the low salt concentration range, the decrease in [η] observed upon increasing the salt content is typical of a polyelectrolyte behavior. Upon further addition of salt, a polyampholyte behavior is found as reflected by the viscosity increase. It should also be noted that the minimum in the curves is shifted to lower salt concentration upon decreasing the net charge.

TABLE 2

Comparison between the theoretical
and experimental parameters controlling
the water solubility

Degree of conversion	$10^2\ \delta f$	$10^2\ \lvert\delta f_1\rvert$
4.43%	1.14	1.89
2.31%	0.62	1.39

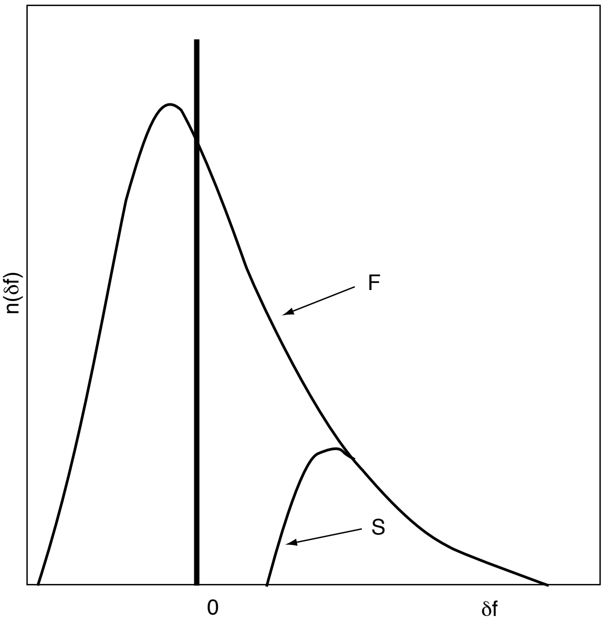

Figure 3

Schematic plot illustrating the distribution of the number of chains with net charge δf versus δf, for small (S) and full (F) conversion. The location of the maximum has been chosen arbitrarily. The areas under the curve (F) on both sides of the ordinate axis are equal.

This behaviour is in qualitative agreement with the model of Higgs and Joanny [2]. The theory predicts for a randomly polyampholyte, charged enough to render it soluble, an expanded configuration at low ionic strength and a collapsed state at a given ionic strength characterized by a Debye-Hückel length:

$$\kappa_s^{-1} = (f\, l_B/a^2)^{-1} \tag{2}$$

At higher ionic strength, the chain should exhibit a gaussian configuration. Experimentally, the signature of the collapse should be the precipitation of the polymer. Again the above scheme has been established without taking into account the excluded volume of the neutral polymer. If the excluded volume is positive, as is the case for PAM in water, the chain, instead of collapsing, exhibits a minimum size which corresponds to the minimum in the intrinsic viscosity shown in Figure 3.

CONCLUSION

The results reported here provide a good qualitative description of the conformational behavior of low charge density polyampholytes. They emphasize the strong effect of the polydispersity in charge distribution on this behavior. This effect is indeed much stronger than the classical polydispersity in size obtained for neutral polymers or even polyelectrolytes. This is due to the occurrence of complexes between chains of opposite net charge.

The above results refer to *low* charge density polymers for which the theories are meant. This implies to prepare terpolymers with all the difficulties inherent to terpolymerization reactions. In particular, the different values of monomer reactivity ratios produce a drift in composition which can be overcome by stopping the reaction at the early stages. This yields homogeneous samples whose net charge and overall charge can be adequately adjusted.

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