Dynamic behaviour of poly(methacrylic acid) in methanolic solutions

M. Sedlák

Institute of Experimental Physics, Slovak Academy of Sciences, Solovjevova 47, 043 53 Košice, Czechoslovakia

and Č. Koňák* and J. Labský

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Heyrovsky sq. 2, 162 06 Prague, Czechoslovakia

Methanolic solutions of poly(methacrylic acid) adjusted to various degrees of neutralization with lithium methoxide were investigated by photon correlation spectroscopy. The results obtained are compared with the dynamic behaviour of aqueous solutions. The influence of the solvent dielectric permittivity ε on the polyelectrolyte dynamics is discussed ($\varepsilon = 31.4$ and 78.5 for methanol and water, respectively). While two diffusive modes corresponding to the dynamics of individual chains and of multi-chain domains can be observed in aqueous solutions, no domains are present in methanolic solutions. The only observable mode (Nernst–Hartley coupled diffusion of polyions and counterions) depends anomalously on the degree of neutralization, indicating the existence of 'excess counterion condensation'. Both phenomena cannot be explained by the classical polyelectrolyte theory, which takes into account only the change of the dielectric permittivity. The role of counterions in these effects is stressed. They influence the solvent quality and cause a chain collapse reflected in excess counterion condensation. The absence of domains in methanol is ascribed to the relatively low osmotic activity of counterions.

(Keywords: poly(methacrylic acid); methanolic solutions; lithium methoxide; degree of neutralization; photon correlation spectroscopy)

INTRODUCTION

The present paper is a continuation of our previous work[1,2] dealing with the properties of polyelectrolyte solutions under conditions of strong electrostatic interactions, namely, with ionized aqueous solutions of poly(methacrylic acid) (PMA) without added salt. This weak polyacid was chosen because of the possibility of varying the charge density on chains by neutralization with a suitable alkali. Quasielectric light scattering measurements were used to study the dynamic behaviour and to correlate it with structural concepts. The first paper[1] dealt with the influence of the degree of neutralization, concentration and molecular weight, the second[2] with the influence of temperature on the solution dynamics. It was found that PMA shows a pronounced polyelectrolyte effect manifesting itself in the presence of two diffusive modes in dynamic light scattering experiments. Both modes can be observed practically under all investigated conditions, in contrast to many cases of strong polyelectrolytes[3,4]. Depending on the molecular weight of the sample, different interpretations of these modes were accepted: (1) for the low-molecular-weight sample ($M_w = 30\,000$), the fast process was attributed to Nernst–Hartley diffusion of individual chains (coupled motion of polyions and counterions) and the slow process to the diffusion of interchain domains (clusters); (2) for the high-molecular-weight sample ($M_w = 400\,000$), where a pronounced overlap of polymer coils must be considered, the fast process was attributed to cooperative diffusion and the slow process to a slow concentration fluctuation with a large correlation length.

The question most frequently discussed is the origin of the slow mode. Based on the angular dependences of the corresponding diffusion coefficient and the scattered light intensity, apparent dimensions of the clusters were established. They exceeded the dimensions of individual chains considerably. Formation of clusters with increasing charge density on macromolecules is accompanied by a destructive interference resulting in a decrease of the total scattered light intensity. It indicates some kind of ordering in solution. The temperature dependences of measured dynamic quantities for the low-molecular-weight sample showed that the clusters in a fully ionized solution are stable up to $T = 95°C$, whereas an irreversible aggregation based on intermolecular hydrogen bonding occurs[2] in partially ionized solutions above $T = 70°C$.

Another quantity that might be important for the electrostatic interactions in a polyelectrolyte solution is the dielectric permittivity of the solvent. Methanol with a relatively low dielectric permittivity ($\varepsilon = 31.4$ for methanol at 25°C *versus* 78.5 for water at 25°C) was therefore used as solvent. In analogy to previous works, a similar low-molecular-weight PMA sample ($M_w = 32\,000$) and dynamic light scattering as the experimental method were used.

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* To whom correspondence should be addressed

EXPERIMENTAL

The PMA sample (molecular weight $M_w = 32\,000$) was prepared by radical polymerization. Methanol was obtained from Lachema and was of PA quality. Samples were neutralized by means of lithium methoxide (CH_3OLi). Because of the high reactivity of lithium (especially the ability to react with CO_2 and to form insoluble salts), special care was devoted to sample preparation. Methanol was purified before use by stirring in a three-necked flask with a reflux condenser under the atmosphere of dry N_2 at room temperature for several hours. Lithium methoxide was prepared by introducing a freshly cut piece of the pure metal into a flask containing purified methanol. The lithium cutting was washed in petroleum ether and petroleum ether/methanol before adding it to methanol. The prepared solution of lithium methoxide (0.32 M) was kept under a N_2 atmosphere. PMA solutions with various degrees of neutralization were prepared by dissolving the polymer in methanol and adding calculated amounts of lithium methoxide. All manipulations were made in a glovebox flushed with dry N_2. Values of the degree of neutralization were checked by potentiometric titration. Solutions were filtered through a glass bacterial filter (Schott) with porosity 5 into glass cells, again under a N_2 atmosphere, and the cells were sealed. Samples prepared in this way showed no turbidity caused by the presence of insoluble salts arising from the reaction with CO_2 and were suitable for light scattering measurements.

A homodyne spectrometer was used for dynamic light scattering experiments. A He–Ne laser (model 125 A, Spectra Physics) and an Ar laser (model ILA 120-1, Carl Zeiss Jena) were the light sources. All measurements were carried out at 26°C. A 96-channel digital laboratory-built correlator operated with three simultaneous sampling times enabled us to measure the multi-time correlation function ($MTCF$) covering 4.5 decades of delay time. The composite correlation functions were constructed by combining two or three $MTCF$s and covered a wide range of delay times (0.5 μs–1 s).

Correlation functions were analysed by the CONTIN program[5] based on a constrained regularized method and by its modified version REPES[6]. No substantial differences between values obtained by these two methods were observed.

RESULTS AND DISCUSSION

Correlation functions were measured for a series of PMA samples with degree of neutralization ranging from $\alpha = 0$ (non-neutralized solution) to $\alpha = 1$ (totally neutralized solution) at concentration $c = 10\,g\,l^{-1}$. It is surprising that in all cases (i.e. at all degrees of neutralization) the correlation function has a single-exponential character. The measured characteristic time τ_c satisfies the relation for a diffusion process:

$$\tau_c = D^2 K^2$$

where D is the corresponding diffusion coefficient and K is the scattering vector. With respect to results obtained for aqueous solutions it can be said that the only observable mode is the fast diffusive process (Nernst–Hartley diffusion). There are no domains (clusters) responsible for the slow diffusive mode in methanolic solutions. This can be seen also with the naked eye, by
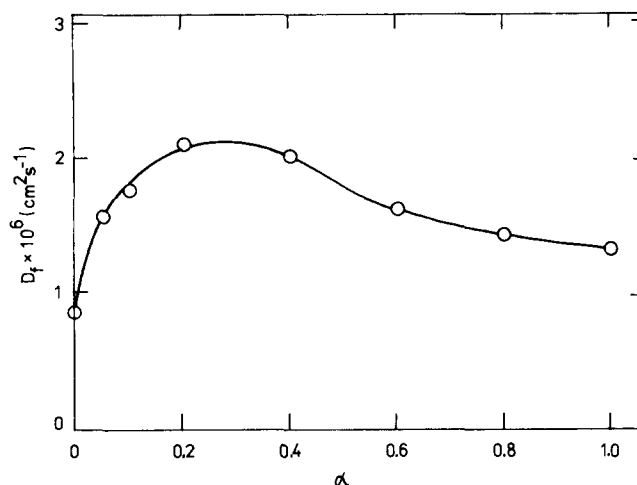

Figure 1 Dependence of the Nernst–Hartley diffusion coefficient D_f on the degree of neutralization α. PMA ($M_w = 32\,000$) in methanol, neutralized by lithium methoxide, $c = 10\,g\,l^{-1}$

observing magnified speckle patterns of scattered light. Typical mosaic patterns characteristic of aqueous solutions are not present when methanol was used as the solvent.

Figure 1 shows the dependence of the diffusion coefficient D_f on the degree of neutralization α. Contrary to aqueous solutions, after an initial rise of D_f at small values of α, D_f passes through a maximum at $\alpha = 0.2$ and decreases for $\alpha > 0.2$. The concentration dependence of D_f was measured for $\alpha = 0.25$, i.e. in the region where D_f reached its maximum value, and hence where the maximum polyelectrolyte effect could be expected. It was the aim of these measurements to investigate in particular the low-concentration region, where the contribution of the slow mode to the total scattered light intensity becomes considerable in the case of aqueous solution (see figure 8 in ref. 1). A series of samples with concentration ranging from $c = 0.3$ to $10\,g\,l^{-1}$ was measured. No slow mode can be observed even for $c = 0.3\,g\,l^{-1}$. The interaction parameter K_D determining the concentration dependence of the fast diffusion coefficient according to the equation:

$$D_f = D_0(1 + K_D c)$$

D_0 = diffusion coefficient at infinite dilution, could not be estimated due to a relatively low accuracy in the measurement of D_f in the low-concentration region. This difficulty was caused by a small light scattering intensity of the polymer in these solutions.

In order to interpret the dependence of the Nernst–Hartley diffusion coefficient on the degree of neutralization, two questions should be answered:

(1) Why does the diffusion coefficient reach its maximum value already for $\alpha = 0.2$ (in comparison with aqueous solutions where this is the case for $\alpha = 0.4$)?

(2) Why is the diffusion coefficient not constant after reaching its maximum value (as in aqueous solutions), but decreases instead?

The shift of the maximum of the Nernst–Hartley diffusion coefficient from $\alpha = 0.4$ in the case of an aqueous solution to $\alpha = 0.2$ in the case of a methanolic solution is related to counterion condensation, which takes place at $\alpha > \alpha_c$. According to Manning's theory[7], α_c corresponds to a situation when the charge-density parameter

$Q/A = 1$ (A is the distance between adjacent charges on polyions, Q is the Bjerrum length defined by $Q = e^2/\varepsilon K_B T$, where e is the elementary charge and $K_B T$ is the kinetic energy of polyions). For $\alpha > \alpha_c$ the charge density on polyions is stabilized, and so are the electrostatic interactions. By inserting the dielectric permittivity value of methanol, $\varepsilon = 31.4$, into the equation $Q/A = 1$, the value $\alpha_c = 0.15$ is obtained[8] for the critical degree of neutralization at the onset of counterion condensation (for aqueous solutions $\alpha_c = 0.36$). This value is close to the experimentally observed maximum of the diffusion coefficient at $\alpha = 0.2$.

It is much more difficult to answer the second question. The effective charge density on a polyion should have a constant value given by the relation $Q/A = 1$ for $\alpha > \alpha_c$. The increasing number of charged groups on chains with α increasing above α_c should be compensated for by the condensation of the fraction of counterions $(1 - A/Q)$. As a consequence of the constant charge density on chains, the Nernst–Hartley diffusion coefficient should be independent of α for $\alpha > \alpha_c$, since it is defined as:

$$D_{NH} = \frac{(1 + Z_p)D_p D_c}{Z_p D_p + D_c} \quad (1)$$

where Z_p is the effective charge of the polyion, D_p is the diffusion coefficient of an isolated polyion, and D_c is the diffusion coefficient of counterions. The experimental fact that D_{NH} decreases with α increasing above α_c cannot be attributed only to the lower dielectric permittivity value of the solvent.

To our knowledge no data on quasielastic light scattering have been published yet for the studied system. However, several papers have been devoted to a study of polyelectrolytes dissolved in low-dielectric-permittivity solvents by other experimental techniques. The results of these experiments bear some resemblance to ours.

Methanolic solutions of PMA with $M_w = 230\,000$ and poly(acrylic acid) (PAA) with $M_w = 290\,000$, neutralized with lithium methoxide, were investigated by potentiometric titration and viscometry[8]. Viscometric measurements showed that the reduced viscosity increased upon neutralization, reached its maximum near $\alpha \simeq 0.2$ and then decreased to the initial value. Similar α dependences of viscosity were observed also upon neutralization of poly(4-vinylpyridine) (P4VP; $M_w = 180\,000$) and poly(2-vinylpyridine) (P2VP; $M_w = 140\,000$) in a mixture of ethanol (45 wt%)–water[9]. A very detailed study concerning neutralization of PAA (mostly the fraction with $M_w = 530\,000$) in methanol by sodium methoxide (CH_3ONa) and lithium methoxide (CH_3OLi) was published by Klooster et al.[10]. Several experimental techniques used in this investigation yielded results also indicating a collapse of chains, more pronounced in the case of sodium methoxide as titrant.

As to the mechanism of the phenomena observed, Klooster et al. have ascribed them to chain conformation changes due to solvent quality changes with ionization of the polymer. It has been postulated that slightly neutralized PAA in methanol at room temperature already approaches the Θ conditions. The Θ temperature of the system—as determined by the macromolecule and the counterions with their electric charge removed—increases upon neutralization. The qualitatively different behaviour of systems with sodium and lithium ions is caused by different solvation of these ions (better

solvation of Li^+). In the case of Li^+ ions, an increase in the Θ temperature of the system (in other words, poorer solvent quality) causes a continuous collapse of chains. In the case of Na^+ ions, the Θ temperature rises above the real solution temperature. This takes place at $\alpha = 0.15$ and causes an immediate and very fast collapse. Khokhlov's theory of the condensation avalanche effect was proposed to explain the mechanism of this collapse. According to this theory a rise in the Θ temperature of the system above the real solution temperature brings about an unstable situation, where condensation of counterions causes reduction of chain dimensions and, consequently, additional condensation of counterions. The result is a very compact chain with minimum charge.

Another mechanism that might be responsible for the collapse of a polyelectrolyte in a low-dielectric-permittivity solvent has been proposed in the paper of Morawetz[8]. The collapse is ascribed to the attraction between ion pairs formed by counterion condensation. Such attractive forces at the intermolecular level are assumed to be effective in ionomers dissolved in a low-dielectric-permittivity solvent. In such a case counterions are preferably bound to the polymer and multi-coil aggregates arise[11,12]. On the other hand, ionomers show classical polyelectrolyte behaviour in a relatively high-dielectric-permittivity solvent, where counterions are dissociated[13].

In spite of different interpretations, it seems that the same mechanism applies to all polyelectrolyte solutions in a relatively low-dielectric-permittivity solvent. Only the intensity of the observed effects is different, depending on the character of the polymer, solvent and types of counterions used. This is supported by studies dealing with the influence of various types of counterions on the behaviour of methanolic solutions of PMA[14,15]. It was shown by viscosity measurements that addition of salt to the solution causes a collapse of polyions. The intensity of this effect depends on the nature of both the cation and the anion, being higher the larger the diameter of the cation and the lower the dissociation constant of the acid corresponding to the respective anion. The latter then determines the degree of dissociation of polyacid due to the addition of salt.

However, the D_{NH} changes cannot be explained only on the basis of chain contraction. In such a case the Nernst–Hartley diffusion coefficient should increase with increasing degree of neutralization above α_c due to the decrease of chain dimensions, contrary to experimental observation. According to equation (1), the experimental results indicate that the effective charge of the polyion should decrease upon neutralization to $\alpha > \alpha_c$. The reduction of the polyion charge should result from some kind of 'excess counterion condensation'. According to Manning's theory, the relation $Q/A = 1$ should hold for $\alpha > \alpha_c$ and the effective charge of the polyion should have a constant value; the real situation is different, however. The introduction of additional counterions into solution at $\alpha > \alpha_c$ is followed not only by their condensation but also by condensation of a part of the free counterions already present. A question now arises with regard to the mechanism of such counterion condensation.

Khokhlov's condensation avalanche effect can be ruled out for two reasons:

(1) In the case of the titration of PAA in methanol[10], where the condensation avalanche effect was pro-

posed, the polymer is close to the Θ conditions. In water, which is a good solvent for PAA, conditions for the condensation avalanche effect are unfavourable. This can explain differences between the behaviour of methanolic and aqueous solutions. In the case of PMA, however, the opposite situation is encountered. Methanol is a better solvent for PMA than is water[16,17], and a lowering of the solvent quality of methanol due to neutralization with lithium methoxide is not so pronounced as in the case of PAA.

(2) The condensation avalanche effect is a very rapid self-induced process. It means that, after reaching conditions for system instability at a certain degree of neutralization α, the condensation results in very small values of chain dimensions (globules) and of the effective polyion charges. A further increase of α upon addition of the titrant practically does not change the situation.

In our case (PMA) the observed process of excess counterion condensation is not self-induced, because changes of properties are continuous over a broad interval of α (from α_c to $\alpha = 1$).

The mechanism of this excess counterion condensation remains a question open to further investigation. What we can say on the basis of current knowledge is the following: the reduction of chain dimension leads to a decrease in the quantity A, which in turn induces a successive condensation of free counterions introduced into the solution before reaching the condition $\alpha = \alpha_c$.

As for the chain collapse, we suppose that an increase of the total content of Li^+ counterions in solution impairs solvent quality and therefore causes a reduction of chain dimensions.

It is possible that the solvent quality begins to deteriorate already at $\alpha = 0$, but is overcompensated in the interval from $\alpha = 0$ to $\alpha = \alpha_c$ by polyion expansion caused by repulsive charge interactions. In any case, the poorer solvent quality is related to ionized COO^- groups, not to COOH ones. This follows from the fact that addition of non-ionizing salt into a polyelectrolyte solution does not result in a collapse[15].

The absence of domains in solution is another important result of this investigation. It is not related only to the excess counterion condensation, because no domains exist over the whole interval of α, not only for $\alpha > \alpha_c$. This is surprising because one would rather expect strengthened charge interactions due to a lower value of dielectric permittivity in a methanolic solution (as compared to water). The principal role in the interactions, however, can be ascribed to counterions. Their osmotic activity in the methanolic solution is (for all values of the degree of neutralization α) absolutely lower

than in an aqueous solution. This is apparent from the measurement of the osmotic coefficient and from conductivity measurements[10]. The counterion motion is restricted more to the polyion territory. This causes a more effective screening compared to aqueous solutions, where counterions are relatively free. Such an effect acts against the strengthening of charge interactions due to the lower dielectric permittivity of methanol. Anyway, the absolute absence of domains is surprising.

Another possible explanation follows from models of attractive interactions between polyions. Ise's two-state model[18] and its electrodynamic analogue presented by Schmitz[19] were developed to explain the presence of domains in polyelectrolyte solutions. According to the electrodynamic variant, the formation of such domains is caused by fluctuations in the distribution of counterions shared by several polyions. Counterions can 'sample' several polyion environments during the time interval required for the fluctuation in the polyion distribution function to relax. The sampling distance of counterions can be shortened by a temporary 'trapping' in the polyion territory. This is more pronounced in a methanolic solution. It is possible that in such a case the sampling distance is not sufficient for mediating the interaction between several polyions.

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