Hydrodynamic Properties of Short NaPMA in Excess Salt: a Dynamic Light Scattering Study*

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Diffusion of short poly(methacrylic acid) (Na-PMA, M = 6600 g/mol) in aqueous solution has been investigated by means of dynamic light scattering at different scattering angles, ionic strengths, pH, and polymer concentrations in the pH range between 2.1 and 8.2. At pH = 2.14, only one fast relaxation mode was observed whereas at higher pH-values a fast and a slow mode could be determined. Whereas the slow mode is due to collective diffusion of polyelectrolyte domains, the fast mode at a sufficiently high ionic strength (I > 0.1 mol/L) is caused by the diffusion of single polyelectrolyte chains. From the dependence on the polymer concentration, self-diffusion coefficients at infinite dilution, the corresponding hydrodynamic radii, and second virial coefficients were determined and discussed. It was concluded that PMA exists as a random coil in excess electrolyte solution in the whole pH range, although a slight stretching was observed for pH > 4.

INTRODUCTION

Synthetic polyelectrolytes are an important class of polymers due to their commercial use (*e.g.*, in detergents) or as model compounds for natural polyelectrolytes of much less defined sizes and structures, like humic acids. Their special properties result from their high charge density, which to a considerable extent modifies the flexibility of the backbone.[1,2] In general, the charge density of weak polyelectrolytes such as polycarboxylates is a function of pH, temperature, ionic strength and type of counterions.[3–9] Most experimental and theoretical investigations have been performed with long chain polyelectrolytes. On the other hand, short chain, variably charged polyelectrolytes may serve as important model compounds for many natural polyelectrolytes and biopolymers, since many of them have medium molecular weight, like dissolved humic acids[10,11] or polyelectrolyte subdomains in some special proteins.[12,13] The methyl group of PMA introduces a small degree of hydrophobicity, which is also typical of many natural polyelectrolytes.

The purpose of this study is detailed experimental investigation and interpretation of the diffusional behavior of a short PMA in aqueous electrolyte solution by means of dynamic light scattering (DLS).[14] Part of the data has already been used for model calculations describing ionization based on a thermodynamic model;[15] here, we will present the complete analysis of experimental DLS results as a function of polymer concentration, pH, and

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* Dedicated to Professor Nikola Kallay on the occasion of his 65th birthday.

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ionic strength. Based on these results, the hydrodynamic size is calculated and discussed, since this is a crucial factor determining the effective charge density, which is also important for the behavior in aqueous solution.

MATERIAL AND METHODS

Poly(methacrylic acid) with a M = 6600 g/mol and a polydispersity of 1.11 was purchased by Polymer Standards Service, Mainz, Germany, and used without further purification. For the dynamic light scattering experiments (DLS), samples of 2 mL NaCl solutions (background electrolyte of given concentration) containing PMA in the concentration range between 3 and 20 g/L were prepared. The pH (2.1 to 8.2) was adjusted by adding HCl and NaOH, respectively. The degree of ionization as a function of pH was reported for the lowest concentration in our previous work.[15]

After preparation, the samples were filtered through 200 nm Anotop (Whatman, Brentford, Middlesex, UK) filters into carefully cleaned cylindrical DLS cuvettes (QS-glass, Hellma, Müllheim, Germany) to exclude dust. The DLS instrument consisted of an ALV goniometer, an ALV-SO-SIPD photomultiplier/discriminator-unit, an ALV5000/E correlator (ALV, Langen, Germany), and an Ar+-Laser operating at 488 nm. The intensity autocorrelation functions g_2 were recorded in VV geometry at a temperature of 20 °C and at scattering angles between 30 and 140°. The intensity autocorrelation functions were recalculated into field autocorrelation functions by means of the Siegert relation:

$$g_2 = 1 + f(g_1)^2 \qquad (1)$$

and g_1 was further analyzed by Contin.[16,17]

$$g_1 = \int_{\Gamma_{min}}^{\Gamma_{max}} S(\Gamma)\exp(-\Gamma t)\,\mathrm{d}\Gamma \qquad (2)$$

Eq. (2) describes an inverse Laplace transform of g_1 and the solution is the distribution function $S(\Gamma)$ of the relaxation rates Γ, from which the mean relaxation rates of each mode $<\Gamma>$ can be calculated. From $<\Gamma>$, the apparent translational diffusion coefficient is calculable according to:

$$D_T = <\Gamma> / q^2 \qquad (3)$$

In Eq. (3), q is the scattering vector ($q = 4\pi\,n\,\sin(\theta/2)\,/\,\lambda$) with the refractive index n, the scattering angle θ and the laser wavelength λ. Eq. (4) relates the apparent translational diffusion coefficient D_T to the polymer concentration c_P and the radius of gyration R_g:[4,18,19]

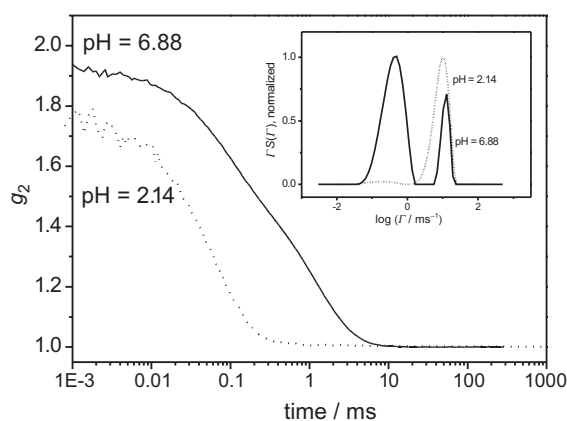$$D_T = D° (1 + k_d c_P + C\,R_g^2 q^2) \qquad (4)$$

Figure 1. Experimental intensity autocorrelation function g_2 of a sample of 10 g/L PMA (M = 6600 g/mol) in aqueous 0.12 mol dm^{-3} NaCl solution at pH = 6.88, t = 20 °C, and at a scattering angle θ = 30°. The inset shows the corresponding distribution function of the relaxation modes obtained by the CONTIN analysis.[16,17,24]

where C is a shape and polydispersity dependent constant and k_d the apparent 2nd virial coefficient.[20] Eq. (4) shows that one has to investigate the translational diffusion behavior at different concentrations and scattering angles in order to obtain reliable translational diffusion coefficients at infinite dilution, $D°$, from which hydrodynamic radii are computable. (For further evaluation of the fast diffusion process, this quantity is termed $D°_f$ in the following, see also the section Results). In the case of sufficiently small radii of gyration, i.e., for short chain lengths and for small scattering angles, one may neglect the third term in the brackets (see also the section Discussion).

RESULTS

Figure 1 shows exemplarily the intensity autocorrelation functions of 9.5 g/L PMA in aqueous 0.12 mol dm^{-3} NaCl solution at pH = 6.88 and pH = 2.14, t = 20 °C at a scattering angle θ = 30°. At high pH, the sample is characterized by a pronounced bimodal exponential decay, whereas only fast monomodal decay is observable for low pH. The corresponding distribution functions of the relaxation rates $S(\Gamma)$ are plotted in the inset. At pH = 6.88, two clearly separated modes are distinguishable, a slow mode with the mean relaxation rate of 0.45 ms^{-1} and a fast mode with the mean relaxation rate of $<\Gamma>$ = 12 ms^{-1}. At pH = 2.14, only the fast mode is observable.

In order to check if the observed modes are caused by diffusive motion, we first analyzed the angular dependence of the autocorrelation functions of PMA at pH = 2.14 and pH = 5.84 in 0.12 mol dm^{-3} NaCl solution. Figure 2 shows the distribution functions of the relaxation rates at both pH values. At all angles, monomodal relaxation was observed at pH = 2.14 whereas at pH = 5.84 the distribution functions were bimodal. From the mean
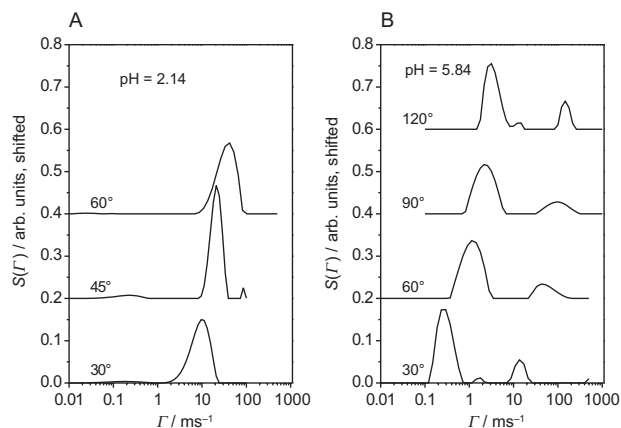
Figure 2. Inverse Laplace transforms of the field autocorrelation functions of 18 g/L PMA at pH = 2.14 (panel A) and pH = 5.84 (panel B) at different scattering angles.
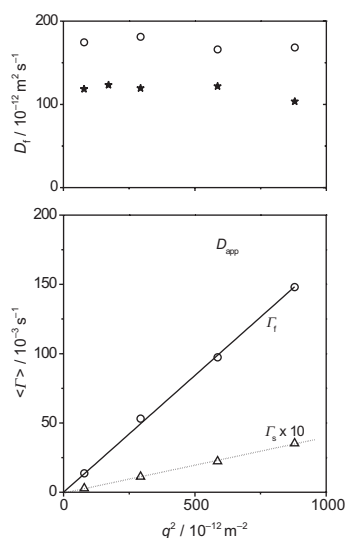

Figure 3. Bottom panel: mean relaxation rates $<\Gamma>$ of fast (O) and slow (Δ) modes at pH = 5.84 and c_p = 18 g/L as a function of the squared scattering vector q^2. Top panel: mean apparent diffusion coefficients at pH = 5.84 (O) and pH = 2.14 (★).

value of each mode, the mean relaxation rates $<\Gamma>$ were calculated and plotted in Figure 3 (bottom) *vs.* q^2. At pH = 5.84, the mean relaxation rates of both the fast ($<\Gamma_f>$) and slow modes ($<\Gamma_s>$) depend linearly on q^2. The same was observed for $<\Gamma_f>$ of the fast mode at pH = 2.14 (not shown). In Figure 3 (top), it is demonstrated that the quotient $<\Gamma_f>/q^2$ at pH = 2.14 and 5.85 is independent of q^2 according to Eq. (3). In the following, this quotient is termed the mean apparent diffusion coefficient D_f of 6600 g/mol PMA under the applied conditions.

It is known that the fast diffusion mode of a polyion in electrolyte solution depends on the salt concentration.[21] This behavior can be described by the coupled mode theory, where the motion of the polyion couples to the motion of the surrounding counterion cloud. For a sufficiently high ionic strength, the theory states that the observed diffusion coefficient is only due to the motion of the

polyion. To confirm this, we investigated the effect of ionic strength on the fast mode. Figure 4 shows the mean relaxation rates of NaPMA at pH = 6.86 and c_P = 3.8 g/L as a function of the total sodium chloride concentration. At low ionic strength, a pronounced dependence of $<\Gamma_f>$ on c_{NaCl} is present, but for $c_{NaCl} > 0.1$ mol/L the mean rate stays constant. The apparent diffusion coefficient is calculated as 135×10^{-12} m^2/s; this value corresponds very satisfactorily with that found by Sedlak[5] for PSS with a molar mass of 5000 g/mol in 0.1 mol dm^{-3} NaCl solution.

Hydrodynamic interactions further affect the apparent self-diffusion coefficient of polymers at finite concentrations; see Eq. (4) above. Figure 5 shows the dependence of apparent diffusion coefficients of NaPMA in 0.12 mol/L NaCl solution on concentration at different pH values. We fitted the data linearly disregarding the third term in Eq. (4), and Table I summarizes the numerical results. For
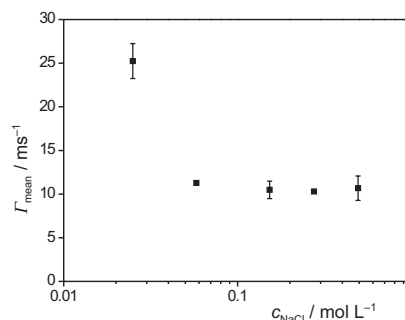

Figure 4. Mean relaxation rates of NaPMA at pH = 6.86 and c_P = 3.8 g/L as a function of the total sodium chloride concentration.
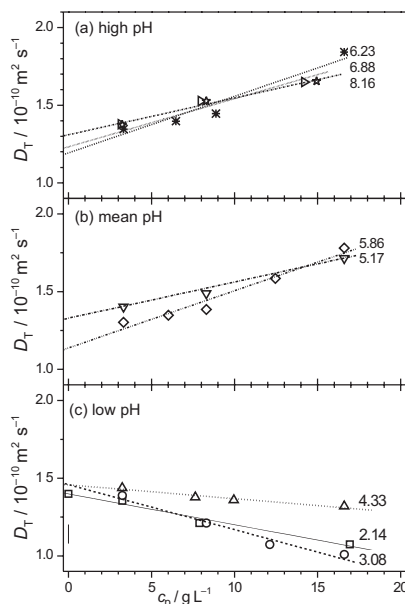

Figure 5. Translational diffusion coefficients obtained by means of Eq. (3) from mean relaxation rates of the fast process (θ = 30°, t = 20 °C, [NaCl] = 0.12 mol/L) at different pH-values and concentrations c_P of the polymer.

TABLE I. Results of the linear regression of fast and slow relaxation modes of PMA (6600 g/mol) in 0.12 mol/L NaCl solution (background electrolyte). The overall ionic strength, defined as $c_{NaCl} + 0.5\ c_{(HCl,\ NaOH)}$, is slightly enhanced by at most 0.01 mol/L for the lowest polymer concentration. Polymer concentrations range from 3 to 17 g/L, α is the degree of deprotonation taken from Ref. 15

pH	α	A_c / l_B	Fast process			Slow process	
			$D°_f / 10^{-10}$ m^2 s^{-1}	R_h / nm	$k_{d,f}$ / L g^{-1}	$D°_s / 10^{-12}$ m^2 s^{-1}	$k_{d,s}$ / L g^{-1}
2.14	0.000	–	1.4	1.51	–0.014	–	–
3.08	0.007	61	1.46	1.45	–0.020	7.0	–0.024
4.33	0.082	8.7	1.46	1.45	–0.006	7.5	–0.004
5.17	0.207	5.2	1.31	1.62	0.018	4.7	–0.0001
5.84	0.458	2.1	1.15	1.84	0.032	5.1	–0.002
6.22	0.583	0.94	1.22	1.74	0.030	8.2	–0.030
6.88	0.771	0.74	1.24	1.71	0.019	6.8	–0.019
8.16	0.977	0.56	1.31	1.62	0.026	8.6	–0.037

pH > 5 (Figures 3a and 3b), the diffusion second virial coefficients are positive between 0.018 and 0.032 L/g, but for pH < 5 negative values are found in the range between –0.006 and –0.02 L/g. Figure 6 shows the dependence of $D°_f$ and k_D on pH and on the inverse Manning parameter (see also Table I). The concentration dependence of the slow mode is simpler. Although there are no established theoretical concepts, we have analyzed the slow mode in the same way as the fast mode according to Eq. (3); the data are also included in Table I.

DISCUSSION

The nature of the slow mode, caused by collective diffusion of polyelectrolyte domains, has been discussed extensively in the literature.[6,14,22] Our observation that the slow mode is not present at very low pH where the polymer is completely protonated and uncharged supports this interpretation. The fast mode in the range of 10 ms^{-1} for $q = 30°$ is in all cases due to the diffusion of single polyions. From its dependence on the NaCl concentration, one can conclude that the influence of the ionic cloud is negligible above a concentration of 0.1 mol/L. Similar behavior is reported in the literature already for PSS[5] and is interpreted by the coupled mode theory, which describes the fast relaxation rates at low salt concentrations as coupled motion of counterions and polyions.[23] For higher ion concentrations, this motion decouples and the observed fast mode is due to diffusion of single polyelectrolytes.
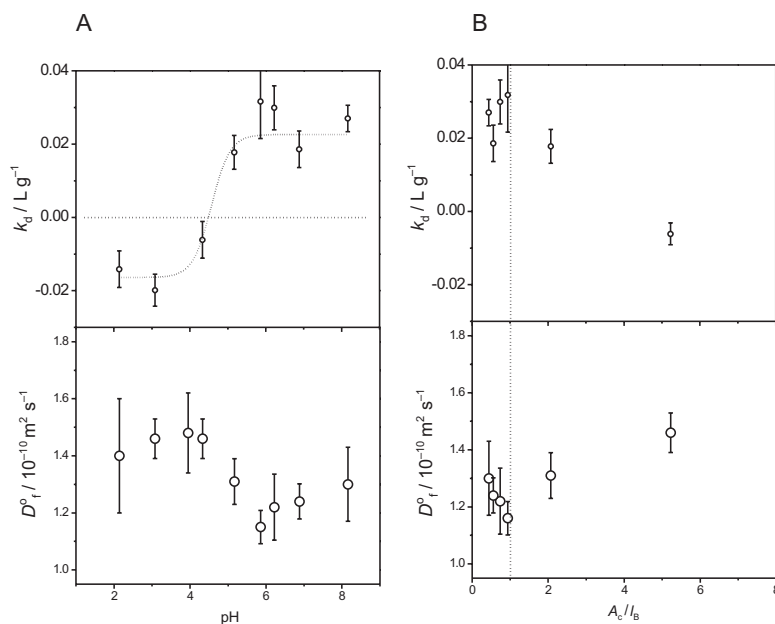

Figure 6. A) $D°_f$ and k_d obtained by fitting Eq. (4) (see text for details) for PMA (M = 6600 g/mol) at different pH and [NaCl] = 0.12 mol/L. Error bars result from the linear regression of the data shown in Figure 5. B) $D°_f$ and k_d plotted *versus* the inverse Manning parameter A_c/l_B (≡ mean distance between charges / Bjerrum length). The vertical dotted line indicates $A_c/l_B = 1$.

No dependence of the ratio $\langle \Gamma_f \rangle / q^2$ on q was observed, indicating that the apparent diffusion coefficient depends only on the polyion concentration.[4] This becomes reasonable if one estimates the third term in Eq. (4) assuming[20] $C = 0.2$ for a linear monodisperse flexible polymer and $R_g \approx 1.5 R_h$. For the lowest investigated concentration, the third term contributes maximally to about 1 % of the concentration term $k_d c_P$, as expectable for such small polymer molecules. This further allows the linear fitting of Eq. (4) to the concentration dependent data; see Figure 5.

The determined hydrodynamic radii agree also with the results of Schweins *et al.*[4] obtained for poly(acrylic acids) with different chain lengths. Assuming $v \approx 0.6$ and the validity of the power law $R_h \propto M^v$, one obtains $R_h \approx 2.2$ nm for this short ($M = 6600$ g/mol) polyelectrolyte, while we determined $R_h \approx 1.8$ nm at pH ≈ 6 in 0.12 mol/L NaCl solution. This slightly smaller size may be caused by the slightly lower hydrophilicity due to the methyl side groups of PMA or a lower degree of deprotonation. We observed a sigmoidal pH dependence of k_d of the diffusion coefficients of single polyions. In this note, however, we do not intend to give a quantitative interpretation of this effect. A qualitative explanation is that under the given conditions of excess salt and low pH the effective degree of ionization (0 to 0.12) is sufficiently low to satisfy the θ conditions. This leads to the observed negative slope for pH < 5. With increasing ionization, PMA gets well solvated and the slope (k_d) gets positive. The diffusion coefficients of single polyions also depend on pH. With increasing pH, $D°_f$ decreases and the corresponding hydrodynamic radii R_h increase; see Table I. A further illustration is the plot of k_d and $D°_f$ as a function of the inverse Manning parameter A_c / l_B (mean distance per charge/Bjerrum length; see Figure 6B), which is calculated from the degree of ionization given in Table I. $D°_f$ shows a minimum and k_d a maximum at $A_c / l_B \approx 1$. The reason is most probably the increased charge of the polymer from low pH to pH ≈ 6. Beyond this pH, newly created deprotonated sites bind Na^+ in the inner-sphere mode, so that the net charge remains approximately constant. This is expectable according to the ion condensation theory as well as the chemical equilibrium approach.[15]

Qualitatively, the expected behavior is an increase of R_h and decrease of k_d, since with increasing charging the backbone gets stiffer and the polyion stretches itself. However, the effect is not so strong for PMA to stretch to its full length at high pH. The reason is a sufficiently high concentration of counterions (electrostatic shielding) in the excess electrolyte medium the allow the polymer to remain rather flexible. This interpretation of the DLS data is also supported by our previous model calculations,[15] showing that an electrostatic model that combines a flexible random coil parameterized by hydrodynamic radii, direct binding of counterions, and additional electrostatic attraction in a Poisson Boltzmann approach describes the measured ionization data very satisfactorily.

REFERENCES

1. M. Borkovec, B. Jönsson, and G. J. M. Koper, *Ionisation Processes and Proton Binding in Polyprotic Systems: Small Molecules, Proteins, Interfaces and Polyelectrolytes*, in: E. Matijević (Ed.), *Surface and Colloid Science*, Vol. 16, Plenum / Kluwer Academic, New York, 2001.
2. H. Dautzenberg, W. Jaeger, J. Kötz, B. Philipp, C. Seidel, and D. Stscherbina, *Polyelectrolytes*, Hanser, München, 1994.
3. R. Schweins and K. Huber, *Eur. Phys. J. E* **5** (2001) 117–126.
4. R. Schweins, J. Hollmann, and K. Huber, *Polymer* **44** (2003) 7131–7141.
5. M. Sedlak, *J. Chem. Phys.* **105** (1996) 10123–10133.
6. M. Sedlak, *J. Chem. Phys.* **116** (2002) 5256–5262.
7. M. Sedlak, C. Konac, P. Stepanek, and J. Jakes, *Polymer* **31** (1990) 253–256.
8. C. Heitz, M. Rawiso, and J. Francois, *Polymer* **40** (1999) 1637–1650.
9. M. Mandel, J. C. Leyte, and M. G. Stadhouder, *J. Phys. Chem.* **71** (1967) 603–612.
10. B. M. Bartschat, S. E. Cabaniss, and F. M. M. Morel, *Environ. Sci. Technol.* **26** (1992) 284–294.
11. T. Miyajima, Y. Kanegae, K. Yoshida, M. Katsuki, and Y. Naitoh, *Sci. Total Environ.* **118** (1992) 129–137.
12. H. G. Körschen, M. Illing, R. Seifert, F. Sesti, A. Williams, S. Gotzes, C. Colville, F. Muller, A. Dose, M. Godde, L. Molday, U. B. Kaupp, and R. S. Molday, *Neuron* **15** (1995) 627–636.
13. S. Haber-Pohlmeier, K. Abarca-Heidemann, H. G. Koerschen, H. Kaur Dhiman, J. Heberle, H. Schwalbe, J. Klein-Seetharaman, U. B. Kaupp, and A. Pohlmeier, *Biophys. J.* **92** (2007) 3207–3214.
14. M. Sedlak, *Langmuir* **15** (1999) 4045–4051.
15. A. Pohlmeier and S. Haber-Pohlmeier, *J. Colloid Interface Sci.* **273** (2004) 369–380.
16. S. W. Provencher, *Comput. Phys. Commun.* **27** (1982) 213–227.
17. S. W. Provencher, *Comput. Phys. Commun.* **27** (1982) 229–242.
18. J. M. Schurr and K. S. Schmitz, *Annu. Rev. Phys. Chem.* **37** (1986) 271–305.
19. M. Mandel, *Physica A* **147** (1987) 99–114.
20. W. Burchard, M. Schmidt, and W. H. Stockmayer, *Macromolecules* **13** (1980) 580–587.
21. M. Sedlak, *Structure and Dynamics of Polyelectrolyte Solutions by Light Scattering*, in: T. Radeva, (Ed.), *Physical Chemistry of Polyelectrolytes*, Marcel Dekker, New York, 2001. pp. 1–58.
22. M. Sedlak, *J. Chem. Phys.* **122** (2005) 151102.
23. K. S. Schmitz, *Macroions in solution and colloidal suspension*, VCH, New York, 1993.
24. H. Ruf, *Adv. Colloid Interface Sci.* **46** (1993) 333–342.

SAŽETAK

Hidrodinamička svojstva kratke NaPMA u suvišku soli: istraživanje pomoću dinamičkog raspršenja svjetla

Sabina Haber-Pohlmeier i Andreas Pohlmeier

Istraživana je difuzija kratke poli(metakrilne kiseline) (Na-PMA, M = 6600 g/mol) u vodenoj otopini pomoću dinamičkog raspršenja svjetla pri različitim kutovima raspršenja, ionskim jakostima, pH i koncentracijama polimera u pH području između 2,1 i 8,2. Pri pH = 2,14 uočena je samo brza relaksacija, dok su pri višim vrijednostima pH određene i brza i spora relaksacija. Spora relaksacija se javlja zbog kolektivne difuzije polielektrolitnih domena, dok do brzog načina pri dovoljno visokoj ionskoj jakosti (I > 0,1 mol/L) dolazi zbog difuzije pojedinačnih polielektrolita. Iz ovisnosti o koncentraciji polimera, određene su i raspravljene vrijednosti koeficijenata samodifuzije pri beskonačnom razrjeđenju, odgovarajući hidrodinamički radijusi i sekundarni virijalni koeficijenti. Zaključeno je, da je PMA u suvišku elektrolita prisutna kao slučajna zavojnica u cijelom ispitivanom pH području, iako je lagano istezanje uočeno pri pH > 4.