LIGHT SCATTERING INVESTIGATION OF AQUEOUS SOLUTIONS OF POLY (METHACRYLIC ACID) AND POLY (SODIUM METHACRYLATE)[#]

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Abstract

Light scattering was used to study the properties of poly (methacrylic acid), PMA, and its sodium salt, NaPMA, in aqueous solutions. The polymer is an atactic one, composed of around 45% heterotactic and 55% syndiotactic triads. The weight-average molar mass of a single PMA chain ($M_{w,0}$ = 131 kg/mol) was estimated from experiments with NaPMA in 0.1 M NaCl. From the scattering data at zero-angle it was concluded that PMA is inter-molecularly associated in 0.1 M HCl. The data were treated according to the Open Association Model of Elias, which yielded M_w for the associated PMA form equal to 188 and 170 kg/mol at 25 °C and 55 °C, respectively. Furthermore, the second virial coefficient and a relatively high value for the apparent association constant were obtained: $A_2 = 1.37 \times 10^{-3}$ and 1.24×10^{-3} mol ml/g^2 and $K_{app} = 3.4 \times 10^5$ and 2.0×10^5 at 25 °C and 55 °C, respectively. The radius of gyration of NaPMA in 0.1 M NaCl is R_g = 47 nm, whereas for PMA in 0.1 M HCl it is equal to 20.4 nm at 25 °C. An increase in temperature from 25 °C to 55 °C brings about a decrease in R_g to 16.9 nm for PMA in 0.1 M HCl. The changes in thermodynamic functions point to a hydrophobically driven association process of PMA chains.

Introduction

Poly (methacrylic acid), PMA, is a weak polyacid with hydrophobic methyl side chains. Their presence leads to a number of peculiarities in solution behavior of PMA, which point that some elements of structure are present in the dissolved polymer. In contrast to poly (acrylic acid), which displays a smooth transition from a more compact coil to an expanded one upon increasing its degree of ionization, PMA resists expansion before a critical charge density is attained.[1] This transition is usually described as a cooperative change from a tightly coiled cluster of the un-ionized polyacid to an extended form of the charged polyion coil.[1] Furthermore, PMA is known to form thermo-reversible gels in concentrated solutions that display a lower critical solution temperature (LCST) behavior; a gel phase is formed upon heating the solution.[2a] From viscometric and thermodynamic studies of un-dissociated PMA it was concluded that the molecule is intramolecularly bonded in dilute solutions.[2b] These intramolecular bonds in the dilute regime eventually lead to agglomeration (e.g. gelation) in concentrated solutions caused by intermolecular association.[2a]

The aim of this paper is preliminary studies of the association behavior of PMA in aqueous HCl solutions. Wide-angle light scattering is a very sensitive method that is able to detect even very small amounts of the associated material. Light scattering measurements will be performed in aqueous solutions of PMA at zero degree of neutralization, $\alpha_N = 0$, and in solutions of its sodium salt, NaPMA, at $\alpha_N = 1$. It has been pointed out frequently that the behavior of PMA depends considerably on the type and degree of stereo-regularity of the chain.[3-7] For example, the isotactic form of PMA displays a partly irreversible potentiometric behavior in aqueous solutions[4-7] in contrast to the atactic and syndiotactic ones. Binding capacity towards various counterions depends considerably on the tacticity of the polyion.[7] In most of the investigations of PMA, however, the tacticity of the polyion is either not known or not reported. It is therefore difficult to correlate the existing data with the detailed structural features of the chain. One of the aims of our study is to also ascertain the stereo-chemical composition of the studied sample.

Experimental section

Materials

Poly (methacrylic acid) was prepared by polymerization of methacrylic acid using a standard procedure.[8] The tacticity of the polymer was determined from the ester form. The polyacid was dissolved in a methanol/water mixture (2:1) and ethereal diazomethane solution was added while stirring to yield the methyl ester, poly (methylmethacrylate), PMMA.[9] The tacticity of the resulting PMMA was determined from the signals of the α-methyl group in the proton[5] and in the ^{13}C NMR spectrum[10] of a $CDCl_3$ solution. The polymer contains around 45% heterotactic and around 55% syndiotactic triads. The amount of the isotactic ones is negligible.

The stock solution of PMA for light scattering measurements was prepared by dissolving the dry acid in ultra pure water obtained with the Milli-Q-Reagent Grade Water System, Millipore. To ensure complete solubilization of the polymer, the solution was stirred overnight at room temperature. Afterwards, it was transferred quantitatively into a volumetric flask and a desired amount of 1 M HCl was added to yield the concentration of HCl equal to 0.1 M. For the preparation of NaPMA stock solution, PMA was first dissolved in water and 1 M NaOH solution was slowly added under continuous stirring and blowing through with N_2 until the pH of the solution was around 8.5. The solution was then transferred into a volumetric flask and the calculated amount of 1 M NaCl was added. All light scattering experiments with NaPMA were performed in 0.1 M NaCl. Before performing light scattering measurements, all solutions were filtered directly into measuring cells through Millipore filters (type GS) with a pore size 0.22 μm using a closed circuit involving a filter holder and a peristaltic pump. The filtering time was around 5-15 minutes.

Light Scattering Measurements

The static light scattering at 25 °C and 55 °C was measured at angles between 40° and 150° using a commercial Amtec MM 100 photometer. A cylindrical cell, containing the solution, was immersed in a thermostatically controlled toluene bath. As the light source, a monochromatic and polarized beam of a He-Ne laser (Spectra Physics, Model 124) operating at 632.8 nm was used. The proper optical alignment of the instrument was checked regularly by measuring the scattering of toluene. The refractive index increment, d*n*/d*c*, for PMA and NaPMA was taken from the literature. The following variation of d*n*/d*c* with the degree of neutralization, α_N, is reported[11]

$$\frac{dn}{dc} = 0.171 + 0.092\alpha_N\,(ml/g) \qquad (1)$$

It gives d*n*/d*c* = 0.171 and 0.263 ml/g for the acid ($\alpha_N = 0$) and for the salt ($\alpha_N = 1$), respectively. These values were used in elaborating the data obtained by static light scattering method. All light scattering experiments were performed in the concentration range of the polymer below 2 g/L.

Analysis of the Light Scattering Data

Concentration dependence. The experimental data were analyzed for the concentration dependence according to the Open Association Model (OAM) of Elias.[12] For a system having a polydispersity index, PI (PI = M_w/M_n, where the indexes w and n denote the weight and the number averages of the molar mass, respectively), the OAM introduces an apparent weight-average molar mass of an associating species, $(M_w)_{ass}$, as[12,13]

$$(M_w)_{ass} = \left[(M_{w,0})^2 + 4000 K_{ass} PI \cdot M_{w,0} c_p\right]^{1/2} \tag{2}$$

In Eq. 2, $M_{w,0}$ is the weight-average molar mass of the fundamental non-associating species (unimer[12]), K_{ass} is the apparent association constant for the process, and c_p is the concentration of the polymer in g/L. By substitution of Eq. 2 into the classical Zimm formula[14,15] for the inverse of the reduced scattering intensity, Kc_p/R_θ, at a scattering angle θ

$$\frac{Kc_p}{R_\theta} = \left(\frac{1}{(M_w)_{ass}} + 2A_2 c_p + \ldots\right)\frac{1}{P(\theta)} \tag{3}$$

the expression for the concentration dependence of scattering at $\theta \rightarrow 0°$ takes the form[13]

$$\left.\frac{Kc_p}{R_0}\right| = \frac{1}{\left[(M_{w,0})^2 + 4000 K_{ass} PI \cdot M_{w,0} c_p\right]^{1/2}} + 2A_2 c_p \tag{4}$$

In Eqs. 3 and 4, K is the optical constant in the light-scattering equation,[15] R_θ is the Rayleigh ratio,[15] A_2 is the second virial coefficient, and $P(\theta)$ is the form factor of a macromolecule (note that $P(0) = 1$).[15] The PI for our sample is not known. Consequently, the product K_{ass}·PI was used as a single fitting parameter, $K_{app} = K_{ass}$·PI, together with $M_{\mathrm{w},0}$ and A_2. The second virial coefficient was considered to be a constant for each series of experiments, irrespective of the extent of association.[13,15] Knowing $M_{\mathrm{w},0}$, Eq. 4 can be used as a two-parameter equation for the evaluation of K_{app} and A_2.

Angular dependence. The form factor $P(\theta)$ depends on θ and on the shape and size of the scattering particle. It can be expressed in relation to the so-called concentration-dependent static correlation length, $\xi(c_\mathrm{p})$, by the expansion[16]

$$P(\theta) = \left[1 - \left(q \cdot \xi\left(c_p\right)\right)^2 + \frac{3}{10}\left(q \cdot \xi\left(c_p\right)\right)^4 - \dots\right] \tag{5}$$

where q is the scattering vector given by the relationship

$$q = \frac{4\pi \cdot n_s \sin\left(\frac{\theta}{2}\right)}{\lambda} \tag{6}$$

In Eq. 6, λ is the wavelength of the incident light and n_s is the refractive index of the solvent (1.33 for water). $P(\theta)$ enables the evaluation of the z-average root mean square radius of gyration, $\left(\left\langle R_g^2 \right\rangle_z\right)^{1/2}$, of the macromolecule. For simplicity, R_g will be used to designate the latter quantity. The radius of gyration is obtained from the static correlation length at infinite dilution, ξ_0, according to Eq. 7

$$R_g = \sqrt{3} \cdot \left(\lim_{c_p \to 0} \xi\left(c_p\right)\right) = \sqrt{3} \cdot \xi_0 \tag{7}$$

where ξ_0 is the result of the extrapolation of $\xi(c_\mathrm{p})$ to $c_\mathrm{p} = 0$.

After substitution of $P(\theta)$ (Eq. 5) into Eq. 3, the $1/P(\theta)$ term can be approximated for small q-values by the usual linear dependence on q^2.[14] One obtains then the following expression for the reduced light scattering intensity at constant c_p, known as the Zimm-approximation

$$\left.\frac{Kc_p}{R_\theta}\right|_{c_p} = \left(\frac{1}{(M_w)_{ass}} + 2A_2c_p\right)\left(1 + \xi^2(c_p)x\right) \tag{8a}$$

where x = q^2. (Although the relation between $\xi(c_p)$ and R_g given by Eq. 7 is strictly valid at infinite dilution only, one can operationally use a similar one

$$R_g^{app} \equiv \sqrt{3}\cdot\xi(c_p) \tag{9}$$

even for finite values of c_p. In this notation, Eq. 8a takes the form

$$\left.\frac{Kc_p}{R_\theta}\right|_{c_p} = \left(\frac{1}{(M_w)_{ass}} + 2A_2c_p\right)\left(1 + \frac{\left(R_g^{app}\right)^2}{3}x\right) \tag{8b)}$$

If the angular dependence of the intensity of scattered light shows a curvature when q^2 approaches zero the linear extrapolation procedure is no longer justified.[14] In the case of a non-linear q^2-dependence of the scattering function, the latter can be approximated by various relationships. A polynomial function of the second order in x

$$\left.\frac{Kc_p}{R_\theta}\right|_{c_p} = \left(\frac{1}{(M_w)_{ass}} + 2A_2c_p\right)\left(1 + \frac{\left(R_g^{app}\right)^2}{3}x + b_2x^2\right) \tag{10}$$

gives a much better fit of the experimental data than the most often used linear approximation. In Eq. 10, b_2 is a constant resulting from the fitting procedure. Eqs. 8-10 were applied for the evaluation of the radius of gyration of PMA and NaPMA.

Results and disccusion

1. NaPMA in 0.1 M NaCl. The completely charged sodium salt of poly (methacrylic acid) was used to estimate the weight-average molar mass of a single PMA chain under the universally accepted assumption that PMA - anions don't associate with each other. Figure 1 shows the Zimm plot[15] for NaPMA in 0.1 M NaCl at 25 °C, i.e., a plot of the reduced light scattering data, Kc_p/R_θ, against $\sin^2(\theta/2) + kc_p$, where k is an arbitrary constant (k = 10 in this case). The angular dependence of scattering (at constant c_p) is close to linear as it can be appreciated from the curves in Figure 1. M_w of the sample is obtained by a double extrapolation procedure, first to $\theta = 0°$ (or $q^2 = 0$, c.f. Eq.6) at constant c_p and then to $c_p = 0$. The zero-angle values, Kc_p/R_0, were obtained in two ways: by a linear (Eq. 8a or b) and by a second order in q^2 polynomial fitting (Eq. 10). The difference between Kc_p/R_0 values obtained by both procedures is small. However, the latter one results in lower values of the sum of the squares of residuals. These Kc_p/R_0 results are therefore included in Figure 1 as full circles, whereas the full triangles are the result of the extrapolation at constant angle to $c_p = 0$.

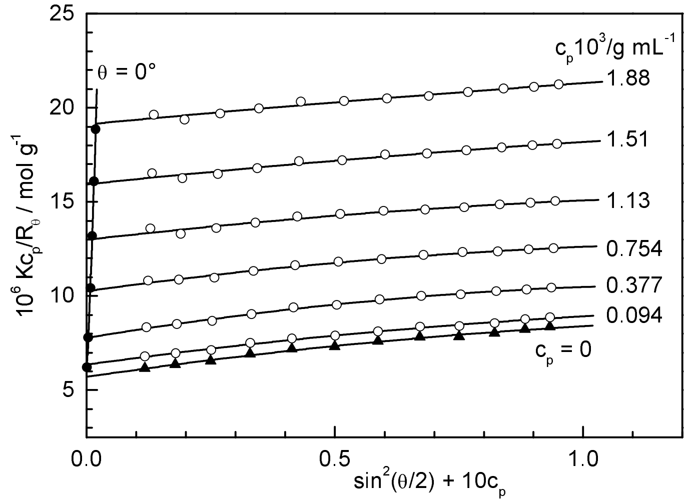

Figure 1. *The Zimm-plot of NaPMA in 0.1 M NaCl at 25 °C.*

The limiting slope of the $\theta = 0°$ curve in Figure 1 is proportional to the second virial coefficient of NaPMA in 0.1 M NaCl. A value $A_2 = 2.64 \times 10^{-3}$ mol ml g^{-2} is obtained.

The extrapolation to $c_p = 0$ was carried out by a second order polynomial fitting in c_p. The resulting M_w for NaPMA is equal to (165±4) kg/mol. From this, one obtains the weight-average degree of polymerization equal to 1528. If one assumes the same degree of polymerization for the polymer also in the acid form, the resulting weight-average relative molecular mass of an isolated PMA chain is equal to 131 000 (i.e., M_w for PMA is equal to 131 kg/mol).

2. PMA in 0.1 M HCl at 25 °C and 55 °C. Scattering studies with PMA in aqueous 0.1 M HCl were performed at 25 °C and at 55 °C. Figure 2a and 2b show the resulting Zimm plots. One can clearly see that these plots are curved, markedly so at lower concentrations, whereas at higher concentrations the curvature is less pronounced. The extrapolation to $\theta = 0°$ was carried out by the usual linear (Eq.8 a and b) and by a polynomial fitting procedure (Eq. 10). In the case of PMA, the latter one gives a much better fit of the experimental data, indicated by the lowest values of the sum of the squares of the residuals. Therefore, the polynomial fitting in q^2 was considered for the evaluation of the Kc_p/R_0 values at both temperatures. These values are plotted in Figure 3. They show a pronounced deviation from linearity in the low c_p range.

The upward curvature in Kc_p/R_0 values when c_p approaches zero is diagnostic for inter-molecular association.[12,13] Therefore, an appropriate association model has to be applied for the treatment of these data. In our case, the Open Association Model of Elias was used,[13] in the first place as a three-parameter equation (Eq. 4: variable $M_{w,0}$, K_{app}, and A_2) to evaluate $M_{w,0}$. The model gives a rather good fit of the data points as can be seen from the curves reported for each temperature in Figure 3. The resulting $M_{w,0}$ for PMA in 0.1 M HCl is (188±4) kg/mol and (170±4) kg/mol at 25 °C and 55 °C, respectively. These values are considerably higher than the value proposed for a single un-associated PMA chain ($M_{w,0}$ = 131 kg/mol, see above. Note that M_w obtained by a linear extrapolation of Kc_p/R_0 points to $c_p = 0$ for $c_p >\sim 3 \times 10^{-4}$ g/L is even higher: M_w = 206 kg/mol and 186 kg/mol at 25 °C and 55 °C, respectively.), thus confirming the significant inter-chain association.

The values of A_2 and K_{app} for the isolated, non-associated chain in the acid form were obtained from the OAM by fixing in the fitting procedure $M_{w,0}$ to the stated value

131 000. The resulting second virial coefficient of PMA in 0.1 M HCl is considerably lower than the one observed previously for NaPMA: $A_2 = 1.37 \times 10^{-3}$ mol ml/g^2 and 1.24×10^{-3} mol ml/g^2 at 25 °C and 55 °C, respectively. A lower A_2 can be ascribed to an essentially

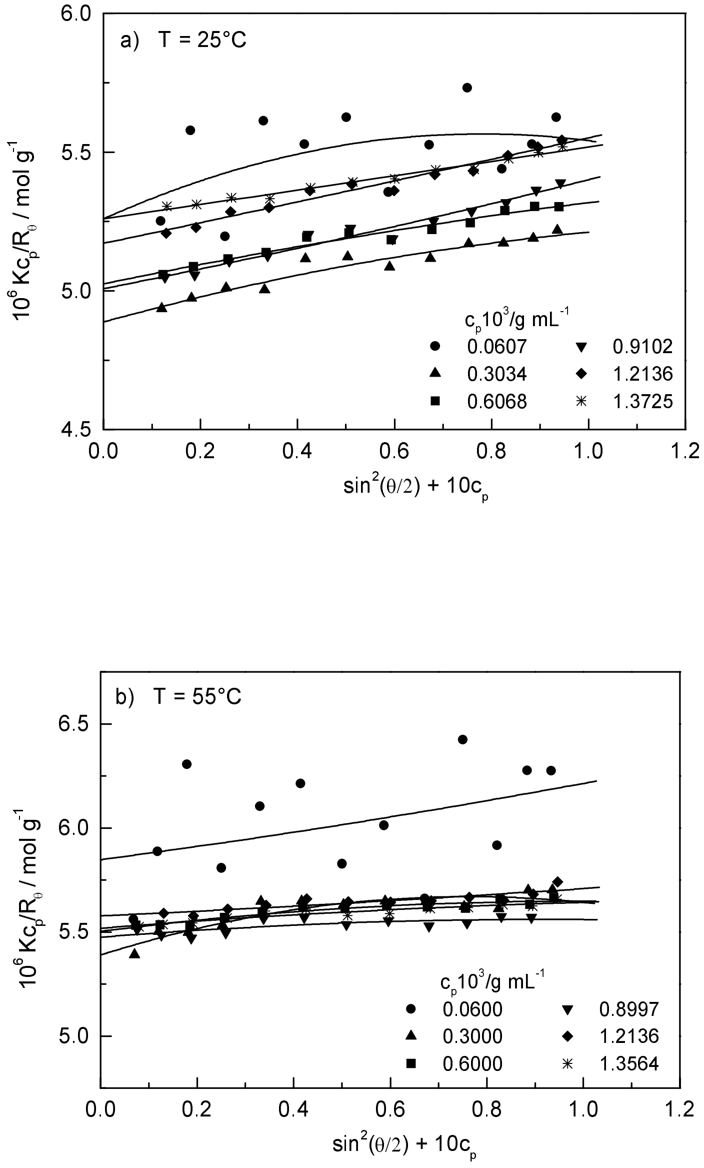

Figure 2. *The Zimm-plots of PMA in 0.1 M HCl: **a)** at 25 °C and **b)** at 55 °C.*

uncharged character of PMA molecules at low pH and to the presence of the hydrophobic methyl side-groups on the PMA main chain. In accordance with the LCST behavior of PMA, A_2 decreases with increasing temperature.[11,17] Katchalsky and Eisenberg[17] have found a value of A_2 close to zero for PMA in 0.02 M HCl at 30 °C.

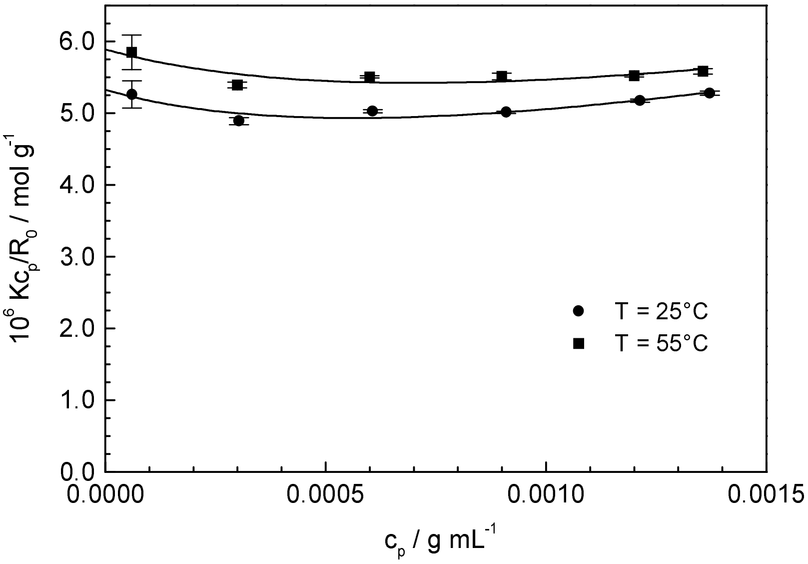

Figure 3. *The dependence of the zero-angle values, Kc_p/R_0, on polymer concentration, c_p, for PMA in 0.1 M HCl at 25 °C and at 55 °C. The lines are the results of the application of Elias Model to the treatment of the data (see text).*

However, the results of Silberberg et al.[18] show that A_2 approaches the zero-value at considerably higher temperatures as reported before, i.e., at 58 °C.[2] Temperatures around room T would then correspond to rather good solvent conditions. The same can be concluded for PMA in 0.1 M HCl in our study. The apparent association constant for PMA in 0.1 M HCl is rather high: $K_{\mathrm{app}} = 3.4 \times 10^5$ and 2.0×10^5 at 25 °C and 55 °C, respectively. These K_{app} values are comparable to those reported for a strongly associating κ-carrageenan system in aqueous salt solutions.[13] The corresponding free enthalpy change of association is more negative at 55 °C ($\Delta G°_{328}$ = -33.3 kJ/mol) than at 25 °C ($\Delta G°_{298}$ = -31.4 kJ/mol), indicating that the increase in temperature promotes intermolecular association of PMA chains. The temperature dependence of both, $\Delta G°$ and A_2, is in accordance with the LCST behavior of PMA.[11,17] From the temperature dependence of $\Delta G°$ one obtains an estimate for the changes in entropy $\Delta S°$ (= 63 J/(K mol)) and enthalpy $\Delta H°$ (= – 12.6 kJ/mol) of the association process. These values, albeit very crude, are comparable with the ones reported for the hydrophobically driven phase separation, e.g., of hydrocarbons in water.[18]

3. Radius of Gyration. The radius of gyration was evaluated by fitting the angular dependence of the scattering data according to different formalisms of Eqs. 8-10. One first obtains for each polymer concentration a value of $\xi(c_p)$ (or of the apparent radius of gyration, R_g^{app}, cf. Eqs. 9, 8b, 10). R_g at zero concentration is then obtained from a plot of $\xi(c_p)$ vs. c_p (or alternatively from a plot of R_g^{app} vs. c_p: cf. Eq. 9) by extrapolating to $c_p = 0$. This extrapolation was in all cases performed by using a polynomial function of the second order in c_p. Both, a linear (Eq. 8 a,b) and a second-order (Eq. 10) polynomial fittings were used, giving comparable results. The average R_g values resulting from both procedures are reported in Table 1 for NaPMA in 0.1 M NaCl and for PMA in 0.1 M HCl.

Table 1. *Radius of gyration, R_g, (in nm) for NaPMA in 0.1 M NaCl at 25 °C and for PMA in 0.1 M HCl at 25 °C and 55 °C.*

system	T / °C	R_g / nm (average values)
NaPMA in 0.1 M NaCl	25	47.0 ± 3.8
PMA in 0.1 M HCl	25	20.4 ± 2.8
	55	16.9 ± 1.9

The average R_g-value for NaPMA in 0.1 M NaCl at 25 °C is 47 nm, whereas the corresponding value for PMA in 0.1 M HCl PMA is 20.4 nm. The increase of temperature to 55 °C causes a decrease of R_g for PMA in 0.1 M HCl to 16.9 nm. One can conclude that the increase of temperature leads to a more compact and concurrently more stable associated state of PMA in aqueous solutions. The length of a fully stretched, all trans, PMA chain, with a degree of polymerization equal to 1528, is around 385 nm. From the value of R_g it can be concluded that the conformation of the PMA-anion in 0.1 M NaCl is far from a fully extended one even at the highest degree of neutralization ($\alpha_N = 1$). The conformation of PMA at low pH ($\alpha_N = 0$) is sometimes approximated by a compact sphere. A value of R_g = 20.4 nm for our sample should correspond to a sphere of radius R = 26 nm. This is a much higher value than the one obtained from the specific volume[11] (= 0.68 mL/g) of PMA by proposing a spherical symmetry of the polymer in aqueous solutions. In this case, a sphere of radius R = 3.3 nm is obtained. One can conclude that molecules of the "contracted" form of PMA are anyway far from being compact spheres.

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Povzetek

Sipanje svetlobe smo uporabili za študij lastnosti polimetakrilne kisline, PMA, in njene natrijeve soli, NaPMA, v vodnih raztopinah. Polimer je ataktičen, sestavljen iz približno 45% heterotaktičnih in 55% sindiotaktičnih triad. Utežno povprečje molske mase ene same PMA verige ($M_{w,0}$ = 131 kg/mol) smo ocenili iz poskusov z NaPMA v 0.1 M NaCl. Iz podatkov sipanja pri kotu nič smo sklepali, da je PMA v 0.1 M HCl intermolekularno asociirana. Podatke smo obravnavali po Odprtem asociacijskem modelu po Eliasu, ki je dal vrednosti za M_w za PMA 188 in 170 kg/mol pri 25 °C in pri 55 °C. Določili smo še drugi virialni koeficient in relativno visoko vrednost za navidezno konstanto asociacije: $A_2 = 1{,}37 \times 10^{-3}$ and $1{,}24 \times 10^{-3}$ mol ml/g^2 in $K_{app} = 3{,}4 \times 10^5$ and $2{,}0 \times 10^5$ pri 25 °C in pri 55 °C. Radij giracije NaPMA v 0.1 M NaCl je R_g = 47 nm, medtem ko je za PMA v 0.1 M HCl pri 25 °C enak 20,4 nm. Dvig temperature na 55 °C vodi do zmanjšanja R_g na 16,9 nm. Spremembe v termodinamskih funkcijah kažejo, da gre za hidrofobno voden asociacijski proces med PMA verigami.