

# Influence of temperature on polyelectrolyte dynamics: partially neutralized solutions of poly(methacrylic acid)

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The influence of temperature on the dynamics of partially neutralized solutions of poly(methacrylic acid) was investigated by photon correlation spectroscopy. A pronounced effect of aggregation above  $T \approx 70^\circ\text{C}$  is observed. The aggregation process is accompanied by a rapid increase of the relative scattering amplitude of the slow diffusive mode occurring in strongly interacting polyelectrolyte systems, by a decrease of the corrected slow diffusion coefficient, and by an increase of the total scattered light intensity. The process is not fully reversible. The aggregation tendency strongly depends on the degree of neutralization  $\alpha$  of the sample. In the interval  $\alpha=0$  to  $\alpha=1$  it reaches a maximum at  $\alpha \approx 0.4$ . An aggregation mechanism based on intermolecular hydrogen bonding between carboxyl groups is proposed.

(Keywords: semidilute polyelectrolyte solutions; diffusion; dynamic light scattering; aggregation)

## INTRODUCTION

Polyelectrolyte solutions with low concentration or in the absence of low-molecular-weight salt represent rather complicated physical systems because of strong long-range electrostatic interactions between unscreened charges on the macromolecular chains. Up to now there is no full understanding of the structure of these solutions. Three different theoretical models were introduced: the cell model theory<sup>1</sup>, supposing more or less parallel ordering of rigid macromolecules, the isotropic model<sup>2</sup>; and the three-dimensional two-state model<sup>3</sup>, proposing formation of ordered regions (domains) in a generally disordered solution. Satisfactory agreement also does not exist in the interpretation of experimental results obtained by the most powerful methods in this field: small-angle X-ray and neutron scattering (SAXS and SANS), static and dynamic light scattering nuclear magnetic resonance (n.m.r.) relaxation measurements, etc. Thus, many open questions remain to be answered.

In our work we use quasi-elastic light scattering (QELS) spectroscopy for the study of solution dynamics. An unexpected result of QELS experiments on polyelectrolyte solutions without added salt is the existence of a slow diffusive mode reported for the first time in the paper of Lin *et al.*<sup>4</sup>. They observed a rapid drop in the apparent diffusion coefficient of poly(L-lysine) with decreasing salt concentration below a certain critical value. Later it was shown that in some circumstances two diffusive modes (slow and fast) can be observed in this 'extraordinary region' of low salt concentration, which arise from a splitting of the apparent diffusion coefficient of the high-salt phase<sup>5,6</sup>. This extraordinary

behaviour was observed in various polyelectrolyte systems regardless of their local chemical structure (e.g. poly(L-lysine)<sup>4</sup>, bovine serum albumin<sup>6</sup>, polynucleosomes<sup>6</sup>, sodium polystyrene sulphonate<sup>5</sup>, etc.). In our previous paper<sup>7</sup> we published the first results obtained with a weak polyelectrolyte, namely poly(methacrylic acid) (PMA). We chose such a system because of the possibility of varying the degree of neutralization of the acid by means of a suitable alkali. Two samples with different molecular weights were investigated over a wide variety of experimental conditions: degree of neutralization, concentration, scattering vector. In all cases two diffusive modes differing in relative scattering amplitudes were observed. The following interpretation of the two diffusive modes based on the detailed discussion of experimental results (including experimental data from SANS on a very similar sample<sup>8</sup>) was given: (i) the fast mode corresponds to a Nernst-Hartley diffusion of individual chains (coupled motion due to interaction of polyions and counterions); (ii) the slow mode can be attributed to diffusion of clusters (domains) of chains with size much greater than the dimensions of individual macromolecules.

The aim of the present paper is to investigate the influence of temperature on polyelectrolyte solution dynamics. We used the same sample as in the previous investigation<sup>7</sup>, so that a direct comparison of experimental data is possible.

## EXPERIMENTAL

Aqueous solutions were prepared by dissolving PMA sample obtained by radical polymerization (molecular weight  $M_w = 30\,000$ , polydispersity  $M_w/M_n = 2.0$ ) in

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deionized water. In order to avoid the effect of possible impurities, solutions were thoroughly dialysed. Degrees of neutralization  $\alpha$  were adjusted potentiometrically by means of sodium hydroxide. Prior to measurement, samples were filtered through a glass bacterial filter G5 (Jena).

The 514.5 nm line of an Ar laser (model ILA 120-1, Carl Zeiss, Jena) and the 632.8 nm line of a He-Ne laser (model 125A, Spectra Physics) were used as the incident light in QELS experiments. The sample was placed in a sample compartment allowing temperature control in the range between 20 and 100°C with an accuracy  $\pm 0.05^\circ\text{C}$ . In order to ensure temperature equilibrium, samples were maintained at the given temperature for 20 min before each measurement. A homodyne spectrometer equipped with a 96-channel digital correlator enabling one to measure the multi-time correlation function (MTCF) covering 3.5 decades of delay time was used. The correlator operated with three simultaneous sampling times. The composite correlation functions  $G^{(2)}(t)$  covering a wide range (typically  $0.5\ \mu\text{s}$ –1 s) were constructed by combining two or three MTCFs.

These correlation functions were analysed by the CONTIN program<sup>9</sup> based on a constrained regularization method, which yields the distribution function of decay times  $A(\tau)$  defined as:

$$G^{(1)}(t) = \int_0^\infty A(\tau) \exp(-t/\tau) d\tau \quad (1)$$

where  $G^{(1)}(t)$  is the normalized heterodyne correlation function,  $t$  is the delay time and  $\tau$  is the decay time. As the distribution function consisted in all cases of two well separated narrow bands (bimodal distribution), correlation functions were also fitted by a double-exponential forced fit in the form:

$$G^{(2)}(t) = [A_f \exp(-t/\tau_f) + A_s \exp(-t/\tau_s)]^2 + B \quad (2)$$

where  $\tau_f$  and  $\tau_s$  are the fast and slow decay times, respectively,  $A_f$  and  $A_s$  are the respective scattering amplitudes and  $B$  is a constant. It was found that centres of gravity of the two bands of decay time distribution obtained by the CONTIN analysis corresponded to  $\tau_f$  and  $\tau_s$ , and the scattering amplitudes  $A_s$  and  $A_f$  agreed well with the zero-moment values of the corresponding bands. A typical example of distribution of decay times is shown in Figure 1.

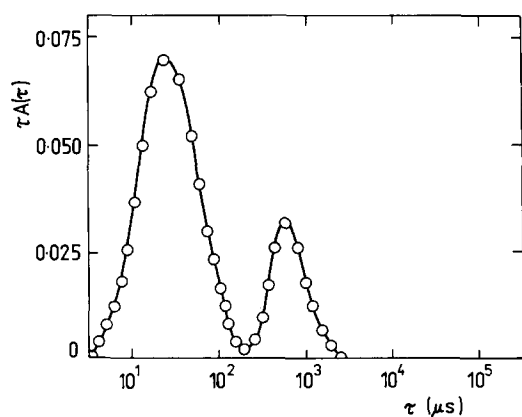


Figure 1 Distribution function of decay times  $A(\tau)$  obtained by the CONTIN method: PMA,  $c = 36\ \text{g l}^{-1}$ ,  $\alpha = 0.05$ ,  $T = 60^\circ\text{C}$ ,  $\theta = 45^\circ$

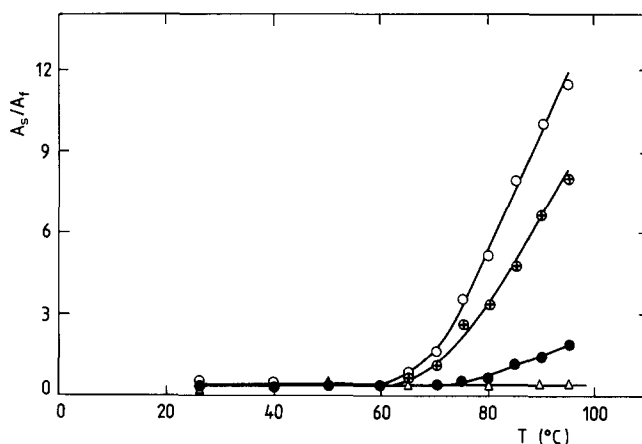


Figure 2 Temperature dependence of the  $A_s/A_f$  ratio: PMA,  $c = 36\ \text{g l}^{-1}$ ,  $\theta = 45^\circ$ ; ( $\Delta$ )  $\alpha = 0$ , ( $\bullet$ )  $\alpha = 0.05$ , ( $\oplus$ )  $\alpha = 0.1$ , ( $\circ$ )  $\alpha = 0.37$

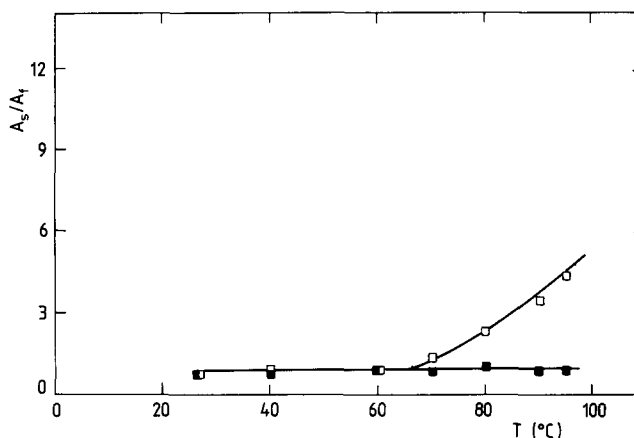


Figure 3 Temperature dependence of the  $A_s/A_f$  ratio: PMA,  $c = 36\ \text{g l}^{-1}$ ,  $\theta = 45^\circ\text{C}$ ; ( $\square$ )  $\alpha = 0.85$ , ( $\blacksquare$ )  $\alpha = 1.0$

## RESULTS AND DISCUSSION

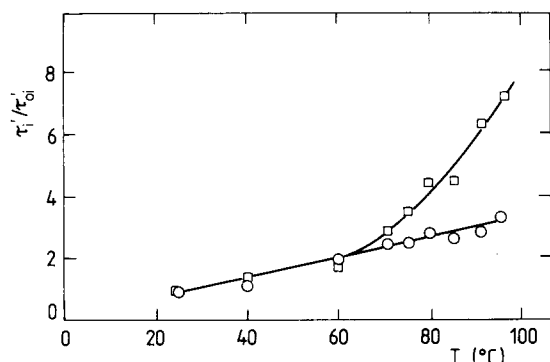
The dynamics of PMA solutions with various degrees of neutralization  $\alpha$  was studied as a function of temperature from  $T = 26^\circ\text{C}$  to  $T = 95^\circ\text{C}$ . Values of the degree of neutralization  $\alpha$  from 0 to 1 correspond to systems of strong polyelectrolytes with high values of salt concentrations to zero values, respectively.

Figure 2 shows the temperature dependence of the  $A_s/A_f$  ratio for PMA samples with  $\alpha = 0, 0.05, 0.1$  and  $0.37$ . The dominant feature of these measurements is the rapid increase of  $A_s/A_f$  above  $70^\circ\text{C}$ . This effect depends strongly on the degree of neutralization  $\alpha$ . For  $\alpha = 0$  it is nearly unobservable and becomes more and more pronounced with increasing  $\alpha$  to  $0.37$ . The rapid change of  $A_s/A_f$  was accompanied by an increase of the total scattered light intensity and was not fully reversible. The sample with  $\alpha = 0.05$  returned to the former state after  $\sim 3$  weeks; samples with  $\alpha = 0.1$  and  $0.37$  did not return to the former state at all. A relatively surprising result is shown in Figure 3. For  $\alpha = 0.85$  the change of  $A_s/A_f$  is less significant than for  $\alpha = 0.37$ , and for  $\alpha = 1.0$   $A_s/A_f$  does not change at all upon heating.

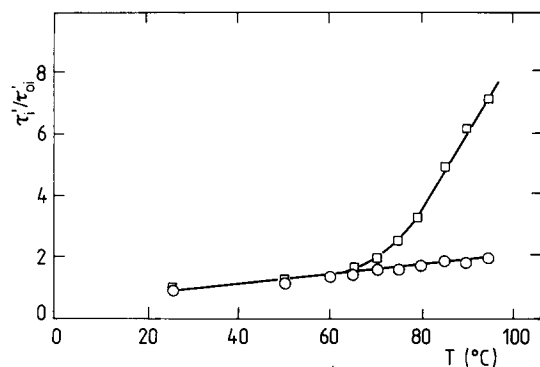
Additional information on the scattered intensity data can be obtained from the temperature dependences of characteristic decay times  $\tau_f$  and  $\tau_s$ . Both these times were found to have a diffusive character (i.e.  $\tau \sim K^{-2}$ ) and the Stokes equation can therefore be assumed to hold for the two corresponding diffusion coefficients  $D_f = \tau_f^{-1} K^{-2}$  and

$D_s = \tau_s^{-1} K^{-2}$ . Here  $K$  is the scattering vector,  $K = [4\pi n_r \sin(\theta/2)]/\lambda_0$ , where  $n_r$  is the relative refractive index of the sample,  $\theta$  is the scattering angle and  $\lambda_0$  is the wavelength of the incident light in vacuum. Thus, the representation of temperature dependences  $\tau_f(T)$  and  $\tau_s(T)$  can be made independent of viscosity and kinetic energy effects by using the normalized variables  $\tau_i/\tau_{0i}$  ( $i=f, s$ ), where  $\tau_i = T\tau_i(T)/\eta(T)$ ,  $\tau_{0i} = T_0\tau_i(T_0)/\eta(T_0)$ ,  $\eta(T)$  is the viscosity at temperature  $T$  and  $T_0$  is a selected reference temperature ( $T_0 = 26^\circ\text{C}$  in our particular case). In the case of the temperature-independent apparent hydrodynamic radius  $R_{H,app}^i$  corresponding to the diffusion coefficient  $D_i$  ( $D_i = k_B T/6\pi\eta(T)R_{H,app}^i$ , where  $k_B$  is the Boltzmann constant), the ratio  $\tau_i/\tau_{0i}$  should be a temperature-independent constant equal to 1. Thus, this plot ( $\tau_i/\tau_{0i}$  versus  $T$ ) is sensitive only to changes of  $R_{H,app}^i$  which reflect structural changes induced by temperature in the studied sample.

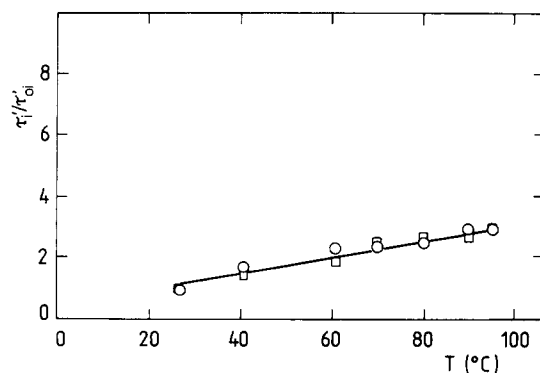
Figures 4, 5 and 6 show the temperature dependences



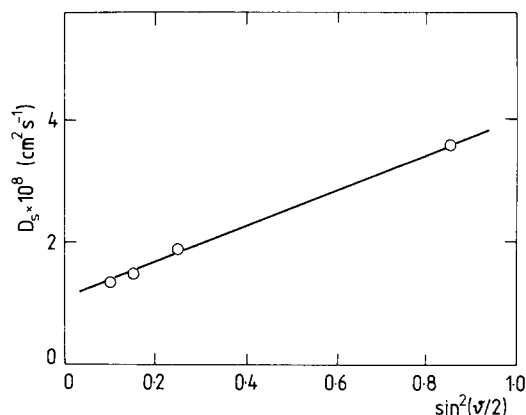
**Figure 4** Temperature dependence of the  $\tau_i/\tau_{0i}$  ratio: PMA,  $c = 36 \text{ g l}^{-1}$ ,  $\theta = 45^\circ$ ,  $\alpha = 0.05$ ; (○)  $\tau_f/\tau_{0f}$ , (□)  $\tau_s/\tau_{0s}$



**Figure 5** Temperature dependence of the  $\tau_i/\tau_{0i}$  ratio: PMA,  $c = 36 \text{ g l}^{-1}$ ,  $\theta = 45^\circ$ ,  $\alpha = 0.1$ ; (○)  $\tau_f/\tau_{0f}$ , (□)  $\tau_s/\tau_{0s}$



**Figure 6** Temperature dependence of the  $\tau_i/\tau_{0i}$  ratio: PMA,  $c = 36 \text{ g l}^{-1}$ ,  $\theta = 45^\circ$ ,  $\alpha = 1.0$ ; (○)  $\tau_f/\tau_{0f}$ , (□)  $\tau_s/\tau_{0s}$



**Figure 7** Dependence of diffusion coefficient  $D_s$  on the scattering angle  $\theta$ : PMA,  $c = 36 \text{ g l}^{-1}$ ,  $\alpha = 0.1$ ,  $T = 90^\circ\text{C}$

of the normalized variables  $\tau_f/\tau_{0f}$  and  $\tau_s/\tau_{0s}$  for  $\alpha = 0.05$ ,  $0.1$  and  $1.0$ , respectively. It can be seen in Figures 4 and 5 that the normalized variable of the fast mode increases only slightly on heating while that of the slow mode increases rapidly with increasing temperature above  $70^\circ\text{C}$ , similarly to the ratio  $A_s/A_f$  in Figure 2. Thus, it can be concluded that the slow mode is appreciably influenced by the temperature change and is responsible for the observed changes of  $A_s/A_f$ . In the case of the sample with  $\alpha = 1$  both normalized variables show no substantial changes above  $70^\circ\text{C}$ , again in agreement with the dependence of  $A_s/A_f$  (cf. Figure 3).

The angular dependence of  $D_s$  for the sample with  $\alpha = 0.1$  heated above  $70^\circ\text{C}$  is shown in Figure 7. On the assumption that the scatterers are isolated particles, an apparent radius of gyration  $R_{G,app}$  can be estimated from this dependence using the formula<sup>10</sup>:

$$D(K) = D_0[1 + C(R_{G,app}K)^2] \quad KR_{G,app} \ll 1 \quad (3)$$

where  $D_0$  is the diffusion coefficient in the limit  $K \rightarrow 0$  and  $C$  is a constant depending on the architecture of scatterers (its value varies from 0.133 for solid spheres to 0.2 for polycondensates<sup>10</sup>). Entering these extreme  $C$  values into equation (4) we obtain  $137 \text{ nm} \lesssim R_{G,app} \lesssim 168 \text{ nm}$ . This calculated  $R_{G,app}$  value is not equal to the real cluster (aggregate) size because of the finite concentration of the sample, but it may be used as an estimate of the cluster size. Anyway, this value of  $R_{G,app}$  is much greater than the dimensions of an isolated PMA chain ( $R_G = 5.3 \text{ nm}$  at  $\alpha = 0.7$ ) and even about three times greater than  $R_{G,app}$  estimated for clusters in the unheated sample at  $\alpha = 1.0$  ( $R_{G,app} = 50 \text{ nm}$ <sup>7</sup>).

The above-mentioned experimental results allow us to summarize the effect of heating on the solution structure and dynamics. The plot of the normalized variable  $\tau_f/\tau_{0f}$  versus temperature shows only a slight increase, which indicates that the Nernst–Hartley diffusion of individual chains (the fast mode) is predominantly influenced by changes in the kinetic energy of macromolecules and in solvent viscosity. The slight shift of  $\tau_f/\tau_{0f}$  from unity with increasing temperature is caused by additional temperature-induced changes in the macromolecular conformation, in the degree of ionization and in the coupling between motion of chains and ions.

The opposite situation is encountered in the case of the slow mode, where pronounced effects are observed due to the formation of large, not fully reversible,

aggregates. As to the mechanism of this formation, the following statements can be made:

(1) Charge density on the macromolecular chains strongly influences the formation of macromolecular aggregates.

(2) The aggregation process cannot be ascribed only to a change of electrostatic interactions and of solvent quality with temperature because the aggregates are not fully reversible.

Two other possible types of attractive interactions should therefore be considered as responsible for aggregate formation: (i) hydrophobic interactions due to the presence of methyl groups and (ii) hydrogen bonds due to the presence of carboxyl groups on PMA chains.

Irreversible aggregation through the hydrophobic interactions could occur in connection with some conformational transition, which might take place at the critical temperature ( $T_c \approx 70^\circ\text{C}$ ) and could enable association of macromolecular chains through the methyl groups. A similar effect at the intramolecular level was used in works of Mandel *et al.*<sup>11,12</sup> and Crescenzi *et al.*<sup>13,14</sup> to explain the titration curves of PMA, which exhibit a shoulder at a low degree of neutralization  $\alpha$ . This was proposed to be caused by a conformational transition of a single chain. At very low  $\alpha$  the compact coil was stabilized by hydrophobic interactions of methyl groups, while at higher  $\alpha$  (after the conformational transition) the electrostatic interactions between charges on the chain dominated and the compact coil changed into a swollen conformation. However, such types of interaction at the intermolecular level cannot explain the  $\alpha$  dependence of aggregation in our experiments. Besides, some recent work<sup>15</sup> indicates that no conformational transition takes place during titration of PMA. It was shown that there are no changes in the difference between the heat capacity of PMA and PAA (poly(acrylic acid)) with increasing degree of neutralization, which means that there are no significant changes in hydration around the methyl group<sup>15</sup>. In addition, the  $\alpha$  dependence of the radius of gyration of a PMA chain and of the Nernst-Hartley diffusion coefficient established by neutron scattering and QELS, respectively, shows no evidence of conformational transition<sup>8,7</sup>.

The second possibility of the aggregation mechanism, i.e. hydrogen bonding, seems to be more realistic. It is commonly known that a physical gel is formed in highly concentrated solutions of PMA (e.g. ref. 16). The gel network arises for purely geometrical reasons from hydrogen bridges between carboxyl groups on different chains. The macromolecules in solution are more and more closely packed with increasing concentration and so the probability of forming a hydrogen bond becomes higher, too. In our case the chains get close together with decreasing thermodynamic quality of the solvent on heating. It was found by light scattering and intrinsic viscosity measurements that water solutions of PMA exhibit a negative heat of dilution and a negative excess entropy of dilution<sup>16,17</sup>. This also implicates the existence of a lower critical solution temperature. When this temperature is approached, aggregates (microgel particles) start to form through hydrogen bonds.

In the region of low degrees of neutralization  $\alpha$  the tendency to aggregation increases with  $\alpha$ . This is caused by the stronger interaction of the carboxyl-group hydrogen with another ionized than with another non-ionized carboxyl group. The number of 'hydrogen-

ionized carboxyl group' pair interactions increases with  $\alpha$  up to  $\alpha=0.5$  because of an increasing total number of ionized carboxyl groups. At  $\alpha=0.5$  there are equivalent amounts of carboxyl-group hydrogens and ionized carboxyl groups on chains and hence there should be a maximum number of their pair interactions. Above  $\alpha=0.5$  the number of pair interactions decreases because of the decreasing total number of carboxyl-group hydrogens on chains. At  $\alpha=1$  there are no hydrogens on carboxyl groups and therefore the aggregation tendency disappears.

Moreover, hydrogen bonding is influenced by counterion condensation, which decreases the effective polyion charge. According to Manning's theory<sup>18</sup> it takes place when the charge density parameter  $Q/A > 1$  ( $Q$  is the Bjerrum length defined by  $Q = e^2/\epsilon k_B T$ , where  $e$  is the elementary charge and  $\epsilon$  the relative permittivity of solvent). For PMA in water the condition  $Q/A > 1$  is fulfilled for  $\alpha > \alpha_M$ , where  $\alpha_M$  varies from 0.36 to 0.44 over the temperature interval studied. The aggregation tendency is therefore diminished above  $\alpha_M$  as a consequence of counterion condensation and should reach its maximum between  $\alpha_M$  and  $\alpha=0.5$ . In accord with the above-mentioned facts, the maximum aggregation is observed for the sample with  $\alpha=0.37$  (cf. Figures 2 and 3).

With regard to the irreversibility of the aggregation process, it is necessary to consider two forces acting on thermally created aggregates during subsequent cooling. The first one tends to strengthen the aggregate via strengthening of hydrogen bonds with decreasing temperature; the second one tends to distort the aggregate via the improvement of the thermodynamic quality of the solvent. The real situation in solution thus results from a balance between these two opposing forces.

Finally, a comment can be made on the results obtained for the solution with degree of neutralization  $\alpha=1$ . In this case the aggregation mechanism does not apply and some information about the direct influence of temperature on the electrostatic interactions can be obtained. At first sight, one can expect a distortion effect of temperature on the ordered domains in solution. This should manifest itself in the decrease of the relative scattering amplitude of the slow mode and in the decrease of the corrected decay time  $\tau'_s$ . However, the opposite is observed experimentally. The relative scattering amplitude does not change with temperature and  $\tau'_s$  increases after the obvious corrections for temperature changes in the kinetic energy and the solvent viscosity are made (cf. Figure 6). These results do not contradict the theory of attractive coulombic interactions suggested by Ise<sup>19,20</sup>, which assumes the intermolecular attraction between polyions to become stronger with increasing temperature. This strengthening, caused by the decrease in the dielectric constant, results in a smaller computed distance  $2D_{\text{exp}}$  between polyions in a cluster, which was demonstrated also experimentally (e.g. ref. 21).

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