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Dynamic light scattering studies on polyelectrolytic derivatives of poly(*N*-isopropylacrylamide)

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Copolymers of *N*-isopropylacrylamide, 2-acrylamido-2-methylpropane sulfonic acid, and 2-acetamidoacrylic acid in various ratios were synthesised by free radical solution polymerisation. Aqueous solutions of the copolymers were studied by dynamic light scattering in order to find out how the lower critical solution temperature and the conformational transition of the polymers at that temperature depend on the chemical composition of the macromolecule. The ratio of the hydrophobic and hydrophilic repeating units was observed to affect considerably the response of the polymers to an increase in temperature. The polyelectrolytes were studied also in aqueous salt solutions. The salts added into the solutions were sodium, nickel and chromium chlorides. The behaviour of the polymers was observed to depend on the chemical nature of the added inorganic salt as well as on the ionic strength of the solutions. The added salts increase the tendency of the polymers to aggregate in solutions. The degree of aggregation, however, is not only dependent on the ionic strength; different cations clearly show a different capability of binding to the polymers. © 1997 Elsevier Science Ltd.

(Keywords: *N*-isopropylacrylamide; polyelectrolytes; dynamic light scattering)

INTRODUCTION

Poly(*N*-isopropylacrylamide), PNIPAAM, has been widely studied owing to the interesting thermal properties of its aqueous solutions. Aqueous PNIPAAM solutions precipitate at lower critical solution temperature (LCST) around 32°C due to a phase transition between hydrated and dehydrated states of the polymer side chains[1–6]. PNIPAAM has been tested for several applications in biotechnology, drug release, film technology, flocculation and water treatment[4,6].

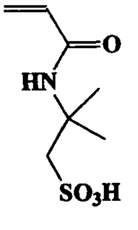
A further level of control of PNIPAAM properties arises from manipulation of the LCST by inclusion of other acrylamide derivatives as comonomers[7]. Since vinyl polyelectrolytes have a dual character as highly charged electrolytes and flexible chain molecules, it is of interest to copolymerise NIPAAM with ionic vinyl monomers in order to prepare polymers which respond to a change in temperature as well as to a change in pH and ionic strength.

2-Acrylamido-2-methylpropane sulfonic acid (AMPS) as well as its sodium salt have been used as comonomers because of their hydrolytic stability. These monomers contain a spacer which allows the charged group to have a relatively high mobility when linked to a polymer backbone[3,8,9]. Since 2-acetamidoacrylic acid (4A) has two functional groups, i.e. carboxyl and acetamido groups, it may be used as a comonomer of NIPAAM to modify the pH sensitive properties of PNIPAAM; 4A is known to complex with metal ions[10].

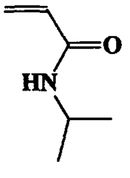
The dynamic properties of PNIPAAM and some of its copolymers have been studied by a wide variety of experimental techniques. These include calorimetry, viscometry, turbimetry, neutron and X-ray scattering, dielectric, fluorescence, n.m.r., EPR and dynamic light scattering. To study polyelectrolytic PNIPAAM copolymers in solution, dynamic light scattering can provide useful information not only on the dynamics of charged chains but also on some aspects of the equilibrium behaviour[11].

This paper reports the synthesis and properties of a series of polyelectrolyte copolymers of NIPAAM, AMPS and 4A. By dynamic light scattering, properties of the aqueous solutions of the copolymers with varying chemical composition were studied as a function of temperature.

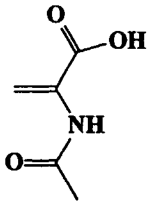
Also, the effect of concentration of the copolymers as well as that of added low molar mass salts on the diffusion coefficients of copolymers were studied. This work forms the basis for further studies of intelligent materials which are responsible to changes in temperature, pH and ionic strength.



AMPS



NIPAAM



4A

EXPERIMENTAL

Materials

N-Isopropyl acrylamide (NIPAAM) purchased from Polysciences Inc. was purified by recrystallisation with hexane. 2-Acetamidoacrylic acid (4A) was prepared by

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Table 1 Synthesised copolymers

Sample	Component/mol ratio			Reaction time	Precipitation	Yield	M_n	M_w
	AMPS	NIPAAM	4A	(h)		(%)	(g mol^{-1})	(g mol^{-1})
SAM 1	2	40	58	20	Cold acetone, three times	41.7	7600	17000
SAM 2	2	68	30	17	Cold acetone, twice	58.2	13000	39000
SAM 3	2	78	20	19	Cold acetone, once	63.8	11000	43000
SAM 4	2	88	10	18	Dry ethanol, twice	68.6	10000	24000
SAM 5	2	93	5	20	Dry ethanol, twice	69.7	6000	12000

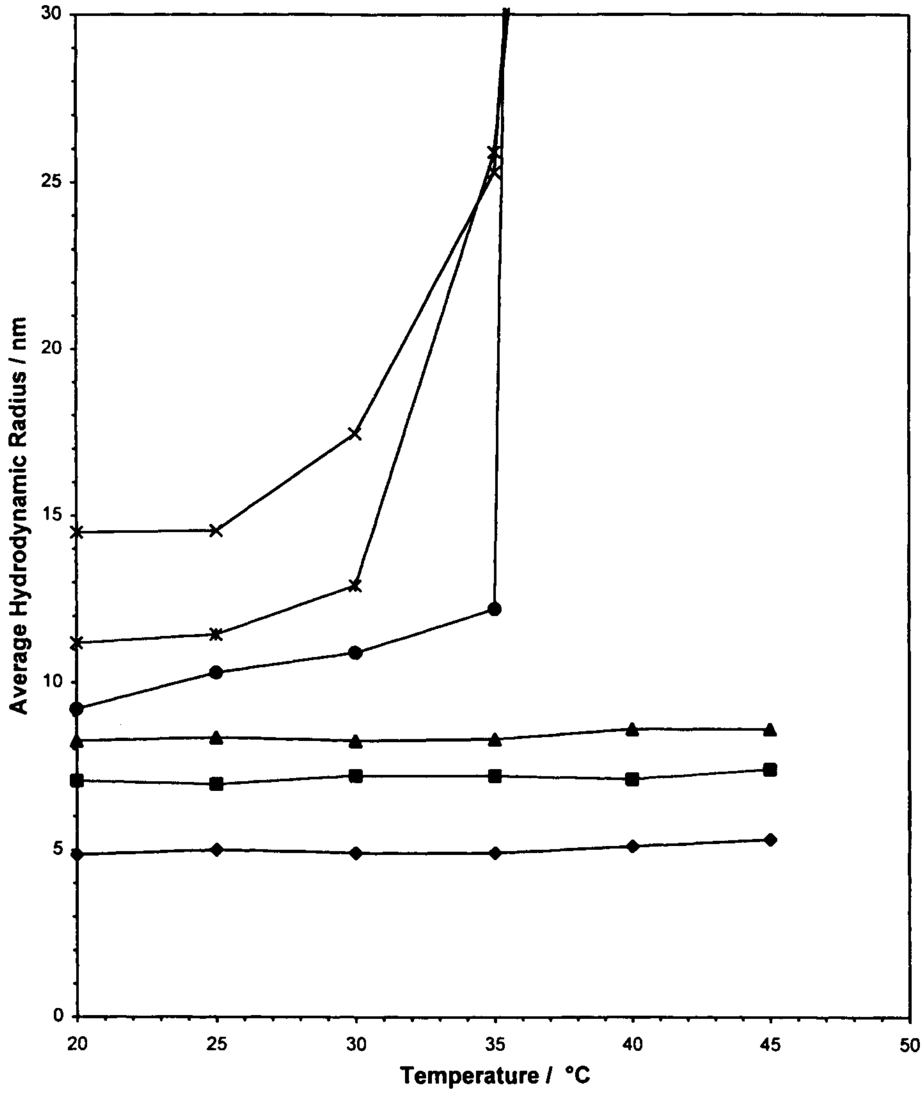

Figure 1 Hydrodynamic radii of the copolymers in aqueous 0.1 M NaCl solutions. Polymers: ◆, SAM1; ■, SAM2; ▲, SAM3; ×, SAM4; *, SAM5; ●, poly(NIPAAM)

refluxing a toluene (500 ml) solution of pyruvic acid (30 ml) and acetamide (14.77 mg) for approximately 4 h. The crude 4A was removed from the supernatant toluene by filtration, then it was purified by recrystallisation from ethanol. 4A monomer was precipitated as white needles and dried in vacuum. The melting point of 4A was 194–195°C. The yield was 21%. 2-Acrylamido-2-methylpropane sulfonic acid (AMPS) was purchased from Merck.

Polymer synthesis

The radical solution copolymerisation was carried out in a 50 ml two-neck flask fitted with a nitrogen bubbling tube and a vent. A total of 5 g of AMPS, NIPA and 4A was dissolved into 15–20 ml DMF in different molar ratios as shown in *Table 1*. (When speaking about the chemical composition of the copolymers, we refer to the molar ratio of the monomers in the feed of the polymerisation reaction.) After the monomer solution was purged with nitrogen for

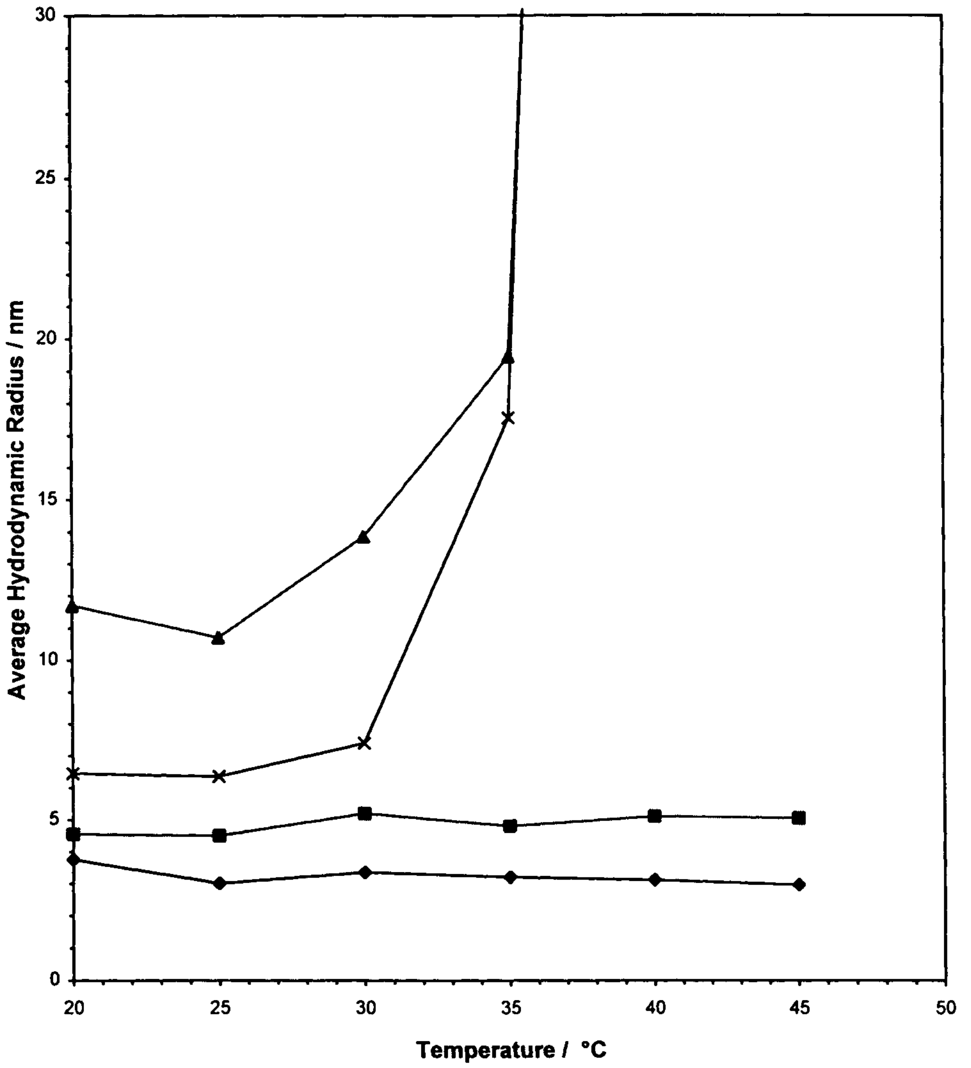

Figure 2 Hydrodynamic radii of the copolymers dissolved in pure water. Polymers: ◆, SAM1; ■, SAM3; ▲, SAM4; ×, SAM5

about 30 min, 0.5 wt% of AIBN in 5 ml DMF was added into the system and the reaction was allowed to proceed at 60°C for 16–20 h. After the reaction, copolymers SAM1, SAM2 and SAM3 were slowly precipitated with cold acetone several times. SAM4 and SAM5 were precipitated dropwise into dry ethanol, then dissolved in THF and reprecipitated into dry ethanol. *Table 1* shows that with increasing molar ratio of NIPAAM, the yield of polymerisation increases. In *Table 1*, also the average molar masses from GPC are shown. In the GPC measurements, 0.1 M aqueous sodium chloride solution was used as an eluent and polyethylene oxide standards were used as a reference. Homopolymer PNIPAAM was synthesised in a similar way to that described above. The M_w measured by light scattering was 26 000.

Dynamic light scattering

Dynamic light scattering measurements were conducted with a Brookhaven Instruments BI-200SM Goniometer and BI-2030AT digital correlator with 136 time channels. The light source was Spectra Physics Model 127 Helium/Neon laser (633 nm, 35 mW). Time correlation functions were analysed with a Laplace inversion program (CONTIN). The samples ranging from 5 to 500 mg were dissolved in 5 ml deionised water and in various aqueous salt solutions. The salts used were sodium chloride, nickel chloride and chromium(III) chloride. Salt concentrations were 0.1, 0.01 and 0.001 M. The solutions were clarified by filtering through Millipore membranes with 0.22 μm pore size. The intensity–intensity time correlation functions $g_2(t,q)$ in the self-beating mode were measured at a scattering angle of 90° as a function of temperature. Temperature ranged from 20 to 45°C. At each temperature, the sample was allowed to equilibrate for 30 min before measurement. Measurements were also conducted at various scattering angles from 30 to 135°. In these measurements, temperature was kept constant at 25°C. In the vast majority of cases, CONTIN program produces no artefact peaks and yields reasonably accurate moments[7], and thus CONTIN was chosen to be used to study the hydrodynamic character of polyelectrolyte solutions.

THEORETICAL BACKGROUND

The intensity–intensity time correlation function $g_2(t,q)$ measured using dynamic light scattering is related to the electric field time correlation function $g_1(t,q)$ as[4,12]:

$$g_2(t,q) = \langle I(t,q)I(0,q)\rangle = A[1 + B|g_1(t,q)|^2] \quad (1)$$

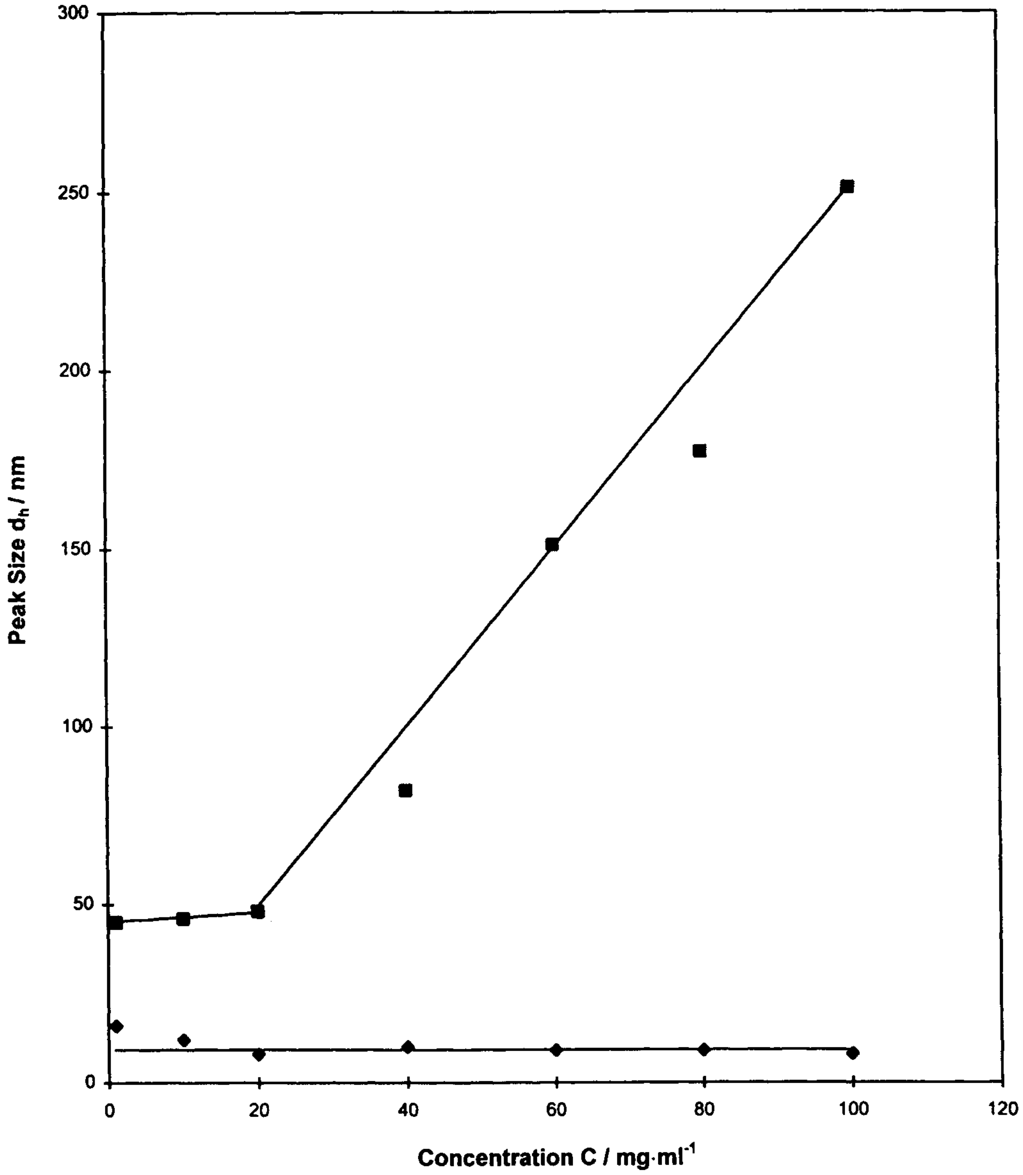

Figure 3 Two hydrodynamic diameters obtained by CONTIN for SAM5 in 0.1 M aqueous NaCl, plotted against the polymer concentration

where A is the baseline, B a parameter depending on the coherence of the detection, and t is the delay time.

Kohlrausch–Williams–Watts (KWW) stretched exponential function[13] may be used to describe various relaxation processes. The KWW function has the form

$$g_1(t) = \sum a_i \exp(t/\tau_i)^{\beta i} \qquad (2)$$

where the parameter a_i corresponds to the weight of various processes and $\Sigma a_i = 1$. τ_i and β_i ($0 < \beta_i \leq 1$) characterise the mean relaxation time $\langle\tau_i\rangle$ which is given by

$$\langle\tau_i\rangle = \tau_i/\beta_i\Gamma(1/\beta_i) \qquad (3)$$

Here, $\Gamma(x)$ is the gamma function. The parameter β is a measure of the width of the underlying distribution of relaxation times. $g_1(t)$ has values $0 \leq g_1(t) \leq 1$. The diffusion coefficient is calculated from the mean relaxation time by equation (4).

$$D = 1/(\tau q^2) \qquad (4)$$

Here, q is the scattering vector defined[12] as $q = 4\pi n_0/\lambda_0 \sin(\theta/2)$, where n_0 is the refractive index of the medium and λ_0 is the wavelength of the incident light in vacuum.

The Laplace inversion program CONTIN was used to analyse the mean value and the distribution of diffusion coefficient. The hydrodynamic radius was obtained from the diffusion coefficient using the Stokes–Einstein relation[12,13]:

$$R_h = k_B T/6\pi\eta_0 D \qquad (5)$$

In equation (5), k_B, T and η_0 are the Boltzmann constant, absolute temperature and the solvent viscosity, respectively. The experimental correlation functions were in some cases fitted by a one exponential KWW function. In some cases, however, the slow and fast relaxation processes were observed as bimodality of the correlation function, and the curve was fitted with a sum of two exponentials in the KWW function.

If the polymer concentration is increased beyond a critical concentration C^*, the solution changes from a dilute solution into a semidilute one. At $C > C^*$ the overall

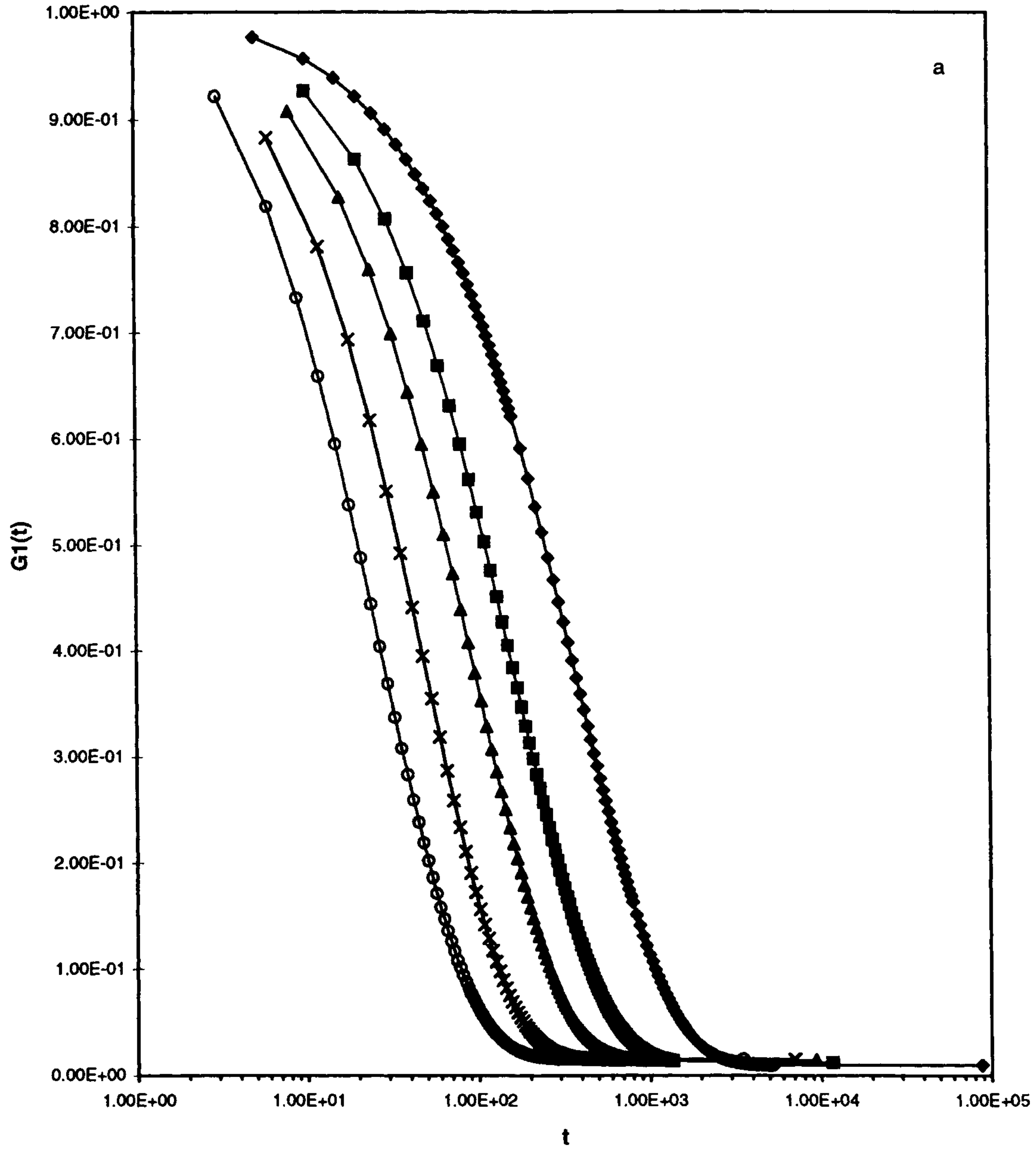

Figure 4 Correlation functions $g_1(t)$ measured at different angles for solutions with the polymer concentration: (a) 1 mg ml^{-1}; (b) 10 mg ml^{-1}; (c) 100 mg ml^{-1}. The curves from right to left are measured at angles of 30, 45, 60, 90 and 135°

concentration equals the segment concentration and linear chains overlap to such an extent that they may be visualised as interpenetrating coils. For flexible linear chains, C^* is defined as follows[11,13,14]

$$C_{\mathrm{Rh}}* = M/(N_{\mathrm{A}}(4\pi/3)R_{\mathrm{h}}^3) \quad (7)$$

RESULTS AND DISCUSSION

Dependence of the hydrodynamic radius on the chemical composition of the copolymers

Aqueous NaCl solutions. The average hydrodynamic radii, R_{h}, of the copolymers in 0.1 M aqueous sodium chloride were measured against increasing temperature. The measurements were conducted at the scattering angle 90°, keeping the copolymer concentration constant at 10 mg ml^{-1}. As can be seen from *Figure 1* for SAM1, SAM2 and SAM3, the average radius remains constant with increasing temperature so that the phase separation typical of poly(NIPAAM) may not be observed. The differences in R_{h} of the copolymers SAM1–SAM3 are evidently due to the differences in molar masses. When the amount of 4A decreases below 20 mol% (samples 4 and 5), the resulting copolymers show a phase separation typical of poly(NIPAAM). These results indicate that the behaviour of the copolymers is mainly determined by a balance between the hydrophobic interactions of isopropyl groups on the one hand, and the electrostatic interactions of ionised carboxylic and sulfonic acid groups on the other.

An interesting feature in *Figure 1* is that the hydrodynamic radii of polymers 4 and 5 are fairly large at $T <$ LCST, considering the chromatographically measured molar masses which are lower than those of polymers 2 and 3. Either the polymer conformation changes dramatically when the composition is changed, or the

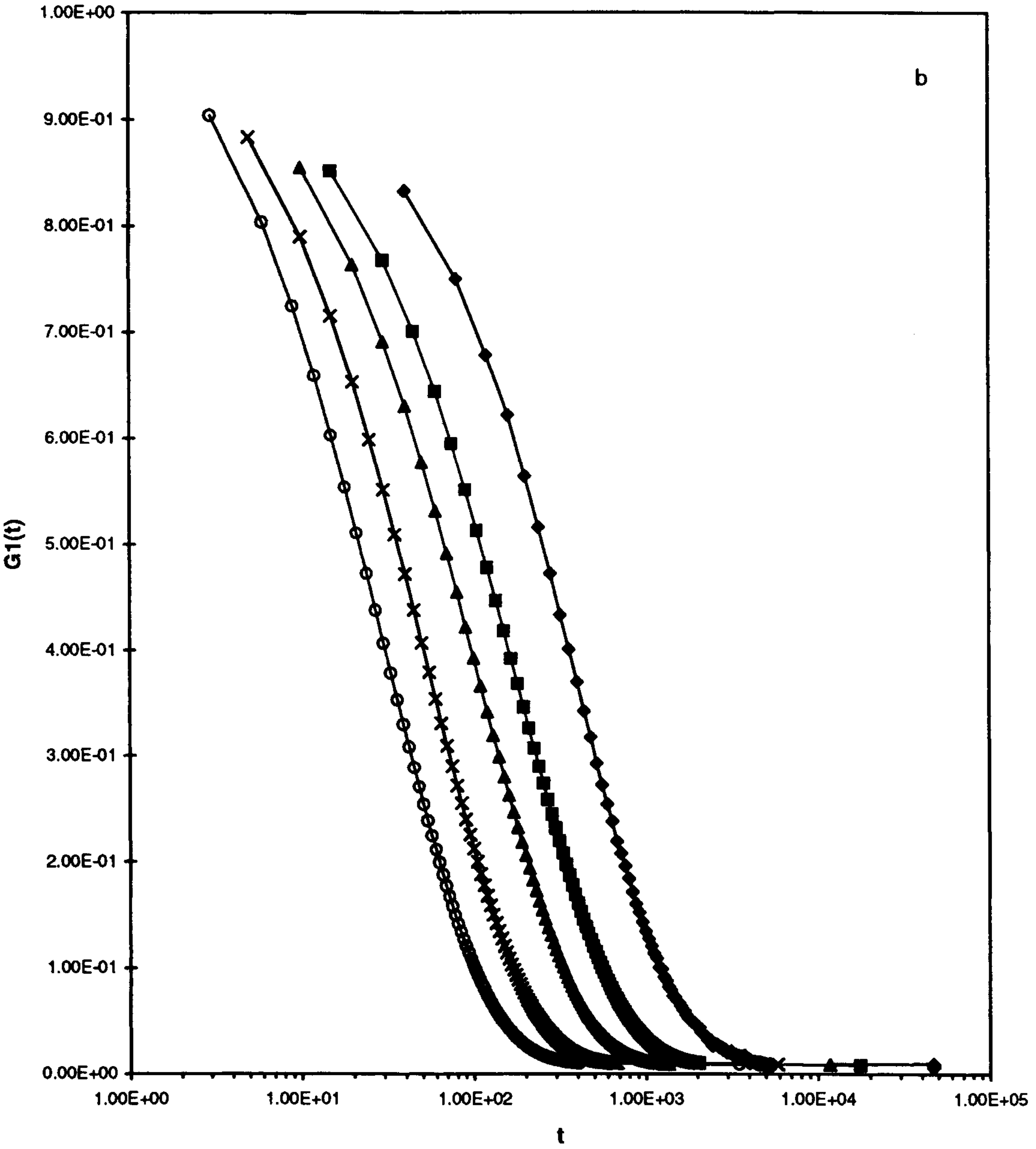

Figure 4 Continued

tendency of aggregation of the polymers changes with the composition.

Aqueous solutions. Counter ion specificity is one of the most widely studied aspects of polyelectrolyte behaviour[11,15,16]. The electrostatic interactions of the counter ions with dissociated polymers is usually assumed to screen the charges of the polyelectrolytes, which makes the polymers behave more or less like electrically neutral ones. Thus, in a dilute aqueous solution, addition of low molar mass electrolytes leads to the compression of the polymer coil, supposing that the counter ion does not induce any aggregation of the chains. Prior to further studies on the specific binding of certain metal ions into the copolymers of AMPS, NIPAAM, and 4A, it was necessary to investigate the copolymers in pure aqueous solutions.

Figure 2 shows the average R_h against temperature, measured for the copolymers in pure water at an angle of 90°. The copolymer concentration was again constant, 10 mg ml^{-1}. The behaviour of the polymers showed the same trend as in aqueous sodium chloride solutions. The radius of SAM1 and SAM3 containing over 20 mol% of 4A, is constant through the measured temperature range and no phase separation appears. When the amount of 4A is less than 20 mol% (SAM4 and SAM5), the sudden increase of the radius at a temperature interval between 30 and 40°C indicates the appearance of the LCST.

Contrary to expectation, the hydrodynamic radius of every copolymer in an aqueous solution is smaller than that measured in 0.1 M NaCl solution. It is concluded that the salt not only screens the charges of the polymers but while doing this also induces the aggregation of the chains; the tendency to aggregate increases the size of the diffusing particles.

Concentration dependence of the solution properties

The intensity of the light scattered from the aqueous polymer solutions was very low compared with the intensity

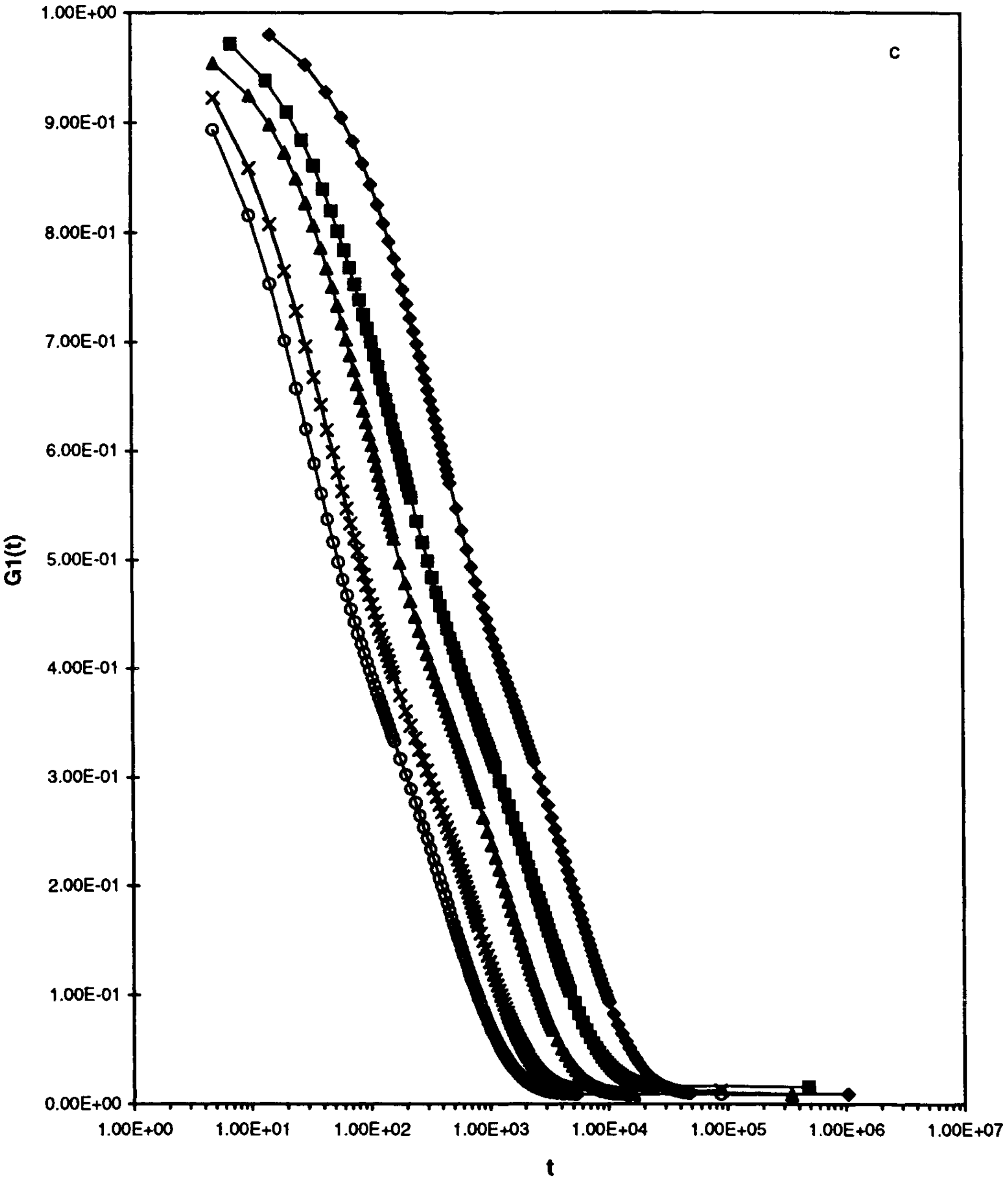

Figure 4 Continued

from the samples containing sodium chloride. To study closer the concentration dependent properties of the solutions it was decided to use the saline solutions of SAM5. SAM5 was considered the most interesting of the copolymers because it shows the phase separation behaviour of PNIPAAM.

The intensity autocorrelation functions were measured for SAM5 with varying polymer concentration, and the distribution of the hydrodynamic diameters of the diffusing particles was calculated using CONTIN. With this program, a bimodal distribution was obtained for every sample. The measured peak sizes are shown against polymer concentration in *Figure 3*. According to this analysis, the polymer solutions contain small particles with a diameter independent of concentration, as well as large particles which start to increase in size when concentration is increased above 20 mg ml^{-1}.

Inspection of the normalised correlation functions $g_1(t)$ plotted against logarithmic time shows that the relaxation time of the fast decay is almost independent of concentration, whereas the relaxation time of a slower process increases with increasing concentration. It is noticeable that for concentrations lower than 20 mg ml^{-1}, $g_1(t)$ can be well fitted with KWW function using only one relaxation time. A possibility remains that the results obtained by CONTIN with dilute samples (polymer concentration below 20 mg ml^{-1}) could be taken as an indication of a broad size distribution better than a distinct bimodal one.

Figure 4 shows the angular dependence of the correlation function $g_1(t)$ at 25°C for samples with concentration 1, 10, and 100 mg ml^{-1} of SAM5 in 0.1 M NaCl solution. The functions $g_1(t)$ describing the samples with concentration of 1 and 10 mg ml^{-1}, could be fitted using one exponent in the KWW equation. Two relaxation modes were needed to fit the curve from solution with concentration 100 mg ml^{-1}. From *Figure 4* it is qualitatively observed that relaxation times of samples with concentration 1 and 10 mg ml^{-1}, as well as both the short and long relaxation times of the

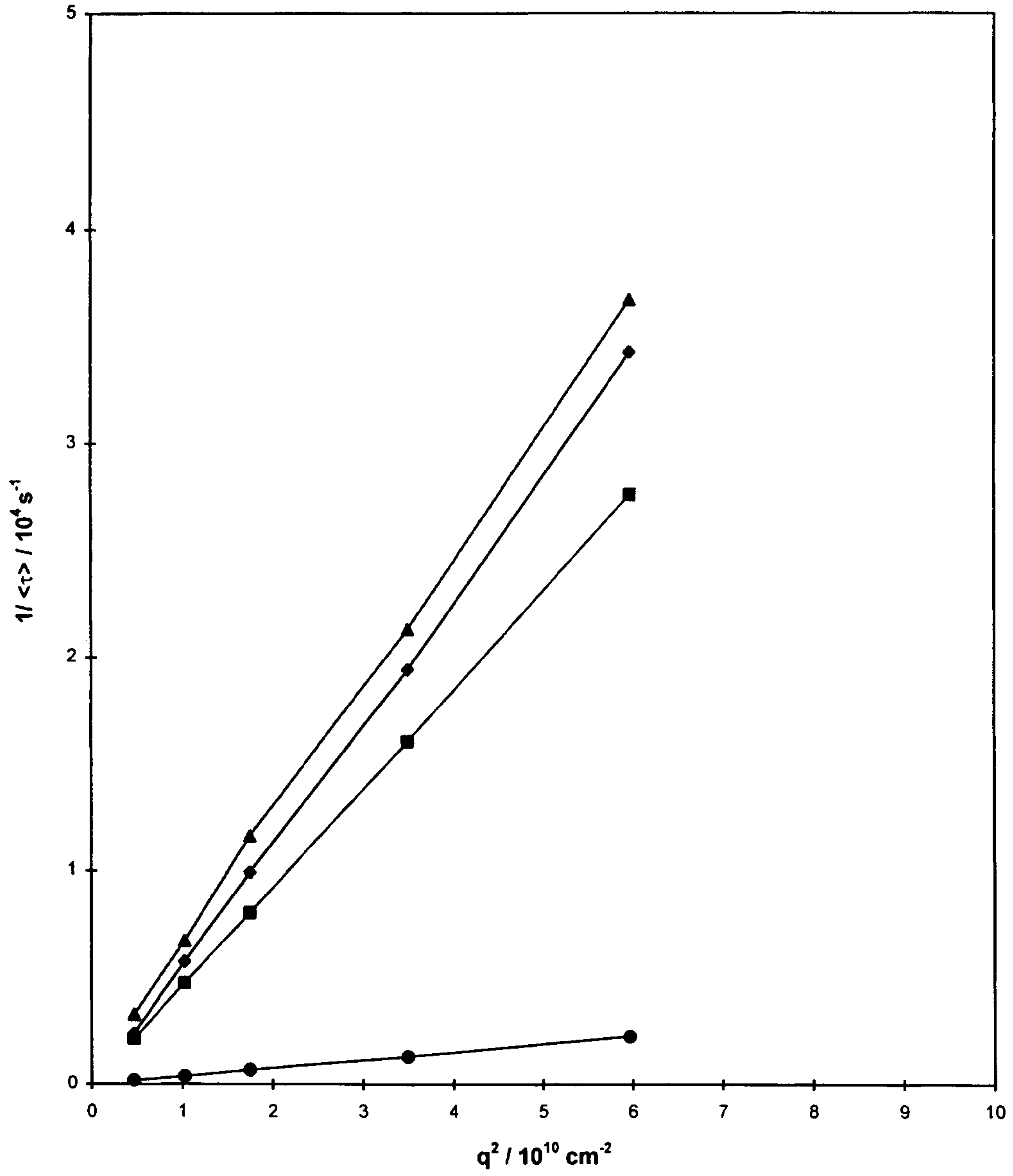

Figure 5 The inverse relaxation times of SAM5 as functions of q^2. Symbols: ◆, polymer concentration 1 mg ml^{-1}; ■, polymer concentration 10 mg ml^{-1}; ▲, polymer concentration 100 mg ml^{-1}, fast relaxation; ●, polymer concentration 100 mg ml^{-1}, slow relaxation

sample with concentration 100 mg ml^{-1} decrease with increasing scattering angle. As is demonstrated in *Figure 5*, all reciprocal relaxation times show linear relation to q^2 as is typical for diffusive processes.

Using equation (7) and taking the lower of the values shown in *Figure 3* as the hydrodynamic diameter of the polymer in dilute solution it may be concluded that solutions with polymer concentration of 10 mg ml^{-1} are in the dilute regime; evidently the critical overlap concentration is between 20 and 40 mg ml^{-1} (cf. *Figure 3*). The fact that in several repeated measurements CONTIN gives a bimodal size distribution even for dilute samples, could be taken as evidence of the existence of two copolymers with different molar masses in SAM5. However, because the hydrodynamic volume of the polymer was observed to be larger in aqueous sodium chloride solution than in pure water, it is more realistic to assume that the salt induces the aggregation of the polymers. To further clarify this point, the effect of some other salts on the diffusion rate of the polymer was studied. Nickel and chromium chlorides were chosen not only to use cations with different valence but also because of the evident importance of finding polymers which could effectively bind these toxic metal ions from water.

Effect of nickel and chromium(III) salts on the diffusion of the polymer

The average R_h of SAM5 was measured against temperature in 0.1 M sodium, nickel and chromium(III) chloride solutions. The scattering angle was 90°, and the polymer concentration was 10 mg ml^{-1}. The diffusion coefficients in water and aqueous salt solutions are compared in *Figure 6*. As may be seen from the figure, all the added salts increase the hydrodynamic size of the polymer at temperatures below the LCST. Furthermore, the increase of the size becomes more evident with increasing valence of the added cations. This result shows that the cations bind to the polyelectrolyte causing the aggregation of the polymers.

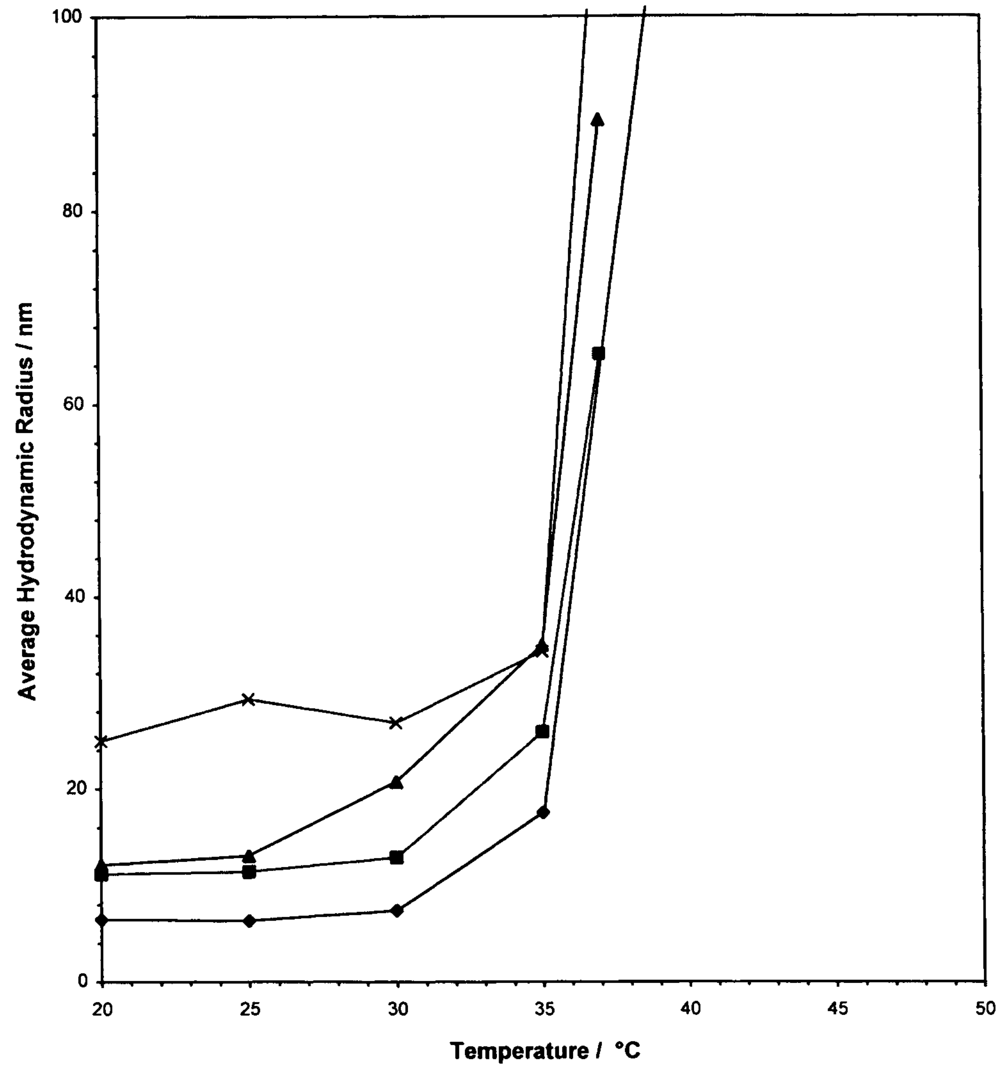

Figure 6 Hydrodynamic radius of SAM5 in aqueous solvents. Solvents are indicated by the symbols: ◆, water; ■, 0.1 M NaCl; ▲, 0.1 M $NiCl_2 \cdot 6H_2O$; ×, 0.1 M $CrCl_3$

The dependence of the salt concentration on the behaviour of the polymers is exemplified in *Figure 7* where R_h of various samples at 25°C is plotted as a function of the ionic strength of the solutions. The difference between the cations used is clear, chromium ions increase the size of the diffusing particles much more effectively than do the nickel ions. As is well known, the two cations have different coordination numbers; in addition to the different electric charges of the cations this is also a factor affecting their binding to the polymers.

CONCLUSIONS

The solution behaviour of the copolymers of AMPS, NIPAAM and 4A has been studied by dynamic light scattering from three aspects, i.e. the chemical composition of the copolymers, the concentration of the solutions and the effects of low molar mass salts. The results show that the relative amounts of AMPS, NIPAAM and 4A in the polymers strongly affect the thermal properties and the conformation of the copolymers. The amount of AMPS has been kept constant (2 mol%) throughout this study. When the amount of 4A is equal to and higher than 20 mol%, the copolymers do not show phase separation, owing to the electrostatic interactions between the acid groups which outweigh the hydrophobic forces between the isopropyl groups. However, when the amount of 4A is lower than 20 mol%, the aqueous solutions of the copolymers show critical temperature, at which point the electrostatic and hydrophobic forces are balanced.

Comparison of the solutions with varying polymer concentration revealed that the copolymer SAM5 when dissolved in aqueous sodium chloride, has a tendency to aggregate even in dilute solutions at $T <$ LCST. By using other metal salts it has been shown that the degree of aggregation in the aqueous solutions is dependent on the valence of the counter ion. The effects of the salt concentration on the behaviour of the polymers depend on the chemical nature of the cation.

ACKNOWLEDGEMENTS

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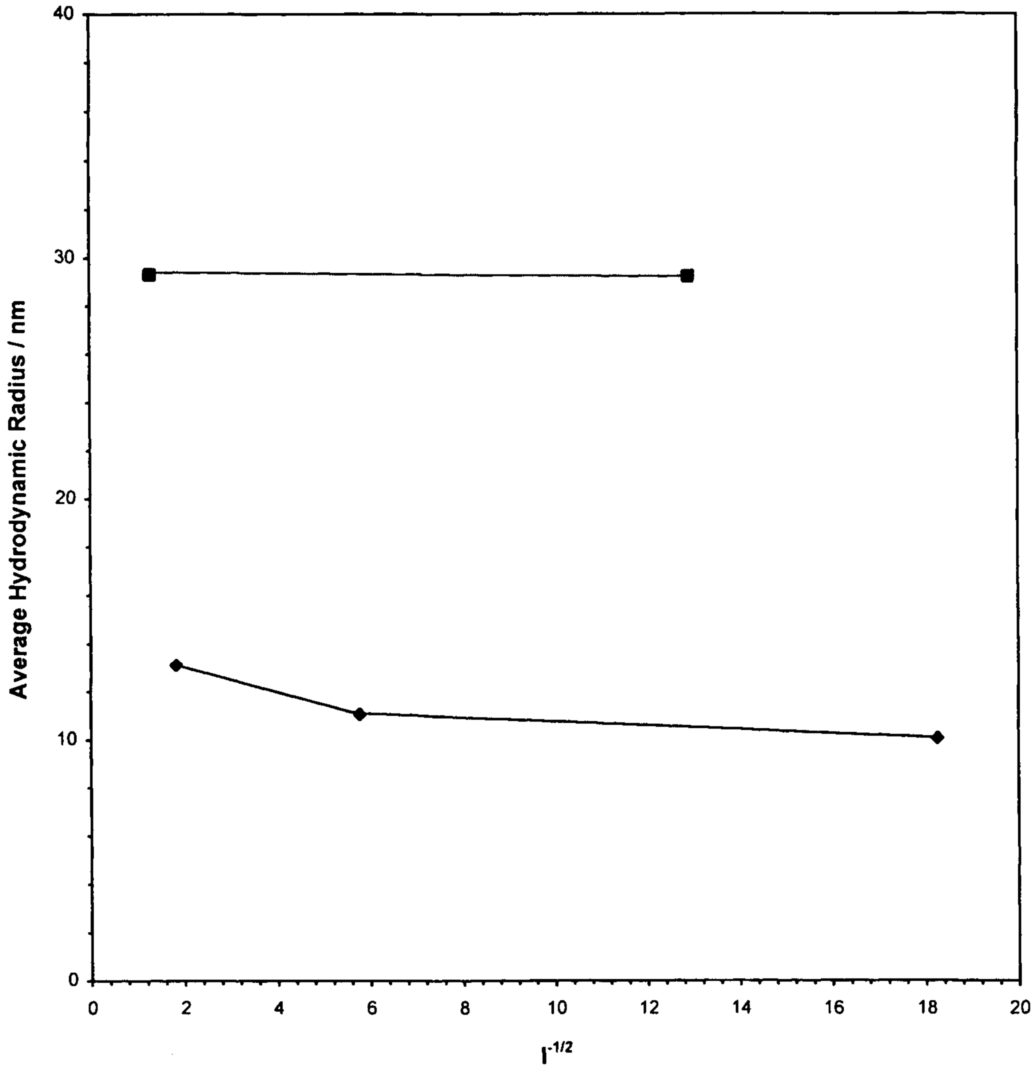

Figure 7 The R_h of SAM5 in aqueous solutions containing metal salts, measured at 25°C. R_h is plotted against the inverse square root of the ionic strength. R_h in pure water was 6 nm. ◆, $NiCl_2$; ■, $CrCl_3$

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