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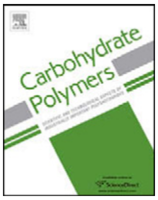

Novel multi-stimuli responsive sodium alginate-*grafted*-poly(N-isopropylacrylamide) copolymers: II. Dilute solution properties

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A B S T R A C T

Multi-stimuli responsive biocompatible and biodegradable materials can be obtained by combining polysaccharides with the thermoresponsive polymer poly(N-isopropylacrylamide)-PNIPAM. Behaviour of dilute aqueous solution of sodium alginate (AgA) grafted with (PNIPAM) (AgA-g-PNIPAM) copolymers as function of composition, temperature and pH has been studied by viscometry coupled with particle size analysis. The effect of grafting on the solution properties has been established. The sol–gel phase transition temperature has been also determined.

1. Introduction

Hydrophobically modified polysaccharides exhibit emulsifying properties that can be adjusted by controlling the process of hydrophobic transformation. Moreover, the polysaccharide backbone can provide biocompatibility, biodegradability and other specific properties. The hydrophobic groups grafted onto the polysaccharide backbone tend to aggregate together, in order to limit their contact with the solvent (Shashkina et al., 2003). Associative polymers based on polysaccharides have been widely studied since the pioneering work of Landoll (1982). The hydrophobically associated water-soluble polymers contain a small proportion of hydrophobic groups, usually in the form of pendant side chains or terminal groups, which raise of increasing interest for a wide variety of industrial applications, such as: flocculants, thickening agents in oil recovery, latex paints, cosmetics, due to the advantage offered both by polyelectrolyte and hydrophobic groups effect (Bock, Valint, & Pace, 1988; Bock, Varadaraj, Schulz, & Maurer, 1994; Kevin & Taylor, 2003; Schulz & Glass, 1991; Ye & Huang, 1999; Zhang, Da, & Hogen-Esch, 1991).

Generally, the graft copolymers of various polysaccharides, such as chitosan (Kim, Cho, Lee, & Kim, 2000; Wang, Zhang, & Wang, 2009; Zhang et al., 2009), dextran (Huh, Hashi, Ooya, & Yui, 2000; Wang et al., 2002) and carboxymethyl celullose (Bokias, Mylonas, Staikos, Bumbu, & Vasile, 2001; Bumbu, Vasile, & Staikos, 2007; Zhang et al., 2009) with PNIPAAm exhibit a lower critical solution temperature (LCST) in aqueous media, where their hydration/dehydration change occurs reversibly and rapidly in response to the small changes in the environment conditions; also, their behaviour depends on pH of the medium (Vasile, 2009, chap. 6).

The rheological properties (viscosity) of dilute and semidilute solutions and of the physical gels (elasticity modulus) of hydrophobically modified self-associated polymers and copolymers have been studied by many researchers (McCormick, Park, & Hester, 1984; Neidlinger, Chen, & Mccormick, 1984; Rogovina, Vasilev, Churochkina, & Pryakhina, 2001).

In our previous papers, it has been shown that multi stimuli-responsive biocompatible and biodegradable polymeric materials can be obtained by combining the properties of alginate (AgA) with a thermo-responsive polymer, such as poly(N-isopropylacrylamide) (PNIPAAm), in various architectures: as interpolymeric complexes, block and graft copolymers or hydrogels (Vasile & Cheaburu, 2008; Vasile, Dumitriu, Cheaburu, & Oprea, 2009).

In this paper, the dilute solution properties of a series of graft copolymers of sodium alginate and poly(N-isopropylacrylamide) (AgA-g-PAIPAAm) have been studied

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by viscosity measurements, coupled with particle size analysis.

2. Experimental

2.1. Materials

The alginic acid (Ag) extracted from brown algae (*Macrocystis pyrifera* kelp), used in the experiments, was purchased from Fluka (Switzerland). It is a straight-chain, hydrophilic, colloidal, polyuronic acid composed primarily of anhydro-β-D-mannuronic acid residues with 1→4 linkage, characterized by reduced viscosity in water at 25 °C for an aqueous solution of $c = 0.2$ wt% is $\eta_{\text{red}} = 2.41$ dl/g, drying loss ≤10 wt% and ash content ≤3 wt%. Sodium alginate, obtained by alkaline hydrolysis with NaOH 1 M, is a an anionic linear copolymer with homopolymeric blocks of (1-4)-linked β-D-mannuronate (M) and its C-5 epimer α-L-guluronate (G) residues, respectively, covalently linked in different sequences of blocks, or in randomly organized blocks. The relative amount of each block type varies with the origin of the alginate. Alternating blocks form the most flexible chains and are more soluble at lower pH than the other blocks. According to the producer's specifications, the mannuronic/guluronic ratio was around 1.3.

PNIPAAm-NH_2 has been synthesized by radical polymerization in aqueous solution using (2-aminoethanethiol hydrochloride, 98% Aldrich) AET HCl as redox coupling agent, and $K_2S_2O_8$ (KPS) as initiator.

Several copolymers with various compositions of sodium alginate (AgA) grafted with poly(N-isopropylacrylamide) (PNIPAAm) (AgA-g-PNIPAAm) have been prepared by a coupling reaction between AgA and PNIPAAm, using 1-3-(3-dimethylaminopropyl)–3-ethyl-carbodiimide hydrochloride 98% (EDC) as condensing agent. Their structure was confirmed by FT-IR, ^{1}H NMR spectroscopy and elemental analysis (Vasile & Cheaburu, 2008). Copolymers composition varied between 20 and 68 wt% PNIPAAm. The actual distribution of the side chains on the AgA backbones remains unknown but there exists certainly some amount of AgA chains bearing more than one PNIPAAm chain.

The weight average molecular weights determined by light scattering measurements varied from 100 to 690 kDa.

2.2. Viscosity measurements

Salt solutions were made up by directly adding 0.1 M of the quantitative solid NaCl into the aqueous solutions followed by stirring to dissolve NaCl. Doubly distilled water was used for the preparation of all solutions. A biopolymer solution was prepared by dissolving 1.0 wt% NaAgA in the 0.1 M NaCl solution, on stirring for at least 4 h to ensure complete dispersion, and then storing overnight at room temperature. The pH of the solutions was varied by adding certain amounts of 0.01 M NaOH and/or 0.05 M HCl solutions. The final studied pH values of the saline solutions varied from 2.4 to 8.0. Prior to measurements, the aqueous solutions were filtered through 0.2 μm filters and kept overnight before measurements. Polymer concentration was checked by weighing the remaining dry substance obtained after letting the solutions for 24 h in an oven, at 110 °C. The solutions were kept about 10 min prior to measurements for temperature equilibrium. All prepared solutions remained clear over the whole range of established concentrations, pHs and temperatures imposed which shows that no macroscopic phase separation ever occurred, as found for other alginate containing solutions (Yang, Chen, & Fang, 2009).

Viscometric measurements of the polymer solutions were carried out on a 0.6 mm Ubbelohde capillary viscometer, at 25.0 ± 0.1 °C. The temperature was adjusted by a circulating bath. No kinetic corrections were required, since we verified that the flow time was proportional to the kinematic viscosity. The kinetic energy was found to be negligible. The density of solution was thought to be approximately the same as that of pure water. As a viscosity characteristic served the reduced viscosity $\eta_{\text{sp/c}}$ (dl/g), which most adequately reflects the structural changes occurring in a system. The measurement error was within 0.12 dl/g.

2.3. Particle size analysis

Particle size analysis of the polymeric samples was done by a *dynamic light scattering technique* (Zetasizer model Nano ZS (Malvern Instruments, UK)) with a red laser wavelength of 633 nm (He/Ne). The system uses a non-invasive back scatter (NIBS) technology (which reduces the multiple scattering effects), wherein the optics are not in contact with the sample, back scattered light being detected. This is the system for which the Mie method is applied over the whole measuring range, from 0.6 nm to 6 μm. Dynamic light scattering (DLS) measurements were performed to obtain the *Z*-average distribution of the apparent hydrodynamic diameter (D_{H}) of the aggregates, using equation:

$$D_{\text{H}} = \frac{kT}{3\pi\eta D} \tag{1}$$

where D_{H} is the hydrodynamic diameter, k is the Boltzman constant, T is the temperature, η is the viscosity, D is the diffusion coefficient.

It is important to note that this mean size (hydrodynamic diameter, often expressed by symbol *Z* or *z*-average) is an intensity mean, and not a mass or number mean, because it is calculated from signal intensity.

Determinations have been done on dilute solutions of copolymers at different pHs over the concentration interval 0.125–0.7 g/dl below the critical concentration of alginate (~0.7 g/dl), where only polymer clusters were formed (Zhao, Teresa Carvajal, Won, & Harris, 2007).

The Zetasizer Nano ZS instrument permits to determine molecular weight and the second virial coefficient, A_2, of the samples. The Zetasizer Nano *S* measures the intensity of static light scattering (SLS) by scattered light of various concentrations of sample at one angle (173°). The intensity of scattered light produced by a macromolecule is proportional to the product of weight-average molecular weight (M) and concentration of the macromolecule. The samples with a relatively large size exhibit non-isotropic scattering profiles with measured intensities dependent on the angle of observation. Nevertheless, the particle size decreases, sample scattering becomes isotropic and the angular dependence of the measured intensity is minimized. Based on this consideration, the Zetasizer Nano system provides a method for measuring the molecular weight of small proteins and polymers at only one angle by using the relationship between the intensity of scattered light and their molecular weight given by the Rayleigh equation (Eq. (2)).

As no clear-cut distinction has been established between the "small" and "large" particles, it is recommended to compare the values of molecular weight and/or the second virial coefficient by two or more methods. The obtained results are useful exclusively for comparative purposes.

A plot of KC/R_θ *versus* C is expected to be linear, with an intercept equivalent to $1/M$ and a slope equal to the second virial coefficient, A_2.

The following relations (Rayleigh equation) are valid:

$$\frac{KC}{R_\theta} = \left(\frac{1}{M} + 2A_2C\right)P(\theta) \tag{2}$$

where

$$K = \frac{2\pi^2}{\lambda_0^4 N_A}\left(n_0 \frac{dn}{dc}\right)^2 \tag{3}$$

$$P_\theta = 1 + \frac{16\pi^2 n_0^2 R_g^2}{3\lambda_0^2} \sin\left(\frac{\theta}{2}\right) \tag{4}$$

and

$$R_\theta = \frac{I_A n_0^2}{I_T n_T^2} R_T \tag{5}$$

where K is the optical constant, M is the molecular weight, A_2 is the 2nd virial coefficient, C is the polymer concentration, R_θ is the Rayleigh ratio of the sample, $P(\theta)$ is the shape factor; n_o is the refractive index of the solvent at the laser wavelength, N_A is the Avogadro constant, and dn/dc is the refractive index increment of the scattering species in the solvent used. R_g is the radius of gyration; θ is the measurement angle, I_A is the intensity of sample, I_T is the intensity of standard, toluene, n_T is the toluene standard refractive index, R_T is the Rayleigh ratio of standard, toluene.

Rayleigh ratio (R_θ) is the ratio of scattered to incident light intensity. The intensity of the incident light interacting with the macromolecule is difficult to measure. Therefore, the standard approach is to measure the scattering intensity of the sample, relative to that of a well-described standard with a known Rayleigh ratio (for toluene, at 633 nm, the Rayleigh ratio is $1.3522 \times 10^{-5}\,\mathrm{cm}^{-1}$). The dn/dc value of alginate of 0.152 ml/g was taken from the literature of Storz et al. (2009) and Martinsen, Skjåk-Brk, Smidsrød, Zanetti, and Paoletti (1991). The radius of gyration (R_g) can be roughly estimated from the hydrodynamic radius (R_H) determined by such experiments, using the shape correction model box for coils: $R_g = 0.816R_H$.

3. Results and discussion

Several semi-empirical equations proposed for the viscosity of dilute and semidilute polymer solutions have been compiled by Sakai (1968) in a mathematical study. The well-known Huggins equation holds true in dilute domains, being generally valid for all polymers, provided that they are not polyelectrolytes. Other equations have been proposed for describing the variation of viscosity up to the semidilute concentration range (Cowman & Matsuoka, 2005, Schulz & Blaschke, 1941), starting from the results on the viscosity of sphere suspensions. All these semi-empirical equations contain two parameters: intrinsic viscosity (related to the hydrodynamic dimensions of the objects in solution) and an empirical constant (related to the interactions between components). All tested equations provide consistent values of intrinsic viscosity (Ma, Liang, Cui, Dai, & Huang, 2003).

Studies on sodium alginate diluted and semi-dilute solutions have been reported in the literature (Yang et al., 2009; Rinaudo & Graebling, 1986).

The viscometric results obtained with water-soluble graft Ag-g-PNIPAAm copolymers have been analyzed using the parameters derived from the Huggins–Kraemer (Eqs. (6) and (7)) and Feodors equations (Eq. (8)). Usually, Huggins equation (Huggins, 1942) was combined with Kraemer equation (Kraemer, 1938) to give the intrinsic viscosity:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c \tag{6}$$

$$\frac{\ln\ \eta_r}{c} = [\eta] - k_B[\eta]^2 c \tag{7}$$

where $[\eta]$ is intrinsic viscosity (dl/g), η_{sp} is specific viscosity and $\eta_{sp/c}$ is reduced viscosity (η_{red}); $\eta_{sp/c} = (\eta - \eta_0)/\eta_0 c$, η is the viscosity of the solution; η_0 is solvent viscosity; c is polymer concentration; and k_H and k_B are the Huggins and Kraemer coefficients, respectively; η_r is relative viscosity. All are empirical dimensionless constants, which depend on molecular architecture and interactions, respectively. For polymers in good solvent conditions, the Huggins coefficient is generally between 0.3 and 0.6, which is the range of reported values for highly hydrophilic polymers in aqueous solutions. When solvent quality is lowered, the experimental value of the Huggins coefficient can largely rise, above unity, as is observed when hydrophobic groups are grafted onto dextran chains (Durand, 2007). All investigated samples exhibit a linear dependence of reduced viscosity ($\eta_{sp/c}$) as a function of polymer concentration. For dilute and moderately concentrated polymer solutions, Fedors proposed Eq. (8) (Fedors, 1974, 1975, 1979) reported as valid for to moderate polymer concentrations of nonassociative polymers (Ayal, Gargallo, & Radic, 1993; Shah & Parsania, 1984; Torres, Dutta, Choudhury, & Matison, 2004). For the second parameter, Fedors equation is the only relation involving a concentration parameter, while the others contain dimensionless constants. Generally, the magnitude of the intermolecular interactions is accounted for by the value of the dimensionless constant. Nevertheless, this concentration parameter can be empirically related to viscometric characteristics (Rotureau, Dellacherie, & Durand, 2006).

Based on numerous measurements, Fedors found out that this equation is generally applicable for η_r values from 1 to about 100:

$$\frac{1}{2(\eta_r^{1/2} - 1)} = \frac{1}{[\eta]}\left(\frac{1}{c} - \frac{1}{c_m}\right) \tag{8}$$

In Eq. (8), $\eta_r = \eta/\eta_s$ is the relative viscosity of the solution and Cm is a concentration parameter.

Fedors equation was first applied to the viscosity of Newtonian suspensions of rigid particles, then it was used to describe the viscosity of dilute to moderately concentrated polymer solutions (Chen & Chen, 1988). Later on, Eq. (3) was applied to various polymer–solvent systems (Bercea & Navard, 2000; Ioan, Simionescu, Neamtu, & Simionescu, 1986; Rao, 1993). Ghimici and Popescu (1998) testified that this equation could be used to describe the viscometric properties of a polyelectrolyte solution over a wide concentration range. Dragan and Ghimici (2001), Dragan, Mihai, and Ghimici (2003) and Ioan, Filimon, and Avram (2006) used it for modified polyelectrolyte solutions and got very good results. In addition Eq. (8) was applied to aqueous solutions of amphiphilic polymers and compared with other equations, but the study was limited to the dilute domain (Ma et al., 2003). Feodors equation has been also applied to several polymeric systems, polysaccharides included (Rotureau et al., 2006).

After measuring relative viscosity (η_r), the viscometric data of polymer dilute solutions with different polymer concentrations could be linearized by different equations. As an example, such type of graph is given in Fig. 1. Addition of NaCl will increase the polarity of solutions and change the behaviour of copolymer molecules. The copolymers had an anti-polyelectrolyte behaviour in salt solutions, *i.e.* the reduced viscosity value decreased with decreasing the concentration of polymer solution, due to the contraction of polymer chains, which is caused by the intra-molecular hydrophobic association between hydrophobic groups (McCormick, Middleton, & Grady, 1992). Thus, Fedors equation exhibited a very good linear fitting degree for two systems – with and without NaCl.

The linear regression correlation coefficients (CLR) of different equations could be used to evaluate the degree of linear fitting. The results showed that, although the CLR values of different equations were different, the intrinsic viscosity values calculated from different equations were closed to each other. Considering the best fitting results of Fedors equation, the $[\eta]$ values obtained by Fedors

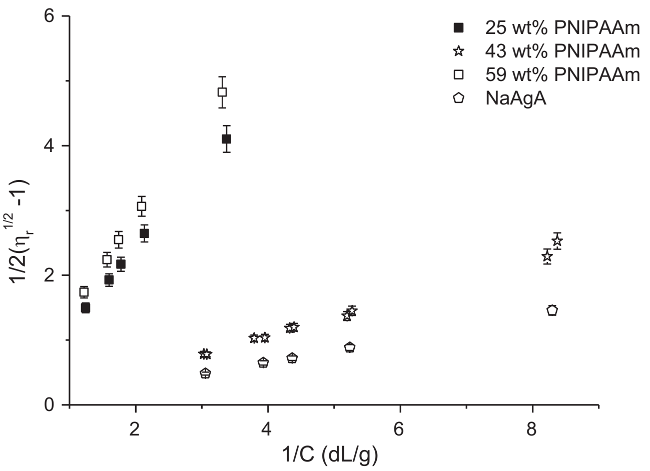

Fig. 1. The Fedors graphs for several of the studied samples.

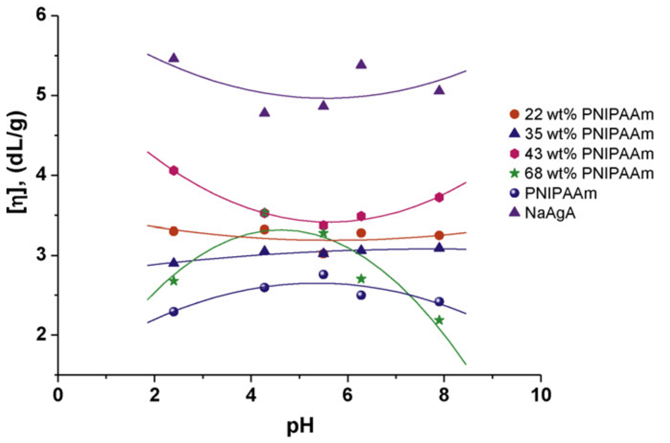

Fig. 3. The dependence of the intrinsic viscosity on the composition and pH of the solution.

equation would be used to describe the behaviour of macromolecular chains of graft copolymers. Addition of NaCl would shield the electrostatic repulsion effect and reinforce the hydrophobic association effect, contraction of the polymer chains decreasing of both $[\eta]_{\text{Fedors}}$ and η_{red}.

Variation of intrinsic viscosity obtained by Fedors equation as a function of copolymer composition is given in Fig. 2 at different pHs, while Fig. 3 plots the dependence of this value on pH.

Intrinsic viscosity linearly decreases with increasing PNIPAAm content, showing a more packed conformation being probably formed for high hydrophobic component content, and also because of the lower molecular weight of PNIPAAm. Decrease in intrinsic viscosity with increasing the PNIPAAm content is expected, because the contour length of the alginate backbone per total polymer unit mass will decreases with the PNIPAAm content, *i.e.* the structure becomes more branched.

Variation of $[\eta]$ on pH depends on copolymer composition. A maximum is found for both PNIPAAm and copolymers with prevalent amount of this polymer at pH = 4–6 while, over the same pH interval, a minimum appears for AgA and for the copolymers containing a high AgA amount. Intrinsic viscosity corresponds to the specific volume of the species present in dilute solution (occurring as either isolated macromolecules or aggregates). For highly hydrophilic polymers, intrinsic viscosity depends on both the molecular weight and stiffness of the macromolecules. The intrinsic viscosity of hydrophobically-modified AgA, varies significantly with the extent of modification. The higher the number of graft groups, the lower the solvent quality and the higher the tendency of macromolecules to interact with each other (because of the well-known "hydrophobic effect"). Decrease of intrinsic viscosity is due to the collapse of individual coils, since modified macromolecules are less hydrophilic. When the degree of modification is high enough or when highly hydrophobic groups are attached, the decrease of intrinsic viscosity reflects the formation of compact aggregates (even in the dilute domain) formed mainly at low pH values.

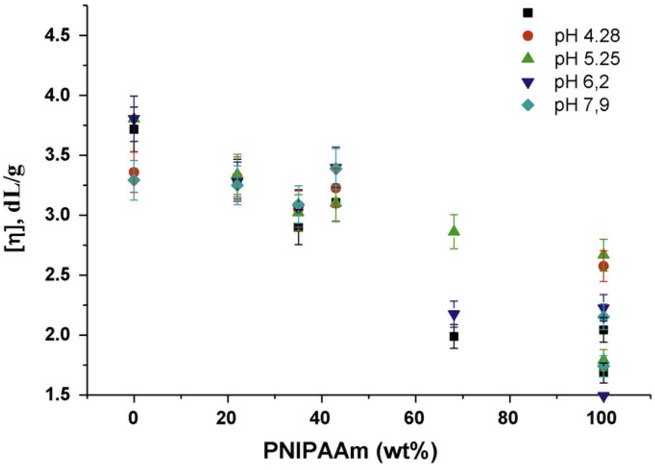

Fig. 2. The dependence of the intrinsic viscosity on the graft copolymer composition.

Yang et al. (2009) found out that the general trend is that viscosity increases with lowering pH, where strong shear-thinning features are detected in the low to the intermediate shear rate region, due to the breakup of intermolecular associations. At pH values below 3.0, macroscopic phase separation also occurs. These results clearly demonstrate that the rheological response of the alginate dilute solutions is sensitive to a change of pH within the low pH range, which probably reflects enhanced intermolecular interactions. With the progressive decrease of pH value from 5.0 to 3.0, the system exhibits a marked viscosity enhancement (Yang et al., 2009). As the pH value of the solution decreases from 6.6 to 5.0, the system generally shows small viscosity changes, which probably indicates no intermolecular interactions owing to electrostatic repellence, while the hydrophobic segments in the alginate chains increase, and the hydrophilic ionized carboxyl groups decrease, suggesting that electrostatic repellence is suppressed, and that the possible intermolecular entanglements and hydrogen bonds are enhanced, association structures being thus formed. Oberyukhtina, Bogolitsyn, and Popova (2001) described the behaviour of sodium alginate at various pHs. With increasing pH of the sodium alginate solution ($6.5 < \text{pH} < 8$), the degree of dissociation of alginic acid increases, thus enhancing the electrostatic repulsion between the COO^- groups of the molecule. This, in turn, results in unfolding of the macromolecule and, consequently, increases the viscosity of the system. The highest viscosity is observed at pH 8 (Tanford, 1963).

Huggins coefficient, k_{H}, is related to the interactions between the species in solution and the solvent molecules. For the copolymers studied under solvent conditions, Huggins coefficient generally varies between 0.3 and 0.7, which is the range of reported values for highly hydrophilic polymers in aqueous solutions. Variation of the interaction parameters k_{H} and k_{B} with copolymer composition is illustrated in Fig. 4. The curves of k_{H} – composition show a minimum over the 25–60 wt% PNIPAAm composition range, while a maximum or a small increase in kB was found in the same range, because of the change

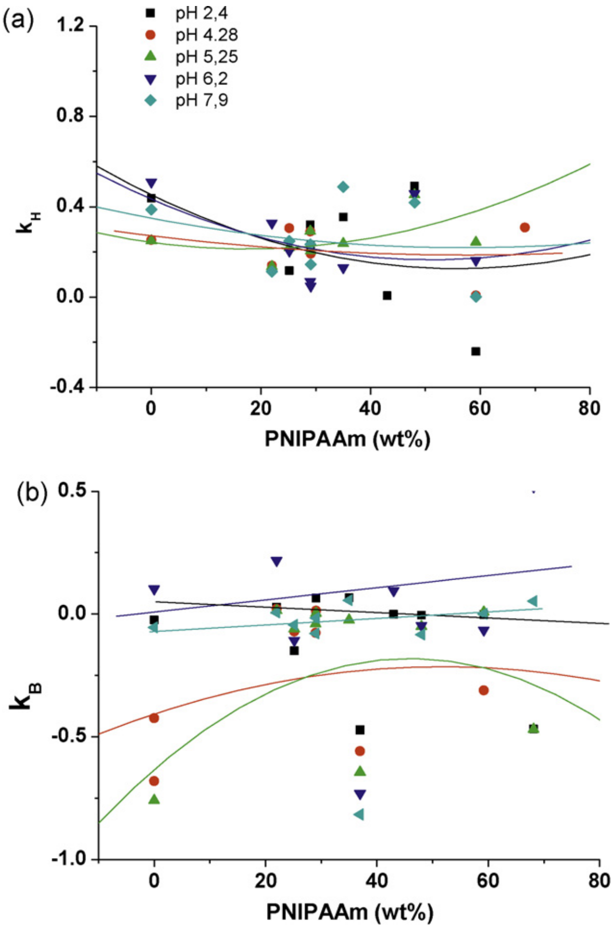

Fig. 4. Dependence of the k_H (a) and k_B (b) on copolymer composition.

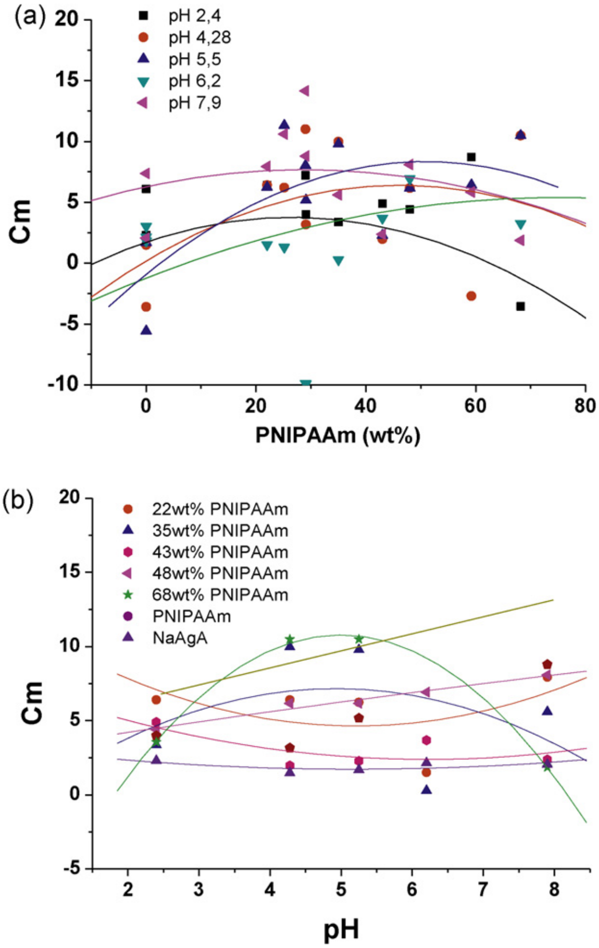

Fig. 5. Variation of the Cm with copolymer composition (a) and pH (b).

induced by the interaction with the solvent by incorporation of hydrophobic groups.

Only a slight pH variation of k_H and k_K may be observed for a certain composition (Fig. 4).

Fedors equation gives the same type of dependence, on both composition and pH, for Cm, although the maximum is much pronounced for a composition range of 20–60 wt% PNIPAAm (Fig. 5).

The interdependence between Fedors parameter and other viscometric characteristics (intrinsic viscosity, Huggins coefficient) is also evidenced. The significance of Cm in Fedors equation is unknown for water-soluble polymer systems. A lower Cm corresponds to a higher k_H, that is to say that a lower Cm means a stronger interaction between different molecules and vice versa as also observed by Durand (2007) for modified dextran and by Ma et al. (2003) for hydrophobically-associated polyacrylamide. As for the hydrophobically-associated water-soluble polymers, the intermolecular hydrophobic association plays a very important role. However, the copolymers had an obvious antipolyelectrolyte effect due to the inter- or intra-molecular hydrophobic association.

3.1. Particle size analysis

The distribution curves of particle size at various pHs (not given) and copolymer compositions show an increase in *Z*-average with increase of pH, due probably because the macromolecule is much extended at high pH.

At a PNIPAAm content below 50 wt%, the distribution curves show three peaks, with the most probable dimensions of 10, 100 and 800 nm at pH 6.2. The last peak becomes narrower with increasing the PNIPAAm content of copolymers, only one peak appearing for copolymers with a high PNIPAAm content. This should indicate the importance of hydrophobic association. At pH 2.4, the distribution curves are much closer to monomodal distribution, with the exception of the samples with 43% PNIPAAm.

As expected, *Z*-average increases with increasing solution concentration and pH; the most significant increase being specific to copolymers with a high AgA content. The difference between samples is much evident at high pH. At low pH, Z-average varies in close limits for all copolymers from 200 to 450 nm, with larger differences at $c = 0.65$ g/dl, while, at high pH, the *Z*-average takes very different values, from 1800 nm for copolymers with a high AgA content, to 300–600 nm for copolymers with a prevalent content of PNIPAAm. These values agree with those found by (Storz et al., 2009) for the gyration radius if, in a rough approximation, this evaluation was done from the hydrodynamic diameters determined here. This should mean that association is much important at a high AgA content, while PNIPAAm favours a much more packed conformation.

The polydispersity index (PDI) is a dimensionless parameter. Values higher than 0.7 for PDI indicate that the sample has a very broad size distribution. The maximum value is arbitrarily limited to 1.0. (frequent question, www.malvern.com). The polydispersity index (PDI) of the particles increases with solution concentration, at all pH values. Its variation with concentration is much more important for solutions with low pH than for the solutions with high pH.

Variation in *Z*-average and PDI with composition of copolymers and pH could be due to the interaction between copolymer components and with the solvent. The samples become more

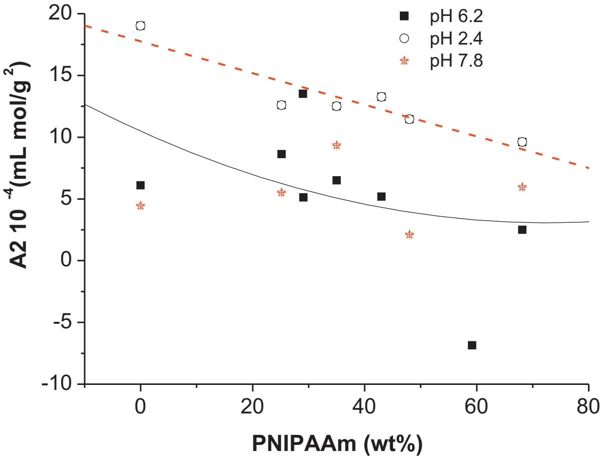

Fig. 6. Dependence of the second virial coefficient on the PNIPAAm content of the graft copolymers AgA-g-PNIPAAm.

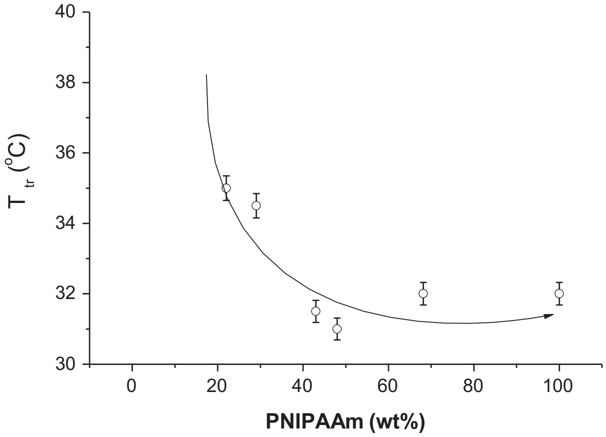

Fig. 8. The dependence of the transition temperature of the AgA-g-PNIPAAm copolymers on composition.

homogeneous at concentrations of 4–5 mg/ml, where PDI is closer to 0.5 being lower at pH 6.2 than at pH 2.4 indicating a better homogeneity. Increase of PDI with concentration for the samples with a prevalent content of PNIPAAm can be also observed at pH 6.2, which means the increase of heterogeneity with concentration, because of the association of hydrophobic groups.

The 2nd virial coefficient, A_2, is representative for the magnitude of particle–solvent interactions. These interactions are evidenced by the A_2 virial coefficient which represents particle interaction strength, being correlated with sample solubility (George & Wilson, 1994). The dependence of A_2 on copolymers composition at different pHs of the solution is shown in Fig. 6.

Decrease in the A_2 values with increase of the PNIPAAm content is linear for pH 2.2, a minimum being found in the 30–70 wt% PNIPAAm interval content, at high pH, in accordance with variation of the k_H and k_B values with composition, which indicates that the interactions are much stronger for copolymers with a high AgA content. The positive value of the 2nd virial coefficient indicates that solvation is more energetically favourable than polymer aggregation, suggesting a high solubility limit for copolymers in the solvent used in the study. When $A_2 = 0$, the molecule solvent interaction strength is equivalent to the molecule-molecule interaction strength, and the solvent is described as a theta solvent. The negative value indicates that the polymer has a slight preference toward aggregation, as opposed to dissolution. Aggregation could occur for a copolymer composition with prevalent PNIPAAm content, where small values of A_2 have been obtained.

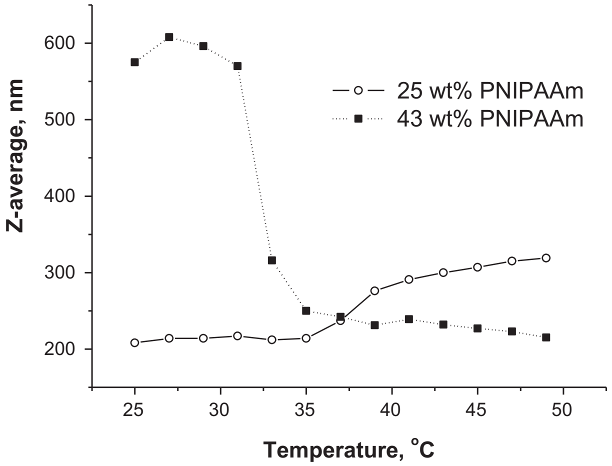

Fig. 7. Z-average *versus* temperature for graft copolymers of AgA with 25 and 43 wt% PNIPAAm.

3.2. Temperature effect

Contrary to native alginate, temperature could have a strong effect on the viscometric parameters of modified alginate. Temperature increase leads to a reinforcement of the hydrophobic effect, which is similar to changing the type of interacting hydrocarbon groups at a given temperature. In other series of experiments, particles size analysis was done in function of temperature. In Fig. 7, *Z*-average was plotted as a function of temperature for two representative samples with different contents of PNIPAAm. It is evident that, for samples with a low PNIPAAm content, an increase in *Z*-average takes place over the temperature interval around 35–37 °C while, for graft copolymers with a high content of PNIPAAm, *Z*-average decreases suddenly at 32–33 °C, a temperature which corresponds to the LCST of PNIPAAm.

The dependence of this transition temperature on copolymer composition is given in Fig. 8.

Transition temperature increases with the increase of the hydrophilic component content and remains approximately constant and close to the LCST of PNIPAAm for a content higher than 50 wt% PNIPAAm.

Hence, by increasing temperature, the copolymers with a high PNIPAAm content become much heterogeneous (PDI increases with temperature for copolymers with a high content of PNIPAAm, and remains approximately unchanged or increases with increasing temperature for copolymers with a high AgA content) because, of phase separation and aggregation. Such phenomenon was observed in other cases too (Yang, Wu, Konák, & Kopecek, 2008).

4. Conclusions

The data on dilute solution of AgA-g-PNIPAAm hydrophobically associating copolymers by NaCl addition of were fitted by three different equations. The results showed that Fedors equation was the most accurate one to describe the dilute solution properties of these kinds of copolymers. The high value of the polymer concentration parameter (Cm) in Fedors equation corresponded to the low value of constant k_H. The copolymers had an anti-polyelectrolyte effect. The second virial coefficient depends on copolymer composition and pH, indicating a weak interaction in the middle interval of composition, which agrees with the variation of Cm and of Huggins and Kraemer coefficients with both composition and pH.

The aqueous solutions of the graft copolymers of sodium alginate with PNIPAAm exhibit a "thermothickening effect", which is dependent on solution copolymer composition and pH. It is much evident at high concentrations, as will be demonstrated in a future paper.

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