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Solution properties of the acrylamide-modified cellulose polyelectrolytes in aqueous solutions

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ABSTRACT

A novel cellulose-based polyelectrolyte (AM-C) containing acylamino (DS = 0.625) and carboxyl (DS = 0.148) groups was homogeneously synthesized from cellulose with acrylamide in NaOH/urea aqueous solutions. Solution properties of AM-C in aqueous solutions were investigated by laser light scattering, rheometry, and viscometry. The results indicated that AM-C could form large aggregates spontaneously in water with or without the addition of salts by the strong hydrogen bonds and electrostatic interaction between acylamino and carboxyl groups. Steady-shear flow study showed a Newtonian behavior of the solutions in the dilute regime while a shear-thinning behavior as the concentration increases. The critical concentration (c_e) for transition from dilute to concentrated solution was determined to be 0.7 wt %. Aqueous solutions of AM-C displayed good thermo-stability, reversible liquid-like characters attributing to the chemical modification. The derivation from Cox–Merz rule at relatively low concentration was related to the co-existence of single chain and large aggregates of AM-C in dilute regime. As the polymer concentration increased, the AM-C system was transformed into a homogeneous entanglement structure, resulting in the disappearance of deviations from the Cox–Merz rule.

1. Introduction

Polysaccharides, including cellulose, starch, chitin, and hemicelluloses, are by far the most abundant renewable resource on the earth, and are expected to play an increasingly important role in, for example, industrial, biochemical, and medical fields with decreasing supply of oil resources.[1] Polysaccharide-based polyelectrolytes are an intriguing class of important polymers with broad scientific and technological appeal.[2,3] The incorporation of ionizable groups within the polymer backbone ensures a better water solubility, as well as a stronger thickening ability, which has a great importance in various areas such as the petrochemical, cosmetics, paint industries, water treatment, and controlled drug release.[4]

Cellulose, a linear β-1, 4-D-glucan, is the most abundant polysaccharide available today worldwide. The chemical modification of cellulose is the dominant route to tailor the functions, modify the properties, and improve the overall utilization of this naturally occurring biopolymer.[5–8] Cellulose-based polyelectrolytes, such as carboxymethyl cellulose (CMC) and cellulose-grafted copolymers, have been widely investigated and used in flocculation, drag reduction, detergents, textiles, paper, foods, drugs, and oil well drilling operation.[9–14] Solution properties of these polyelectrolytes have been extensively studied for their wide industrial applications.[8] Ghannam et al. carried out a complete and comprehensive study of the rheological properties of CMC solutions.[9] They found that the rising concentration of CMC in the solutions transforms the behavior from Newtonian to shear thinning and accompanied by stronger time-dependence of the rheological properties. Abdelrahim et al. reported that CMC solutions showed power-law flow behavior and that the consistency coefficient and flow behavior index were significantly affected by both temperature and concentration.[10] Kulicke et al. found that the rheological behavior of an aqueous CMC solution was mainly influenced by the molar mass of the dissolved CMC and its concentration.[11] The stiffness of the polymer chain due to the cellulose backbone is not really influenced by the introduction of more ionic groups, especially in the technically relevant salt solutions. Enebro et al. investigated two model sodium CMCs with similar monomer composition but with significant differences in the viscoelastic properties.[12] According to their analytical method, CMC with the strongest intermolecular interactions in solution also contains the longest nonsubstituted segments. Wei et al. suggested that the rheological properties of a novel cellulose-based hydrophobically polyelectrolyte, cellulose octaonate sulfate (COS), were similar to hydrophobically associating polymers.[13] As the shear rate increased, the COS solution passed through a shear-thickening region before exhibiting a sharp

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decrease in viscosity, eventually exhibited Newtonian behavior. Biswal et al. reported that the viscosities of CMC-*g*-polyacrylamide (PAM) copolymer gradually increased with increase in PAM side chains.[14]

Based on the Michael addition (the nucleophilic addition of a carbanion to an α, β unsaturated carbonyl compound) and the saponification of acylamino groups to carboxyl groups in alkaline media,[15] we successfully synthesized acrylamide-modified cellulose (AM-C) polyelectrolytes,[16] which contain acylamino and carboxyl groups (chemical structure as shown in Scheme 1), in NaOH/urea aqueous solutions. In the present work, the solution properties of AM-C solutions in dilute and concentrated regimes were studied, and the effects of concentration and ionic strength on the evolutionary aspect of the rheological properties were investigated. We suppose to supply some useful information to develop applications of this novel cellulose-based polyelectrolyte.

2. Experimental

2.1. Materials

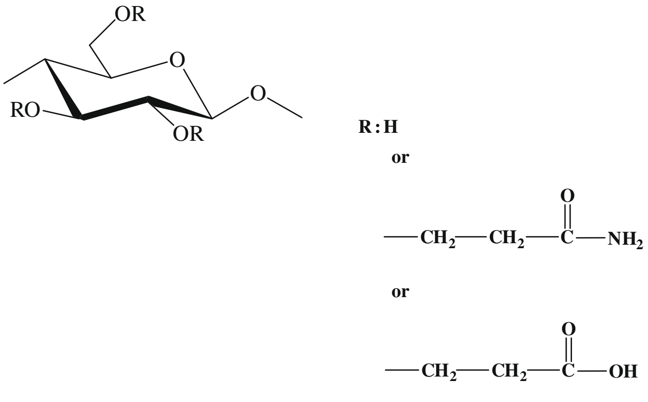
The cellulose (cotton linter pulp) was supplied by Hubei Chemical Fiber Group Ltd. (Xiangfan, China), and the viscosity-average molecular weight (M_η) of the cellulose was determined by viscometry in cadoxen[17] to be 11.2×10^4 g/mol. Acrylamide and other reagents were of analytical grade and were used without further purification.

2.2. Preparation of AM-C

AM-C sample was prepared according to our previous work.[16] Briefly, cellulose was dissolved in NaOH/urea aqueous solutions to obtain a transparent solution (4 wt %),[18] then a certain amount of acrylamide aqueous solution was added dropwise into it and the mixture was stirred for a certain time at 25 °C. The reaction product was neutralized with acetic acid, dialyzed, and freeze-dried to obtain AM-C derivative. According to its nitrogen content (3.588 wt %) in the acidic derivative and ^{13}C NMR spectrum,[16] the DS of acylamino and carboxyl groups was calculated to be 0.625 and 0.148, respectively.

2.3. Characterization

The viscosity of AM-C in different solvents was measured at 25 ± 0.1 °C with an Ubbelodhe capillary viscometer. The kinetic energy correction was always negligible. The light-scattering intensities were determined with a modified commercial light scattering spectrometer (ALV/SP-125, ALV, Germany) equipped with an ALV-5000/E multi-τ digital time correlator and a He–Ne laser ($\lambda = 632.8$ nm) in an angular range from 30 to 150° at 10° intervals at 25 °C. The test AM-C solutions were prepared in distilled water and in 0.1 M NaCl aqueous solution, respectively, and made optically clean by filtration through 0.45 μm Millipore filters. The specific refractive-index increments (dn/dc) of AM-C were measured with an Optilab refractometer (Wyatt Technology) at 632.8 nm and 25 °C and were found to be 0.135 cm^3/g.



Scheme 1. Chemical structure of AM-C.

The rheological properties of AM-C solutions were characterized using the steady shear and dynamic oscillator tests. All rheological measurements were performed on a Rheometric Scientific ARES-RFS III strain-controlled rheometer with couettee cups (TA Instruments, New Castle, DE, USA). Plots were made of the log apparent viscosity versus log shear rate (from 0.1 to 1000 s^{-1}) to determine zero-shear viscosities. The dynamic rheology measurements were carried out to measure dynamic viscoelastic parameters such as $G'(\omega)$ and $G''(\omega)$ as functions of angular frequency (ω), or temperature (T). The rheometer was equipped with two force transducers allowing the torque in the range from 0.004 to 1000 g cm. The values of the strain amplitude were set at 10%, which is within a linear viscoelastic regime. For each measurement, the sample was poured into the couettee geometry instrument, which had been maintained at each measurement temperature without pre-shearing or oscillating. Temperature control was established by connection with a Julabo FS18 cooling/heating bath kept within ±0.2 °C of the desired temperature over an extended period of time. To prevent dehydration during rheological measurements, a thin layer of low-viscosity paraffin oil was spread on the exposed surface of the measured solution. For the frequency sweep measurements, time $t = 0$ min was defined when the temperature reached the desired value. The frequency range was from 0.01 to 100 rad/s.

3. Results and discussion

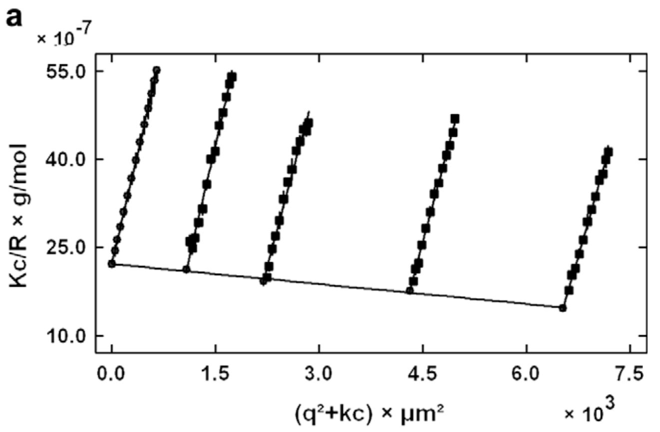
3.1. Dilute solution properties

Figure 1 shows the Zimm plots for AM-C in distilled water and in 0.1 M NaCl aqueous solution at 25 °C, respectively, and the molecular parameters are listed in Table 1. From the results, weight-average molecular weight (M_w) of AM-C in distilled water and in 0.1 M NaCl aqueous solution was estimated to be 4.5×10^5 g/mol and 14.0×10^5 g/mol, respectively, which was much larger than the molecular weight of AM-C (about 1.5×10^5 g/mol) calculated from its DS value and the M_η of the original cellulose (11.2×10^4 g/mol). The results suggested that AM-C could form large aggregates spontaneously in water with or without the addition of salts by the strong inter- and intramolecular hydrogen bonds and electrostatic interaction between the acylamino and carboxyl groups. Furthermore, AM-C could form larger aggregates in NaCl solution than in distilled water because the electrostatic repulsion was screened with the addition of salts, according to the apparent M_w, radius of gyration (R_g), second virial coefficient (A_2) of AM-C in distilled water and in 0.1 M NaCl.

The reduced viscosity η_{sp}/c of AM-C in pure water at 25 °C is shown in Figure 2. The reduced viscosity of AM-C exhibits typical polyelectrolyte behavior, which remarkably increases with decreasing polymer concentration due to the expanded polyelectrolyte chains and chain-chain repulsion.[19] The curves shown in Figure 2 can be linearized applying Fuoss equation:[20]

$$\eta_{sp}/c = [\eta]/(1 + Ac^{1/2}) \tag{1}$$

where A is a constant, to account for the interactions of polyelectrolyte. The curve obtained by calculating the viscometric data for AM-C in terms of the Fuoss equation is presented in inset of Figure 2. As



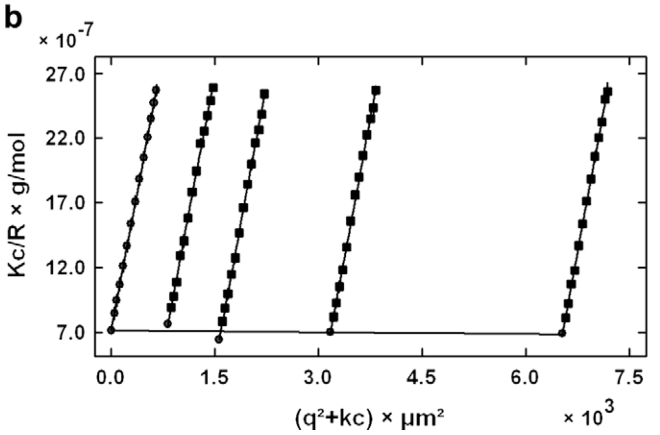


Figure 1. Zimm plot of AM-C in distilled water (a) and in 0.1 M NaCl aqueous solution (b).

Table 1
The experimental results of weight-average molecular weight (M_w), radius of gyration (R_g), and second virial coefficient (A_2) of AM-C in distilled water and in 0.1 M NaCl aqueous solution

Solvent	M_w ($\times 10^5$ g/mol)	R_g (nm)	A_2 (mol mL/g^2)
H_2O	4.50	82.6	-6.133×10^{-7}
0.1 M NaCl	14.00	109.3	-3.550×10^{-8}

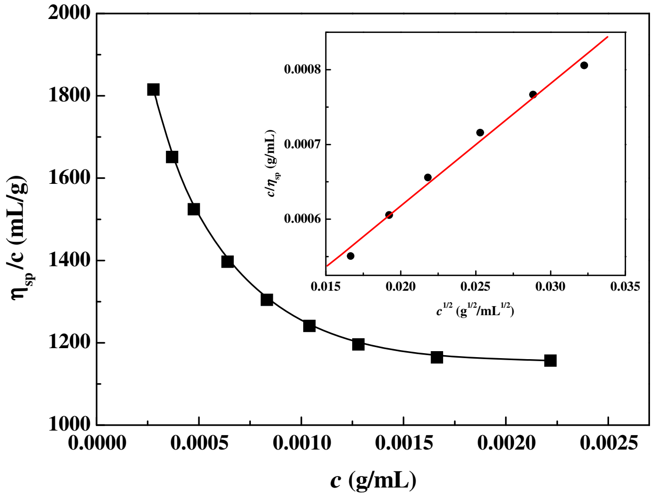


Figure 2. Dependence of the reduced viscosity (η_{sp}/c) on concentration (c) for AM-C in distilled water at 25 °C. Inset is the dependence of c/η_{sp} on $c^{1/2}$.

observed, straight line was obtained over a wide range of concentrations, and the intrinsic viscosity ([η]) value of AM-C was calculated to be 3442 mL/g. Compared to other random coil polymers, the [η] value of AM-C is very high. It can be deduced that the AM-C had more extended coil geometry in water at 25 °C, which attributed to the electrostatic repulsion of the polyelectrolyte solutions and to the stiffness of cellulose backbone.

In order to further probe the effects of electrostatic repulsion on the conformation of AM-C in solution, the intrinsic viscosity was studied as a function of salt concentration. Figure 3 depicts the respective [η] values for AM-C in NaCl solutions, which were obtained from Huggins equation[21] by extrapolation of concentration to be zero. When NaCl concentration increased from 0.05 M to 0.5 M, the [η] values decreased from 393 mL/g to 302 mL/g, because the electrostatic repulsion was screened and the macromolecules displayed more flexible chain conformation.[22] The extent of polyelectrolyte contraction from an extended conformation to the flexible chain conformation is dependent upon the inherent stiffness of the polymer.[23] Smidsrød parameter B is often used as an empirical measure of the relative stiffness of polyelectrolyte chains.[24] The lower the B is, the stiffer the chain becomes. By construction of a plot wherein the intrinsic viscosity is extrapolated to infinite ionic strength, a linear relationship can be found in which the slope of the line (S) relates to the inherent stiffness of the polymer (B):

$$[\eta]_I = [\eta]_\infty + B([\eta]_{0.1\ \mathrm{M\ NaCl}})^v (I^{-1/2}) \tag{2}$$

where $[\eta]_\infty$ was the [η] at infinite ionic strength. As shown by Smidsrød, Haug, and others,[25] the parameter v exhibits a small amount of variation as a function of polyelectrolyte species, thus an average exponent value of 1.3 was employed in this study. From the slope (S) determined from Figure 3 and the [η] measured in 0.1 M NaCl, the stiffness parameter B was calculated to be 0.058. It was similar to the values reported for several ionic polysaccharides such as CMC (0.044–0.065), alginate (0.04), and λ-carrageenan (0.05),[1,24,25] indicating that AM-C was an inherently stiff polymer attributing to the stiffness of cellulose backbone.

3.2. Steady-shear flow behavior

Figure 4 presents the steady shear curves in terms of shear stress–shear rate relationships for 0.1–5 wt % AM-C aqueous

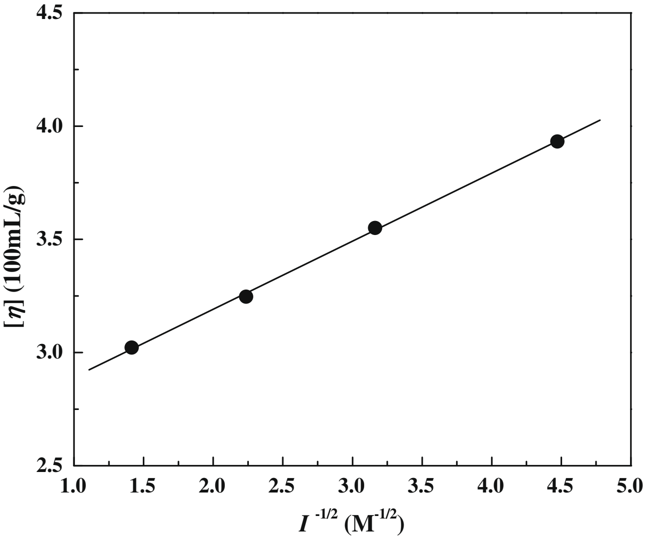


Figure 3. Plot of intrinsic viscosity ([η]) as a function of the inverse square root of ionic strength ($I^{-1/2}$) depicted for AM-C in various concentrations of NaCl solution at 25 °C.

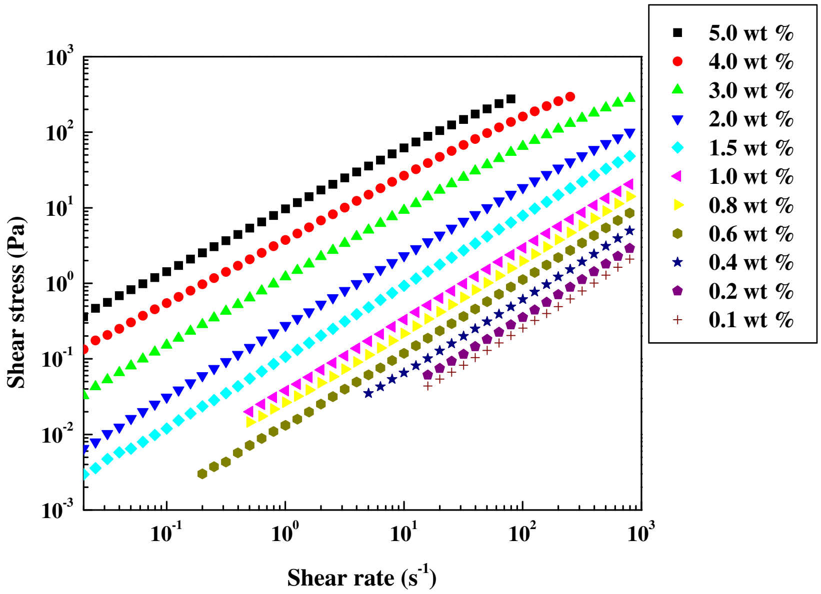


Figure 4. Dependence of the shear stress on shear rate for AM-C in distilled water at various concentrations at 25 °C.

solutions. When flow and viscosity curves are plotted in double logarithmic scales the curves give straight lines, which indicate that the Ostwald-de-Waele equation fitting is suitable for AM-C solutions. This can be written as:

$$\tau = k\dot{\gamma}^n \tag{3}$$

where τ (Pa) is shear stress, $\dot{\gamma}$ (s^{-1}) is shear rate, k (Pa s^n) is the consistency index, and n is the flow behavior index. k and n are typical rheological parameters used in power-law models. Figure 5 shows the n value as a function of log k from Ostwald-de-Waele equation. As shown, n decreased slightly with increasing AM-C concentration. The values of n for dilute AM-C solutions were approximated to 1 (n = 0.96–0.99), and the n against log k curve was leveled, showing that the flow was close to Newtonian liquid. However, the increase in AM-C concentration led to a slight drop in n (n = 0.81–0.94), the n value was a linear function to log k, which corresponded to a shear-thinning behavior for the higher range of concentrations, and as expected, this shear-thinning tendency became more pronounced as the concentration increased.

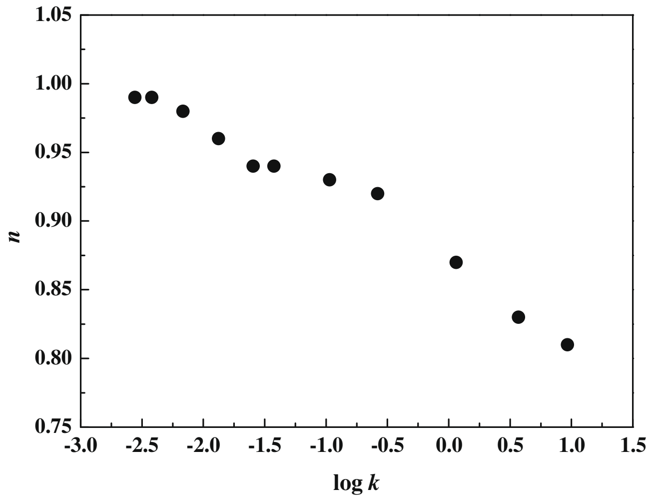


Figure 5. n versus log k plot for AM-C in distilled water at various concentrations at 25 °C.

The similar shear behavior can be seen in Figure 6, which shows the steady shear viscosity dependence on the shear rate at 25 °C. It displayed a Newtonian behavior of the solutions in the dilute regime and a shear-thinning behavior as the concentration increased. The approximate value of the zero-shear viscosity (η_0) could be obtained from the viscosity at shear rate tending to be 0. Clearly, the η_0 values increased when the polymer concentration increased, and at the same time the Newtonian plateau limit shifted to a lower shear region. The critical shear rate ($\dot{\gamma}_c$) corresponding to the transition from Newtonian to shear-thinning behavior moved to lower values with an increase in the AM-C concentration, similar to the general polymer solutions.[26] These effects can be explained that the increase of concentration resulted in the increase of molecular chains, leading to the interactions or entanglements of the polymer chains, and restriction of the motion of individual chains. Thus, the Newtonian behavior was lost progressively and shear-thinning behavior tendency became more pronounced with increasing polymer concentration.[27]

It is well known that at higher shear rate the viscosity decreases by power law dependence with the shear rate:

$$\dot{\gamma} \propto \eta^{-m} \tag{4}$$

By using the exponent (m), the dependence of $-m$ on the polymer concentration (c) is shown in Figure 7. Clearly, the plot of $-m$ against c was linear, and the m value decreased with a decrease in the AM-C concentration. Our m values were smaller than the predicted value (0.818) from the concept of Graessley,[28] suggesting the existence of strong association between AM-C chains, which is consistent with the above result of light scattering study.

In order to estimate the influence of the solvent on the viscosity, AM-C solutions (1–3 wt %) were analyzed in pure water and NaCl aqueous solutions (0.05–0.5 M). As illustrated in Figure 8, at all NaCl concentrations, there was negligible influence on the shear viscosity of AM-C solutions. This might be attributed to the stiffness of AM-C molecules in entanglement network as mentioned already. The stiffness of the polymer chain was not really influenced by the introduction of more ionic groups in the salt solutions. Even in the presence of salts, the polymer–polymer interactions remain the main factor influencing the rheological behavior for AM-C solutions.[26]

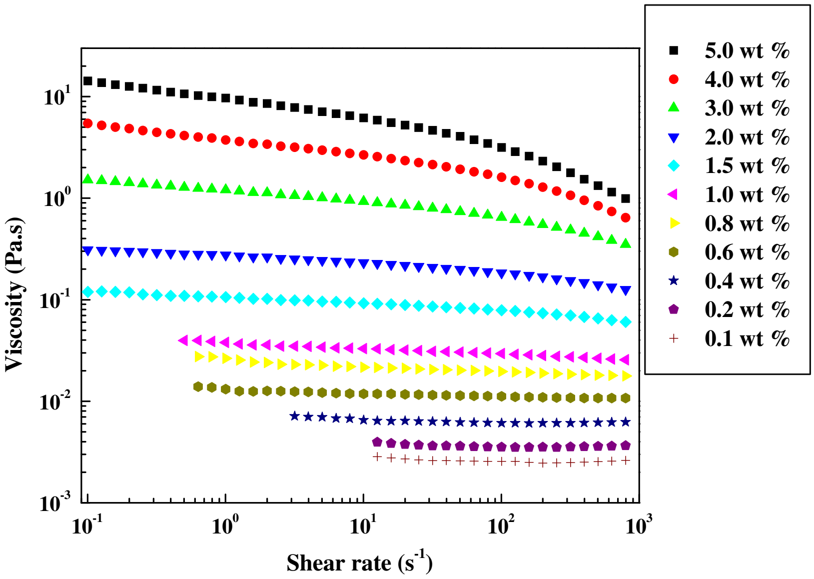


Figure 6. Dependence of the steady shears viscosity on the shear rate for AM-C in distilled water at various concentrations at 25 °C.

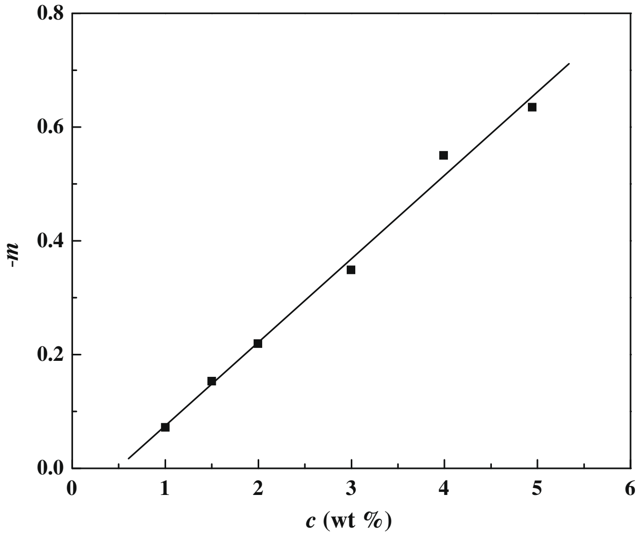


Figure 7. Slopes in the pseudo-plastic domain of $\eta\dot{\gamma}$ determination on steady flow curves for AM-C in distilled water at 25 °C.

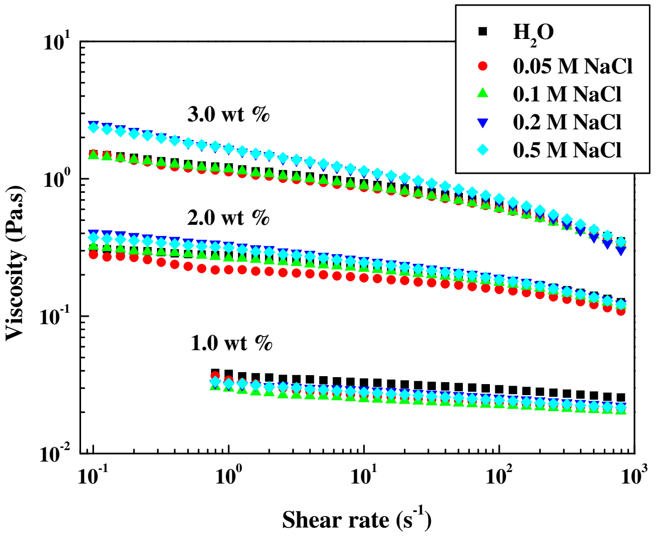


Figure 8. Dependence of the steady shears viscosity on the shear rate for AM-C in various concentrations NaCl aqueous solution at 25 °C.

3.3. Transition from the dilute to concentrated regime

Generally, the physical properties of a polymeric solution are greatly dependent on its concentration. It is well known that the transition from a dilute solution of independently moving coils or rods to an entangled network is usually accompanied by a very marked change in the concentration dependence of solution viscosity.[26] In order to further investigate the transition from dilute solution to the concentrated regime, the zero-shear viscosity (η_0, values estimated from Figure 6) was monitored as a function of AM-C concentrations in pure water at 25 °C (Fig. 9). The critical entanglement concentration (c_e) was determined to be about 0.7 wt %. For polyelectrolyte above the critical overlap concentration c^* and below c_e, the polymer chains can overlap without making effective entanglements.[4] In this regime, the viscosity increased with AM-C concentration according to a power law with an exponent of 0.76, slightly higher than the theoretically predicted value (0.5).[29,30] Scaling theory also predicts polyelectrolyte behavior above c_e based on a model of electrostatic blob interactions in which the polymer behaves as a neutral, randomly coiled entity in the entangled regime. A critical exponent of 3.3 was experimentally found here, similar to those found for various polysaccharides such as CMC and alginate,[31] also in reasonable agreement with the theoretical scaling exponents.[29]

Intrinsic viscosity usually reflects the hydrodynamic volume of individual polymer coils and conformation, when multiplied by concentration gives a dimensionless reduced concentration ($c[\eta]$) which was sometimes wrongly called the coil overlap parameter.[32] An important observation of Morris et al.[31] is that for polysaccharides, a plot of the specific viscosity $\eta_{sp,0}$ as a function of $c[\eta]$ yields a master curve to that obtained from plots of η_0 versus c, and the similar result was found later.[33–35] For AM-C solutions, the plots of $\eta_{sp,0}$ versus $c[\eta]$ gave exponents of 0.75 and 3.3, respectively (as shown in inset of Fig. 9). The values were well accorded with those obtained from the plots of η_0 versus c. The break of the plots of $\eta_{sp,0}$ versus $c[\eta]$ occurred at $c[\eta] \approx 20$, which was far higher than

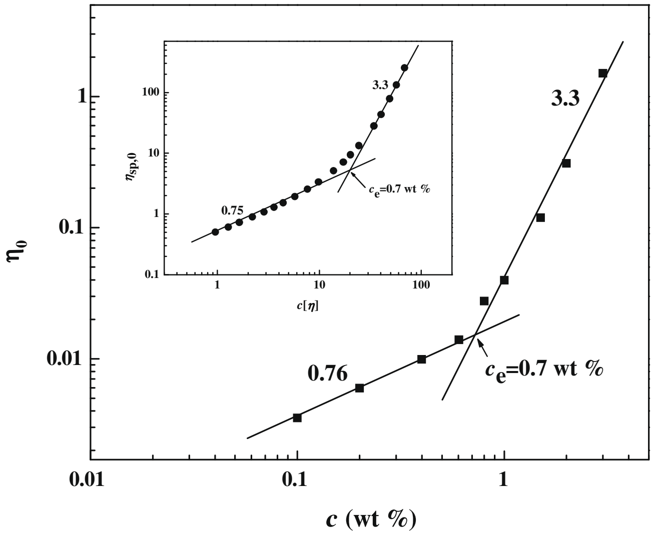


Figure 9. Determination of c_e for AM-C in distilled water from a plot of η_0 versus c at 25 °C. Inset depicts $\eta_{sp,0}$ versus $c[\eta]$ at 25 °C.

~4 for most disordered polysaccharides.[31] This may be attributed to the compression and subsequent interpenetration of AM-C coils in response to increasing space-occupancy, and also to the high viscosity of polyelectrolyte in water. In addition, the AM-C was a polyelectrolyte, and showed considerable stiffness with larger chain size. From $c[\eta] \approx 20$, c_e can be calculated to be about 0.7 wt %, which is consistent with the result from plots of η_0 versus c.

Examination of c_e as a function of ionic strength is shown in Figure 10. Compared to 0.7 wt % in pure water, the c_e shifted to lower values (0.56–0.62 wt %) with increasing of ionic strength, which indicated an increased occurrence of intermolecular interactions at higher salt concentrations.[23] However, the shift extent was not obviously, indicating that the ionic strength had little influence on the system because of the dominant polymer–polymer interactions. The plots of $\eta_{sp,0}$ versus $c[\eta]$ in NaCl solutions gave slopes of ~1.1 and ~3.4, respectively, in reasonable agreement with the theoretical scaling results of polyelectrolytes in excess salt.[30,31]

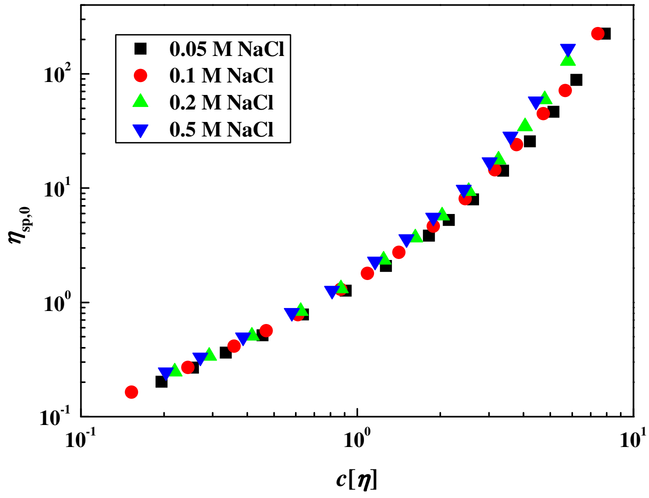


Figure 10. Plot of zero specific viscosity ($\eta_{sp,0}$) versus $c[\eta]$ for AM-C in various concentrations NaCl aqueous solution at 25 °C.

3.4. Dynamic oscillation behavior

To gain better understanding of the influence of concentration on viscoelasticity of the AM-C solutions, dynamic sweep measurements were carried out in solutions with different concentrations. Figure 11 depicts the plot of G', G'' versus ω for AM-C in pure water at 25 °C. The magnitudes of G'' were greater than those of G' for all frequencies studied without any evidence of gel-like character, which meant that viscosity property was the dominant of the AM-C solutions. As the AM-C concentration increased, the value of the module rose due to the increasing number of entanglements. While tan δ decreased as concentration increased (not shown), indicating that the elasticity was enhanced by increasing polymer concentration.[22]

The effect of temperature on the viscoelastic properties of AM-C solutions (2 wt %) containing NaCl ranging from 0.05 M to 0.5 M was also studied. It was expected that when the temperature increased, the viscosity decreased as a result of the heating. Here slight decrease occurred to all solutions (Fig. 12 shows in 0.2 M NaCl aq). At all temperature measured, obviously liquid-like character was observed with $G'' > G'$. It was found that the modulus decreases linearly upon heating, and the curves of heating and cooling superposed well, indicating that the change of modulus with temperature was reversible for the AM-C solution. On the other hand, the fact that no gel formation occurred indicates that the intrinsic hydrophobic structure for the native cellulose had been influenced by the chemical modification.[36] Tan δ showed no change during the heating and cooling process, indicating a good thermo-stability of the solutions.

The Cox–Merz rule is an empirical correlation between the large and nonlinear deformations in steady shear to the small and linear deformations in oscillatory shear. This empirical rule has been shown to apply successfully for a number of polymer melts and homogeneous solutions, but with relative success for aggregating polymers. It provides a sensitive practical test to detect the presence of aggregates in the solutions.[1] The Cox–Merz plots of the flow and dynamic rheological data of AM-C aqueous solution at various concentrations are shown in Figure 13. At relatively high concentrations (>1.0 wt %), the Cox–Merz rule was followed in the full test range: shear rate or frequency, that is, complex viscosity $|\eta^*(\omega)|$ = apparent shear rate $\eta(\dot{\gamma})$.[37] However, at lower concentrations (<1.0 wt %), the Cox–Merz rule with the $|\eta^*(\omega)|$ values lower than those of $\eta(\dot{\gamma})$ at high shear rate or frequency, and the extent of the deviation decreased as the polyelectrolyte concentration increased. The departures from the Cox–Merz rule were also found in other polysaccharides study,[38–40] and were considered to be due to the highly branched structure of the starch, two-phase system of pectin micro-aggregates dispersed in solvent and heterogeneous nature of the starch dispersions, respectively. In the AM-C aqueous solution, therefore, the deviation from the Cox–Merz rule could be attributed to the co-existence of AM-C single chain and large aggregates in the dilute regime. As the polymer concentration increased, AM-C single chains fully associated with each other to form aggregates, and the solution system transformed into a more uniform and homogeneous entanglement architecture in the concentrated region, resulting in the disappearance of deviations from the Cox–Merz rule at relatively high concentrations.[41]

4. Conclusions

Solution properties of an acrylamide-modified cellulose polyelectrolyte (AM-C) have been investigated. AM-C formed large aggregates spontaneously in aqueous solution because of the strong hydrogen bonds and electrostatic interaction between acylamino and carboxyl groups. The rising concentration of AM-C in

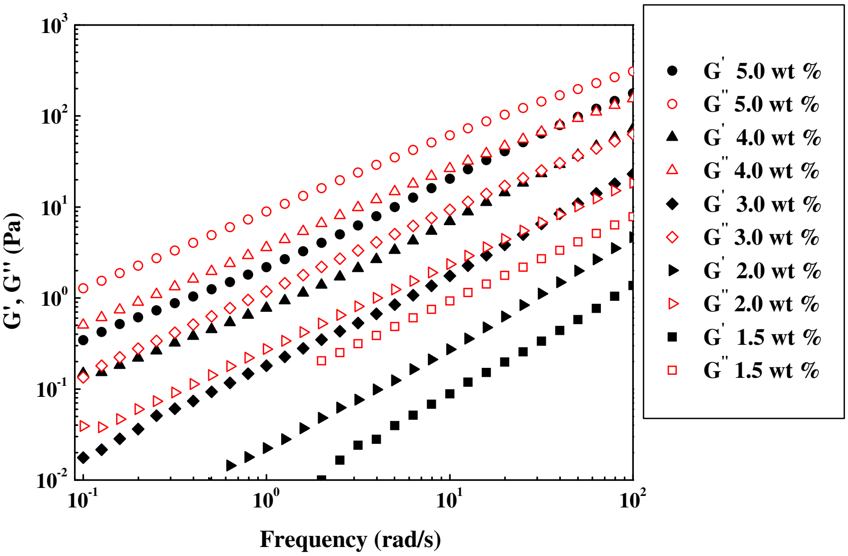


Figure 11. Plot of *G*′, *G*″ versus frequency (ω) for AM-C in distilled water with various concentrations at 25 °C.

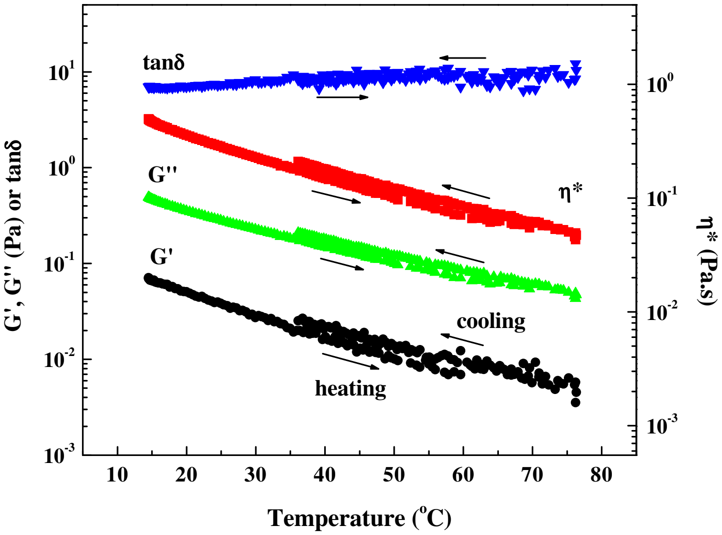


Figure 12. Influences of the temperature on the rheological properties of AM-C in 0.2 M NaCl aqueous solution.

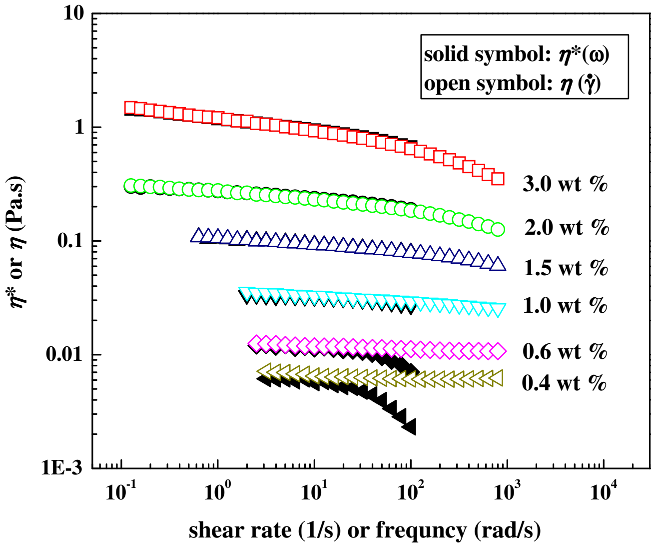


Figure 13. Cox–Merz plot of AM-C in distilled water with various concentrations at 25 °C.

the solutions transformed the rheological behavior from Newtonian to shear thinning. The critical concentration for transition from dilute to concentrated solution was determined to be 0.7 wt %. AM-C solutions displayed good thermo-stability and reversible liquid-like behavior, and the influences of salt adding on the rheological behavior were negligible attributing to the stiffness of the polymer chain. The derivation of complex viscosity and shear viscosity from Cox–Merz rule in dilute regime is related to the co-existence of AM-C single chain and large aggregates in solution. As the concentration increased, the AM-C system was transformed into a homogeneous entanglement structure. The unique rheological properties of AM-C solutions would have wide applications in industries such as pharmaceutical, cosmetics, and oil recovery and so on.

Acknowledgments

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