

## Solution Properties of Low Charge Density Amphoteric Terpolymers *via* Aqueous Dispersion Polymerization

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Solution properties of low-charge-density ampholytic terpolymers (amPAM) of acrylamide (AM), acrylic acid (AA) and 2-methyl acryloylxyethyl trimethyl ammonium chloride (DMC) prepared *via* free-radical dispersion polymerization and poly(2-methylacryloylxyethyl trimethyl ammonium chloride) (PDMC) as cationic polymeric stabilizer in the aqueous ammonium sulfate media (D-amPAM) were studied with the reduced viscosities and hydrodynamic radii by variation of the polymer concentration, salt concentration and type and temperature. In D-amPAM solutions, it is found that the influences of hydrogen bonds, the relationships between PDMC and amPAM chains, the microenvironmental salt concentrations around the polymer chains, typically the network structures formed by the effects of salt ( $Mg^{2+}$ ) and PDMC chain bridges and microaggregation in the solution played important roles which directly relieved the transitions of polymer chain conformation. And the linear manner of the reduced viscosities was different and complicated as a function of the D-amPAM concentrations in different concentration of NaCl media or at different temperature conditions. In concentrated solutions, the data of apparent viscosities and apparent phenomena indicated that the phase-separation behaviors (solution and swollen phases) occurred when the D-amPAM concentrations exceeded 1.92 g/dL and the solutions exhibited typically pseudoplastic viscosity profiles.

**Key Words:** Polyampholyte, Low charge density, Dispersion polymerization, Viscosity, Network structure.

### INTRODUCTION

Polyampholytes, as one kind of polyelectrolytes, bear cationic and anionic groups along the polymer chain<sup>1,2</sup>. The special molecular structure makes the polyampholytes exhibit markedly different behaviour from common polyelectrolytes composed of single cationic or anionic group in aqueous solution. In salt-free aqueous solution, polyampholytes are insoluble due to the electrostatic attraction between opposite charges<sup>3</sup> and adding low-molecular electrolytes to the system can promote

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the solubility, *i.e.*, so-called antipolyelectrolyte effects or polyampholyte effects<sup>4</sup>. In recent decades, polyelectrolyte-polyampholyte complexes and polyampholyte solution properties were lucubrated by Kudaibergenov<sup>5,6</sup>, Dobrynin<sup>7,8</sup>, McCormick<sup>9,10</sup> and their coworkers. The previous studies favoured our investigation in the solution properties of low-charge-density amphoteric terpolymer *via* aqueous dispersion polymerization. Low-charge-density amphoteric terpolymers based-on acrylamide have been successfully prepared *via* aqueous dispersion polymerization by our research group. Through the studies, it is expected that the ampholytic terpolymer dispersions could be widely used in practical applications and enrich the theories on the polyelectrolyte-polyampholyte complexes and polyampholyte solution properties.

In the system, low-charge-density amphoteric terpolymers composed of acrylamide (AM), acrylic acid (AA) and 2-methylacryloylxyethyl trimethyl ammonium chloride (DMC) were prepared *via* free-radical dispersion polymerization and the poly(2-methylacryloylxyethyl trimethyl ammonium chloride) (PDMC) as cationic polymeric stabilizer in the aqueous ammonium sulfate media. So polyampholyte-polyampholyte, polyelectrolyte-polyelectrolyte, polyampholyte-polyelectrolyte, polymer-solvent and polymer-added salt interactions exist in the dispersion dilute and semi-dilute solution (D-amPAM) and effects of environment on the D-amPAM solution are complicated. In present work, the effects of D-amPAM concentration, low-molecular-mass electrolyte concentration, various electrolyte and temperature on D-amPAM solution properties were discussed.

## EXPERIMENTAL

Acrylamide (AM, Chemical Grade, Dia-Nitrix. Co., Ltd., Japan) and 2-methylacryloylxyethyl trimethyl ammonium chloride (DMC, Chemical Grade, YTETDZ Spark Chemicals Co., Ltd., China) were directly used. Acrylic acid (AA, A.R. Grade, Tianjin Damao Chemical reagent Factory, China), ammonium sulfate (AS, A.R. Grade, Sinopharm Chemical Reagent Co., Ltd., China) and 2, 2'-azobis (2-amidinopropane) dihydrochloride (V-50, A.R. Grade, Wako Pure Chemical Industries, Ltd., Japan) were used as received, respectively. Ethylenediamine tetraacetic acid disodium salt (EDTA·2Na, A.R. Grade, Yantai Sanhe Chemical Reagent Co., Ltd., China) and isopropyl alcohol (IPA, A.R. Grade, Yantai Sanhe Chemical Reagent Co., Ltd., China) were used as 0.004 mol/L solution, respectively. Sodium chloride (NaCl, A.R. Grade, Tianjin Damao Chemical reagent Factory, China), potassium chloride (KCl, A.R. Grade, Yantai Sanhe Chemical Reagent Co., Ltd., China), potassium bromide (KBr, A.R. Grade, Sinopharm Chemical Reagent Co., Ltd., China), magnesium chloride (MgCl<sub>2</sub>, A.R. Grade, Sinopharm Chemical Reagent Co., Ltd., China), sodium hydroxide (NaOH, A.R. Grade, Yantai Sanhe Chemical Reagent Co., Ltd., China), hydrochloric acid (HCl, A.R. Grade, Yantai Sanhe Chemical Reagent Co., Ltd., China) were used as some concentrations. Deionized water was used throughout this work.

**Characterization of terpolymer structure:** The polymers were redissolved into 60 wt % ethanol mixture with deionized water and were further purified by precipitation in acetone, followed by vacuum drying for 2 days at 80 °C. The  $^{13}\text{C}$  NMR spectrum of the terpolymer sample was obtained at 125 MHz with Bruker Avance DRX500 Mhz NMR spectrometer (Bruker Co.) using *ca.* 10 wt % aqueous ( $\text{D}_2\text{O}$ ) polymer solution containing 0.5 M NaCl. The polymer compositions were analyzed with MestRe-C spectral analysis software (Universidad de Santiago de Compostela)<sup>4</sup>.

**Sample preparations:** D-amPAM was prepared as follows: the monomers (AM, DMC and AA), AS, PDMC and DI water were added into a 250 mL three-neck flask equipped with a stirrer, reflux condenser, thermometer and  $\text{N}_2$  inlet tube. The flask was placed in 60 °C temperature bath and the contents were sparged for 0.5 h. The pH of the resulting solution was adjusted to 7-8 prior to initiating the polymerization. The water-soluble V-50 was then added to the flask by constant-pressure dropping funnel. The polymerization was allowed to proceed under  $\text{N}_2$  and constant stirring speeds (100 rpm or so) for 8 h.

Stock solution were prepared through the dissolution of D-amPAM samples in inorganic salt media and kept 48-72 h to obtain homogeneous systems; the D-amPAM concentrations were 1.0 and 0.5 g/dL; the samples of concentrated solutions were directly prepared and used in 1 M NaCl media.

**Solution property testing:** Dilution solution viscometric measurements were taken with an Ubbelohde viscometer (105.11 s for DI-water at  $25.00 \pm 0.01$  °C, Shanghai Liangjing Co., China) and testing temperatures were controlled *via* ZH-ZB glass thermostatic water bath (Nangjing University Hengtong S and T Development Co., China). The solution viscosity terms and relationship between each other are listed as follows:

$$\text{Relative viscosity: } \eta_r = \frac{t_1}{t_0} \quad (1)$$

$$\text{Specific viscosity: } \eta_{sp} = \frac{(t_1 - t_0)}{t_0} = \eta_r - 1 \quad (2)$$

$$\text{Reduced viscosity: } \eta_{rd} = \frac{\eta_{sp}}{C} = \frac{(\eta_r - 1)}{C} \quad (3)$$

$$\text{Inherent viscosity: } \eta_i = \frac{\ln \eta_r}{C} \quad (4)$$

where  $t_0$  (s) is the flow time of the pure solvent and  $t_1$  (s) the flow time of the D-amPAM solution;  $C$  (g/dL) is the D-amPAM concentration. The apparent viscosities of concentrated D-amPAM solutions were determined with a Brookfield LVDV+ programmable viscometer (Brookfield Engineering Laboratories, Inc., US), the temperatures were controlled by the thermostatic water bath pan (CS501 series,  $\pm 0.1$  °C Shanghai Yanguang Laboratories Co. Ltd., China). The states of amPAM and PDMC could be indicated well by the average hydrodynamic radius with the Zetasizer Nano ZS90 (Malvern Instruments Ltd., UK) at different temperatures.

## RESULTS AND DISCUSSION

Fig. 1 presented a  $^{13}\text{C}$  NMR spectrum of amPAM. The carbonyl resonances were listed as follows: C<sub>1</sub>,  $-\text{COO}-\text{Na}^+$ ; C<sub>2</sub>,  $-\text{CONH}_2$ ; C<sub>5</sub>,  $-\text{CH}_2$  nearly attached to the quaternary ammonium salt group; C<sub>8</sub>,  $-\text{CH}_3$  attached to the quaternary ammonium salt group; C<sub>9</sub>, C of polymer main chains; C<sub>10</sub>, CH of polymer main chains; C<sub>3</sub> and C<sub>4</sub>, C=O of DMC units; C<sub>6</sub> and C<sub>7</sub>,  $-\text{O}-\text{CH}_2-$ ; C<sub>11</sub> and C<sub>12</sub>,  $-\text{CH}_2$  of polymer main chains; C<sub>13</sub> and C<sub>14</sub>,  $-\text{CH}_3$  of polymer main chains. The C<sub>3</sub>, C<sub>4</sub>, C<sub>6</sub>, C<sub>7</sub>, C<sub>13</sub> and C<sub>14</sub> indicated that the PDMC stabilizers were taken off completely from the dispersion systems. The amPAM composition (AM:AA:DMC = 8.3:0.48:1.1) incompletely agreed with the feed composition (8.5:0.5:1.0), which also proved the PDMC existing in the power and supported by previous report<sup>11</sup>.

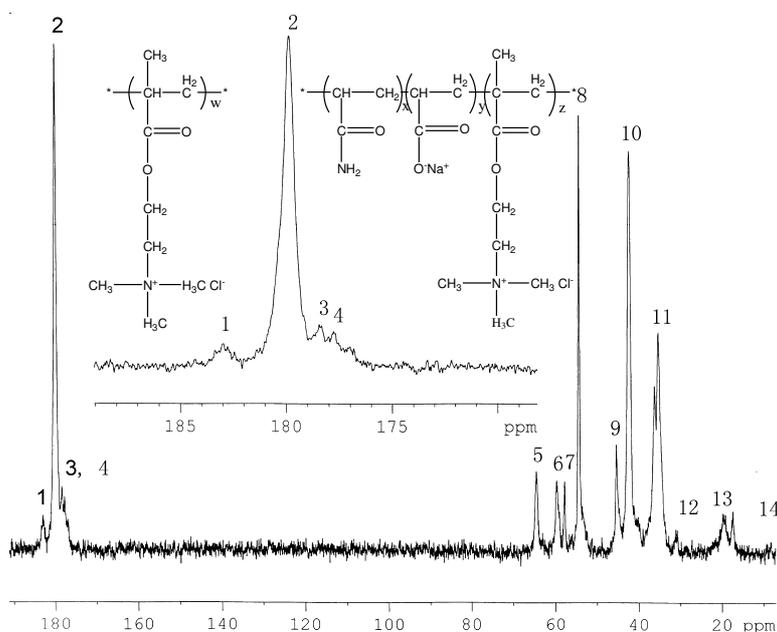


Fig. 1.  $^{13}\text{C}$  NMR spectrum of amPAM

**Effect of D-amPAM concentration:** The viscometric behaviour of charge-balanced D-amPAM solution in 1 M NaCl medium was presented in Fig. 2 as a function of polymer concentration. When the D-amPAM concentrations were varied from 0.0078-0.117 g/dL, the reduced viscosities increased first and then decreased, but the inherent viscosities increased in the entire region and the two lines tend to closing and overlapping. The solution behaviours indicated that D-amPAM solutions had obviously polyelectrolyte behaviours when the D-amPAM concentrations were varied from 0.0026-0.0078 g/dL, the reduced and inherent viscosities of D-amPAM solutions decreased sharply and overlapped. In the region from 0.065-0.117 g/dL,

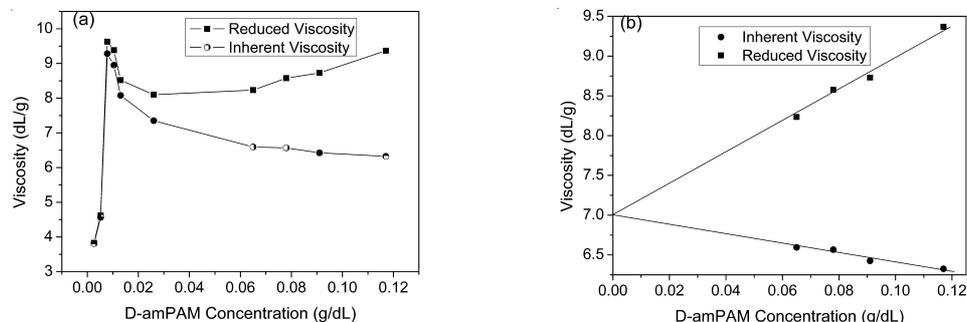


Fig. 2. Reduced viscosity of D-amPAM as a function of the D-amPAM concentration at 25 °C, pH = 7.0-7.5. The NaCl concentration was 1 M and D-amPAM concentration was varied from 0.0026-0.117 g/dL

the linear manners of reduced and inherent viscosities coincide with the Huggins equation and extrapolating the reduced and inherent viscosity to zero concentration. It is found that the two lines arrived to a point to give the intrinsic viscosity of D-amPAM ( $\eta_r = ca. 7 \text{ dL/g}$ ). We plotted out three concentration regions to explain the viscometric behaviors of D-amPAM solutions. (a) In 0.078-0.117 g/dL region, the micro-environmental concentrations of counter ions around polymer chains increased with increasing the D-amPAM concentrations leading to the counter ions being not easily disassociated from the polymer chains. Hence, the linear manners were similar to the viscometric behaviours of nonionic polymers. (b) In 0.026-0.078 g/dL region, the micro-environmental concentrations of counter ions around polymer chains decreased with decreasing the D-amPAM concentrations leading to the counter ions being easily disassociated from the polymer chains and net charge densities increasing so that the structural conformations easily extended (the effect of counter ionic increasing viscosity) and decreasing the D-amPAM concentrations, having enough rooms that the bridging effects occurred in between neighboring amPAM chains *via* cationic polyelectrolyte PDMC. The two reasons mentioned attributed to the viscosity increasing sharply phenomena in the region. (c) In 0.0026-0.0078 g/dL region, the effects of counter ions increasing viscosities were not obvious, the salt bridges are destroyed between PDMC and amPAM and the complexes of PDMC and amPAM chains *via* cationic and anionic groups disassociating. Hence, the viscosities decreased in the region.

Fig. 3 showed the viscometric behaviours of D-amPAM solutions in different NaCl concentration media as a function of the D-amPAM concentration. The reasons, leading to the linear manners, were very complicated. The results revealed that the behaviours related with not only D-amPAM concentrations and ionic strengths but also structural conformations of polymer chains and the relationship between amPAM and PDMC chains.

At  $[\text{NaCl}] = 0.2 \text{ M}$ , the intra-chain interactions were stronger between fixed charges of amPAM chains, the amPAM chains collapsed and aggregated, the

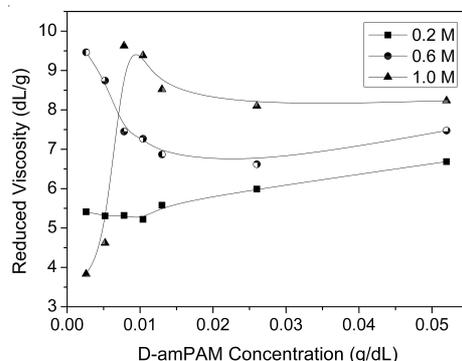


Fig. 3. Reduced viscosity of D-amPAM as a function of the D-amPAM concentration at 25 °C, pH = 7.0-7.5. The NaCl concentrations were 0.2, 0.6 and 1.0 M

behaviours were similar to nonionic polymer behaviours. In lower concentration region, the effects of counter ionic increasing viscosities around PDMC chains were more obvious and PDMC wrapped tightly by amPAM chains leading to network structures formed not easily destroyed, so the reduced viscosities slightly increased and not decreased sharply. At [NaCl] = 0.6 M, the screened electrostatic interactions were stronger, the complexions occurred in the D-amPAM solutions formed by PDMC chains directly or *via* salts attached to amPAM chains, the amPAM chains and network structures were more extended. Hence, the reduced viscosities decreased firstly and then increased with decreasing the D-amPAM concentrations which exhibited the typical behaviors of polyelectrolytes.

Fig. 4 showed the viscometric behaviours of D-amPAM solutions at different temperatures (30 and 35 °C) as a function of the D-amPAM concentration. At lower D-amPAM solution concentrations, the reduced viscosities of D-amPAM solutions were lower at 35 °C than at 30 °C, the inflexion was not more obvious than at 30 and 25 °C and the increasing decreases were faster than at 30 °C so that exceed 30 °C, D-amPAM solution over some concentration point. Increasing the temperatures,

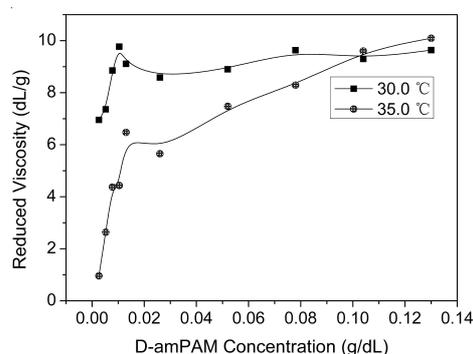


Fig. 4. Reduced viscosity of D-amPAM as a function of the D-amPAM concentration at 30 and 35 °C, pH = 7.0-7.5. The NaCl concentration was 1 M

the molecular motions were more vigorous so that the screened electrostatic layers formed by electrolyte molecules, hydrogen bonds and network structures were weakened and destroyed; the polymer chains coil, collapse and aggregate and the higher the D-amPAM concentrations were, the more the microaggregations were, the more the amount of bigger particles formed by the aggregations were.

**Effect of low-molecular-mass electrolyte concentration:** Fig. 5 showed the reduced viscosities of D-amPAM as a function of the NaCl concentration at 25 °C,

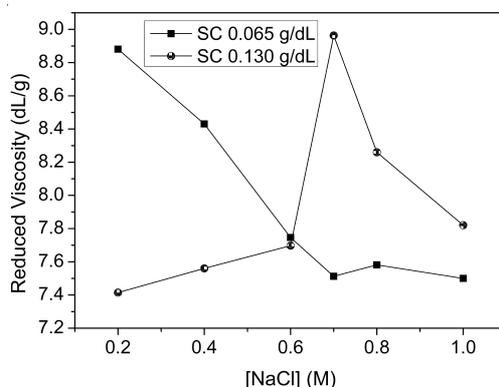


Fig. 5. Reduced viscosity of D-amPAM as a function of the NaCl concentration at 25 °C, pH = 7.0-7.5. The D-amPAM concentrations were 0.056 and 0.13 g/dL

when the D-amPAM concentrations were 0.056 and 0.13 g/dL. Fig. 4 indicated that the tendencies of 0.056 and 0.13 g/dL D-amPAM solutions, changing [NaCl] from 0.2-1.0 M, were markedly different, which are attributed to two factors: the influence of NaCl concentration on the chain states of the PDMC and amPAM, polysalt bonds existing in between PDMC and amPAM chains. In the range of NaCl concentrations from 0.2-0.7 M, at lower D-amPAM concentrations, the polyelectrolyte effects of PDMC were much stronger than antipolyelectrolyte effect of amPAM. On the other hand, the network structures, formed by PDMC linking with two or more neighbouring amPAM chains, become weaker due to the PDMC chains seriously curling with increasing NaCl concentrations. The previous two reasons led to the reduced viscosities of D-amPAM solutions acutely decreasing. At higher D-amPAM concentrations, the interactions of cationic and anionic charged groups attached to neighboring amPAM chains became by far stronger, internal polysalt complexes and intermolecular aggregations are easily formed. The network structures formed by PDMC chains do not easily exist in the solution because of the rooms of amPAM chains. With the NaCl concentrations increasing, the intermolecular charge screening effects increased so that amPAM chains separated from each other. The rooms, however, were not enough to forming intermolecular salt bonds due to the repulsive electrostatic interactions between fixed charges and the steric effects in other amPAM chains. But the polyelectrolyte effects of PDMC chains would result in the

reduced viscosities of D-amPAM solutions decreasing. The two opposite tendencies made the viscosities increase gently.

In the range of NaCl concentrations from 0.7-1.0 M, at lower D-amPAM concentrations, with increasing electrolyte concentrations, the PDMC chains continually collapsed and the amPAM chains continually extended, which led to the tend changing gently. At high D-amPAM concentrations, the rooms, existing in between amPAM chains, become larger due to screened electrostatic repulsions of the intermoleculars so that intramolecular polysalt bonds were easily formed, which would result in the reduced viscosities of D-amPAM solutions decreasing. However, the screened effects of the amPAM intra-chains favoured the expansion of amPAM chains so that the viscosities were depressed.

**Effects of various electrolytes:** Fig. 6 showed the dilute-solution ( $C = 0.056$  g/dL) reduced viscosities as a function of the anionic concentration at  $25\text{ }^{\circ}\text{C}$ ,  $\text{pH} = 7.0-7.5$ . The tendencies revealed that the influences of different electrolytes on the reduced viscosities of D-amPAM solutions were apparently different. Under the same anionic ( $\text{Cl}^-$ ) conditions, the reduced viscosities of  $\text{Mg}^{2+}$  solutions were much greater than  $\text{Na}^+$  and  $\text{K}^+$  solutions. The reason was that the  $\text{Mg}^{2+}$  was easily associated with the  $-\text{NH}_2$  and  $-\text{COO}^-$  of PDMC and amPAM, which favoured the ionically crosslinked networks to form. The structures depressed the decrease of reduced viscosities due to the PDMC chains' hydrophobization. The hydrodynamic radius of  $\text{K}^+$  was larger than the one of  $\text{Na}^+$  and the ionic structure of  $\text{K}^+$  was not compacted. Therefore, the polyelectrolyte effects of D-amPAM solutions were more apparent in NaCl media at the lower electrolyte solutions. The antipolyelectrolyte effects (polyampholyte effects) of D-amPAM solutions were more apparent at higher electrolyte, conversely. The hydrodynamic radius of  $\text{Br}^-$  was larger than the one of  $\text{Cl}^-$  and was more easily induced, which led to forming the association with the quaternary ammonium groups ( $-\text{R}_4\text{N}^+$ ) and the net charge densities of amPAM chains increased. Therefore, the reduced viscosities of D-amPAM solutions in KBr media were greater than in KCl media.

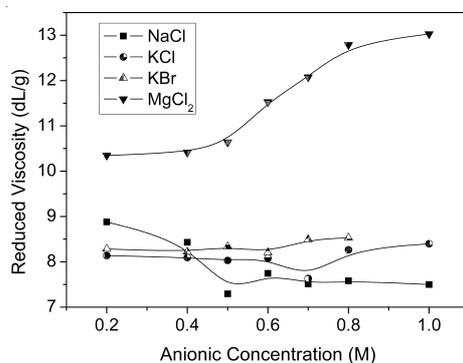


Fig. 6. Reduced viscosity of D-amPAM as a function of the anionic concentration at  $25\text{ }^{\circ}\text{C}$ ,  $\text{pH} = 7.0-7.5$ . The D-amPAM concentration was  $0.056$  g/dL

**Effect of temperature:** Fig. 7 showed the influences of temperature on the reduced viscosities of charge-balanced D-amPAM. The plot gave that the viscosities decreased with increasing the temperatures from 25–60 °C. Increasing the temperatures, on the one hand, that resulted in weakening a large number of hydrogen bonds which originate from existing in between the surfaces of polymer chains and water molecules. The hydrophobization of polymer chains increased, the hydrophobic associations became stronger and the polymers lightly tangled with each other so that the decreasing tends became gently at late stage. On the other hand, that results in the molecular motions becoming violent which led to the polyelectrolyte PDMC and NaCl being disengaged from the amPAM chains. So the net charge densities of amPAM chains were decreased and then the intra-chain electrostatic repulsions became weaker and the chains collapsed. The results are that the decreased tends of reduced viscosities in 0.6 and 1.0 M NaCl media were more gently than in 0.2 M NaCl media.

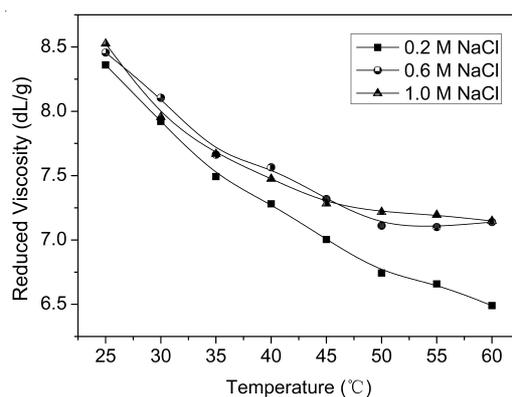


Fig. 7. Reduced viscosity of D-amPAM as a function of the temperature, pH = 7.0–7.5. The D-amPAM concentration was 0.056 g/dL and NaCl concentrations were 0.2, 0.6 and 1.0 M

Fig. 8 showed the influence of temperatures on the structural conformations in 0.2 M NaCl media, pH = 7.0–7.5, keeping the D-amPAM concentration 0.056 g/dL. The plot had a grade in the range of temperature from 35–45 °C. There existed two kinds of polyelectrolyte in the D-amPAM solution: anionic polyelectrolyte PDMC and ampholytic polyelectrolyte. Generally, with the low weight inorganic electrolytes increasing in the some concentration range, the chains of cationic or anionic polyelectrolyte would collapse and the structural conformations would undergo the coil-to-globule transition near the isoelectric point (IEP), the chains of ampholytic polyelectrolyte would undergo the globule-to-coil transition. With the temperature increasing, the electrolyte concentrations would decrease in the micro-environmental regions of polymer chains, leading to the hydrodynamic radii of D-amPAM chains vary gently in the region of 25–45 °C; when the temperature was more than 45 °C,

the hydrophobic interaction played an important role in increasing the hydrodynamic radii because of the hydrogen bonds weakening.

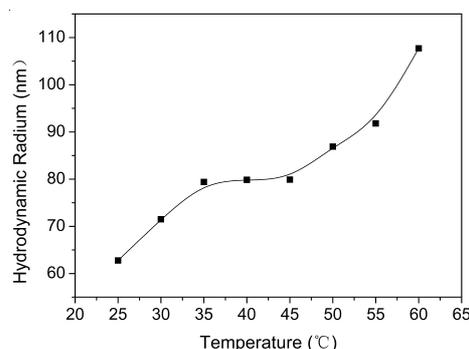


Fig. 8. Hydrodynamic radius of D-amPAM as a function of the temperature, pH = 7.0-7.5. The D-am PAM concentration was 0.056 g/dL and NaCl concentration was 0.2 M

In Fig. 9, the size distribution states of D-amPAM were given for different temperature in 0.2 M NaCl media. From the plots, the size distributions generally moved toward the bigger size regions and generally centralized toward two regions; the higher the temperatures were, the more apparent the boundaries were. On the one hand, the PDMC chains took off from the amPAM chains and they would become alone relatively; on the other hand, the aggregates, formed by a large number of amPAM chains, may be also disorganized, restructured and the sizes would be redistributed due to amPAM molecules irregular motion because of an increase of the temperature. The two reasons mentioned maybe well explain the phenomena.

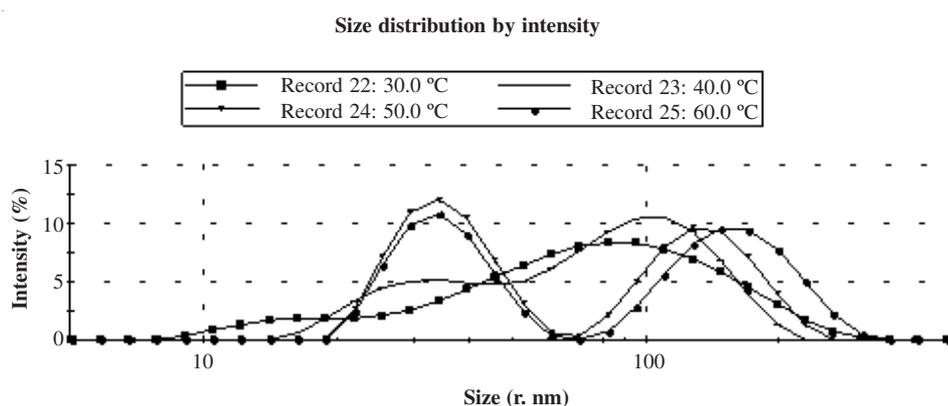


Fig. 9. Size distribution of D-amPAM as a function of the temperature (30, 40, 50 and 60 °C) by intensity, pH = 7.0 -7.5. The D-am PAM concentration was 0.056 g/dL and NaCl concentration was 0.2 M

**Effect of D-amPAM concentration on solution apparent viscosity:** In Fig. 10, it is observed that the line had a apparent turning point at  $C^* = 1.92$  g/dL, keeping shear rate = 12 rpm, in 1 M NaCl media. Preponderating over the point, the apparent viscosities increased slowly with the D-amPAM increasing and a large amount of apparent like-gel materials occurred in the D-amPAM solutions. The dissolving progress of water-soluble D-amPAM latex particle, formed in aqueous saline medium, may be described as follows: firstly, the water molecules penetrated into the inside of latex particles due to the chemical potential differences between the inside and outside particles; secondly, amounts of hydrogen bonds were formed between the polymers and water molecules, electrolyte ions moved toward aqueous phase from the surfaces of polymer chains and then the screened electrostatic layers of micro-environments would be diminished. In the end, the polymers were swollen, the polymer chains would move toward rich aqueous phase on the chains not being tightly fixed and dissolve into the media forming homo-phase systems. With the polymer chains transferring from the swollen systems to the rich solvent phases, when polymer chain concentration increased to critical overlap concentration, the viscosity of D-amPAM system rapidly increased leading to depressing the chains transferring. Continually increasing to the critical phase-separation concentration ( $C^* = 1.92$  g/dL), when driving force of polymer chain transferring into solution phase was nearly equal with resistance originating from the viscosities of solution, the solution phase and swollen phase kept relatively constant. In the same solvent volume, the more the added D-amPAM latex particles were, the more the D-amPAM were in swollen phase, but amounts of D-amPAM were increased limitedly. Hence, the apparent viscosities increased slowly when amounts of D-amPAM added were more than 1.92 g/dL.

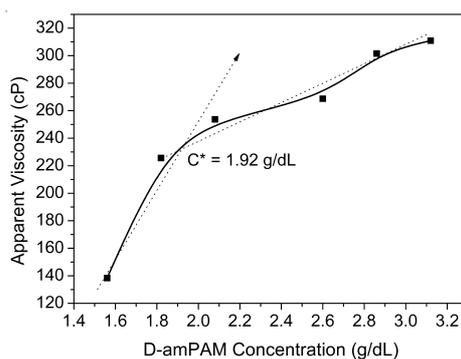


Fig. 10. Apparent viscosity of D-amPAM solution as a function of the D-amPAM concentration. The NaCl concentration was 1 M, shear rate = 12 rpm

**Concentrated-solution rheology behaviours:** Fig. 11 showed the apparent viscosities of concentrated-solution D-amPAM ( $C = 1.56$  and  $1.82$  g/dL) in 1 M NaCl media as a function of the shear rate. The solutions exhibited typically

pseudoplastic viscosity profiles: the apparent viscosities decreased with the increase of shear ratio. In D-amPAM solutions, polymer chains entangled and curled between each other and were distributed irregularly in the systems. A large number of salt bonds existed in between amPAM chains, amPAM and PDMC chains, polymer chains and electrolytes and many hydrogen bonds existed in the amPAM chains and water molecules. With increasing the shear ratio, on the one hand, the polymer chains were disentangled and orientated in the solutions. On the other hand, kinds of salt bonds in the surfaces of polymer chains and the network structures existed in between the polymer chains would be destroyed, the screened electrostatic layers would be dismissed so that the lone amPAM chain is easily coiled and the hydrogen bonds became weaker so that the water molecule layers around the polymer chains would be token off leading to the hydrophobization increasing. The two reasons would attribute to the decrease of apparent viscosities with increasing the shear rates.

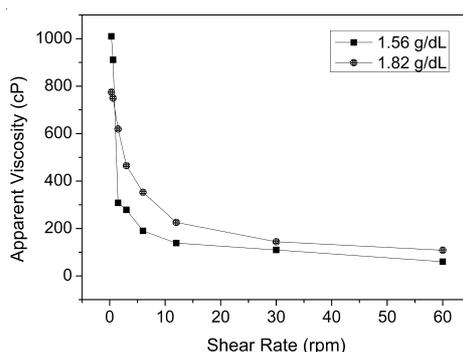


Fig. 11. Reduced viscosity of D-amPAM as a function of the temperature, pH = 7.0-7.5. The D-amPAM concentrations were 1.56 and 1.82 g/dL and NaCl concentration was 1 M

## Conclusion

In the aqueous dispersions of low-charge-density terpolymers based on acrylamide, they contain two kinds of water-soluble polymers *i.e.*, ampholytic terpolymers (amPAM) and cationic polyelectrolytes (PDMC). The former, mainly composed of acrylamide monomers, are easily formed hydrogen bonds with water molecules and exhibit the effects of antipolyelectrolytes (effects of polyampholytes) near the IEP when added salts into their solutions; the latter are a cationic homopolymer and they will exhibit the effects of polyelectrolytes. Moreover, the quaternary ammonium groups of the PDMC chains and the amPAM chains may directly or indirectly form the network structures and the divalent metal-ion (such as  $Mg^{2+}$ ) also favour the network structure formations. Through present studies, the results are as follows: (a) Keeping other conditions, the D-amPAM concentrations varied in some region which favour the network structures formation; (b) The salt concen-

trations *via* the influences on the conformations of amPAM and PDMC chains determined the ranges of D-amPAM concentrations existing network structures in the solutions; (c) At higher temperatures, a large number of hydrogen bonds would be weakened, the salt concentrations would decrease in the microenvironments around the polymer chains and the network structures would be destroyed, but the microaggregations and even water-soluble micro-particles were easily formed in the regions of higher D-amPAM concentrations and the higher temperatures also favored the large microaggregations and regular micro-particles forming and the boundary of the distributions of polymer sizes became more obvious; (d) The larger radii of cation (such as  $K^+$ ) and anion (such as  $Br^-$ ) were easily bonded to the carboxyl and quaternary ammonium groups of the amPAM chains respectively leading to the net charge densities increasing which contributed to the amPAM chains expanding; the  $Mg^{2+}$  could associate with the carboxyl groups on the neighboring amPAM chains, which contributed to the network structures forming; (e) When the polymer concentrations extended over 1.92 g/dL, the homo-phases and swollen phases existed in the solution systems; the concentrated D-amPAM solutions exhibited typically pseudoplastic viscosity profiles.

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