

## Dynamics Simulation on the Associative Properties of Amphiphilic Functional Monomer Modified Polyacrylamide Copolymers<sup>\*</sup>

Pan Zhang<sup>a</sup>, Lin Yao<sup>a</sup>, Jian-hui Luo<sup>b</sup>, Bin Ding<sup>b</sup>, Ge Zhou<sup>a\*\*</sup> and Bo Jiang<sup>a</sup>

<sup>a</sup> Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610065, China

<sup>b</sup> Research Institute of Petroleum Explorations and Development of Petro China, Beijing 100083, China

**Abstract** A kind of amphiphilic functional monomer was selected to modify polyacrylamide (PAM) or partially hydrolyzed polyacrylamide (HPAM). The relative properties of the modified polyacrylamide (HM-PAM) and modified partially hydrolyzed polyacrylamide (HM-HPAM) such as radius of gyration ( $R_g$ ), hydrodynamic radius ( $R_H$ ), and radial distribution functions (RDFs) have been studied to find the intrinsic relation between the microstructure of the polymer chain and the intrinsic viscosities with changing the amount of modified monomers from 1% to 4%. The simulation results show that, compared to HPAM, HM-HPAM has a better performance in increasing viscosity when the percentage of modified monomers is 2% and has a stronger salt tolerance when the modified monomers is 4%. Furthermore, a complex hydrogen bonding network was revealed with the analysis of radial distribution functions (RDFs) and the pair correlation function was used to investigate the diffusivity of  $\text{Na}^+$  and carbon atoms in the  $\text{COO}^-$  group.

**Keywords:** Intrinsic viscosity; Molecular dynamic simulation; Pair correlation function; Radial distribution function; Salt-tolerance.

### INTRODUCTION

Hydrophobically modified water-soluble polymers been extensively studied over the past two decades in both academic and industrial laboratories. In particular, hydrophobically modified acrylamide (HM-PAM) and partially hydrolytic polyacrylamide (HM-HPAM), which are derived from polyacrylamide and containing a small fraction of hydrophobic groups, have received increasing attention because of their unique association characteristics and wide applications in oil recovery due to the viscosity of their solution with good temperature and salt tolerance caused by both the polyelectrolyte and the hydrophobic groups' effect<sup>[1–3]</sup>. Polyelectrolyte macromolecules undergo the diverse conformational transitions corresponding to the changes of the conditions (ionic strength, pH, concentration) driven by interplay between attractive short-range van der Waals and repulsive long-range Coulomb interactions. With increasing ionic strength, electrostatic interactions are screened and the electrostatic repulsion between the polymer segments is reduced, which affects the conformation of the polymer chains and also the ability to flocculate. It is therefore very important to characterize the electrostatic properties of polyelectrolytes, used in such processes<sup>[4]</sup>. Unfortunately, when the HM-PAM solution is continuously exposed to mechanical shearing action, either by strong mechanical stirring in the process of injection allocation or by passing through capillary pores in the petroleum reservoirs, the viscosity of the polymer solution rapidly declines, it indicated a rapid breakdown of the polymer molecules<sup>[2]</sup>.

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<sup>\*\*</sup> Corresponding author: Ge Zhou (周歌), E-mail: zhougekk@scu.edu.cn

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Although much progress has been made on the preparation and characterization of HM-PAM, there are still many questions unsolved in this area. This research is still in its infancy and the corresponding knowledge produced is scarce. The influence of chain architecture and composition on the morphology of HM-PAM is very important and must be explored within a wide parameter space, requiring a tremendous amount of experimental efforts. However, changing experimental parameters in a systematic manner may also be hindered by technical difficulties. Furthermore, it is difficult to detect the nature of hydrophobic associations or visualize the evolution of the association directly by experiments<sup>[3]</sup>.

However, computer simulation is a powerful tool that can complement experimental work. The reasons are not only its operation within a wider parameter space but also its less cost yet high efficiency. Molecular simulations<sup>[5, 6]</sup>, one of computer simulation techniques, can provide a preview of the answers to questions that can guide future experimental research and lead to valuable molecular-level information. The simulations can provide useful information that may contribute to a future rational design and synthesis of novel anti-salt and anti-temperature polyacrylamides<sup>[3]</sup>.

In the past research, our group has studied the various properties of the PAM/HM-PAM and HPAM/HM-HPAM in aqueous solution with different salt concentrations using computational method (MD simulation) and experimental method<sup>[7-9]</sup>, such as the radius of gyration ( $R_g$ ), the hydrodynamic radius ( $R_H$ ), the ratio of  $R_g$  and  $R_H$ . However, some disadvantages, such as the poor salt tolerance, need to be further studied at the present stage. The goal of the present work is to study further improving the salt tolerance and tackification of PAM and HPAM.

Two main ways are introduced to solve the problems mentioned above. First, a kind of amphiphilic functional monomer, which is a saturated hydrophobic functional monomer, is copolymerized into the polymer chain (Fig. 1). The modified monomer possesses a benzene ring in side chains to achieve the tackification of PAM and HPAM. The side chains with alkyl ether bonds will increase the hydrophilicity to greatly enhance the emulsification ability, decrease interfacial tension, increase the viscosity of the solution and hence allowing greater recovery efficiency. The monomers with the steric hindrance would reduce the curliness of molecular chains and, consequently, enhance the temperature resistance and improve the salt tolerance.

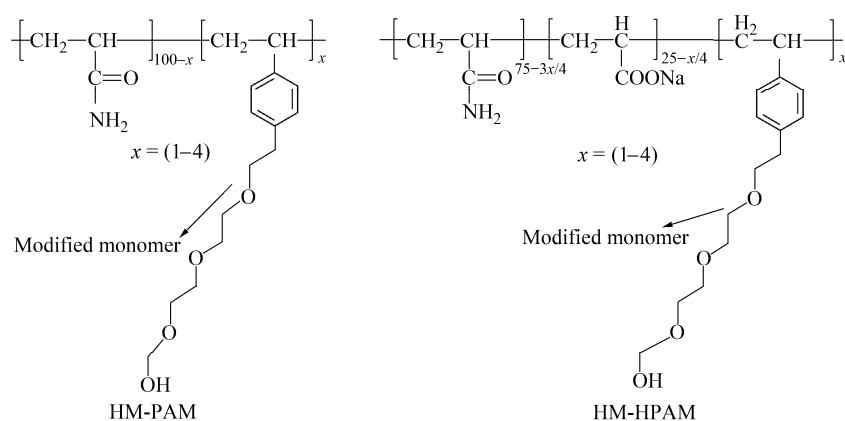


**Fig. 1** Structures of a series of designed HM-PAM and HM-HPAM

Secondly, we will change the percentage of monomer, which is used to modify PAM and HPAM, from 1% to 4%. Different amounts of monomers have different amounts of hydrophobic groups and hydrophilic groups. For these differences, the polymer chains which are modified by these monomers exhibit different properties, such as the hydrophobicity, the thickening efficiency, the shear thinning and the salt-tolerance.

In this work, the dynamic properties of polymer chains, such as  $R_g$ ,  $R_H$ , the intrinsic viscosity  $[\eta]$ , the salt tolerance and tackification of the HM-PAM and HM-HPAM with different amounts of the modified monomer in aqueous solutions with the ionic strengths from  $I = 0$  mol/L to  $I = 0.33$  mol/L are studied. But more

investigations have been focused towards the variation tendency of these parameters, which indicates the influence of the properties of the HM-PAM and HM-HPAM dilute solutions in different ionic strengths by introducing different percentages of the modified monomers. At the same time, the radial distribution functions (RDFs) between O ( $-\text{CONH}_2$ ) of HM-PAM (or  $\text{O}^-$  ( $-\text{COO}^-$ ) of HM-HPAM) and H ( $\text{H}_2\text{O}$ ) in various NaCl solution models are investigated in hopes of revealing the inherent structure-performance relationship of the dilute modified polyacrylamide solutions.

## SIMULATION THEORY AND METHOD

Molecular simulation is a new computational chemistry technique, developed by the combination of computer science and theoretical chemistry. According to the dimension of the modeling system, molecular simulations include molecular scale simulation and mesoscale simulation. The simulation methods are used to study molecular-scale interactions including quantum mechanics, molecular mechanics, molecular dynamics (MD) and Monte Carlo methods. Among these methods, MD simulation is a widely applied method in the fields of chemistry, biology and materials science<sup>[3]</sup>.

In our work, for all models, construction, minimization, molecular dynamics simulation and properties analyses were carried out using Materials Studio program<sup>[10, 11]</sup> (MS, version 4.2 Accelrys Software Inc., United States). The simulation procedures were as follows.

The simulations performed for amorphous unit cells of each investigated polymer with the degree of polymerization of 100. Previous researchers have reported reasonable results when they used less monomer for polymer simulation<sup>[12, 13]</sup>.

Firstly, the 3D Sketcher is used to create the modified monomer (Fig. 1),  $\text{H}_2\text{O}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$  and sodium acrylate (NaAA) monomers. The HM-PAM chain (Fig. 1) is constructed using the build polymer module. The polymer chain consists of 100 repeat units with a probability of  $(100 - x):x$  ( $x = 0 - 4$ ) for the occurrence of vinyl-amide unit and various monomers configurations. The HM-HPAM chain (Fig. 1) which consists of 100 repeat units with a probabilities of  $(75 - 3x/4):(25 - x/4):x$  for the occurrence of vinyl-amide unit, sodium acrylate unit monomer configurations is built. The tacticity of HM-PAM/HM-HPAM chains is that of a random copolymer. Reasonable energy minimization was performed for the HM-PAM chain, the HM-HPAM chain,  $\text{H}_2\text{O}$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  using Smart Minimizer method. Second, optimized molecules and ions were embedded into the cubic cells full of 2000 water molecules with  $1 \text{ g}\cdot\text{cm}^{-3}$  density to form all kinds of initial polymer aqueous solution models with different NaCl concentrations, which are constructed by Amorphous Cell module. During this process, the Period Boundary Condition (PBC)<sup>[14]</sup> was taken and a cutoff radius of 1 nm was applied for both non-bonded electrostatic and van der Waals interactions. The solution model is named according to the percentage of the modified monomer, for example, the HM-PAM1 means that it contains one polymer chain with 1% of the modified monomer and 2000  $\text{H}_2\text{O}$  molecules (with a series of different ionic strengths). Parts of the models are shown in Fig. 2. These solutions were submitted to 5000 steps of the smart minimization by the Discovery module.

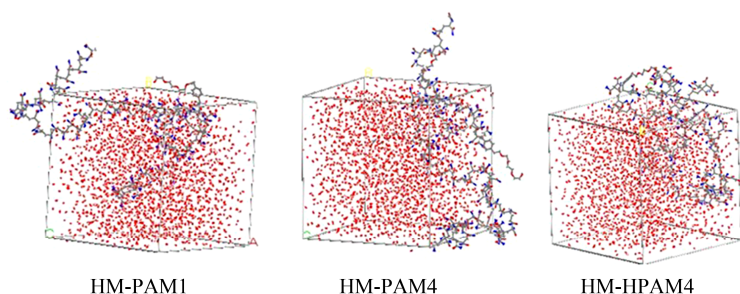


Fig. 2 The parts of HM-PAM-2000 and HM-HPAM-2000 solution models in pure water

A 100 ps MD equilibration runs for all the systems that is performed in the NPT ensemble (constant number of particles, pressure, and temperature,  $P = 1.01 \times 10^{-5}$  MPa,  $T = 298$  K) to obtain the equilibrium density. For MD process, the temperature of the systems was kept through the Andersen<sup>[15]</sup> method and the pressure in the systems was kept through the Berendsen barostat<sup>[16]</sup>, the collision ratio is 1.00 and the press decay constant is 0.10. An additional 1000 ps NVT (constant number of particles, volume, and temperature  $T = 298$  K) dynamics is performed on the last frame of the NPT equilibrium stage. The time step was 1.0 fs and the total dynamics time was 1100 ps. All the motion trajectories and coordinate parameters were saved and the frames of the trajectory were output every 10 ps for the subsequent analysis. The non-bond cutoff distance was 1 nm. In all simulations, all calculations are performed using the PCFF force field. PCFF, which was used to polymers and organic materials more and more, is developed based on CFF91<sup>[17–19]</sup>. The validity of the force field, which was used here, has already testified by previous researchers<sup>[18, 19]</sup>. All force field parameters come from the PCFF force field. Therefore, under a wide range of conditions of temperature and pressure, this force field can guarantee accurate and simultaneous prediction of structural, conformational, vibrational and thermophysical properties for a broad range of molecules in isolation and in condensed phases.

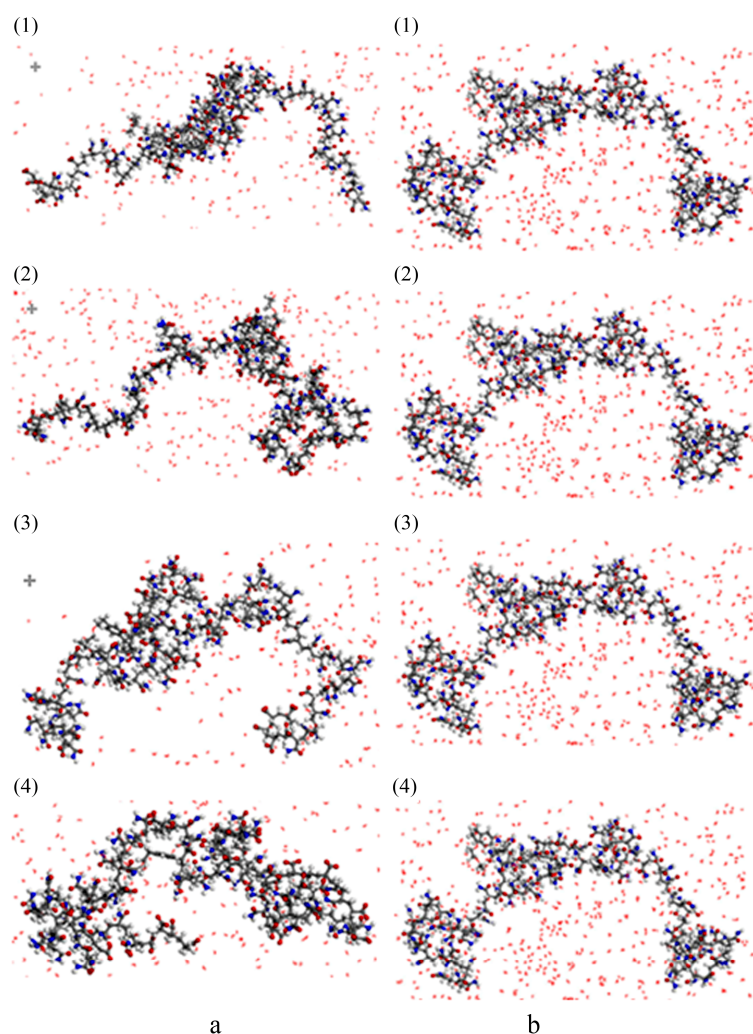


**Fig. 3** Snapshots of HM-HPAM1 and HM-PAM1 molecule conformations in solution models derived from MD simulations: (a) the ionization degree  $\alpha = 0.25$ , (b) the ionization degree  $\alpha = 0$ ; (1)  $I = 0$  mol/L, (2)  $I = 0.03$  mol/L (3)  $I = 0.19$  mol/L (4)  $I = 0.33$  mol/L

## RESULTS AND DISCUSSION

### Size and Shape

From all simulations above, the mean conformation of every polymer in the solution models can be gained. Figure 3 presents some snapshots of the equilibrated HM-HPAM1 and HM-PAM1 chain configurations, which were collected during simulations.

HM-PAM or HM-HPAM molecule assumed a variable shape under various simulation conditions. It was difficult to define unequivocally a characteristic linear dimension such as the end-to-end length or  $R_g$ . For the sake of conveniences, we have introduced here the effective length parameter ( $L_{ef}$ ) which can be a useful measure of molecule dimensions if it assumes an elongated shape. That parameter also facilitates the interpretation of dynamic viscosity measurements in terms of the hydrodynamic theory. The  $L_{ef}$  was calculated as a value of the distance between the surfaces of two outermost atoms of the molecule averaged at the fluctuating equilibrium state<sup>[20, 21]</sup>. The procedure of the calculations of  $[\eta]$  of HM-PAM and HM-HPAM is explained in the next part of the paper.

Figure 4(a) for the 25% ionization degree indicates that for low ionic strength the molecule assumes an extended, worm-like shape characterized by the average  $L_{ef} = 4$  nm (for  $I = 0$  mol/L). For increasing ionic strength, decreasing of the contour implies the folding of the molecule, becoming 3.5 nm for  $I = 0.03$  mol/L, 2.9 nm for  $I = 0.19$  mol/L, and 2.5 nm for  $I = 0.33$  mol/L. A similar behavior was predicted in the simulations of Adamczyk<sup>[20, 21]</sup>, who studied conformations of poly(allylamine hydrochloride) in electrolyte solutions. For the lower ionic strength, the polyelectrolyte chain becomes more extended. Nevertheless, for  $I = 0.19$  mol/L and  $I = 0.33$  mol/L, the mean conformations of HM-HPAM1 have not shrunk any longer and the average effective lengths ( $L_{ef}$ ) of HM-HPAM1 change little. Even for the highest ionic strength 0.33 mol/L, the

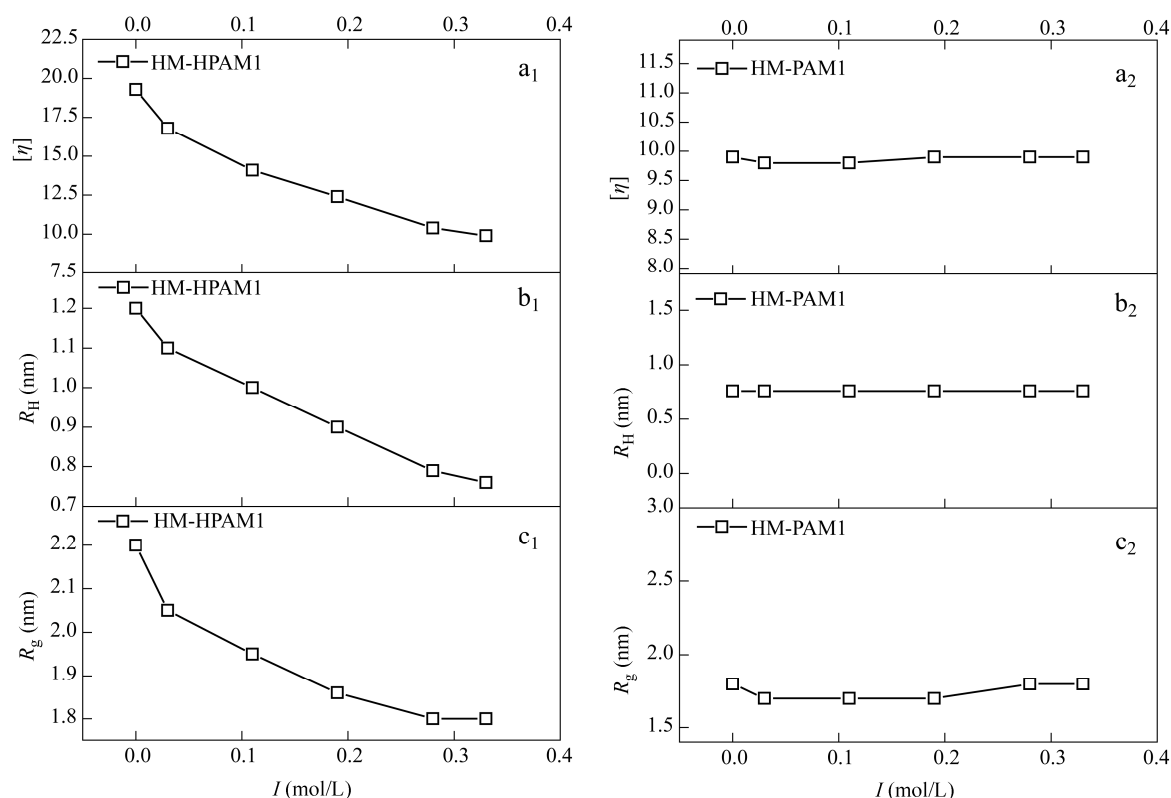


**Fig. 4** Intrinsic viscosity ( $a_1$  and  $a_2$ ), hydrodynamic radius ( $b_1$  and  $b_2$ ) and radius of gyration ( $c_1$  and  $c_2$ ) versus ionic strength for HM-HPAM1 and HM-PAM1 solution models at 298 K

polyelectrolyte chain did not collapse and still kept bent spheroid. For the HM-PAM1 with zero ionization degree (Fig. 4b), the average  $L_{ef}$  has no significant change in increasing the ionic strength. A similar behavior was seen in HM-HPAM (2, 3, and 4) and HM-PAM (2, 3, and 4).

The  $R_g$  ( $s$ ) represents the molecular size of the polymer explored for this work, which is defined as the root mean square distance of the atoms in the molecule from their common center of mass<sup>[22]</sup> that is,

$$s^2 = \frac{\sum_{i=1}^N m_i s_i^2}{\sum_{i=1}^N m_i} \quad (1)$$

where  $s_i$  denotes the distance of atoms  $i$  from the center of mass,  $N$  denotes the total number of atoms in the above expression.

The  $R_H$  and  $[\eta]$  for HM-PAM and HM-HPAM molecules can be calculated through the following equations<sup>[20, 21]</sup>. For the bent spheroid,

$$\begin{aligned} \lambda &= l / 2b > 1 \\ 2l/\pi &= L_{ef} \\ R_H &= \frac{l}{2(\frac{11}{12}\ln\lambda - 0.31)} \\ [\eta] &= \frac{\lambda^2}{15} \left[ \frac{3}{\ln(2\lambda) - 0.5} + \frac{1}{\ln(2\lambda) - 1.5} \right] + \frac{8}{5} \end{aligned} \quad (2)$$

where  $l$  is the extended length and  $\lambda$  is the aspect ratio of bare molecule<sup>[20, 21]</sup>.  $L_{ef}$  is the effective length (mentioned above). The results are represented in Table 1.

**Table 1.**  $R_H$  and  $R_g$  for HM-HPAM and HM-PAM in the different ionic strength solutions

| Solution Model | $R_g$ (nm) (From simulation) |      |      |      |      |      | $R_H$ (nm) (Calculated by Eq. (2) ) |      |      |      |      |      |
|----------------|------------------------------|------|------|------|------|------|-------------------------------------|------|------|------|------|------|
|                | $I$ (mol/L)                  |      |      |      |      |      | $I$ (mol/L)                         |      |      |      |      |      |
|                | 0                            | 0.03 | 0.11 | 0.19 | 0.28 | 0.33 | 0                                   | 0.03 | 0.11 | 0.19 | 0.28 | 0.33 |
| HM-HPAM1       | 2.20                         | 2.05 | 1.95 | 1.86 | 1.80 | 1.80 | 1.20                                | 1.10 | 1.00 | 0.90 | 0.79 | 0.76 |
| HM-HPAM2       | 3.55                         | 2.90 | 2.50 | 2.40 | 2.20 | 2.00 | 1.67                                | 1.57 | 1.39 | 1.28 | 1.23 | 1.18 |
| HM-HPAM3       | 2.50                         | 2.23 | 2.16 | 1.97 | 1.95 | 1.90 | 1.43                                | 1.33 | 1.22 | 1.16 | 1.10 | 1.08 |
| HM-HPAM4       | 2.26                         | 2.14 | 2.00 | 1.95 | 1.86 | 1.70 | 1.29                                | 1.24 | 1.15 | 1.09 | 1.06 | 1.04 |
| HM-PAM1        | 1.8                          | 1.7  | 1.7  | 1.7  | 1.8  | 1.8  | 0.76                                | 0.76 | 0.76 | 0.76 | 0.76 | 0.76 |
| HM-PAM2        | 2.5                          | 2.3  | 2.7  | 2.7  | 2.3  | 2.5  | 1.18                                | 1.18 | 1.18 | 1.18 | 1.18 | 1.18 |
| HM-PAM3        | 2.4                          | 2.3  | 2.3  | 2.3  | 2.3  | 2.2  | 1.08                                | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 |
| HM-PAM4        | 1.9                          | 2.0  | 2.1  | 1.9  | 1.8  | 1.9  | 1.04                                | 1.04 | 1.04 | 1.04 | 1.04 | 1.04 |

According to Table 1,  $R_g$  for HM-HPAM decreases gradually with increasing the ionic strength and has no significant change with increasing ionic strength for HM-PAM. The tendency of  $R_g$  was consistent with the one of  $L_{ef}$ . The theoretical values of  $R_H$  for various molecule shapes can be calculated from the Eq. (2). The variation tendency towards the  $R_H$  was in accordance with  $L_{ef}$  and  $R_g$  as show in Table 1. The reason for this is as follows.

When the HM-HPAM is dissolved in deionized water, the HM-HPAM macromolecule with the carboxylate groups ( $-\text{COO}^-$ ) can form electrical double layer and thick hydration film, which can pack more  $\text{H}_2\text{O}$  molecules. Thus, the HM-HPAM will extend and have larger hydrodynamic volume, and accordingly  $R_H$  and  $R_g$  will be higher. The NaCl added to the HM-HPAM solution can release  $\text{Na}^+$ , which can destroy the electrostatic repulsion between the  $-\text{COO}^-$  groups of the HM-HPAM molecule chain and compress the electrical double layer around the  $-\text{COO}^-$  groups and make the hydration film thinning<sup>[23]</sup>. This leads to the HM-HPAM chain

possessing a more collapsed conformation and the smaller overall dimension. As a result,  $R_H$  and  $R_g$  of the system decrease. The higher the concentration of the NaCl is the lower  $R_g$  and  $R_H$  are. As shown in Table 1, the  $R_g$  and  $R_H$  for HM-HPAM solutions decrease gradually with increasing NaCl concentration. In Table 1, for HM-PAM the  $R_g$  and  $R_H$  have no significant change with increasing NaCl concentration. This lies in the absence of ionic groups in the HM-PAM chain.

### The Viscosity Promoting

The ability of hydrophobically associating polymers to enhance viscosity of aqueous solutions is extensively exploited in a variety of practical applications. For instance, blocking water in enhanced oil recovery and the application in enhanced oil recovery of particular interest are associating polymers based on HM-PAM<sup>[24]</sup>.

From all simulations above, the mean conformation of HM-HPAM1 and HM-PAM1 in solution models can be gained as Fig. 3, the other solution models have the similar tendency towards the HM-HPAM1 and HM-PAM1. Adamczyk *et al.*<sup>[20, 21]</sup> have reported that  $[\eta]$  for a polymer can be calculated by the parameters ( $l$  and  $\lambda$ ) of the molecule shape, which is determined by the mean conformation and the Eq. (2). The results are represented in Table 2 below. According to Table 2, with the ionic strength increasing, the  $[\eta]$  of the HM-HPAM decreases and the HM-PAM has no significant change and the  $[\eta]$  values for HM-PAM are lower than the values for HM-HPAM.

**Table 2.** The influence of ionic strength on intrinsic viscosities of the HM-PAM and HM-HPAM solutions

| Solution model         | The intrinsic viscosity $[\eta]$ (Calculated by Eq. (2)) |       |       |       |       |       |
|------------------------|----------------------------------------------------------|-------|-------|-------|-------|-------|
| Ionic strength (mol/L) | 0                                                        | 0.03  | 0.11  | 0.19  | 0.28  | 0.33  |
| HM-HPAM1               | 19.30                                                    | 16.80 | 14.10 | 12.40 | 10.40 | 9.90  |
| HM-HPAM2               | 40.00                                                    | 35.00 | 26.80 | 22.00 | 20.70 | 18.70 |
| HM-HPAM3               | 28.30                                                    | 24.00 | 20.00 | 17.90 | 16.60 | 15.40 |
| HM-HPAM4               | 22.90                                                    | 20.80 | 17.50 | 16.00 | 15.00 | 14.20 |
| HM-PAM1                | 9.90                                                     | 9.80  | 9.80  | 9.90  | 9.90  | 9.90  |
| HM-PAM2                | 18.70                                                    | 18.70 | 18.70 | 18.70 | 18.70 | 18.70 |
| HM-PAM3                | 15.40                                                    | 15.40 | 15.40 | 15.40 | 15.40 | 15.40 |
| HM-PAM4                | 14.20                                                    | 14.20 | 14.20 | 14.20 | 14.20 | 14.20 |

Thus, the HM-HPAM backbone will extend and have larger hydrodynamic volume, and accordingly its  $[\eta]$  will be higher than that of HM-PAM because of the electrical double layer<sup>[25]</sup>. The NaCl added to the HM-HPAM solution can release  $\text{Na}^+$ . It leads to a significant compensation for the nominal charge of HM-HPAM, which was reduced to a small fraction of its initial value. Besides, according to  $L_{\text{ef}}$ ,  $R_g$ , and  $R_H$ , its shape and the characteristic linear dimensions of the molecule under various conditions were determined<sup>[20]</sup>. As a result, the higher ionic strength of the solution possesses, the lower intrinsic viscosity is. Nevertheless, when the  $[\eta]$  decreases to a certain degree, the intrinsic viscosity keeps constant, which is in accordance with the experimental results very well<sup>[26]</sup>. As show in Table 2, the intrinsic viscosity for HM-HPAM, at the same ionic strength, the value of the intrinsic viscosity of HM-HPAM2 is the maximum. For the HM-PAM, the order is HM-PAM2 > HM-PAM3 > HM-PAM4 > HM-PAM1, the intrinsic viscosity for HM-PAM2 is also the maximum. Therefore, we can get the conclusion that HM-HPAM2/HM-PAM2 has good performance in increasing viscosity.

In addition,  $R_H$  and  $R_g$  of a polymeric molecule in a solvent can be used to predict an approximation of the  $[\eta]$  via<sup>[27, 28]</sup>,

$$[\eta] = \frac{6^{3/2} \Phi R_g^3}{M_w} \quad (3)$$

$$[\eta] = 2.5 \frac{4/3 \pi R_H^3 d N_A}{M_w} \quad (4)$$

with  $d$  the specific gravity of the solute,  $N_A$  the Avogadro number,  $M_w$  the molecular weight, and  $\Phi$  the value

reflecting the solvent quality. According to Eq. (4), it is clear that the  $[\eta]$  is only affected by  $R_H$  and proportional to  $R_H^3$ . While for Eq. (3), the intrinsic viscosity is determined by both  $R_g^3$  and  $\Phi$ .

As in Fig. 4, we can investigate  $R_H$  for HM-HPAM1 or HM-PAM1, the change trends of which reflect the trends of intrinsic viscosity in the polymer solutions with different ionic strength in the MD simulations. Simultaneously,  $R_g$  for HM-HPAM or HM-PAM can be gained using MD simulations to explore solvation power of the polymer under different ionic strengths. In Fig. 4(a, b, c), the  $[\eta]$ ,  $R_H$  and  $R_g$  for HM-HPAM1 or HM-PAM1 versus ionic strength are shown. It is clear that the trends of the  $[\eta]$  changes in increasing ionic strength are in good agreement with the  $R_g$  and  $R_H$  ones. Therefore, we can use  $R_g$  and  $R_H$  to predict  $[\eta]$  changes for HM-HPAM or HM-PAM solutions with different ionic strengths as Eqs. (3, 4) shown. Similar results were seen in HM-HPAM (2, 3, and 4)/HM-PAM (2, 3, and 4). This result agrees with the theoretical calculations of other investigators<sup>[27, 28]</sup>.

### The Salt Tolerance

To investigate the salt tolerance of HM-HPAM, we define a parameter  $D$  as the declined proportion of the  $[\eta]$  from  $I = 0$  mol/L to  $I = 0.33$  mol/L, for example,

For HM-HPAM1, the expression about  $D$  is following,

$$D_1 = \frac{[\eta]_{I=0 \text{ mol/L}} - [\eta]_{I=0.33 \text{ mol/L}}}{[\eta]_{I=0 \text{ mol/L}}} \times 100\% \quad (5)$$

$[\eta]_{I=0 \text{ mol/L}}$  represents the value of the intrinsic viscosity for  $I = 0$  mol/L,  $[\eta]_{I=0.33 \text{ mol/L}}$  represents the value of the  $[\eta]$  for  $I = 0.33$  mol/L.

$D$  represents declined proportion of the intrinsic viscosity from  $I = 0$  mol/L to  $I = 0.33$  mol/L. Therefore, we can calculate the  $D_0$ ,  $D_1$ ,  $D_2$ , and  $D_3$  through the expression above as shown in Fig. 5. It can be seen from Fig. 5 that the HM-HPAM has a stronger salt tolerance compared to HPAM<sup>[7-9]</sup>. It can also be concluded that the salt tolerance increases gradually from HM-HPAM2, HM-HPAM1, to HM-HPAM3, HM-HPAM4. Therefore, the molecular design of modified polyacrylamide is good for the stronger salt tolerance. The monomers with the steric hindrance would reduce the curliness of molecular chains and, consequently, improve the salt tolerance<sup>[26]</sup>. With increasing the percentage of modified monomer, the effect of the curliness of molecular chains will be weakened further; the salt tolerance of the HM-HPAM will be improved further. Such advantages provide the modified HPAM with great potential for enhanced oil recovery fields.

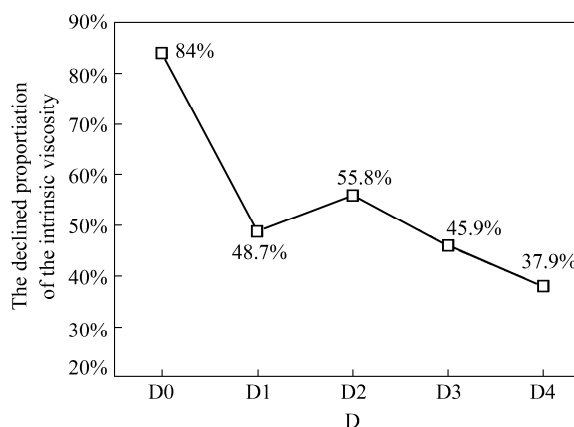


**Fig. 5** The declined proportion of the intrinsic viscosity for HPAM and HM-HPAM from  $I = 0$  mol/L to  $I = 0.33$  mol/L ( $D_0$  represents the declined proportion of the intrinsic viscosity of the HPAM from  $I = 0$  mol/L to  $I = 0.33$  mol/L;  $D_1$  represents the declined proportion of the intrinsic viscosity of the HM-HPAM1 from  $I = 0$  mol/L to  $I = 0.33$  mol/L;  $D_2$  represents the declined proportion of the intrinsic viscosity of the HM-HPAM2 from  $I = 0$  mol/L to  $I = 0.33$  mol/L;  $D_3$  represents the declined proportion of the intrinsic viscosity of the HM-HPAM3 from  $I = 0$  mol/L to  $I = 0.33$  mol/L;  $D_4$  represents the declined proportion of the intrinsic viscosity of the HM-HPAM4 from  $I = 0$  mol/L to  $I = 0.33$  mol/L.)

### The Radial Distribution Function

The radial distribution function (RDF)  $g(r)$  gives the probability density of finding a particle at a distance  $r$  from a given particle position. The radial distribution function  $g(r)$  is calculated as follows:

$$g(r) = \frac{dN}{\rho 4\pi r^2} \quad (6)$$

where  $N$  is the number of molecules (or atoms) in a spherical crown at a distance  $r$  from the reference atom, with thickness  $r$ , and  $\rho$  is the mean concentration in the computing box.

Therefore, the  $g_{O-H}(r)$  of the  $O^-$  of the  $-COO^-$  group of the HM-HPAM1 and  $H_2O$  and the  $g_{O-H}(r)$  of the O of the  $-CONH_2$  group of the HM-PAM1 and  $H_2O$  have been shown in Fig. 6 with different NaCl concentrations. For HM-PAM4, the  $g_{O-H}(r)$  is nearly zero when  $r$  is less than 0.25 nm, it means that the  $-CONH_2$  group cannot appear around the  $H_2O$  molecule when their distance is below 0.25 nm; the peak of RDF appears when  $r$  is about 0.25 nm. For HM-HPAM, the position of the peak is the same as that for HM-PAM at about 0.25 nm. Nevertheless, the peak heights are different. For HM-HPAM4, it is about 1.7 for  $I = 0$  mol/L and 1.1 for  $I = 0.33$  mol/L, which means that the appearance probability of  $O^-$  around 0.25 nm of  $H_2O$  is higher in the system with  $I = 0$  mol/L than that in the system with  $I = 0.33$  mol/L. As shown in Fig. 6, the repulsion between  $-COO^-$  groups of the HM-HPAM is reduced and the adsorption amount of sodium ions at the interface is increased. The other systems have the same tendency.

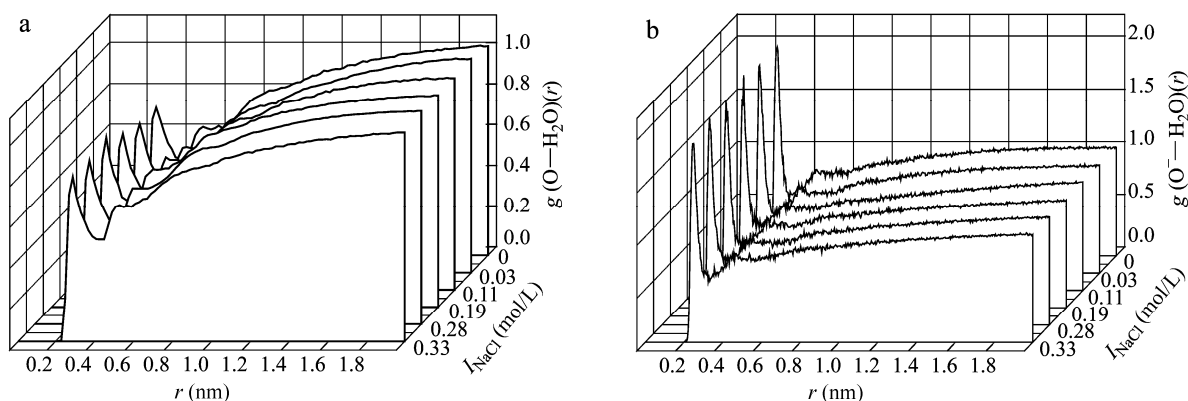


**Fig. 6** (a) RDF for O ( $-CONH_2$ ) of HM-PAM1 and H ( $H_2O$ ) in different ionic strength solutions; (b) RDF for O ( $-COO^-$ ) of HM-HPAM1 and H ( $H_2O$ ) in different ionic strength solutions

This verifies that the NaCl in the aqueous solution destroys the hydration layer of the  $O^-$  of the HPAM, which weakens the electrostatic repulsion between the  $-COO^-$  groups of the HM-HPAM. Therefore, the HM-HPAM chain will be pinched in the middle as the NaCl concentration increases. Even for the highest ionic strength 0.33 mol/L, the polyelectrolyte chain did not collapse and still keep bent spheroid and the peak of RDF for HM-HPAM changes little. This implies the hydration of the O of the HM-HPAM is very weak and not influenced basically by increasing NaCl concentration, at the same time, which explains the HM-HPAM has a good salt tolerance from microscopic view. The similar results can be obtained for HM-HPAM (2, 3, and 4)/HM-PAM (2, 3, and 4).

### Hydrogen Bonding

For the HM-HPAM containing one hydrogen bonding donor amidogen hydrogen (N-H) and two possible acceptors (carbonyl oxygen (C=O), carboxyl oxygen ( $COO^-$ )), it is widely speculated that there are three types of hydrogen bonding interaction in the HM-HPAM solutions. The intermolecular RDFs between carboxyl O and carbonyl O and H of  $H_2O$ , amidogen H and O of  $H_2O$  were calculated by averaging the last 1 ns of the MD trajectory respectively. The corresponding RDFs are depicted in Fig. 7, Fig. 8 and Fig. 9, respectively. The inter

molecular RDFs of carboxyl O and H of H<sub>2</sub>O with changing the amount of modified monomers from 1% to 4% in different ionic strength solutions are shown in Fig. 7. It can be found that there are two main peaks of 0.15 nm and 0.3 nm (generally, the length of hydrogen bond is less than 0.3 nm) in all HM-HPAM solutions. At the distance near 0.15 nm, the peak heights of the intermolecular hydrogen bonding RDFs decrease with the increasing of the ionic strength, and the decrease for the intermolecular hydrogen bonding of HM-HPAM2 is more obvious, which indicates the intermolecular hydrogen bonding is more sensitive to the NaCl concentrations. At the distance near 0.3 nm, we can find a small peak with the intensity lower than 0.8 arising from the intermolecular hydrogen bonding. The similar trends can be found just as the small peaks.

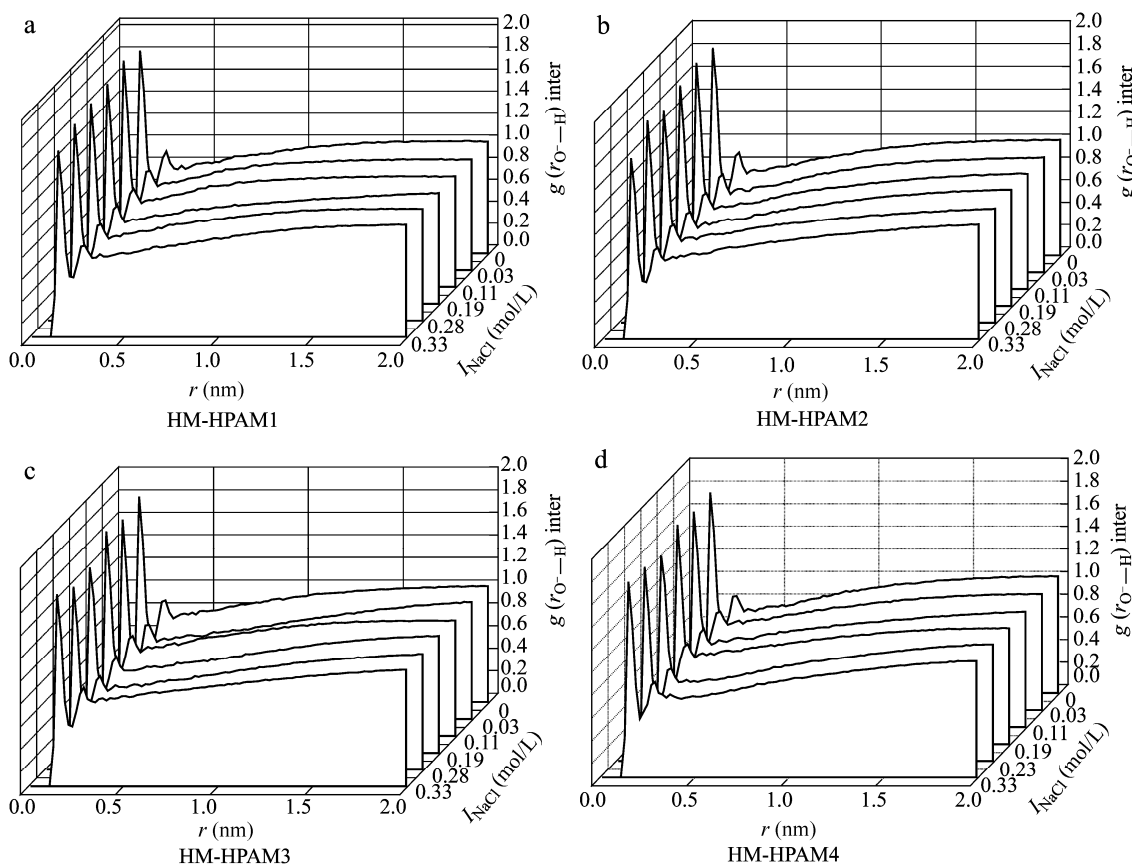


**Fig. 7** RDFs for the hydrogen bonding between carboxyl O (COO<sup>-</sup>) and H (H<sub>2</sub>O) with changing the amount of modified monomers from 1% to 4% in different ionic strength solutions

The order of the influence of the NaCl concentrations on the intermolecular hydrogen bonding is HM-HPAM2 > HM-HPAM1 > HM-HPAM3 > HM-HPAM4 and the order of the salt tolerance of HM-HPAM is just the opposite. It also appears to provide some evidence why the salt tolerance is in the order as shown in Fig. 5. The hydrogen bonding in the HM-HPAMs is much stronger, the COO<sup>-</sup> combines with water more closely and the conformations of the HM-HPAMs in the aqueous solutions will be more stable, which will make the solution viscosity remain nearly the same. Therefore, the order of the influence of the NaCl concentrations on the intermolecular hydrogen bonding is opposite with the order of the salt tolerance. However, the  $[\eta]$  decreases gradually with the increasing of the ionic strength because the intermolecular hydrogen bonding is broken partly and the electrostatic force weakens gradually.

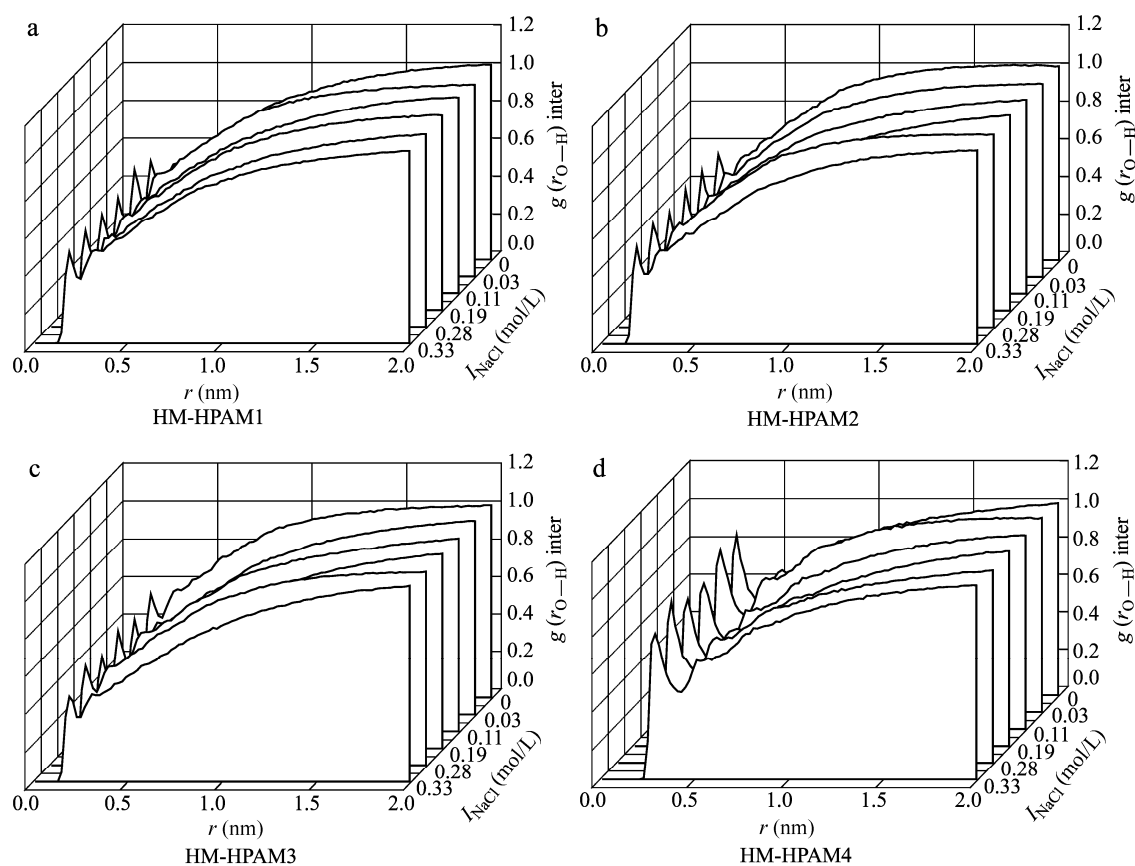


**Fig. 8** RDFs for the hydrogen bonding between carbonyl O (C=O) and H (H<sub>2</sub>O) with changing the amount of modified monomers from 1% to 4% in different ionic strength solutions

The RDFs for carbonyl O (C=O) and H (H<sub>2</sub>O) in different ionic strength solutions are given in Fig. 8. At the distance near 0.2 nm, we can find a main peak of the intensity about 0.7 arising from the intermolecular hydrogen bonding and the peak heights have no significant change with increasing the salt concentration. Compare to Fig. 7, the hydrogen bonding between carbonyl O (C=O) and H (H<sub>2</sub>O) is far weaker than the hydrogen bonding between carboxyl O (COO<sup>-</sup>) and H (H<sub>2</sub>O). The similar trends can be found just as the amidogen H (NH<sub>2</sub>) and O (H<sub>2</sub>O) as seen in Fig. 9. In the fourth figures of Fig. 8, there is an interesting phenomenon that the first peak is shifted to 0.29 nm, while in the first three figures the first peak is at 0.25 nm, which indicates that the hydrogen bonding is weakened. With changing the percentage of modified monomers from 1% to 4%, the increasing oxygen atoms of modified monomers will compete with carbonyl O in forming hydrogen bonding with H (H<sub>2</sub>O). When the percentage of modified monomers reached 4%, the competition effect achieve maximum, and relatively to Figs. 7 and 9, the hydrogen bonding between carbonyl oxygen and water in Fig. 8 is the weakest, competition effect is more outstanding. Predictably, continue to increase the amount of modified monomers, the phenomenon will be more obvious.

The peak of the hydrogen bonding C=O...H is not obvious just as that of (NH<sub>2</sub>) H...O (H<sub>2</sub>O), much lower than that of COO<sup>-</sup>...H. It indicates that the hydrogen bonding COO<sup>-</sup>...H is the predominant hydrogen bonding interaction and the probability of hydrogen bonding C=O...H and (NH<sub>2</sub>) H...O (H<sub>2</sub>O) is little.

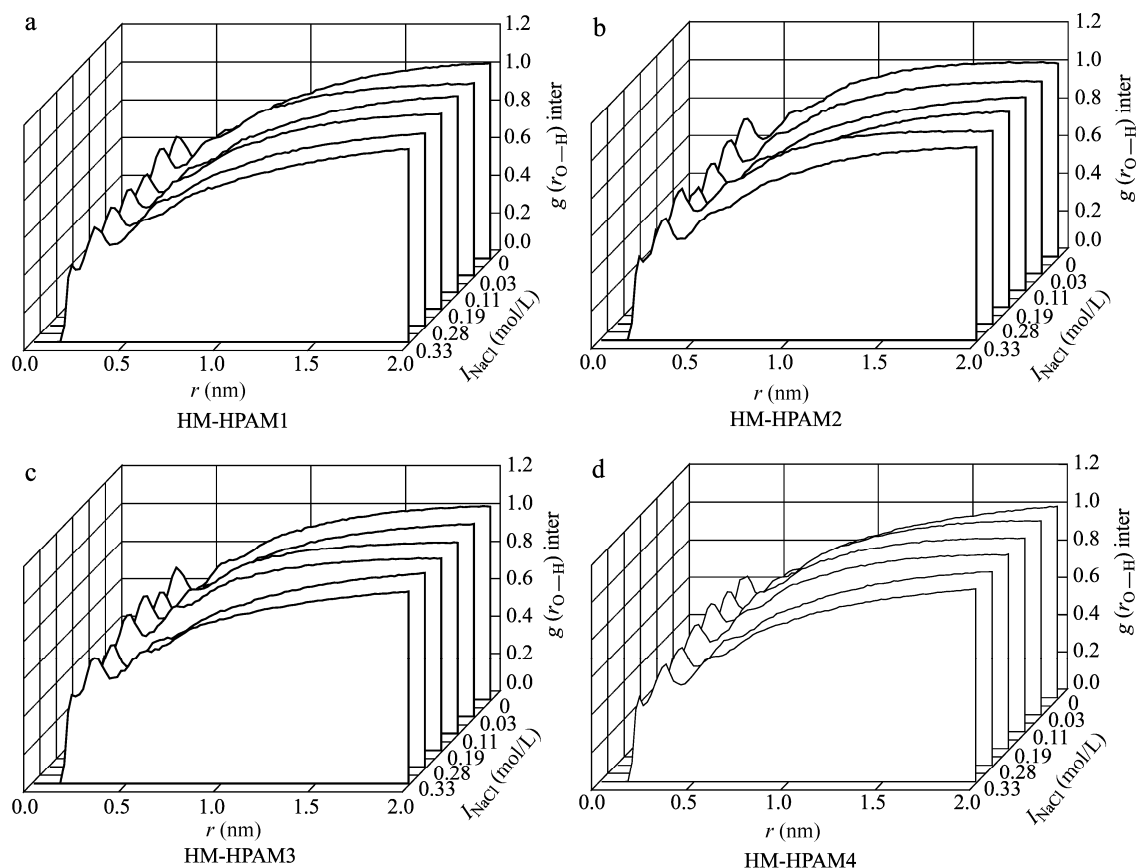


**Fig. 9** RDFs for the hydrogen bonding between amidogen H ( $\text{NH}_2$ ) and O ( $\text{H}_2\text{O}$ ) with changing the amount of modified monomers from 1% to 4% in different ionic strength solution

### Pair Correlation Function

The correlation between carbon atoms of the  $\text{COO}^-$  is consistent with these groups being spread out on the exterior of the globule. Figure 10 depicts the pair correlation function between carbon atoms of the  $\text{COO}^-$  and sodium ions with changing the amount of modified monomers from 1% to 4% in different ionic strength solutions. At the distance near 0.25 nm, we can find a set of main peaks and the peak heights gradually increase with the increasing salt concentration in the HM-HPAMs. However, the intensity of the HM-HPAM2 peak is the strongest and the intensity of HM-HPAM4 peak is the weakest with the same ionic strength. The order of the intensity for HM-HPAM peak is  $\text{HM-HPAM2} > \text{HM-HPAM1} > \text{HM-HPAM3} > \text{HM-HPAM4}$ , which is opposite to the order of the hydrogen bonding or the salt tolerance. This is because the HM-HPAM4 has the strongest hydrogen bonding interaction and restrains the interaction between the  $\text{COO}^-$  and  $\text{Na}^+$ . Therefore, the HM-HPAM4 has the better salt tolerance.

### CONCLUSIONS

In this paper, the modification of PAM/HPAM in aqueous solutions by introducing one kind of amphiphilic functional monomer was investigated by molecular dynamics simulation with the PCFF force field. The characteristics of the HM-PAM/HM-HPAM (such as  $R_H$ ,  $R_g$ , the viscosity-promoting and the salt-tolerance) have been studied to find the intrinsic relation between the microstructure of the polymer chain and the intrinsic viscosity with changing the amount of modified monomers from 1% to 4%. The simulation results show that the  $R_g$ ,  $R_H$  and the  $[\eta]$  of the HM-HPAM chain decrease with the increase in NaCl concentration, and those of the HM-PAM chain have no significant change. Furthermore, compared to HPAM, the HM-HPAM which are

obtained by molecular design has a stronger salt tolerance and a good performance in increasing viscosity. HM-PAM/HPAM has the better performance in increasing viscosity when the percentage of modified monomers is 2% and has a stronger salt tolerance when the percentage of modified monomers is 4% compared with the other percentages of modified monomers.

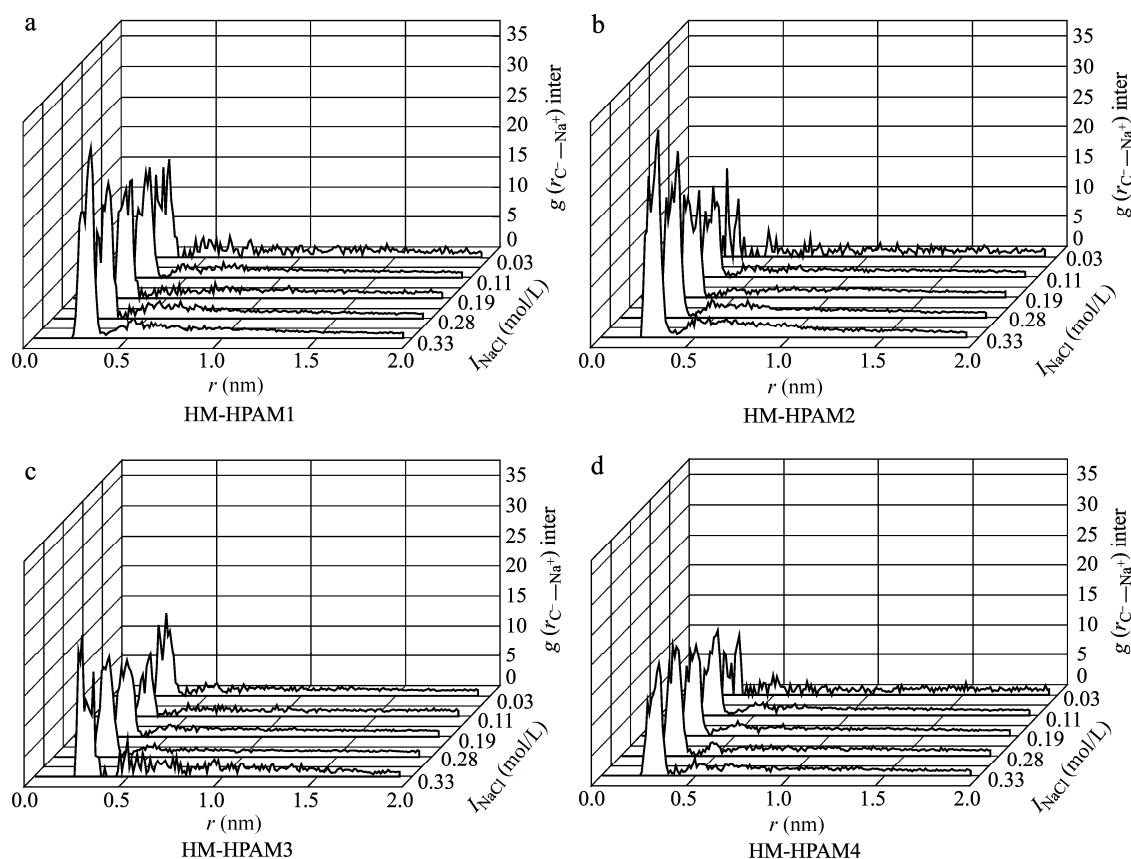


**Fig. 10** Pair correlation function between carbon atoms of the  $\text{COO}^-$  groups and sodium ions with changing the amount of modified monomers from 1% to 4% in different ionic strength solutions

The RDF of the  $\text{O}^-$  in the  $-\text{COO}^-$  group of the HM-HPAM with  $\text{H}_2\text{O}$  and the O in the  $-\text{CONH}_2$  group of the HM-PAM with  $\text{H}_2\text{O}$  in a series of the solutions with various ionic strengths have been investigated. It explained the effect of NaCl on the hydration of the  $-\text{COO}^-$  groups of the HM-HPAM from microscopic view.

Ultimately, the intermolecular RDFs between carboxyl O and carbonyl O and H in the  $\text{H}_2\text{O}$ , amidogen H and O in the  $\text{H}_2\text{O}$  were calculated by averaging the last 1 ns of the MD trajectory respectively. The results show that the peak for the hydrogen bonding  $\text{C}=\text{O}\cdots\text{H}$  is not obvious just as that of  $(\text{NH}_2)\text{H}\cdots\text{O}(\text{H}_2\text{O})$ , much lower than that of  $\text{COO}^-\cdots\text{H}$ . It indicated the hydrogen bonding  $\text{COO}^-\cdots\text{H}$  is the predominant hydrogen bonding interaction and the probability of hydrogen bonding  $\text{C}=\text{O}\cdots\text{H}$  and  $(\text{NH}_2)\text{H}\cdots\text{O}(\text{H}_2\text{O})$  is little. It also appears to provide some evidence that why the salt tolerance is in the order as shown in Fig. 5.

The pair correlation function has been used to investigate between carbon atoms in the  $\text{COO}^-$  and sodium ions with changing the amount of modified monomers from 1% to 4% in different ionic strength solutions. The order of the intensity of HM-HPAM peak is  $\text{HM-HPAM2} > \text{HM-HPAM1} > \text{HM-HPAM3} > \text{HM-HPAM4}$ , which is opposite to the order of the hydrogen bonding or the salt tolerance. This is because the HM-HPAM4 has the strongest hydrogen bonding interaction and restrains the interaction between the  $\text{COO}^-$  and  $\text{Na}^+$ . Therefore, the HM-HPAM4 has the better salt-tolerance.

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