Study on the Molecular Behavior of Hydrophobically Modified Poly(Acrylic Acid) in Aqueous Solution and Its Emulsion-Stabilizing Capacity

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ABSTRACT: In this article, molecular conformation and aggregation behavior of partly hydrophobically modified poly(acrylic acid) (HMPAA) in aqueous solution has been studied by mesoscale simulation approach dissipative particle dynamics for the purpose to find out how the chemical structure and environmental conditions effect its capacity. It has been found that, as a kind of pH-sensitive polymer, the chemical structure variation of HMPAA carried by adjusting pH and grafting degree influence the taking place of intermolecular and intramolecular associations, which induced the formation of molecular network and help to maintain high bulk phase viscosity of its aqueous solution in larger pH range or under higher salinity comparing with PAA. There exists an optimum grafting degree, above which the increase of the possibility of the intramolecular associations enhance the coiling of the polymer chain and result in destroy of the network. The experimental determination of properties of aqueous solutions of poly(acrylic acid) (U10) and poly alkyl acrylate (U20), such as the bulk phase viscosity and oil/water interface tension, accord well with the molecular simulation conclusion, by which the mechanisms of elevated stability of surfactant-free O/W emulsion stabilized by the HMPAA comparing with PAA has been discussed. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Water-soluble polymers have been widely used in petroleum exploitation, cosmetic products, and pharmaceutical industry in recent years.[1–6] In many cases, they are applied as thickening agents due to their outstanding rheological behavior, for instance act as oil-in-water (O/W) emulsion stabilizer. Emulsion instability is related to intricate progresses with different mechanisms, such as creaming or sedimentation, coagulation or flocculation, coalescence, and Ostwald ripening.[7,8] All these aspects are relevant to the diffusion of the emulsion droplets. Einstein-Stokes equation[9] is used well-known to describe the diffusion of spherical particle:

$$D = \frac{k_B T}{6\pi\eta r} \tag{1}$$

where D is the diffusion coefficient of spherical particle, k_B is the Boltzmann's constant, T is the absolute temperature, η is the bulk phase viscosity, r is the radius of the spherical particle.

O/W emulsion droplet can be approximately treated as spherical particle under statistic states. Consequently, the decrease of the

diffusion coefficient of emulsion droplet induced by bulk viscosity increase would result in the enhancement of emulsion stability, because all the above processes correlated with the emulsion unstable would be slowed down. For instance, in the creaming process, the rising velocity of emulsion droplet obeys the below equation:[9]

$$v = \frac{2gr^2(\rho_0 - \rho)}{9\eta} \tag{2}$$

where v is the rising velocity of emulsion droplets, ρ_0 and ρ are the densities of continuous and dispersed phase, respectively. The rise of emulsion droplet decelerates because of the high bulk viscosity and emulsion stability would be enhanced.

Hydrophobically modified polymers (HM polymers), which were synthesized by grafting hydrophobic side chains on to the hydrophilic backbone of polymer, such as cellulose derivatives, poly(acrylic acid) derivatives, protein derivatives, and polysaccharide derivatives, have been reported to have better thickening properties,[10–17] which resulting in excellent emulsion stability. And adsorption of HM polymers at the oil–water interface
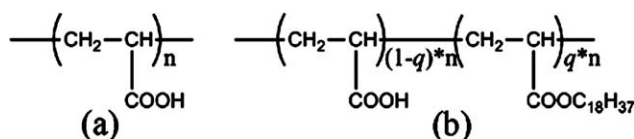
Figure 1. Molecular structures of PAA (a) and HMPAA (b). The grafting degree q is the partial ratio of the hydrophobic modification part.

because of their amphiphilic character was thought to provide contribution on the enhancement of the emulsion stabilization, too.[18,19]

Both the thickening capacity and the oil/water interfacial activity of HM polymers are determined by their molecular conformation and behavior, which would be affected by molecular chemical structure and environmental conditions, while be not always coherent. Therefore, the detailed information about its behavior in molecular level is not only helpful for understanding the mechanism of emulsion stability better but also important to find out the optimum molecule design direction, while relevant references are still scarce.

This article investigated the molecular behavior of hydrophobically modified poly(acrylic acid) HMPAA and PAA in aqueous solution using dissipative particle dynamics (DPD) method,[20–24] in which a simplified bead-and-spring model is used to represent polymer chain, thereby the simulation of a tremendous polymer solution system containing large number of particles could be achieved. Effect of pH and grafting degree on the conformations and aggregation behavior of the polymers were investigated. Accordingly, properties of aqueous solutions of poly(acrylic acid) (U10) and poly alkyl acrylate (U20) and their emulsion stability capacity were determined experimentally. By combining molecular simulation and experimental results, how chemical structure of the polymers affects molecular behavior in aqueous solution and their capacity of emulsion stability has been investigated.[25–27]

DPD SIMULATION DETAILS

Chemical structures of PAA and HMPAA investigated in DPD simulation are shown in Figure 1, their coarse-grained model was shown in Figure 2. The main chain of the polymers was constructed by connecting acrylic acid beads for PAA and embedded connecting acrylic acid beads with acrylate beads, the variation of ratio of the two kinds of beads corresponds to the change of chemical structure induced by pH adjusting. The hydrophobic-modifying group octadecyl is presented as three contiguous hexyl beads.

BLEND was used to calculate Flory-Huggins parameters χ between different kinds of beads. Interaction parameters a_{ij} in DPD can be calculated by $a_{ij} = 25 + 3.27\chi$. The size of the simulation box is $30 \times 30 \times 30$ r_c^3 (r_c is the DPD length unit), where three-dimensional edges are all periodic. The bulk density $\rho = 3.0$. All simulations were carried out by Materials Studio 4.3 from Accelrys.

EXPERIMENTAL SECTION

For experimental determination, poly acrylic acid Carbopol® Ultrez 10 (U-10) and poly alkyl ($C_{10–30}$) acrylate Carbopol®

Ultrez 20 (U-20), provided by Lubrizol Corporation, were used as received.

Bulk Phase Viscosity

The aqueous solutions of polymers were prepared by keep whisking for 24 h at 50°C. pH value of polymer solutions were adjusted by adding 0.25 mol L^{-1} NaOH stock solution, and ionic strength of polymer solution was adjusted by adding 0.85 mol L^{-1} NaCl stock solution. Bulk viscosity of polymer solution was tested with Rheometer RS75 (HAAKE, Germany).

Confocal Laser Scanning Fluorescence Microscopy

The visualization investigation of polymer aqueous solution was carried out with Olympus FV500 Confocal Microscope (Olympus, Japan). Rhodamine B (0.0002%, w/w) was used as the fluorescence label of the polymer chain. The excitation laser source was $\lambda_{ex} = 543$ nm, the fluorescence emission was recorded between 580 and 630 nm.

Interfacial Tension

The interfacial tension between polymer solution and mineral oil was tested with TRACKER interfacial rheometer(TECLIC, France). The area of oil droplet was fixed as 8 mm^2 and the tested time was 3000 s. The polymer concentration was 0.01 wt%.

Emulsion Stability Evaluation

O/W emulsions were prepared using homogenizer (Shanghai Forerunner M&E, China). First, the mixture of polymer aqueous solution and mineral oil was homogenized (3000 r/min) for 5 min at 80°C. Then, the emulsion samples were centrifuged at 1000 r/min for 5 min, the volume fraction of the upper emulsion phase and the lower separated water phase represent the emulsion stability on one side, that is the capacity of keeping water for the emulsions. The size distribution of oil droplets in the emulsion was analyzed according to images determined by Olympus CX31-P polarizing microscope (Olympus, Japan), which represent the emulsion stability on another side.
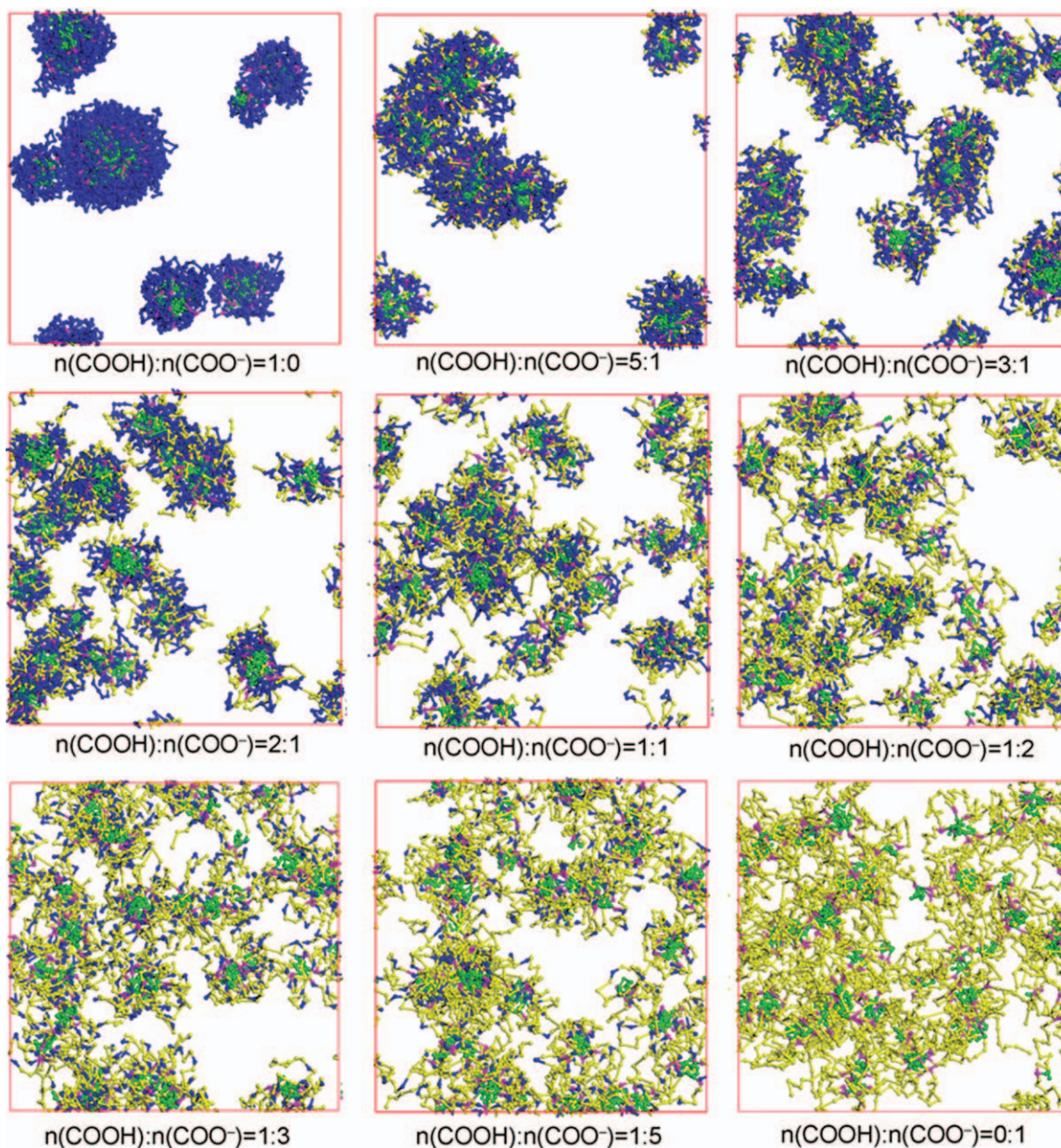
RESULTS AND DISCUSSION

pH-Responding Behavior of HMPAA

DPD simulation was adopted to investigate the molecular conformation of HMPAA in aqueous solution. The variation of the pH value of solution was achieved by adjusting the ratio of COOH and COO$^-$ on the polymer chains, results are shown in
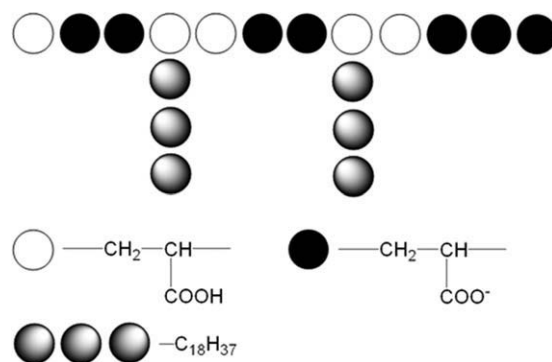
Figure 2. Topologic structure of HM polymer in DPD simulation.

Figure 3. Snapshots of conformations of HMPAA in aqueous solution with various pH, where blue beads sign acrylic groups, yellow beads sign acrylate groups, green and pink beads sign hydrophobic groups. Water beads are removed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3. It could be found that the COOH groups and the hydrophobic modification side chains both showed clearly gathering tendency, the former should be driven by hydrogen bond connection, and the latter induced by hydrophobic interaction. The polymer chain was coiled at low pH, with the kernel formed by the hydrophobic groups covered by a shell formed by COOH groups. The curled polymer molecules are isolated, and it is reasonable that the viscosity of the solution would be very low. The polymer chain got release gradually with the proportion of COO^- increases, accompanied by building up of intramolecular and intermolecule associations. The RMS end-to-end distance of polymer chain was calculated, of which the variation as a function of x_{coo-} was shown in Figure 4. The

proportion of blank area in snapshots in Figure 3 was calculated and shown in Figure 4, too.

The conformation variation of polymer U-20 affected by pH was investigated by LSCFM, the images were shown in Figure 5. The polymer chains curled up at low pH and got stretching gradually while pH increases, which agree well with the molecular simulation results.

Effect of Hydrophobic Modification on Formation of Molecular Network and the Bulk Phase Viscosity of HMPAA Aqueous Solution

In DPD simulations, the water diffusivity for the different systems was calculated to quantitatively characterize the formation
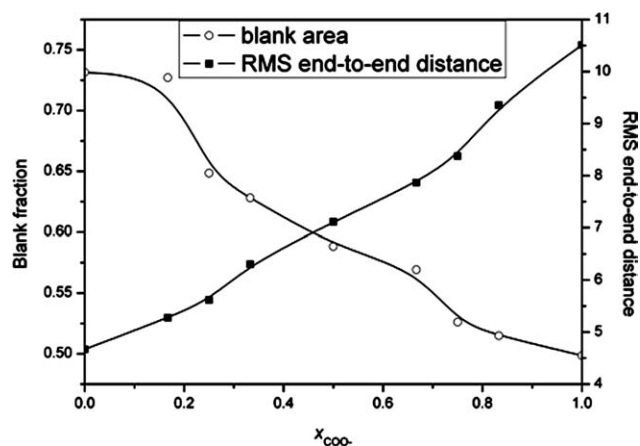
Figure 4. RMS end-to-end distance (■) of polymer chain and blank fraction (○) of snapshots in Figure 3 as a function of x_{COO^-}.

and elimination of the polymer molecular network, because the formation of network would course the increase of the astriction degree of water molecules, which correspond to the increase of the bulk phase viscosity of the solution. Figure 6 shows the water diffusivity in HMPAA and PAA solutions with different pH as a function of time. For the cases molar ratio of COOH : COO− equal to 0 : 1 and 1 : 3, the water diffusivity was lower in HMPAA solution than in PAA solution, which means that no matter at higher pH or medium pH, the viscos-
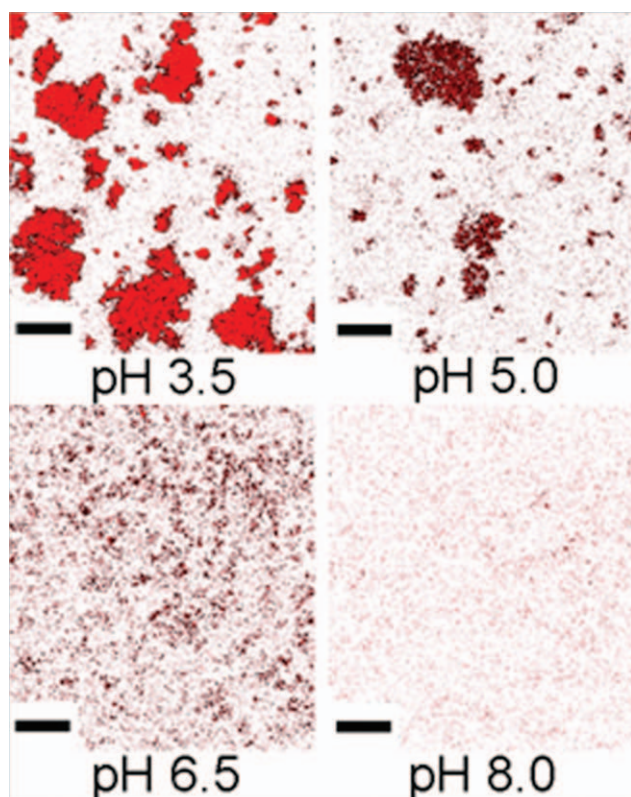

Figure 5. LCFM images of U-20 aqueous solution (The scale on the picture is 20 μm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
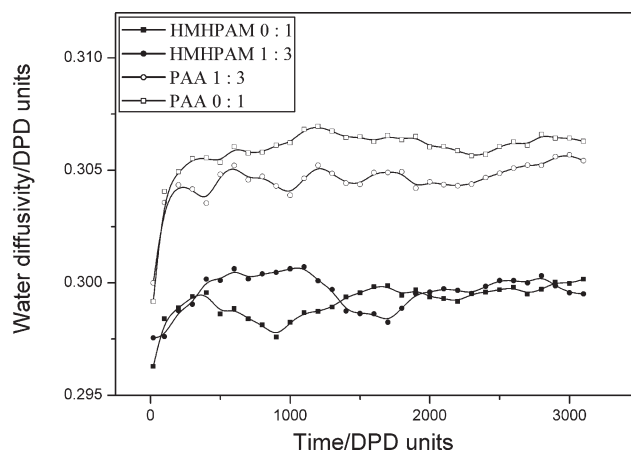

Figure 6. Water diffusivity in HMPAA and PAA solution with the ratio of COOH and COO⁻ was apparently 1 : 3 and 0 : 1.

ity of HMPAA solution could be higher than that of PAA at the same concentration. Another interesting phenomenon is that, the diffusivity of water molecules in PAA solution with medium pH was lower than that in solutions with higher pH, so the intermolecular and intramolecular associations induced by COOH benefit the molecular network formation for PAA, there would be an optimum pH region to get high bulk phase viscosity for their solutions. For HMPAA, the diffusivity of water molecules is similar in the two situations, means that the impact of pH on the bulk phase viscosity of HMPAA solution would be not as remarkable as on that of PAA solution.

The viscosity of the aqueous solutions of polymer U-10 and U-20 at various pH was shown in Figure 7. The viscosity of PAA solution increases with pH initially and performs the peak value at pH 6.5–7.5, then decreases lentamente as pH increases continuously. When pH of the solution is larger than 7.5, more and more COOH groups are neutralized by NaOH and change to COO⁻ group, the hydrogen bond interaction becomes weak and electrical repulsion interaction is enhanced, resulting in the extension of the polymer chain and dramatic increase of
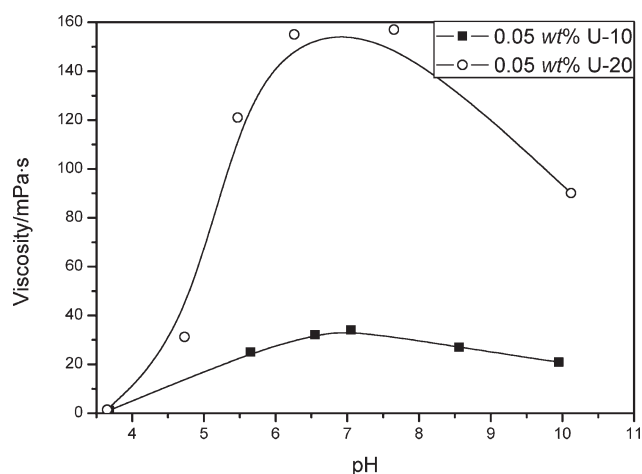
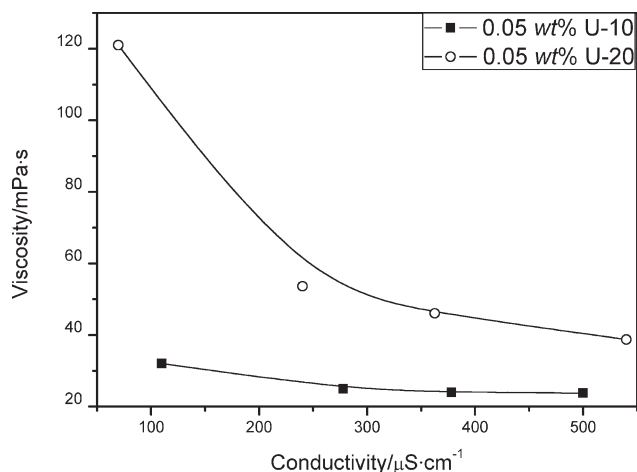**Figure 7.** Variation of bulk phase viscosity of polymer solutions as a function of pH.
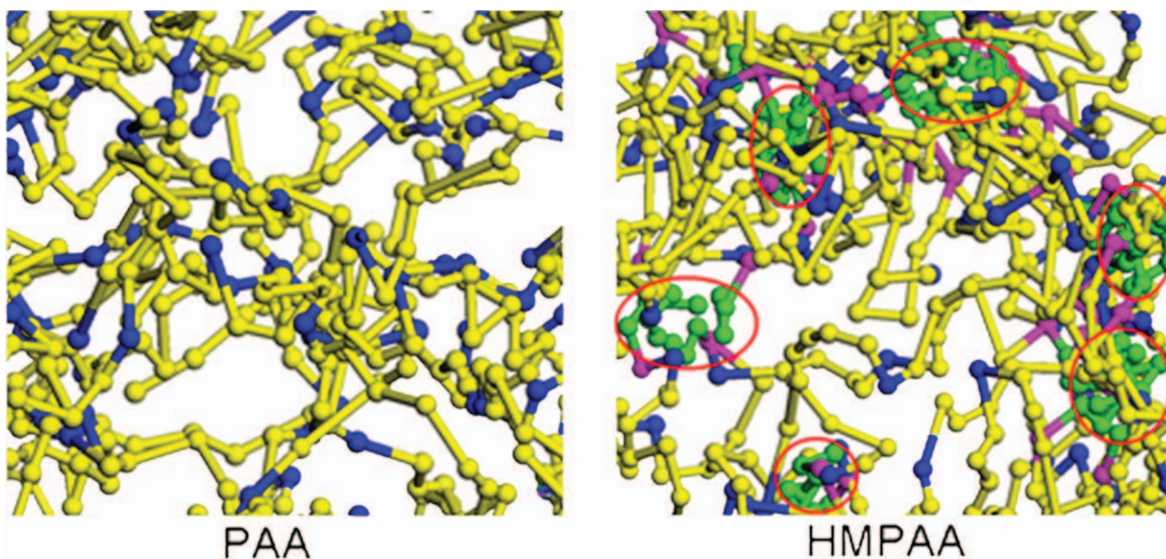
Figure 8. Snapshots of PAA and HMPAA in solution in DPD simulation. The ratio of COOH and COO$^-$ was 1 : 3. The blue beads sign acrylic groups, yellow beads sign acrylate groups, green and pink beads sign hydrophobic groups. Water beads are removed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

viscosity. But at higher pH value, the high electric repulsion interaction hindered the gathering among polymer chains, and bulk phase viscosity decreases. Figure 8 shows DPD snapshots of conformations of PAA and HMPAA in aqueous solution with the same pH value, the hydrophobic associating tendency of the polymer molecules induced by the side chains is more distinct than the COOH groups, which do a great favor on increasing of bulk phase viscosity.
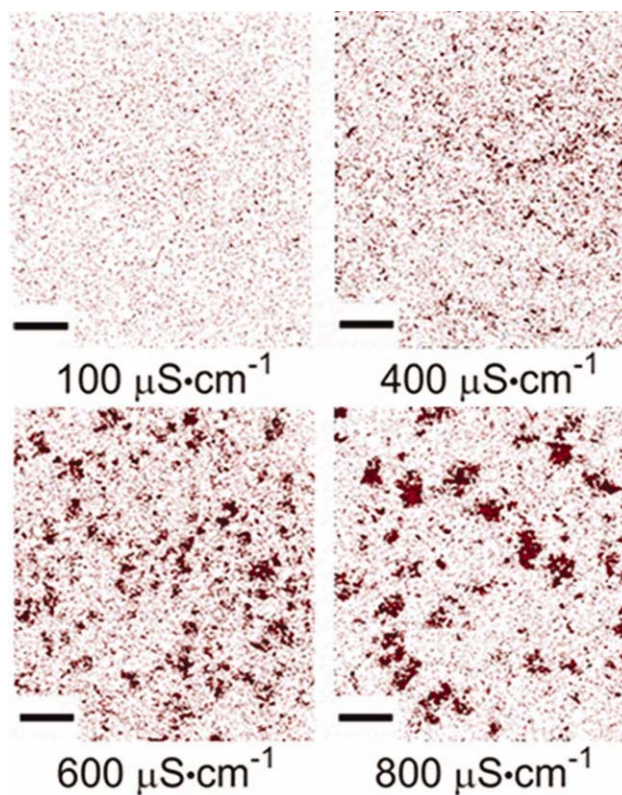
Effect of Ionic Strength on the Bulk Phase Viscosity and Conformation of Polymer

The effect of ionic strength on the conformation of polymers is investigated, results shown in Figures 9 and 10. The viscosity of polymer solution sharply decreases as ionic strength increased. The chain conformation of HMPAA changes from extending to coiling as ionic strength increases, because the static repulsion

between COO$^-$ groups on polymer chain has been screened at higher salt concentration, the decrease of the electric repulsion interaction and the increase of hydrophobiciy of the polymer chain induce the intramolecule association, so that the viscosity

Figure 10. Effect of ionic strength on LCFM images of 0.05 wt % U-20 in aqueous solution (The scale on the picture is 20 μm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9. Viscosity of polymer solutions as a function of electric conductivity.
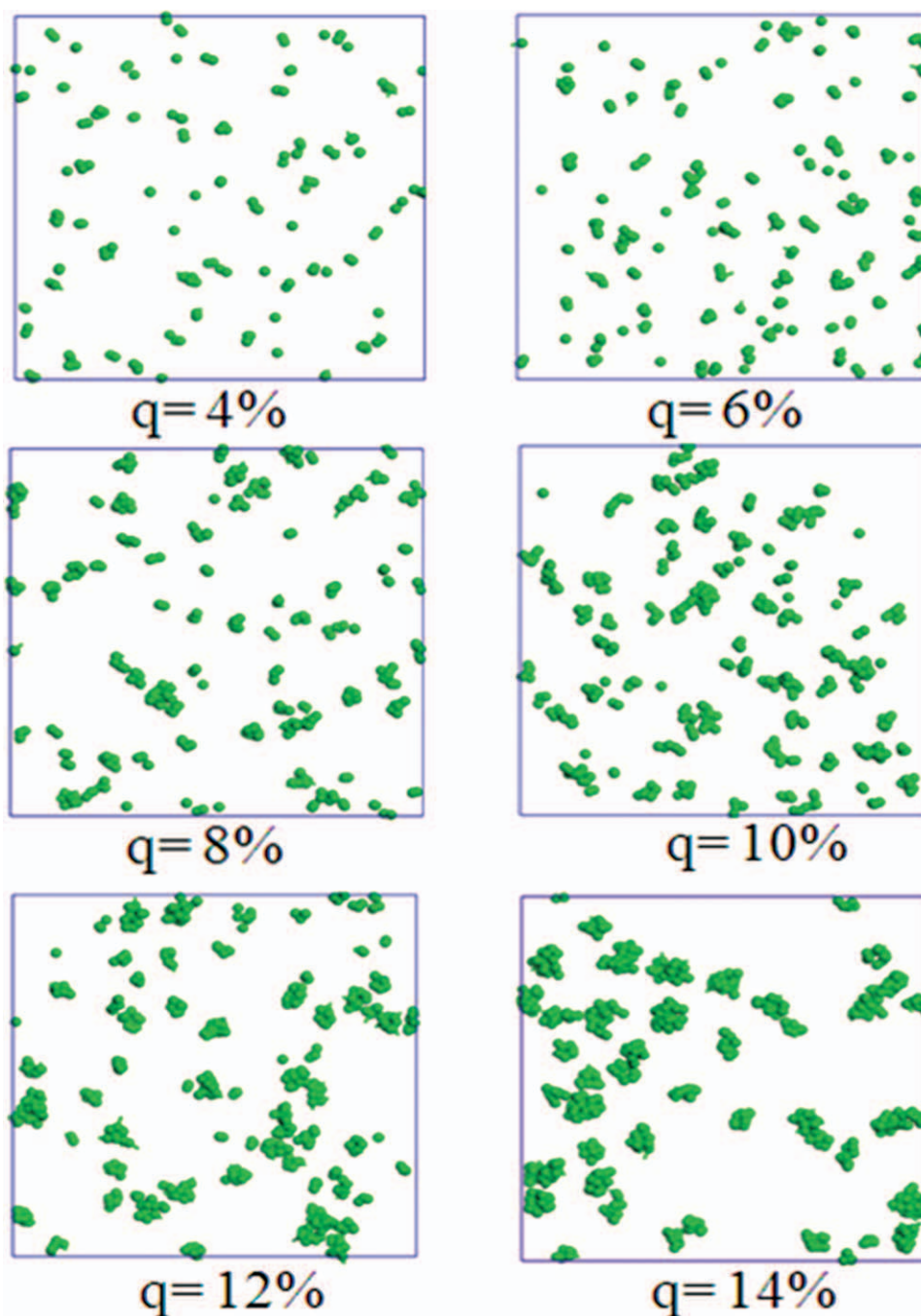
Figure 11. Effect of grafting degree q on aggregation behavior of polymer chain (there are only hydrophobic group beads visual). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of solution decreases. For U-10, the polymer got to be coiling when the electricity conductivity is 200 μS cm^{-1}, and the bulk phase viscosity decreased sharply as the electricity conductivity increasing. So, the HMPAA could maintain the stretching conformation and the molecular network at higher salinity than PAA.

Effect of Grafting Degree of HMPAA on Its Conformation and Aggregation Behavior

Grafting degree of HMPAA has been adjusted in DPD simulation to investigate the effect on the conformation of polymer, as shown in Figure 11. It could be found that the degree of the hydrophobic association got stronger with the increasing grafting degree.

The influence of grafting degree on diffusivity of water is shown in Figure 12. The water diffusivity decreased as the grafting degree increase from 0 to 10%, but when the grafting degree got to be over 10%, the water diffusivity increases. According to the snapshots of DPD, when the grafting degree is low, the hydrophobic association mainly happened between hydrophobic
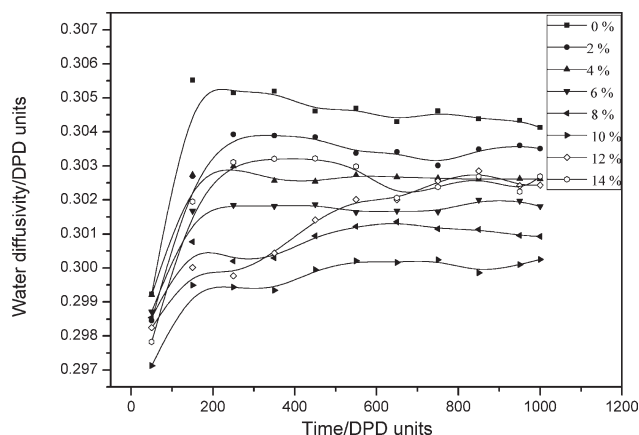
Figure 12. Water diffusivity in polymer solution with different grafting degrees q as a function of time.

side groups belong to different polymer chain, which linked the polymer chains together to form network, so the viscosity of solution increases and the water diffusivity decreases. However, for the higher grafting degree, the hydrophobic association interaction could be too strong, and the possibility of intramolecule interaction increase, lead to the polymer chains being crouched and the molecular network destroyed, so viscosity of the solution decreases and the water diffusivity increases.

Effect of pH and Ionic Strength on Interfacial Activity of HMPAA

The oil/water interfacial tension γ of polymer solution was tested as shown in Table I. $\Delta\gamma$ means the difference of the interface tension between the polymer solution of which the pH value is apparently 4.5 and 6.5. Mineral oil is used as oil phase.

As it is shown in Table I, no matter for PAA and HMPAA, the interfacial tension of polymer solution and oil phase at pH 6.5

Table I. Effect of pH on Interfacial Tension

Time	0.05 wt % U-10			0.05 wt % U-20		
	γ(pH 4.5)/mN m^{-1}	γ(pH 6.5)/mN m^{-1}	$\Delta\gamma$/mN m^{-1}	γ(pH 4.5)/mN m^{-1}	γ(pH 6.5)/mN m^{-1}	$\Delta\gamma$/mN m^{-1}
$t = 20$ s	38.04	42.58	4.54	35.58	36.76	1.18
$t = 200$ s	35.72	40.54	4.82	30.81	31.18	0.37
$t = 2000$ s	30.82	34.62	3.80	23.42	23.44	0.02

Note: $\Delta\gamma = \gamma$(pH 6.5) $- \gamma$(pH 4.5).

Table II. Effect of Ionic Strength on Interfacial Tension

Time	0.05 wt % U-10			0.05 wt % U-20		
	$\gamma(\kappa_1)$/mN m^{-1}	$\gamma(\kappa_2)$/mN m^{-1}	$\Delta\gamma$/mN·m^{-1}	$\gamma(\kappa_1)$/mN m^{-1}	$\gamma(\kappa_2)$/mN m^{-1}	$\Delta\gamma$/mN m^{-1}
$t = 20$ s	41.38	37.58	−3.80	37.24	36.78	−0.46
$t = 200$ s	38.23	34.79	−3.44	29.92	29.34	−0.58
$t = 2\,000$ s	31.74	29.42	−2.32	22.86	22.56	−0.30

Note: $\kappa_1 = 100$ μS·cm^{-1}, $\kappa_2 = 200$ μS·cm^{-1}, $\Delta\gamma = \gamma(\kappa_2) - \gamma(\kappa_1)$.
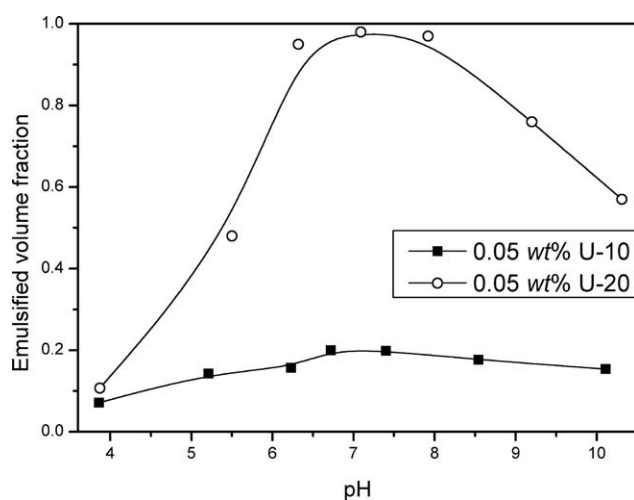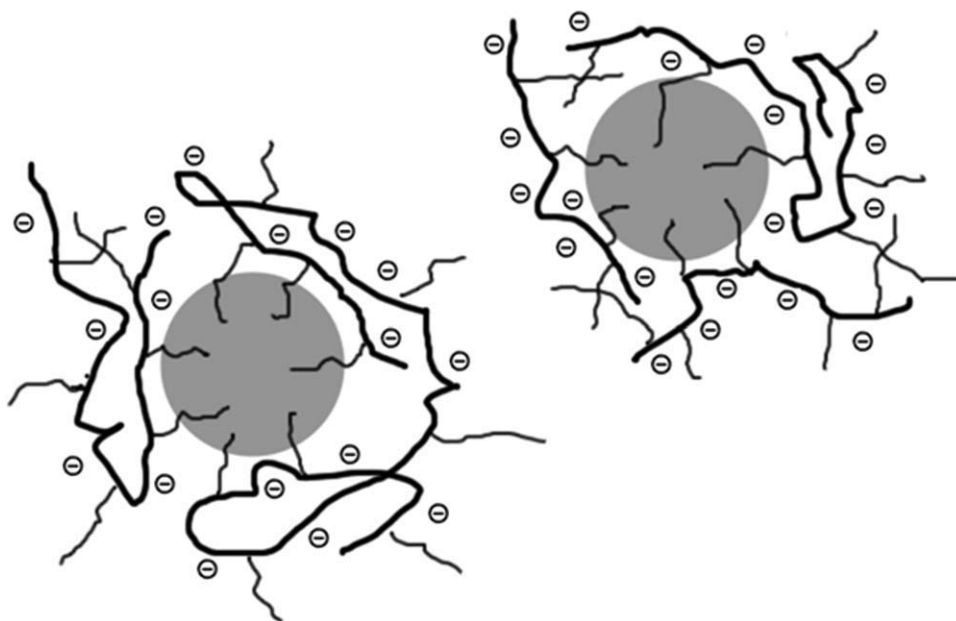

Figure 13. Volume fraction of emulsion with polymers as a function of pH.


Figure 14. Volume fraction of emulsion with polymers as a function of ionic strength.

Figure 15. Schematic diagram of O/W emulsion stabilization mechanism for HMPAA.

is higher than it is at pH 4.5, means that COOH group is relatively hydrophobic comparing with COO$^-$. For HMPAA, the $\Delta\gamma$ is much lower than that of PAA at the same condition, and the

interface tension decreases more quickly, the HM polymer have stronger trend in adsorbing onto the oil/water interface, and it is obvious that the extend of the influence of pH on the
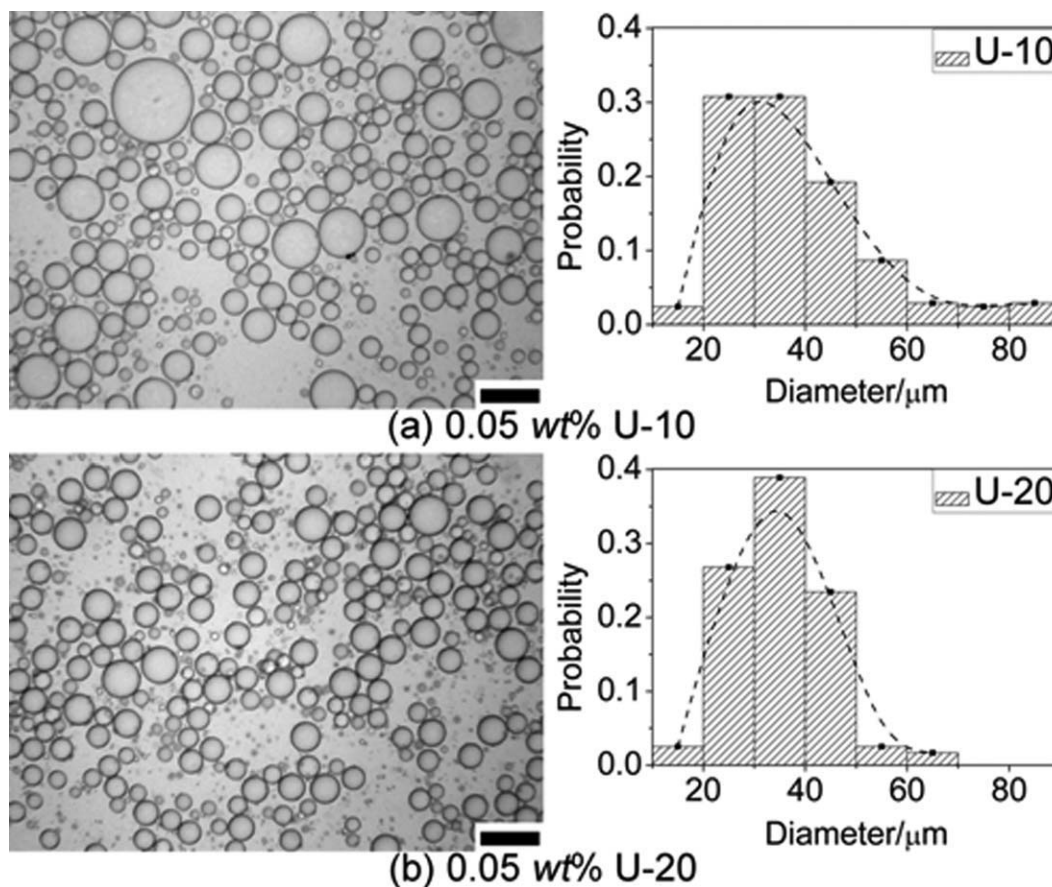
Figure 16. Optical microscopy photos of emulsions stabilized by 0.05 wt % U-10 (a) and U-20 (b). The scale on the picture is 100 μm.

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interface activity decrease for HMPAA comparing with PAA. The effect of ionic strength on the interface tension of oil and polymer solution is also investigated, see Table II. For both U-10 and U-20 solution, the interfacial tension decreased as ionic strength increasing, while $\Delta\gamma$ is much smaller for the later one and get to the equilibrium more quickly, which also stated the strong tendency of HMPAA to adsorb onto the oil/water interface.

Contribution of Thickening Effect and Interfacial Activity of HMPAA on Its Emulsion Stabilization Capacity

The volume fraction of emulsions formed by dispersion of mineral oil in aqueous polymer solution with different pH was determined after being centrifuged for 5 min, as shown in Figure 13. The stability of emulsion stabilized by U-20 is much higher than that of U-10, and the variation of the stability as a function of pH has the same trend with that of viscosity, according to Figure 13, the emulsion stabilized by HMPAA and PAA are all most stable at pH = 6.5–7.5, though the interface activity is higher when pH is lower.

The effect of ionic strength on emulsion stability is shown in Figure 14. The emulsion stabilized by HMPAA and PAA both become less stable as ionic strength increases, which is in consist with Figure 10, but be inconsistent with their interfacial activity. Consequently, for the surfactant-free emulsion stabilized by polymer, the bulk phase viscosity plays more important role in emulsion stabilization than interface activity. However, the prominent oil/water interfacial adsorption of HMPAA still help to fix the oil drops inside the molecular network, which give assistance to prohibit the coalescence of oil drops and the oil/water phase separation, as shown in Figure 15.

The optical microscopy images of residual emulsion stabilized by U-10 and U-20 of the same concentration are shown in Figure 16. The most probable diameter of droplets is about 39.18 μm for U-10 and 34.03 μm for U-20, and the distribution for the former is wider than the later. Undoubtly, the stability of the latter is better than the former, which accorded with the above analyzation.

CONCLUSION

It is concluded that, conformation variation of polymer chain depended on the chemical structure of the molecular chain determines the viscosity of the bulk phase solution. The molecular conformation of PAA and partly hydrophobically modified PAA in aqueous solution shown by DPD simulation revealed that the increase of the grafting degree of hydrophobic group of HMPAA and appropriate pH value benefit the formation of molecular network, which agrees well with the experimental determination results of viscosity of the polymer solutions at different pH. Combining the experimental investigation results of the stability of emulsion stabilized by HMPAA at different pH and the molecular aggregation behavior got by DPD molecular simulation, it is revealed that the optimization of the emulsion stabilizing capacity of HMPAA with no surfactant existing derive mainly from the increase of dynamic stabilization factor which come from the strengthening of intermo-

lecular and intramolecular associations that benefit the formation of molecular network, and the increase of viscosity plays the most important role in emulsion only stabilized by HMPAA.

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