Study on the Morphology of the Novel Hydrophobically Associative Acrylamide-Based Terpolymer in Aqueous Solution by AFM Measurements

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ABSTRACT: The synthesized hydrophobically associating water-soluble polymer P(AM-BST-NaAMPS) (PASA) exhibits good viscosification properties in the aqueous and brine solution. To study the viscosifying mechanisms of the polymer in the aqueous solution and brine solution, atomic force microscope (AFM) was applied to observe the micromorphology of the polymer solution. The AFM measurements show that continuous network structures have been formed in the aqueous solution of 0.05 g dL^{-1} PASA, and with the increase in PASA concentration, the network structures become much bigger and more condensed. The network structures of PASA are collapsed by the addition of salt, and tree-like crystals are formed, leading to the decrease in the apparent viscosity of PASA solution. However, by increasing the NaCl concentration or the polymer concentration in the brine solution, the sizes of crystals increase. These results are consistent with the ESEM and viscosity study results. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3996–4002, 2006

Key words: hydrophobically associating water-soluble polymer; acrylamide; butyl styrene; morphology; atomic force microscopy

INTRODUCTION

Hydrophobically associating water-soluble polymers have been extensively studied in recent years because of their potential industrial applications in enhanced oil recovery (EOR), drag reduction, flocculation, cosmetics, etc.[1–4] When dissolved in the aqueous solution above the critical concentration (C*), these polymers containing a small fraction of hydrophobic groups exhibit unique solution properties such as high viscosity, antishearing, salt resistance, which are attributed to intermolecular hydrophobic interaction.

At present, numerous studies on hydrophobically modified polymers have been devoted to copolymers containing acrylamide (AM) and a hydrophobic monomer, which are commonly the derivatives of acrylamide, propionate and its derivatives[5–9] and are easy to hydrolyze under acidic or basic conditions at high temperature, resulting in the abrupt decrease in the viscosities of the polymer solution. Consequently, their technical applications have been restricted.[10,11] To solve the key problem, we studied the synthesis, the molecular structure characterization and ESEM measurements of the novel terpolymer (PASA) containing AM, butyl styrene (BST), as the hydrophobic monomer and sodium 2-acrylamido-2-methylpropane sulfonate (NaAMPS).[12] In this article, to reveal the viscosification mechanisms of the hydrophobically associating water-soluble polymers in the aqueous solution and brine solution, atomic force microscope (AFM) was used to explore the hydrophobically associating microstructures.

EXPERIMENTAL

Reagents

AM was recrystallized twice from $CHCl_3$, 2-acrylamido-2-methylpropane sulfonate (AMPS) was purchased from Lubrizol Co., and used directly. Butyl styrene was prepared in the laboratory. Other reagents were analytically pure and used without further purification.

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Synthesis of copolymers

The PASA terpolymers were prepared by the micellar free radical copolymerization using sodium dodecyl sulfate (SDS) as the surfactant and potassium persulphate as the initiator. The typical micellar copolymerization process is as follows. A 100 mL, three-necked, round flask was equipped with a mechanical stirrer, and a nitrogen inlet and outlet. Four grams (0.0563 mol) AM, 1.31 g (6.326×10^{-3} mol) AMPS, 47.79 g distilled water and suitable SDS were added into the reaction flask and NaOH was used to control the PH value of the reaction solution. The mixture was stirred for 15 min, and then 0.25 g (1.566×10^{-3} mol) butyl styrene (BST) was added into the reaction flask. The flask was purged with N_2 for half an hour until a clear homogeneous mixture was observed. The solution was heated to 50°C and the initiator then was added. The polymerization proceeded for 12 h, after which the reaction mixture was diluted with 10 volumes of distilled water, followed by precipitation into two volumes of reagent-grade acetone while stirring. The polymers were washed with acetone twice and extracted with ethanol for 2 days to remove all traces of water, surfactant, residual monomers, and initiator. Finally, the polymers recovered by filtration were dried under reduced pressure at 50°C for 3 days.

The copolymer of NaAMPS with AM was synthesized and purified under the same experimental conditions as mentioned earlier.

Elemental analysis

The elemental analysis of the polymers was conducted by CARLO ESRA-1106 elemental analyzer (Italy) to determine carbon, nitrogen, and sulfur content. The molar compositions of P(AM-NaAMPS) and PASA used in this study were obtained by the elemental analysis of the carbon, nitrogen, and sulfur content, which are AM : NaAMPS = 84.27 : 15.73 and AM : NaAMPS : BST = 82.62 : 14.58 : 2.8, respectively.[12]

UV spectral analysis

The UV spectrum was obtained with a UV-240 spectrophotometer (Shimadzu, Japan). The purified PASA polymer was dissolved in pure water, and the polymer concentration was 0.1 g dL^{-1}.

FTIR

The FTIR spectroscopy was done with a NICOLET-560 FTIR spectrophotometer (USA), whose resolution capacity was 1 cm^{-1} and scanning number was 32. The KBr pellets were prepared with the purified polymer sample.

^{1}H NMR

The purified PASA copolymer solution in D_2O was studied at room temperature by a 400 MHz INOVA-400 instrument (America Varian Company, USA) to determine whether butyl styrene hydrophobic units are incorporated into the polymer molecules.

Solution viscosity measurement

Polymer solutions were prepared by dissolving the purified polymer in the distilled water or NaCl aqueous solution. The apparent viscosities of the polymer solutions were measured with a Brookfield DVIII R27112E viscometer, at a temperature of 25°C and the shear rate of 6 s^{-1}.

Atomic force microscopic measurement

The atomic force micrographs were obtained from SPA400 AFM made from (Seiko, Japan), and all measurements were performed in tapping mode. All samples were covered on the mica flakes and dried naturally.

RESULTS AND DISCUSSION

Molecular structure characterization

The characteristic UV absorption peak at 230 nm attributed to the phenyl group proves that butyl styrene hydrophobic units are incorporated into the polymer molecules.

The characteristic FTIR absorption peaks of PASA are as follows: —NH stretch, 3433 cm^{-1}; C═O stretch, 1647 cm^{-1}; —CH_3, —CH_2, —CH stretch, 2928cm^{-1}, 2863cm^{-1}, 2787cm^{-1}; —CH_3, —CH_2—, —CH bending, 1455 cm^{-1}, 1354 cm^{-1}, 1325 cm^{-1}; —C═C— in

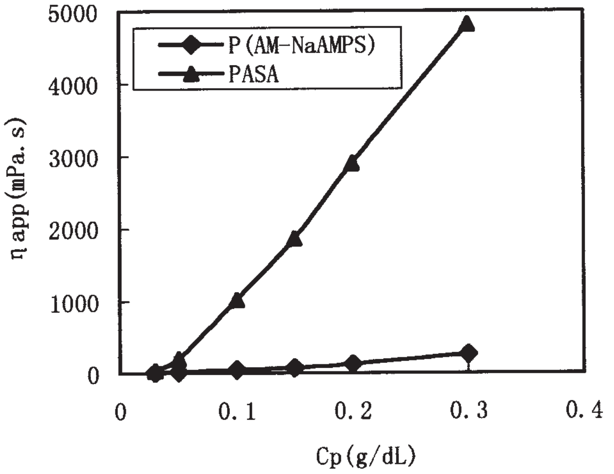


Figure 1 Effect of polymer concentration on the apparent viscosity of copolymer aqueous solution.

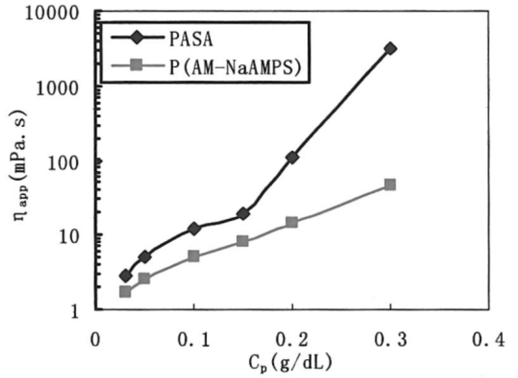


Figure 2 Effect of polymer concentration on the apparent viscosity of copolymer in 0.256 mol L^{-1} NaCl solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

phenyl stretch, 1647 cm^{-1} (overlap with C—O), 1455 cm^{-1} (overlap with —CH_3, —CH_2— bending); —SO_3^-: 1205 cm^{-1}, 1120 cm^{-1}, 1041 cm^{-1}, 634 cm^{-1}.

All the resonances of protons of PASA are as follows: 4H(—CH of phenyl), δ 7.028–7.787 ppm; 2H(—CH_2 of butyl styrene main-chain), δ 2.105 ppm; 1H(—CH of butyl styrene main-chain), δ 2.772 ppm; 6H(—CH_3 of NaAMPS side chain), δ 1.674 ppm; 2H(—CH_2 of AMPS side chain), δ 3.439 ppm; 2H(—CH_2 of NaAMPS main-chain), δ 1.781 ppm; 1H(—CH of AMPS main chain), δ 2.355 ppm; 2H(—CH_2 of AM main chain), δ 1.500 ppm; 1H(—CH of AM main chain), δ 2.246 ppm; H(—NH_2 of AM side chain and—NH of AMPS side chain), δ 4.716–4.967 ppm.

Effects of copolymer concentration on the viscosity

Figures 1 and 2 show increasing apparent viscosities with the increase in polymer concentrations for PASA with the hydrophobic monomer of BST and P(AM-NaAMPS) without BST, in the aqueous and 0.256 mol L^{-1} NaCl solution, respectively. A dramatic increase in solution viscosity with increasing polymer concentration is clearly exhibited above 0.05 g dL^{-1} for PASA in Figure 1, indicating that the critical association concentration of the polymer is about 0.05 g dL^{-1}. For comparison, the concentration dependence of the viscosity for poly(AM-NaAMPS) is also shown in Figure 1, but the critical concentration (C*) of poly(AM-NaAMPS) is not observed in the concentration range investigated. The remarkable increase in the apparent viscosity of the PASA polymer solution is attributed to the strong intermolecular associations. The same concentration effect was observed for the brine solution of polymers, and the critical concentration of PASA increases because of the ionic shielding on —SO_3^- groups along the polymer chains.

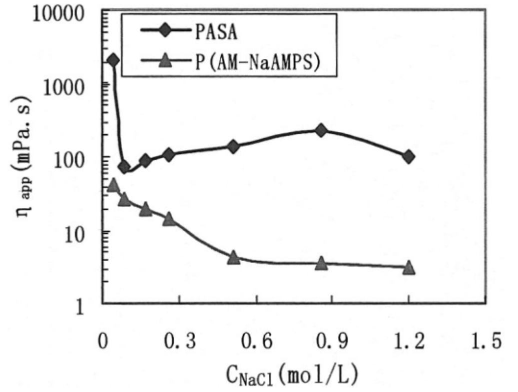


Figure 3 Effect of NaCl concentration on apparent viscosity of copolymer brine solution. Copolymer concentration: 0.2 g dL^{-1} PASA; 0.2 g dL^{-1} P(AM-NaAMPS). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

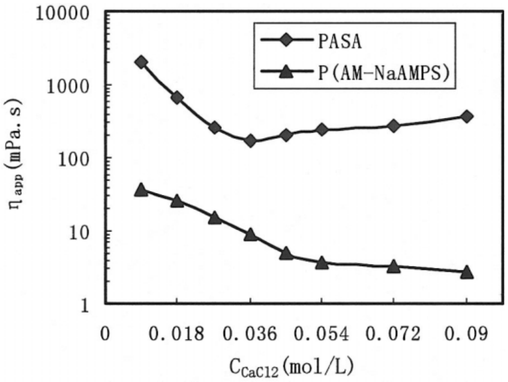


Figure 4 Effects of $CaCl_2$ concentration on apparent viscosity of copolymer brine solution. Copolymer concentration: 0.2g/dL PASA; 0.2g/dL P(AM-NaAMPS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

Effects of electrolytes on the viscosity

The effects of salt on solution viscosity for PASA and P(AM-NaAMPS) were shown in Figure 3. The solution

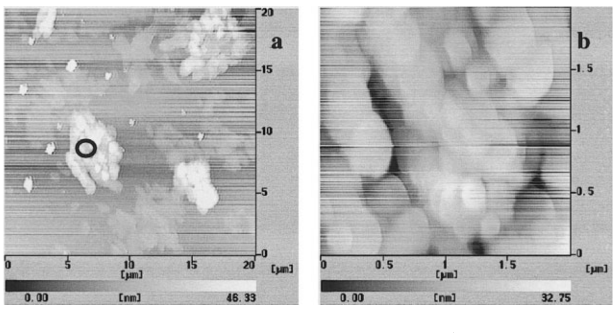


Figure 5 The AFM images of 0.03 g dL^{-1} PASA aqueous solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

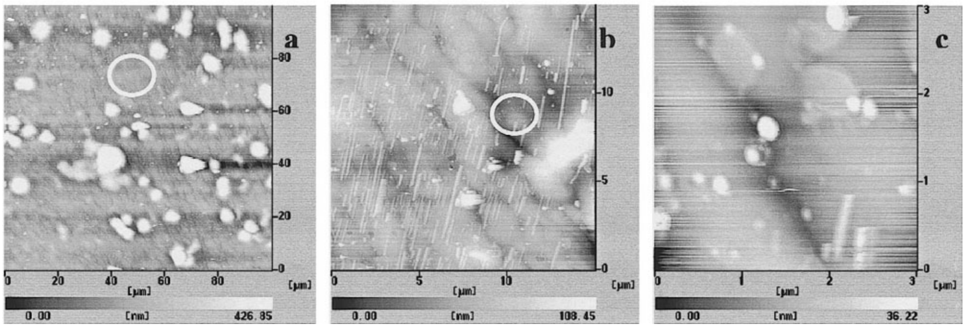


Figure 6 The AFM images of 0.05 g dL^{-1} PASA aqueous solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

viscosity of PASA decreases with the increase in NaCl concentration in the range of 0.0428–0.0855 mol L^{-1} because of charge shielding of repulsive ionic interactions along the polymer chain. However, in the range of 0.0855–0.855 mol L^{-1}, the shielding effect tends to reach equilibration, and with an increase in salt concentration, the polarity of solution induced by electrolytes increases, resulting in the reinforced intermolecular association of the hydrophobic groups and the good salt-thickening behavior of the polymer solution. When the salt concentration increases continually, the hydrophobic microstructures turn more compact, and then condensed aggregates associate with each other to form larger aggregates, resulting in the visible phase separation and the decrease in the apparent viscosity. P(AM-NaAMPS) behaves differently from the PASA polymer, and shows the conventional polyelectrolyte behavior because of the shielding of charges, leading to the abrupt reduction of viscosity of Poly(AM-NaAMPS) in the brine solution. In Figure 4, the similar polyelectrolyte effect is observed for P(AM-NaAMPS) with the $CaCl_2$ concentration of 0–0.09 mol L^{-1}; with increasing $CaCl_2$ concentration, the solution viscosity of PASA first decreases below 0.036 mol L^{-1} $CaCl_2$, and then increases. The results show that the electrostatic shielding effect of $CaCl_2$ is stronger than that of NaCl because of bivalent Ca^{2+}.

The associating morphologies of polymer in aqueous solutions

0.03 g dL^{-1} PASA: Figures 5(a) and 5(b) shows aggregation morphologies of 0.03 g dL^{-1} PASA aqueous solution. hydrophobic aggregates with different sizes are observed in Figure 5(a), but the network structures spanned in the whole solution are not formed, resulting in the viscosity of 42 mPa s of 0.03 g dL^{-1} PASA solution. As seen in Figure 5(b), the amplified aggregate consists of ellipsoid-like clusters.

0.05 g dL^{-1} PASA: As observed in Figures 6(a) and 6(b), with increasing polymer concentration from 0.03 to 0.05 g dL^{-1}, the aggregate morphologies change from separated aggregates to continuous network distributed in the aqueous solution, leading to the rapid increase in viscosity from 42 to 203 mPa s. On the other hand, independent column-like, sphere-like aggregates are also observed in Figures 6(b) and 6(c).

0.1 g dL^{-1} PASA: Figure 7 shows associative morphologies of 0.1 g dL^{-1} PASA aqueous solution. The integrated three-dimensional networks are formed because of the intermolecular hydrophobic association, and the diameter of network bones is about 5 μm, compared with the morphology of 0.05 g dL^{-1} PASA solution, the network bones become bigger and more compact, and there are almost no separated aggregates.

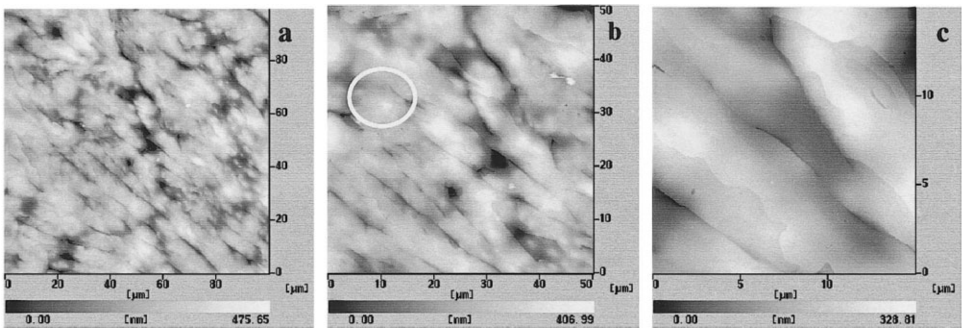


Figure 7 The AFM images of 0.1 g dL^{-1} PASA aqueous solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

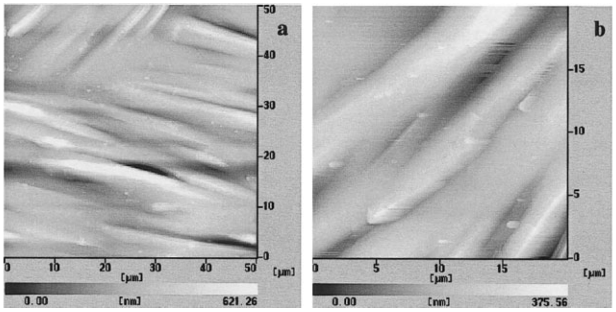


Figure 8 The AFM images of 0.23 g dL^{-1} PASA aqueous solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

0.23 g dL^{-1} PASA: As shown in Figures 8(a) and 8(b), Compared with Figure 7, network bones of 0.23 g dL^{-1} PASA become apparently much bigger and more compact, and small amounts of compact separated aggregates were observed. The results show that on increasing the polymer concentration, the intermolecular associations are reinforced, charge-charge repulsions act to expand the polymer molecules, and are not sufficient to disrupt hydrophobic interactions, resulting in the dramatical increase in viscosity. With the increase in polymer concentration from 0.1 to 0.23 g dL^{-1}, the solution viscosity increases abruptly from 1020 to 3400 mPa s.

0.3 g dL^{-1} PASA: Figure 9 shows the AFM morphologies of 0.3 g dL^{-1} PASA aqueous solution. Figure 9(b) exhibits the morphologies of amplified network bones. As observed in Figure 9(c), The PASA molecule chains aggregate together via intermolecular hydrophobic association and form block-like aggregates, which connect each other to form string-like network bones. The results of AFM measurements suggest that with increasing the polymer concentration in the range of 0.05–0.3 g dL^{-1}, the intermolecular hydrophobic association is reinforced, and the network structures of the polymer become much more huge and condensed, which lead to the improvement of the apparent viscosity from 203 mPa s at C_p = 0.05 g dL^{-1} to 4817 mPa s at C_p = 0.3 g dL^{-1}.

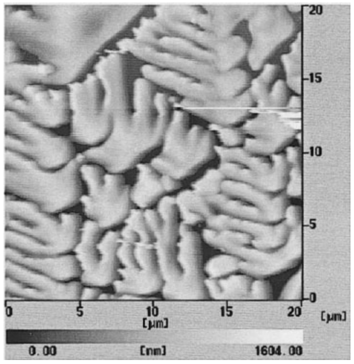


Figure 10 The AFM images of 0.513 mol L^{-1} NaCl salt solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

Influence of added NaCl on the associating morphologies of the polymer

Figure 10 shows AFM images of 0.513 mol L^{-1} NaCl solution with no polymer. Typical salt crystal structures are observed in the images. As shown in Figure 11, for 0.23 g dL^{-1} PASA in 0.256 mol L^{-1} NaCl solution, the continuous networks spanned in the whole solution are collapsed by the addition of salt, lots of condensed aggregates with different sizes are formed and connect with each other to form huge tree-like crystal structures, which are completely different with the polymer hydrophobic associating structures, and salt crystals, resulting in the decrease in the solution viscosity compared with the aqueous solution of the same polymer concentration. Figure 12 shows morphologies of the polymer for 0.3 g dL^{-1} PASA in 0.256 mol L^{-1} NaCl solution. By comparison with Figure 11, with the increase in the polymer concentration in the brine solution, the sizes of aggregates increase obviously, which is the same as the case in the pure water.

As seen in Figure 13, with increasing NaCl concentration from 0.256 to 0.855 mol L^{-1}, the sizes of crystals and tree-like structures formed by crystal increase apparently, indicating that intermolecular associations of hydrophobic groups may be strengthened. The result is in good agreement with the apparent viscosity versus NaCl concentration plot.

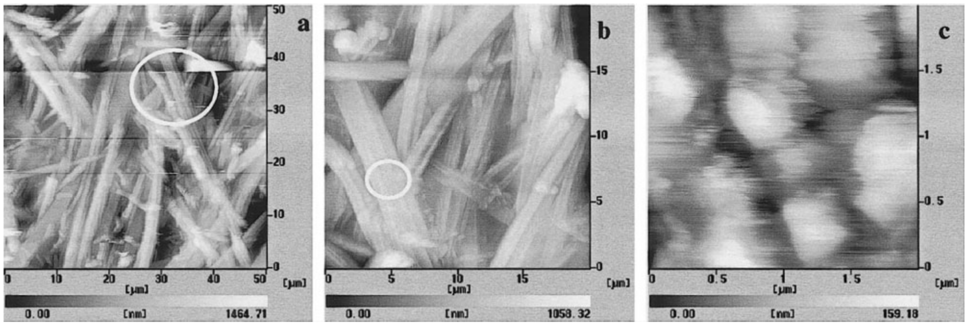


Figure 9 The AFM images of 0.3 g dL^{-1} PASA aqueous solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

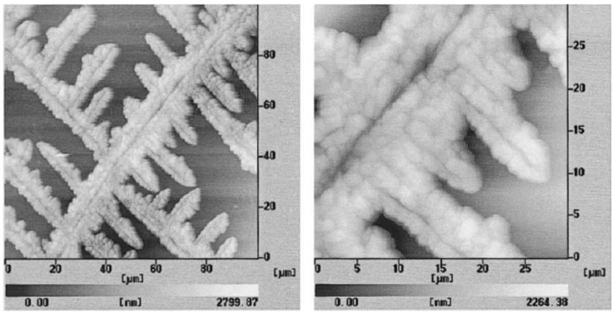


Figure 11 The AFM images of 0. 23 g dL^{-1} PASA in 0.256 mol L^{-1} NaCl aqueous solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

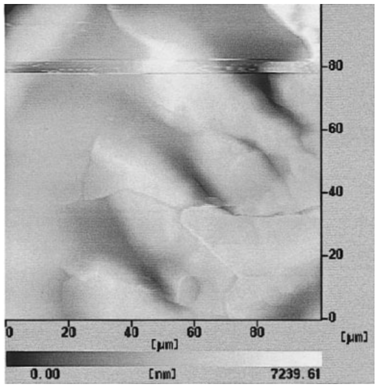
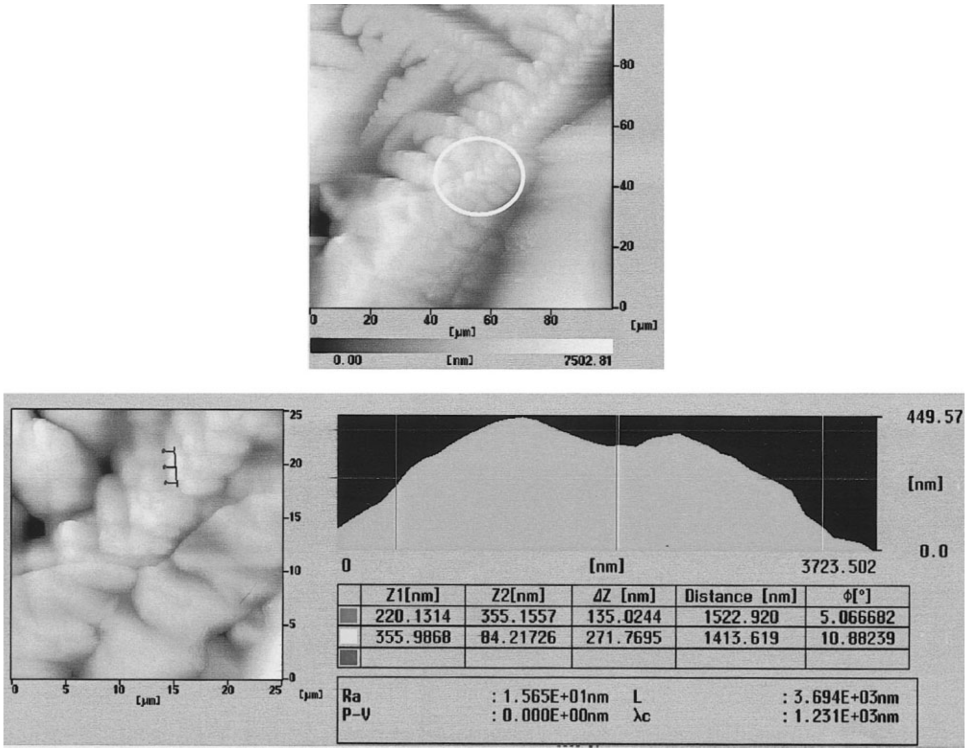


Figure 12 The AFM images of 0.3 g dL^{-1} PASA in 0.256 mol L^{-1} NaCl aqueous solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

CONCLUSIONS

The PASA terpolymer exhibits excellent viscosification properties in the aqueous and brine solution, where the critical association concentration of the polymer is about 0.05 and 0.15 g dL^{-1} respectively, indicative of strong intermolecular association of butyl styrene units. AFM was applied to observe the micromorphology of hydrophobically associating water-soluble polymers solution. The AFM images of continuous network structures of hydrophobically associating water-soluble copolymer in aqueous solution are obtained. AFM measurements show that continuous network structures have been formed in the aqueous solution of 0.05 g dL^{-1} PASA, proving that the PASA molecules have strong hydrophobically associating effects in the aqueous solution and the critical association concentration of the polymer is about 0.05 g dL^{-1} With the increase in PASA concentration, the network structures become much bigger and more condensed. The network structures of PASA are collapsed by the addition of salt, and tree-like crystals are formed, leading to the decrease in the apparent viscosity of PASA solution. However, with the increase in NaCl concentration or polymer concentration, the sizes of crystals increase, which may be caused by the in-



	Z1[nm]	Z2[nm]	ΔZ [nm]	Distance [nm]	ϕ[°]
■	220.1314	355.1557	135.0244	1522.920	5.066682
□	355.9868	84.21726	271.7695	1413.619	10.88239
■					

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Ra      : 1.565E+01nm    L       : 3.694E+03nm
P-V     : 0.000E+00nm    λc      : 1.231E+03nm
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Figure 13 The AFM images of 0. 23g dL^{-1} PASA in 0.855 mol L^{-1} NaCl aqueous solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

creased intermolecular association, resulting in the increase of the apparent viscosity of PASA solution. These results reveal the viscosifying mechanisms of the polymer in the aqueous solution and salt solution, and the relationship of molecular structure, associating structure, and thickening properties of the polymer.

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