

Study on the Morphology of the Hydrophobically-Modified Polyelectrolyte in Aqueous Solution by AFM Measurements

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Abstract: This work focuses on the AFM study of the aggregation morphology and association mechanism of the hydrophobically-association water-soluble polymer P (AM-AA-BPAM) in aqueous solution. It shows that the P (AM-AA-BPAM) molecule chain, which has hydrophobic and hydrophilic ionic groups, forms the "spherical" aggregations as micelles below $0.2 \text{ g} \cdot \text{dL}^{-1}$, and then connect each

other to form the string-like aggregations, which produce large viscosity for the polymer solution. It is also coincident with the FCS, DLS, and viscosity study result. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1175–1178, 2004

Key words: polyelectrolytes; morphology; atomic force microscopy (AFM)

INTRODUCTION

Hydrophobically associating water-soluble polymers contains a small proportion of hydrophobic groups ($\leq 3 \text{ mol } \%$) usually in the form of pendant side chains or terminal groups, which are capable of nonspecific hydrophobic association (intra- or intermolecular) in aqueous solution. These polymers exhibit particular rheological properties such as high viscosity, salt resistance, mechanic stable, shear thinning, and the reversible physical links under shear application, which has prove to be of great technological importance, especially for tertiary oil recovery, latex paint systems, drug delivery, cosmetic formulation, drag reduction, flocculation, biological/medical purposes, etc.^{1–5}

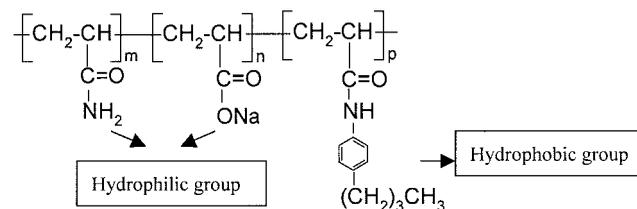
The structure characterization of the hydrophobically associating water-soluble polymers has been a long-term problem.^{6–9} To understand the association mechanism of such polymers, in this article, the hydrophobically modified polyelectrolyte P (AM-AA-BPAM) was synthesized. Viscosity study, fluorescence correlation spectroscopy (FCS), dynamic light scattering (DLS), and atom force microscope (AFM) were used to explore the conformational behaviors, which

are dependent on the electrostatic and hydrophobic interactions.

EXPERIMENTAL

Materials and methods

The copolymers of acrylamide, *N*-(4-butyl) phenylacrylamide, and sodium acrylic acid [abbreviation: P (AM-AA-BPAM)] were synthesized and characterized as the method described before.¹⁰ The composition of the copolymer used in this study is: AM:AA:BPAM = 72.8:26.6:0.61.¹⁰



Viscosity measurements were conducted on a Bohlin CS rheometer with a cone/plate or double-gap concentric cylinder measuring geometry with a cone angle 4° and a diameter 40 mm, and the double-gap device is applicable for low viscous liquids. The measurement temperature was 25°C , and shear rate was 6 s^{-1} unless otherwise indicated. Fluorescence correlation spectroscopy (FCS) was measured by ConfoCor2 FCS microscope. The atom force electron micrographs (AFM) were made using a Digital Instruments Nano-

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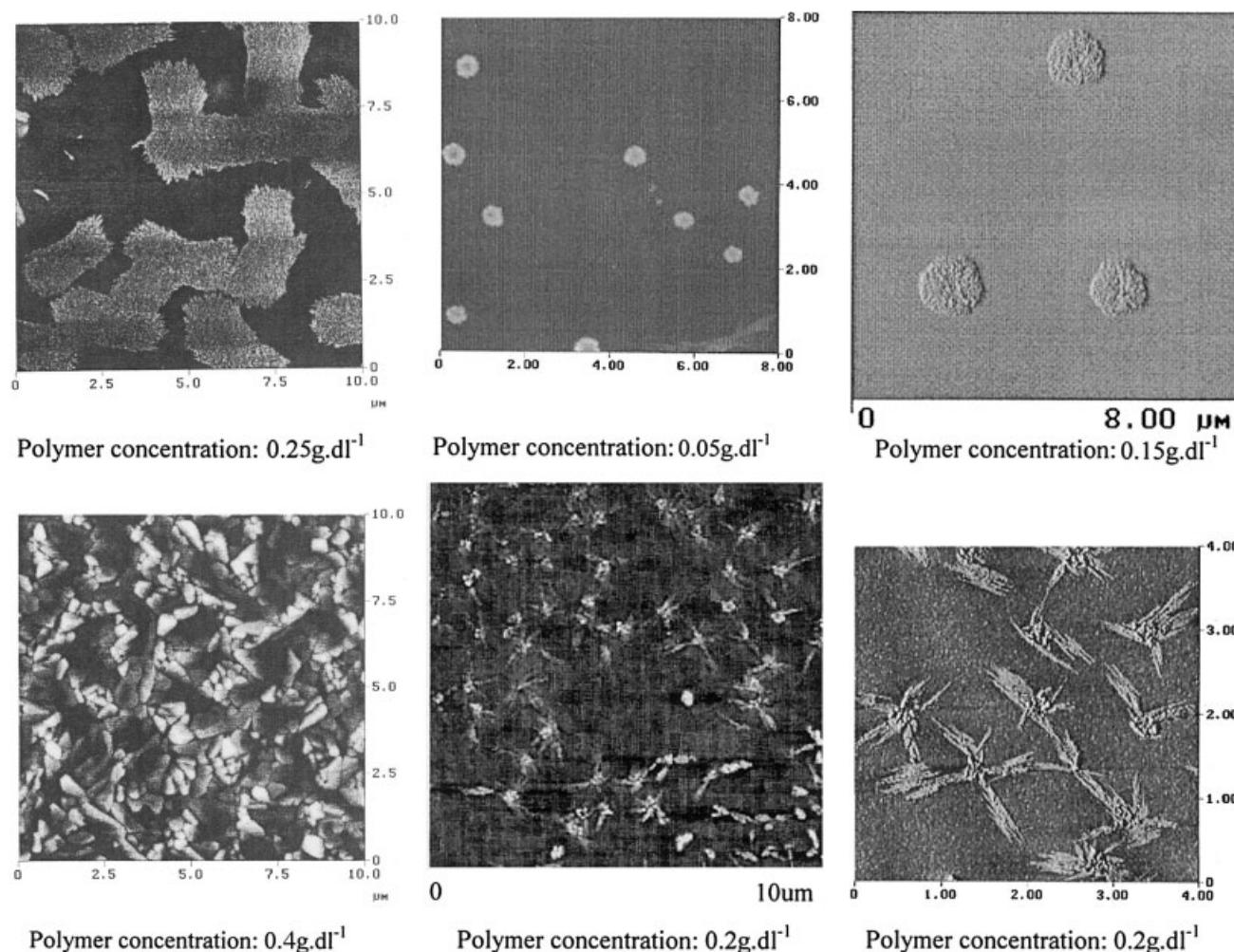


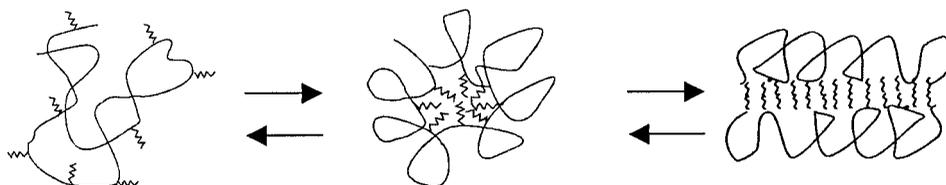
Figure 1 The supramolecule structure of P (AM-AA-BPAM) at different polymer concentrations in 1.5% NaCl solution.

scope III controller with a Dimension 3100 microscope, and all measurements were performed in Tapping Mode. Mica wafers was employed as the substrate for the measurements. Dynamic light scattering (DLS) was performed on an ALV/DLS/SLS-SP 5022F compact goniometer system using an ALV 5000/E correlator and a He-Ne laser ($\lambda = 632.8$ nm). Prior to the light-scattering measurements, the sample solutions were filtered using Teflon filters with a pore size of 3 μm . Effective hydrodynamic diameters were calculated using the algorithm CONTIN and associated software.

RESULTS AND DISCUSSIONS

The aggregation morphology change with the concentration of the polymer solution

Figure 1 shows the change of the supramolecule structure of P (AM-AA-BPAM) in 1.5% NaCl solution with the polymer concentration. With the increase of the polymer concentration, the aggregations becomes increasingly larger from small particles at polymer concentration $0.01 \text{ g} \cdot \text{dl}^{-1}$ to spherical aggregations at the polymer concentration $0.05\text{--}0.15 \text{ g} \cdot \text{dl}^{-1}$, further to string-like aggregations above the polymer concentra-



Scheme 1 The polymer aggregation formation model.

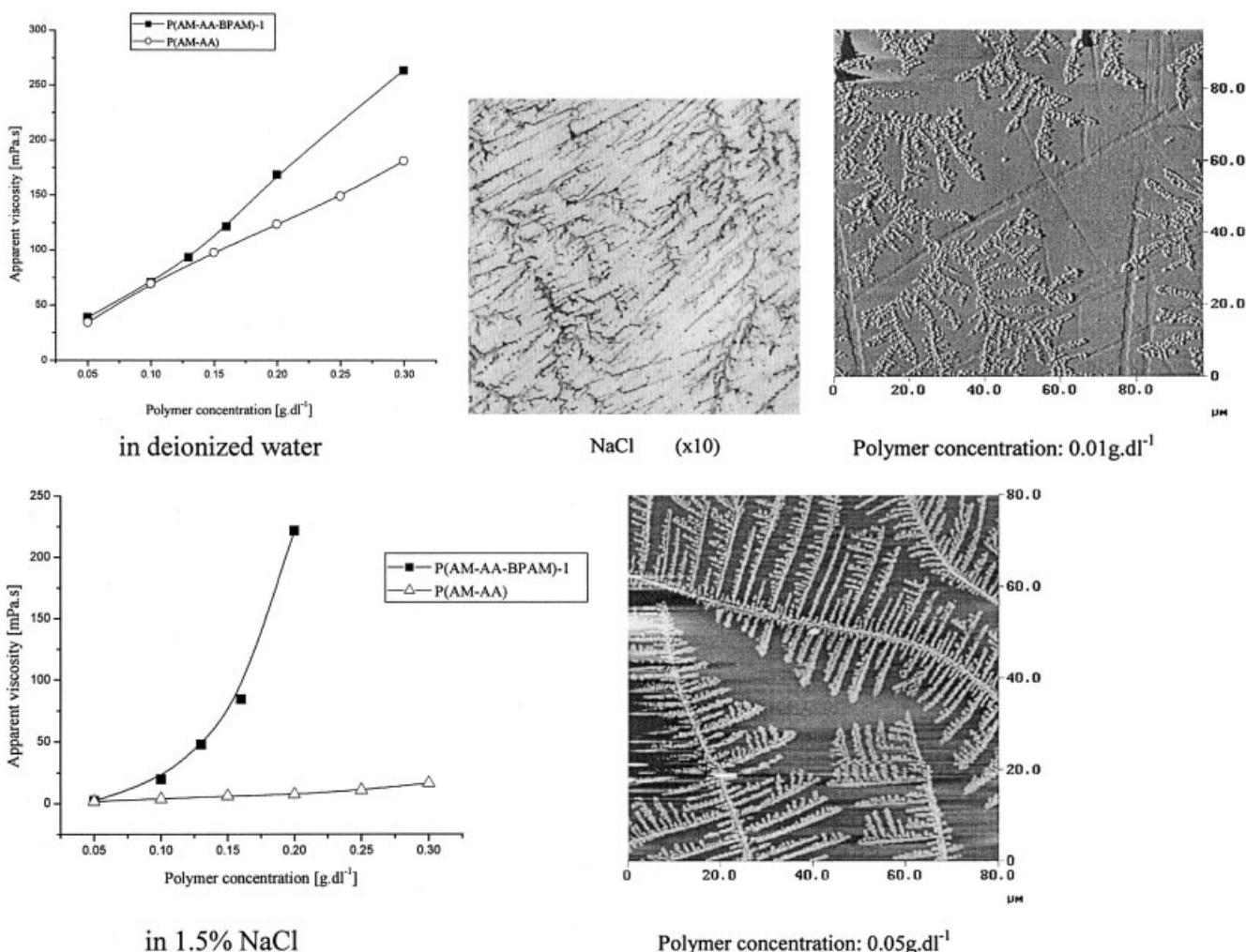


Figure 2 The effect of polymer concentration on the apparent viscosity of P(AM-AA-BPAM) solution.

tion $0.2 \text{ g} \cdot \text{dl}^{-1}$, and to the very regular crystal-like aggregations at $0.4 \text{ g} \cdot \text{dl}^{-1}$. The diameter of the spherical aggregation at $0.05 \text{ g} \cdot \text{dl}^{-1}$ is about 600 nm, and the diameter of the string at $0.2 \text{ g} \cdot \text{dl}^{-1}$ is about 15 nm. In Figure 2, the viscosity–polymer concentration relationship study displays that there is a dramatic increase of viscosity at about the polymer concentration $0.15 \text{ g} \cdot \text{dl}^{-1}$. In Figure 3, FCS measurement also shows that the aggregation starts at about the polymer concentration $0.2 \text{ g} \cdot \text{dl}^{-1}$. So the above research results all show that the critical association concentration of the polymer is $0.2 \text{ g} \cdot \text{dl}^{-1}$. The aggregation morphology is formed by the intermolecular hydrophobic association and the ionic repulsion of the functional groups of the polymer. As shown in Figure 1, the P (AM-AA-BPAM) molecule chain, which has hydrophobic and hydrophilic ionic groups, forms the “spherical” aggregation as micelles, and then connect each other to form the string-like aggregation, which produce large viscosity for the polymer solution. The micelle dimensions are comparable to those measured in solution by DLS. The formation model is displayed in the Scheme 1.

The change of the salt crystal morphology with the concentration of polymer solution

As shown in Figure 4, for the same salt concentration in different concentrations of polymer solution, the

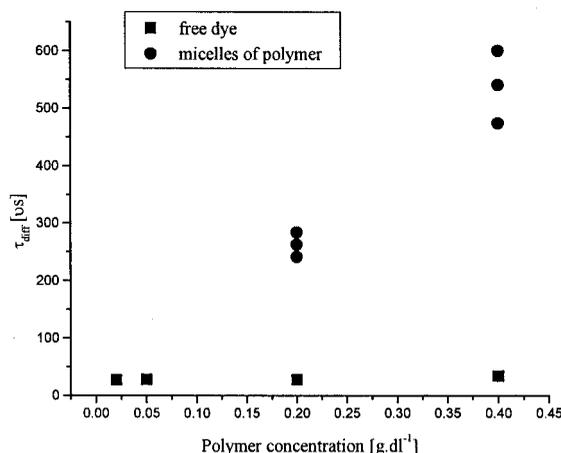
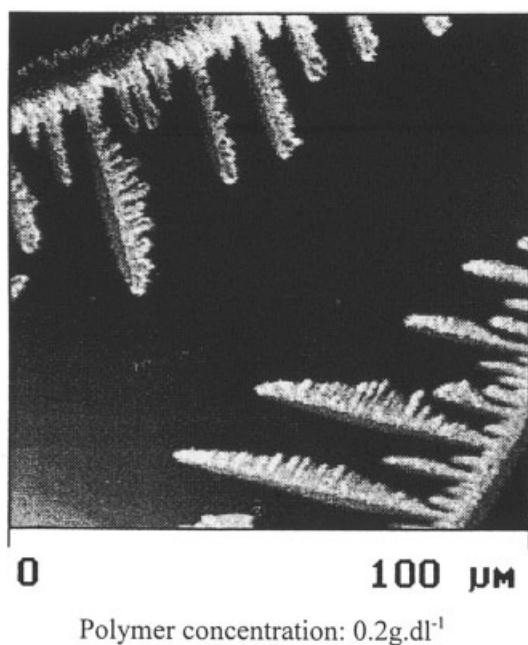
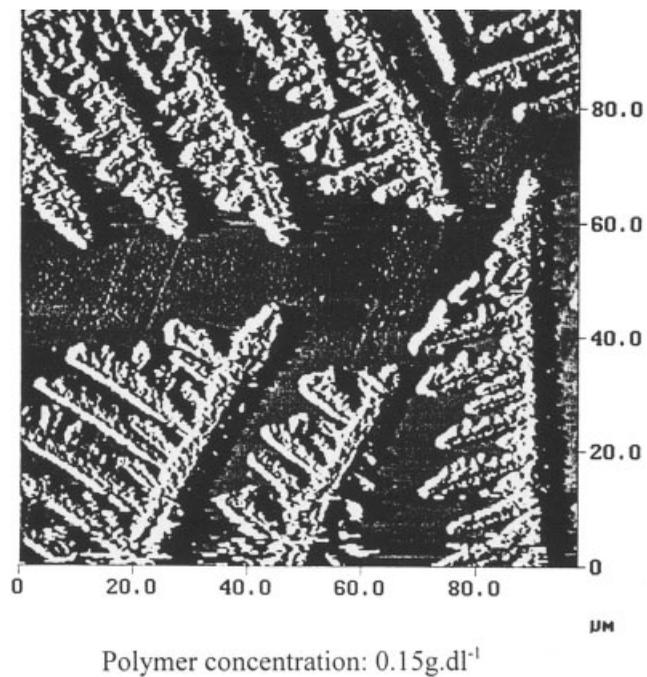


Figure 3 FCS measurement for P(AM-AA-BPAM) in 1.5% NaCl solution.



salt crystals become much bigger and bigger and in more regular arrangement with the increase of polymer concentration. It may be caused by the increased polymer molecule aggregation, which can be regarded as the crystal cores. The salt can form beautiful huge tree-like crystals in the high-concentration polymer solution.

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Figure 4 The NaCl crystal configuration at different polymer concentrations (NaCl concentration: 0.15%).