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ORIGINAL CONTRIBUTION

L. Ye
R. Huang
J. Wu
H. Hoffmann

Synthesis and rheological behavior of poly[acrylamide–acrylic acid–*N*-(4-butyl)phenylacrylamide] hydrophobically modified polyelectrolytes

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L. Ye (✉) · R. Huang · J. Wu
The State Key Laboratory of Polymer Materials Engineering,
Polymer Research Institute
of Sichuan University,
610065 Chengdu, Sichuan,
China
E-mail: sklpme@scu.edu.cn

H. Hoffmann
Physical Chemistry I, NWI,
University of Bayreuth,
95440 Bayreuth,
Germany

Abstract Hydrophobically modified polyelectrolytes were prepared by an aqueous micellar copolymerization technique from acrylamide, *N*-(4-butyl)phenylacrylamide, and a third monomer, sodium acrylate. The amounts of surfactant and anionic monomers used in the synthesis have great effects on the molecular structures and the association behaviors of the resultant polymers. Rheological properties have been studied as a function of polymer concentration, ionic strength, temperature, shear rate, viscoelasticity, and so on. As expected, the copolymers exhibit improved thickening properties owing to the strong synergistic viscosification effects of the ions and the hydrophobic groups of the polymer molecules. Atomic force microscope studies were used to explore the aggregation morphology and association mechanism of such polymers.

Keywords Hydrophobically associating · Polyelectrolytes · Synthesis · Solution behavior

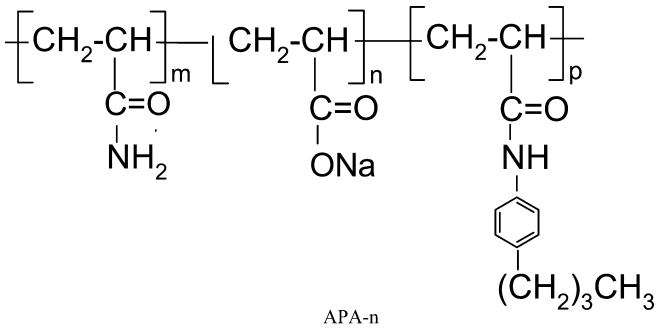
Introduction

Hydrophobically associating water-soluble polymers have become of great interest in recent years. These kinds of polymers contain a small proportion of hydrophobic groups (3 mol% or less) usually in the form of pendant side chains or terminal groups, which are capable of nonspecific hydrophobic association (intramolecular or intermolecular) in aqueous solution. In dilute aqueous solution, the intramolecular associations are dominant. Above a certain polymer concentration (critical association concentration, c^*), the hydrophobes attached to the polymer backbone begin to aggregate and produce a transitory three-dimensional network of polymer chains. Thereby, these polymers exhibit particular rheological properties, such as high viscosity, salt resistance, mechanic stability, shear shinning, the reversible physical links under shear application, which has proved to be of great technological importance especially for tertiary oil recovery, latex paint systems, drug delivery, cosmetic formulation, drag reduction, flocculation, and biological/medical purposes [1, 2, 3, 4].

Although the subject has been studied over several decades, there are still some substantial problems to be solved. It is difficult to prepare copolymers with both high associativity and high water solubility. The degree of hydrophobic substitution has to be kept low, otherwise the polymers become insoluble in water. So c^* cannot be made low enough.

As a consequence, the range of hydrophobic modification is rather limited, and therefore the rheological properties cannot be controlled over a large range.

Hydrophobically modified polyelectrolytes exhibit solution properties combining both the association of the hydrophobes (intramolecular or intermolecular) and the electrostatic expansion of ions in the polymer molecules. These two synergetic interactions may improve the



APA-n

Scheme 1

viscosification of the copolymers [5]. In this work, the polyelectrolyte poly[acrylamide–acrylic acid–*N*-(4-butyl)phenylacrylamide] [P(AM–AA–BPAM)] was synthesized. The rheological properties were investigated in more detailed. Pyrene probe fluorescene, dynamic light scattering, and atom force microscopy (AFM) were used to explore the conformational behaviors which are dependent on the electrostatic and hydrophobic interactions.

Experimental

Materials and synthesis of monomers and polymers

AM, 4-butylaniline, was purchased from Fluka Chemical Co. and was used as received. AA was purified by recrystallization from deionized water.

Monomer synthesis

BPAM was synthesized from the reaction of 4-butylaniline with acryloyl chloride, with triethylamine as the acid receptor, using the method described by McCormick et al. [6]. The crude product was recrystallized twice from ethanol at −25 °C and a white product obtained. The melting point was 92–93 °C. FTIR (KBr): C=C–H 3,079, 3,029 cm^{-1}; N–H 3,283 cm^{-1}; C=C 1,636 cm^{-1}; C=O 1,662 cm^{-1}; phenol 1,608 cm^{-1}; CH_3 2,952, 2,870 cm^{-1}; CH_2 2,927, 2,855 cm^{-1}. ^1H NMR($CDCl_3$): CH_2= 6.3947, 6.2463; =CH 5.7740; NH 7.2239; benzyl–CH_2 7.1266, 7.4601; CH_3 0.9177; CH_3-CH_2 1.3244; CH_3-CH_2-CH_2 1.5782; CH_3-CH_2-CH_2-CH_2- 2.5798.

Polymer synthesis

A micellar polymerization technique was used to prepare polymers using sodium dodecyl sulfate (SDS) as the surfactant and potassium persulfate as the free-radical initiator [6]. The appropriate amount of ionizable monomer (AA) was dissolved in deionized water and the pH was adjusted to 9–10 with NaOH to form the water-soluble sodium salt (sodium acrylate). AM, BPAM, and SDS were added respectively, and stirred under N_2 until a clear solution was observed. The solution was then heated to 50 °C, and the initiator was added. The polymerization was conducted for 12 h. The polymer mixtures were diluted with water and precipitated into acetone and then washed with acetone. The polymer was dried under reduced pressure at 40 °C for 4 h. The polymers (abbreviation APA-*n*, Scheme 1) used in this study are listed in Table 1.

Measurements

Elemental analysis was performed with a Elementar-CHNO-Rapiol to determine the carbon, nitrogen, and hydrogen content. The Fourier transform IR measurement was conducted using a Biorad/Digilab FTS40, and the ^1H NMR measurements were carried out on the BPAM solution in $CDCl_3$ using a Bruker Ac250. UV spectra were obtained with a Spektralphotometer DMR 10. Pyrene fluorescence studies were performed with a Shimadzu RF-5301 PC spectrofluorophotometer (λ_{EX} = 335 nm, I_1 = 373 nm, I_2 = 384 nm). Viscosity measurements and oscillatory rheological measurements were conducted with a Bohlin CS rheometer with a cone/plate or double-gap concentric cylinder measuring geometry with a cone angle of 4° and a diameter of 40 mm. The double-gap device is applicable for low-viscosity liquids. The zero-shear viscosity in dilute solution was measured with a Paar OCR-D oscillating capillary rheometer. The measurement temperature was 25 °C, and shear rate was 6 s^{-1} unless otherwise noted. The atom force electron micrographs were made using a Digital Instruments Nanoscope III controller with a Dimension 3100 microscope, and all measurements were performed in tapping mode. Mica wafers were employed as the substrate for the measurements and the sample was prepared by dip-coating and drying up. Dynamic light scattering studies were performed at 60–120° and the signals were processed with a Brookhaven Instruments BI-2030AT autocorrelator. Effective hydrodynamic diameters were calculated using the algorithm CONTIN and associated software.

Table 1 Synthesis parameters of APA terpolymers

Sample	Acrylamide concentration (mol%)	Acrylic acid concentration (mol%)	*N*-(4-Butyl) phenylacrylamide concentration (mol%)	Monomer concentration (%)	Initiator concentration (mol%)	Sodium dodecyl sulfate concentration (%)	Temperature (°C)
APA-0	75	25	0	8	0.5	0	50
APA-1	84.5	15	0.5	8	0.5	7	50
APA-2	84.5	15	0.5	8	0.5	3.25	50
APA-3	84.5	15	0.5	8	0.5	2.2	50
APA-4	84.5	15	0.5	8	0.5	1.5	50
APA-5	74.5	25	0.5	8	0.5	1.5	50
APA-6	74.5	25	0.5	8	0.5	3.25	50
APA-7	94.5	5	0.5	8	0.5	3.25	50

Table 2 Polymer composition analysis

Sample	Feed composition (mol%) Acrylamide:acrylic acid:*N*-(4-butyl)phenylacrylamide	Polymer composition (mol%)		
		Acrylamide	Acrylic acid	*N*-(4-Butyl)phenylacrylamide
APA-0	75:25	70.7	29.3	0
APA-1	84.5:15:0.5	75.0	24.5	0.5
APA-2	84.5:15:0.5	71.6	27.7	0.69
APA-3	84.5:15:0.5	72.8	26.6	0.61
APA-5	74.5:25:0.5	63.0	36.4	0.6
APA-6	74.5:25:0.5	59.3	40.2	0.45
APA-7	94.5:5:0.5	83.7	15.8	0.56

Results and discussion

Synthesis studies

Polymer composition analysis

UV spectroscopy and elemental analysis were used to determine the polymer composition. The model compound *N*-(4-butyl)phenylamidopropionic acid was synthesized to obtain the Beer–Lambert plot, its absorbance was compared with polymer absorbance, and the BPAM content of the polymers was obtained. The AM and AA contents of the polymers can be obtained from the elemental analysis result. The composition of the polymers is shown in Table 2.

AA effect

The incorporation of ion groups into polymer chains may enhance the solubility of the polymers, and the electrostatic repulsion of the ionic groups results in chain expansion, which may favor the intermolecular associations of hydrophobic groups. This can be called synergistic effects. But too many ionic groups along the polymer chain may be susceptive to the small electrolytes. The extended chain may collapse in the electrolyte solution, and disrupt hydrophobic associations, as shown in Fig. 1. Therefore, it is important to determine the suitable AA content.

SDS effect

The concentration of surfactant used during micellar polymerization can have a significant effect on the resultant hydrophobe-containing polymer, because the length of the hydrophobic blocks in the polymer chains can be determined by adjusting the surfactant-to-hydrophobe concentration ratio (c_{surf}/c_{HM}) [7]. A schematic illustration of the polymer structure under

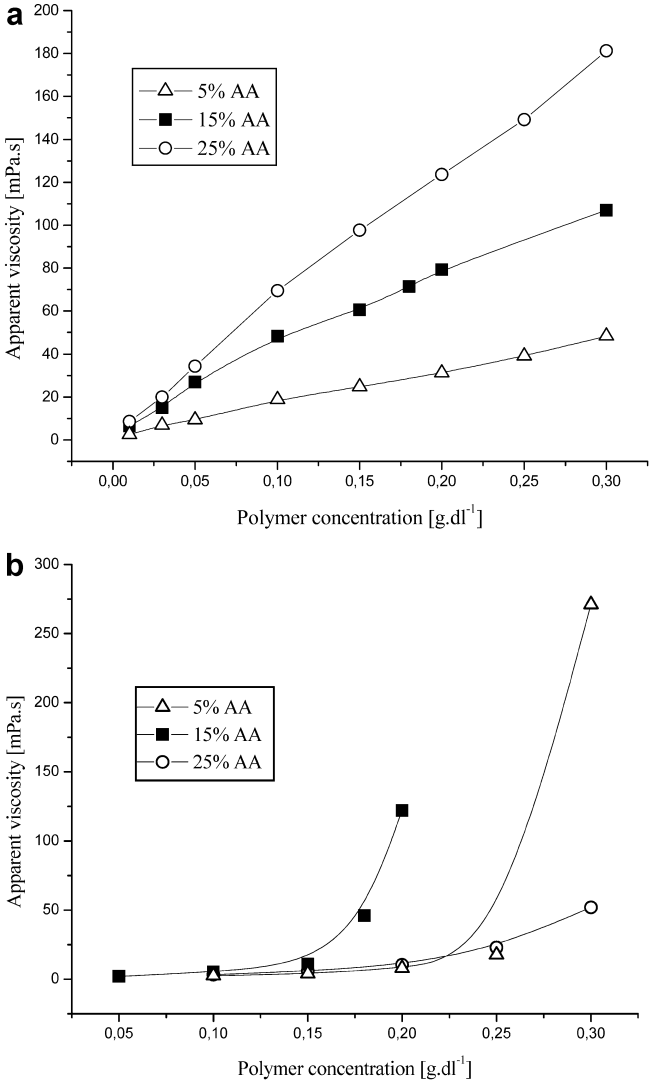


Fig. 1a,b The effect of polymer concentration on the apparent viscosity of the polymer solution for different acrylic acid (*AA*) concentrations used in the synthesis

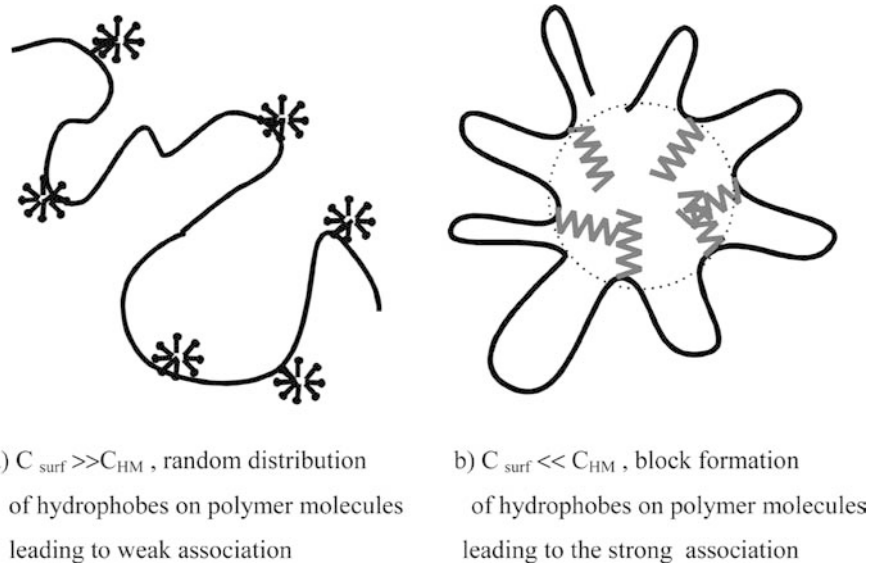


Fig. 2a,b Schematic illustration of the polymer structure under different synthesis conditions

different synthesis conditions is shown in Fig. 2. As shown in Fig. 3, for the polymers of 15% AA content, with the decrease of SDS concentration, the viscosities of the polymers increase, especially in brine solution. And when 1.5% SDS concentration is reached (APA-4), the polymer forms small gels and cannot dissolve in NaCl solution well. During polymer synthesis, the lower the SDS concentration, the more hydrophobic groups in a SDS micelle, the longer the hydrophobe block, and the association of hydrophobic groups is stronger. But the very low concentrations of surfactant result in polymers with poor solubility in brine solution. By increasing the concentration of AA in the polymer, the solubility of the polymer can be enhanced. For the polymer of 25% AA content, the polymer can be soluble in water at 1.5% SDS concentration, and a dramatic increase in solution viscosity was observed at about 0.15 g dl^{-1} It can be seen that there is an optimum concentration of surfactant at which the maximum solution viscosity is attained.

Solution properties

Ionic strength effect

The ionic strength of the polymer solution was found to influence the degree of hydrophobic association and the size of the micellar clusters. Two effects on the solution behavior compete with each other on the addition of salt. It first enhanced the intermolecular association owing to the increased polarity of the solvent. The polymer molecules contained ion groups, and addition of salt shielded the intermolecular repulsion and made the polymer molecules contract. As shown in Fig. 4, for APA-3 and APA-5, the viscosities first increase rapidly owing to the strong hydrophobic intermolecular association. And at high NaCl concentration, the molecules aggregate to small gels and the viscosity drops. For APA-2 and APA-7, the viscosity first decrease with NaCl concentration, and then increases greatly. The hydrophobic intermolecular association predominates after charges of the polymer molecules are all shielded by NaCl. For APA-0 and APA-1, the viscosities decrease with NaCl concentration. This is the typical behavior of polyelectrolytes for APA-0, and the intermolecular association of hydrophobic groups are very weak for APA-1.

Oscillatory-shear experiments were used to explore the viscoelastic characteristics of the polymer solutions in terms of the storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, (ω is the frequency) [8, 9]. Measurements of G' and G'' as a function of frequency at different NaCl concentration for APA-2, APA-3, and APA-5 copolymers are shown in Fig. 5. With the increase in the NaCl concentration, the elasticity of the polymer solution was enhanced. Above 5% NaCl, the system is more elastic than viscous ($G' > G''$).

Temperature effect

The effect of temperature on the viscosity of the polymer solutions is displayed in Fig. 6. For APA-2, APA-3, and APA-7, a sharp decrease in viscosity is observed with increasing temperature. But for APA-5, the viscosity first drops before 40 °C, and then increases to a stable value. The temperature increase

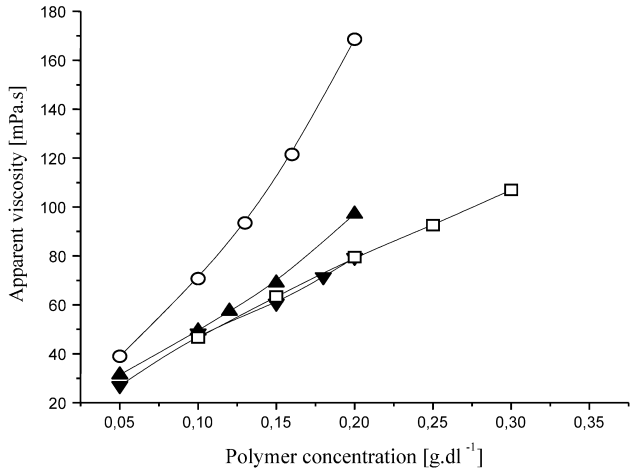


Fig.3a) The effect of SDS concentration used in synthesis on the apparent viscosity of the polymer solution (in deionized water)

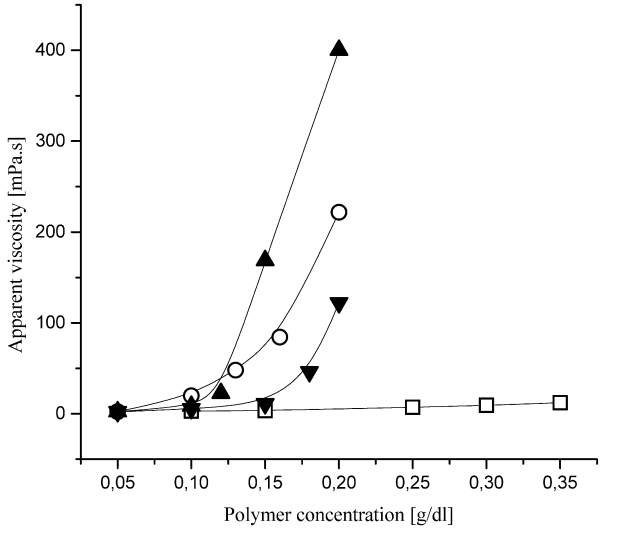


Fig.3b) The effect of SDS concentration used in synthesis on the apparent viscosity of the polymer solution (in 1,5% NaCl solution)

Fig. 3 The effect of sodium dodecyl sulfate (*SDS*) concentration used in the synthesis on the apparent viscosity of the polymer solution **a** in deionized water and **b** in 1.5% NaCl solution

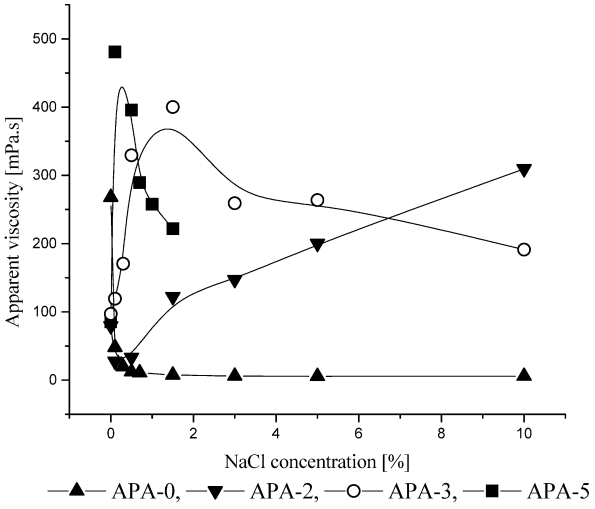


Fig.4a) The effect of NaCl concentration on the apparent viscosity of the polymer solution (Polymer concentration: 0.2g.dl^{-1})

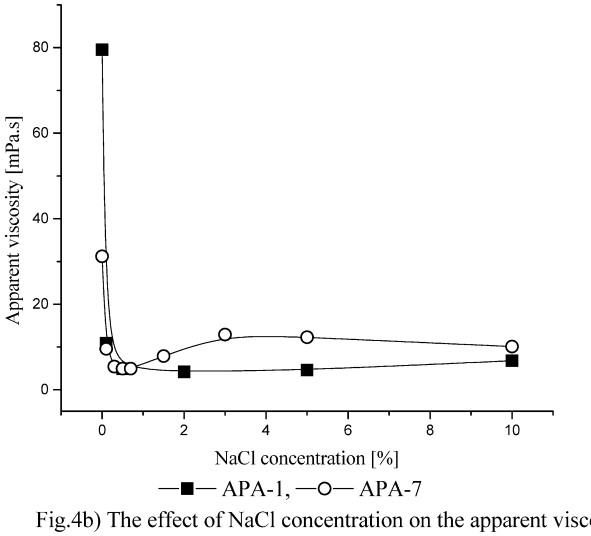


Fig.4b) The effect of NaCl concentration on the apparent viscosity of the polymer solution (Polymer concentration: 0.2g.dl^{-1})

Fig. 4a,b The effect of NaCl concentration on the apparent viscosity of the polymer solution (polymer concentration 0.2 g dl^{-1})

makes the movement of water molecules and hydrophobic groups increase, and the hydration spheres of the hydrophobic groups change a great deal, which are not favored for the interchain association of the copolymers. Hydrophobic hydration is exothermic, while hydrophobe–hydrophobe interaction is endothermic, and the viscosity increases observed upon heating are consistent with an entropy-driven increase in hydrophobic bonding.

Shear rate effect

The apparent viscosity of APA copolymers is shown as a function of increasing then decreasing shear rates in Fig. 7. APA-0 is almost not affected by the shear rate, and can be regarded as a Newtonian fluid. For APA-3 copolymers, their viscosities decrease with increasing shear rates and show pseudoplastic behavior. After removing the shear, the viscosities of these polymers can recover immediately. There is a dynamic equilibrium between intermolecular association and dissociation.

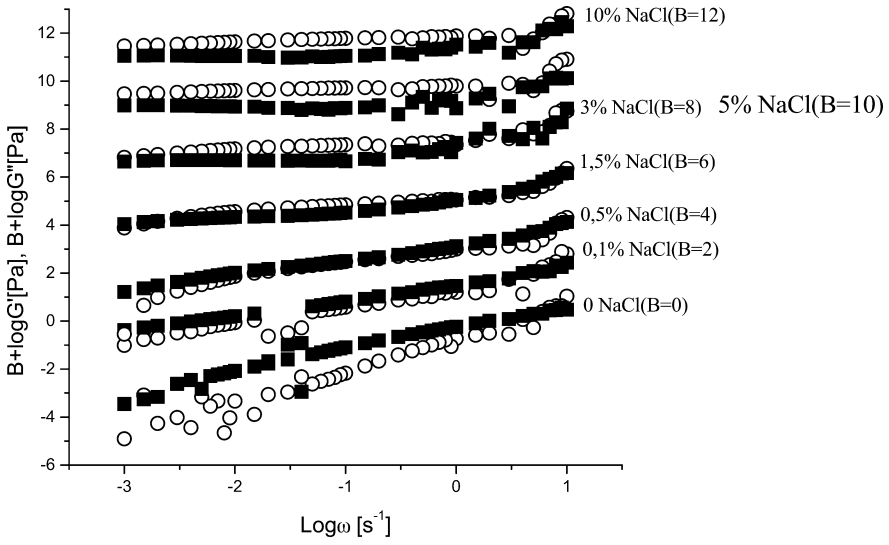


Fig. 5 G' and G'' versus frequency measured for different NaCl concentrations of copolymers (polymer concentration 0.2 g dl^{-1})

Fig.5 G′(○) and G′′(■) versus frequency measured for different NaCl concentration of APA-3 copolymer (Polymer concentration: 0.2g.dl^{-1})

Aging effects

The aging effect for the polymer in 1.5% NaCl solutions at 50 °C is shown in Fig. 8. The apparent viscosities decreased with time. APA-5 (0.15 g dl^{-1}) displayed a slower drop in viscosity than the two others. For APA-3 and APA-5 (0.1 g dl^{-1}), a constant viscosity was reached after 1 month or so. The degradation and reduction of some hydrophobe groups may be the reason for the drop in the viscosity.

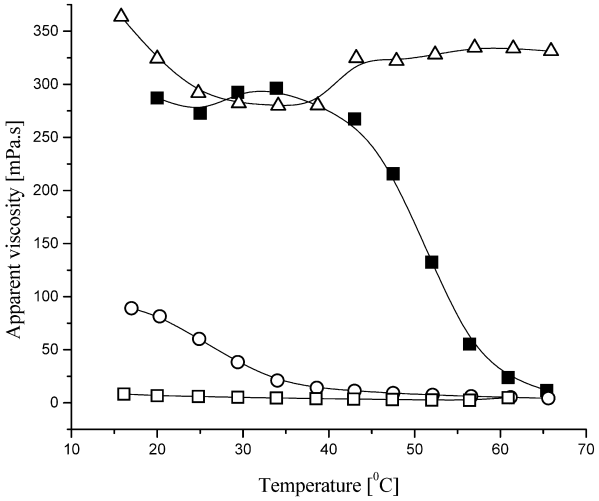


Fig.6 The effect of temperature on the apparent viscosity of the polymer in 1.5% NaCl solutions at 6s^{-1} (Polymer concentration: 0.2g.dl^{-1})
—△— APA-5, —■— APA-3, —○— APA-2, —□— APA-7

Fig. 6 The effect of temperature on the apparent viscosity of the polymer in 1.5% NaCl solution at 6 s^{-1} (polymer concentration 0.2 g dl^{-1})

Pyrene fluorescene studies

Pyrene probe experiments were performed to investigate the aggregation of the polymer molecules. The ratio of the pyrene fluorescence intensity of the first band to that of the third band (I_1/I_3) is related to the polarity of the local enviroment. The plot of I_1/I_3 as a function of polymer concentration for APA-3 in 1.5% NaCl solution is shown in Fig. 9. The I_1/I_3 values decrease with increasing polymer concentration, indicating that the copolymer provides hydrophobic microdomains for the pyrene molecules formed through association of the hydrophobic groups with increasing polymer concentration.

AFM measurements

For the understanding of why the polymer solutions show high viscosoties, the morphology of the polymer in solution was investigated by AFM. The supramolecule structure of APA-3 in NaCl solution is displayed in Fig. 10. For a polymer concentration of 0.2 g dl^{-1} above c^*, there are some stringlike aggregations in solution, and the diameter of each string is about 15 nm, and the

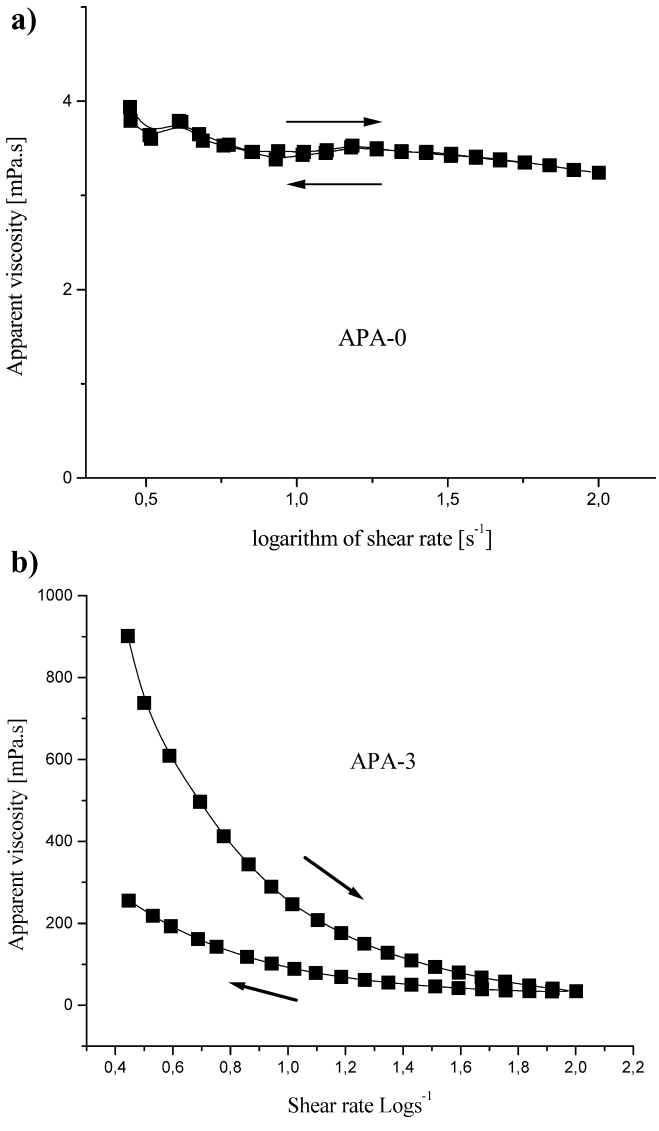


Fig. 7a,b The effect of shear rate on the apparent viscosity of the polymer solution (polymer concentration 0.2 g dl^{-1}, NaCl concentration 1.5%)

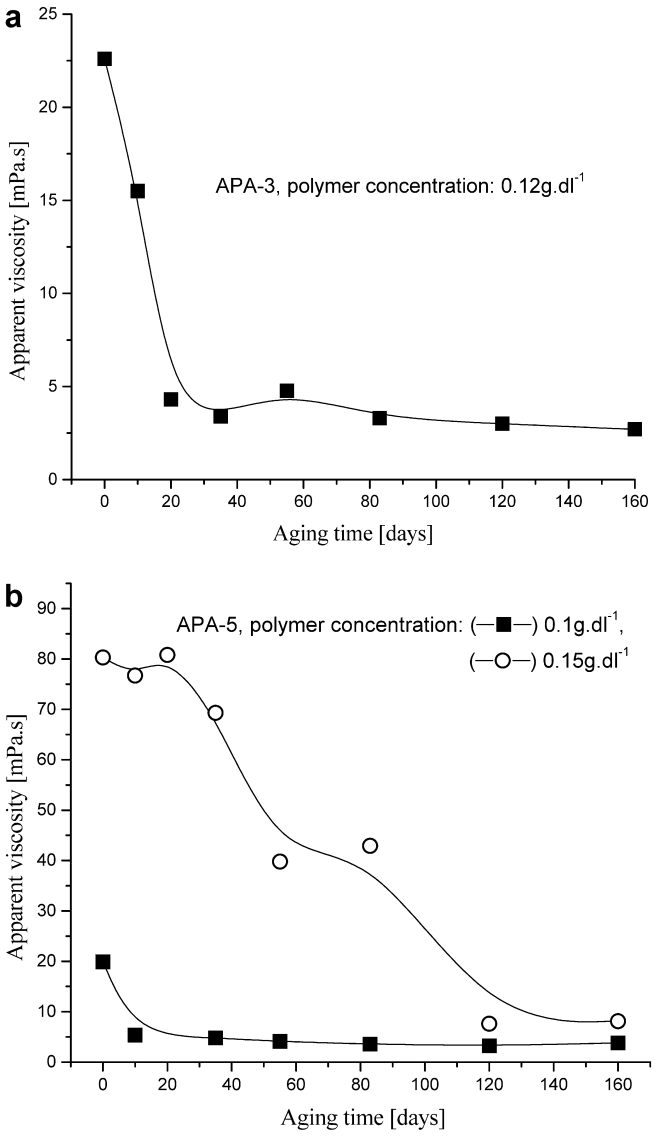


Fig. 8 Aging effect for the copolymers in 1.5% NaCl solution at 50 °C

aggregations are formed by the networks of intermolecular hydrophobic association. For a polymer concentration of 0.05 g dl^{-1}, there are only some spherical aggregations in solution. For a polymer solution without NaCl, no supramolecule aggregations can be observed. According to the computation by statistical mechanics of the polymer configuration, the concentration of the hydrophobic groups in one molecule coil of the polymers is high enough to result in micellelike aggregations being formed. The formation model of the supramolecule structure of hydrophobically modified polyelectrolyte in the presence of salt is exhibited in Fig. 11. The micelle dimensions are comparable to those measured in solution by dynamic light scattering.

Conclusions

The hydrophobically modified polyelectrolytes APA-*n* were prepared by an aqueous micellar copolymerization technique from AM, BPAM, and a third monomer. sodium acrylate. The polymer APA-*n* with both high water solubility and high associativity can be achieved when suitable amounts of surfactant and anionic monomers are used in the synthesis. S tudy of the rheological properties showed that APA-*n* has remarkably improved thickening properties, especially in electrolyte aqueous solution, owing to the strong synergistic effects of the ions and the hydrophobic groups of the polymers.

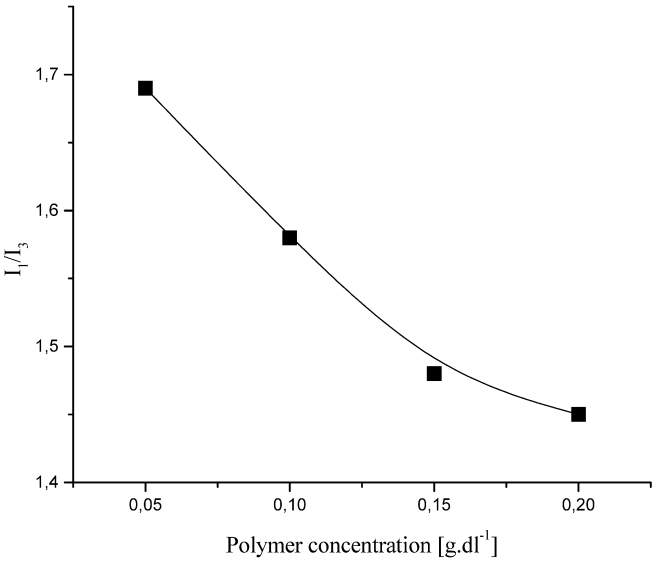


Fig. 9 I_1/I_3 as a function of polymer concentration for APA-3 in 1.5% NaCl solution

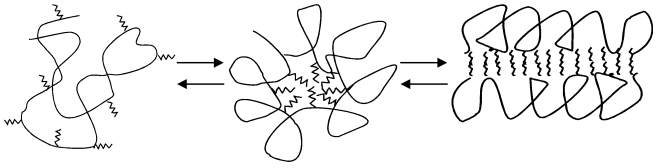
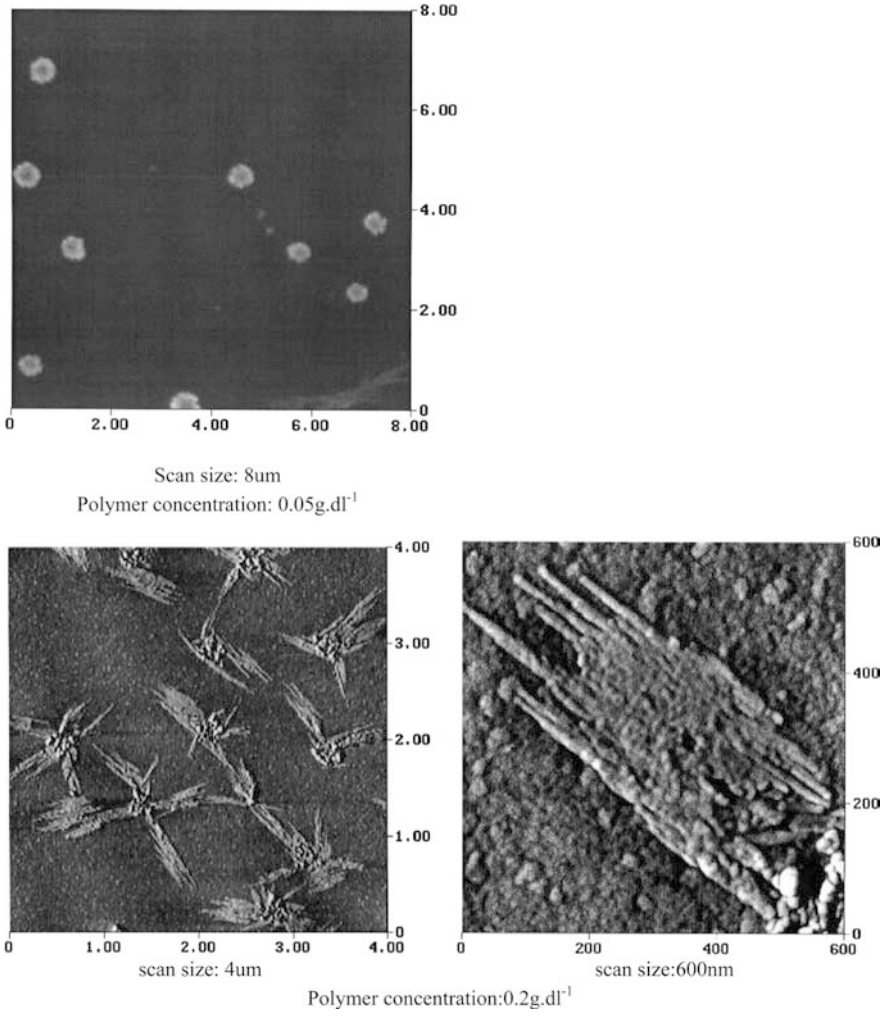


Fig. 11 The supramolecule structure of hydrophobically modified polyelectrolyte in the presence of salt

APA-*n* also exhibits improved long-term heat resistance. The aggregation morphology of APA-*n* was explored by AFM, which showed that the polymer molecules form stringlike aggregations when the critical association concentration of the polymers is reached.

Acknowledgements This work was supported by the Chinese Ph.D. fund (98061027) and the 973 National Key Basic Research (G1999022502) project.

Fig. 10 Atomic force microscope images of APA-3 in 1.5% NaCl solution



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