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Synthesis and solution behavior of hydrophobic association water-soluble polymers containing arylalkyl group

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Abstract

Copolymers of acrylamide (AM) and *N*-arylalkylacrylamide (AAM) have been synthesized by free radical micellar copolymerization in aqueous solution utilizing sodium dodecyl sulphate (SDS) as the surfactant and ammonium persulfate/sodium bisulfite as the redox initiator. Some factors affecting synthesis, such as the amount of AAM, SDS and 2-acrylamide-2-methylpropane sulfate, are described. Solution behaviors of these polymers were studied. The results show that with the increase of AAM content, the intrinsic viscosity decreases, Huggins constant increases and the viscosification effect increase. The addition of NaCl and $CaCl_2$ results an increase of solution viscosity, and the addition of surfactant has a significant and complex effect to solution viscosities. The polymers exhibit good temperature tolerance property, shear-thickening and thixotropy behavior. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrophobic association; Acrylamide copolymers; Arylalkyl group; Micellar copolymerization; Solution behavior; Viscosity

1. Introduction

Hydrophobic association water-soluble polymers are synthetic water-soluble polymers containing a small proportion of hydrophobic groups usually in the form of pendent side chains or terminal groups, which are of increasing interest for a wide variety of industrial applications such as: flocculants, thickening agents in oil recovery, latex paints, cosmetics due to the advantage both of the polyelectrolyte and the hydrophobic groups effect [1–11]. In aqueous solution, the hydrophobic groups aggregate to minimize their exposure to water and thereby form inter- or intra-molecular association resulting in the hydrophobic microdomains. Above a certain concentration (C^*), intermolecular hydrophobic interactions lead to the formation of a three-dimensional network of polymer chain resulting in a rapid increase in the apparent viscosity.

The addition of salt enhances this interaction because of the increased polarity of the solvent, so this kind of polymer exhibit good salt-tolerant property [12–14]. Upon elevated shear action, the polymer network structures are disrupted. However, the associations between the polymer chains reform and the viscosity recover to its initial value. Consequently, irreversible mechanical degradation characteristic of high molecular weight polymers in high shear applications can be avoided [15–17].

Up to now, however, the hydrophobic association water-soluble polymers haven't been applied widely. Many problems appearing in synthesis and performances limit their usage. For example, the critical aggregate concentration (C^*) is little high, and their viscosities below C^* are not high enough to be used in practice. At high temperature, the viscosities will decrease because of the existence of weak bond in polymer chemical structure, which result in the breakage of hydrophobic side chain from polymer backbone [14].

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This kind of polymers can be prepared by chemical modification of precursor polymers or by free radical copolymerization. The precursor polymers mainly include the derivatives of cellulose [18], poly(oxyethylene) [15,19] and poly(acrylic acid) [20]. The latter route concerns essentially copolymers based on acrylamide. The micellar copolymerization is the most convenient way to ensure the solubilization of the hydrophobic monomer within the surfactant micelles and the copolymerization occurring in the water continuous medium [21–24]. The most commonly used hydrophobic monomers are *n*-alkyl series, such as *N*-alkylacrylamide, *n*-alkyl (meth)acrylate, polyethoxy *n*-alkyl (meth)acrylate and vinyl alkylates [7,9,14,16,23–25]. The study on the hydrophobic monomers containing aryl group is seldom [21,26–28], The phenyl groups is well known to induce Van Der Walls interactions due to its plane and polarizable structure, so the incorporation of an aromatic group in hydrophobic groups can stabilize the hydrophobic associations involved by alkyl chain. Furthermore, the phenyl groups can act as spacer increasing the rigidity of the structure [24]. The UV-active property of aryl groups can also be used to characterize the microstructure of the copolymers and the content of hydrophobe in the copolymers [4,28].

In this paper we report the synthesis and solution behavior of the copolymer of acrylamide (AM) and a new kind of hydrophobic monomer (*N*-arylalkylacrylamide, AAM) prepared by free radical micellar copolymerization in the presence of sodium dodecyl sulfate (SDS). The synthesis study was conducted on the effect of the amount of AAM, SDS and ionic monomer. Solution behavior of polymers was examined as function of the content of AAM, polymer concentration, salt, surfactant, temperature and shear. The purpose of this study is to get idea of the effect of the introduction of aryl-group on the solution behavior of copolymers and on the temperature tolerance property.

2. Experimental

2.1. Materials and monomer synthesis

AM was recrystallized twice from $CHCl_3$, 2-acrylamide-2-methylpropane sulfate (AMPS) was obtained from Lubrizol Co. and was recrystallized twice from a mixture of methanol and 2-propanol. AAM were synthesized from the reaction of 4-alkylaniline (purchased from Aldrich Co. and redistilled at 133–134 °C/14 mmHg) with acryloyl chloride (self-produced, vacuum distilled at 30–32 °C/140 mmHg) in *n*-hexane, the crude products were washed with *n*-hexane, then recrystallized from acetone and dried overnight under vacuum at room temperature.

Ammonium persulfate and sodium bisulfite were recrystallized from deionized water respectively. Other analytically pure grade agents were used without further purification.

2.2. Polymer synthesis

The copolymers of acrylamide with *N*-arylalkylamide were prepared by micellar copolymerization [21,22] using SDS as the surfactant and ammonium persulfate/sodium bisulfite as the redox free radical initiator. Each reaction was conducted in a 100-ml, three-necked, round flask equipped with a mechanical stirrer, nitrogen inlet and outlet. AM, SDS and AAM were added respectively into the reaction flask, and then dissolved in deionized water. The mixture was stirred under N_2 until a clear homogeneous mixture was observed. The total monomer concentration in water was constant at 4% (w/w) and the initiator concentration was 0.2% (w/w) relative to the monomer feed. After the addition of initiator, the polymerization was conducted at 30 °C for 12 h followed by dilution of mixtures with water and precipitation into excess acetone. The polymers were washed with acetone and extracted with ethanol for 8 h to remove all traces of water, surfactant and residual monomer before dried under reduced pressure at room temperature for 24 h.

Homopolyacrylamide and terpolymer of AM–AAM–AMPS were prepared under identical experimental conditions except for homopolyacrylamide without the addition of AAM, and for terpolymer with the addition of AMPS (adjusting pH value to 8–9).

The polymers (abbreviation: PABA-*n*) prepared in this study are listed in Table 1.

2.3. Measurements

Stock polymer solutions were prepared by dissolving the dried polymer in deionized water or aqueous salt solution and being gentle shaken on an orbital shaker for at least five days.

Intrinsic viscosities were measured by a 0.6 mm Ubbelohde capillary viscometer at 30.0 ± 0.1 °C. The kinetic energy and shear rate were found to be negligible. The density of solution was thought to be approximately the same as that of pure water. Apparent viscosities were measured using NXE-1 coneplate viscometer and HAAKE RV20N/C20 rotational rheometer (CV20 system, PK45-4.0 spindles). All viscosities were measured at 25 ± 0.1 °C without special statement. Relationship between apparent viscosity and temperature were studied by Brookfield DV III rotational viscometer with UL adapter accessories (temperature range, 20–75 °C, shear rate, 7.68 s^{-1}).

Table 1
Synthesis of PABA polymers

Polymers	The feed of amount of hydrophobic monomer AAM (mol%)	The feed of amount of anionic monomer AMPS (mol%)	SDS (wt.%)	Solubility[a]
PAM	0		3.0	+
PABA-1	0.1		3.0	+
PABA-2	0.2		3.0	+
PABA-3	0.5		3.0	+
PABA-4	0.7		3.0	+
PABA-5	0.9		3.0	−
PABA-6	0.5		6.0	+
PABA-7	0.5		9.0	+
PABA-8	0.5	15	3.0	+

[a] +: soluble; −: insoluble.

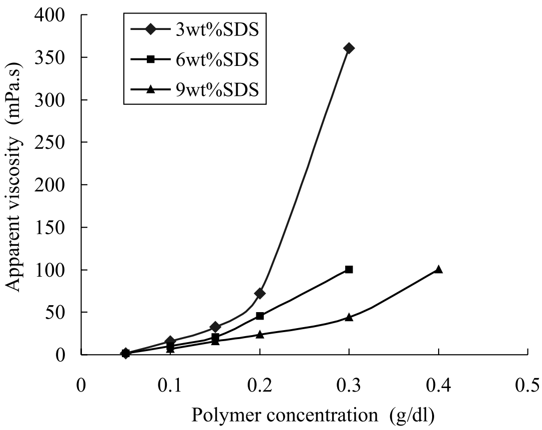

Fig. 1. Relationship of apparent viscosity and polymer concentration with different SDS concentration during polymerization.

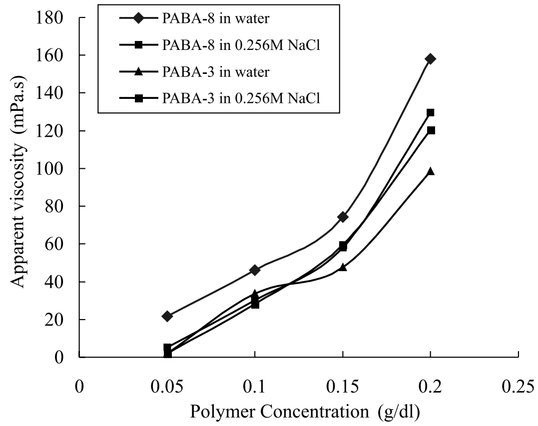

Fig. 2. Effect of polymer concentration on the apparent viscosity of copolymer PABA-3 and terpolymer PABA-8 in both water and 0.256 mol/L NaCl solutions.

3. Results and discussion

3.1. Synthesis studies

3.1.1. Effect of AAM amount

The incorporation of hydrophobic monomer AAM to water-soluble polymers will change the solubility of polymers [29,30]. Less content of AAM cannot result effective intermolecular association, but excessive incorporation will decrease the solubility of polymers in water. As seen in Table 1, when the mole content of AAM reaches to 0.9% (PABA-5), the copolymer cannot be dissolved in water after five day stirring.

3.1.2. Effect of SDS amount

Fig. 1 shows the effect of SDS amount used in the micellar polymerization on the viscosities of copolymer solution. SDS dissolves in water and form micellar, which can solubilize hydrophobic monomer. The number of micelle in solution will affect the hydrophobe number per micelle, control the block length and distribution of the hydrophobic groups in the macromolecules backbone, and consequently influence the viscosification effect [21,26,31]. As shown in Fig. 1, for PABA-3, 3 wt.% SDS was required to achieve maximum viscosity.

3.1.3. Effect of the ionic group

As shown in Fig. 2, 15% mol NaAMPS terpolymer (PABA-8) has a higher viscosity than precursor PABA-3 both in aqueous and 0.256 mol/L NaCl solutions. The incorporation of ionic groups into polymer chains may enhance the solubility of terpolymers, and the electrostatic repulsion of the ionic groups results in chain expansion, which may favor the intermolecular associations of hydrophobic groups. This is called synergistic effects [29,31]. The effect of the amount and the type of ionic groups will be studied in details in a forthcoming research.

3.2. Solution behavior

3.2.1. Effect of AAM content

Dilute solution behavior of polymers were evaluated by intrinsic viscosity, $[\eta]$, and Huggins constant, K_H, and the relationship between polymer concentration and its reduced viscosities. $[\eta]$ and K_H were determined by measuring the viscosities of polymer solution of different concentration. Then Huggins equation, a linear model, was used to fit the data:

$$\frac{\eta_{sp}}{c} = [\eta] + K_H[\eta]^2 c \qquad (1)$$

Table 2
Intrinsic viscosity and Huggins constant of polymers

Sample	AAM content (mol%)	$[\eta]$ (g/dl)	K_H	L_f[a]
PAM	0	6.32	0.5	0.9973
PABA-1	0.1	3.94	1.32	0.9809
PABA-2	0.2	2.76	3.66	0.9784
PABA-3	0.5	2.51	4.25	0.9377
PABA-4	0.7	2.44	4.91	0.9271

[a] L_f is the degree of linear fitting that can show the accuracy of the application of Huggins equation.

where c is the concentration of polymers in g/dl and $[\eta_{sp}]$ is the reduced viscosities.

The introduction of hydrophobic groups will affect η and K_H. Table 2 lists the intrinsic viscosity and Huggins constant obtained by use of Eq. (1). The degree of linear fitting (L_f), which can show the accuracy of the application of Huggins equation, is also listed in the table. The intrinsic viscosities of the copolymers decrease with increasing AAM content. This phenomenon was attributed to the decrease of the molecular weight and to the intramolecular association that leads to the contraction of polymer chains. The Huggins constant increases with increasing AAM content and is bigger than that of common random coil polymers (0.3–0.8). It means that the interactions between the polymer molecular and water, and between different polymers molecules are very strong. The tendency of Huggins constant increased with increasing hydrophobe content may reflect the possibility of intermolecular association, which is consistent with the results of some other researchers [30,32]. As shown in Figs. 3 and 4, at same polymer concentration, apparent viscosity increases with the increase of AAM content (from PAM to PABA-4).

3.2.2. *Effect of polymer concentration*

Figs. 3 and 4 show the concentration dependence of the solution viscosity for polymers with or without hydrophobic composition AAM in aqueous and 0.342 mol/L NaCl solution, respectively. In both cases, almost the same solution behavior was observed. The viscosities of solution increase with increasing polymer concentration. From the curves in both figure, it's also can be seen that the polymer solution viscosities increase dramatically above a certain concentration (C^*), which correspond to the formation of three-dimensional network in solution. And after C^*, the more the content of hydrophobic monomer in polymer structure, the higher the viscosities of solutions can be observed.

3.2.3. *Effect of additives on the viscosities*

3.2.3.1. NaCl and $CaCl_2$. The effect of salt on the viscosities of the polymer solution was investigated using PABA-1 (Fig. 5). As shown in the figure, the viscosities of polymer solution increase with the increase of electrolyte concentration in the range of 0–0.6 mol/L. These increases were attributed to the increase of polarity of solvent induced by electrolytes. The tendency of the intermolecular association and the formation of dimensional network were reinforced. So these polymers exhibit good salt-resistant performance. Similar result can be obtained by comparing Fig. 3 with Fig. 4.

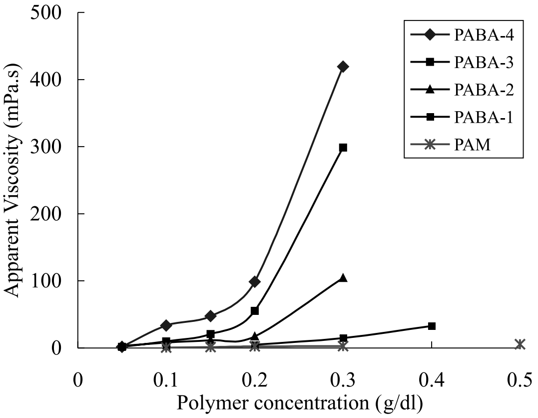

Fig. 3. Effect of polymer concentration on the apparent viscosity of aqueous solution (25 °C, shear rate 19.2 s^{-1}).

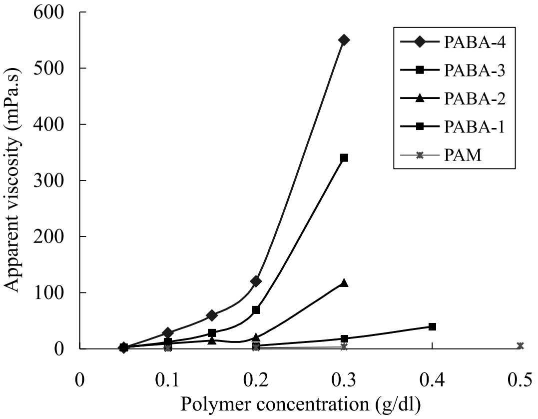

Fig. 4. Effect of polymer concentration on the apparent viscosity of 0.342 mol/L NaCl solution (25 °C, shear rate 19.2 s^{-1}).

3.2.3.2. Surfactants. Fig. 6 shows the effect of ionic surfactant, SDS, on the solution viscosities. The curve in the figure can be divided into three regions with regards to SDS concentration: (1) from 0–0.75 wt.%, viscosity increases remarkably with increasing SDS concentration and reaches a maximum value, 11.75 mPa s; (2) further addition of SDS (to 2.5 wt.%) make the viscosities to decrease to even less than un-added one; (3) after 2.5 wt.%, the viscosities are almost not affected by the ad-

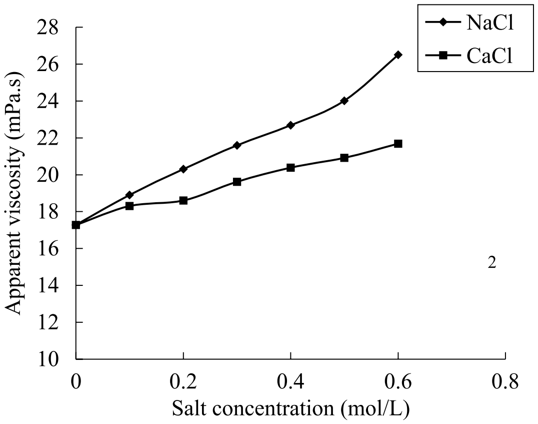

Fig. 5. Effect of ionic strength of NaCl and $CaCl_2$ solution on the apparent viscosity of 0.2 g/dl PABA-2 aqueous solution (25 °C, shear rate 19.2 s^{-1}).

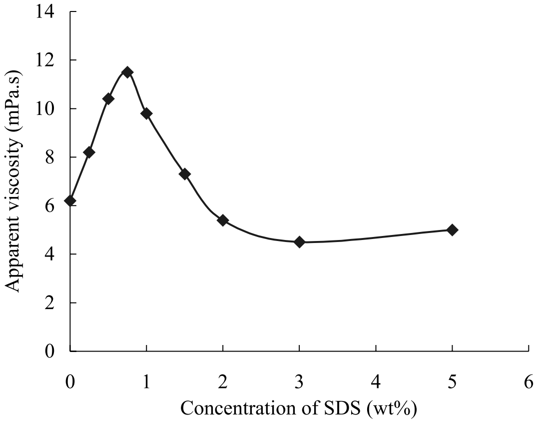

Fig. 6. Effect of surfactant concentration on the apparent viscosity of 0.25 g/dl PABA-1 aqueous solution (25 °C, shear rate 9.60 s^{-1}).

dition of SDS. Surfactant molecules can adsorb to the hydrophobic moieties of polymer, which increase the hydrophobicity of polymer chains resulting more intermolecular association. Furthermore, with the increase of SDS, the formation of micelle will link the hydrophobic groups of different polymer molecular and result in dimensional network, so the viscosities increase. However, further addition of SDS just increases the number of surfactant micelle in the solution. These micelles cannot solubilize more than one hydrophobic group, so the crosslinking are destroyed and the viscosities decrease.

3.2.4. *Effect of temperature on the viscosities*

Fig. 7 shows the apparent viscosity versus temperature for PABA-3 and PABA-4 respectively. For PABA-4, its solution viscosity decreases slowly from 79.32 mPa.s (20 °C) to 24.06 mPa.s (75 °C). But for PABA-3, with the increase of temperature, the viscosities of solution increase slowly (20–40 °C), then drop down a little and keep unchanged, and decrease after 55 °C. The viscosity retention ratio of PABA-3 is 59.53%. It's well known that hydrophobic hydration is exothermic while hydrophobe–hydrophobe interaction is endothermic [33,34]. The results indicate that the interaction of interchain association of polymers is favored by increasing the temperature at least to an extent. A higher temperature will destroy the "iceberg structure" around the hydrophobic groups, and quicken the molecular movement, weaken the hydrophobic association effect, and make the viscosity decrease. The good temperature retention may be due to the increase of rigidity of polymer chain introduced by aryl group.

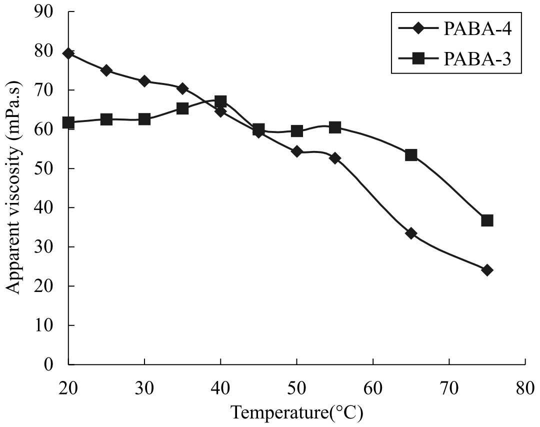

Fig. 7. Effect of temperature on the apparent viscosity of polymer aqueous solution (polymer concentration: 0.2 g/dl, shear rate 7.68 s^{-1}).

3.2.5. *Effect of shear*

The effects of shear on polymer solution behavior were studied by measuring the time-dependent relationship of PABA-3 at different shear rate in 25 °C. As shown in Fig. 8, at low shear rate (5, 10, 20 s^{-1}), the viscosities of polymer increase with increasing time (shear-thickening) and then drop down gradually. But at high shear rate (100 s^{-1}), the viscosities decrease quickly. In this study, PABA copolymers exhibit thixotropy behavior, and the viscosities will recover gradually after stopping the shear. The time-dependent relationship demonstrates that the association and disassociation are exit simultaneously in the solution, and these two effects are not finished instantaneously.

The model put forward by Ballard can explain these phenomena [35]. Under certain shear rate, the polymer molecular will experience the transition of the intramolecular association to intermolecular association, which is favor to the physical crosslinking of different chains.

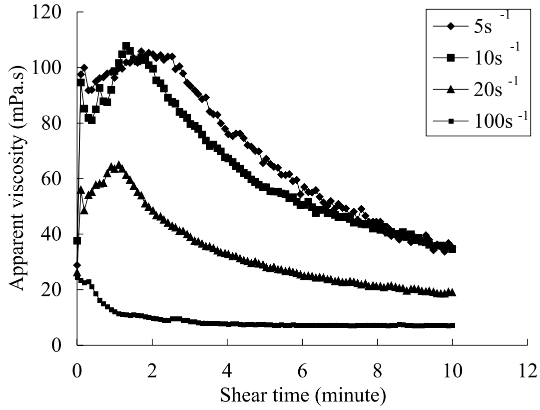

Fig. 8. Time-dependent relationship of the apparent viscosity of PABA-3 aqueous solution at different shear rate (polymer concentration: 0.25 g/dl, 20 °C).

Higher shear rate will break all association and molecular chains will orientate in the fluid field, so the viscosities decrease.

4. Conclusions

Copolymers of AM/AAM have been synthesized by micellar free radical copolymerization in aqueous solution utilizing SDS as the surfactant and ammonium persulfate/sodium bisulfite as the redox initiator. With the increase of AAM content, intrinsic viscosity decreases and Huggins constant increases, which reflect the tendency of intermolecular association. The amount of SDS used in polymerization will affect the microstructure of produced polymers and their viscosification effect. The use of AMPS results in synergistic effects, which will be studied in details in a forthcoming research. Solution viscosities increase with the addition of inorganic salts (NaCl, $CaCl_2$). A complex viscosity behavior of the polymer solution is observed upon the addition of surfactant (SDS). Intermolecular association of hydrophobic groups is favored by increasing temperature in the range of 20–40 °C. Even in 75 °C, the solution viscosity of PABA-3 can retain 59.53% which may be due to the introduction of aryl group. The time-dependent relationship of polymers at different shear rate demonstrates that both the association and the disassociation are dynamic and time-dependent, which is explained by the model of Ballard. Here the direct relationship between the introduction of arylalkyl group and the solution behavior of this kind of polymers was still lack of evidence, some compare will be done in the future work. Further studies will be concerned with the nature of intermolecular association by use of fluorescent and NMR methods, and with the relationship between polymer microstructure and vicosification efficiency.

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