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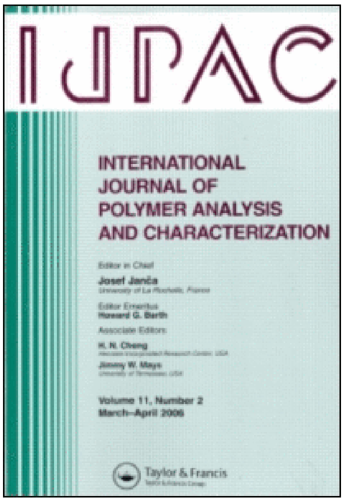

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Synthesis and Characterization of Hydrophobically Modified Cationic Acrylamide Copolymer

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Abstract: Hydrophobically modified cationic acrylamide copolymers were synthesized by free radical solution copolymerization using potassium persulfate as the initiator. Epichlorohydrin, acrylamide, and tridodecylamine were used to synthesize the hydrophobically modified cationic monomer, i.e., 3-acrylamido-2-hydroxypropyltridodecylammonium chloride (AHPTDAC), which was then copolymerized with acrylamide. The intrinsic viscosity, molecular weight, and charge density of the copolymers depend on the ratio of AHPTDAC and acrylamide used. Fourier transform-infrared (FT-IR) and transmission electron microscopy (TEM) were used to elucidate the structure of the copolymer. The solid copolymer is insoluble in water but only swells in the aqueous medium.

Keywords: Cationic acrylamide copolymers; Charge density; Molecular weight; Tridodecylamine

INTRODUCTION

Hydrophobically modified polymers have recently become the subject of extensive research.[1–2] These hydrophobically modified systems have

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received increasing attention due to their unique characteristics and applications such as in enhanced oil recovery, drilling fluids, hydraulic fracturing, superabsorbency, flocculation and drag reduction.[3–6] In aqueous solution, the hydrophobic groups have a strong tendency to associate together yielding intra- and intermolecular networks.[7–8] Due to the intermolecular cross-linking of hydrophobic units, hydrophobically modified polymers were found to be capable of minimizing their exposure to water by blocking water and increasing the viscosity of the solution at high hydrophobic units concentrations; hence, hydrophobically modified polymers can be used as thickeners.[9–10]

Hydrophobically modified polymers are generally constituted by a hydrophilic main chain (uncharged or charged) and associating of hydrophobic group at the polymer backbone.[11–12] Hydrophobic modification of synthetic polyelectrolytes can be performed through chemical grafting or copolymerization.[13] Acrylamide-based polyelectrolytes also received a great extent of utility in the industry due to their useful monomer for obtaining water-soluble high molecular weight polymers.[14] They have been used to copolymerize with various hydrophobic comonomers.[2,4,15,16] Acrylamide has been hydrophobically modified with 3-acrylamido-2-hydroxypropyltrialkylammonium chloride,[17] in which alkyl groups used were ethyl, butyl, and octyl groups. It was found that flocculation performance increases with increasing of the chain length of the hydrophobically modified copolymer. The increase in the hydrophobicity of the copolymer is accompanied by a decrease in sludge weight during the flocculation process due to the elimination of water trapped in the sludge.

In the present work, hydrophobically modified cationic acrylamide copolymers were synthesized via copolymerization of acrylamide and 3-acrylamido-2-hydroxypropyltridodecylammonium chloride in which a longer chain dodecyl group was used. Free-radical solution copolymerization was carried out to synthesize the hydrophobically modified copolymers. The method of synthesis was based on previously published procedures.[17–19] Characterization of the copolymers was conducted by FT-IR and TEM.

EXPERIMENTAL SECTION

Materials

Epichlorohydrin and tridodecylamine ($>95\%$ purity) were obtained from Merck, and potassium persulfate (analytical grade) and acrylamide (analytical grade) were supplied by R&M Chemicals. Analytical grade silver nitrate and potassium chromate were used in charge density determination. Deionized water was used throughout the experiment.

Synthesis of Comonomer

The synthesis procedure of hydrophobically modified cationic acrylamide was described by previous researchers.[17–19] First, 10% of acrylamide solution was prepared in deionized water. Acrylamide solution then reacted with epichlorohydrin in a three-necked flask equipped with a condenser, mechanical stirrer, rubber septum cap, and thermometer. The reaction was carried out at 75°C for 6 h to obtain the Mannich base, which was cooled to ambient temperature. The Mannich base was then added gradually to tridodecylamine in a reaction flask at 50°C for 40 min to produce the quaternized ammonium cationic monomer 3-acrylamido-2-hydroxypropyltridodecylammonium chloride. The monomer solution was then cooled to ambient temperature and kept without any further precipitation. The synthesis equations are shown in Figure 1.

Synthesis of Copolymers

Fourier transform-infrared (FT-IR) spectroscopy was used to analyze the composition of quaternized ammonium cationic monomer 3-acrylamido-2-hydroxypropyltridodecylammonium chloride (AHPTDAC). Acrylamide and AHPTDAC were then copolymerized using free-radical solution polymerization. Various molar ratios between acrylamide and AHPTDAC were used to prepare different characteristics of cationic copolymers. The mixture of acrylamide and AHPTDAC was well stirred in aqueous medium. The reactor was purged with nitrogen gas to deoxygenate the reaction medium, them 0.5 mL of 5% $K_2S_2O_8$ solution was

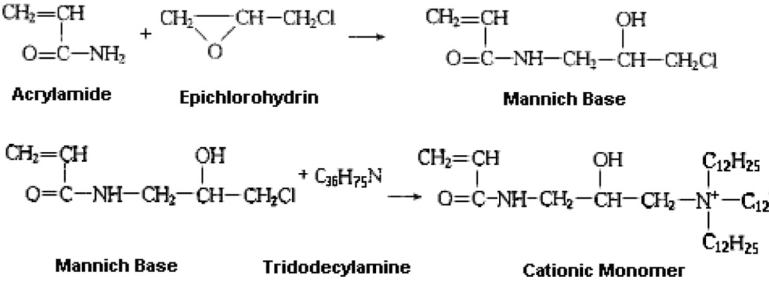

Figure 1. Synthesis of quaternized ammonium cationic monomer 3-acrylamido-2-hydroxypropyltridodecylammonium chloride (AHPTDAC).

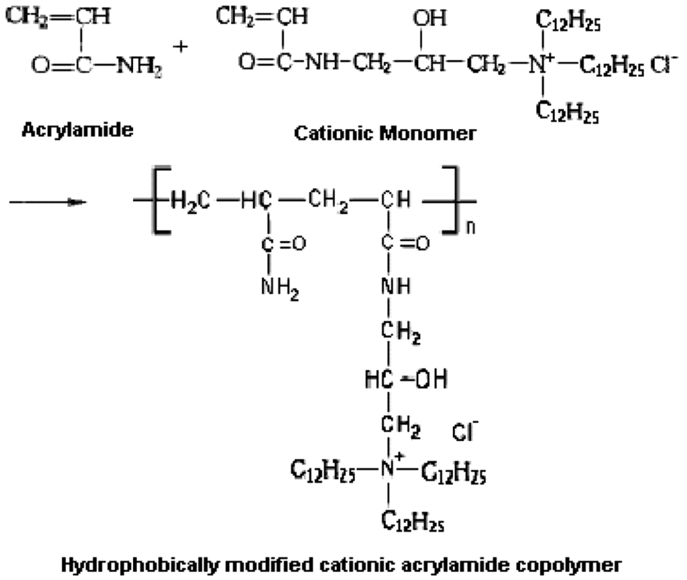

Figure 2. Synthesis of cationic acrylamide copolymer.

injected into the system to initiate the polymerization. The copolymerization process was carried out for 6 h at 60°C under acidic condition. The mechanism of copolymerization is shown in Figure 2. The copolymers obtained were cooled to ambient temperature. FT-IR analysis was then carried out to determine the composition of the copolymer produced.

Characterization

FT-IR Spectra Analysis

Monomer and copolymer chemical compositions were determined by a Perkin Elmer FT-IR spectrophotometer. Its window of was thinly coated with polymer solution after completion of the spectrum of blank. The sample was then dried to prevent interference from the presence of water in the sample. The FT-IR equipment was operated with a resolution of 4 cm^{-1} and scanning range from 4000 to 400 $cm^{-1.}$

Intrinsic Viscosity and Molecular Weight Determination

Intrinsic viscosity measurement was carried out using an Ubbelohde viscometer with 1.0 M NaCl aqueous solution as solvent at 25°C. Intrinsic viscosity $[\eta]$ of the copolymers was obtained using the dilution extrapolation method. The intrinsic viscosity measurement is an approximation method ascribed to the effect of intramolecular hydrophobic interaction on the determination of viscosity-average molecular weight for polymer.[6] The average molecular weight of the acrylamide copolymer was determined by using the Mark-Houwink equation:

$$[\eta] = k(M_v)^{\alpha}$$

where $k = 19.1 \times 10^{-3}\,mL/g$ and $\alpha = 0.71$.

Viscosity Measurement

Viscosity of the copolymer solutions was measured by using the 1.0 M NaCl solution as the solvent. Copolymer solution was prepared by dissolving a known weight of polymer in this solvent. The copolymer solutions were agitated to ensure complete dissolution. For each concentration, the flow time of the solution was measured using Ubbelohde viscometer. The viscosity of the solution was determined by:

$$\eta = A\rho t$$

where η = viscosity, A = calibration constant of the viscometer, ρ = density of solution, and t = flow time.

Charge Density Determination

Charge density was measured by titrating 1 g/L polymer solution with 0.05 M silver nitrate using potassium chromate as the indicator. The charge density is calculated by considering the percentage of cationic monomer in the copolymer using the equations:

$$\text{Charge density}(\%) = \frac{n_c}{(n_c + n_{AM})} \times 100\%$$

$$\text{Charge density}(\%) = \frac{CV}{[(m - MCV)/M_{AM} + CV]} \times 100\%$$

where n_c = mole of cationic comonomer, n_{AM} = mole of acrylamide, C = concentration of silver nitrate, V = volume of silver nitrate used, m = weight of the polymer, M = molecular weight of cationic monomer, and M_{AM} = molecular weight of acrylamide.

Transmission Electron Microscopy

Copolymer in 1.0 g/L aqueous solution was analyzed by Philips CM12 transmission electron microscopy to investigate its polymer molecular formation. One drop of the copolymer aqueous solution was carefully placed on the copper grid and dried with filter paper. The copolymer solution-coated copper grid was then put under TEM for image viewing.

RESULTS AND DISCUSSION

Synthesis

Cationic polyelectrolytes were produced generally using quaternary ammonium salt groups by homopolymerization and copolymerization of monomers containing quaternary N atoms, i.e., the quaternization of polymers containing tertiary amine group with suitable alkylation agents.[20] It was claimed that the properties of hydrophobically modified copolymers can be tuned by varying the number of hydrophobic groups and their chain length.[21] This was further explained by Ren et al.,[17] who carried out hydrophobic modification by extending the alkyl chain length of quaternary ammonium group. The longer the chain, the higher its hydrophobicity. The long alkyl chain, the like dodecyl group, was found to be relatively difficult to incorporate into the Mannich base. This was due to the high hydrophobicity of the dodecyl chain compared with the lower homologous series groups. According to Biggs et al.,[1] the copolymerization of acrylamide and hydrophobic monomer by aqueous solution polymerization has not been reported so far. Considering the limitations of solution polymerization processes, relatively low monomer concentrations were used in order to prevent high viscosity of the polymer product.[5,15,22] For this reason, the total monomer concentration in this study was fixed at a relatively low concentration, 0.01 mol, to prevent the formation of highly viscous copolymer gel product.

In this study, a series of hydrophobically modified cationic acrylamide copolymers with different feed molar ratios of acrylamide and AHPTDAC have been synthesized by solution copolymerization. Potassium persulfate was used as an initiator. The different feed molar ratios are given in Table I. At low content (low molar ratio) of AHPTDAC in the feed, the copolymer solution was optically transparent, which is in agreement with the observation by Grassl et al.[11] The copolymer becomes turbid as the concentration of AHPTDAC comonomer is increased. Attempts to produce copolymers in solid form have been done by precipitating the copolymer solution with methanol and drying it under vacuum. Nevertheless, copolymers did not dissolve in aqueous solution but formed a solid, which makes it difficult for them to be applied in wastewater treatment. The copolymer only swells in water and could not untangle itself, an observation similar to that of a previous report.[24] As explained by Ren et al.,[17] increasing chain length, i.e., octyl chains in

Table I. Copolymerization of AHPTDAC with acrylamide

AHPTDAC feed concentration (mol%)	AM feed concentration (mol%)	Charge density (%)	Intrinsic viscosity [η] (mL/g)	Molecular weight (g/mol)	AHPTDAC composition in copolymer (%)
0	100	—	192	4.3×10^5	0
20	80	84.99	9.9	6.6×10^3	15
33	67	46.96	6.7	3.8×10^3	27
45	55	44.19	67.0	9.8×10^4	33
60	40	34.90	52.6	6.9×10^4	44
75	25	22.12	28.8	2.9×10^4	58
100	0	22.36	22.0	2.0×10^4	100

the polymer molecule, will increase entanglement between the polymer molecules. In this study, this entanglement phenomenon is further enhanced by the presence of dodecyl chains, which causes the insolubility of polymer in water after precipitation. To overcome this problem, copolymer products obtained were not further precipitated with methanol.[23] Solution copolymerization produces a copolymer that is free from entanglement and avoids insolubility in aqueous medium.

Characterization

FT-IR

The compositions of the resulting comonomer and copolymers were determined by FT-IR. The FT-IR spectrum in Figure 3 shows the peaks of AHPTDAC (OH-, 3386.18 cm^{-1}; $-CH_3$, 2922.14 cm^{-1} and 2852.39 cm^{-1}; $-CONHR$, 1652.75 cm^{-1} and 1284.05 cm^{-1}; $R-OH$, 1435.38 cm^{-1}; $C-(CH_3)_2$, 1361.30 cm^{-1}; $>CH-O-H$, 1040.87 cm^{-1}; $-CH{=}CH_2$, 971.93 cm^{-1}). Hence, it is confirmed that the FT-IR spectrum corresponds to the structure of AHPTDAC. Hydrophobically modified cationic acrylamide copolymers are shown in Figure 4 ($-NH_2$ and $-OH$, 3353–3391 cm^{-1}; $-NH_2$, 3201–3210 cm^{-1}; $-CH_2-$, 2953 cm^{-1}; $-CONH_2$, 1665–1673 cm^{-1}; $-NH_2$, 1603–1621 cm^{-1}; $-OH$, 1428–1436 cm^{-1}; $C-N$ stretch, 1352–1361 cm^{-1}; $-CONHR$, 1280–1285 cm^{-1}; $-C-NH_2$, 1108–1112 cm^{-1}; $>CH-O-H$, 1042–1044 cm^{-1}; $-CH{=}CH_2$, 967–985 cm^{-1}; $C-Cl$, 812 cm^{-1}; $-CH{=}CH-$, 619–700 cm^{-1}). Thus, FT-IR spectra obtained confirm the structure of the hydrophobically modified cationic acrylamide copolymers. According to Ghimichi et al.,[20] it is often impossible to determine the degree of hydrophobic incorporation, especially for comonomers consisting of

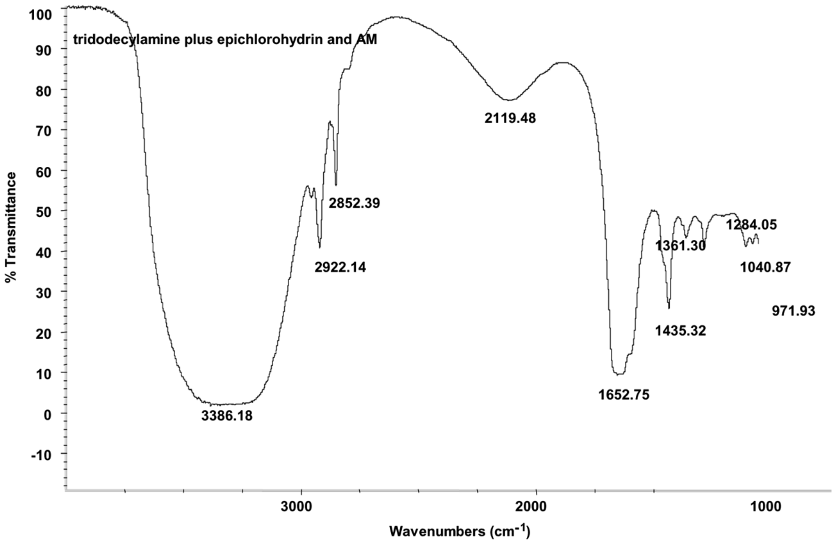

Figure 3. FT-IR spectrum for AHPTDAC monomer.

alkyl chains; consequently, it was assumed that the hydrophobic amine content was the same as in the initial feed composition, as usually supposed for the low contents of hydrophobic component included in

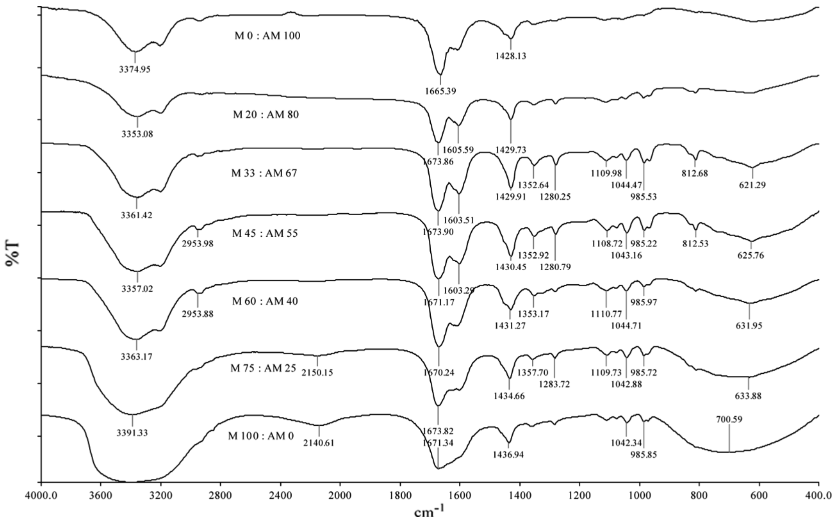

Figure 4. FT-IR spectra for hydrophobically modified cationic acrylamide copolymers.

the hydrophilic-hydrophobic copolymers. However, the chemical compositions of the copolymers can be estimated from the FT-IR spectra by investigating the monomer conversion as shown in Table I.

Intrinsic Viscosity and Molecular Weight Measurements

Table I shows the intrinsic viscosities of the copolymers. It is found that the intrinsic viscosity increases (6.7–67 mL/g) with the increase of AHPTDAC hydrophobic monomer concentration from 20 to 45 mole %. Hydrophobic monomer association is divided into two stages. First, the copolymer dissolves in water, resulting in intra- and intermolecular associations. Beyond the first critical associating concentration (CAC_1), the molecular network forms and causes a rapid increase in viscosity.[25–27] The associating of hydrophobic group at the second critical associating concentration (CAC_2) leads to a decrease in viscosity until a constant value is reached due to its intramolecular association.[25] This observation is in agreement with the intrinsic viscosity reported in our study (Table I), i.e., association of hydrophobic group concentration occurs between 60 and 100 mole%. In addition, further increase of cationic AHPTDAC hydrophobic monomer ratio would lead to the repulsion among hydrophobic comonomer, which inhibits molecular chain bonding and hence decreases the molecular weight.[17]

At low polymer concentration ($C < 0.01$ M), the viscosity of the copolymers is generally lower than that of polyacrylamide (PAM).[11]

Viscosity Measurement

Figure 5 shows that the viscosity increases gradually and linearly with the copolymer concentration. In dilute copolymer solution, copolymer molecules behave as individual chains. It was explained by Poh and Ong[28] that the polymer coils are expanded by the excluded volume effect at low concentration. The coils contract with increasing concentration as the excluded volume repulsion between segments in the same chain becomes screened by segments of neighboring chains. In dilute solution, the molecular chains do not interact with each other. The viscosity increases with copolymer concentration until the copolymer chains are able to approach each other and their overlapping occurs.

Charge Density Determination

Charge density of the cationic copolymers is given in Table I. The charge densities decrease when the intrinsic viscosity increases from monomer feed concentration of 20 to 45 mole %. The trend is consistent with the published work[24] at lower feed concentration of hydrophobic monomer.

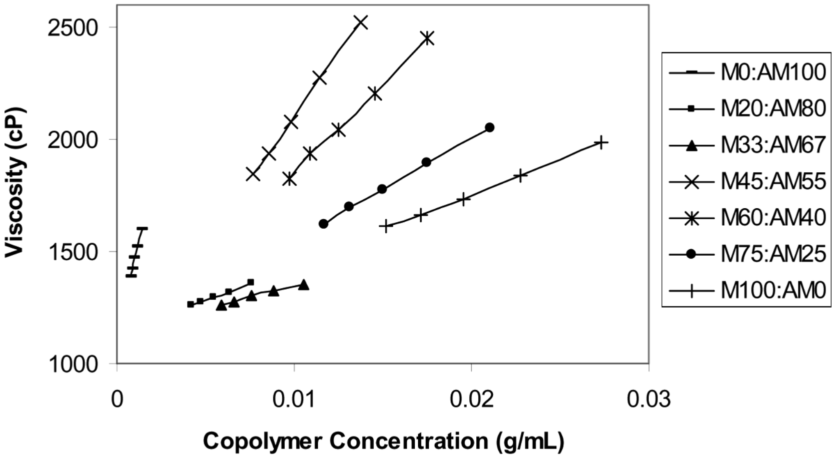

Figure 5. Viscosity of the hydrophobically modified cationic acrylamide copolymers in 1.0 M NaCl solution.

The charge density also decreases with the increase of AHPTDAC hydrophobic cationic monomer, especially after 20 mole % concentration. This observation is attributed to the increase of the hydrophobicity of the molecule when the feed ratio of cationic hydrophobic monomer increases. As a consequence, polymer solubility decreases as reflected by a drop of charge density.[17]

TEM

The TEM image of the copolymer is shown in Figure 6. The monotonous molecule of the highest molecular weight hydrophobically modified cationic acrylamide copolymer (ratio 45:55) appears to be long, thin, and branched in its molecular structures. The telechelic copolymer with hydrophobic group in the polymer molecule is stretched and forms an enlarged structure. The molecular chain length of the monotonous copolymer is estimated to be approximately 900 nm at magnification of 220,000× . The repulsive force in the high hydrophobicity chain groups prevents chain bonding. Hence, the association of the hydrophobic group was found to be stretched and thin.[17]

CONCLUSIONS

Solution copolymerization of hydrophobic AHPTDAC monomer and acrylamide with relatively low feed concentration (0.01 mol) was found

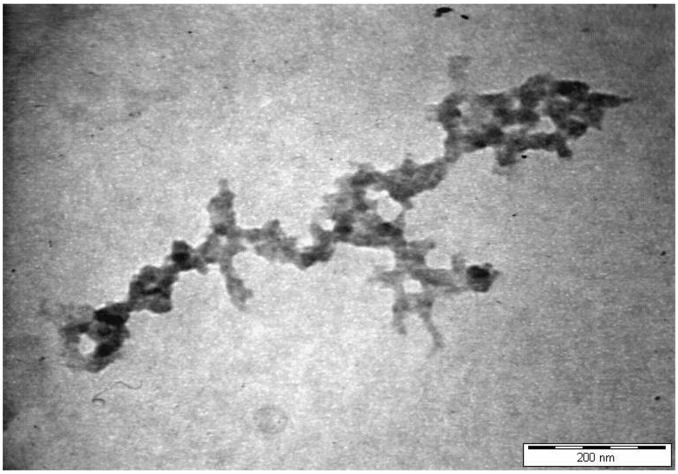

Figure 6. TEM image of the hydrophobically modified cationic acrylamide copolymer (45:55).

to be the best condition for the copolymerization of this hydrophilic and hydrophobic monomer couple. Solid copolymer is insoluble in water but swells in aqueous medium. The copolymers were produced in solution without any precipitation after copolymerization. The intrinsic viscosity of copolymer aqueous solution depends on the molecular weight and charge density of the copolymer. Viscosity of the copolymers increases linearly with concentration in the dilute region. The addition of cationic hydrophobic group in the acrylamide copolymers yields lower molecular weight than with polyacrylamide homopolymer. TEM indicated the monotonous structure of the copolymer of ratio 45:55.

REFERENCES

[1] Biggs, S., A. Hill, J. Selb, and F. Candau. (1992). Copolymerization of acrylamide and a hydrophobic monomer in an aqueous micellar medium: Effect of the surfactants on the copolymer microstructure. *J. Phys. Chem.* **96**, 1505–1511.

[2] Volpert, E., J. Selb, and F. Candau. (1997). Associating behaviour of polyacrylamides hydrophobically modified with dihexylacrylamide. *Polymer* **39**(5), 1025–1033.

[3] Zhang, J., L.-M. Zhang, and Z.-M. Li. (2000). Synthesis and aqueous solution properties of hydrophobically modified graft copolymer of sodium carboxymethylcellulose with acrylamide and dimethyloctyl(2-methacryloxyethyl) ammonium bromide. *J. Appl. Polym. Sci.* **78**, 537–542.

[4] Wei, X., I. W. Hamley, V. Castelletto, and P. D. Olmsted. (2004). Synthesis and characterization of hydrophobically modified polyacrylamides and some observations on rheological properties. *Eur. Polym. J.* **40**, 47–56.

[5] Zhu, Z., O. Jian, S. Paillet, J. Desbrieres, and B. Grassl. (2007). Hydrophobically modified associating polyacrylamide (HAPAM) synthesised by micellar copolymerization at high monomer concentration. *Eur. Polym. J.* **43**(3), 824–834.

[6] Gao, B., L. Jiang, and K. Liu. (2007). Microstructure and association property of hydrophobically modified polyacrylamide of a new family. *Eur. Polym. J.* **43**(10), 4530–4540.

[7] Feng, Y., L. Billon, B. Grassl, G. Bastiat, O. Borisov, and J. Francois. (2005). Hydrophobically associating polyacrylamides and their partially hydrolyzed derivatives prepared by Post-modification. 2. Properties of non-hydrolyzed polymer in pure water and brine. *Polymer* **46**, 9283–9295.

[8] Feng, Y., L. Billon, B. Grassl, A. Khoukh, and J. Francois. (2002). Hydrophobically associating polyacrylamides and their partially hydrolyzed deriavatives prepared by post-modification. 1: Synthesis and characterization. *Polymer* **43**, 2055–2064.

[9] Shaskina, Yu. A., Y. D. Zaroslov, V. A. Smirnov, O. E. Philippova, A. R. Khokhlov, T. A. Pryakhina, and N. A. Churochkina. (2003) . Hydrophobic aggregation in aqueous solutions of hydrophobically modified polyacrylamide in the vicinity of overlap concentration. *Polymer* **44**, 2289–2293.

[10] Wu, S., R. A. Shanks, and G. Bryant. (2006). Properties of hydrophobically modified polyacrylamide with low molecular weight and interaction with surfactant in aqueous solution. *J. Appl. Polym. Sci.* **100**, 4348–4360.

[11] Grassl, B., J. Francois, and L. Billon. (2001). Associating behaviour of polyacrylamide modified with a new hydrophobic zwitterionic monomer. *Polym. Int.* **50**(10), 1162–1169.

[12] Penott-Chang, E. K., L. Gouveia, I. J. Fernandez, A. J. Muller, A. Diaz-Barrios, and A. E. Saez. (2006) . Rheology of aqueous solutions of hydrophobically modified polyacrylamides and surfactants. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **295**(1–3), 99–106.

[13] Bratskaya, S., V. Avramenko, S. Schwarz, and I. Philippova. (2006) . Enhanced flocculation of oil-in-water emulsions by hydrophobically modified chitosan derivatives. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **275**, 168–176.

[14] Chagas, B. S., D. L. P. Machado Jr., R. B. Haag, C. R. de Souza, and E. F. Lucas. (2004). Evaluation of hydrophobically associated polyacrylamide-containing aqueous fluids and their potential use in petroleum recovery. *J. Appl. Polym. Sci.* **91**, 3686–3692.

[15] Candau, F., and J. Selb. (1999). Hydrophobically-modified polyacrylamides prepared by micellar polymerization. *Adv. Colloid Interface Sci.* **79**, 149–172.

[16] Yahaya, G. O., A. A. Ahdab, S. A. Ali, B. F. Abu-Sharkh, and E. Z. Hamad. (2001). Solution behavior of hydrophobically associating water-soluble block copolymers of acrylamide and n-benzylacrylamide. *Polymer* **42**, 3363–3372.

[17] Ren, H., W. Chen, Y. Zhen, and Z. Luan. (2007) . Effect of hydrophobic group on flocculation properties and dewatering efficiency of cationic acrylamide copolymers. *React. Funct. Polym.* **67**, 601–608.

[18] Ma, X.-P. and D.-B. Shao. (1999). The synthesis and flocculating property of cationic polyacrylamides. *Oilfield Chem.* (in Chinese) **16**(4).

[19] Lu, L. and G.-Q. Wu. (2002). Synthesis of high charge density cationic polyacrylamide. *Technol. Dev. Chem. Ind.* (in Chinese) **31**(3), 8–11.

[20] Ghimici, L., I. Dranca, S. Dragan, T. Lupascu, and A. Maftuleac. (2001) . Hydrophobically modified cationic polyelectrolytes. *Eur. Polym. J.* **37**, 227–231.

[21] Miller, D. and M. Loffler. (2006). Rheological effects with a hydrophobically modified polymer. *Colloids Surf. A Physicochem. Eng. Aspects* **288**, 165–169.

[22] Hernandez-Barajas, J., and D. J. Hunkeler. (1996). Inverse-emulsion copolymerization of acrylamide and quaternary ammonium cationic monomers with block copolymeric surfactants: Copolymer composition control using batch and semi-batch techniques. *Polymer* **38**(2), 449–458.

[23] Billmeyer, F. W., Jr. (1984). *Textbook of Polymer Science*. New York: John Wiley & Sons, p. 127.

[24] Zhao, H.-Z., Z.-K. Luan, B.-Y. Gao, and Q.-Y. Yue. (2002). Synthesis and flocculation properties of poly(diallyldimetyl ammonium chloride-vinyl trimethoxysilane) and poly(diallyldimethyl ammonium chloride-acrylamide-vinyl trimethoxysilane). *J. Appl. Polym. Sci.* **84**, 335–342.

[25] Sun, S.-R., H.-J. Zhu, J.-H. Luo, J.-X. Tang, B.-L. Kong, and J.-B. Yang. (2004). A study on critical associating concentrations of water soluble hydrophobically associating polymers for EOR. *Oilfield Chem.* (in Chinese) **21**(2), 173–176.

[26] Ye, L. K. Luo, and R. Huang. (2000). A study on P(AM-DMDA) hydrophobically associating water-soluble copolymer. *Eur. Polym. J.* **36**, 1711–1715.

[27] Ye, L., L. Mao, and R. Huang. (2001). Synthesis and aqueous solution behavior of hydrophobically modified polyelectrolytes. *J. Appl. Polym. Sci.* **82**, 3552–3557.

[28] Poh, B. T., and B. T. Ong. (1984). Dependence of viscosity of polystryrene solutions on molecular weight and concentration. *Eur. Polym. J.* **20**, 975–978.