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Synthesis and Characterization of Hydrophobically Modified Cationic Polyacrylamide with Low Concentration of Cationic Monomer

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Hydrophobically modified cationic polyacrylamides were synthesized via free radical solution copolymerization using ammonium persulphate/sodium hydrogen sulphite as the redox initiator. Epichlorohydrin, acrylamide and trialkylamine were used to synthesize the hydrophobic cationic monomer 3-acrylamido-2-hydroxypropyltriakylammonium chloride (AHPTAAC) in which the trialkyl group was trihexylamine (AHPTHAC), trioctylamine (AHPTOAC) and tridodecylamine (AHPTDAC). Low concentration (1–6 mol%) of cationic monomer from each group were copolymerized with acrylamide to obtain hydrophobically modified cationic polyacrylamide. Results show that the intrinsic viscosity and molecular weight of the copolymers decreases with the concentration of the hydrophobic cationic group, whereas charge density indicates the reverse behaviour. Fourier Transform Infrared (FTIR) and Transmission Electron Microscopy (TEM) were also carried out to elucidate the structure of the copolymer.

Keywords: Cationic polyacrylamide, charge density, molecular weight

1 Introduction

Acrylamide-based polymers have received a great extent of utility in industry because of high molecular weight and water soluble property (1, 2). Generally, these polymers are classified into nonionic, anionic and cationic species according to the nature of their covalently bond ionic groups (3). The addition of a charged group often offer a more effective system as a flocculant. Hence, many cationic polyacrylamides are prepared by copolymerizing acrylamide with monomers having cationic charged groups (4, 5). In spite of a great variety of commercially available flocculants, there is still a need for improvement of their efficiency for special applications. Hydrophobic modification of synthetic polymers was suggested as one of possibilities to enhance polymer performance (6). Hydrophobically modified polymers have recently become the subject of extensive research due to their unique characteristics and applications such as in enhanced oil recovery, drilling fluids, hydraulic fracturing, super absorbency, flocculation and drag reduction (1, 7–16). These polymers are tailored on the basis of a hydrophilic structure by introducing a relatively small amount of hydrophobic monomer into a hydrophilic macromolecular chain (10). Hydrophobic modification of synthetic polyelectrolytes can be performed through chemical grafting or copolymerization (6). The chain flexibility, the molecular weight, the solubility, the charge density are the main factors which determine the applications of these polymers in the waste and surface water purification process (5).

In the present work, hydrophobically modified cationic polyacrylamides were synthesized via free radical solution copolymerization of acrylamide with low concentration (1–6%) of 3-acrylamido-2-hydroxypropyltrialkylammonium chloride in which alkyl groups used were hexyl, octyl and dodecyl groups where the longer the alkyl chain having higher hydrophobicity. FT-IR and TEM were used to characterize the copolymers.

2 Experimental

2.1 Materials

Epichlorohydrin (>99% purity), trioctylamine (>93% purity) and tridodecylamine (>95% purity) were obtained

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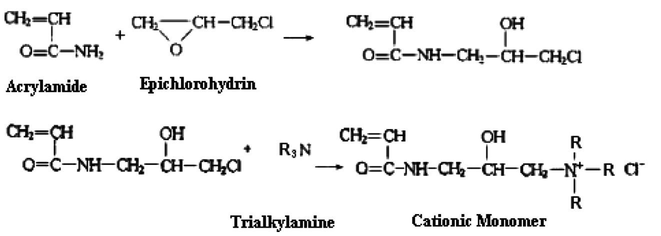
*Address correspondence to: Beng Teik Poh, School of Industrial Technology, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia; E-mail: btpoh@usm.my from Merck, whereas trihexylamine (>96% purity) was supplied by Aldrich. Acrylamide (AM) (>98% purity, Fluka) was used without further purification. Ammonium persulphate (AR, Systerm) and sodium hydrogen sulphite (GR, Acros Organics) were used as redox initiators. Potassium chromate (Bendosen), silver nitrate (ARChem), chloroform (QReC) and sodium chloride (R&M Chemicals) were analytical grade reagents and used as received. Deionized water was used throughout the experiment.

2.2 Synthesis of Comonomers

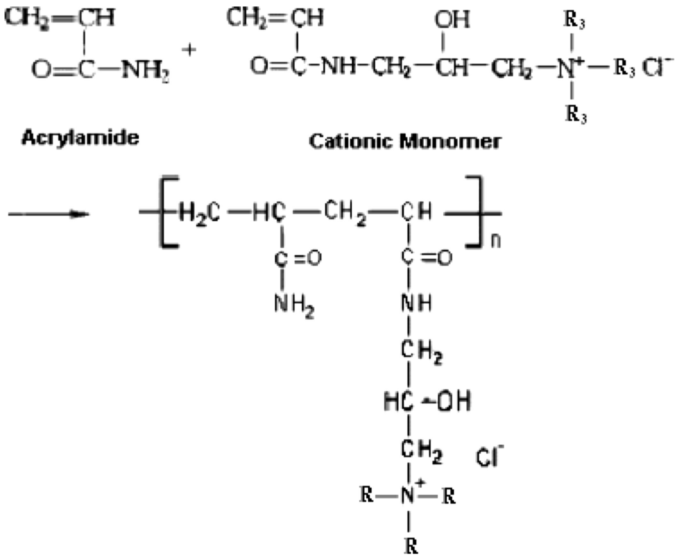
The synthesis route of hydrophobically modified cationic acrylamide monomer was described in a previous paper (1). Synthesis equations are shown below.



An equivalent mole ratio of acrylamide and epichlorohydrin was reacted in a three-necked flask equipped with a condenser, water bath stirrer, rubber septum cap, and thermometer. The reaction was carried out at 50°C for 3.5 h to obtain 3-acrylamido-isopropanol chloride. The sample was cooled to an ambient temperature and then reacted with trihexylamine, trioctylamine and tridodecylamine separately in chloroform at 50°C for 20 h. After the reaction, samples were shelved for several days to obtain the quaternized ammonium cationic monomer 3-acrylamido-2-hydroxypropyltrialkyl-ammonium chloride solution. Fourier transform-infrared (FT-IR) spectroscopy was used to elucidate the functional groups of comonomers prior to copolymerization process.

2.3 Copolymerization

P(AHPTHAC-co-AM), P(AHPTOAC-co-AM) and P(AHPTDAC-co-AM) copolymers were synthesized using free-radical solution copolymerization. A small mole ratio (1–6 mol%) of quaternized ammonium cationic monomers was used to prepare different characteristics of cationic polyacrylamides. The 0.1 mol mixture of AM and comonomers were thoroughly stirred in an aqueous medium and purged with nitrogen gas for 30 min to deoxygenate the reaction medium. 2×0^{-5} M of ammonium persulphate and 5×10^{-6} M of sodium hydrogen sulphite were used as redox initiator to initiate the copolymerization at 50°C for 6 h. The scheme of copolymerization is shown below.



The copolymers obtained were precipitated with methanol, then vacuum dried and ground into powder. FT-IR analysis was then carried out to determine the composition of the copolymer produced. The polymers are referred as C6, C8 and C12 indicating P(AHPTHAC-co-AM), P(AHPTOAC-co-AM) and P(AHPTDAC-co-AM) copolymers, respectively. The subsequent two digits indicate the percentage of the hydrophobic monomer present in the chain. For example, C601 means that the polymer is obtained from copolymerizing acrylamide with 1 mol% of AHPTHAC (trihexylamine-based cationic comonomer).

2.4 Characterization

2.4.1. *Fourier transform infrared (FTIR) spectra analysis*

The chemical compositions of comonomers and copolymers were determined using a Avatar 360 FT-IR spectrophotometer. Monomer solutions were coated thinly on the FT-IR windows, whereas powder form polymers were prepared into platelets with potassium bromate. The samples were tested after completion of the blank spectrum scanning. The FT-IR equipment was operated with a resolution of 4 cm^{-1} and scanning range from 4000 to 400 cm^{-1}.

2.5 Intrinsic Viscosity and Molecula Weight Determination

Intrinsic viscosity measurements were 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 a 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 (16). The average molecular weight of the hydrophobically modified cationic polyacrylamides was determined using the Mark-Houwink equation:

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

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

2.6 Viscosity measurement

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

2.7 Charge Density Determination

Charge density was measured by titrating 0.1 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 over copolymer as shown by the equations below:

$$\begin{aligned}\text{Charge density}\,(\%) &= \frac{n_c}{(n_c + n_{AM})} \times 100\% \\ &= \frac{CV}{[(m - MCV)/M_{AM} + CV]} \times 100\%\end{aligned}$$

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.

2.8 TEM (Transmission Electron Microscopy)

Copolymer in 2.0 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.

3 Results and Discussion

3.1 Monomer Synthesis

Cationic polyacrylamide is generally prepared by copolymerizing acrylamide with quaternary ammonium salt (5). In this study, cationic monomer containing quaternary ammonium groups was prepared using epichlorohydrin, trialkylamine and acrylamide. The opening of epoxy chain allows acrylamide to react and form the intermediate compound 3-acrylamido-isopropanol chloride (21). In view of the immiscibility of the trihexylamine, trioctylamine and tridodecylamine with 3-acrylamido-isopropanol chloride, an organic solvent which is a solvent for the two reactants and a non-solvent for the reaction product was used. According to Reimschuessel et al. (22), chloroform is particularly suitable for this purpose. The reaction proceeds readily at temperatures within the range of 0°C to 50°C.

3.2 Polymer Synthesis

In this study, a series of hydrophobically modified cationic polyacrylamide with different feed molar ratios of acrylamide and AHPTHAC, AHPTOAC and AHPTDAC have been synthesized by solution copolymerization. Ammonium persulphate and sodium hydrogen sulphite were used as redox initiator. To avoid crosslinking between molecular chains and insolubility problems which occurred, a relatively low hydrophobic cationic monomer was used, i.e., 1–6 mol% feed mole ratios. At low content (low mole ratio) of AHPTHAC, AHPTOAC and AHPTDAC comonomer in the feed, the copolymer solution is optically transparent, the copolymer becomes turbid as the concentration of AHPTHAC, AHPTOAC and AHPTDAC comonomer is increased which is in agreement with the observation reported by Grassl et al. (23).

The yield of the hydrophobically modified cationic polyacrylamides obtained were high (>80%), as shown in Table 1. In general, it is often impossible to determine the degree of hydrophobic incorporation, especially for comonomers consisting of alkyl chains; consequently, it is assumed that the hydrophobic content is the same as in the initial feed composition, as is usually supposed for the low contents of hydrophobic component included in the hydrophilic-hydrophobic copolymers (5, 10). Several days are needed to dissolve the copolymers completely in the aqueous and brine media. For comparison of the solubility between AHPTHAC, AHPTOAC and AHPTDAC copolymer, it is observed that the time of dissolution increases with the chain length. Thus the solubility is related to the nature of the hydrophobic unit. It is well known that a slight increase in the length of hydrophobic alkyl chain can strongly modify the solubility properties (11). A copolymer with the highest AHPTDAC content requires the longest time for complete dissolution. The increase of concentration of long chain monomer in the polymer molecule will increase the physical chain crosslink and causes the insolubility of polymer (1).

Table 1. Copolymerization of hydrophobically modified cationic polyacrylamide.

Polymer	*Feed Amount of Cationic Monomer (mol%)*	*Yield (%)*	*Intrinsic Viscosity [η] (mL/g)*	*Molecular Weight (g/mol)*	*Charge Density (%)*
Nonionic	0	97.03	895.82	3.79×10^6	—
C601	1	97.42	595.53	2.13×10^6	1.17
C602	2	96.40	461.25	1.48×10^6	1.61
C603	3	95.30	367.40	1.08×10^6	2.15
C604	4	87.14	357.31	1.03×10^6	2.60
C605	5	82.95	300.82	8.15×10^5	3.10
C606	6	88.25	287.82	7.64×10^5	3.45
C801	1	98.87	569.02	2.00×10^6	1.14
C802	2	99.57	293.48	7.88×10^5	1.27
C803	3	99.74	266.08	6.86×10^5	1.42
C804	4	92.37	224.40	5.39×10^5	1.91
C805	5	85.01	201.18	4.62×10^5	1.97
C806	6	86.44	143.34	2.87×10^5	2.06
C1201	1	94.68	52.44	6.96×10^4	0.95
C1202	2	98.55	31.43	3.38×10^4	1.14
C1203	3	99.45	28.40	2.93×10^4	1.29
C1204	4	99.45	24.79	2.42×10^4	1.46
C1205	5	99.09	20.14	1.81×10^4	1.71
C1206	6	95.92	19.42	1.72×10^4	1.96

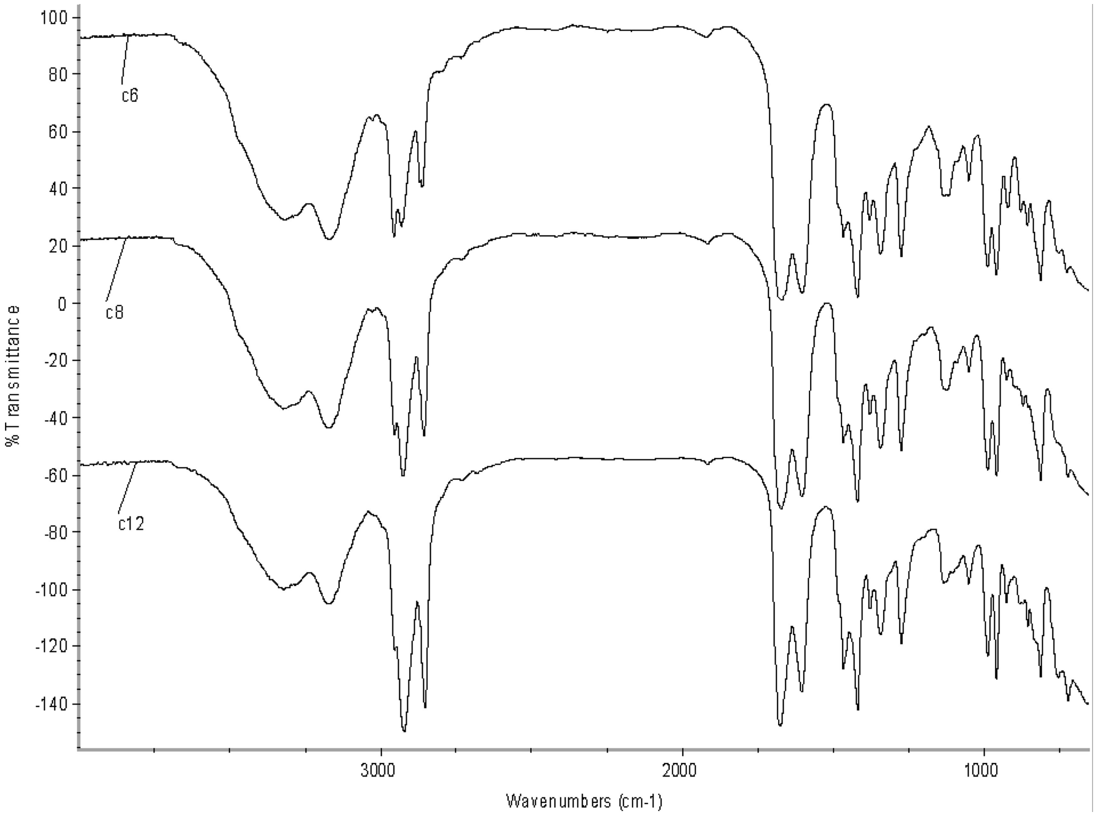


Fig. 1. FT-IR spectra for AHPTHAC, AHPTOAC and AHPTDAC comonomers.

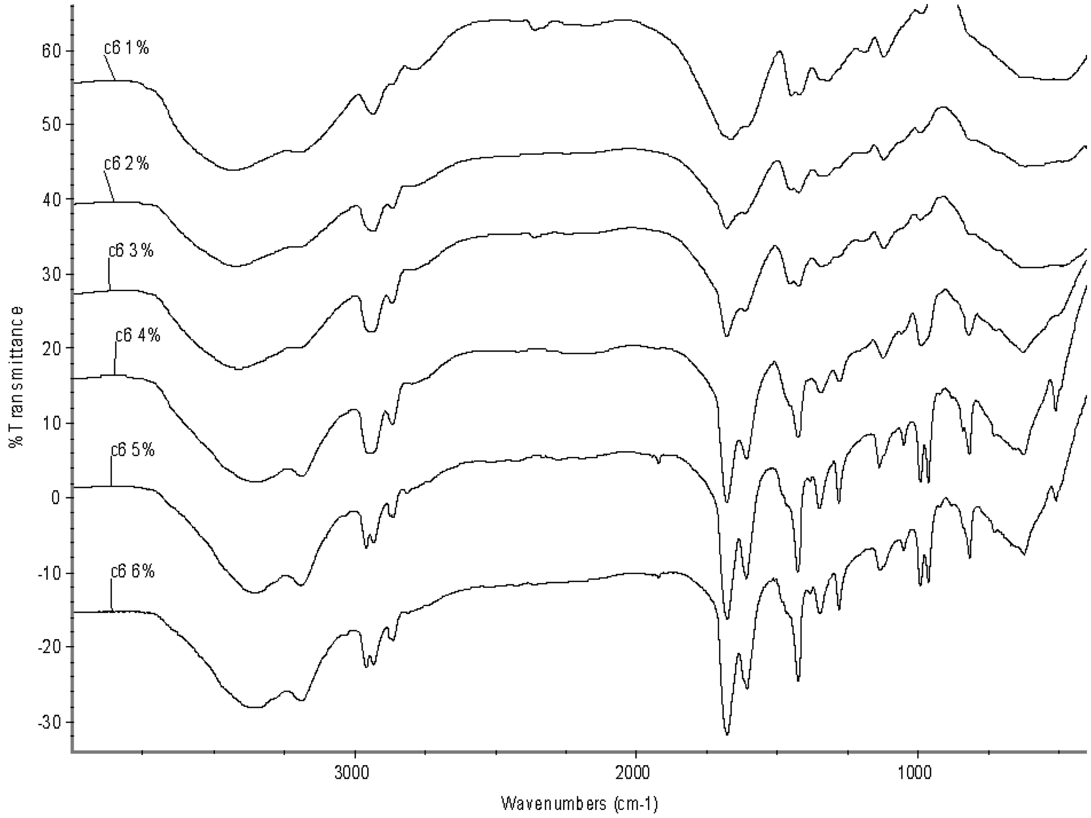


Fig. 2. FT-IR spectra for AHPTHAC group polymers.

3.3 Characterization

Cationic copolymers are characterized by their copolymer composition or charge density, molecular weight and chain architecture (24). Hence, FT-IR, TEM, molecular weight, charge density and solution behavior are particularly important in this study to characterize the hydrophobically modified cationic polyacrylamides that have been synthesized.

3.4 FourierTransform Infrared (FTIR) Spectra Analysis

Compositions and functional groups of the resulting comonomers and copolymers were determined by FT-IR. The FT-IR spectra in Figure 1 show the peaks of AHPTHAC, AHPTOAC and AHPTDAC monomers. From the spectra, it is observed that increasing alkyl chain length from hexyl, octyl to dodecyl group is accompanied by the increase in the composition of alkyl group (2980–2850 cm^{-1}). NH_4^+ (3260–3150 cm^{-1}) and -CONHR (1680–1640 cm^{-1}) groups are also observed in the spectra. Hence, it is confirmed that the FT-IR spectra corresponds to the structure of AHPTHAC, AHPTOAC and AHPTDAC monomers.

FT-IR spectra of hydrophobically modified cationic polyacrylamide obtained from AHPTHAC, AHPTOAC and AHPTDAC groups are shown in Figures 2, 3, and 4, respectively. The functional groups, alkyl (2980–2850 cm^{-1}), NH_4^+ (3260–3150 cm^{-1}) and -CONHR (1680–1640 cm^{-1}) from the three copolymers are observed in the spectra. Hence, elucidation of FT-IR spectra confirms that the hydrophobically modified cationic polymers are successfully synthesized.

3.5 Intrinsic Viscosity and Molecular Weight Measurements

Intrinsic viscosity of the polymer is shown in Table 1. The intrinsic viscosities of the hydrophobically modified polymers are lower than that of its unmodified analogue due to reduced intramolecular interactions in dilute regions (19). The decrease of the molecular weight and intramolecular association would lead to the contraction of polymer chains (25). In contrast with neutral associating copolymers, the presence of ionic sites of similar charge along the hydrophilic backbone of associating polyelectrolyte leads to a great variety of behavior. The addition of cationic hydrophobic comonomer concentration results in repulsion within a polymer chain which would lead to coil expansion in water. The interchain electrostatic repulsions lower the

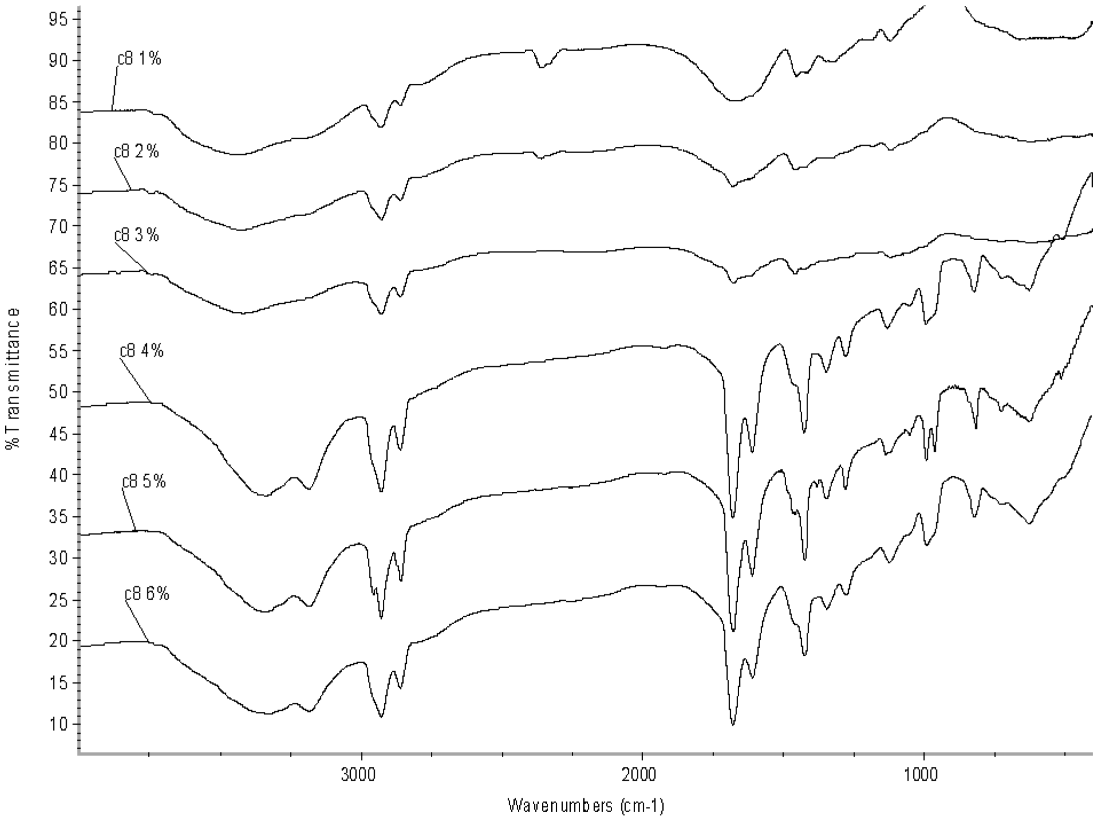


Fig. 3. FT-IR spectra for AHPTOAC group polymers.

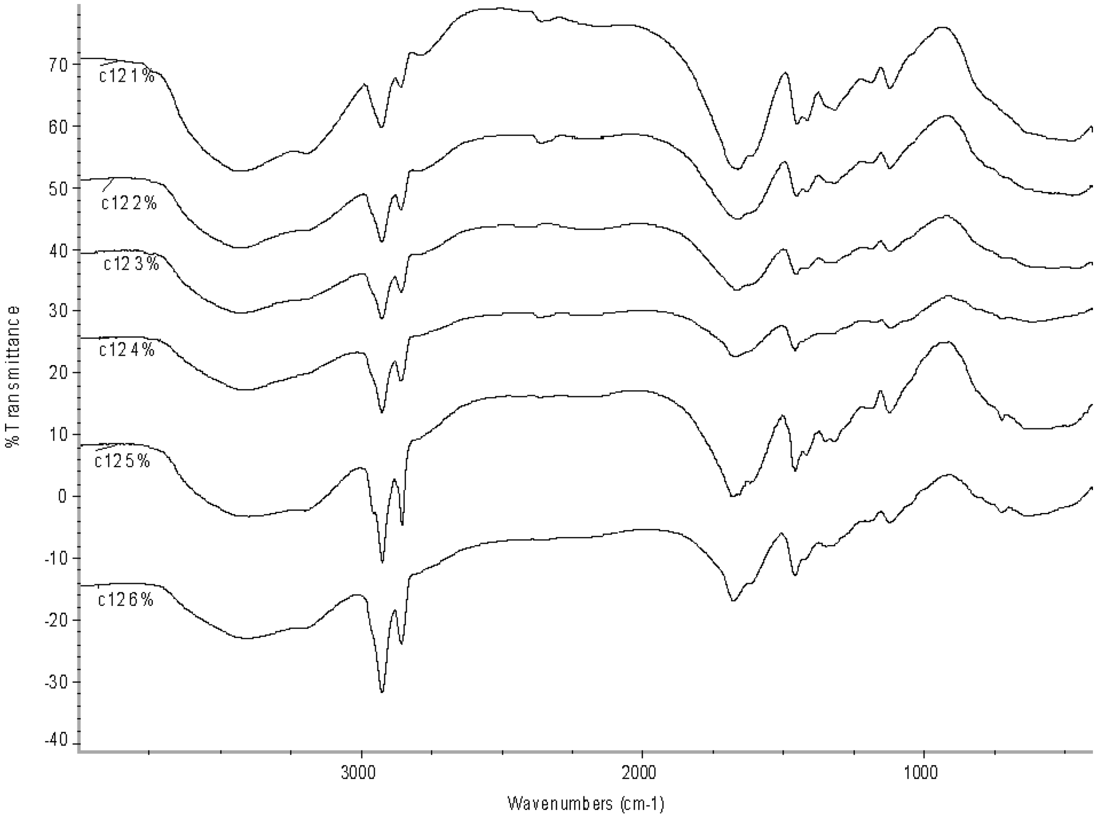


Fig. 4. FT-IR spectra for AHPTDAC group polymers.

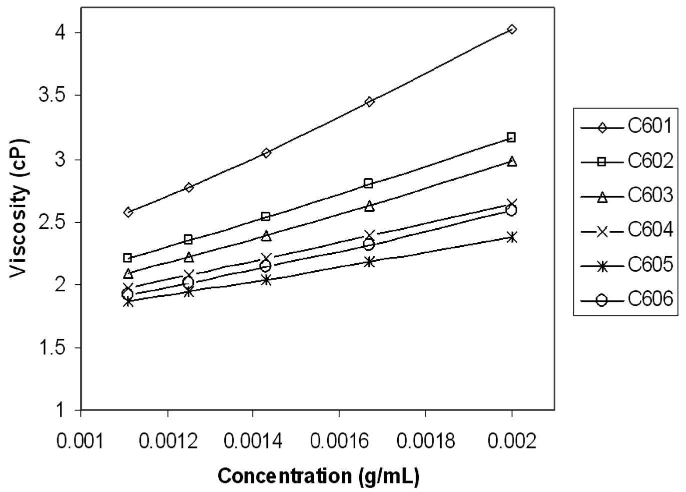


Fig. 5. Effect of AHPTHAC group copolymer concentration on the viscosity in 1.0 M NaCl solution.

degree of hydrophobic association which inhibits molecular chain bonding and hence decreases the molecular weight (20).

A significant difference ($p < 0.05$) was reported between AHPTHAC, AHPTOAC and AHPTDAC group copolymers using one way ANOVA analysis in comparing the intrinsic viscosity and molecular weight. The intrinsic viscosity and molecular weight is found to decrease with increasing chain length in the sequence of AHPTHAC > AHPTOAC > AHPTDAC. This observation is attributed to the longer comonomer chain which increases the steric hindrance, hence, lower molecular weight copolymer is observed.

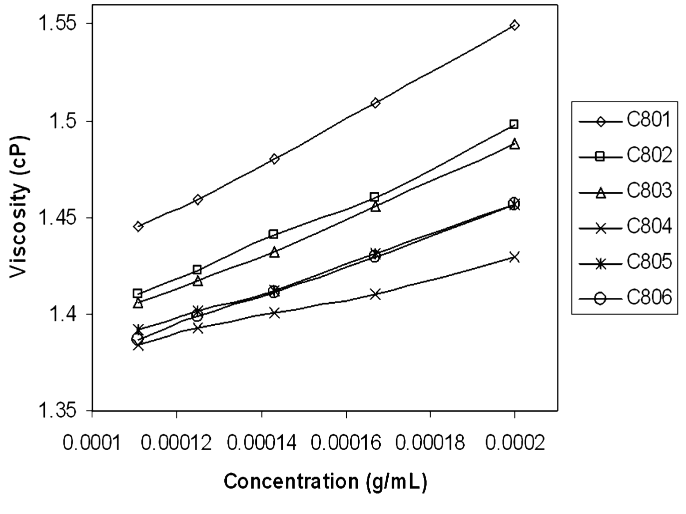


Fig. 6. Effect of AHPTOAC group copolymer concentration on the viscosity in 1.0 M NaCl solution.

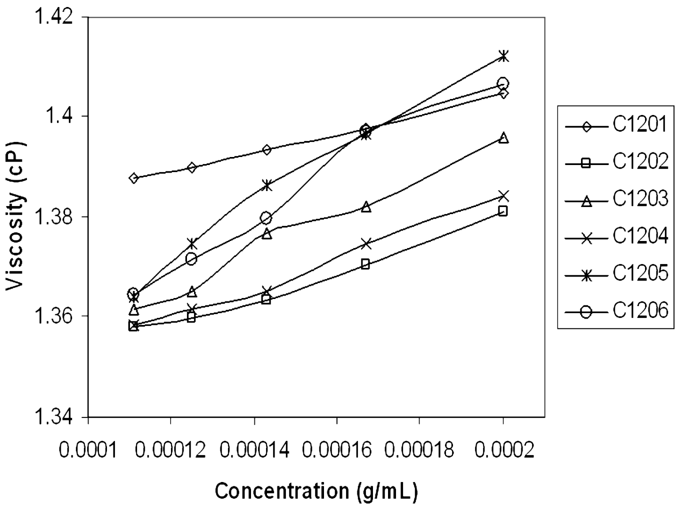


Fig. 7. Effect of AHPTDAC group copolymer concentration on the viscosity in 1.0 M NaCl solution.

3.6 Solution Behavior of Polymer in NaCl Solution

The viscosities of the polymer solution were investigated in NaCl solution. Figures 5, 6, and 7 show the viscosity of polymer solution at different polymer concentration. The viscosity of copolymers in NaCl solution is found to have significant difference ($P< 0.05$) between AHPTHAC, AHPTOAC and AHPTDAC group copolymers using one way ANOVA analysis. In view of a slow dissolution problem, relatively low copolymer concentrations were used to dissolve in NaCl solution. The viscosity of the copolymer increases gradually and linearly with the polymer concentration which is in agreement with the general regularity (14). Poh and Ong (26) explained 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. At low polymer concentration, hydrophobic chains have little chance of interacting with each other, thus leading to the formation of small aggregates with a small hydrodynamic volume. Intramolecular associations are dominant compared to intermolecular associations in this dilute solution, thus the interactions produce a decrease in the hydrodynamic radius of the copolymer coil. As the copolymer concentration is increased, hydrophobic intermolecular associations are more probable, giving rise to a network structure of polymer chains by approaching each other leading to increase of solution viscosity (27).

NaCl salt was added to increase the polarity of solvent in order to reinforce the tendency of the intermolecular association and the formation of dimensional network (24). Zhang (14) stated that the polarity of solvent promoted by NaCl motivates intermolecular hydrophobic association, which results in increase of viscosity. The electrostatic shield of Cl^- to cation of quaternary ammonium will weaken the

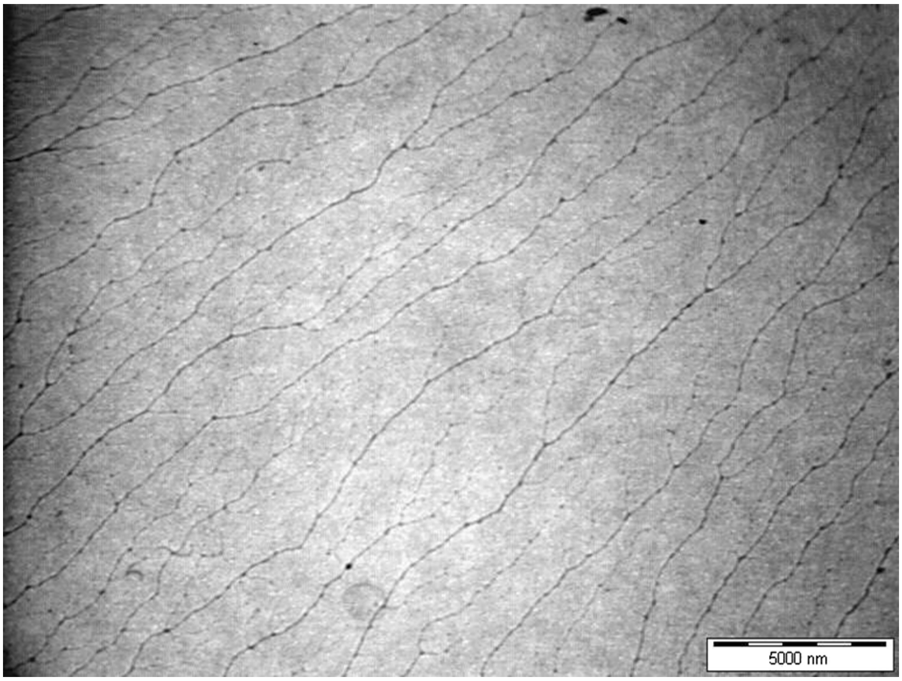


Fig. 8. TEM image of C601 copolymer under magnification power 6400×.

repulsion between polymer molecules, thus leading to easier hydrophobic association. In addition, the ionic species may enhance ordering of the hydrophobic microdomains in favor of viscosity enhancement.

3.7 Charge Density Determination

Charge density in the polymer is very important if used as cationic flocculants because it is closely related to flocculation properties of the polymer (4). Charge density of the

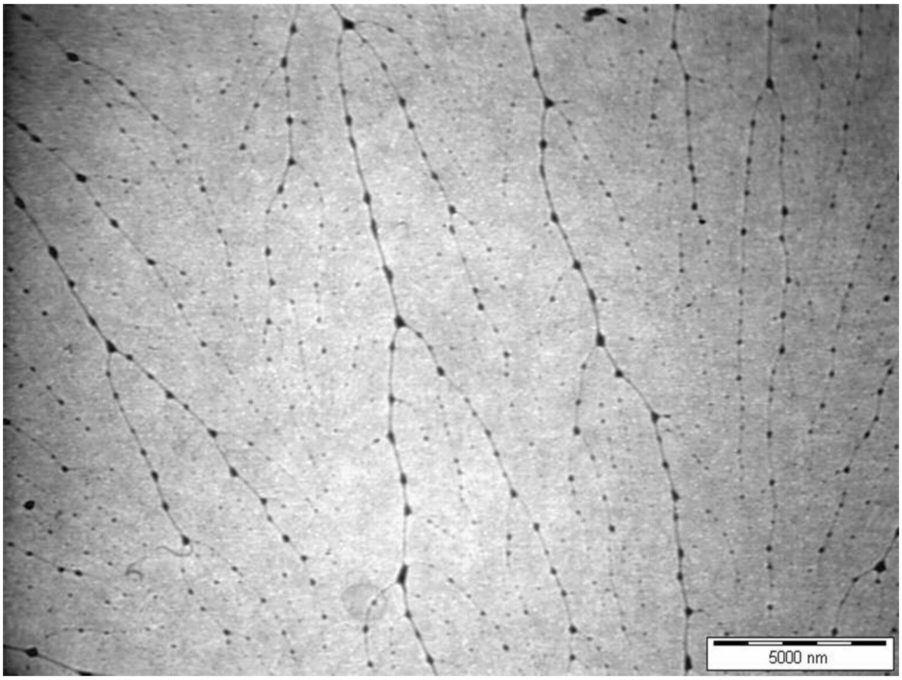


Fig. 9. TEM image of C801 copolymer under magnification power 6400×.

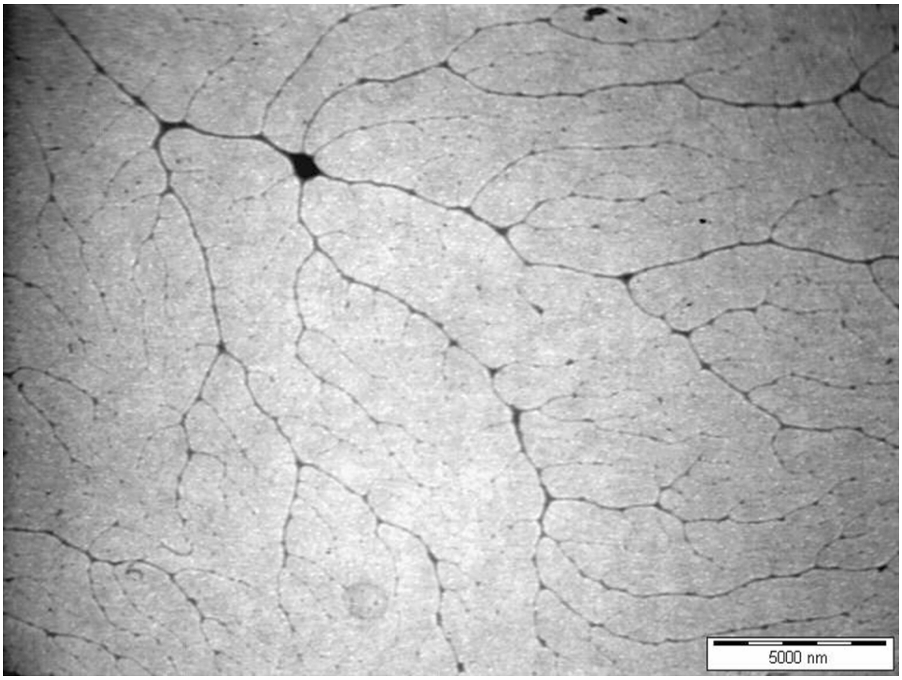


Fig. 10. TEM image of C1201 copolymer under magnification power 6400×.

hydrophobically modified cationic polyacrylamide is depicted in Table 1. The charge density increases as the intrinsic viscosity is decreased from monomer feed concentration of 1 to 6 mol%. Silver nitrate titration method used in this study is to determine the Cl^- ions of quaternary ammonium in the polymer solution. The charge density is found to increase with the increasing of cationic monomer concentrations in polymers. However, the increment of charge density differs between the hydrophobic groups. The difference of the charge densities between AHPTHAC, AHPTOAC and AHPTDAC group copolymers is significant ($p< 0.05$). The shorter chain hydrophobic group polymer exhibits higher charge density compared to longer chain groups in each ratio where the charge densities decrease in the sequence of AHPTHAC > AHPTOAC > AHPTDAC. This phenomenon can be explained by weaker attraction force between the quaternized ammonium group and Cl^- ion when the alkyl chain length increases.

3.8 TEM

The TEM images of the hydrophobically modified cationic polyacrylamide from AHPTHAC, AHPTOAC and AHPTDAC group are shown in Figures 8, 9, and 10, respectively. The molecular chain of AHPTHAC group can be described to be large, bulky and net-like nature under magnification power of 6,400×. With the increasing chain length, the bulkiness of the molecule structure decreases; while a more branchy structure is obtained. This is further elucidated by the AHPTOAC and AHPTDAC groups which have longer chain length. The micrographs also prove that the associations of hydrophobic group in the polymer chain are helpful to enlarge molecule. This is due to the repulsive force among the hydrophobic group which prevents the molecular chain bonding (20).

4 Conclusions

A series of hydrophobically modified cationic polyacrylamides have been synthesized by free radical solution copolymerization using ammonium persulphate/sodium hydrogen sulphite as the redox initiator. Three groups of polyacrylamide-based copolymers containing the hydrophobic cationic comonomers AHPTHAC, AHPTOAC and AHPTDAC groups are investigated. The yield of solid copolymers is more than 80%.Comparison between AHPTHAC, AHPTOAC and AHPTDAC-based copolymers shows significant difference in intrinsic viscosity, molecular weight, charge density and viscosity of the polymers. With an increase of AHPTHAC, AHPTOAC and AHPTDAC ratios, lower molecular weight polymer with higher charge density is obtained. For a fixed feed ratio, molecular weight and charge density decreases with an increase of chain length in the sequence of AHPTHAC > AHPTOAC > AHPTDAC. The viscosity of polymer in NaCl solution indicates similar trend between the three hydrophobic groups. TEM images show that the molecular structure becomes less bulky but branchier with the increase of the alkyl chain length of hydrophobic groups. The hydrophobicity increases with chain length resulting in greater repulsive force among the hydrophobic group which prevents the molecular chain bonding.

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