

# Amphibious Water-Soluble Copolymer. I. Its Synthesis and Dispersing Ability on Barium Titanate

Lung-Pin Chen, Kuo-Liang Ying, Kung-Chung Hsu

Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan 116, Republic of China

Received 10 February 2003; accepted 10 September 2003

**ABSTRACT:** An amphibious water-soluble copolymer, polyacrylamide/( $\alpha$ -*N,N*-dimethyl-*N*-acryloyloxyethyl) ammonium ethanate (PAAM/DAAE), was synthesized and used as a dispersion agent for BaTiO<sub>3</sub> particles. PAAM/DAAE was prepared from acrylamide and ( $\alpha$ -*N,N*-dimethyl-*N*-acryloyloxyethyl) ammonium ethanate under basic conditions through a free-radical polymerization. The structure of this copolymer was verified with IR and <sup>1</sup>H-NMR spectra. The dispersing effects of PAAM/DAAE were examined through the measurement of the viscosity and sedimenta-

tion of BaTiO<sub>3</sub> suspensions and the green density. The results indicated that this copolymer could uniformly disperse the particles, reduce the viscosity, stabilize the suspensions, and produce high-density green compacts. In comparison with a commercial dispersant, the ammonium salt of poly(methylacrylic acid), PAAM/DAAE was clearly more effective. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2232–2239, 2004

**Key words:** polyelectrolytes; synthesis; dispersions

## INTRODUCTION

Water-soluble polymers have been applied in many areas, such as mineral processing, water treatment, and coatings.<sup>1,2</sup> Another important area is the wet processing of ceramic powder.<sup>3,4</sup> These polymers, called polymeric surfactants or polyelectrolytes, have often been used as dispersants or stabilizers. Their roles are mainly to uniformly disperse solid particles and to stabilize ceramic slurries with less agglomeration or segregation during processing. Therefore, ceramic green parts with a uniform microstructure and a high packing density can be prepared, and sintered compacts without defects or pores can be obtained.

The dispersing mechanism of these polymeric surfactants is that, after being adsorbed onto ceramic particles, they create electrostatic, steric, or electrosteric forces.<sup>4–7</sup> This results in the dissociation of the agglomerates into primary particles with a significant reduction in the viscosity and a stable cloudy state of suspensions. Among commercial dispersants, acrylic acid based polyelectrolytes are commonly used for ceramic powders. For example, Cesarano and coworkers<sup>5,6</sup> showed that alumina suspensions could be stabilized with sufficient amounts of the sodium salt of poly(methacrylic acid), the ammonium salt of poly(methacrylic acid) (PMAAN), or poly(acrylic acid)

(PAA). Chen et al.<sup>7</sup> and Jean and Wang<sup>8</sup> found that either PAA or PMAAN could stabilize barium titanate slurries under certain pH conditions. De Laat and Van den Heuvel<sup>9</sup> reported that the molecular weight fraction of adsorbed PAA salts onto BaTiO<sub>3</sub> depended on the molecular weight distribution of the dispersants. Shih and Hon<sup>10</sup> studied the stability of colloidal silicon nitride suspensions with PMAAN and concluded that the conformation of the polymer chain, along with the electrostatic interactions, was the major factor in determining the stability of the slurries. Although some good results have been achieved, there are still some aspects that could be further improved. Specifically for barium titanate powder, it has been suggested that the resulting slurries be processed under basic conditions because of the substantial amount of Ba<sup>+2</sup> that leaches out from particles to solutions at pH values of less than 7.<sup>11,12</sup> However, the adsorption of acrylic acid based dispersants onto BaTiO<sub>3</sub> particles has been found to decrease with increasing pH because the polymers are more negatively dissociated.<sup>8,13</sup> Usually, more adsorption or greater surface coverage of the dispersants is preferred, and this generates larger electrostatic, steric, or electrosteric forces. In addition, the added dispersant molecules are expected to enhance Ba<sup>+2</sup> leaching because of their interactions with barium ions. This would generate exaggerated grain growth in the later sintering process and a low sintered density.<sup>11,12,14</sup> Therefore, new and more effective dispersants are worth developing.

In this study, we synthesized an amphibious water-soluble copolymer as a dispersant for barium titanate powder. Barium titanate was selected because of its

Correspondence to: K.-C. Hsu.

Contract grant number: National Science Council of the Republic of China; contract grant number: NSC-89-2211-E-003-003.

wide use in electronic devices such as multilayer capacitors, communications filters, and piezoelectric sensors. The synthesized copolymer was polyacrylamide/( $\alpha$ -*N,N*-dimethyl-*N*-acryloyloxyethyl) ammonium ethanate (PAAM/DAAE), which was prepared from acrylamide (AAM) and ( $\alpha$ -*N,N*-dimethyl-*N*-acryloyloxyethyl) ammonium ethanate (DAAE) through a free-radical polymerization. The dispersion effects of PAAM/DAAE on BaTiO<sub>3</sub> suspensions were examined and evaluated from the viscosity and sedimentation measurements, and the density of the green compacts was also measured.

## EXPERIMENTAL

### Materials

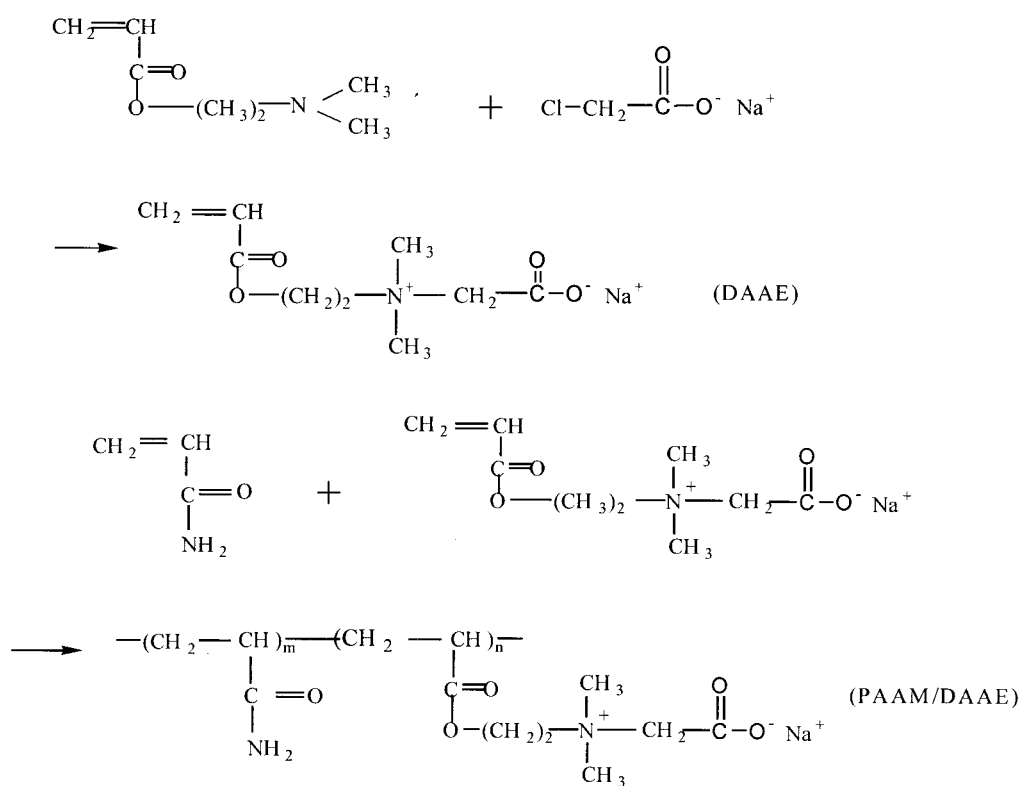
AAM, 2-dimethylamino ethyl acrylate, and sodium chloroacetate were used without further purification. PAAM/DAAE was prepared from the chemicals mentioned previously. The prepared PAAM/DAAE polymer had a fixed AAM/DAAE ratio of 10/1 and a weight-average molecular weight of  $1.2 \times 10^4$ . In addition, a commercial dispersant, PMAAN, with a

weight-average molecular weight of  $1.0 \times 10^4$ , was used for comparison. The molecular weights of the PAAM/DAAE and PMAAN polymers were measured with gel permeation chromatography (GPC), as discussed later.

The ceramic powder was high-purity BaTiO<sub>3</sub> from Prosperity Dielectrics (Taoyuan, Taiwan). The powder had a Ba/Ti ratio of 1/1, a median size of 0.9  $\mu\text{m}$ , and a Brunauer-Emmett-Teller (BET) specific surface area of 2.45 m<sup>2</sup>/g. Table I lists the characteristics of the BaTiO<sub>3</sub> powder. Deionized and distilled water was used, and the pH was adjusted by the addition of aqueous NaOH.

### Preparations of the PAAM/DAAE resins

PAAM/DAAE was prepared according to Kuo et al.'s<sup>15</sup> procedure, that is, from AAM and DAAE through a free-radical polymerization. Ammonium persulfate, along with sodium thiosulfate, was used as the initiator. DAAE was prepared from 2-dimethylamino ethyl acrylate and sodium chloroacetate. The reaction equations for preparing DAAE and PAAM/DAAE are as follows:



DAAE and PAAM/DAAE with 10/1 AAM/DAAE were prepared as follows. 2-Dimethylamino ethyl acrylate (12.2 g) and sodium chloroacetate (8.1 g) were dissolved in 60 mL of distilled water, and the mixture was added to a 250-mL stirred reactor. The reaction pro-

ceeded for 24 h at room temperature. After the reaction, the mixture was precipitated and purified with a 1/1 acetone/water solution. The acetone solution was removed in a vacuum oven at about 1.0 Torr and room temperature. The dried precipitate was DAAE (17 g).

TABLE I  
Basic Properties of the BaTiO<sub>3</sub> Powder

Ba/Ti	1/1
Purity (%)	99.76
SrO (%)	0.0667
Nb <sub>2</sub> O <sub>5</sub> (%)	0.008
Al <sub>2</sub> O <sub>3</sub> (%)	0.0428
SiO <sub>2</sub> (%)	0.0152
Median particle size (μm)	0.9
Moisture (%)	0.16
Ignition loss (%)	0.23
Compressed density (g/cm <sup>3</sup> )	3.269
BET specific surface area (m <sup>2</sup> /g)	2.45

AAM (30 g) and DAAE (8.12 g) were dissolved in 110 mL of distilled water, and then the mixture was added to a 250-mL stirred reactor. The reactor was purged with N<sub>2</sub> gas. Ammonium persulfate (1.91 g) and sodium thiosulfate (0.43 g) were added to the reactor, and the polymerization was carried out at room temperature for 7 days, the reactor being sealed. After the reaction, the mixture was precipitated and purified with a 1/1 acetone/water solution. The acetone solution was removed in a vacuum oven at about 1.0 Torr and room temperature. The dried precipitate was a PAAM/DAAE resin (26 g).

#### Identification of the prepared resins

The dried DAAE and PAAM/DAAE resins were further ground into a powder before the determination of the structure and other procedures. In identifying the chemical structure, we mixed the proper amount of powder samples with predried KBr and pressed them into disks. Transmission IR spectra of the disks were recorded with a PerkinElmer Paragon 500 Fourier transform infrared spectrometer (Boston, MA). Moreover, some powder samples were also dissolved in D<sub>2</sub>O and analyzed with a JEOL JNM-ECX 400 NMR spectrometer (Tokyo, Japan).

#### GPC measurements

The molecular weight of the dispersants was determined with a gel permeation chromatograph, which consisted of a Jasco liquid chromatograph (Tokyo, Japan) equipped with three coupled columns (Shodex OHpak KB802.5, KB804, and KB806), a pump (Jasco PU-980), and a refractive-index detector (Jasco RI-203). The samples were analyzed with a 0.1M KCl/methanol (80/20) aqueous solution as an eluant at a flow rate of 1 mL/min. Monodispersed polystyrene sulfonates of different molecular weights (1600, 4000, 6500, and 16,000) were used as calibration standards.

#### Preparation of the BaTiO<sub>3</sub> suspensions

Aqueous suspensions (100 g) containing either 22.7 wt % (5 vol %) or 60 wt % BaTiO<sub>3</sub> were prepared. They contained 0–4.8 wt % dispersant with respect to the weight of the dry BaTiO<sub>3</sub> powder. The suspensions were milled and mixed in a ceramic jar with a fixed number of zirconia balls for 24 h. The 24-h period of milling was believed to be long enough for a homogeneously dispersed state to be reached.

#### Viscosity measurements

The viscosity of 60 wt % BaTiO<sub>3</sub> aqueous suspensions at pH 12 with or without dispersants present was determined with a Brookfield LVDV-II viscometer (Middleboro, MA) with a #1 or 4 spindle at a rotation speed of 60 rpm.

#### ζ-potential measurements

BaTiO<sub>3</sub> aqueous suspensions (5 vol %, 22.7 wt %) at pH 12 with or without dispersants present were prepared. After ball-milling and centrifugation, a small amount of the supernatant was taken, and the ζ potential of the remaining powder in the supernatant was measured with a model 501 ζ meter (Pen Kem, Inc., New York, NY).

#### Sedimentation tests

BaTiO<sub>3</sub> aqueous suspensions (5 vol %) with or without dispersants present at pH 12 were prepared and poured into 200-mL graduated cylinders. These suspensions were left in the cylinders for 30 days, and the changes in the sedimentation volumes with the time were measured and recorded.

#### Measurements of the green compact density

Compacts were made through the gravitational settlement and consolidation of 60 wt % BaTiO<sub>3</sub> suspensions with or without dispersants. The density of the green compacts was evaluated by the Archimedes method.

#### Scanning electron microscopy (SEM) observations

The microstructures of BaTiO<sub>3</sub> green compacts with or without dispersants were observed with a JEOL JSM-6300 scanning electron microscope.

## RESULTS AND DISCUSSION

#### Structures of the prepared resins

The structures of typically prepared DAAE and PAAM/DAAE were verified with their IR and <sup>1</sup>H-NMR spectra, as shown in Figures 1 and 2, respectively. The IR spec-

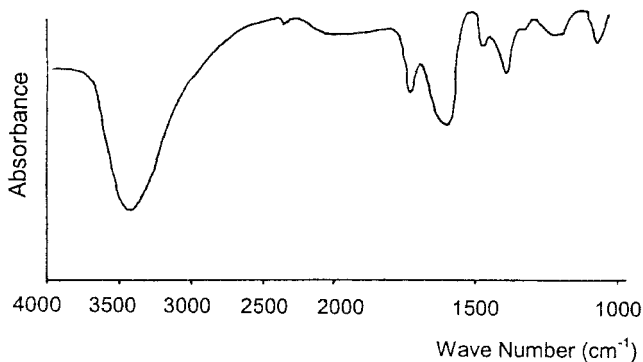


Figure 1 IR spectrum of DAAE.

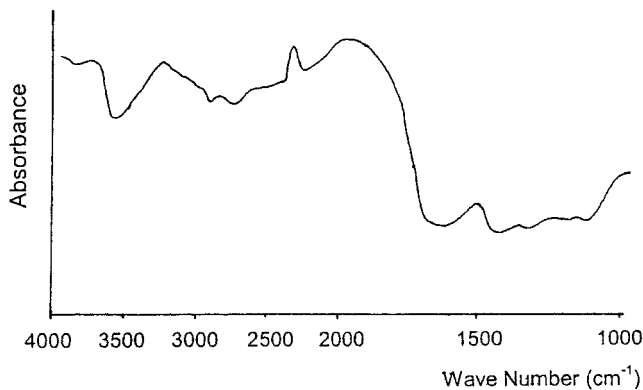


Figure 3 IR spectrum of PAAM/DAAE.

trum displays bands at 3432 (O—H), 1731 (C=O), 1620 (C=C), 1300 (C—O), and 1239 and 1010  $\text{cm}^{-1}$  (C—O—C). The  $^1\text{H-NMR}$  spectrum shows signals at  $\delta = 2.8$  (s, 1H), 3.1 (s, 2H), 3.6 and 3.8 (t, 3H, 4H), and 4 ppm (s, overlap of 5H, 6H, and 7H). Figures 3 and 4 show the IR and  $^1\text{H-NMR}$  spectra of prepared PAAM/DAAE. The IR spectrum displays bands at 3480 (overlap of O—H and N—H), 2757 ( $\text{NH}_2$ ), and 1659  $\text{cm}^{-1}$  (C=O). The  $^1\text{H-NMR}$  spectrum shows signals at  $\delta = 1.6$  (overlap

of 1H and 5H), 2.2 (6H), 3.1 (2H), 4.1 (overlap of 3H and 4H), and 10.3 ppm (7H).

In comparison with Figure 1, the IR spectrum in Figure 2 lacks a C=C absorption band at 1620  $\text{cm}^{-1}$  and contains a new N—H absorption band at 2757  $\text{cm}^{-1}$  as a result of the polymerization of AAM and DAAE. Furthermore, the signal at  $\delta = 4$  ppm (related to the protons in  $\text{CH}_2=\text{CH}-$ ) in Figure 3 should

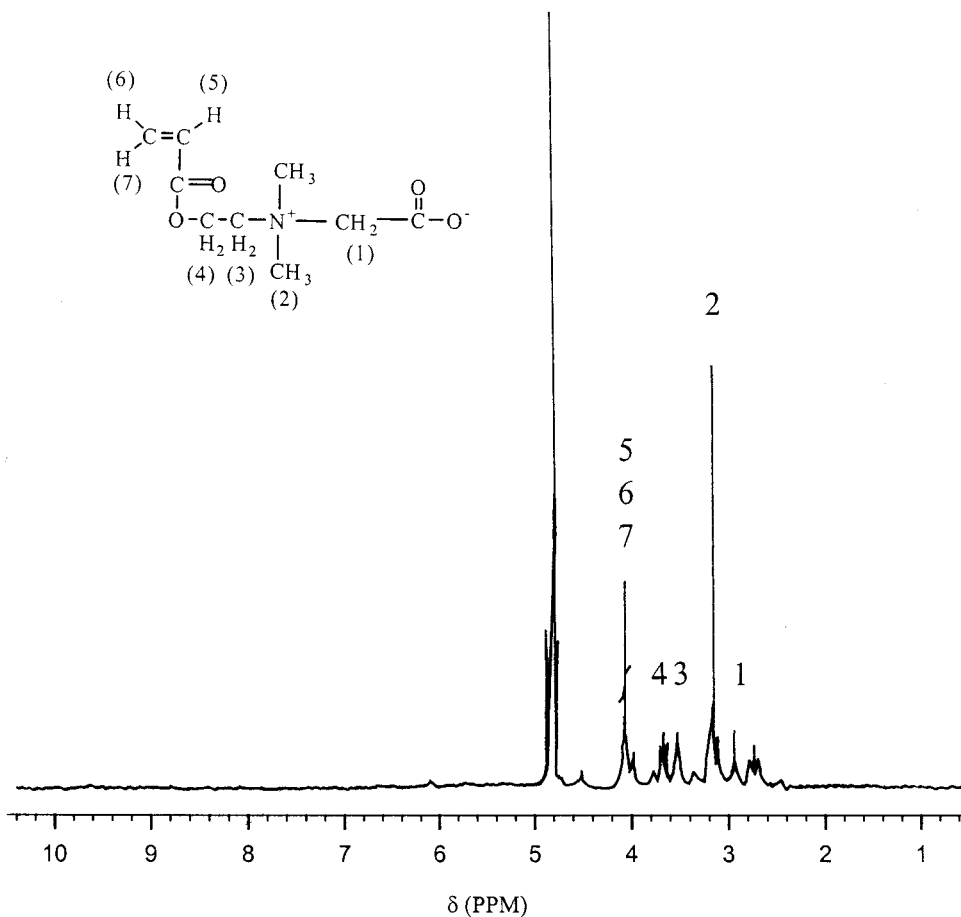


Figure 2  $^1\text{H-NMR}$  spectrum of DAAE.

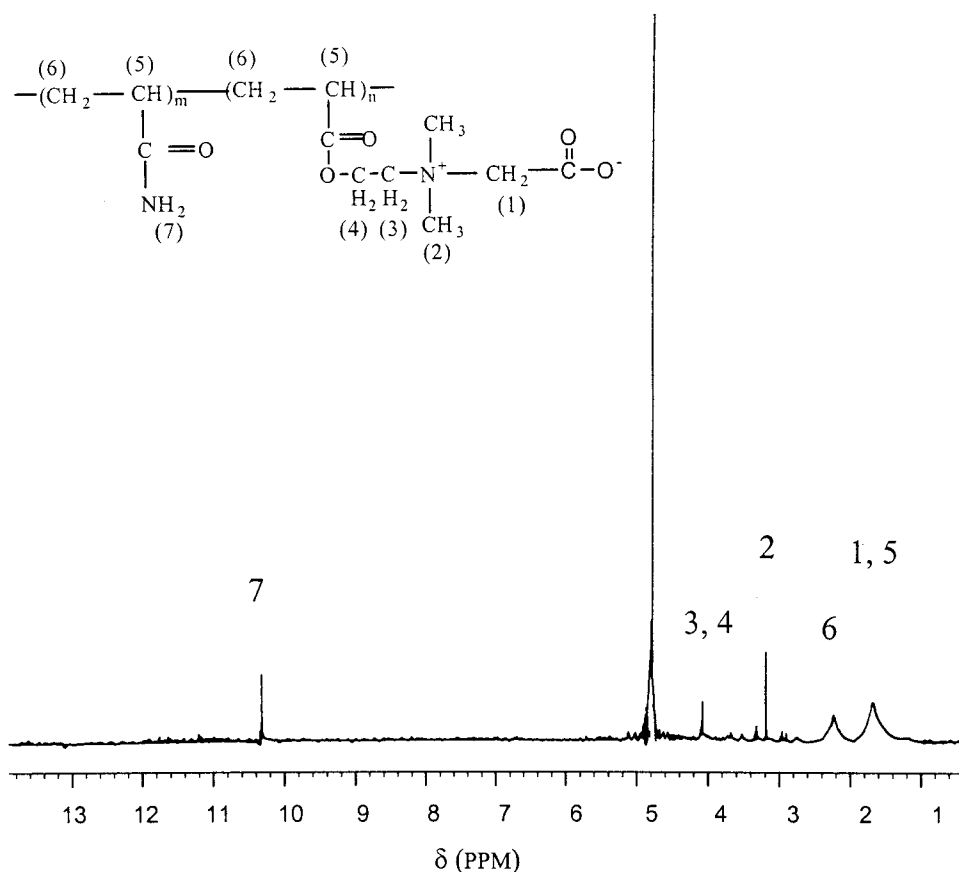


Figure 4 <sup>1</sup>H-NMR spectrum of PAAM/DAAE.

disappear in Figure 4, and new signals at  $\delta = 1.6$  and 2.2 ppm (related to the protons in  $-\text{CH}_2-\text{CH}-$ ) and at  $\delta = 10.3$  ppm (related to the proton in  $-\text{NH}_2$ ) appear in Figure 4. The signal at  $\delta = 4.1$  is related to the protons in  $-(\text{CH}_2)_2-$ . This indicates the formation of the copolymer from its two monomers.

### Rheological behavior

For concentrated suspensions, viscosity measurements are an appropriate means of evaluating the extent of dispersion.<sup>13</sup> Figure 5 shows the viscosity of 60 wt %  $\text{BaTiO}_3$  suspensions at pH 12 as a function of the dispersant concentration. Generally, the viscosity of suspensions depends on the viscosity of polymer solutions and the volume fraction of solid particles. When the polymer concentration increases, the resulting suspensions are expected to be more viscous. However, the viscosity of suspensions can be reduced if the added polymer is able to disperse particles. As shown in Figure 5, the viscosity of  $\text{BaTiO}_3$  suspensions without a dispersant is about 2000 cps. The values decrease when PAAM/DAAE is incorporated, and this indicates that PAAM/DAAE can enhance the dispersion of  $\text{BaTiO}_3$  particles. As the PAAM/DAAE concentration is increased, the viscosity

of suspensions decreases first and then reaches a plateau. The critical optimum dispersant concentration, that is, the amount that gives the lowest viscosity, is about 1.5

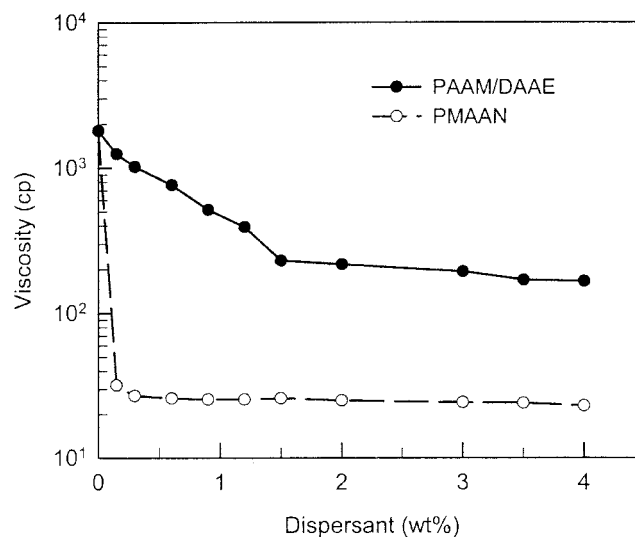
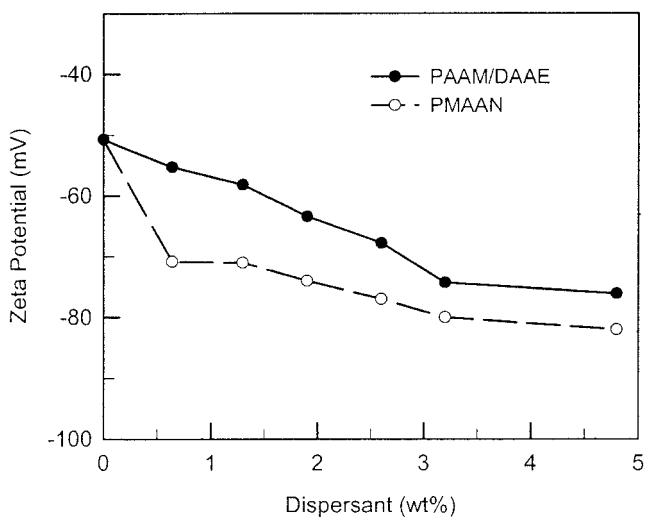


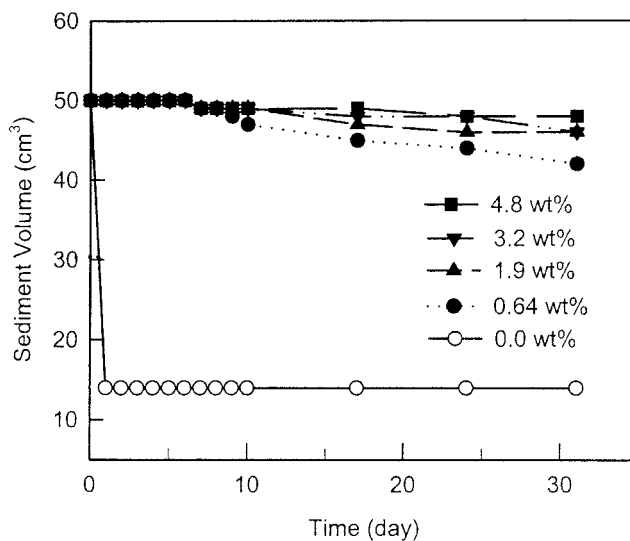
Figure 5 Effect of the dispersant concentration on the viscosity of 60 wt %  $\text{BaTiO}_3$  suspensions at pH 12.



**Figure 6** Effect of the dispersant concentration on the  $\zeta$  potential of 5 vol % BaTiO<sub>3</sub> suspensions at pH 12.

wt %. In contrast, the viscosity of suspensions decreases rather sharply with the PMAAN concentration, and then it reaches a minimum value. The amount of PMAAN required to achieve the lowest viscosity is about 0.16 wt %, which is much less than the amount of PAAM/DAAE required. Furthermore, the minimum viscosity of the suspensions with PMAAN is lower than that with PAAM/DAAE.

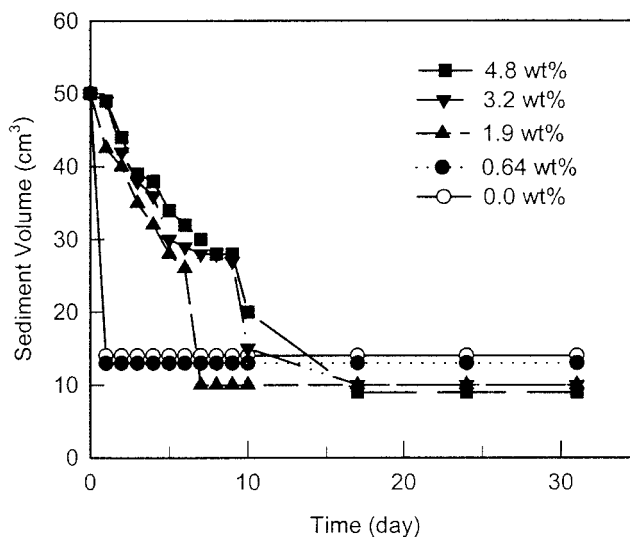
As PMAAN and PAAM/DAAE have similar molecular weights, the difference in their rheological behavior is believed to be due to their different dispersion effects. PMAAN molecules are anionic polyelectrolytes, which cause mainly electrostatic repulsions when adsorbed onto BaTiO<sub>3</sub> particles. In contrast, PAAM/DAAE molecules also cause electrostatic repulsions when adsorbed onto BaTiO<sub>3</sub> particles. However, the effect should be less than that by PMAAN molecules because they belong to amphibious polyelectrolytes. Figure 6 shows the effect of the dispersant concentration on the  $\zeta$  potential of 5 vol % BaTiO<sub>3</sub> suspensions at pH 12. The  $\zeta$  potential of suspensions without a dispersant is -50.8 mV. This value becomes more negative when a dispersant is present in the suspensions. For suspensions with PAAM/DAAE, the  $\zeta$  potential decreases with increasing dispersant concentration and then approaches a constant value (-76.1 mV). For suspensions with PMAAN, the initial decreasing rate of the  $\zeta$  potential is greater, and the final constant value (-82 mV) is more negative. This confirms that PMAAN causes stronger electrostatic repulsions than any other dispersant. However, PAAM/DAAE is expected to produce greater steric effects than PMAAN because the former molecules contain longer side chains.



**Figure 7** Effect of the PAAM/DAAE concentration on the sedimentation of 5 vol % BaTiO<sub>3</sub> suspensions at pH 12.

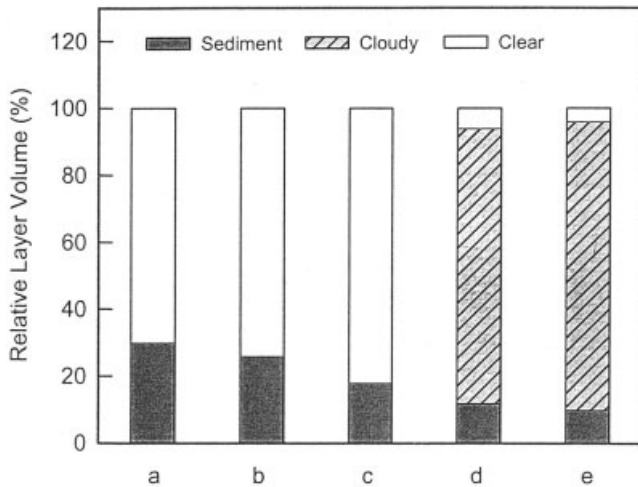
**Sedimentation**

Observing and measuring the sedimentation is another way of examining the colloidal stability. A good dispersant will make suspensions cloudy and result in a small final sedimentation height.<sup>7,8</sup> Figure 7 shows the sedimentation of 5 vol % BaTiO<sub>3</sub> suspensions with various amounts of PAAM/DAAE at pH 12. Suspensions without any dispersants are not stable and separate into two layers after 1 day of sedimentation; a clear boundary exists between a sediment layer and an upper clear aqueous layer. When PAAM/DAAE is added, the resulting suspensions remain stable and cloudy for 30 days. Moreover, a clear layer above the



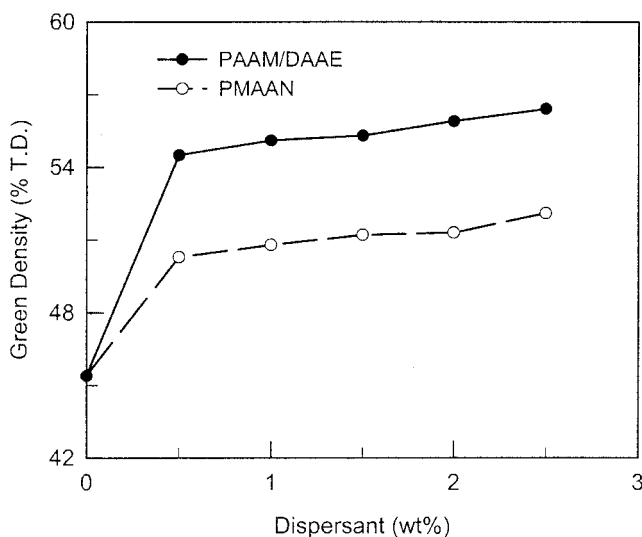
**Figure 8** Effect of the PMAAN concentration on the sedimentation of 5 vol % BaTiO<sub>3</sub> suspensions at pH 12.



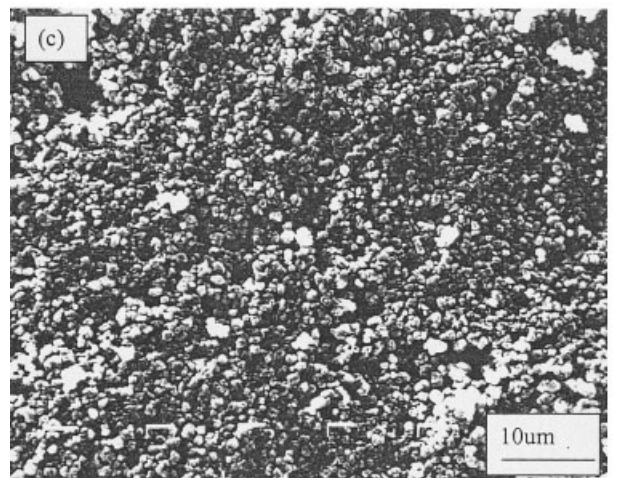
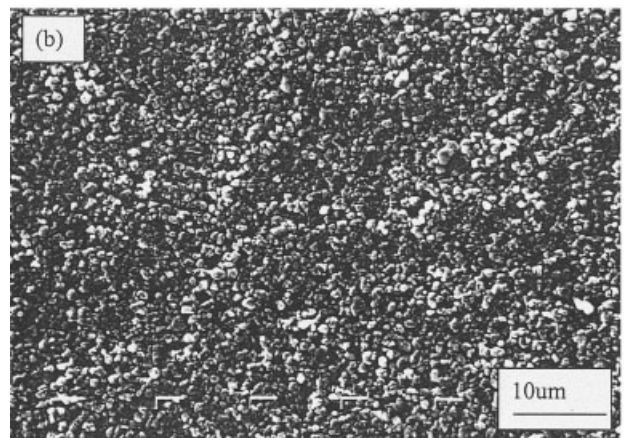
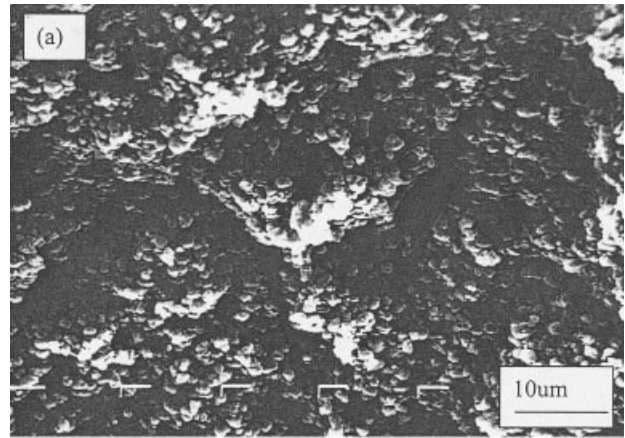


**Figure 9** Relative layer volume of 5 vol %  $\text{BaTiO}_3$  suspensions (a) without any dispersant, (b) with 0.64 wt % PMAAN, (c) with 3.2 wt % PMAAN, (d) with 0.64 wt % PAAM/DAAE, and (e) with 3.2 wt % PAAM/DAAE at pH 12 after 30 days of settling.

cloudy layer appears in suspensions when the sedimentation time is longer than 5 days. Different amounts of PAAM/DAAE only cause some changes in the thickness of the cloudy layer. Figure 8 shows the effect of the PMAAN concentration on the sedimentation of 5 vol %  $\text{BaTiO}_3$  suspensions at pH 12. When the amount of added PMAAN is less than 0.64 wt %, the suspensions separate quickly into two layers within 1 day; they become more stable and remain in a cloudy state longer if more PMAAN is incorporated. Nevertheless, the suspensions become unstable and separate into two layers when the sedimentation time is longer than 20 days even if the amount of added PMAAN reaches 4.8 wt %.



**Figure 10** Effect of the dispersant concentration on the green density of the  $\text{BaTiO}_3$  compacts.



**Figure 11** SEM micrographs of  $\text{BaTiO}_3$  green compacts (a) without any dispersant, (b) with 2.5 wt % PAAM/DAAE, and (c) with 2.5 wt % PMAAN.

Figure 9 shows the relative volume of each layer of 5 vol %  $\text{BaTiO}_3$  suspensions with different dispersant concentrations at pH 12 after 30 days of settling. Two layers, that is, a clear layer and a sediment layer, can be observed for suspensions without any dispersant present. The volume of the top layer is 70%, and that of the other layer is 30%, if we assume that the total

volume is 100%. Similarly, the PMAAN suspensions also contain two layers. However, the sediment height of suspensions with PMAAN present is less than that of suspensions without PMAAN. Suspensions with greater PMAAN concentrations contain smaller final sediment heights. In contrast, three layers, that is, a clear layer, a cloudy layer, and a sedimentation layer, can be observed for BaTiO<sub>3</sub> suspensions incorporated with PAAM/DAAE. This indicates that both dispersants can enhance the colloidal stability, and PAAM/DAAE appears to be more effective than the other.

### Green compact density

The green density of the powder compact obtained from the gravitation, sedimentation, and consolidation of a suspension is shown in Figure 10. The green density is an index of the extent of powder packing. As shown in Figure 10, the green density of BaTiO<sub>3</sub> compacts is 45.4% with respect to the true density of the powder. This value is higher when dispersants are incorporated. Along with an increasing dispersant concentration, the green density is also increased. Furthermore, compacts with PAAM/DAAE show higher density than those with PMAAN, and this confirms that the former generates better packing efficiency than the latter because of the formation of more stable suspensions.

Figure 11 shows SEM micrographs of BaTiO<sub>3</sub> green compacts with or without the presence of a 2.5 wt % dispersant. The compact with no dispersant appears to be more porous, and the particles are less uniformly dispersed. In contrast, the suspensions with the dispersant show lower viscosity and form denser and more consolidated compacts. Apparently, the particles in the compacts with PAAM/DAAE are more uniformly dispersed than those with PMAAN. This proves that PAAM/DAAE is better than PMAAN in dispersing BaTiO<sub>3</sub> particles.

### CONCLUSIONS

In this study, an amphibious water-soluble copolymer, PAAM/DAAE, has been synthesized, and its chemical structure has been verified with IR and <sup>1</sup>H-NMR spectra. As PAAM/DAAE can uniformly disperse BaTiO<sub>3</sub> particles, the resulting suspensions with this copolymer become less viscous and more stable, and the green compact is more consolidated and shows higher green density. PAAM/DAAE has been proved to be a good dispersant or stabilizer. This copolymer appears to be even more effective for BaTiO<sub>3</sub> suspensions than the commercial dispersant PMAAN.

The authors are grateful to the Academic Paper Editing Clinic of the National Taiwan Normal University.

### References

1. Molyneux, P. *Water-Soluble Synthetic Polymers: Properties and Behavior*; CRC: Boca Raton, FL, 1984.
2. Piirma, I. *Polymeric Surfactants*; Marcel Dekker: New York, 1992.
3. Reed, J. S. *Introduction to the Principles of Ceramic Processing*, 2nd ed.; Wiley: New York, 1995.
4. Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic: New York, 1983.
5. Cesarano, J., III; Aksay, I. A.; Blier, A. *J Am Ceram Soc* 1988, 71, 250.
6. Cesarano, J., III; Aksay, I. A. *J Am Ceram Soc* 1988, 71, 1062.
7. Chen, Z. C.; Ring, T. A.; Lemaitre, J. *J Am Ceram Soc* 1992, 75, 3201.
8. Jean, J. H.; Wang, H. R. *J Am Ceram Soc* 1998, 81, 1589.
9. De Laat, A. W. M.; Van den Heuvel, G. L. T. *Colloids Surf A* 1995, 98, 53.
10. Shih, C. J.; Hon, H. M. *Mater Chem Phys* 1998, 57, 125.
11. Blanco-Lopez, M. C.; Rand, B.; Riley, F. L. *J Eur Ceram Soc* 1997, 17, 281.
12. Neubrand, A.; Lindner, R.; Hoffmann, P. *J Am Ceram Soc* 2000, 83, 860.
13. Carlos, G. Y.; Heberto, B. R.; Froylan, M. *Ceram Int* 2000, 26, 209.
14. Nanni, P.; Leoni, M.; Buscaglia, V.; Aliprandi, G. *J Eur Ceram Soc* 1994, 14, 85.
15. Kuo, P. L.; Kao, R. F.; Lai, G. J. *R.O.C. Pat.* 65966 (1994).