

# Functional Polymers for Colloidal Applications. XIV. Syntheses of Styrene–Maleic Anhydride Copolymers with Different Charges and Their Ability to Disperse Kaolinite Particles

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**ABSTRACT:** Four kinds of styrene/maleic–anhydride (SMA) copolymer-derived dispersants with different charged forms were synthesized and characterized with <sup>1</sup>H-NMR. These four different dispersants contained carboxylic acid groups and exhibited characteristics indicative of anionic, cationic, zwitterionic, or nonionic surfactants as pH was changed. The charge properties of these copolymers changes with pH, and their ability to disperse clay particles under low and high pH were assessed by measuring viscosity or sedimentation, as well as Scanning Electron Microscopy (SEM). The results showed that the dispersing abilities are functions of pH of the system. It was found that SMA-N [Poly(styrene-co-β-N,N-dimethylpropylamino) maleic acid, sodium salt)] exhibits the best dispersing ability, the fastest rate of sedimentation, and the smallest sedimentation volume at pH = 2, and SMA-Na [poly(styrene-co-maleic acid, disodium salt)] exhibits the better dispersing ability at pH = 7 and 12. In addition, the aggregation behavior of the dispersants characterized by fluorescence spectroscopy revealed that the degree of aggregation for all dispersants at high concentration increases in the order: SMA-Na < SMA-B [poly(styrene-co-B-imino-propyl-N-trimethylammonium acetate) maleic acid, disodium salt)] < SMA-N < SMA-Q [poly(styrene-co-β-imino-propyl-N-trimethylammonium sulfate) maleic acid, sodium salt)]. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 592–602, 2000

**Key words:** SMA copolymers; colloidal application; kaolinite particles

## INTRODUCTION

A colloidal suspension with particles dispersed in solution is thermodynamically unstable; thus, dispersants are normally used to stabilize the system. The main function of the dispersant is to provide the particles with an electrostatic barrier<sup>1–4</sup> and/or steric hindrance,<sup>5,6</sup> to prevent the coagulation of particles, or to modify the surface properties of the particles to be more compatible with the medium.<sup>7</sup> An effective dispersant normally has a tendency to effectively adsorb on particles. Thus, the structure and functional group of a dispersant can be designed for a specific type of particle to be dispersed. As a result of the importance of dispersing technology in industry, it attracts a wide range of attention in both academic research and industrial applications.<sup>1,8</sup>

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Kaolinite is an important raw material for fine ceramics. In this field, it is very important to be able to effectively disperse kaolinite particles. Kaolinite contains the aluminum hydroxide group that is protonated at low pH and ionized at high pH; thus, the charge properties on the edge of the kaolinite flake change with pH; i.e., the kaolinite flakes show zwitterionic properties at low pH and anionic properties at high pH. It is interesting to prepare polymers containing different types of charges and to study the dispersing ability of these polymers with kaolinite particles at different pH.

Due to their economic price, styrene–maleic anhydride copolymers (SMA) have been widely used as dispersants after neutralization with alkali to form salts, and/or modified by alcohol to form esters.<sup>9–11</sup> However, zwitterionic types of SMA have never been studied. In this article, SMA copolymers that incorporate anionic, cationic, zwitterionic, or nonionic groups (as shown in Scheme 1) were synthesized and characterized. The charge properties of these copolymers change with pH. Their ability to disperse clay particles under low and high pH were assessed by methods such as viscosity, sedimentation, and Scanning Electron Microscopy (SEM). These results were correlated and interpreted in terms of the charge properties and polymer structure.

## EXPERIMENTAL

### Materials

Styrene Maleic Anhydride copolymer, SMA (Arco, SMA1000,  $M_n = 1600$ , 50% styrene), *N,N*-dimethyl-1,3-propanediamine (T.C.I., GR grade), dimethyl sulfate (Wako, EP grade), sodium chloroacetate (Merck, >99%), and sodium hydroxide (Wako, EP grade), were used without further purification. Kaolinite (Akima 35, 48.57% SiO<sub>2</sub> and 36.92% Al<sub>2</sub>O<sub>3</sub>) were used as supplied. The water used in these experiments was ion exchanged and distilled, with a pH between 6.8–7.2, and conductivity of  $4.4 \times 10^{-6} \Omega^{-1} \cdot \text{m}^{-1}$ .

### Synthesis and Characterization of Dispersants

**Synthesis of SMA-Na (poly(2-phenyl-3,4-disodium carboxylate butylene)) (poly(styrene-co-maleic acid, disodium salt)) (Scheme 1)**

In a 1000-mL reaction kettle, 80 g (0.05 mol) of SMA was added to 400 mL of 1 N NaOH solution.

The reaction was carried out at room temperature for 8 h. pH values were adjusted to 9–10 by adding 1 N NaOH aqueous solution. The reaction product was then dried by a rotavapor (Buchi RE111, Swiss) and reprecipitated in acetone. The residue was dried in a vacuum oven at 38°C/3 mmHg for 48 h to give the product, with a yield of 80%.

**Synthesis of SMA-N [poly(2-phenyl-3-(sodium carboxyl)-4-(carbonyl imino propyl dimethyl amino) butylene] [Poly(styrene-co-β-N,N-dimethylpropylamino) maleic acid, sodium salt] (Scheme 1)**

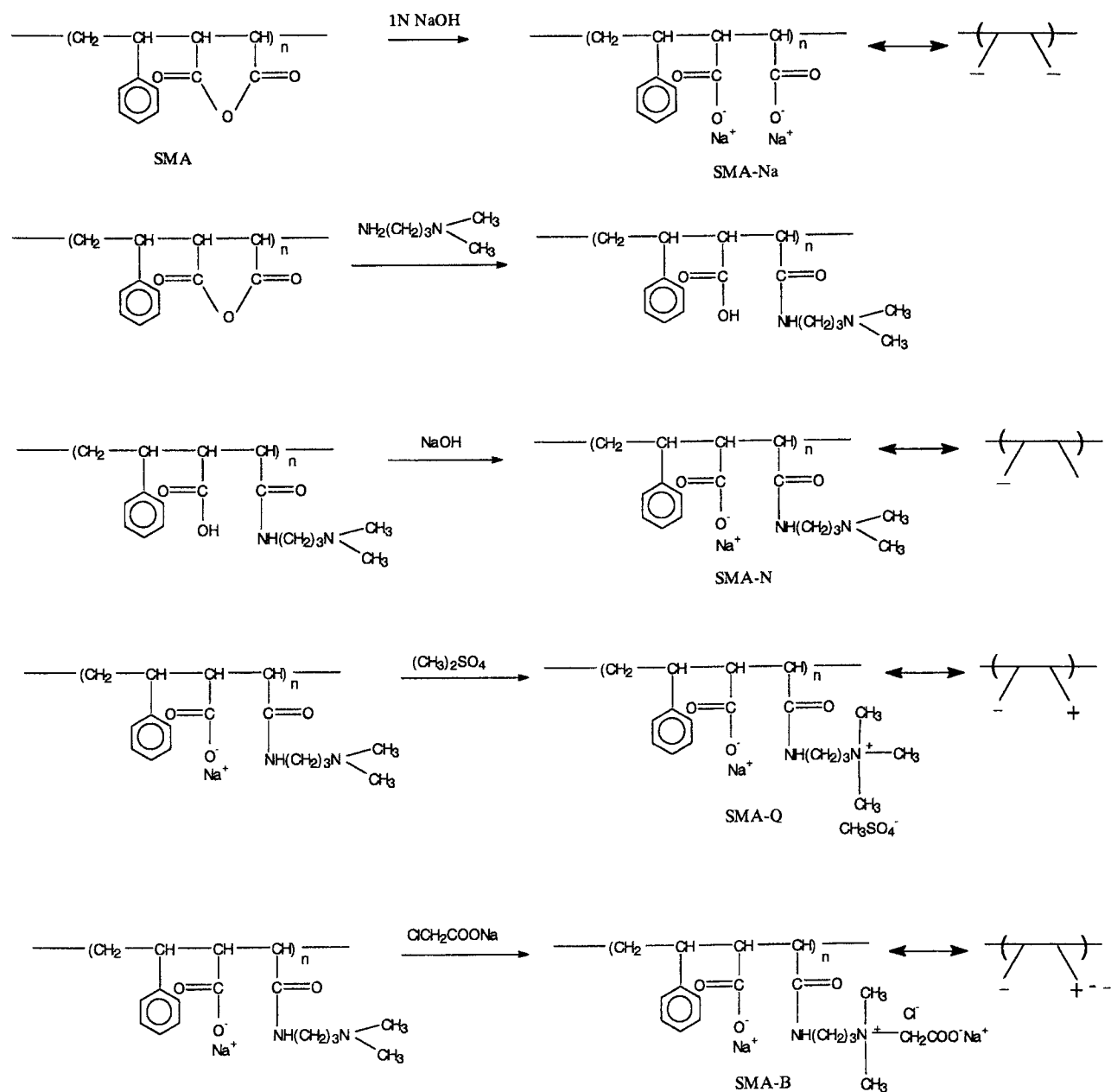
In a 500-mL reaction kettle, 40 g (0.025 mol) of SMA and 22.48 g (0.22 mol) of *N,N*-dimethyl-1,3-propanediamine were added to 300 g of 1,4-dioxane. The reaction was refluxed at 100°C for 24 h, and then cooled to room temperature. The solvent was removed with a rotary evaporator (rotovac) to give the solid residue. The residue was dissolved in water, the pH adjusted to 9–10 with 1 N NaOH solution. Water was then removed with a rotovac. The polymer was reprecipitated in acetone and dried in a vacuum oven at 40°C for 48 h to give the final product.

**Synthesis of SMA-Q [poly(2-phenyl-3-(sodium carboxyl)-4-(carbonyl imino propyl dimethyl ammonium sulfate) butylene] [poly(styrene-co-β-imino-propyl-N-trimethylammonium sulfate) maleic acid, sodium salt] (Scheme 1)**

In a 500-mL reaction kettle, 32.4 g (0.0125 mol) of the above SMA-N polymer and 12.81 g (0.11 mol) of dimethyl sulfate were added to 200 g of distilled water. The solution was adjusted to a pH of 13 by adding an aqueous solution of 1 N NaOH. The reaction was run for 6 h at room temperature. The solution was then dried using a rotavapor to remove residual and water, then reprecipitated in acetone to give the product. The final polymer was obtained upon drying under vacuum at 40°C for 2 days.

**Synthesis of SMA-B [poly (2-phenyl-3-(sodium carboxyl)-4-(carbonyl imino propyl dimethyl ammonium acetic ion) butylene] [poly(styrene-co-B-imino-propyl-N-trimethylammonium acetate) maleic acid, disodium salt] (Scheme 1)**

This reaction was carried out in a similar manner as SMA-Q except that sodium chloroacetate



Scheme 1

(12.81 g, 0.11 mol) was added instead of dimethyl sulfate, and the pH was adjusted to ca. 10.

#### Characterization of Dispersants

SMA itself and the other dispersants were dissolved in acetone- $d_6$  and  $\text{D}_2\text{O}$  respectively, and then characterized with  $^1\text{H-NMR}$  (Bruker WP 100).

#### Assessment of the Dispersing Abilities of Dispersants

Dispersed clay/water systems were prepared using the different dispersants. The dispersant

0–3.36 g (0–8 wt % based on kaolinite) was dissolved in water (78 g) and mixed with the kaolinite-type clays (42 g); then milled balls (2 mm, 84 g) were added for milling. The mixture was shaken mechanically (Red Devil, USA) for 1 h at room temperature. All of the prepared pastes were assessed by the following methods:

Rheological method: ten milliliters of the above dispersed paste were put in a Brookfield viscometer adapter outfitted with a SCS-31 spindle, and the viscosity was measured by using a rotating cylindrical viscometer (Brookfield DVII LVT).

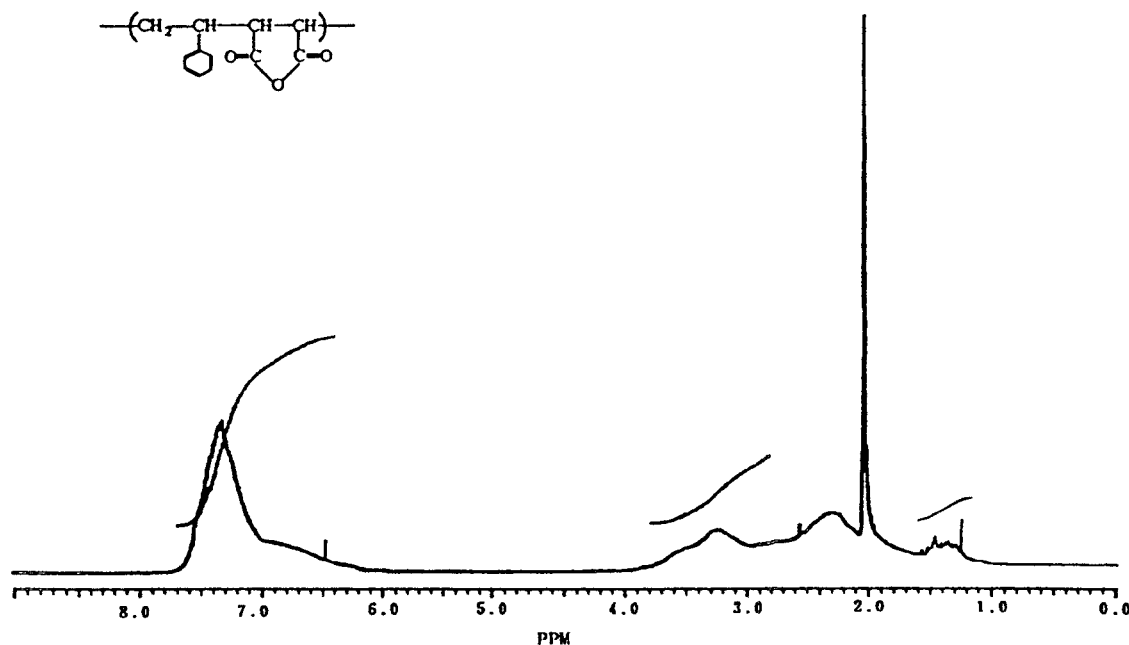


Figure 1  $^1\text{H-NMR}$  spectrum of SMA.

The apparent viscosity (under a fixed shear rate) was used as a parameter to evaluate the dispersing ability of the various prepared dispersants. All of the viscosities were measured at  $25^\circ\text{C}$ .

Scanning electron microscopy (SEM): the dispersed paste (ca. 1 g) was coated (ca.  $25\ \mu\text{m}$  wet film thickness) on a thin copper plate. After drying at room temperature for 1 day, a small piece of the paste (ca.  $4 \times 4\ \text{mm}^2$ ) was cut and put on an aluminum sheet (with diameter of 20 mm) and electrodeposited with a layer of gold. The surface of the coating film was observed by an SEM electron probe microanalyzer (Hitachi F-4100).

Sedimentation method: The dispersed pastes (ca. 20 mL) were put into 50-mL graduated cylinders, and the tops of the cylinders were sealed. The heights of the precipitates were recorded after given time intervals; thus, the rate of precipitation and the final volume ratio could be measured.

Fluorescence spectroscopy: Fluorescence spectroscopy measurement was carried out with an Hitachi F-4010 fluorescence spectrometer. Polymers with different concentrations were dissolved in a saturated pyrene/ethanol solution mixed with a buffer solution of  $\text{pH} = 7$ . The absorption intensity ratios of  $I_1/I_3$  ( $I_1 = 372.4\ \text{nm}$ ,  $I_3 = 383\ \text{nm}$ ) were recorded.

## RESULTS AND DISCUSSION

### Polymer Synthesis

Four types of dispersants with different charged forms were synthesized. The  $^1\text{H-NMR}$  spectra of SMA copolymer and the derived dispersants are shown in Figures 1–5, respectively. For the SMA copolymer, the resonance peak at 7.2–7.4 ppm is ascribed to the protons of the benzene ring, while the peak at 2.35 ppm is associated with the protons of the maleic anhydride backbone. As compared to Figure 1, the resonance peak at 2.1 ppm for SMA-N (Fig. 3) is assigned to the protons of two methyl groups on the nitrogen atom, indicating a successful linking of *N,N*-dimethyl-1,3-propanediamine to SMA copolymer. In the case of SMA-Q, as seen in Figure 4, the resonance peak shifts from 2.1 to 3.0 ppm, indicating the transformation of a tertiary amine to a quaternary amine salt. Figure 5 shows the  $^1\text{H-NMR}$  spectrum of SMA-B. Compared to Figure 4, the resonance peak at 3.0 ppm is also ascribed to the formation of a quaternary amine salt. Moreover, the resonance peak at 3.67 ppm is assigned to the protons of  $-\text{N}^+-\text{CH}_2-\text{COO}^-$ , indicating the methylenation of SMA-N by  $\text{ClCH}_2\text{COONa}$  to a detached zwitterionic-type quaternary amine salt.

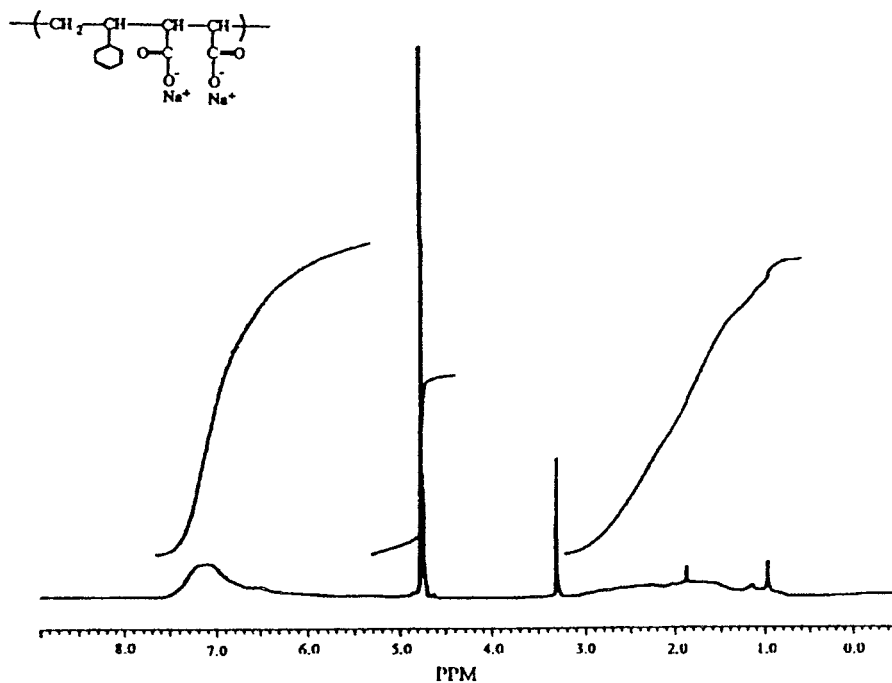


Figure 2 <sup>1</sup>H-NMR spectrum of SMA-Na.

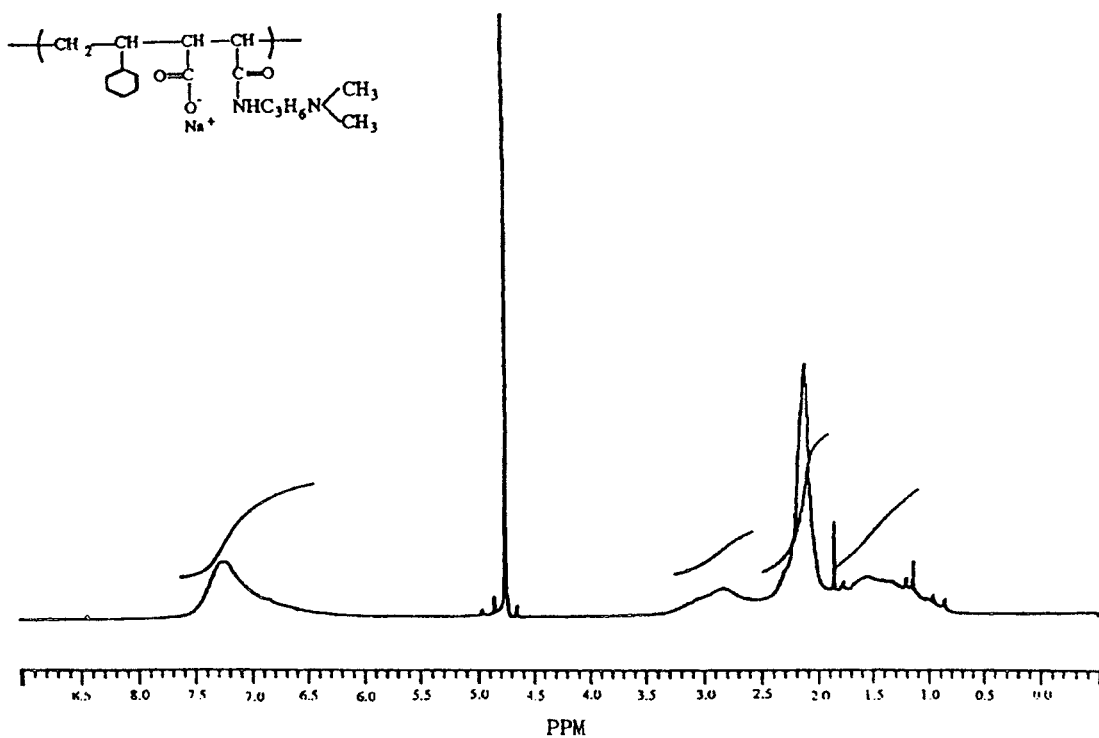


Figure 3 <sup>1</sup>H-NMR spectrum of SMA-N.

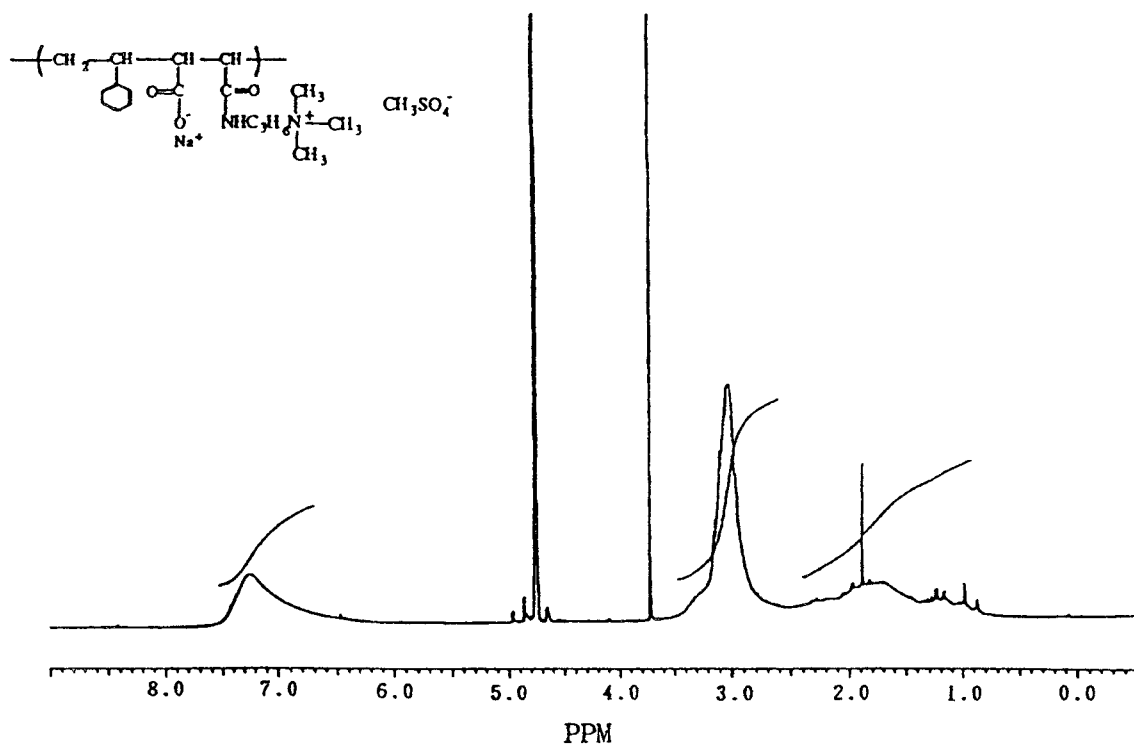
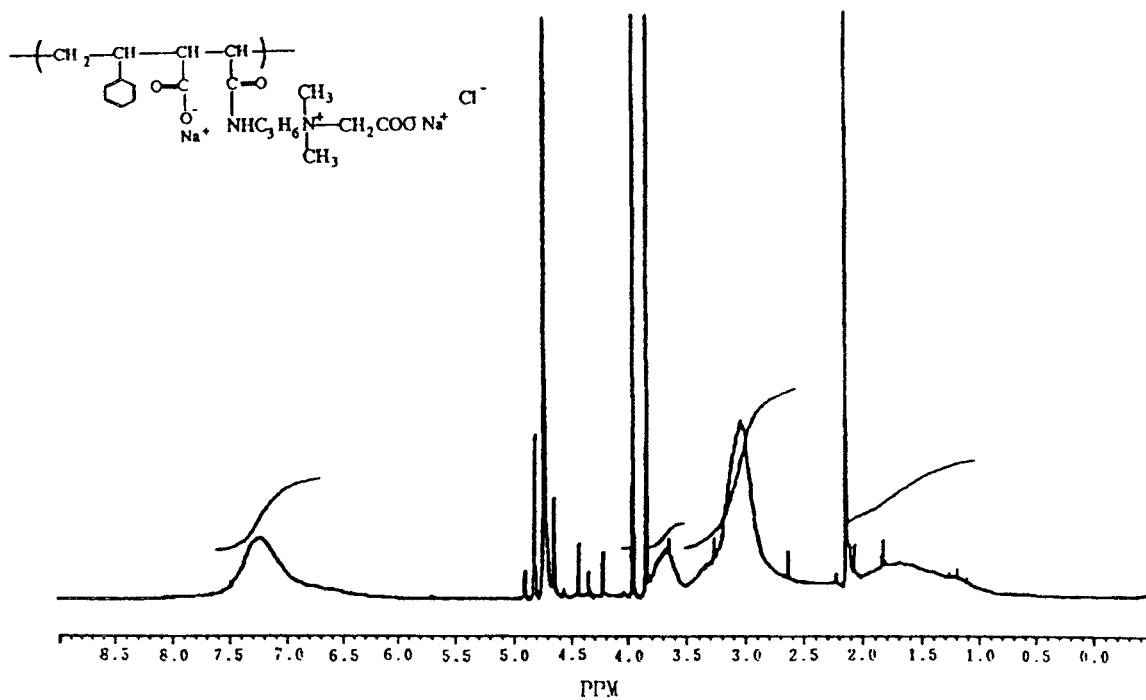
Figure 4  $^1\text{H-NMR}$  spectrum of SMA-Q.Figure 5  $^1\text{H-NMR}$  spectrum of SMA-B.

Table I Different Charged Forms of the Four Dispersants at Different pH Values

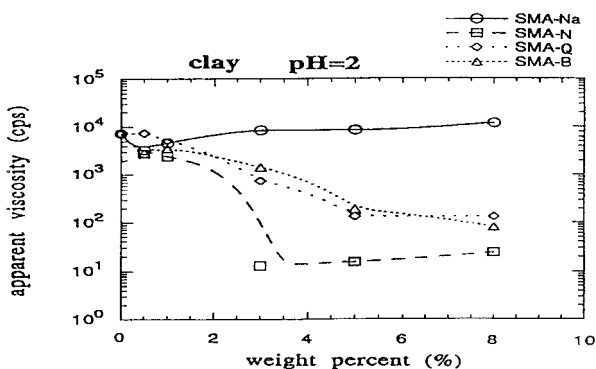
pH	2	7		12
	100%	19%	81%	100%
SMA-Na				
SMA-N				
SMA-Q				
SMA-B				

### Polymer Characterization

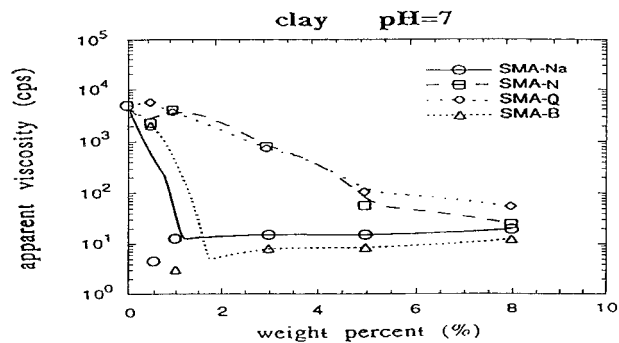
According to the degree of dissociation data for poly(acrylic acid), poly(acrylic acid) is a pure acid at pH = 2, a pure COO<sup>-</sup> polyanion at pH = 12, and 81% polyanion at pH = 7, respectively.<sup>12</sup>

Because the four different dispersants contain carboxylic acid groups, they are all sensitive to changes in pH. Thus, they develop characteristics of anionic, cationic, zwitterionic, or nonionic surfactants depending on the pH change, as illustrated in Table I. To discern the charge sign of the substrate in a disperse system, the pH value at the isoelectric point may be used. When the pH value is larger, equal, or smaller than that of the isoelectric point of the substrate, the substrate will be negatively charged, neutral, or positively charged, respectively.

In the present study, we have focused on the dispersed system of kaolinite-type clays in water. Kaolinite-type clays mainly consist of SiO<sub>2</sub> and Al(OH)<sub>3</sub>. Its isoelectric point is ca. 4.6.<sup>13</sup> However, there are regions of positive charges at the edges of the clay platelets at pH < 4.6, probably due to



**Figure 6** Apparent viscosity of the dispersed clay as a function of the concentration of dispersants at pH = 2.



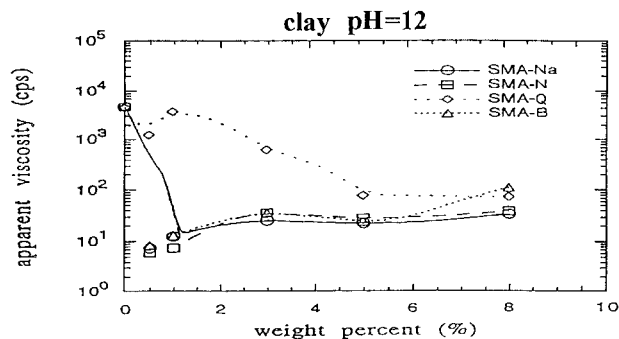
**Figure 7** Apparent viscosity of the dispersed clay as a function of the concentration of dispersants at pH = 7.

linking of Al—OH with H<sup>+</sup> to form Al—OH<sub>2</sub><sup>+</sup> ions. Hence, there is partial flocculation in this case. However, deflocculation will occur if pH > 4.6. This study concerns the effect of different dispersants on a clays/water dispersed system at pH = 2, 7, and 12.

### Rheological Analysis

In the measurement of apparent viscosity as a function of the concentration of dispersants, as shown in Figures 6 to 8, the dispersing ability of the four different type of dispersants are readily evaluated.

As is evident from Figure 6, at pH = 2, the viscosity decreases as a function of increasing concentration of the dispersant for each surfactant except SMA-Na. For SMA-N, it has a significantly drop in viscosity at low concentration, and remains almost constant until high concentrations (8 wt %). In the case of SMA-Q and SMA-B, the viscosities decrease gradually and reach minima. However, the minimum viscosity that SMA-Na can reach is remarkably higher than the other



**Figure 8** Apparent viscosity of the dispersed clay as a function of the concentration of dispersants at pH = 12.



ers. The viscosity rises to even higher values after the minimum viscosity. It is apparent that SMA-Na acts as a nonionic dispersant at  $\text{pH} = 2$  and has no dispersing ability in this case. It seems that the adsorption phenomenon occurring in this stage is mainly caused by the interaction of the polymer backbone with the clay particle surface. After the adsorption of nonionic SMA-Na, aggregation of neutral clay particles occurs. Consequently, the viscosity increases due to the increased extent of aggregation at higher concentrations of the dispersant. For the other three dispersants, all of them are cationic surfactants and exhibit remarkable dispersibilities over the range of measurement. The decreases in viscosity may be attributed to the adsorption of polyelectrolytes onto the clay particle surfaces. After the adsorption of dispersants, the clay particles are positively charged and the viscosities decrease with an increase in repulsion forces at higher dispersant concentrations. In comparison, SMA-N has the best dispersing ability, independent of concentrations among the three dispersants. This may be ascribed to the higher hydrophilic characteristic of the  $-\text{N}^+(\text{CH}_3)_2\text{H}$  group compared to the other dispersants. The hydrophilicity of cationic groups of dispersants may be ranked in the order:  $-\text{N}^+(\text{CH}_3)_2\text{H} > -\text{N}^+(\text{CH}_3)_3 \cong -\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COOH}$ .

The measurement results presented in Figure 7 were carried out at a  $\text{pH}$  of ca. 7. At this  $\text{pH}$ , the clay particles are negatively charged. Consequently, more positive charges on the SMA-N and SMA-Q copolymers increase the interaction between the dispersants and the clay particles. Aggregation may occur due to bridging between clay particles at low concentrations; hence, the dispersing abilities of SMA-Na and SMA-Q are reduced. It seems that negative charges of the  $\text{COO}^-$  groups present in SMA-N and SMA-Q are less competitive in their interaction with clay particles than the positive charged groups in this case. Next, as the concentrations of SMA-N and SMA-Q increase, the charge on the clay particles passes the neutral state and becomes negatively charged. Consequently, at higher concentrations of SMA-N and SMA-Q, similar viscosities and dispersing abilities compared to SMA-Na and SMA-B are observed. However, they are inferior dispersants at low concentrations due to the occurrence of aggregation, as mentioned above. On the other hand, the viscosities for SMA-N and SMA-B reach minimum values at relatively low concentrations, indicating that the strongly neg-

atively charged clay particles are dispersed more homogeneously due to the repulsion.

As the  $\text{pH}$  value increases up to 12, SMA-Q has inferior dispersing abilities compared to other dispersants at low concentrations, as seen in Figure 8. The reason for this may be explained by the presence of positively charged  $-\text{N}^+(\text{CH}_3)_3$  groups that interact with the negative-charged groups on the clay particle surface. Hence, after the neutral state is passed, clay particles become negatively charged and attain similar viscosities compared to the other dispersants at higher concentration of SMA-Q.

### Scanning Electron Microscopy

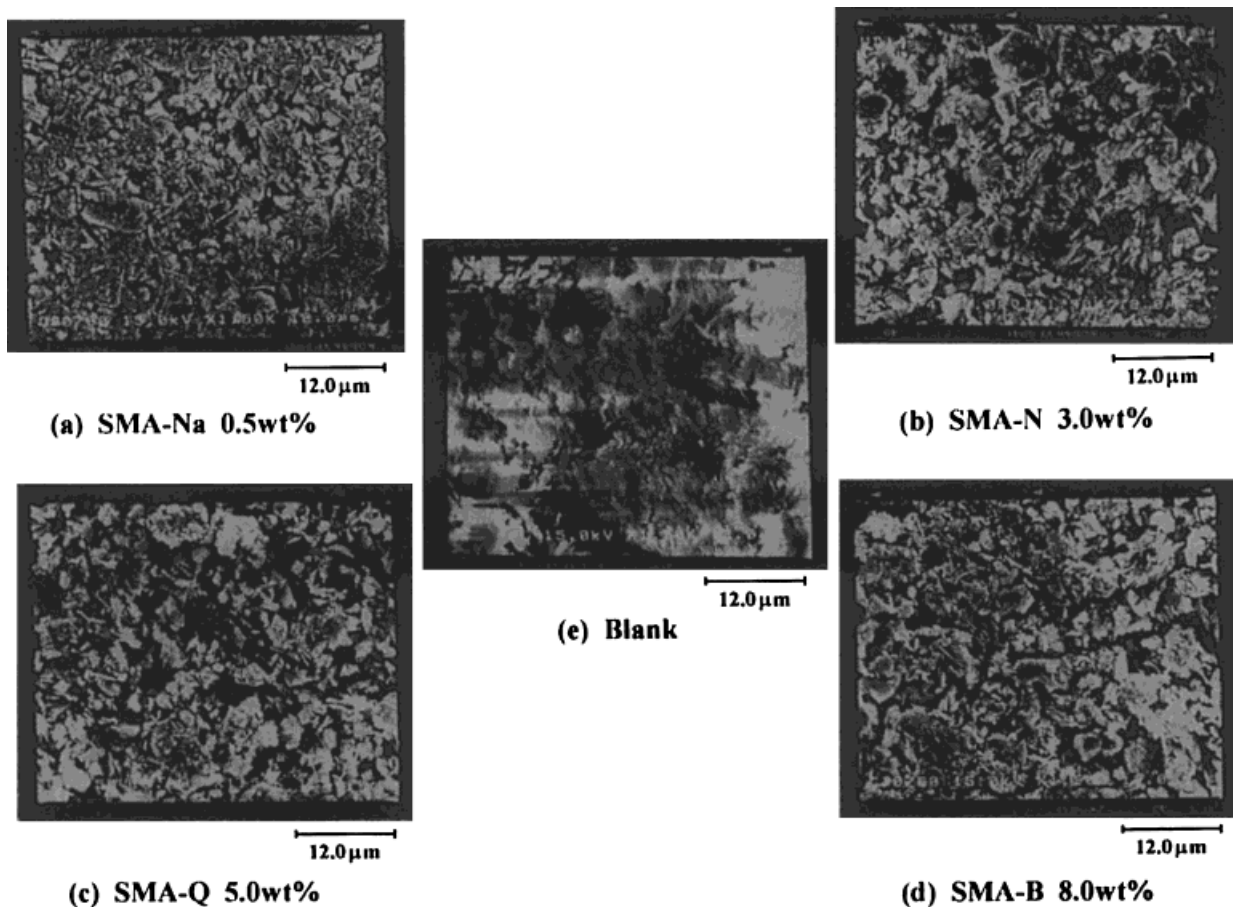
To provide more information about the dispersion state of the clay particles in solution, SEM may also be used. However, because all images were obtained at the optimum dispersant concentration, i.e., at the minimum viscosity for each dispersant, in many cases there are many distinct differences. Hence, only one representative case was shown and discussed. As seen in Figure 9, in the case of  $\text{pH} = 7$ , all of the dispersing systems show distinguishable effects on the dispersibility of the clay particles compared to the blank. Nevertheless, it is hard to tell which one has the best dispersing ability. The micrographs of other cases (under different  $\text{pH}$  values) show similar results.

### Sedimentation Method

A sedimentation method is another effective approach to evaluate the dispersing ability of the SMA copolymers as dispersants. Because the sedimentation volume increases as the particle size increases, the system with less aggregation may have a faster sedimentation rate and a smaller sedimentation volume.

The sedimentation results shown in Figure 10 are in line with the observations from the viscosity measurements. The smallest sedimentation volume was obtained in the case of SMA-N, confirming that SMA-N acted as the best dispersant under acidic conditions ( $\text{pH} = 2$ ). On the other hand, under neutral conditions (Fig. 11), there is a little difference in ranking the dispersibilities of the four dispersants. The dispersing ability of the SMA derivative increases in the order:  $\text{SMA-Q} < \text{SMA-N} < \text{SMA-B} < \text{SMA-Na}$ . Because the partially cationic characteristic of SMA-B adversely affects the dispersion, it seems that these sedimentation results are more reasonable than

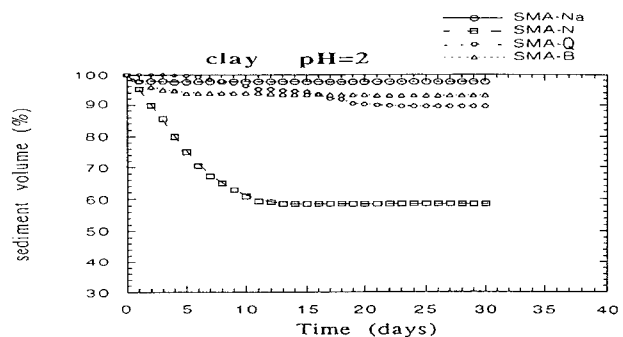




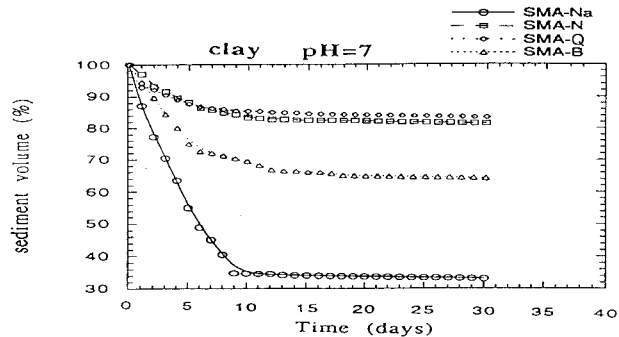
**Figure 9** SEM micrographs of clay dispersed in water using dispersants at each optimum concentration at pH = 7: (a) SMA-Na (0.5 wt %); (b) SMA-N (3.0 wt %), (c) SMA-Q (5.0 wt %); (d) SMA-B (8.0 wt %); and (e) blank.

those obtained from the viscosity measurements. Figure 12 shows the sedimentation volume measured under alkaline conditions (pH = 12). It is evident that the dispersing ability also increases

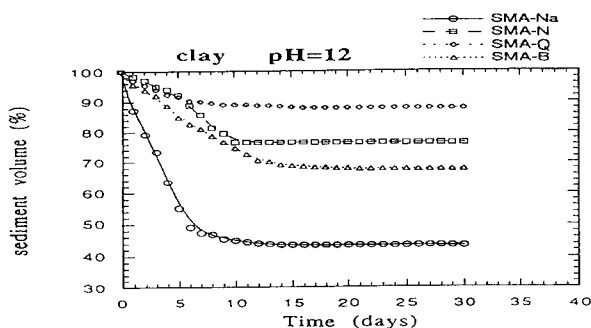
in the order: SMA-Q < SMA-N < SMA-B < SMA-Na. Although it is hard to explain the difference of sedimentation results with the viscosity measurements at low and high concentrations, it is evi-



**Figure 10** Sedimentation volume of the dispersed clay using dispersants at each optimum volume as a function of time at pH = 2.



**Figure 11** Sedimentation volume of the dispersed clay using dispersants at each optimum volume as a function of time at pH = 7.



**Figure 12** Sedimentation volume of the dispersed clay using dispersants at each optimum volume as a function of time at pH = 12.

dent that the dispersing ability of the SMA derivative are ranked much similar to those viscosity results measured over the medium range of concentration. Moreover, the difference with the viscosity results may be within the error range of the viscosity measurement.

Combining the above described results, it is generally concluded that all four of the dispersants could successfully disperse clay particles. Each dispersant exhibits its optimum degree of dispersibility under different concentrations and pH values.

### Fluorescence Spectroscopy

To characterize the aggregation behavior of the dispersants in clay/water systems, the adsorption intensities of fluorescence as a function of increasing concentration of polymer solution were also examined.

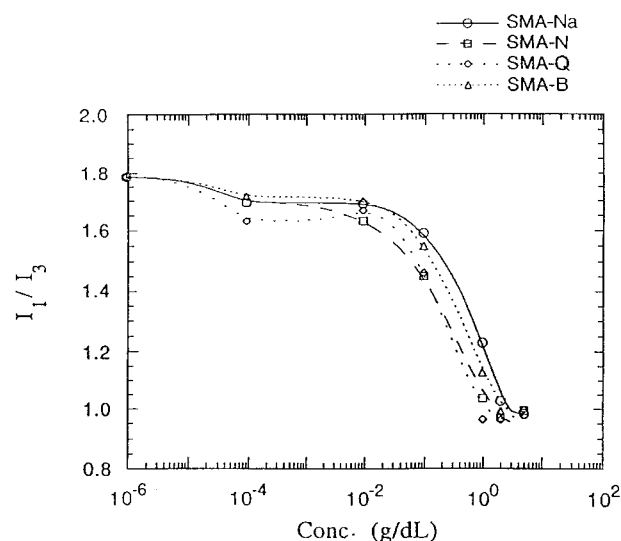
It has been shown that the adsorption intensity ratio  $I_1/I_3$  of pyrene at wavelengths of 372.4 and 383 nm in different solvents is an indication of dispersion or aggregation phenomenon of polymers in solution.<sup>14</sup> When the value of  $I_1/I_3$  decreases, pyrene is dissolved in a less polar solvent, indicating the formation of particle aggregates in solution.

It is evident that all polymer dispersants are well extended at low concentrations and aggregate at high concentrations, as seen in Figure 13. The degree of aggregation for all dispersants at high concentrations increase in the order: SMA-Na < SMA-B < SMA-N < SMA-Q. Because the measurement was carried out in a buffer solution (pH = 7), it is reasonable that SMA-Na is the polyelectrolyte that aggregates to the lowest degree because it carries only negative charges. On the other hand, the most severe aggregation

behavior observed for SMA-Q may be explained by the strong interaction between SMA-Q molecules due to its symmetrical zwitterionic characteristics.

### CONCLUSIONS

This work has shown that SMA copolymers with anionic, cationic, zwitterionic, and nonionic groups could be successfully synthesized, and their ability to disperse clay particles in water at low and high pH can be assessed by measuring viscosity, or sedimentation, as well as SEM. From the measurement of apparent viscosity as a function of the concentration of the dispersants, it is apparent that SMA-Na acts as a nonionic dispersant and has no dispersing ability at pH = 2. In comparison, SMA-N exhibits the best dispersing ability, regardless of its concentration compared to the other three dispersants. This is further conformed by SEM and sedimentation measurements. On the other hand, while evaluating the dispersibilities of these four dispersants under neutral (pH = 7) and alkaline conditions (pH = 12), the results show that the sedimentation method may be a better approach. It is apparent that SMA-Na has a faster sedimentation rate and a smaller sedimentation volume. Alternatively, the aggregation behavior of the dispersants characterized by fluorescence spectroscopy revealed that the degree of aggregation of all dispersants



**Figure 13** The adsorption intensity ratio  $I_1/I_3$  as a function of the concentration of dispersant.

at high concentrations increase in the order:  
SMA-Na < SMA-B < SMA-N < SMA-Q.

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