Functional Polymers for Colloidal Applications. II. Hydrophobic Effects of Polyacrylic Copolymer on Dispersing Polar and Nonpolar Particles

PING-LIN KUO and TA-CHENG CHANG

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 70101, Republic of China

SYNOPSIS

The polyacrylic acids with fixed molecular weights are specifically esterified by lauryl alcohol and methyl alcohol to prepare copolymers. These copolymers are used as dispersants for dispersing TiO_2 and carbon black. It was found that lauryl-esterified copolymers decrease the minimum viscosity and optimum concentrations both for TiO_2 and carbon black due to strong hydrophobic interactions. However, the methyl esterified polyacrylic acid significantly broadens the range of optimum concentrations due to the interruption of polymer interactions between particles by methyl groups. Four different dispersion systems (LB/carbon black, LB/TiO_2, MB/carbon black, and MB/TiO_2) are used. These results are discussed and correlated to the structure of dispersant. The bridging effect of esterified lauryl group and the antibridging effect of esterified methyl group are used to interpret the viscosity phenoma of those dispersed systems.
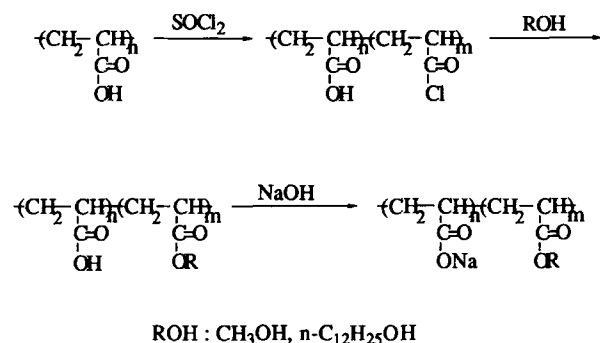
INTRODUCTION

Dispersion is an important technology widely used in the paper, paint, textile, and agriculture industries.[1] It is also used to disperse coal in water (coal–water slurry) or in oil (coal–oil mixture) to create new sources of energy.

The particles in a dispersed system are stabilized mainly by charge stabilization and steric stabilization. Polymers are widely used as dispersants since they provide a high charge density and efficient steric hindrance.[2–4] A widely used polymer type dispersant is sodium polyacrylate, in which the polymer chains contain acrylic acid only. If other components, such as alkyl acrylate, are introduced into the polymer, the second component influences the adsorption of the polymer,[5] the charge density of the particles adsorbed by it, and consequently the dispersing ability of that polymer.

In the previous study, different ratios of methyl groups were introduced to convert the acid group of the polymer into a methyl ester. It was found that the viscosities of dispersed TiO_2 were decreased to a certain value, and the optimum concentrations were significantly increased. The existence of the methyl ester on polymer chains probably inhibits bridging between particles. In this study, the polyacrylic acid moieties were partially esterified by both lauryl groups and methyl groups of different ratios. These copolymers were used to disperse nonpolar particles (carbon black) and polar particles (TiO_2). The structural effects of polymers on dispersion have been investigated.[6,7]

In order to study the structural effects of polymers on their dispersing ability, polymers with different percentages of esterified alkyl groups must have a fixed molecular weight, since the molecular weight of a polymer influences its dispersing ability significantly. Therefore, the lauryl-esterified and methyl-esterified polyacrylic acids are prepared as shown in Scheme 1, and are not prepared by direct copolymerization[8–10]:

$$\{CH_2\text{-}CH\}_n \xrightarrow{SOCl_2} \{CH_2\text{-}CH\}_n\{CH_2\text{-}CH\}_m \xrightarrow{ROH}$$
$$\quad C=O \qquad\qquad C=O \qquad C=O$$
$$\quad OH \qquad\qquad OH \qquad Cl$$

$$\{CH_2\text{-}CH\}_n\{CH_2\text{-}CH\}_m \xrightarrow{NaOH} \{CH_2\text{-}CH\}_n\{CH_2\text{-}CH\}_m$$
$$\quad C=O \quad C=O \qquad\qquad C=O \quad C=O$$
$$\quad OH \quad OR \qquad\qquad ONa \quad OR$$

ROH : CH_3OH, $n\text{-}C_{12}H_{25}OH$

Scheme 1 Synthesis of P(MA–AANa) and P(LA–AANa)

It was shown in the previous study[11] that the viscosity method can be used to measure the dispersing ability of a polymer and that the results parallel other methods such as precipitation rate and the electron microscopic method.[12] In this study, the viscosity method is used to investigate the structural effects of polymers on their dispersing ability for particles with polar or nonpolar surfaces.

EXPERIMENTAL

Materials

Acrylic acid (Wako), benzoyl peroxide (Kanton Chemical Co.), n-butyl mercaptan (Tokyo Kasei), thionyl chloride (Fluka), dioxane, methanol, and dodecanol are EP grade, and are used as supplied without further purification. Titanium dioxide (DuPont R-900), carbon black (Acarb SRFN-774), and a polymer binder (Eternal 1118) are all com-

mercial products. The water used in this experiment is ion-exchanged and distilled. The pH is 6.8–7.2 and conductivity is $4.4 \times 10^{-6}\ \Omega^{-1}\ m^{-1}$.

Methods

Synthesis and Characterization of the Polymer

(a) Polyacrylic Acid and Its Salt (PAA and PAANa). PAA and PAANa at four molecular weights A, B, C, and D were prepared by the same procedures and conditions as described in the previous paper.[11] The molecular weights for A, B, C, and D are 8.2×10^3, 13.0×10^3, 15.5×10^3, and 24.6×10^3, respectively.

(b) Sodium Salt of Poly(lauryl acrylate–acrylic acid) [P(LA–AANa)] (Table I). In a four-neck reaction kettle, polyacrylic acid (15 g) dissolved in 1,4-dioxane (30 g) was heated to 50°C, and the required amount of thionyl chloride was added. After reacting 1 h, excess dodecanol was added, and allowed to react for 0.5 h. HCl and SO_2 in the reactor were chased out with N_2. By adjusting the pH of the copolymer to 8.5 and reprecipitating in CH_3OH, the sodium salt was obtained as a white solid.

Evaluation of the Dispersing Ability of Polymers[11]

Many dispersed systems were prepared by using different polymers as dispersants. The commercial TiO_2 (DuPont R-900, TiO_2 94%, Al_2O_3 4.5%, particle size 200 nm, density 4 g/cm^3, and surface area 57.6 m^2/g) and carbon black (carbon 99.8%, H_2O 0.2%, particle size 60 nm, density 0.53 g/cm^3, and surface area 26 m^2/g) were used for dispersion. The formulation for dispersing TiO_2 is 39.4%, H_2O 13.4%,

Table I Composition of the Sodium Salts of Alkyl Acrylate–Acrylic Acid Copolymers

Copolymer	Abbreviation	Copolymer Composition (mol %)		
		Sodium Acrylate	Methyl Acrylate	Lauryl Acrylate
P(LA10–AANa)A	LA10	90.3	9.7	—
P(LA10–AANa)B	LB10	90.4	9.6	—
P(LA10–AANa)C	LC10	89.8	10.2	—
P(LA10–AANa)D	LD10	89.6	10.4	—
P(LA5–AANa)B	LB5	95.5	4.5	—
P(LA20–AANa)B	LB20	81.3	18.7	—
P(MA5–AANa)B	MB5	94.3	—	5.7
P(MA10–AANa)B	MB10	89.6	—	10.4
P(MA20–AANa)B	MB20	78.8	—	21.2
P(MA30–AANa)B	MB30	68.7	—	31.3

polymer binder 47.2%; and that for dispersing carbon black is carbon black 16.7%, water 16.7%, and polymer binder 66.6%. The dispersant is at 0–7 wt % based on TiO_2 or carbon black. Polymer binder (Eternal 1118) is a pure acrylic latex of 50% solid content. The latex particles of which the average particle size is 0.2 μm and the surfaces of which are anionic-charged, are water-insoluble. The mechanical stirring was 600 rpm for 60 min, and the temperature was maintained at 25°C. The mechanical stirring is equipped with a paddle of diameter 34 mm, i.e., the peripheral rotation speed is 64 $m/$min. The properties of polymer binder, such as the particle size and solid content, and the shape and the diameter of the paddle influence the effort of dispersion and consequently the viscosity of the dispersed paste. However, in this experiment, the polymer binder and stirring conditions were kept the same in order to compare the dispersing effect of different dispersants. Thus, those two factors will not influence the comparison of the dispersing ability.

The prepared dispersed paste was evaluated by the following methods:

(a) Viscosity: A viscosity meter (Brookfield DVII LVT) was used to evaluate the samples; 10 g of a dispersed paste was put in a small sample adaptor, the temperature was maintained at 25°C, and apparent viscosity was measured by using an SC4-34 spindle at 60 rpm.

(b) Sedimentation: The dispersed paste (60 g) was poured into a 100 cc graduated cylinder. The height of the separation phase after standing many days and the final volume of the solid phase were recorded.

(c) Electron microscopy: The dispersed paste (1 g) was used to make a film (ca. 50 μm) on a thin layer of copper. After drying, it was put on an aluminum sheet and electrodeposited with a layer of gold. The surface of film was observed by an SEM electron probe microanalyzer (Jeol TXA-840).

RESULTS AND DISCUSSION

Synthesis of Sodium Salts of Lauryl-Esterified Polyacrylic Acid, P(LA–AANa)

Poly(methyl acrylate–acrylic acid) or poly(laurylacrylate–acrylic acid) copolymers were prepared

from acid chlorination and subsequent esterification as described in Scheme 1.

Four kinds of copolymers with different molecular weights (MW) (A, B, C, and D) were prepared by changing the concentration of initiator, the chain transfer agent, and the reaction temperature as shown by the previous study. The compositions of the copolymers with different esterified alkyl groups, the percent alkylation, and the different molecular weights are shown in Table I. The ratio of methyl or lauryl acrylate in the copolymer can be determined from the ^{1}H-NMR. In the ^{13}C-NMR, the methylene portion attached to $-COONa$ and CH_3 in $-COOC_{12}H_{25}$ has a peak at $\delta = 183.92$ and 164 ppm, respectively. In ^{1}H-NMR, the proton of the CH_3- in $-O$ ($C_{11}H_{22}$)CH_3 appears at $\delta = 1.0$ ppm, and the methylene proton of the polymer back bone appears at $\delta = 1.7–2.5$ ppm. Those two peaks were also used to determine the ratio of $-COOR/$$-COONa$.[13,14]

Evaluation of the Dispersing Ability of Copolymers

In this study, Brookfield DVII LVT, a low-shear-rate viscometer, with a spindle of SC4-34 was used to measured the apparent viscosity $\eta_{app} = \tau/\gamma$, where τ = shear stress and γ = shear rate. For all dispersions of carbon black and TiO_2 with different concentrations of dispersant, the viscosity decreases at the beginning and then reaches a stable value.

Figure 1 shows the relationship of apparent viscosity vs. wt % PAANa–B, D for the dispersed carbon black. A minimum in the plot of apparent viscosity vs. dispersant concentration can be observed. The apparent viscosity at this point is called minimum viscosity and the concentration at that point is called optimum concentration[15] for both B and D. PAANa–B can reach a lower minimum viscosity than PAANa–D, consistent with the tendency of dispersing TiO_2 with PAANa–B and PAANa–D due to the lower molecular weight of PAANa–B. However, PAANa–B shows a higher optimum concentration than PAANa–D for dispersing carbon black.

As the polyacrylic acid is partially esterified by hydrophobic groups, the dispersing ability of polyacrylic acid for carbon black is significantly increased. Figure 2 shows the apparent viscosity of dispersed carbon black as a function of dispersant P(LA–AANa) concentration. As the copolymer is partially esterified by 5% lauryl alcohol. P(LA5–AANa)B, the minimum viscosity significantly decreases from 260 to 210 cP, but the optimum con-

centration increased from ca. 1.5 to 2.1 wt %. As the percentage of esterification increases from 5 to 10 and 20%, the optimum concentration significantly decreases from ca. 2.1 to 0.3%, but the minimum viscosity slightly increases from ca. 210 to 220 and 230 cP, respectively.

Compared with PAANa-B, P(LA5-AANa)B has a higher hydrophobicity, which results in a stronger interaction with carbon black particles thus a higher adsorption.[16] Therefore, the lower minimum viscosity for P(LA5-AANa)B can be attributed to the better dispersion of carbon black due to the higher adsorption. For P(LA5-AANa)B, the stronger adsorption on carbon black particles is accompanied by a lower concentration in the bulk phase for a given total concentration. Therefore, the total concentration needed for P(LA5-AANa)B to form bridging becomes higher, so that it shows a higher optimum concentration.

On the other hand, the lauryl group in P(LA-AANa) adsorbed on carbon particles readily causes
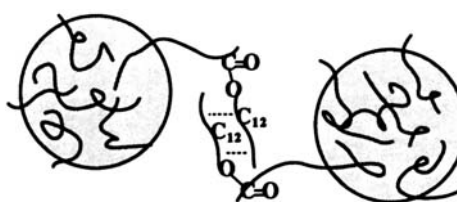
bridging between particles due to the strong hydrophobic interactions of the long chain group (Scheme 2):
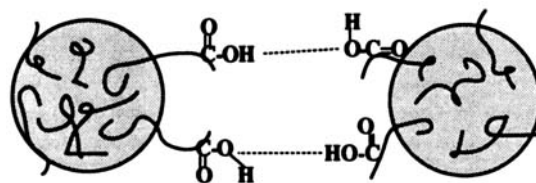
(a) Bridging by the hydrogen bonding of carboxylic gruop in PAANa
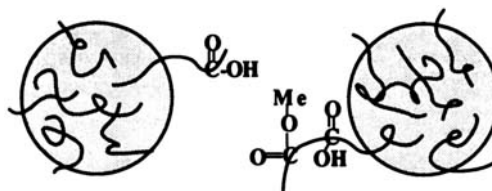
(b) Antibridging by easter gruop in PAANa

(c) Bridging by the hydrophobic interaction of lauryl group in PAANa

Scheme 2 Bridging and bridging inhibition between polymer absorbed particles

This also occurs when the particles are adsorbed by surfactants.[16] As the percentage of esterification increases from 5 to 20%, there is an increase in apparent viscosity and a decrease in optimum concentration. This can be attributed to bridging between polymers adsorbed on different carbon particles (Scheme 2). It means that a higher percentage of esterification by the lauryl group causes bridging more readily. Also, the trend of the minimum viscosity increasing with the increase of percentage of

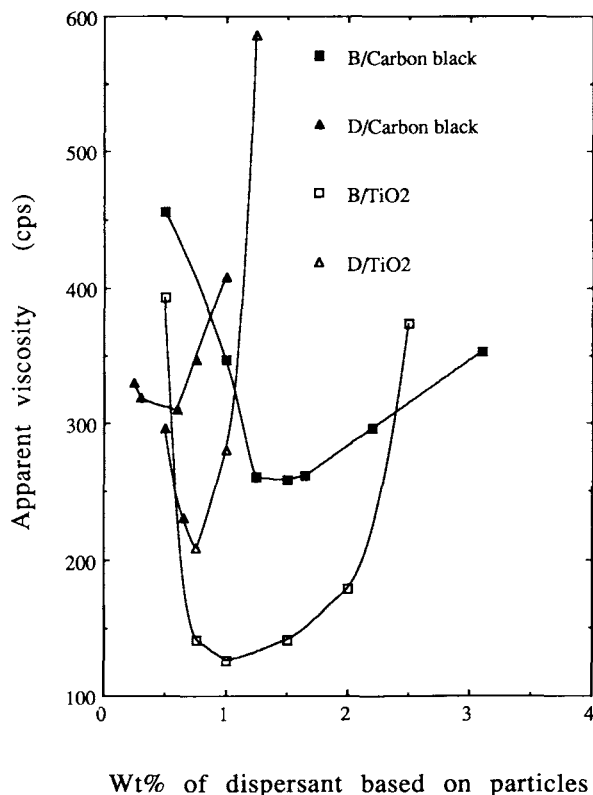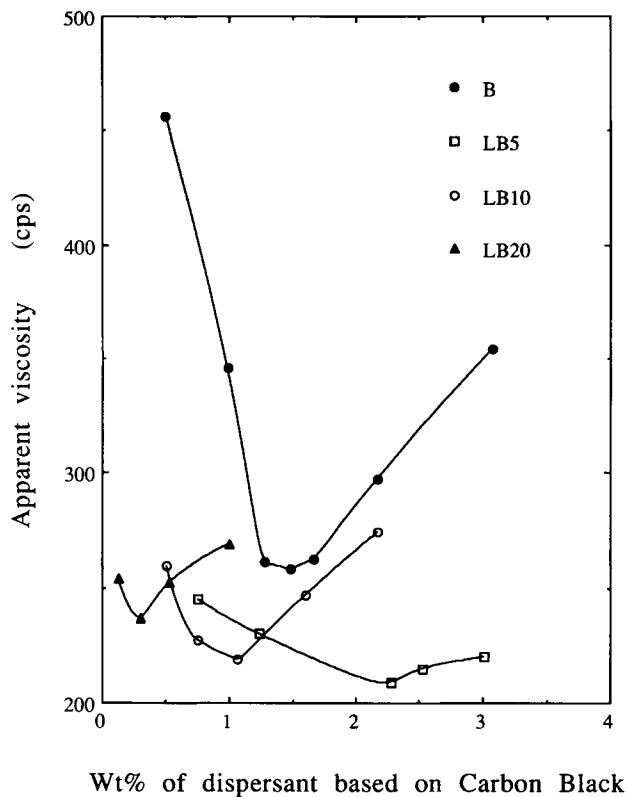**Wt% of dispersant based on particles**

Figure 1 Relationship between apparent viscosity and dispersant concentration: (——) dispersants PAANa-B, D/carbon black; (· · ·) dispersant PAANa-B, D/TiO$_2$.

Figure 2   Relationship between apparent viscosity and dispersant concentration (dispersants LB series/carbon black).

esterification demonstrates the increase in hydrophobic interaction and bridging effect between particles.[17,18]

The effect of lauryl ester substitution in LB10 on dispersing TiO_2 is demonstrated by the apparent viscosity as a function of dispersant concentration as shown in Figure 3. When PAANa is 5% esterified by lauryl alcohol, P(LA5-AANa)B, the apparent viscosity does not drop as low as PAANa-B does until ca. 5 wt % of dispersant is added. The concentration at which bridging begins is ca. 6 wt %. This means that P(LA5-AANa)B has a lower adsorption so that the concentration for saturated adsorption is higher. As the percentage of esterification is increased, bridging occurs at lower concentrations around 1 wt %, and the minimum viscosity increases due to the strong hydrophobic interaction of lauryl group between particles.

Compared with the dispersing ability of P(LA-AANa)B for carbon black, there are two similar trends: the optimum concentration decreases and

the minimum viscosity increases as the percentage of esterification increases. This can be regarded as a characteristic of the esterified lauryl group, which has a strong hydrophobicity,[19] thus easily causing a hydrophobic interaction and bridging between particles. However, there is a different trend for the carbon black system. The minimum viscosity is decreased compared to the TiO_2 system, due to the esterification with the lauryl group. This indicates that the introduction of lauryl ester to PAANa increases the adsorption on carbon particles but decreases that on TiO_2.

The effect of the methyl ester group on P(MA-AANa)B on carbon black dispersion is shown in Figure 4. Due to the negatively charged surface of latex particles, the adsorption of the dispersants (with negative group of $-COO^-Na^+$) on latex particles is not important, and dispersants mainly adsorb on the particles of carbon black. Also, dispersing abilities of dispersants are compared based on the same amount of polymer binder (latex), and thus
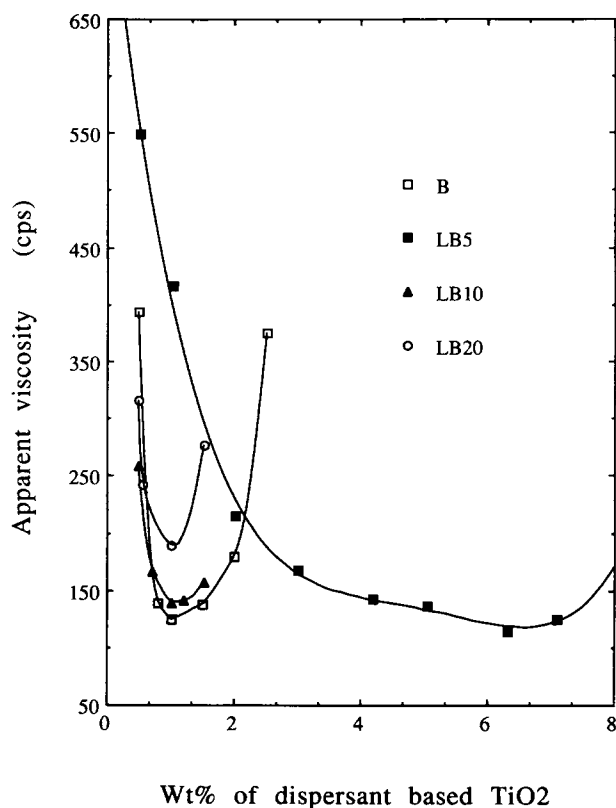

Figure 3   Relationship between apparent viscosity and dispersant concentration (dispersants LB series/TiO_2).

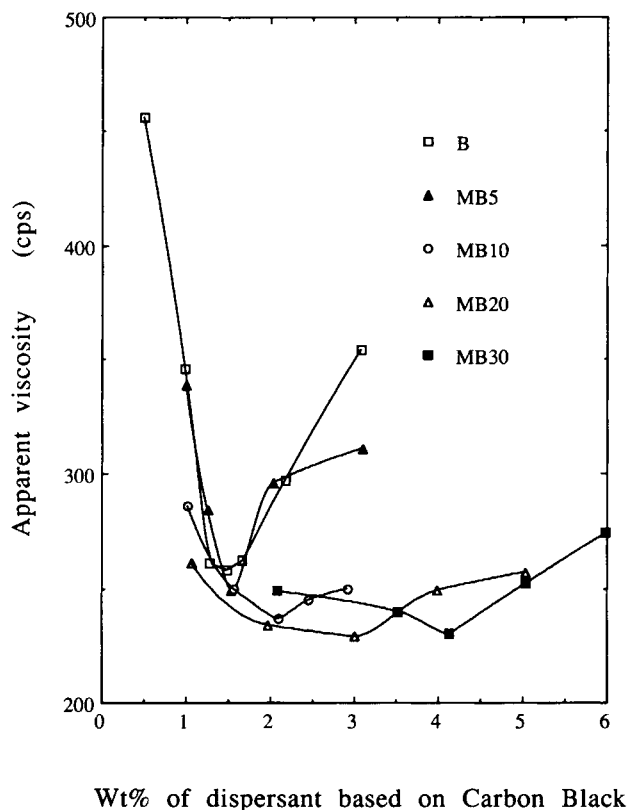Wt% of dispersant based on Carbon Black

Figure 4 Relationship between apparent viscosity and dispersant concentration (dispersants MB series/carbon black).

are not influenced by the trace adsorption of dispersants on the latex particles. In Figure 4, the minimum viscosity decreases gradually as the percentage of methyl group is increased up to 20%. This trend is similar to that observed for the lauryl-esterified PAA [P(LA-AANa)B/carbon black system]. Again, the decrease in minimum viscosity means more effective adsorption of dispersant on carbon particles and a better dispersion. The optimum concentration increases with increasing percentage of methyl esterification. This means that a higher dispersant concentration is needed for bridging of polymer chains adsorbed on different particles. The methyl ester on the polymer chains probably hinders the interaction and interrupts the bridging between them. This trend is completely different from that observed for the lauryl-esterified PAANa/carbon system where lauryl causes a strong bridging effect and the optimum concentration decreases with the increasing percentage of esterified-lauryl group.

In order to investigate the bridging inhibition of methyl ester on the dispersion of carbon black, precipitation (Fig. 5) and electron microscopic methods (Fig. 6) are used to study the liquid state and the surface of dried film of carbon dispersion, respectively. It is better to compare each best dispersed system before bridging; therefore, the point at optimum concentration is chosen for each dispersant. The precipitation rate is PAANa-B > P(MA20-AANa)B > P(MA30-AANa)B (Fig. 5). This means that the dispersed system prepared by P(MA30-AANa)B is more stable than that by P(MA20-AANa)B and PAANa-B. From electron microscopy of the film (× 1200), it is obvious that the film prepared from MB30 has a more homogeneously dispersed surface than MB20 and PAANa-B. From the results of Figures 5 and 6, it can be concluded that MB30 shows a better dispersion than MB20 and PAANa-B at optimum concentrations. This demonstrates that the methyl esters on PAA-Na, which inhibit bridging, also improve the dispersing ability of PAA-Na onto carbon black.
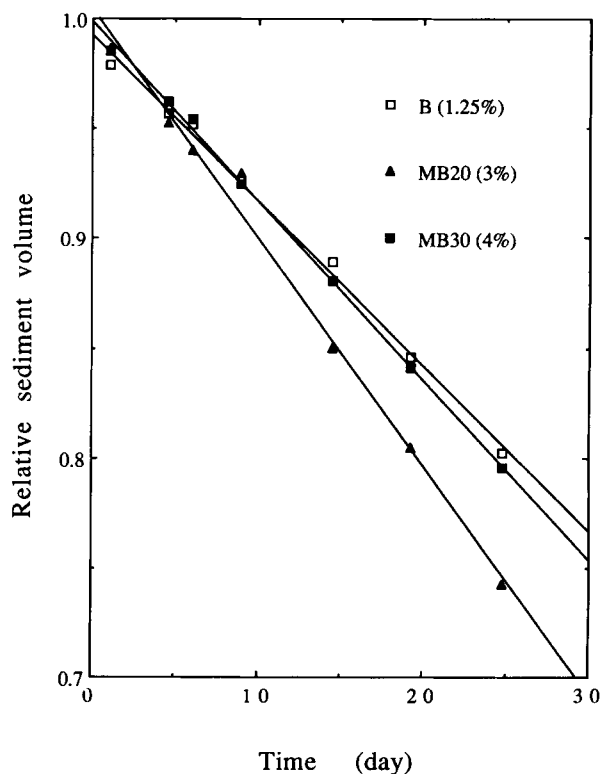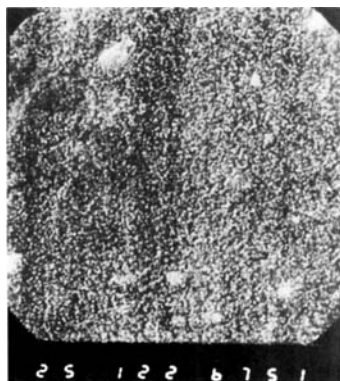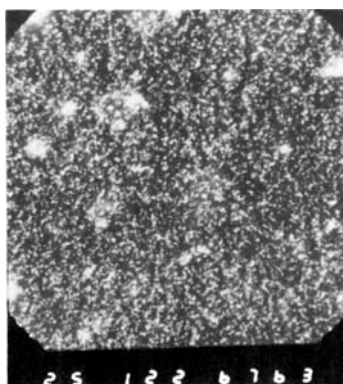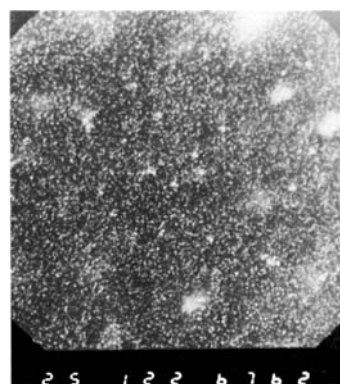

Time   (day)

Figure 5 Effect of settling rate and sediment volume of dispersant MB series/carbon black.

(a)

(b)

(c)

Figure 6 Photographs of particle dispersions (carbon black, $\times$ 1200): (a) dispersant, PAANa-B (1.25 wt %); (b) dispersant, MB20 (3 wt %); (c) dispersant, MB30 (4 wt %).

In the methyl-esterified polyacrylic acid [P(MA–AANa)B]/TiO_2 system reported in the previous paper,[11] when the percentage of esterification increases, the optimum concentration increases and the minimum viscosity does not change initially but then increases slightly (Fig. 7). Comparing this with P(LA–AANa)B/TiO_2 (Fig. 3), there is a similar trend of decreasing minimum viscosity as a function of the percentage of esterification, due to less efficient adsorption. However, there is a different trend between these two systems, i.e., when the percentage of esterification increases, the optimum concentration decreases for the P(LA–AANa)B/TiO_2 system, but it increases for P(MA–AANa)B/TiO_2. This can be attributed to the strong hydrophobic bridging effect of lauryl groups.

In comparing the system of P(MA–AANa)B/TiO_2 (Fig. 7) with P(MA–AANa)B/carbon black (Fig. 4), there is a similar trend such in that the optimum concentration increases with increasing percentage of esterification. It can be concluded that the existence of a methyl ester on the polymer chain adsorbed on a particle surface can inhibit bridging between particles. However, these two systems show different trends so that the minimum viscosity decreases with increasing percentage of esterification for the P(MA–AANa)B/carbon black system while the minimum viscosity does not initially change but then slightly increases for the P(MA–AANa)B/TiO_2 system. The different trends can be attributed to the difference in adsorption between the two systems.
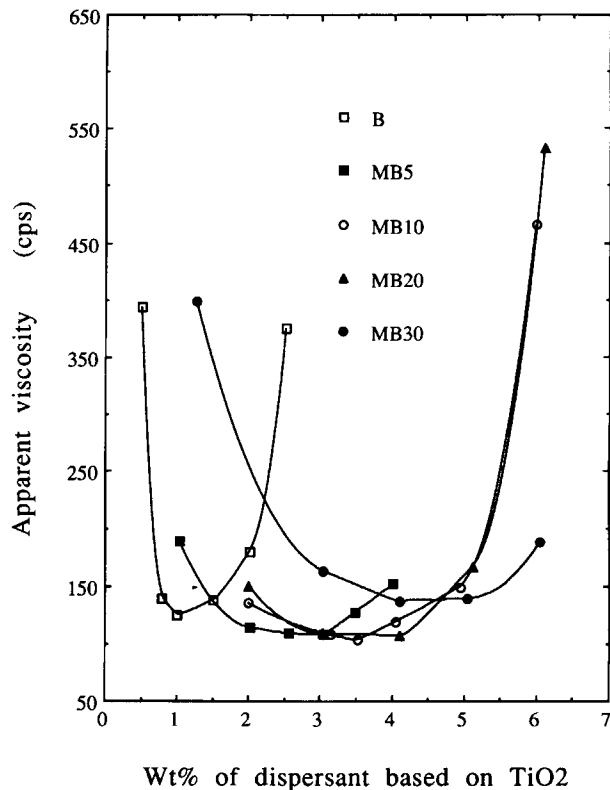
Figure 7 Relationship between apparent viscosity and dispersant concentration (dispersants MB series/TiO$_2$).

REFERENCES

1. R. L. Grant, *Pap. Technol.*, **3**, 539 (1962).
2. B. Vincent, P. F. Luckham, and F. A. Waite, *J. Colloid Interface Sci.*, **73**, 2 (1980).
3. D. H. Napper and A. Netschey, *J. Colloid Interface Sci.*, **37**, 3 (1971).
4. B. Vincent, *Adv. Colloid Interface Sci.*, **4**, 193 (1974).
5. P. Somasundaran and Joy T. Kunjappu, *Colloids Surface*, **37**, 245 (1989).
6. G. D. Parffit and D. G. Wharton, *J. Colloid Interface Sci.*, **38**, 431 (1972).
7. S. G. Dick, T. W. Healy, and D. W. Fuerstenau, *J. Colloid Interface Sci.*, **37**, 595 (1971).
8. O. Griot and J. A. Kitchener, *Faraday Soc. Trans.*, **61**, 1026 (1965).
9. I. O. Sutherland, *Comprehensive Organic Chemistry*, Vol. 2, Pergamon, Elmsford, 1979.
10. K. J. Saunders, *Organic Polymer Chemistry*, Wiley, New York, Vol. 2, 1976.
11. P.-L. Kuo, L.-M. Lu, and T.-C. Chang, *J. Appl. Polym. Sci.*, to appear.
12. (a) Noboru Moriyama, *Bull. Chem. Soc. Jpn.*, **48**, 1713–1719 (1975); (b) G. D. Parfitt, *Dispersion of Powder in Liquids*, 3rd ed., Elsevier, New York, 1981.
13. (a) Quang Tho Pham, Roger Pe Tiaud, Marie-France Llauro, and Hugues Waton, *Proton and Carbon NMR Spectra of Polymers*, Wiley, New York, 1984; (b) Charles J. Pouchert, *The Aldrich Library of NMR Spectra*, Edition II, Aldrich Chemistry, Milwaukee, 1983, Vols. I and II.
14. Temple C. Patton, *Paint Flow and Pigment Dispersant*, 2nd ed., Wiley, New York, 1979.
15. E. D. Guddard and B. Vincent, *Polymer Adsorption an Dispersion Stability*, ACS Symposium Series 240, Am. Chem. Soc., Washington, DC, 1984.
16. (a) J. A. Kitchener, *Br. Polym. J.*, **4**, 217 (1972); (b) P. Somasundaran, T. W. Healy, and D. W. Fuerstenau, *J. Colloid Interface Sci.*, **22**, 599 (1966).
17. Stephen L. Rosen, *Fundamental Principle of Polymeric Materials*, Wiley, New York, 1982.
18. A. Tentorio and L. Canora, *Colloids Surface*, **39**, 311 (1989).
19. Milton J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley, New York, 1978.