

Functional Polymers for Colloidal Applications. I. Structural Effects of Lipophile-Modified Polyacrylates on Adsorption and Dispersion Ability

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SYNOPSIS

Polyacrylic acids of four molecular weights are prepared. A series of poly(methylacrylate-acrylic acid) copolymers with four specific methylacrylate/acrylic acid ratios and molecular weights has been successfully synthesized from the corresponding polyacrylic acids. These polymers and copolymers are used as dispersants for dispersing TiO_2 into aqueous phase. Viscosity, sedimentation, and electron microscopy are used to evaluate their dispersion ability. The extent of adsorption and the zeta potential are measured to evaluate their adsorption behaviors on the surface of TiO_2 . The viscosity, sedimentation, and electron microscopy results are comparable parallel for showing the dispersing ability of a polymer or a copolymer. The polymer (or copolymer), which results in a lower viscosity, shows a slower sedimentation rate and a more homogeneous distribution of particles in microphotographs. The minimum viscosity needed to disperse TiO_2 decreases with the decreasing molecular weight of polyacrylic acid. It was found that partial esterification of polyacrylic acid results in a broader range of minimum viscosity. The trend of the amount adsorbed is similar to that of zeta potential. These two results are used to interpret the viscosity curve.

INTRODUCTION

Dispersion technology is widely used in many industries, such as paint, pigment, textile, paper, electronics, etc.¹ For an effective dispersion, the dispersed particles can display their function efficiently (e.g., a better dispersed pigment can show a stronger color strength) so that the quality of the products is improved and the cost is decreased.

The particles in a dispersed system are stabilized mainly by two factors: (1) charge stabilization due to the repulsion of the same charge on particles; (2) steric stabilization due to the hindrance of the bulky adsorbant on particles.²⁻⁴ Polymers are widely used as dispersants because they can provide a high charge density and efficient steric hindrance. Also, a polymer type dispersant does not produce the foam problems that a surfactant type dispersant does.

A widely used polymer type dispersant is sodium polyacrylate,⁵ in which the polymer chains contain

acrylic acid only. If other components such as an alkyl acrylate are introduced into the polymer, the second component would influence the adsorption of the polymer, the charge density of the particles adsorbed by it, and, consequently, the dispersing ability of that polymer. In this study, different ratios of methyl ester were introduced, by converting the acid group of the polymer into a methyl ester, and the effects of the methyl ester on the dispersing ability were investigated.⁶

The molecular weight of a polymer dispersant influences its dispersing ability tremendously. Therefore, the structural effect of polymer dispersants can be studied only when their molecular weights are fixed to a certain value.

A methyl esterified polyacrylic acid can be easily obtained by copolymerizing acrylic acid with methyl acrylate. However, a polymer with different ratios of methyl acrylate to acrylic acid, but, with a fixed molecular weight, cannot be prepared by copolymerization directly. In this study, these kinds of polymers are prepared according to Scheme 1.

The dispersing properties of the prepared polymers were investigated both from the liquid state and from the dried film of a dispersed system. For the liquid state, the viscosity of dispersed system, the precipitation rate, and the final precipitation volume were compared. The dried film studies used electron microscopy to observe the dispersed particles directly by SEM.^{4,7,8}

The amount adsorbed and the zeta potential of particles were also measured^{9,10} and compared to the dispersing ability. This was done to investigate the structural effects of a polymer dispersant on its dispersing ability, its adsorption behavior, and the zeta potential of adsorbed particles.

EXPERIMENTAL

Materials

Acrylic acid (Wako), benzoyl peroxide (Kanton Chemical Co.), *n*-butyl mercaptan (Tokyo Kasei), thionyl chloride (Fluka), dioxane, and methanol are EP grade, and are used as supplied without further purification. Titanium dioxide (DuPont R-900)¹¹ and the polymer binder (Eternal 1118) are commercial products. The water used in these experiments is ion-exchanged and distilled, the pH is 6.8–7.2, and conductivity is $4.4 \times 10^{-6} \Omega^{-1} \text{ m}^{-1}$.

Methods

Synthesis and Characterization of Polymer

(a) Polyacrylic Acid and Its Salt (PAA and PAANa). In a four-neck reaction kettle, 400 g of 1,4-dioxane were heated to 90°C under mechanical stirring and a nitrogen blanket. Acrylic acid (90 g), the required amount of *n*-butyl mercaptan, and the required amount of benzoyl peroxide were dissolved in 110 g of 1,4-dioxane, and added slowly to the reaction kettle for 1 h (Table I). The temperature was maintained at 90°C for 2 h more to complete the polymerization.

The solvent was removed by a Rotavapor to obtain polyacrylic acid which is further purified by reprecipitation with H₂O/CH₃OH. The sodium salt of polyacrylic acid was obtained by adjusting the pH of the aqueous solution of polyacrylic acid to 8.5, followed by reprecipitation in CH₃OH. The white solid salt of PAANa was dried at 60°C under vacuum for 48 h.

(b) Sodium Salt of Poly(methyl acrylate–acrylic acid) [P(MA–AANa)] (Table II). In a four-neck reaction kettle, polyacrylic acid (15 g) dissolved in 1,4-dioxane (30 g) was heated to 50°C,

Table I Reaction Conditions for Preparing PAA and Molecular Weights of PAA

Polymer Type	BPO (wt %)	C ₄ H ₉ SH (wt %)	Reaction	
			Temp (°C)	\bar{M}_w
A	4	2	90	8.2×10^3
B	2	1	90	13.0×10^3
C	1	0.5	90	15.5×10^3
D	1	0	80	24.6×10^3

and then the required amount of thionyl chloride was added. After 1 h reaction time, methanol was added and left to react for 0.5 h. HCl and SO₂ in the reactor were chased out with N₂. By adjusting the pH of the copolymer to 8.5 and reprecipitating in CH₃OH, a white solid sodium salt was obtained.

Evaluation of the Dispersing Ability of Polymers

Many dispersed systems were prepared by using different polymers as dispersants. The commercial TiO₂ (DuPont R-900, TiO₂ 94%, Al₂O₃ 4.5%, particle size 0.2 μm, density 4 g/cm³, and surface area 57.6 m²/g) was used for dispersion. The formulation is TiO₂ 39.4%, H₂O 13.4%, polymer binder 47.2%, and dispersant 0–7 wt % of TiO₂. 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 by 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 with the following methods:

- Viscosity: By using a viscosity meter (Brookfield DVII LVT), 10 g of a dispersed paste was put in a cylinder with the temperature maintained at 25°C and its apparent viscosity was measured by using a spindle of SC4-34 with 60 rpm.
- Sedimentation: The dispersed paste (60 g)

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

Copolymer	Abbreviation	Copolymer Composition (mol %)	
		Sodium Acrylate	Methyl Acrylate
PAANa–A	A	100	0
PAANa–B	B	100	0
PAANa–C	C	100	0
PAANa–D	D	100	0
P(MA10–AANa)A	MA10	89.9	10.1
P(MA10–AANa)B	MB10	89.6	10.4
P(MA10–AANa)C	MC10	90.0	10.0
P(MA10–AANa)D	MD10	90.5	9.5
P(MA5–AANs)B	MB5	94.3	5.7
P(MA20–AANa)B	MB20	78.8	21.2
P(MA30–AANa)B	MB30	68.7	31.3

was poured into a 100 cc graduated cylinder. The heights of the separation phase after standing for days, and the final volume of 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 film surface was observed by an SEM electron probe microanalyzer (Jeol TXA-840).

Characterization of the Adsorption of Polymer

(a) **Zeta Potential of Adsorption Layer.** In a 250-mL flask, TiO_2 (10 g) was put into 100 mL of the prepared polymer solutions with a series of concentrations. After shaking in a thermal bath (25°C, 300 rpm) for 48 h, the suspension was centrifuged (Centrikon H-401, Kontron). A tiny amount of centrifuged solid was dispersed in a large amount of the supernatant to prepare the samples for measurement. The potential at which the particles did not move was determined as the zeta potential of the dispersed particles using a Lazer Zee Meter 501 (PEN KEM).

(b) **Adsorption Amount.** Hyamine 1622 solution 40 mL (1000 ppm) was added into the prepared polymer solution (60 mL) at a series of concentrations (4–44 ppm). After stirring for 5 min, the turbidity was measured (Orebeco-Heuige digital turbidimeter) and the relation between turbidity and polymer concentration was plotted as a calibration curve (Fig. 1). The supernatant after centrifugation of 5 mL, was diluted to 60 mL, and Hyamine solution (1000 ppm) (40 mL) was added. The polymer concentration of the supernatant can be determined from the turbidity by using Figure 1. From the poly-

mer solution of supernatant ($C_{B,\text{eq}}^D$) and the concentration of the polymer solution before adding particles (C^D), the amount adsorbed¹² C_{ad} was calculated as

$$C_{\text{ad}} = \frac{(C^D - C_{B,\text{eq}}^D) \times V}{m}$$

where m = mass of particles, $C_{B,\text{eq}}^D$ = the concentration of dispersant in bulk phase at equilibrium, and V = the volume of the solution.

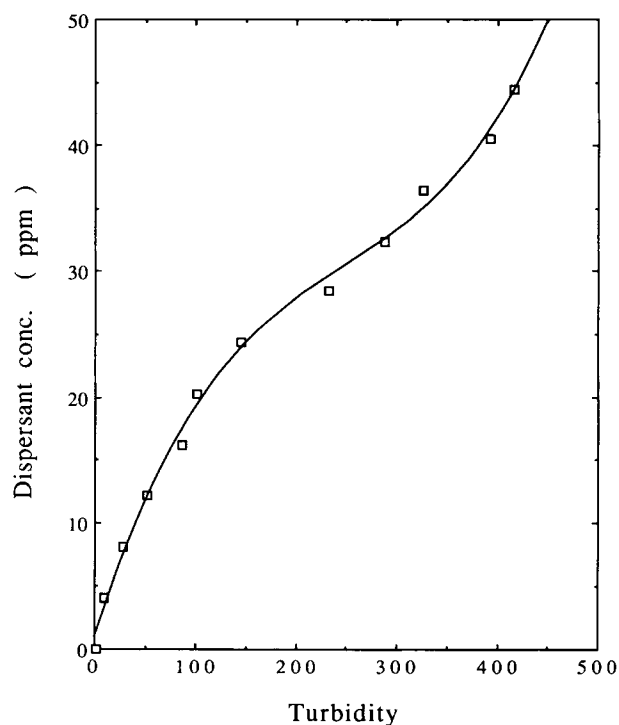
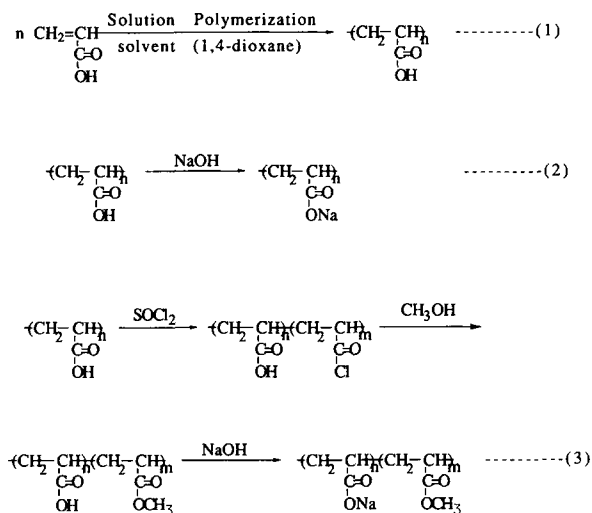


Figure 1 Adsorption calibration curve of the dispersant concentration vs. turbidity for PAANa–B.

RESULTS AND DISCUSSION

Synthesis of Sodium Salts of Poly(methylacrylate-acrylic acid) [P(MA-AANa)]

P(MA-AANa) copolymers were prepared from chlorination and consequent methyl esterification as described in Scheme 1^{13,14}:



Scheme 1 Synthesis of PAANa and P(MA-AANa).

Four kinds of copolymers with different molecular weight (A, B, C, and D) were prepared by changing the concentration of initiator and chain transfer agent and reaction temperature as shown in Table I. PAANa polymers A, B, C, and D containing 10% of methyl ester (MA-10, MB-10, MC-10, MD-10), and B with four kinds of methylacrylate ratio (MB5, MB10, MB20, MB30) were also prepared. The ratio of methyl acrylate in the copolymer can be determined from the ¹H-NMR and ¹³C-NMR. Figure 2 shows the ¹H-NMR and ¹³C-NMR of MB30 as an example. In the ¹³C-NMR, the methylene attached to -COONa or -COOCH₃ has a peak at $\delta = 185.74$ and 180.98 ppm, respectively. In the ¹H-NMR, the -OCH₃ appears at $\delta = 3.8$ ppm, and the methylene portion of the polymer backbone appears between $\delta = 1.2$ and 2.5 ppm, which peaks were used to determine the ratio of -COOCH₃-COONa.^{15,16}

Evaluation of the Dispersing Ability of Copolymers

Viscosity is used by industry to evaluate dispersions of fine particles in liquid. In this study, Brookfield DVII LVT, a low-shear-rate viscometer, with a spindle of SC4-34 was used to measured the apparent

viscosity, $\eta_{app} = \tau/\dot{\gamma}$, where τ = shear stress and $\dot{\gamma}$ = shear rate. Apparent viscosity is always used for measuring a non-Newtonian system, which shows different viscosities under different shear rates. As shown in Figure 3, for all dispersions of TiO₂ with different concentrations of dispersant, the viscosity decreases at the beginning and then reaches a stable value.

The relation of η_{app} vs. concentration of dispersant is used to study the dispersing ability of a dispersant. Brookfield DVII, LVT type is a low-shear-rate viscometer (maximum shear rate 16.8/s). For a well-dispersed system, the aggregation of particles is small, so that the spindle senses a smaller hindrance from aggregates under a given shear rate, and consequently detects a smaller shear stress and a lower viscosity. Conversely, the agglomerates of a poorly dispersed system form a network which drags on the spindle and causes it to sense a higher shear stress and to show a higher viscosity.^{8,17}

Choice of a pigment weight concentration (PWC) is important in studying a dispersed system. If the PWC is too high, the pigment is easy to precipitate and a stable apparent viscosity cannot be acquired. If the PWC is too low, the dispersing ability of different dispersants can not be easily discriminated. From many tests, a PWC of 40% is found to be appropriate. This can show a stable η_{app} .¹⁸

Figure 4 shows the relation of η_{app} vs. [dispersant], where the dispersants are the sodium salts of polyacrylic acids (PAANa) with four different MW (A, B, C, and D, the MW of A < B < C < D, as shown in Table I). In the absence of dispersants, η_{app} of the dispersed system is ca. 3000 cPs. By the addition of small amount of dispersant (0.5 wt % based on solid), the viscosity decreases sharply to ca. 300 cP. For B, C, and D, the viscosity decreases to 130–220 cP, and then increases sharply again showing a viscosity inversion. For A, the viscosity decreases sharply to 130 cP, then slowly down to 110 cP, and slowly increases again, showing a viscosity plateau. In Figure 4, the lowest viscosity in the curve of viscosity inversion is called minimum viscosity and the dispersant concentration corresponding to the minimum viscosity is called optimum concentration.⁷

Figure 5 shows the precipitating rate for B and D at the minimum viscosity concentrations of (1 and 0.75%, respectively). B shows a slower precipitating rate than D, meaning that the dispersed system of B is more stable than that of D. Figure 6 shows the electron microscopy (SEM) of a film prepared from the dispersed system of A and D (at 2 wt %), enlarged by 720, 5400, and 11,000 times.

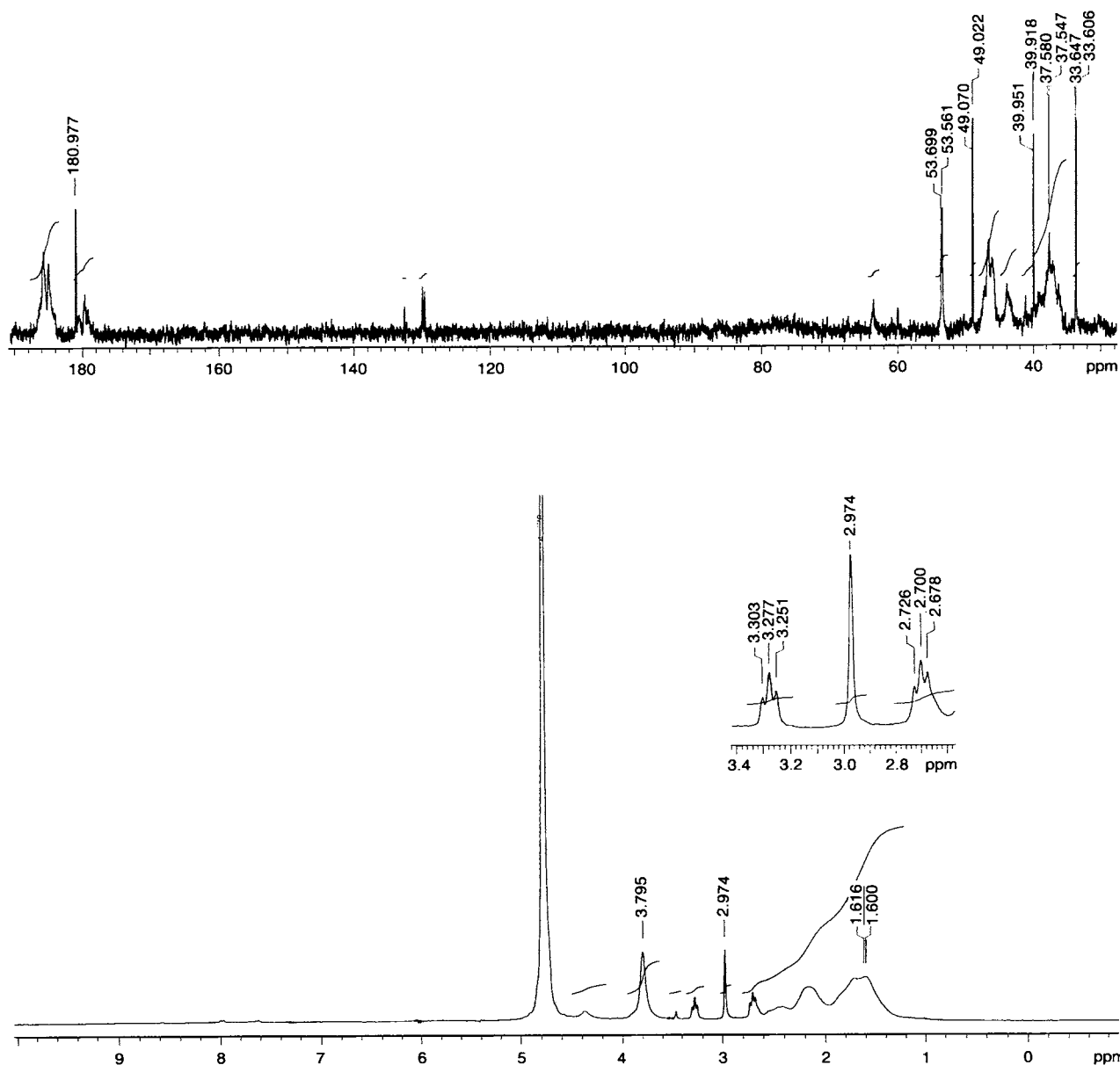


Figure 2 ^{13}C -NMR and ^1H -NMR spectra of acrylic acid-methyl acrylate copolymer sodium salt (MB30).

Compared with D, A shows a smoother surface [Fig. 6(a)] and a more homogeneous distribution of particles [Fig. 6(c)], with less agglomerate [Fig. 6(e)]. In the viscosity curve (Fig. 4), the viscosity of 2 wt % is still at the bottom of the curve for A, so that the particles are well dispersed. However, for C and D that is already in the steep slope area, so that the particles are partially flocculated. The fact that the viscosity, precipitating, and electron microscopy experiments (Figs. 4–6) show similar trends indicates the viscosity method is a reliable method for evaluating a dispersed system. Also, it can be concluded that the relative dispersing ability is $A > B > C > D$,

i.e., the dispersing ability of PAANa with the same composition increases with decreasing MW in the range studied and is consistent with the reported trend.¹⁹

In order to investigate the effect of methyl ester in the polyacrylic copolymer on its dispersing ability, 10% methyl esterification of polyacrylic acid was performed for A, B, C, and D (Table II). Figure 7 shows the curve of the viscosity vs. concentration for the sodium salts of poly(methyl acrylate-acrylic acid) copolymer [P(MA-AANa)]. According to Scheme 1, the MW of MA10, MB10, MC10, or MD10 are the same as A, B, C, or D, respectively,

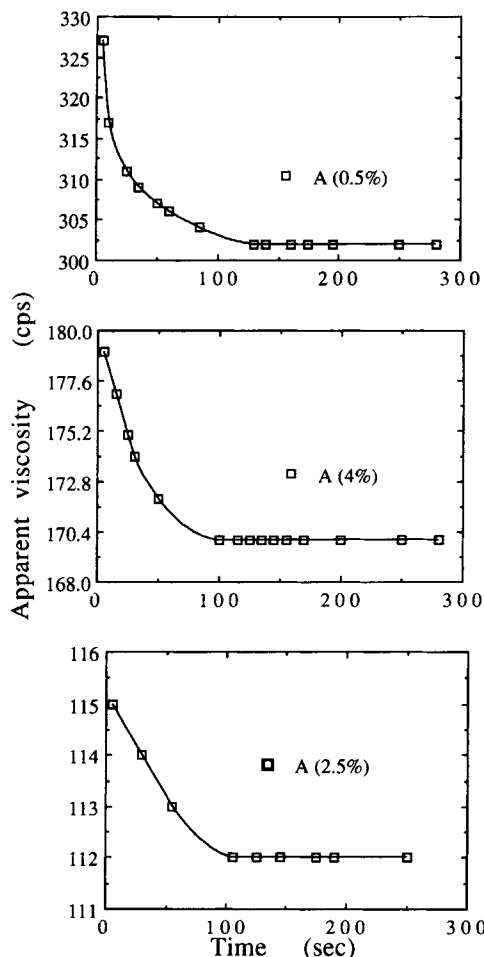


Figure 3 Relationship between apparent viscosity and time for dispersant in PAANa (A/TiO₂).

since the former are prepared from the latter by direct methyl-esterification. Comparing Figures 4 and 7, it is found that the bottom of the curve (the plateau) becomes wider and the optimum concentration shifts to a higher value due to the 10% methyl esterification of polyacrylic acid, but the minimum viscosity is about the same. From the viewpoint of industrial application, the wider the plateau of minimum viscosity, the more convenient for application. As shown in Figure 7, the dispersing ability is MA10 > MB10 > MC10 > MD10, which is the same trend as A > B > C > D (Fig. 4).

In order to confirm the effects of the methyl acrylate in the backbone of sodium polyacrylates, 5, 10, 20, and 30% methyl esterification of polyacrylic acid (B, MW of 13×10^3) were performed to obtain the same MW copolymer of MB5, MB10, M20, and MB30, respectively. Figure 8 shows the curve of η_{app} vs. [dispersant] for MB, MB10, MB20, and MB30. The curve for B, MB5, MB10, MB20, and MB30 shows that 5% methyl esterification broadens the

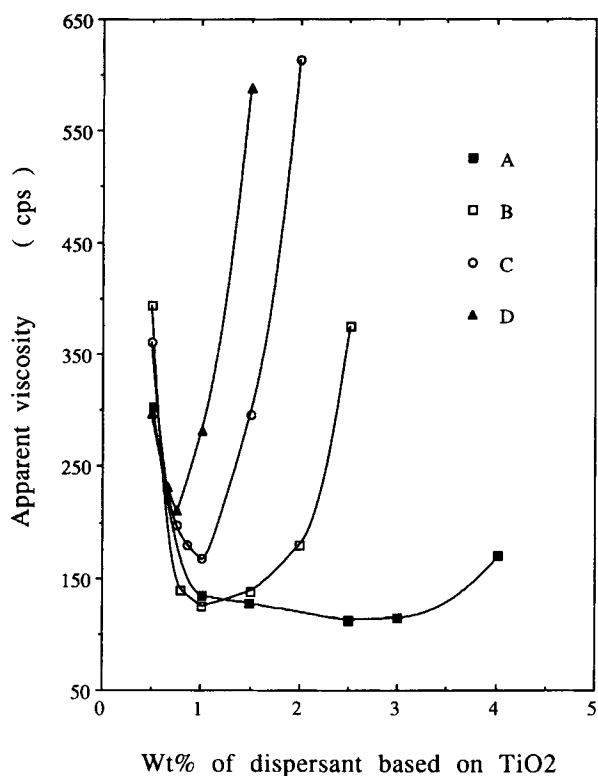


Figure 4 Relationship between apparent viscosity and dispersant concentration (dispersant PAANa-A, B, C, D/TiO₂).

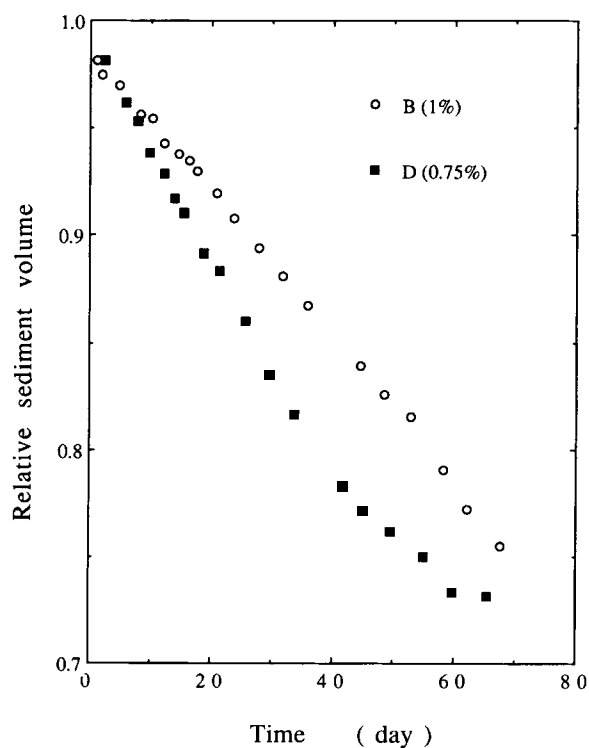


Figure 5 Relationship of settling rate and sediment volume for dispersants PAANa-B, D/TiO₂.

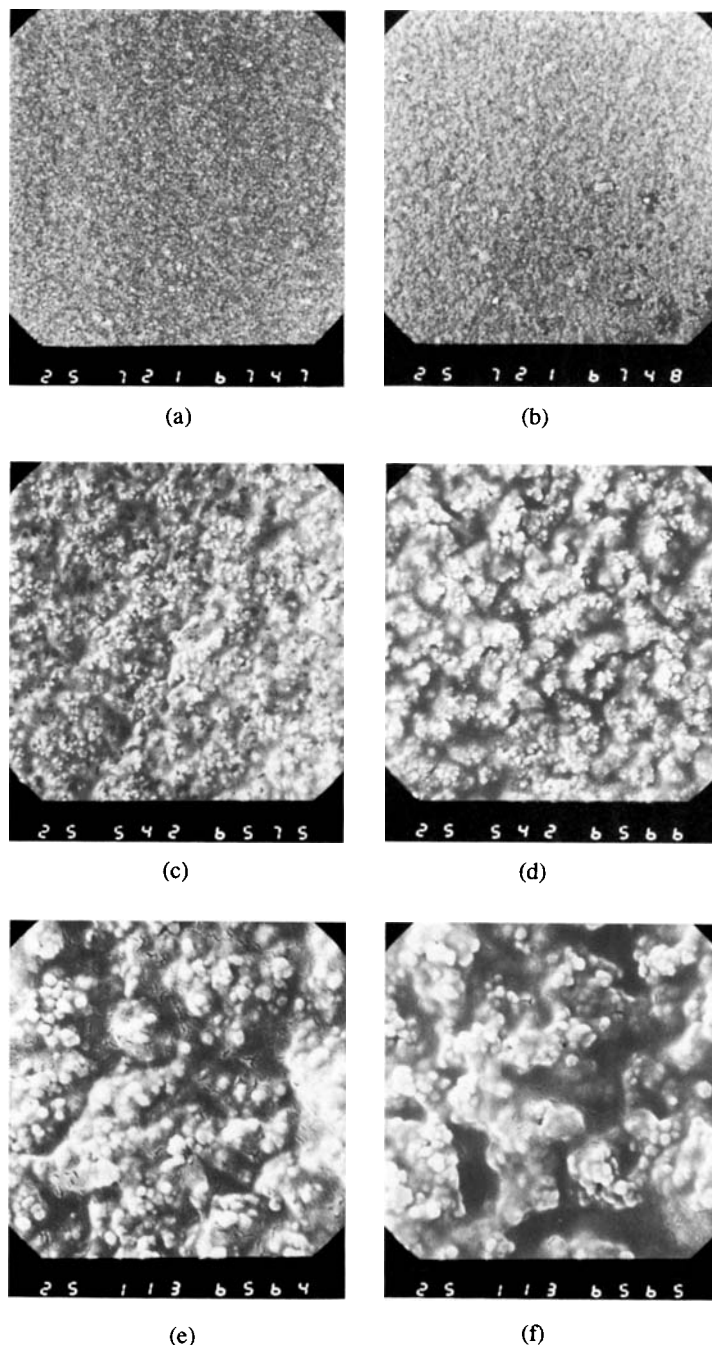


Figure 6 Photographs of dispersed TiO_2 particles using dispersant PAANa-A and PAANa-D: (a) PAANa-A, $\times 720$; (b) PAANa-D, $\times 720$; (c) PAANa-A, $\times 5400$; (d) PAANa-D, $\times 5400$; (e) PAANa-A, $\times 11,000$; (f) PAANa-D, $\times 11,000$.

plateau of the viscosity curve. The range of the plateau does not change, but the maximum concentration shifts to a higher value as the percentage of methyl esterification increases. Figure 8 also shows that the minimum viscosity decreases slightly as methyl esterification increases from 5 to 10 and 20% esterification, but increases for 30% esterification.

It can be concluded from the results of Figures 7 and 8 that the methyl ester group in the P(MA-AANa) significantly increases the range of the viscosity plateau, and increases the optimum concentration. This means that the bridging between the polymer chains adsorbed by different particles is inhibited by the methyl ester. Probably the methyl

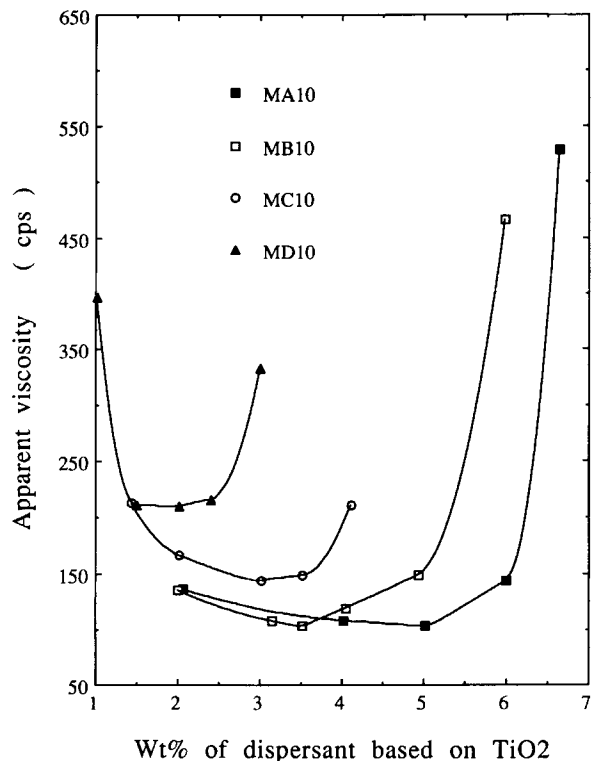


Figure 7 Relationship between apparent viscosity and dispersant concentration (dispersants MB10 series/ TiO_2).

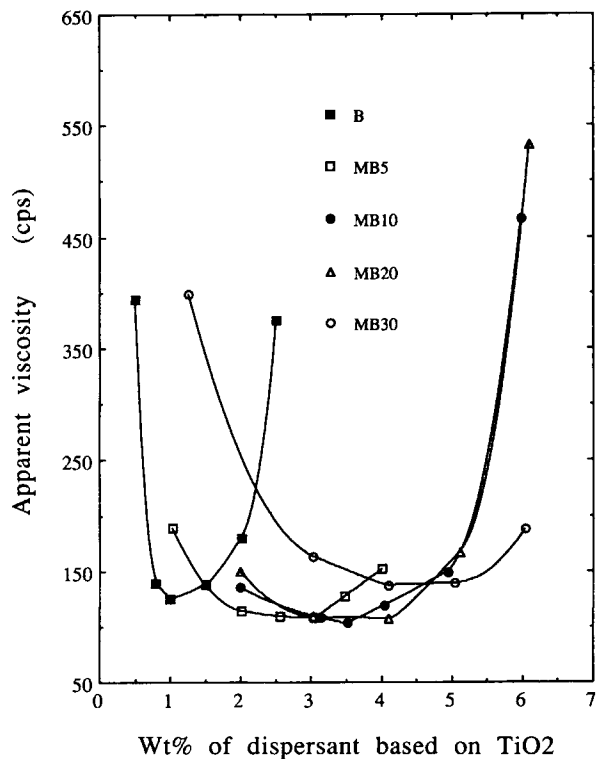


Figure 8 Relationship between apparent viscosity and dispersant concentration (dispersants MB series/ TiO_2).

esters hinder the interaction of polymer PAANa chains on different particles.

Relations between Polymer Adsorption and Dispersing Ability

A dispersant can keep different particles apart by providing electrostatic repulsion and/or steric hindrance on the surface of particles. Therefore, an effective adsorption of a dispersant on particles is necessary for efficient dispersion.²⁰

The concentration of dispersant in the bulk phase was determined by the turbidity of P(MA-AANa) following addition of Hyamine 1622, using the calibration curve (Fig. 1). The adsorption amount of PAANa for B and D is shown in Figure 9. The $C_{B,eq}^D$ for the saturated adsorptions are 7 and 10 g/L for B and D, respectively, but the saturated adsorption amount for B and D are similar (close to 25 mg PAANa/g TiO_2). This means that saturated adsorption is easier to reach for the polymer with smaller MW, but the amount of saturated adsorption is independent of the MW of polymer (B and D).

Zeta potentials for the polymer-adsorbed particles as a function of $C_{B,eq}^D$ are also measured as shown in Figure 10. The zeta potential is negative as TiO_2 is adsorbed by PAANa and the absolute value increases as $C_{B,eq}^D$ increases. For B and D, the zeta potential becomes a plateau after C_B^D is ca. 9 g/L, but is ca.

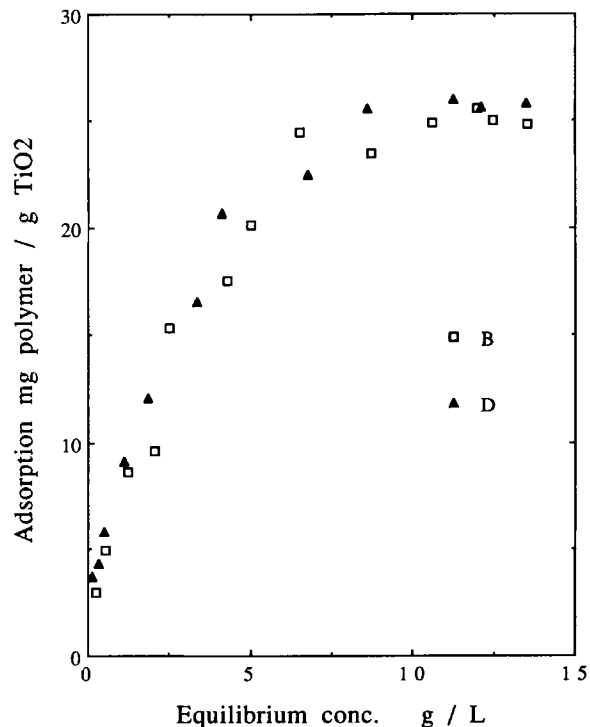


Figure 9 Adsorption isotherms of PAANa-B, D/ TiO_2 .

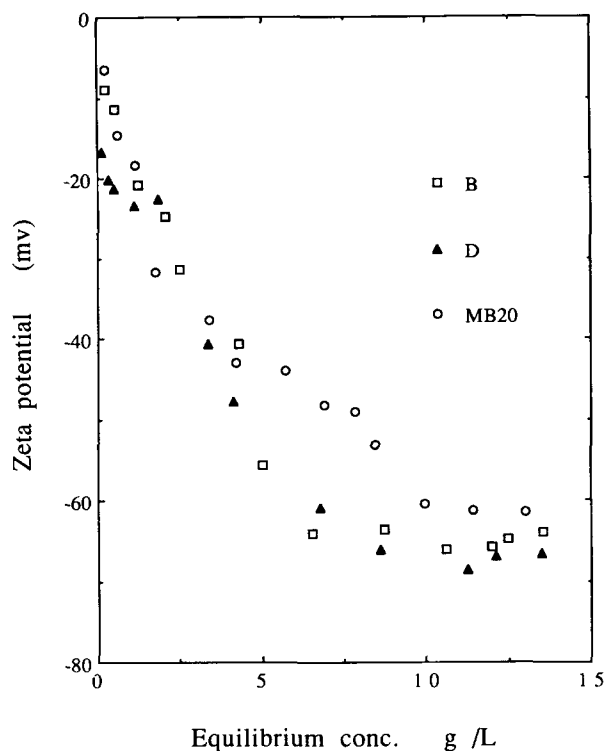


Figure 10 Zeta potential of PAANa-B, D and MB20/TiO₂.

13 g/L for MB20. Figures 9 and 10 show that the trend of adsorption amount as a function of $C_{B,eq}^D$ is similar to that of the zeta potential. It can be concluded from those results that the adsorption amount and zeta potential for PAANa are almost independent of the MW; however, those for P(MA-AANa) decrease due to the methyl ester group in the PAANa chain.

The sharp increase above the optimum concentration in the curve of η vs. [dispersant] for D (in Fig. 4) is due to bridging between the particles by polymers (a flocculation phenomena). A less sharp increase observed for polymers C, B, and A, for which MW is decreased gradually, demonstrates that the bridging effect become less as the MW of the polymer decreases. Since the bridging effect also influences the viscosity of the dispersed system, the minimum viscosity in a curve cannot be simply interpreted by the maximum value of the amount adsorbed or the zeta potential.

The presence of methyl esters in P(MA-AANa) copolymer causes a plateau to occur in the curve of η_{app} vs. [dispersant] and a shift of the optimum concentration to a greater value as shown Figures 7 and 8. These results can be interpreted by the curve of the zeta potential vs. $C_{B,eq}^D$ (Fig. 10). A higher

$C_{B,eq}^D$ for saturated adsorption of P(MA-AANa) (MB20), caused by the introduction of the methyl ester unit, means that the ability of P(MA-AANa) to adsorb onto TiO₂ particles is less. Also methyl ester groups inhibit the bridging effect²¹ of PAANa. These result in a more obvious plateau area in the curve of η_{app} vs. [dispersant] and a higher optimum concentration.

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