Functional Polymers for Colloidal Applications (III): Structural Effects of Lipophile-Modified Styrene-Maleic Anhydride Copolymers on Dispersing Polar and Nonpolar Particles

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SYNOPSIS

Styrene-maleic anhydride copolymer (SMA) with the molecular weight (MW: 7100) suitable for acting as a dispersant was synthesized and then ring-opened with alkylamine to prepare the n-butyl and n-dodecyl-substituted SMA. The prepared lipophile-modified SMA copolymers were used as dispersants to disperse both polar and nonpolar particles (TiO_2 and carbon black). Upon dispersing TiO_2 and carbon black, the antibridging effect (a larger optimum concentration and a less sharp increase after optimum concentration) was observed for SMA as well as n-butylamide-substituted SMA as compared to sodium polyacrylate. The bridging effect, however, is obvious for n-dodecylamide highly substituted SMA (12N45). For dispersing TiO_2, both for n-butyl and n-dodecylamide-substituted SMA, the curve of viscosity vs. concentration increases less sharply after optimum concentration except for 12N45. In the case of dispersing carbon black, the n-butylamide-substituted SMA shows a pronounced antibridging effect, while the n-dodecylamide-substituted SMA shows a significant bridging effect. The minimum viscosity and the optimum concentration for both n-butyl and n-dodecylamide-substituted SMA are correlated to conclude that: (a) at low percentage of alkylamide in SMA, both for n-butyl and n-dodecyl group cause bridging phenomena and increase the viscosity; (b) as the percentage of alkylamide in SMA increase, the adsorption effect is more important for n-butylamide-substituted SMA (e.g., 4N45), and the bridging effect is more important for n-dodecylamide-substituted SMA (e.g., 12N45); (c) the decrease in optimum concentration for 12N45 can be interpreted by the bridging effect.

INTRODUCTION

Many industries involve the process of dispersing solid particles in liquids, such as paint, pigment, resin textile, paper, agriculture, etc.[1,2] Therefore, dispersing process has attracted a wide range of interests in both theoretical studies and practical applications.[3,4] In order to acquire a stable dispersion, a dispersant is usually added to help suspend solid particles in liquid.[5] The main function of the dispersant is to provide the particles with electrostatic barriers[6] or with steric hindrance[7] to produce a bar-rier to prevent coagulation. Surfactants and polymers are usually used as dispersants.[8,9]

Due to the ability to provide a high density of charges and an efficient steric hindrance, polymers are widely used as dispersants in industry.[9,10] To disperse particles effectively, polymers have to interact with and adsorb on the surface of particles effectively. Therefore, the dispersion ability of a polymer is strongly affected by its structure. The hydrophobicity and the functional groups of polymers have to be adjusted to effectively disperse particles with different surface properties. Polycarboxylates, such as the sodium salts of polyacrylic acid[11-16] and styrene-maleic anhydride copolymer (SMA),[17,18] have been widely used as dispersants for inorganic pigments with polar surface,[19,20] such

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as TiO_2 and $CaCO_3$. For particles with nonpolar surfaces (such as carbon black) polycarboxylates, however, is not an effective dispersant.

In addition, an appropriate molecular weight is an important factor for polymer dispersants. Polymers that have inadequate molecular weight could possibly act as a flocculant. To obtain an appropriate molecular weight and hydrophobicity, the SMA copolymer was synthesized following the reported methods[21,22] and then lipophile modified by further reaction with different lengths and percentages of alkylamines to generate the poly(carboxylic acid-alkylamide) copolymers that have a series of hydrophobicities as shown in Figure 1. The dispersing abilities of these copolymers for both polar and nonpolar particles in aqueous solutions were studied and correlated with their structures.

In the previous study,[23,24] a series of lipophile-modified polyacrylic acids were used to study the correlation between the polymer structure and the dispersing ability. The bridging and the antibridging effects were observed for the dodecyl group and the methyl-group-substituted polyacrylic acids, respectively. In the present study the main features in the structure of the alkylamide-substituted SMA are: (a) There is a styrene group in every four carbons along the polymer chain; (b) the alkylamide group is next to the —COONa group; and (c) Some of —COONa groups are next to each other.

EXPERIMENTAL

Materials

Maleic anhydride (Hayashi Pure Chemical Industries Ltd.), styrene (Tokyo Kasei), benzoyl peroxide (Kanton Chemical Co.), n-butyl mercaptan (Tokyo Kasei), n-butylamine (Aldrich), n-dodecylamine (Aldrich), dioxane and acetone are E.P. grade and are used as received. Titanium dioxide (DuPont R-900) and polymer binder (Eternal 1118) are all commercially available products. Polymer binder is a pure acrylic latex of 50% solid content. The latex particles of which the average particle size is 0.2 μm and surface is anionic charged are water insoluble. The water used in the experiments is ion-exchanged and distilled, with the pH of 6.8–7.2 and the conductivity of $4.4 \times 10^{-6}\Omega^{-1}\,m^{-1}$.

Methods

Synthesis and Characterization of Polymers

Synthesis of the SMA Copolymer. In a four-neck reaction kettle, 300 g of 1,4-dioxane was heated to
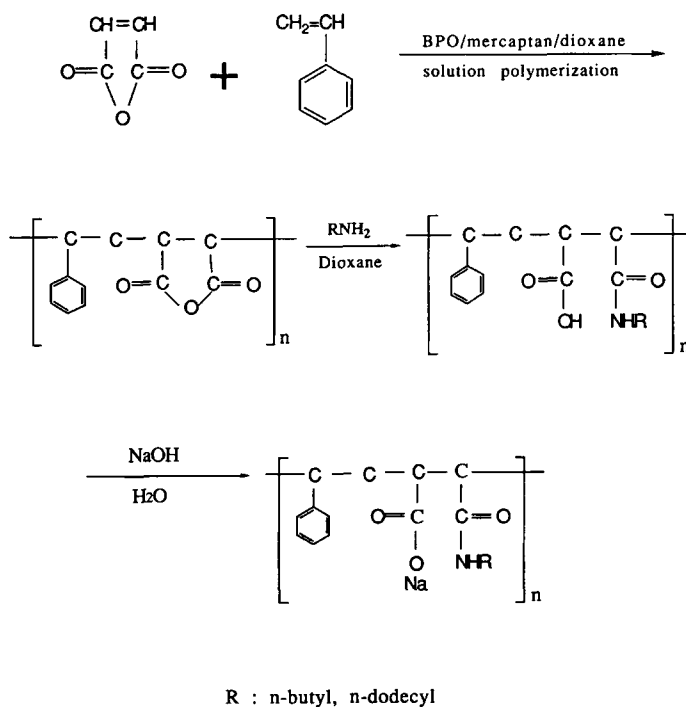

R : n-butyl, n-dodecyl

Figure 1   Synthesis of the SMA and the substituted SMA.

90°C under mechanical stirring and nitrogen blanket. The mixture of maleic anhydride (49 g), styrene (52 g), n-butyl mercaptan (2.02 g), and benzoyl peroxide (4.04 g), dissolved in 140 g of 1,4-dioxane were slowly added into the reaction kettle for 1 h. The temperature was maintained at 90°C for another 2 h to have the polymerization completed.

The solvent was removed from the final solution to obtain the SMA copolymer, which is further purified by dissolving it in dioxane and reprecipitating it in H_2O. The white solid of SMA copolymer was further dried at 60°C at vacuum for 48 h.

Sodium Salt of the n-Butyl Amine, n-Dodecylamine-substituted SMA (SMA-NR).

In a four-neck reaction kettle, 15 g of the SMA copolymer in 1,4-dioxane (30 g) was heated to 50°C, and then an appropriate amount of n-butylamine, n-dodecylamine was added. The sodium salt of amine-substituted SMA was obtained by adjusting the pH of the aqueous solution to 8.5, followed by reprecipitating it in acetone. The sodium salt of n-butylamine, n-dodecylamine-substituted SMA (white solid) was dried at 60°C at vacuum for 48 h.

Evaluation of the Dispersing Ability of Polymers

Many dispersed systems were prepared by using different polymers as dispersants. Titanium dioxide (DuPont R-900, TiO_2 94%, Al_2O_3 4.5%, particle size: 200 nm, density: 4 g/cm³, and surface area: 57.6 m²/g) and carbon black (carbon 99.8%, H_2O 0.2%, particle size: 60 nm, density: 0.53 g/cm³, surface area: 26 m²/g) were used for dispersion. The formulations are as follows: TiO_2, 39.4%; H_2O, 13.4%; polymer binder, 47.2%; and carbon black, 16.7%, water, 16.7%; polymer binder, 66.6%. The dispersant is 0.5–7 wt % of TiO_2 or carbon black. The mechanical stirring was spun at 600 rpm for 60 min, and the temperature was maintained at 25°C. The final dispersed paste was evaluated by the following viscosity method. Without dispersant, the mixture cannot form a paste and its viscosity is too high to measure.

Ten grams of a dispersed paste was put in a small sample adaptor and the temperature maintained at

25°C, and its apparent viscosity was measured by a viscometer (Brookfield DVII LVT) using a spindle of SCS-34 with 60 rpm.

RESULTS AND DISCUSSION

Many SMA copolymers with different molecular weights can be synthesized in dioxane by adding chain transfer agents and by changing the amount of initiators. In this study only one kind of molecular weight of SMA (MW: 7100) was synthesized. Due to the low value of monomer reactivity ratio (r_1 and r_2), the $r_1 r_2$ value close to zero. The synthetic SMA is an alternative copolymer and has a strong alternative tendency.[25] An alternative SMA is useful for acquiring the polycarboxylates of which charges are homogeneously separated. A SMA copolymer with MW of 7100 determined by gas phase chromatography (GPC) was shown to be effective for dispersing TiO_2 and carbon in aqueous solution. This copolymer was used to prepare a series of derivatives of alkylamines that can be used as dispersants. n-Butylamine and n-dodecylamine were used to open part of the anhydride ring in SMA to form the alkylamine-substituted SMAs (SMA-NR), which contain a series of different percentages of amides (Table I). In the ^1H-NMR spectra of SMA-NR, the H of CH_3^- of the alkyl group and that of the benzene ring of styrene appear at $\delta = 0.9$ and 7.2 ppm, respectively. Those two sets of the hydrophobic group are used to determine the degree of substitution of alkylamine.

Apparent viscosity is always used to measure a non-Newtonian fluid that shows different viscosities under different shear rate.[26,27] For a well-dispersed system, the aggregate 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. In contrast, the agglomerate of a poorly dispersed system forms a network that hinders the spindle and results in a higher shear stress and thereby showing a higher viscosity. In this study a low-shear-rate viscometer (Brookfield DVII, LVT), with a spindle of SC4-34 was used to measure the apparent

Table I   Composition and Abbreviation of N-Alkyl Amide-Modified SMA

Alkyl	Degree of Substitution, A% (Abbreviation)				
n-Butylamine (4N)	5.75% (4N05)	15.62% (4N15)	30.19% (4N30)	42.98% (4N45)	49.03% (4N50)
n-Dodecylamine (12N)	4.94% (12N05)	15.30% (12N15)	29.34% (12N30)	42.49% (12N45)	48.71% (12N50)

A% = CONR/(COONa + CONR) in the N-alkylamide-modified SMA (final product in Fig. 1).

viscosity, $\eta_{app} = \tau/\gamma$, where τ is shear stress and γ is shear rate. For all dispersion of carbon black and TiO_2 with different concentrations of dispersant, the viscosity decreases gradually at the beginning (before 100 s) and then reaches a stable value.

The difference in structure between the sodium salt of polyacrylic acid (PAANa-B, MW: 1300)[23] and that of SMA is that half of the acid group of the former is replaced by styrene groups. The dispersing behaviors of these two types of polymers to both polar and nonpolar particles (TiO_2 and carbon black) are shown in Figures 2 and 3. For the dispersion of TiO_2 (Fig. 2), a minimum in the plot of viscosity vs. dispersant concentration can be observed for PAANa-B. The apparent viscosity at the minimum point is called minimum viscosity, and the concentration at that point is called optimum concentration. For SMA, the minimum viscosity is close to that for PAANa-B; however, the increase after minimum viscosity in the plot is not so obvious. The increase after minimum viscosity in the plot is contributed to the bridging effect among the dispersed particles. The less sharp increase after minimum viscosity for SMA can be interpreted by the phenomenon of less bridging as compared with PAANa-B. The phenomenon of less bridging has been observed for the dispersion of partially methyl-
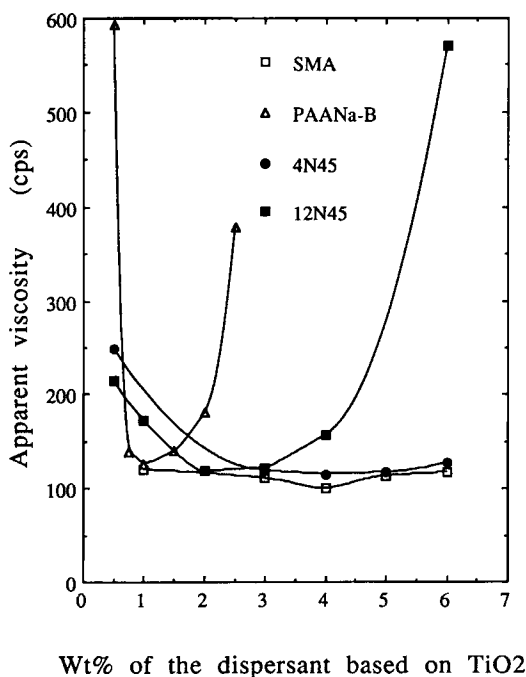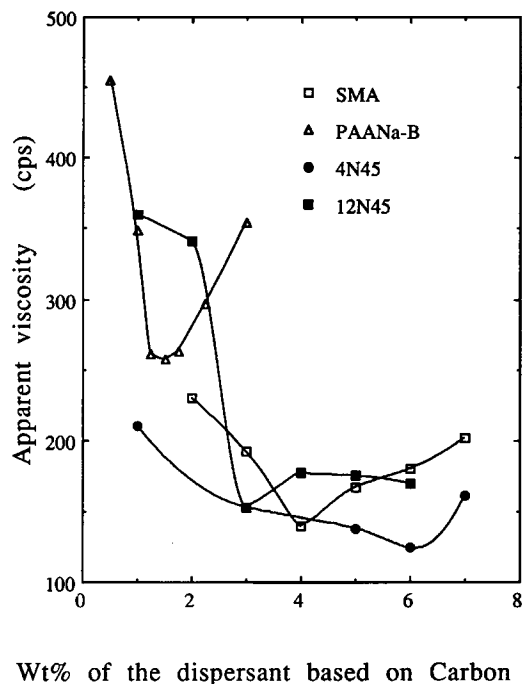

Figure 3 Relationship between viscosity and dispersant concentration for polymers to disperse Carbon black (data of PAANa-B are cited from Ref. 23).

esterified polyacrylic acid.[23] This phenomenon is interpreted by the effect of antibridging of the methyl ester in polymer. From the difference in structure between SMA and PAANa-B, it is seen that the styrene group in SMA has the same of antibridging effect as the methyl group in PAANa-B. When 45% of maleic anhydride in SMA is ring opened by n-butylamine (4N45) and by n-dodecylamine (12N45), 4N45 gives a similar plot with less bridging effect while 12N45 has a more obvious bridging effect (Fig. 2). The phenomenon for the latter is similar to that for the dispersion of partially dodecyl-esterified polyacrylic acid and can be interpreted by the same reason that the bridging effect is caused by the strong hydrophobic interaction of dodecyl group among polymers that adsorb on different particles. The similarity between 4N45 and SMA means that the existence of 45% n-butylamide in SMA does not result in the bridging or antibridging effect, or these two effects compensate each other.

For dispersing carbon black in aqueous solution, SMA shows a much lower minimum viscosity as compared with PAANa-B. This can be attributed to the strong hydrophobicity of SMA, which results in a strong adsorption on carbon black and an efficient dispersion to it. The increase after minimum viscosity of the plot for SMA is less sharp. This could

Figure 2 Relationship between viscosity and dispersant concentration for polymers to disperse TiO_2 (data of PAANa-B are cited from Ref. 23).

be due to the antibridging effect of the phenyl group in SMA. As 4N45 is used as a dispersant, the minimum viscosity decreases as a result of the stronger adsorption on carbon black and the optimum concentration increases due to the antibridging effect. For 12N45, the minimum viscosity increases and the optimum concentration decreases. This trend is identical with that observed in the dodecyl-esterified polyacrylic–TiO_2 system. This can be interpreted by the bridging effect due to the strong hydrophobic interaction of the dodecyl groups.

In order to investigate the effect of hydrophobic group in SMA, different percentages of n-butylamine and n-dodecylamine were used to open the ring of maleic anhydrides. These copolymers are used to disperse TiO_2 and carbon black, and the plots for viscosity as a function of the dispersant concentration are shown in Figures 4–7. The dispersing ability of n-butylamide-substituted SMA (4N05-4N45) to TiO_2 in aqueous solutions is shown in Figure 4. All of these polymers or copolymers result in similar less-curved plots. The different percentage of substitution obviously does not influence the minimum viscosity and the optimum concentration, which are close to that for SMA. This could imply that 5–45% n-butylamide substitution in SMA does not increase or decrease the antibridging effect. The dispersing ability of the n-dodecylamide partially substituted SMA to TiO_2 in aqueous solutions is shown in Figure
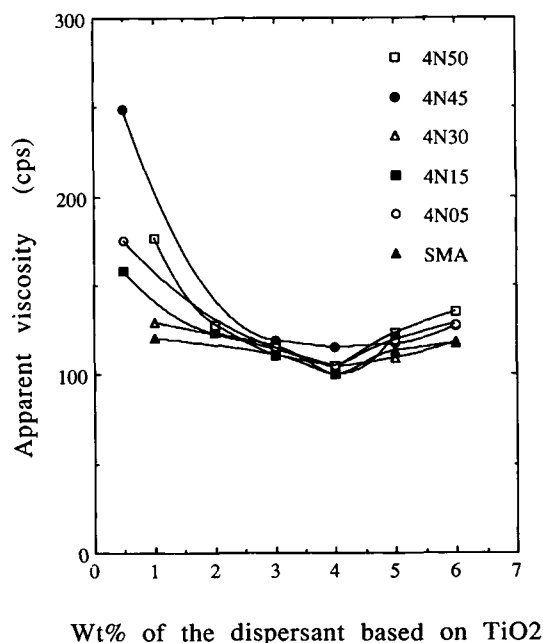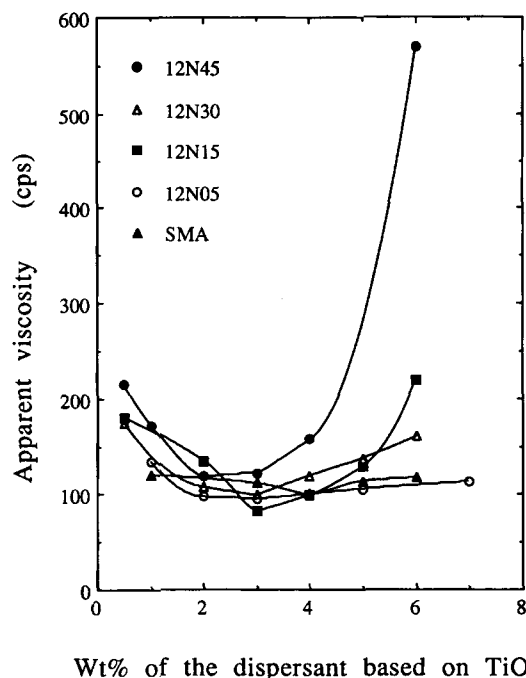

Figure 5 Relationship between viscosity and dispersant concentration (12N series/TiO_2).

5. Except for 12N45, the shapes of the plots are similar to those for the n-butylamide-substituted SMA (Fig. 4). As the percentage of substitution increases from 5 to 45%, the optimum concentration decreases gradually and the minimum viscosity decreased and then increases slightly. For 12N45, the viscosity increases sharply after the minimum concentration is reached. This trend is identical to that observed in the dodecyl-esterified polyacrylate–TiO_2 aqueous system, and can be interpreted by the bridging effect, which is deduced from the hydrophobic interaction of dodecyl groups.
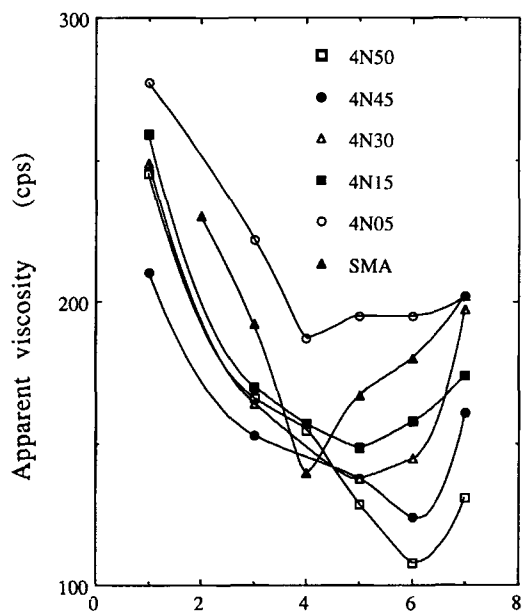
When the n-butylamide-substituted SMA is used to disperse the carbon black in aqueous solution (Fig. 6), the minimum viscosity increases for 4N05. As the percentage of substitution increases, the minimum viscosity decreases and the optimum concentration increases slightly. This trend is similar to that observed in the methyl-esterified polyacrylate–carbon black aqueous system reported in the previous study.[23] As the percentage of substitution increased, the decrease in minimum viscosity can be interpreted by the better dispersion due to the increased adsorption of the n-butylamide-substituted SMA, which is a result of the increased adsorption, while the increase in optimum concentration can be attributed to the increase in the antibridging effect.

For the n-dodecylamide-substituted SMA used

Figure 4 Relationship between viscosity and dispersant concentration (4N series/TiO_2).

to disperse carbon black in aqueous solution (Fig. 7), it is observed that as the percentage of substitution increases from 5 to 30%, the optimum concentration does not change, and the minimum viscosity increases then decreases. As the percentage increases to 45%, the viscosity increases and the optimum concentration decreases. Again, this is a phenomenon of the bridging effect among carbon black.
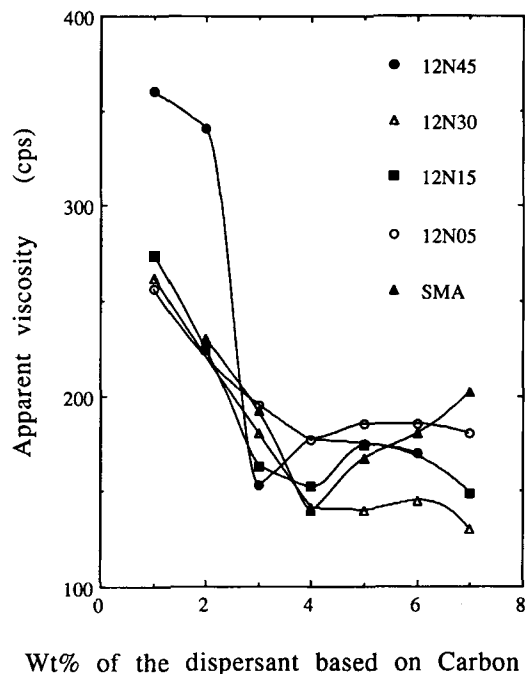
For dispersing carbon black in aqueous solution (Figs. 6 and 7), n-dodecylamide-substituted SMA and n-butylamide-substituted SMA show similar trends for low percentage of substitution and different trend for high percentages of substitution in both minimum viscosity and optimum concentration (Fig. 8).

For the SMA with low percentage of substitution (4N05 and 12N05), part of n-butyl or n-dodecyl groups are probably oriented toward the water phase due to the hydrophilicity properties of the amide groups and the neighboring carboxylic groups. Therefore, those n-butyl and n-dodecyl groups cause the bridging phenomenon and increase the viscosity of the dispersed system. On the other hand, as the percentage of n-alkyl group in SMA increase, the adsorption of n-alkylamide-substituted SMA on carbon black increases, and the viscosity of the system decreases. The factor that increases the ad-

Wt% of the dispersant based on Carbon black

Figure 7 Relationship between viscosity and dispersant concentration (12N series/carbon black).

Wt% of the dispersant based on Carbon black

Figure 6 Relationship between viscosity and dispersant concentration (4N series/carbon black).

sorption is at equilibrium with the bridging effect. The adsorption factor is more important for n-butylamide-substituted SMA, and the bridging effect is more important for the n-dodecylamide-substituted SMA. For the SMA with high substitution of n-dodecyl groups (12N45), the bridging effect is more important and results in a higher viscosity. The decrease in optimum concentration for 12N45 (Fig. 8) can also be interpreted by the bridging effect.

CONCLUSIONS

For dispersing TiO$_2$ in aqueous solution, SMA shows the minimum viscosity close to that for PAANa-B; however, the increase after minimum viscosity in the plot is not so obvious (Fig. 2). Degree of substitution of n-butylamine to SMA obviously does not influence the minimum viscosity and the optimum concentration (Fig. 4). However, as the degree of substitution of n-dodecylamine to SMA increases from 5 to 45%, the optimum concentration decreases gradually and the minimum viscosity decreased and then increases slightly (Fig. 5).

For dispersing carbon black in aqueous solution, SMA shows a much lower minimum viscosity as compared with PAANa-B (Fig. 2). This can be at-
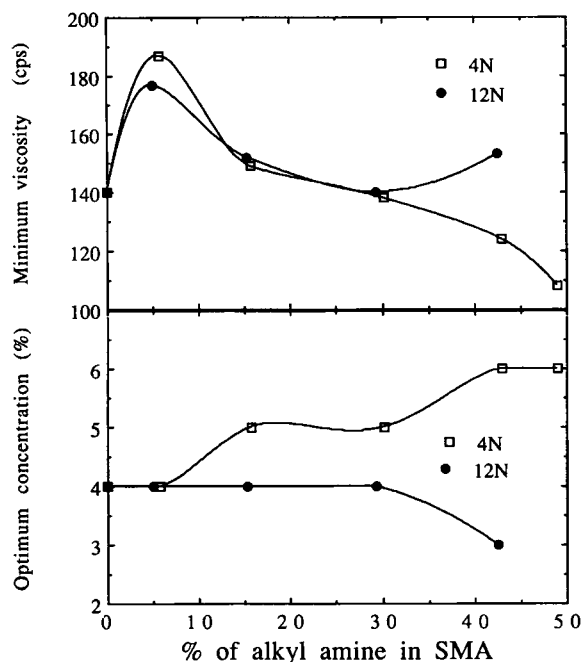
Figure 8 Relationship between apparent viscosity, optimum concentration, and percentage of alkyl amine in SMA.

tributed to the stronger hydrophobicity of SMA, which results in a strong adsorption on carbon black. As the percentage of n-butylamide substitution increases (higher than 5%), the minimum viscosity decreases and the optimum concentration increases slightly. And as the percentage of n-dodecylamide substitution increases from 5 to 30%, the optimum concentration does not change and the minimum viscosity increases then decreases again (Figs. 6–8).

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