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Polymerization of Styrene Adsolubilized in Surfactant Adsorbed Bilayer on Pigments

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The polymerization of styrene adsolubilized in a surfactant-adsorbed bilayer formed on the surface of inorganic pigments (iron oxide, titanium dioxide) was attempted in order to modify their surface properties. After the polymerization, the amount of polystyrene formed on the pigments gradually increased with an increase in the amount of styrene adsolubilized. Further, the molecular weight of the polystyrene formed changed with an increase in the amount of styrene. The surface properties of pigments after the polymerization were characterized by FTIR-PAS, turbidity, and zeta potential measurements.

Recently, seeded polymerization has been employed to modify the surface properties of particles. Cho et al.[1] have studied the mechanism with respect to the emulsion polymerization of PMMA-seeded styrene. Similar research has been achieved by Okubo,[2,3] Whang,[4] Hawkett,[5] Morgan,[6] and Hergeth.[7] From their studies, it has been confirmed that the polymerization of organic polymers on the surfaces of organic substances occurs easily. However, when the polymerization of organic monomers is performed in the presence of inorganic particles, it is known that seed nucleation and the growth of organic monomers progress independently of the inorganic particles due to a deficiency of the affinity between monomers and inorganic particles.[8]

On the other hand, it has been reported that inorganic particles can be encapsulated by organic polymers due to an enhancement of the interfacial affinity by a treatment of water-soluble polymers[8,9] or monomers of the hydrophilic acrylic series.[10] It is also well-known[11] that ionic surfactants form adsorbed bilayers on particle surfaces. By using such adsorbed bilayers, there is a great possibility that hydrophobic monomers can be adsolubilized into the surfactant adsorbed bilayers which exhibit hydrophobic properties and can then be polymerized.

In this work, styrene was adsolubilized into surfactant bilayers on the surface of a pigment and the polymerization of styrene adsolubilized was examined.

Experimental

Materials. Iron oxide (α-Fe_2O_3) and titanium dioxide (anatase) used were supplied by Titan Kogyo Co. Ltd. The surface area of the former was 3.4 $m^2 g^{-1}$, and 40.7 $m^2 g^{-1}$ for the latter. Sodium dodecyl sulfate (SDS) was supplied by Wako Pure Chemical Industries, Ltd., which was purified twice by recrystallization from ethanol. Styrene obtained from Wako Pure Chemical Industries, Ltd., was distilled under reduced pressure. Other chemicals were of all analytical grade.

Procedure. All the polymerization was performed in a 1-liter separable flask under nitrogen gas purging. The polymerization temperature was controlled at 70 °C by a thermostatic water bath. Before polymerization, 1 g of the pigment and 100 ml of aqueous electrolyte solution ($FeCl_3$ for iron oxide, $AlCl_3$ for titanium dioxide) were mixed in order to obtain a pigment with a high positive zeta potential.[11] Then, in order to form adsorbed bilayers of surfactant on the pigment, 100 ml of a 15 mM SDS solution was added, whereas the zeta potential of the adsorbed bilayer on pigment surface was negative. Styrene (as a monomer) was adsolubilized into the adsorbed bilayers of the surfactant on the pigment under 400 rpm of agitation speed for 2 h and then potassium peroxodisulfate (as an initiator) was added into the solution. The weight ratio of potassium peroxodisulfate to styrene was 1:100. The obtained products were washed several times with ethanol.

The amount of ethylbenzene adsolubilized was determined by using the same solution mentioned above; the concentration of ethylbenzene was obtained by measuring the absorbance at 260 nm.

Measurements. The coated amount of polystyrene on the pigments was determined gravimetrically: The total amounts of polystyrene on the pigments were obtained from the difference of weight before and after the calcination of the samples at 500 °C. The THF-unextractive coated amount of polystyrene was also determined gravimetrically.

The zeta potential of uncoated and polystyrene-coated pigments was measured with an Electrophoresis apparatus (Laser Zee 500, Pen Kem, Inc.) in ethanol. The zeta potential of styrene latex prepared by using SDS alone was also measured for a comparison.

The turbidity of pigments in water or hexane was measured as follows: A known weight of sample was put into a sedimentation tube in which deionized water or hexane was contained and then the obtained suspension was treated by sonication for ten minutes. After one hour standing, the absorbance of the suspension was measured at 500 nm with a spectrophotometer (Hitachi, Ltd., 220A).

The weight-average molecular weight of polystyrene which had been extracted from the coated pigments with THF was determined by gel permeation chromatography (Japan Spectroscopic Co. Ltd.).

The surfaces of the coated pigments were measured using a FTIR-PAS (FPA-84, Japan Spectroscopic Co., Ltd.).

Results and Discussion

It is known[11] that positively charged particles can be flocculated and redispersed by the addition of anionic surfactants, resulting in the formation of an adsorbed

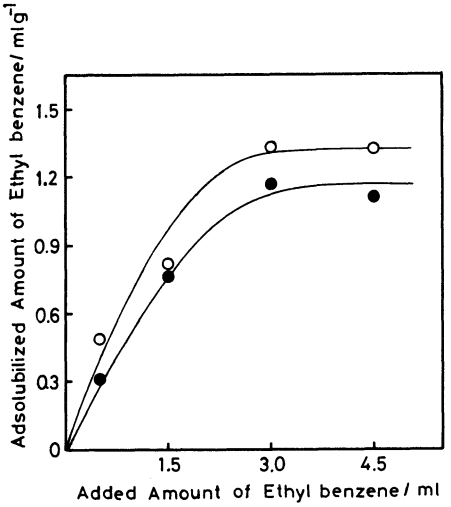


Fig. 1. The change in the amount of ethylbenzene adsolubilized into SDS-double layer on the pigment as a function of added amount of ethylbenzene at 25°C; (○) iron oxide, (●) titanium dioxide.

bilayer of surfactant on the particles. This adsorbed bilayer is expected to provide a field of polymerization of hydrophobic monomers since it exhibits hydrophobic property.

Figure 1 shows the amount of ethylbenzene adsolubilized into an SDS-adsorbed bilayer on the pigments as a function of the added amount of ethylbenzene at 25°C. Here, it is postulated that the amount of ethylbenzene adsolubilized is similar to that of styrene. In both pigments, the amount of ethylbenzene adsolubilized gradually increased and attained a constant value.

Then, the polymerization of adsolubilized styrene was carried out at 60°C using potassium peroxodisulfate as an initiator for 3 h. From a measurement of FTIR-PAS for the samples after polymerization, the absorption bands attributable to polystyrene (3200—2900 cm^{-1}, 1480—1360 cm^{-1}, 1130—1100 cm^{-1}) and SDS (1220 cm^{-1}, 1040 cm^{-1}) were observed, indicating that the surface of pigments are covered with a polystyrene layer.

Figure 2 shows the total amount of polystyrene and the THF-unextractive amount of polystyrene on pigments as a function of added amount of styrene. In the case of iron oxide, it is apparent that the THF-unextractive amount is approximately constant in spite of various added amounts. On the other hand, for titanium dioxide, the THF-unextractive amount was very small, but the THF-extractive amount increased with the added amount of styrene. The change in the weight-average molecular weight of the THF-extractive polystyrene as a function of the added amount of styrene is shown in Fig. 3. In the case of iron oxide, the weight-average molecular weight of the THF-extractive polystyrene decreased with an increase of the added amount of styrene. This result can be explained

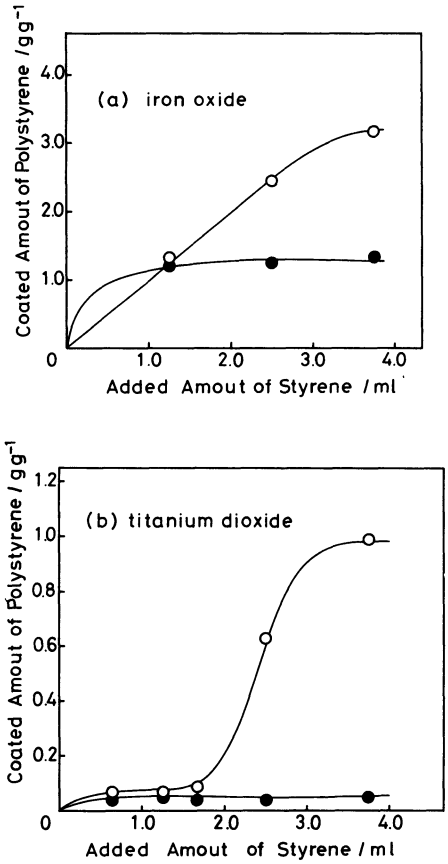


Fig. 2. The change in the coated amount of polystyrene on pigments as a function of added amount of styrene; (●) amount of unextractive polystyrene after THF extraction, (○) total coated amount of polystyrene.

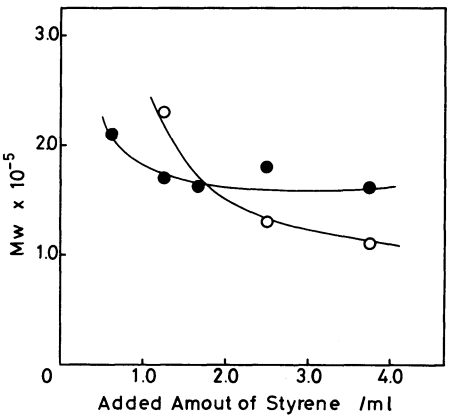
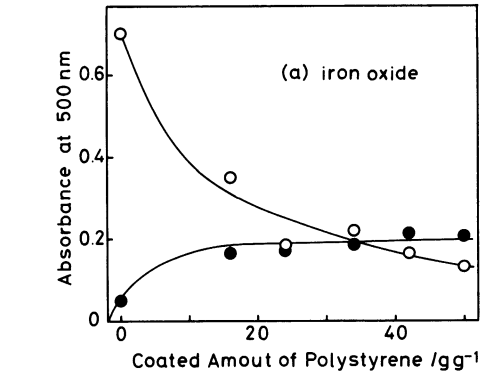


Fig. 3. The change in the weight-average molecular weight of THF-extractive polystyrene on pigment as a function of added amount of styrene; (○) iron oxide, (●) titanium dioxide.

as follows: The adsolubilized amount of styrene gradually increases with the added amount of styrene, while the amount of the initiator becomes in excess against the adsolubilized amount of styrene, resulting in a decrease in the molecular weight. Similarly, in the case of titanium dioxide, the weight-average molecular



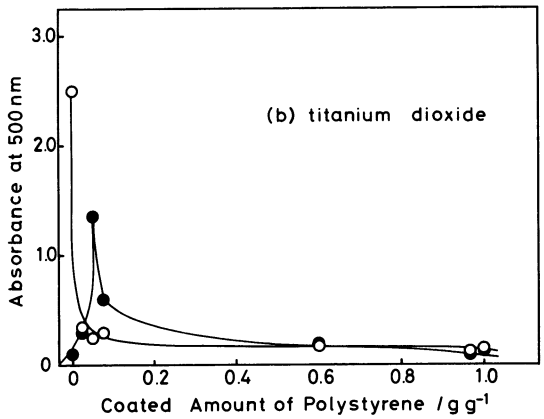


Fig. 4. The change in the absorbance at 500 nm as a function of coated amount of polystyrene on pigment; (○) in water, (●) in hexane.

weight decreases slightly. The zeta potential of the pigments after the polymerization was measured: the zeta potential was almost zero in ethanol compared with both the untreated sample and the latex prepared by using SDS alone having a large zeta potential, suggesting that the pigment surface is reasonably coated by polystyrene for both pigments.

Figure 4 shows the change in the absorbance of pigments after polymerization, in water and hexane, respectively. Here, a high absorbance value indicates a high stability. In water, the absorbance of both pigments decreased upon increasing the coated amount of polystyrene; however, in hexane an opposite change was observed for iron oxide, indicating that the surface of pigment becomes hydrophobic after polymerization. On the other hand, the absorbance of titanium dioxide in hexane showed a maximum value at some coated amount of polystyrene.

Schematics of the adsorbed bilayer of a surfactant adsolubilized with styrene and of pigment particles

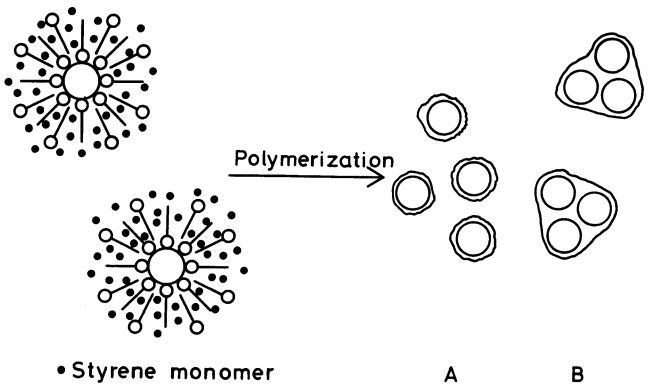


Fig. 5. Models of coated pigments by polystyrene.

after polymerization are presented in Fig. 5. For both iron oxide and titanium dioxide, there is a possibility that the coated pigments belong to model A or B since the coated amount of polystyrene and the molecular weight changed gradually with an increase in the added amount of styrene. Thus, it is concluded that this method of using a surfactant adsorbed bilayer is a useful encapsulation technique for the modification of a particle surface.

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