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ORIGINAL CONTRIBUTION

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Estimation of the adsorption state of nonionic emulsifier molecules onto styrene–methacrylic acid copolymer particles by in situ ^{1}H NMR measurements

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Abstract The adsorption behavior of poly(oxyethylene) nonyl phenyl ether nonionic emulsifier molecules onto polystyrene (PS) and styrene–methacrylic acid copolymer [P(S-MAA)] particles dispersed in D_2O was evaluated by in situ ^{1}H NMR measurements at room temperature. The resonance due to the protons of the emulsifier molecules was only observed. Normalized NMR integrals of the resonance due to the protons of hydrophobic groups (nonyl and phenyl groups) and the hydrophilic group, poly(oxyethylene) chain, at a certain concentration of the emulsifier decreased with an increase in the total surface area of the PS particles dispersed in the system. The decrease for the hydrophobic groups was much larger than that for the hydrophilic groups. In the dispersion system of P(S-MAA) particles, ionized carboxyl groups at the particle surface decreased the amount of the emulsifier adsorbed.

Introduction

It was found that submicron-sized, styrene–butyl acrylate–methacrylic acid [P(S-BA-MAA)] (50.4/40.9/8.7 molar ratio) terpolymer particles were changed to nanoparticles with diameter of about 30 nm in the presence of a certain concentration of poly(oxyethylene) nonyl phenyl ether nonionic emulsifier (Emulgen 930) at 40 °C under alkaline conditions [1]. Hereafter, this method is named the particle dissolution method. Some effects, such as treatment temperature, alkaline concentration, and the kind and amount of nonionic emulsifier, on the preparation of the nanoparticles were examined in detail and the formation mechanism was proposed [2]. Moreover, in order to prepare nonhydrolyzable nanosized polymer particles having high T_g, submicron-sized P(S-MAA) particles having T_g above 100 °C were treated by the particle dissolution method [3]. Nanoparticles were prepared from P(S-MAA) particles having 6–8 mol% MAA content, but not from those having MAA contents of more than 10 mol% [3, 4]. The reason why the P(S-MAA) particles having the high MAA content were not changed to the nanoparticles seems to be based on less interaction between the emulsifier and the copolymer [5].

By the way, the adsorption behavior of the nonionic emulsifier molecules has been actively studied. For example, Colombie et al. reported with ^{1}H NMR measurements the adsorption isotherm of nonionic surfactant on PS particles [6] and competitive adsorption of the anionic and nonionic surfactants on PS particles [7].

In this article, the adsorption behavior of the emulsifier molecules on PS and P(S-MAA) particles having different MAA contents is estimated from in situ ^1H NMR measurements to clarify the particle dissolution method in more detail.

Experimental

Materials

S and MAA were purified by distillation under reduced pressure in a N_2 atmosphere. Reagent-grade potassium persulfate was purified by recrystallization from distilled water. Analytical grade dimethyl sulfoxide (DMSO), potassium hydroxide, 3-(trimethylsilyl)propionic acid sodium salt-*d*4 (TSP-*d*4), and deuterium oxide (D_2O) were used without further purification.

A commercial grade poly(oxyethylene) nonyl phenyl ether nonionic emulsifier (Emulgen 930; Kao Corp., Tokyo, Japan) was used without further purification. Deionized water was distilled.

Preparations of polymer emulsions

The PS emulsion was prepared by emulsifier-free emulsion polymerization, and P(S-MAA) emulsions having various MAA contents were prepared by emulsion copolymerizations under the conditions listed in Table 1. It was confirmed by a gravimetric method that each polymerization had been completed.

Characterizations of particles

The particle diameter was measured at room temperature using an Otsuka Electronics DLS-700 dynamic light scattering spectroscope at 90° of the light scattering angle. The specific surface area of the particles after purification was measured by the Brunauer–Emmett–Teller method using a Shimadzu Micromeritics Jemini with N_2 gas.

^1H NMR measurement for the estimation of adsorption of emulsifier on particles

Various amounts of PS and P(S-MAA) particles, which had been purified by ultracentrifuging with distilled water five times, were dispersed in Emulgen 930 D_2O solutions including 0.1 wt% TSP-*d*4 and 0.069 wt% DMSO in 5-mm NMR tubes. ^1H NMR spectra were measured with a Bruker DPX250 NMR spectrometer operating at 250 MHz for protons with 200 scans at room temperature. Chemical shifts were obtained relative to methyl groups of TSP-*d*4. DMSO was used as an internal reference. In order to clarify the adsorption behavior of the nonionic emulsifier, the survival percentage of normalized NMR integrals was estimated on the basis of the normalized NMR integrals of the system without polymer particles.

Results and discussion

A ^1H NMR spectrum of the nonionic emulsifier Emulgen 930 (2.1 g/l) in D_2O including 0.1 wt% TSP-*d*4 and 0.069 wt% DMSO is shown in Fig. 1. The resonances of the emulsifier molecule appeared around 1, 3.7, and 7 ppm, which correspond to the protons of the nonyl group, the poly(oxyethylene) chain, and the phenyl group, respectively. The concentrations of their groups were calculated by integrals in ranges of 0.8–1.3, 3.3–4.2, and 6.6–7.4 ppm, respectively. Good linear relationships were established for all the integrals and the emulsifier concentration below and above the critical micelle concentration (Emulgen 930, 0.1 g/l at 25 °C). This indicates that quantitative analysis of the emulsifier molecules even in the presence of the micelle is possible with the ^1H NMR measurement without anxiety about the decline of their mobilities. Similar linear relationships were obtained regardless of pH in the range 2–13.

^1H NMR spectra of Emulgen 930 molecules in D_2O in which various amounts of purified PS particles prepared by emulsifier-free emulsion polymerization were dispersed are shown in Fig. 2. ^1H NMR spectra

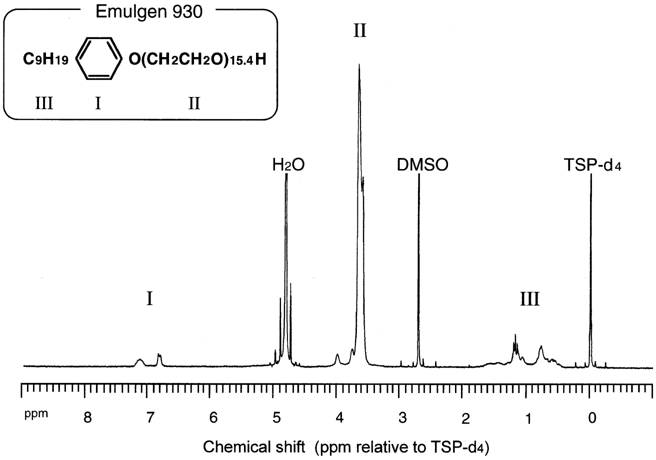

Fig. 1. ^1H NMR spectrum of Emulgen 930 (2.1 g/l) in D_2O solution including 0.1 wt% 3-(trimethylsilyl)propionic acid sodium salt-*d*4 (*TSP-d4*) and 0.069 wt% dimethyl sulfoxide (*DMSO*)

Table 1. Recipes of emulsion polymerizations for preparations of polystyrene (*PS*) particles and styrene–methacrylic acid copolymer [*P(S-MAA)*] particles having various MAA contents. N_2; 70 °C; 48 h for PS or 24 h for P(S-MAA); stirring rate, 120 rpm

	MAA content (mol%)		
	0	6	10
Styrene (g)	60	57	16.5
MAA (g)	0	3.0	1.5
Potassium persulfate (g)	0.99	0.24	0.12
Emulgen 911 (g)	0	2.5	2.0
Water (g)	1,000	540	270
Specific surface area (m^2/g)[a]	12.0	13.9	15.4

[a] Measured by the Brunauer–Emmett–Teller method

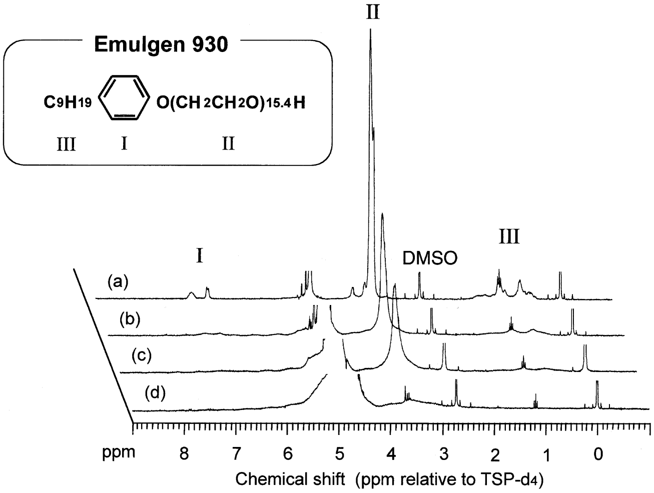

Fig. 2. ^{1} NMR spectra of Emulgen 930 (2.1 g/l) in D_2O solution including 0.1 wt% TSP-d4 and 0.069 wt% DMSO at pH 6.5 in the presence of polystyrene (*PS*) particles (g/l): (*a*) 0; (*b*) 41.4; (*c*) 76.3; (*d*) 192.8

due to the protons of the PS particles were not observed, because of the extremely low mobility of PS molecules in the particle. Each peak decreased gradually with an increase in the amount of PS. This is due to the emulsifier molecule losing mobility by being adsorbed on the particle.

In Fig. 2, spectrum d, where the PS concentration is 2.3 m^2/ml, three peaks are seen around 1.2 ppm. The peaks around 1.2 ppm were not observed for the medium from which the PS particles and the Emulgen 930 molecules adsorbed thereon were removed, TSP-d_4, DMSO, and water. These results suggest that the peaks around 1.2 ppm are from the end methyl groups in the nonyl group of the Emulgen 930 molecule, and the mobility of the end methyl groups still remains even if the Emulgen 930 molecule is adsorbed onto the PS particle.

The variations of the survival percentage of the normalized NMR integrals of Emulgen 930 molecules as a function of the total surface area, A_t, of the PS particles are shown in Fig. 3. The integrals due to the protons of the phenyl and the nonyl groups, which are hydrophobic groups, decreased with an increase in A_t and became zero at 1.8 m^2/ml. This indicates that the PS particles dispersed in the system adsorbed all the emulsifier molecules at $A_t = 1.8$ m^2/ml. From this A_t value, the occupied area per emulsifier molecule adsorbed on the PS particles was calculated to be 1.30 nm^2, which agreed with the result reported by Colombie et al. [6]. They found that the area occupied by the Triton X-405 molecule, which has 42 poly(oxyethylene) units, on PS particles was 1.72 nm^2 by ^{1}H NMR measurement. On the other hand, the integral due to the protons of the poly(oxyethylene) chain also decreased monotonously with the increase in A_t above 1.8 m^2/ml. The A_t value at which the integral for the hydrophilic poly(oxyethylene) chain becomes zero could not be measured. Since the NMR sample was in a highly viscous slurry state at $A_t > 2.5$ m^2/ml, it was difficult to obtain a lock and signal-to-noise ratio was extremely small in the ^{1}H NMR measurement. These results suggest that the adsorption state of the emulsifier molecules on the PS particle is changed with the increase in A_t above 1.8 m^2/ml, as shown in Fig. 4.

At $A_t = 1.8$ m^2/ml, the hydrophobic nonyl and phenyl groups completely occupy the PS particle surface and the hydrophilic poly(oxyethylene) chains extend into the D_2O medium. With the increase in A_t above that value, because a bare PS surface appears, the poly(oxyethylene) chains are partially adsorbed thereon, which may correspond to the adsorption form where poly(oxyethylene) chains are folded [8].

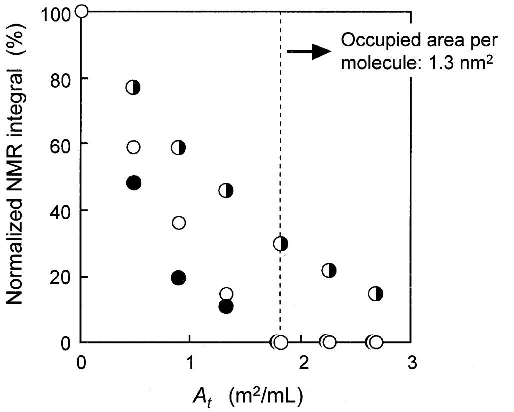

Fig. 3. Variations of the normalized NMR integrals due to the protons of phenyl groups (*open circles*), poly(oxyethylene) chains (*half-filled circles*), and nonyl groups(*filled circles*) of Emulgen 930 (2.1 g/l) at pH 6.5 as a function of the total surface area, A_t, of PS particles

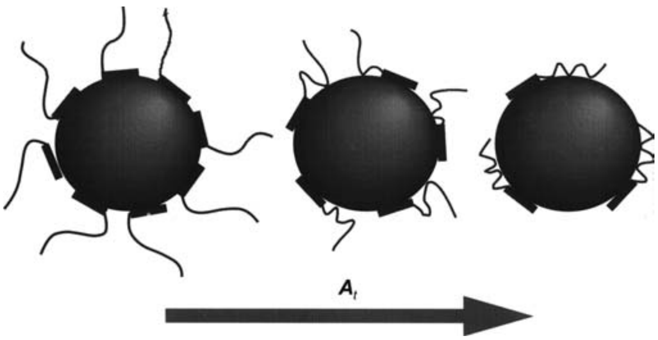

Fig. 4. A possible model for the variation of the adsorption state of Emulgen 930 emulsifier (2.1 g/l) on PS particles as a function of A_t above 1.8 m^2/ml

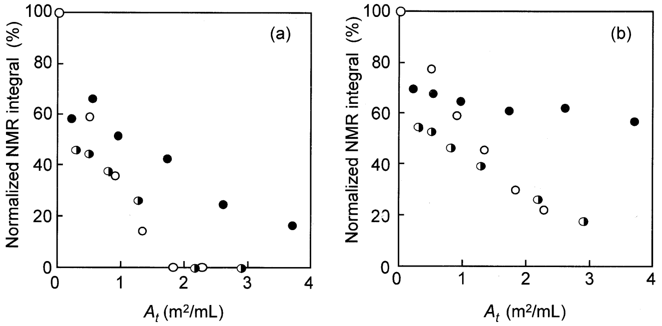

Fig. 5. Variations of the survival ratios of the normalized NMR integrals due to the protons of **a** phenyl groups **b** and poly(oxyethylene) chains of Emulgen 930 (2.1 g/l) as a function of A_t of styrene–methacrylic acid copolymer [*P(S-MAA)*] particles at pH 6.5. MAA contents (mol%); 0 (*open circles*); 6 (*half-filled circles*); 10 (*filled circles*)

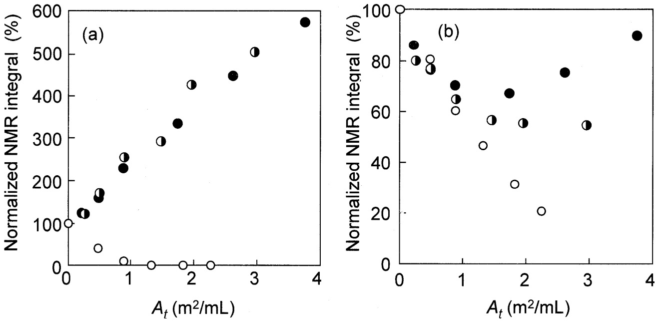

Fig. 6. Variations of the survival ratios of the normalized NMR integrals due to the protons of **a** phenyl groups and **b** poly (oxyethylene) chains of Emulgen 930 (2.1 g/l) as a function of A_t of P(S-MAA) particles at pH 13. MAA contents (mol%); 0 (*open circles*); 6 (*half-filled circles*); 10 (*filled circles*)

Figure 5 shows the variations of the survival percentage of the normalized NMR integrals due to the protons of the phenyl group and the poly(oxyethylene) chain of the emulsifier molecule at pH 6.5, at which carboxyl groups partially ionized at the P(S-MAA) particles surface, as a function of A_t of the P(S-MAA) particles having different MAA contents. In case of 6 mol% MAA, both the integrals decreased similarly to those of the PS particles, whereas in 10 mol% MAA they decreased more gradually. These results indicate that the emulsifier molecule is difficult to adsorb on the P(S-MAA) particle having a high MAA content because of the high surface hydrophilicity due to a lot of ionized carboxyl groups. This result supports our assumption that the reason why the P(S-MAA) particle with a high MAA content was not changed to the nanoparticles by the particle dissolution method is because of less interaction between the emulsifier and the polymer molecule [5], as described in the Introduction.

Figure 6 shows the variations of the survival percentage of the normalized NMR integrals due to the protons of the phenyl groups and the poly(oxyethylene) chain at pH 13, at which all the carboxyl groups ionized at the P(S-MAA) particles surface, as a function of A_t. In case of the PS particles, both the integrals at pH 13 decreased with an increase in A_t similarly to those at pH 6.5 shown in Fig. 5. Inversely, in the cases of the P(S-MAA) particles having MAA contents of 6 and 10 mol%, both the integrals increased with the increase in A_t in comparison with those at pH 6.5. These increases in Figs. 6 seem to be based on the balance between the decrease due to adsorption onto P(S-MAA) molecules and the increase due to elutions of P(S-MAA) molecules having high MAA content and low molecular weight [9] and of Emulgen 911 molecules included inside the particle during the polymerization. Emulgen 911 was used as an emulsifier in the emulsion polymerization for the production of the P(S-MAA) particles. The adsorption of Emulgen molecules onto the P(S-MAA) particles having 10 mol% MAA content is prevented more than that onto the P(S-MAA) particles having 6 mol% MAA content.

From these results, it is concluded that the adsorption behavior of the nonionic emulsifier molecules onto PS and P(S-MAA) particles dispersed in D_2O was estimated by in situ ^1H NMR measurements, and the state depends on the adsorption concentration and the surface concentration of carboxyl groups. This strongly supports the formation mechanism of nanoparticles by the "particle dissolution method" proposed in a previous article [4].

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