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Chemical Immobilization of Polymeric Microspheres onto Inorganic Solid Surfaces

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SUMMARY: Reactive polymer microspheres with active ester groups on their surfaces were synthesized via emulsifier-free emulsion copolymerization of styrene (ST) with methacryloxyphenyldimethylsulfonium methylsulfate (MAPDS). Glass or steel substrates aminated with coupling agents were immersed into P(ST-*co*-MAPDS) latex to chemically immobilize polymeric microspheres. Coverage of the aminated inorganic substrates with the microspheres increased with increasing the solid content of latex. Proper addition of an electrolyte decreased electrostatic repulsion between microspheres to form stable particle monolayer.

Introduction

The fabrication of highly ordered monolayers of colloidal particles on solid substrates using polymer latexes has received much attention because of the potential use in surface imaging [1-7]. Several attempts, such as electrostatic aggregation, solvent evaporation, Langmuir-Blodgett method, electrohydrodynamic manipulation and scanning probe nano-fabrication, have been made to organize closely packed colloidal monolayers. Each technique for the formation of patterned structure is based on particle adsorption onto the solid supports, and the utilization of chemical bond between polymeric microspheres and substrates has not been reported. We have succeeded in synthesis of reactive polymer particles with a high surface density of active ester groups via emulsifier-free emulsion copolymerization of styrene (ST) with methacryloxyphenyldimethylsulfonium methylsulfate (MAPDS) (Figure 1) [8]. As the active ester groups at the surface of P(ST-*co*-MAPDS) microspheres show a high reactivity toward primary amine compounds, the microspheres would be suitable for the fabrication of regulated particle structure through chemical bond formation. In this study, we report results on the chemical immobilization of reactive polymeric microspheres onto the surfaces of the inorganic solid surface.

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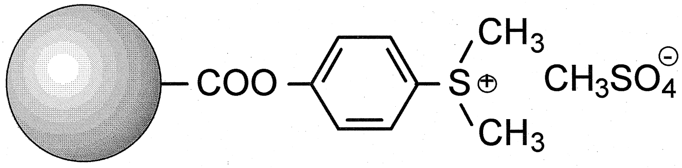

Figure 1. P(ST-*co*-MAPDS) microsphere.

Experimental

Preparation of P(ST-co-MAPDS) microspheres. MAPDS was prepared according to the method described before [8]. The polymer microspheres used in this study were prepared by emulsifier-free emulsion copolymerization of ST (320 mmol) with MAPDS (3.2 mmol) using 2,2′-azobis(2-amidinopropane)dihydrochloride (AIBA) (3.2 mmol) as a radical initiator in water (160 mL) at 60 °C for 6 h. The resulting polymer latex was purified by centrifugation and washing with ion-exchanged water several times. The number-average diameter, d_n, the volume-average diameter, d_v, the standard deviation, σ, and the coefficient of variation, C_v, were determined using scanning electron microscopy (SEM) (JOEL, JSM-5310). Surface charges of the particles were measured by colloidal titration using potassium polyvinylsulfate as a titrant.

Immobilization of P(ST-co-MAPDS) microspheres. Glass substrates used for the chemical deposition of P(ST-*co*-MAPDS) microspheres were cleaned with boiling HNO_3 solution for 1 h, and dipped into 0.1 N NaOH solution prior to use. After being rinsed in deionized water, the glass substrates were treated with a dioxane solution of 3-aminopropyl-2-aminoethyltriethoxysilane (AAPS). Steel plates were washed with toluene to remove grease. Isopropyl alcohol solution of isopropyltri(*N*-aminoethyl-aminoethyl)titanate (KR-44) was dropwised at the surface of the plates and the steel substrates were baked at 100 °C for 2 h. The surface composition of the substrates treated with coupling agents was analyzed by an ESCA (Shimadzu, ESCA-1000). Aminated glass or steel plates were immersed into P(ST-*co*-MAPDS) latex for several hours to immobilize polymeric microspheres onto the substrates (Figure 2). Surface morphology of the substrates modified with P(ST-*co*-MAPDS) microspheres was observed by a SEM.

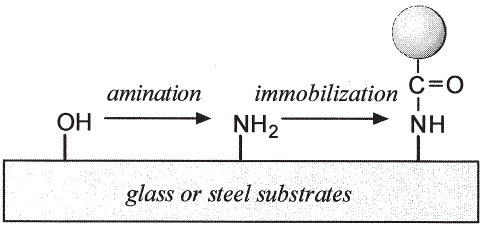

Figure 2. Processes for the immobilization of polymeric microspheres onto inorganic solid surfaces.

Results and Discussion

Preparation of P(ST-co-MAPDS) microspheres. Table 1 summarizes the values of d_n, d_v, σ and C_v obtained by SEM observation of P(ST-*co*-MAPDS) microspheres. Polymeric microspheres with ca. 200 nm in diameter were obtained in quantitative yield (> 90 %) for the copolymerization system containing 1 mol% of MAPDS against ST in feed. The values of σ and C_v were 3.01 and 1.38, respectively, which indicate the formation of well-defined polymer microspheres with a narrow distribution of particle size. The results obtained from surface charge measurement show that a high concentration of active ester groups exists at the surface of P(ST-*co*-MAPDS) microspheres.

Table 1. Characteristics of P(ST-*co*-MAPDS) microspheres [a)]

d_n [nm]	d_v [nm]	σ	C_v [%] [b)]	Surface charge [μeq/g-latex]
218	218	3.01	1.38	15.5

a) Copolymerization: ST, 320 mmol; MAPDS, 3.2 mmol; AIBA, 3.2 mmol; water, 160 mL; 60 °C; 6 h. b) d_n, number-average diameter; d_v, volume-average diameter; σ, standard deviation; C_v, the coefficient of variation.

Immobilization of P(ST-co-MAPDS) microspheres. Figure 3 shows ESCA spectrum of glass substrate treated with AAPS dioxane solution. The peak around 404 eV represents existence of N(1s) at the surface of substrate. In the case of steel plates, ESCA peaks of Ti(2p) arisen from KR-44 coupling agent were observed at around 459 eV in addition to that of N(1s).

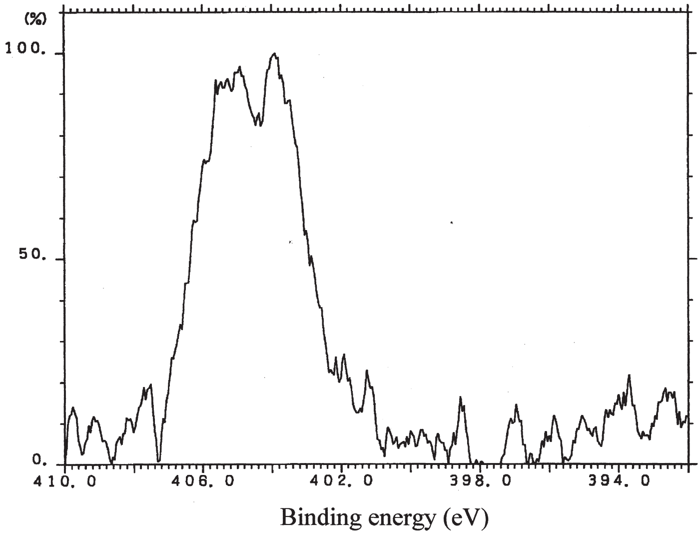

Figure 3. ESCA spectrum of a glass substrate aminated with AAPS dioxane solution.

When aminated glass plates were immersed into P(ST-*co*-MAPDS) latex solution, the coverage of the glass surface was low (ca. 13 %). This is probably because of the high surface charge density of the microspheres used here. Although a high ionic strength by the addition of NaCl results in the aggregation of polymer particles, electrostatic repulsion between polymer microspheres is effectively suppressed with a proper addition ($\leq$ 0.2 M), and 90 % of the glass substrates were uniformly covered with the microsphere monolayer. Figure 4 shows the SEM photograph of the glass substrate modified with polymeric microspheres. The SEM photograph of boundary region of particle monolayer revealed that physisorbed particles were easily left from the solid surfaces after a treatment of sonication or rinse of colloidal particle films and that particle monolayers remained at the solid surfaces. This particle monolayer is stable against sonication in a basic aqueous solution. Similar immobilization of polymeric microspheres onto the steel plates can be also accomplished using KR-44 coupling agent. Coverage of the aminated steel plate modified with polymer microspheres increased with increasing the solid content of P(ST-*co*-MAPDS) latex.

Immobilization of reactive polymer microspheres would be suitable for the stable formation of 2D particle array and other patterned structures at the solid surfaces.

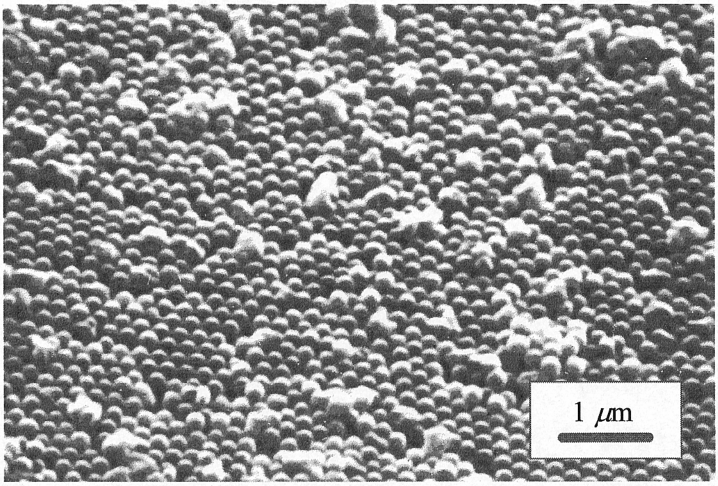

Figure 4. SEM photograph of the monolayer of P(ST-*co*-MAPDS) microspheres chemically immobilized at the surface of glass substrate.

Conclusion

Reactive polymeric microspheres were synthesized in nearly quantitative yield by emulsifier-free emulsion copolymerization of styrene with methacryloxyphenyldimethylsulfonium methyl sulfate. The microspheres are chemically immobilized at the surface of glass or steel plates aminated with coupling agents to form stable particle monolayer. Suppression of electrostatic repulsion between the microspheres with a proper addition of an electrolyte was crucial for the fabrication of closely packed particle monolayer.

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