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ELECTROPHORETIC POLYMER PARTICLES WITH HIGH ZETA-POTENTIAL IN DIELECTRIC MEDIUM

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Polystyrene particles were polymerized at neutral medium (pH 7) for electrophoretic particles that can be moved in dielectric medium by electric field. The poly(ethylene glycol) methyl ether methacrylate (PEG-MMA) and methacrylic acid (MA) were used as surface charge-generating comonomers. The zeta potentials of three kinds of polystyrene particles were measured in dielectric medium by means of ELS-8000 dynamic light scattering. As PEG-MMA concentration increased, the zeta potential became higher. The highest zeta potential of polymer surface was measured to be about 183 mV at a polymer of PEG-MMA 5 mol% relative to styrene. However, as the ratio of [MA]/[PEG-MMA] increased, the zeta potential and electrophoretic mobility of the PS particles decreased.

Keywords: electrophoretic mobility; poly(ethylene glycol) methyl ether methacrylate; zeta potential

INTRODUCTION

Latex polymer colloids with sub-micrometer diameter are important in many areas of technology, such as paint and coatings, ceramics processing, and electrophoretic particles [1,2]. Emulsifier-free emulsion polymerization has been known to one of useful methods to give monodisperse polymer particles with a diameter of less than 1 μm [3]. The stabilization of emulsion

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can be achieved by enhancement of surface zeta potential and/or steric hindrance on surface [4]. Polymer surface charge agents such as polyisobutyl succinimide, poly(*N*-vinyl pyrrolidone), and poly(12-hydroxystearic acid) have been known to useful agents to increase zeta potential of surface. For example, the zeta potential TiO_2 particles with a surface charge agent has been reported to be about 120 mV [5]. In this study, we attempted to manufacture crosslinked polystyrene (PS) particle with higher surface charge and faster mobility in dielectric medium by means of an introduction of ethylene glycol and/or carboxylic acid unit on the particle surface at polymerization. We observed the particle morphology using scanning electron microscopy and measured the zeta potential of the particle slipping plane in dielectric medium using ELS-8000 dynamic light scattering.

EXPERIMENTAL

Particle Preparation and Characterization

All copolymerization was carried out in a 500 ml, three-neck glass flask equipped with a stirrer, condenser, nitrogen inlet and thermometer. After the polymerization, polystyrene emulsion was purified by dialysis for 5 days, treated in ultrasonic bath, and then dried by freeze drying method to give fine polymer powder. The particle size and distribution of the polystyrene particle was observed by scanning electron microscopy (Hitachi Co., S-2500C) and particle analyzer (Beckman Coulter Co., LS230). Zeta potential of polymer surface was measured in dielectric medium by means of ELS-8000 dynamic light scattering (Otsuka Co.).

RESULTS AND DISCUSSION

Synthesis of Polymer Particles using Comonomers

As summarized in polymerization recipes of Table 1, polystyrene particles with ethylene glycol units (P-1 ∼ P-4) and/or carboxyl (PM-1 ∼ PM-3) on surface were synthesized by an emulsifier-free emulsion polymerization using styrene, poly(ethylene glycol) methyl ether methacrylate (PEGMMA, Mn 475), and/or methacrylic acid (MA) at pH 7. All polymerization was conducted with divinylbenzene 4 mol% as a crosslinking agent. Also, PM-2 particles were treated with zinc acetate in order to react the surface carboxyl to give particles (PZ-1 ∼ PZ-4) with zinc-diester salt form $[(-RCOO^-)_2Zn^{2+}]$.

TABLE 1 Properties of Polystyrene Powders[a]

Sample codes	PEG-MMA (mol%)[b]	MA (mol%)[b]	D[c] (nm)	S.D.[d] (nm)	Zeta potential (mV)	Mobility (cm^2/Vs)
P-1	2	–	310	62	104	12.4×10^{-6}
P-2	3	–	307	61	119	14.2×10^{-6}
P-3	4	–	306	63	138	16.7×10^{-6}
P-4	5	–	303	68	183	22.1×10^{-6}
PM-1	2	5	305	68	56	6.74×10^{-6}
PM-2	2	10	351	71	80	9.60×10^{-6}
PM-3	2	20	353	70	51	6.07×10^{-6}

[a] Polymerization condition: potassium persulfate 0.7 g, water 200 g, styrene 20 g, divinylbenzene 1 g, 6 hours, 250 rpm, 70 ± 1°C.

[b] mol% relative to styrene.

[c] Number-average diameter of PS powders.

[d] Standard deviation.

Particle Size and Distribution

All polymerization yielded stable emulsion without coagulum at neutral polymerization medium due to nonionic PEG-MMA. As shown in Table 1, the particle size of polymers (P1 ~ P4) was in the range of 300 ~ 350 nm with a relatively good monodispersity (for example, see P-3 in Fig. 1(a)). As PEG group concentration increased, the particle size decreased a little and their standard deviation increased. Over 5 mol% of PEG-MMA, polymer particle became polydisperse and irregular. Interestingly, the particle surface shape of the polymer particles (PM1 ~ PM3) containing both

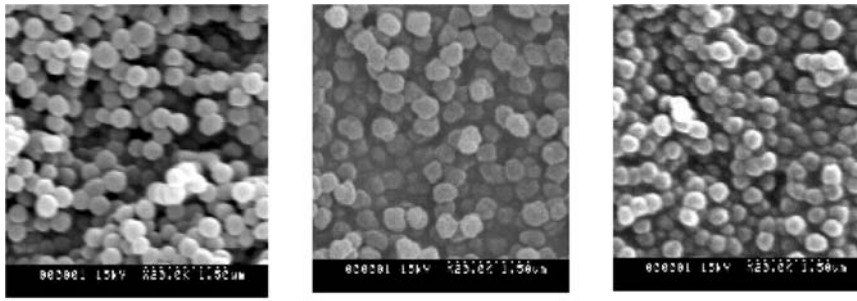

FIGURE 1 Representative scanning electron micrographs of polystyrene powders (x20,000); mol% relative to styrene (a) PEG-MMA 3 mol% (P-2), (b) MA 10 mol%, PEG-MAA 2 mol% (PM-2), (c) Zinc acetate 5 wt% (PZ-1).

TABLE 2 PM-2 Particles Reacted with Zinc Acetate[a]

Sample codes	Zinc acetate (wt%)[b]	D[c] (nm)	S.D.[d] (nm)	Zeta potential (mV)	Mobility (cm^2/Vs)
PZ-1	5	340	71	55	6.57×10^{-6}
PZ-2	10	337	78	41	4.93×10^{-6}
PZ-3	20	–	–	25	3.05×10^{-6}
PZ-4	40	–	–	26	3.10×10^{-6}

[a] Reaction condition: Ethanol 10 ml, 3 hours, 250 rpm, room temp.
[b] wt% relative to PM-2.
[c] Number-average diameter of PS powders.
[d] Standard deviation.

PEG-MMA and MA group became remarkably irregular (Fig. 1(b)). Stable colloidal polymer solution could be obtained at a concentration of below MA 10 mol% relative to styrene with PEG-MMA 2 mol%. As shown in Table 2, with an increase of zinc acetate content, the uniformity of the particle size became worse, the particle distribution became broader.

Zeta Potential and Electrophoretic Mobility of Polymer Powders

The zeta potentials of polymer powders were determined in order to investigate the ingredients that were the most effective to increase the electrophoretic mobility. For this, we prepared three kinds of polymer particles, 1) particle with PEG units, 2) particle with PEG and COOH units, and 3) particle with PEG and $(COO^-)_2Zn^{2+}$ units. Table 1 and Table 2 shows the zeta potential and electrophoretic mobility of polystyrene powders in dielectric medium (mixture of Halocarbon® 0.8 and Isopar® G). The zeta potential of polystyrene powders with PEG unit was considerably high in the medium and increased with increasing PEG concentration. This nonionic ethylene glycol unit must have acted on surface stabilizing agent effectively on polymer surface in dielectric medium because PEG unit had an oligomeric long chain together with dipole moment. The highest zeta potential (183 mV) could be achieved at a feeding 5 mol% of PEG-MMA relative to styrene. Besides, we had to note that polymer particles (P-1 $\sim$ P-4) showed a very high mobility ranging $6 \sim 22 \times 10^{-6}\,cm^2/Vs$ that was one-order magnitude higher mobility compared to inorganic TiO_2 particle reported so far. On the other hand, in second attempt of polystyrene powder with both PEG and COOH units, the zeta potential decreased unexpectedly. The zeta potential of these particles was measured to be 80 mV at a polymer of MA 10 mol% relative to styrene with PEG-MMA 2 mol%. As a

result, we found that carboxyl units affected negatively on zeta potential and mobility in dielectric medium. However, the surface COOH unit of the particle can be later applied a post-reaction with other functional unit. Thirdly, as shown in Table 2, the zeta potential of polymer particle reacted with zinc acetate was rapidly dropped as zinc acetate concentration increased. The treated particles were precipitated in reaction medium (ethanol) due to perhaps density increase and therefore their SEM photographs showed that polymer particles were coagulated seriously.

CONCLUSION

Crosslinked polystyrene particles were successfully synthesized by emulsion polymerization using PEG-MMA and/or MA at pH 7 to give stable particles with high zeta potential. Among the three kinds of polystyrene powders prepared in this study, polymeric powder only with PEG unit on surface showed the highest zeta potential and high mobility. The carboxylic and zinc diester salt units gave a negative influence on zeta potential and mobility. The highest zeta potential value of particle was measured to be 183 mV at a polymer of PEG-MMA 5 mol% relative to styrene. These highly mobile polymeric particles can be a potential candidate to reduce a working voltage in electrophoretic display.

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