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Preparation of Thermosensitive “Snowman-like” Composite
Gel Particles Incorporating an Ionic LiquidHideto Minami^{1*}, Hiroko Ichikawa¹ and Toyoko Suzuki¹**Key words :** Thermosensitive, Composite particle, Ionic liquid, Free-standing gel

Thermosensitive polymers, such as poly(*N*-isopropyl acrylamide) (PNIPAM), are well known to exhibit a lower critical solution temperature (LCST) in aqueous media. The hydrogels of these polymers respond to a change in temperature in terms of their degree of swelling; i.e., a volume-phase transition is observed. This volume-phase transition can be exploited in an actuator and switching devices. Ionic liquids (ILs) have received considerable attention because of their nonvolatility, high thermal stability, and nonflammability. Poly(benzyl methacrylate) and poly(2-phenylethyl methacrylate) (PPhEMA) exhibit LCST-type phase-transition behavior in ILs¹. Thermosensitive polymer gel particles with an IL that exhibit a volume-phase transition around the LCST have also been successfully prepared. Such gel particles are particularly interesting because the nonvolatility of ILs implies that degradation due to evaporation of the solvent is not expected. However, the volume-phase transition phenomenon should be observed only in the presence of dispersed media such as water or IL (“dispersed state”). Recently, we reported the successful preparation of thermosensitive composite gel particles that exhibit volume-phase transition and shape change behaviors in the absence of dispersed media (“nondispersed state”), which are expected to be used as a solid materials: “free-standing gel”. This behavior was due to translation of an IL between PPhEMA and poly(methyl methacrylate) (PMMA) phases². The PMMA phase

is swollen with IL (1-butyl-3-methylimidazolium bis(trifluoro methanesulfonyl)amide) irrespective of the temperature. However, the changes in the volume of each phase and in the particle shape were small. In this communication, we further developed the preparation of free-standing composite gel particles that exhibit a greater volume change.

Fig. 1 Consecutive optical micrographs of PPhEMA/IL (a-d) and P(PhEMA-MAA)/IL (e-h) seed gel particles dispersed in water. Observation temperature: (a, d, e, h) *r.t.*, (b) 60°C, (c) 70°C, (f) 75°C, (g) 90°C.

To prepare such composite gel particles, P(PhEMA-methacrylic acid (MAA))/IL gel particles were used as seeds; these gel particles become more hydrophilic and are expected to form complete phase-separated “snowman” composite gel particles. P(PhEMA-MAA)/IL gel particles including the IL were prepared by suspension polymerization at 30°C at a temperature less than the LCST (70°C in water). The obtained gel particles were approximately 10 μm in size and polydisperse; they were also observed to be homogeneous at *r.t.*, indicating that the P(PhEMA-MAA) was swollen with the IL. **Fig. 1** shows the volume-phase transition behavior of

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PPhEMA/IL seed gel particles (a-d), which were prepared in our previous work, and that of P(PhEMA-MAA)/IL seed gel particles (e-h). The IL began to separate from gel particles at approximately 60°C and 75°C, (b, f) and completely separated above 70°C and 90°C (c, g), respectively, in which the volume ratios between the gel particles and the IL were actually consistent with the values calculated according to the polymerization methodology. In the case of the P(PhEMA-MAA) system, the phase-separated IL protruded from the gel particles (snowman-like) (g) in comparison with the PPhEMA system (c). When the temperature was decreased, both groups of gel particles were gradually swollen with IL and were observed to be homogeneous at *r.t.* (d, h).

The composite gel particles were prepared by seeded polymerization of methyl methacrylate (MMA) in the presence of the P(PhEMA-MAA)/IL seed gel particles at 85°C (i.e., above the LCST). Although the obtained composite gel particles exhibited volume phase transition behavior, the shape of the composite gel particles did not completely reflect the snowman-like shape of the phase that separated from the seed gel particles at temperatures greater than the LCST. The volume-phase transition behavior was not clear, likely because of the absorption of MMA into the P(PhEMA-MAA) phase during the seeded polymerization. Actually, when we observed the gel particles swollen with MMA and IL for 20 min using a hotplate maintained at 85°C, the P(PhEMA-MAA) phase of the gel particles shrunk completely immediately after the sample was placed on the hotplate; however, later, it gradually reswelled with MMA in a short time.

Therefore, photopolymerization was conducted to complete the seeded polymerization prior to the reswelling of P(PhEMA-MAA) with MMA. Fig. 2 shows optical micrographs of P(PhEMA-MAA)/IL/PMMA gel particles prepared using a photoinitiator; the particles were dispersed in water and observed at various temperatures (heating rate of 0.5°C/min). The composite gel particles clearly exhibited the volume-phase transition behavior, in which the P(PhEMA-MAA) phase in the composite gel particles shrunk, and the PMMA phase increased in size at 85°C. Although the PMMA phases changed depending on the temperature, the total volume of the composite gel particles did not change. This fact indicates that the incorpo-

Fig. 2 Consecutive optical micrographs of the composite gel particles prepared by seeded polymerizations in water in the presence of a photoinitiator at 85°C. Observation temperature: (a, c) *r.t.*; (b) 85°C.

rated IL transferred between the P(PhEMA-MAA) and PMMA phases without leaking from the composite gel particles.

Moreover, the composite gel particles were expected to exhibit volume-phase transition behavior in the dry state (the LCST is 97°C in the dry state), because the IL is nonvolatile. As shown in Fig. 3, the composite gel particles were observed in a nondispersed state. When observed in air (a-c), the composite gel particles also exhibited the volume-phase transition behavior; under vacuum conditions (d-f), the shape of a composite gel particle was changed reversibly without leakage of the IL.

Fig. 3 Optical micrographs (a-c) and SEM images (d-f) of the composite gel particles in their nondispersed state, as prepared by seeded polymerization at 85°C in the presence of a photoinitiator. Observation temperature: (a, c, d, f) *r.t.*; (b, e) 120°C.

References

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