Preparation of Submicron-sized Snowman-like Polystyrene Particles via Radiation-induced Seeded Emulsion Polymerization

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In this paper, we have successfully prepared submicron-sized snowman-like polystyrene (PS) particles by radiation-induced seeded emulsion polymerization at room temperature. The monodispersed crosslinked PS particles with an average size of 358 nm acted as seed particles. The influence of polymer/monomer weight ratio on the morphology was studied. The results showed that snowman-like PS particles could be fabricated in high yield about 90% when the polymer/monomer weight ratio was 0.2:1.

In recent years, there has been increasing attention to the design and preparation of nonspherical particles because of their unique physical properties which are useful for controlling light scattering and fluid properties.[1] Since the 1970s, Okubo and other researchers have reported various nonspherical particals, such as snowman-like,[2] confetti-like,[3] Hamburg-like,[4] golfball-like,[5] popcorn-like,[6] and octopus ocellatus-like.[7] Most of the nonspherical particles composed of multicomponent or one-component with a crosslinked structure generally are prepared by seeded polymerization. Formation of the one-component nonspherical particles is mainly due to phase separation, which is that the swelling monomer in the seed particles is separated from the crosslinked network of the seed particles during polymerization.[8] The morphology of polymer particles depends on thermodynamic and kinetic factors.[9]

Many reports have clarified the effect of the thermodynamic parameters on morphology of PS/PS latex particles, such as the monomer/polymer swelling ratio, the crosslinking degree of the seed particles, the polymerization temperature, the size of seed particles, and the crosslinker (divinylbenzene) concentration in the swelling monomer.[10] It has been confirmed that the higher polymerization temperature and the larger size of seed particles make for a higher degree of phase separation in the final particles.[8a] Lager seed particles would have a smaller interfacial pressure at the swollen particle/water interface and hence larger separated domains. And a higher polymerization temperature would bring in a greater elastic–retractile force, resulting in a larger separated domain. Simultaneously, it gives a faster polymer relaxation rate and a higher mobility of monomer and polymer molecules, which is also helpful for the increase of the separated domain. So far, all of the snowman-like particles reported are microsized and prepared at a high polymerization temperature by chemical methods, as we know. In this study, we first employ the radiation-induced seeded emulsion polymerization method to prepare submicron-sized snowman-like PS particles at room temperature.

Figure 1 shows the schematic illustration of the snowman-like PS particles prepared by radiation-induced seeded polymerization of styrene (St) with submicron-sized, monodispersed, crosslinked PS as seed particles. The first step is to prepare monodisperse PS particles by emulsifier-free polymerization[11] in a standard method: 10 g of St, 0.8 g of acrylic acid (AA), 0.05 g of potassium persulfate (KPS), and 0.05 g of divinylbenzene (DVB) are added to a 250-mL three-neck reaction flask followed by bubbling nitrogen gas at room temperature for 30 min, and then the flask was moved to a 70 °C water bath and stirred at 300 rpm for 20 h to ensure a complete polymerization. After that, it is necessary to neutralize the –COOH groups on the surface of PS particles with sodium hydroxide (NaOH) to pH 7 before a certain amount of second monomer styrene is added to the seeded emulsion. The neutralized PS particles with $–COO^-$ groups on their surface have an appropriate amphipathic property to stabilize the seeded emulsion system. Subsequently, the emulsion is stirred by a mechanical stirrer at room temperature for 24 h. During this period, the styrene monomer diffuses into the PS seed particles gradually. In other words, the PS seed particles are swollen by monomers. After the monomer diffuses entirely into the PS seed particles, the seeded emulsion is bubbled with nitrogen gas for 20 min to remove oxygen and then sealed to be irradiated in the field of a 1.30×10^{15} Bq ^{60}Co γ-ray source with an absorbed dose of 53 kGy at a dose rate of 11 Gy min^{-1} at room temperature about 20 °C.

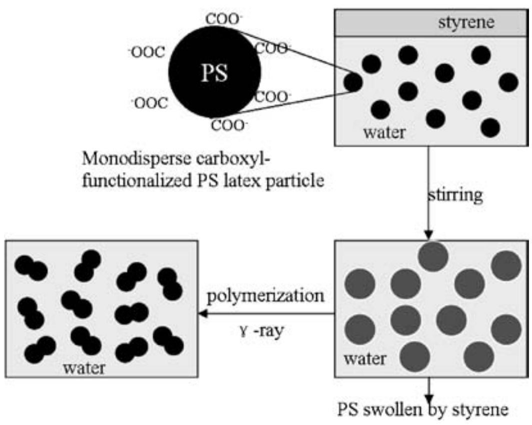

Figure 1. Schematic illustration of the snowman-like PS particles prepared by radiation-induced seeded emulsion polymerization.

The SEM micrographs of crosslinked PS seed particles prepared by emulsifier-free polymerization and various morphologies of PS particles prepared with different polymer/monomer weight ratios of 0.3:1 (sample 1), 0.2:1 (sample 2), and 0.1:1 (sample 3) by radiation-induced seeded emulsion polymerization are shown in Figure 2. From Figure 2A, it is observed that all of the crosslinked PS seed particles are spherical with the quite narrow size distribution. The average particle size is

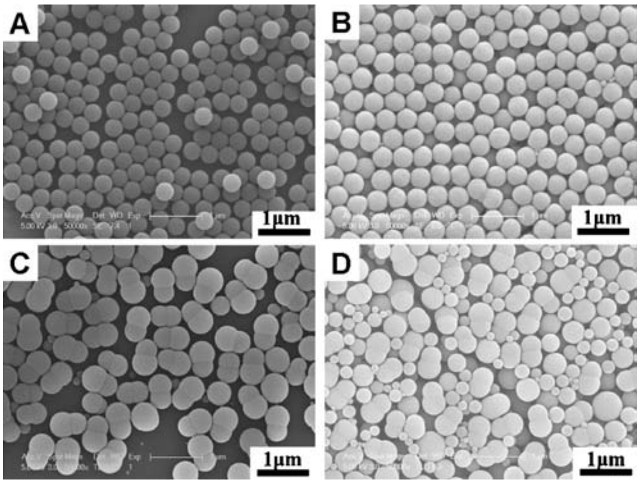

Figure 2. SEM micrographs of crosslinked PS seed particles prepared by emulsifier-free polymerization A) and various morphologies of PS particles with different polymer/monomer weight ratio by irradiating seeded polymerization: B) 0.3:1, C) 0.2:1, and D) 0.1:1.

358 nm calculated by 100 particles in a SEM micrograph. When the polymer/monomer weight ratio is 0.3:1, only spherical particles are formed with an average particle size of 400 nm (Figure 2B). As the polymer/monomer weight ratio is decreased to 0.2:1, snowman-like PS particles only with few smaller sphere particles are obtained (Figure 2C). However, when the polymer/monomer weight ratio is 0.1:1, snowman-like PS particles accompanied by many smaller spherical particles are observed (Figure 2D). The above results indicate that snowman-like PS particles can be formed in high yield with an appropriate polymer/monomer weight ratio. If the polymer/monomer weight ratio is high, no snowman-like PS particles are obtained, whereas many small spherical PS particles are formed accompanied by snowman-like particles at a low polymer/monomer weight ratio.

These phenomena can be attributed to the capability of the crosslinked network structure to accomodate the swelling monomer and the degree of the phase separation. The latter is related to the monomer–polymer mixing force, the particle–water interfacial tension force, and the polymer network elastic–retractile force.[8] If the elastic–retractile force increasing with temperature exceeds the sum of the monomer–polymer mixing force and the particle–water interfacial tension force, phase separation takes place. When the polymer/monomer weight ratio is high (0.3:1), the increased elastic–retractile force caused by the heat release from the polymerization of styrene cannot exceed the sum of the mixing force and the interfacial tension force, leading to the formation of spherical particles without the occurrence of phase separation (shown in Figure 2B). If the polymer/monomer weight ratio is moderate, the elastic–retractile force would outweigh the sum of the mixing force and the interfacial tension force owing to the decrease of the mixing force and the interfacial tension force. Thus, the swelling monomers in the crosslinked network structure are extruded to form a bulb on the surface of seed particles (a new domain) due to the contraction of swollen crosslinked PS seed, leading to formation of snowman-like PS particles as shown in Figure 2C. However, when the polymer/monomer weight ratio is low (0.1:1), the crosslinked network structure cannot accomodate all the monomers, resulting in the existence of monomer droplets. In the γ-ray irradiation field, these droplets would nucleate and grow to form the small spherical particles along with the formation of the snowman-like PS particles whose formation mechanism is the same as sample 2 (see Figure 2D).

In summary, submicrosized snowman-like particles can be prepared via radiation-induced seeded emulsion polymerization at room temperature, and the reproducibility is very well. The phase separation and the capability of the crosslinked network structure to accomodate the swelling monomer are keys to the formation of snowman-like particles. This method should be also applied in other polymer system, such as PB and PMMA.

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