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LETTER

Poly(methyl methacrylate)/polystyrene composite latex particles with a novel core/shell morphology

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The development of colloidal chemistry and nanotechnology make it possible to precisely control the architecture of the latex particles of submicron and micron size [1–4]. Seeded polymerization is a useful technique for the design and preparation of latex particles with desirable morphology. Recently, our group has found various internal and surface morphologies in the synthesis of composite latex particles through seeded soap-free emulsion or seeded dispersion polymerization [5–9]. The particle morphologies are tunable by exquisitely controlling the thermodynamic and kinetic factors during reaction.

We report here the synthesis of poly(methyl methacrylate)/polystyrene (PMMA/PS) composite latex particles which have a novel core/shell morphology. The particles were synthesized via seeded soap-free emulsion polymerization of styrene in the presence of PMMA particles by using a water-soluble nonionic azo-initiator, 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (VA086). Though the seeded emulsion or soap-free emulsion polymerization of styrene with PMMA latex has been widely investigated, the use of this kind of initiator was the first time to our knowledge. The polymerization kinetics and the morphology of the resulting PMMA/PS particles was studied and compared with the case using the ionic potassium persulfate (KPS) initiator.

All polymerizations were performed in a 300 mL round-bottom separated flask equipped with a nitrogen inlet, a sampling syringe and a mechanical agitator. PMMA seed latex was prepared via a standard soap-free emulsion polymerization at 70 °C for 5 h using KPS as initiator. The seed latex was dialyzed against deionized water for 3 days before use. A typical seeded soap-free emulsion polymerization was as follows. Appropriate amount of PMMA seed latex, deionized water and initiator VA086 or KPS were charged into the flask and bubbled with nitrogen gas for 30 min. Then, the oxygen-free styrene monomer was added, followed by the initiation of the polymerization by immersing the flask into the water bath thermostated at 70 °C. The seeded polymerization was carried out for 4 h with continuous stirring. During the polymerization, fractions of 1.5 mL were withdrawn from the reaction mixture at various time intervals. The typical recipes for the preparation of PMMA seed and PMMA/PS composite latex particles were given in Table 1.

The latex particles sampled during the polymerization were analyzed using a particle size analyzer (Microtrac S3500). It was confirmed that no appreciable agglomeration and new particle formation occurred during polymerization whether VA086 or KPS was used. The measurement of these samples by Fourier transform infrared spectroscopy (FT-IR, JASCO FT/IR-8000) showed that some new absorption peaks such as those near 700 and 3026 cm^{-1} appeared as compared with the IR spectrum of PMMA seed particles. These peaks could be reasonably assigned to the characteristic absorptions of aromatic C–H bending and aromatic C–H stretching vibrations. The above results suggested that PS component was successfully introduced into the PMMA seed particles. The PS content (relative to PMMA) was quantified by the absorbance ratio of the peak at 700 cm^{-1} (for PS) to that at 1375 cm^{-1} (CH_3 bending, for PMMA), with a calibration curve obtained from mixtures of PMMA and PS latex particles. From the PS content, the monomer conversion was calculated.

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Table 1 Typical polymerization recipes for the preparation of PMMA seed and PMMA/PS composite latex particles

Run no.	PMMA seed latex (mL)	MMA (g)	Styrene (g)	Water (g)	KPS (mmol/L)	VA086 (mmol/L)
1	–	15	–	185	3.19	–
2	18	–	1.46	112	0.42	–
3	18	–	1.46	112	–	0.42
4	18	–	1.46	112	–	4.60

PMMA seed latex was adjusted to contain 0.6 g solid polymer

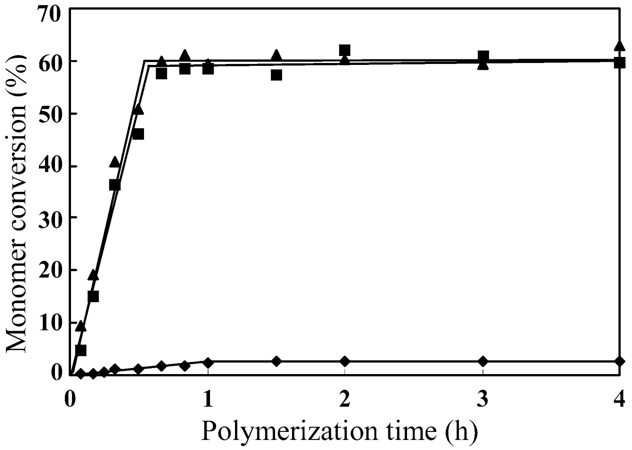


Fig. 1 Typical monomer conversion versus time profiles for the seeded soap-free emulsion polymerization using initiator of KPS (*triangle*, Run 2), VA086 (*diamond*, Run 3), and VA086 (*square*, Run 4), respectively

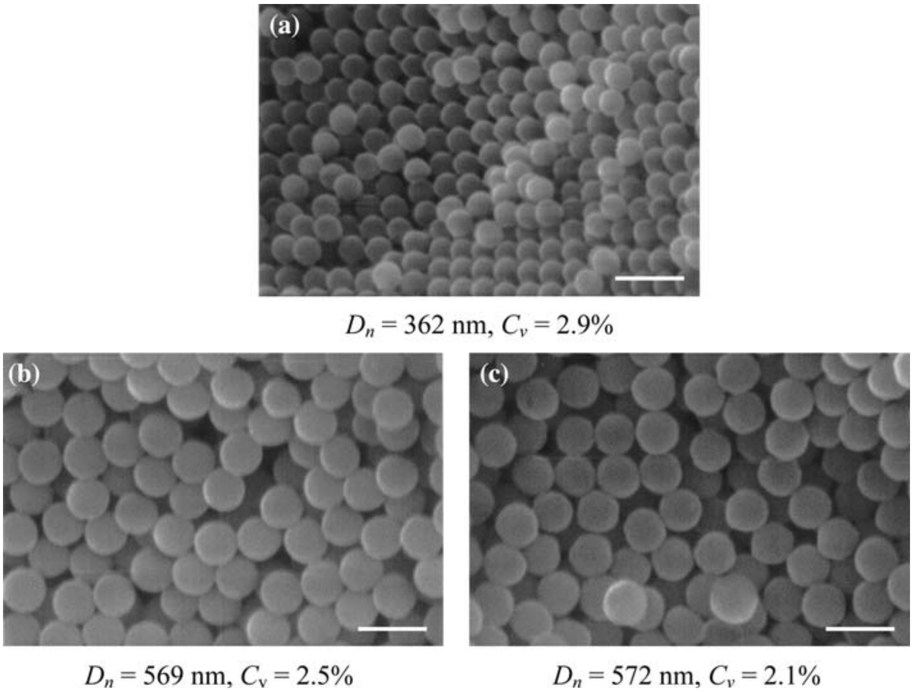
Figure 1 shows the monomer conversion versus time profiles for the seeded polymerization initiated by either VA086 or KPS. As compared to KPS, VA086 was found to initiate polymerization in an extremely low rate when the same concentration was used (cf. Run 3 with Run 2 in Table 1). The final monomer conversion was only about 2.9%. To increase the polymerization rate and monomer conversion, the seeded polymerization was conducted at various concentrations of VA086. As a result, a polymerization rate comparable to the KPS was obtained when the initiator concentration was increased to about 11 times that of KPS (Run 4 in Table 1). The polymerization was nearly complete within 40 min and the monomer conversion finally attained to about 60%.

The PMMA seed and PMMA/PS composite latex particles were freeze-dried and observed by scanning electron microscopy (SEM, JEOL JSM-5300) after sputter-coating with gold (200 Å). The number-average diameter (D_n) and coefficient of variation (C_v) of the particles were determined from the micrographs. The typical SEM micrographs are shown in Fig. 2. The PMMA seed particles prepared under the condition listed in Table 1 (Run 1) are spherical and have a D_n of 362 nm with a good monodispersity (Fig. 2a). The seeded soap-free emulsion polymerization of styrene on PMMA seed led to the increase of particle diameter from 362 nm to about 570 nm for both VA086 and KPS initiators (Fig. 2b, c). The monodispersity of the particle size remained almost unchanged after seeded polymerization. In addition, the formation of new particles was not observed, indicating that the seeded polymerizations proceeded in the absence of the secondary nucleation.

The internal morphology of PMMA/PS composite latex particles was observed by transmission electron microscopy (TEM, JEOL JEM-1200EXII). The latexes were coagulated by centrifugation and vacuum-dried. Two or three pieces of the obtained solid chips were embedded in epoxy, cured at 60 °C for 24 h, and ultramicrotomed. The ultrathin cross-sections (ca. 60 nm in thickness) were exposed to ruthenium tetraoxide (RuO_4) vapor for 3 h at ambient temperature to stain the PS phase. Figure 3 shows the TEM micrographs of ultramicrotomed PMMA/PS composite latex particles. It is obvious that both VA086 and KPS initiators generated the composite latex particles with a well-defined core/shell structure. The hydrophilic PMMA formed the core that was encased by the hydrophobic PS shell, indicating that the morphology development of the PMMA/PS composite latex particles in this study is a kinetically controlled process. However, in contrast to the case of KPS, there existed many occlusions of downy PS phase in the PMMA core and the PS shell was much smoother and more continuous in the case of VA086.

The number-average molecular weight (M_n) of PS polymer formed in the seeded polymerization was determined by gel permeation chromatography (GPC, Tosoh HLC-802A) according to the method described in the literature [10]. VA086 and KPS produced PS polymers with no significant difference in the molecular weight. The thermal decomposition of VA086 gives the less polar, uncharged primary radicals, whereas KPS gives negatively charged ones (sulfate ions). Thus for VA086-initiated polymerization, some oligomer or polymer chains, which have the end group of the less polarity, are capable of diffusing into the particle interior due to the weaker anchoring effect [11]. However, the relatively high internal viscosity of the polymerizing particles limited the diffusivity of the entered polymer chains. This prevents the polymer chains from undergoing Ostwald ripening to form the separate

Fig. 2 SEM micrographs of PMMA seed and PMMA/PS composite latex particles. **a** PMMA (Run 1), **b** PMMA/PS (VA086, Run 4), and **c** PMMA/PS (KPS, Run 2). *Scale bars*: 1 μm



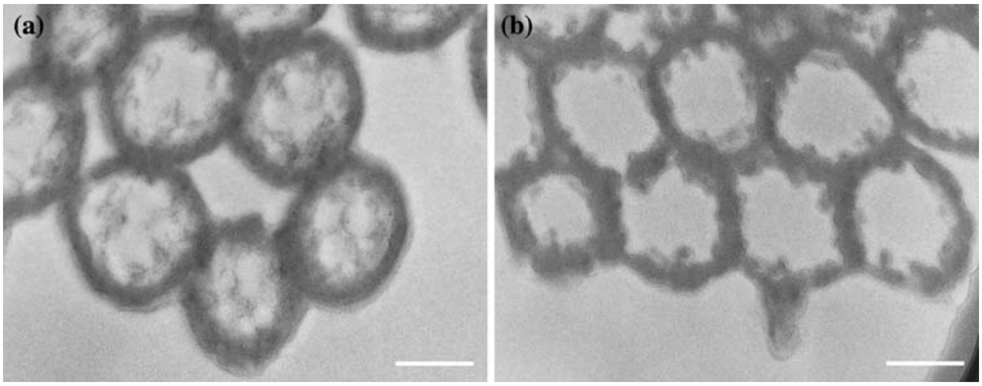


Fig. 3 TEM micrographs of PMMA/PS composite latex particles: **a** VA086 initiator (Run 4) and **b** KPS initiator (Run 2). *Scale bars*: 300 nm

spherical microdomains in the core region. As a result, the PMMA core with several fluffy PS microdomains being occluded was formed. On the other hand, because of the absence of the electrostatic repulsion between the polymer or oligomer chains [12], the uncharged character of the VA086 also led to the development of more contiguous PS shell.

In summary, this study demonstrated that the type of the initiators used in the seeded emulsion polymerization may strongly affect the internal morphology of the resulting composite latex particles. If the polymerization produces kinetically controlled core–shell morphology, it is possible to concurrently control the structure of both core and shell region by using water-soluble initiators with different charged properties.

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