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SCIENCE DIRECT
Polymer 46 (2005) 3567–3570
polymer
www.elsevier.com/locate/polymer

Polymer Communication

Poly(methyl methacrylate)/polyacrylonitrile composite latex particles with a novel surface morphology

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Received 13 September 2004; received in revised form 20 February 2005; accepted 25 February 2005
Available online 2 April 2005

Abstract

Precipitation polymerization of acrylonitrile in aqueous phase was performed in the presence of submicrometer-sized poly(methyl methacrylate) (PMMA) seed particles. The resulting PMMA/polyacrylonitrile (PAN) composite latex particles showed a novel well-defined surface morphology like rambutan. The formation of such surface structure was ascribed to the facts that PAN polymer is crystalline and scarcely swollen by its monomer. The composite particles had a core/shell structure with a PAN shell surrounding a PMMA core.

Keywords: Composite latex particle; Surface morphology; Core/shell structure

The preparation and formation mechanism of two-stage non-spherical latex particles have been the subject of many investigations [1–7]. The formation of these particles offered an excellent approach to study phase separation behavior in heterogeneous polymer system [6,7]. The latex particles with anomalous shape have exhibited several advantages over the conventional spherical particles when utilized as architectural paints or plastic pigments [8,9]. Recently, we reported a series of non-spherical composite latex particles obtained from the two-stage soap-free emulsion polymerization of styrene on cross-linked poly(2-acetoxyethyl methacrylate) seed latexes. These particles had a wide variety of surface morphologies such as 'confetti-like', 'raspberry-like', 'popcorn-like', 'void-containing' particles, 'doublets' and 'triplets'. They showed a strong dependence on the polystyrene content, second-stage monomer addition mode and initiator type [10,11].

In addition, the precipitation polymerization of a highly water-soluble monomer, acrylonitrile (AN), was performed in aqueous phase in the presence of poly(methyl methacrylate) (PMMA) seed particles. The resulting PMMA/polyacrylonitrile (PAN) composite latex particles were found to assume an anomalous surface morphology owing to the unique characters of PAN polymer. We report on the preparation and characterization of these particles in this communication.

All polymerizations (both seed and second-stage) were carried out in a 300 ml four-neck, round-bottom separated flask equipped with a nitrogen inlet and a mechanical marine-type agitator (three-blade, ϕ50 mm). Methyl methacrylate (MMA) and AN (Wako Pure Chemical Ind., Ltd) were purified by distillation under reduced pressure. Potassium persulfate (KPS, Wako Pure Chemical Ind., Ltd), used as a radical initiator, was recrystallized from deionized water shortly before use. PMMA seed latex particles, which have a number-average diameter of 307 nm with a narrow size distribution (C_v=3.1%), were prepared by a soap-free emulsion polymerization at 70 °C for 5 h. The seed latex was dialyzed against deionized water for 3 days. For the second-stage polymerizations, appropriate PMMA seed latex, deionized water and initiator were charged into the reaction vessel and dried nitrogen was bubbled through for 30 min. Then, the oxygen-free AN monomer was added and the polymerization was initiated. The second-stage polymerization was carried out at 70 °C for 8 h with stirring constantly at 250 rpm. The recipes for the polymerizations of PMMA seed latex and PMMA/PAN composite latex particles were given in Table 1, along with some characteristics of the latex particles prepared.

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doi:10.1016/j.polymer.2005.02.106

Table 1
Polymerization recipes and characteristics for the latex particles prepared

Symbol	Ingredients					Characteristics	
	PMMA latex (ml)[a]	MMA (g)	AN (ml)	Water (ml)	KPS (mg)	Particle diameter (nm)[b]	BET surface area ($m^2\ g^{-1}$)
PMMA		30		170	60	307	20.5
PMMA/PAN-3	9		3	121	20	459	45.9
PMMA/PAN-4	9		4	121	20	496	40.8
PMMA/PAN-5	9		5	121	20	632	34.5

[a] Adjusted to contain 0.6 g solid polymer.
[b] Determined from FE-SEM measurement for PMMA seed particles and from TEM measurements for PMMA/PAN composite latex particles.

Three PMMA/PAN composite latexes were synthesized with no appreciable agglomeration. Fourier transform infrared spectroscopy (FT-IR, JASCO FT/IR-8000) analysis confirmed the presence of PAN in the composite particles. The latex particles were dried onto double-sided carbon tape and observed by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F). As shown in FE-SEM micrographs (Fig. 1), the PMMA/PAN particles prepared were not the normal spheres with featureless smooth surface. In contrast, a number of small projections were randomly distributed on the whole particle surface. The size of these projections, ranging from a few nanometers to tens of nanometers, increased as the amount of the second-stage monomer increased.

It should be noted that all samples were sputter-coated with gold (150 Å) prior to FE-SEM examinations in order to minimize sample charging. To exclude the possible artifact introduced by this treatment, transmission electron microscopy (TEM, JEOL JEM-1200EXII) observations were made on the diluted latex dried on carbon-coated copper grids. As expected, TEM micrographs (Fig. 2) showed a much finer surface structure. The particles seemed to be covered by short fleshy thorns and we call them rambutan-like particles (rambutan: fruit of *Nephelium lappaceum*). The deformation of some particles shown in Fig. 2(a) was probably caused by the decomposition of PMMA polymer under electron beam irradiation [12,13].

The extremely uneven surface structure of PMMA/PAN composite latex particles led to a large specific surface area. The BET surface area (BELSORP28SA, using nitrogen as adsorbate at 77 K) of freeze-dried PMMA/PAN-3 particles was more than twice that of PMMA seed particles despite the increase of particle size from 307 to 459 nm (Table 1). The BET surface area of PMMA/PAN composite latex particles decreased with increasing the amount of AN monomer added in the second-stage polymerization.

Since PAN is more hydrophilic than PMMA, PAN polymer will be preferentially located at the outer particle surface in the second-stage polymerization [14–16]. X-ray photoelectron spectroscopy (XPS, Perkin-Elmer ESCA5600) analysis revealed that the outermost layer of the particles comprised mostly of C and N atoms originating from PAN molecules. In addition, the internal morphology was visually examined by TEM observation on the ultrathin cross-sections (ca. 60 nm in thickness) of PMMA/PAN composite latex particles (Fig. 3). In the micrographs, PAN appears as dark phase. It is obvious that all PMMA/PAN composite particles had a definite core/shell structure. PAN formed the shell encasing the PMMA core. The location of PAN phase on the particle surface was also evident from the smaller dark images. They were the cross-sections, which were sliced from the outer edge of composite particles. The size of them indirectly provided information in regard to the thickness of PAN shell.

It was considered that the present AN polymerization in water in the presence of seed particles included: (i) initiation

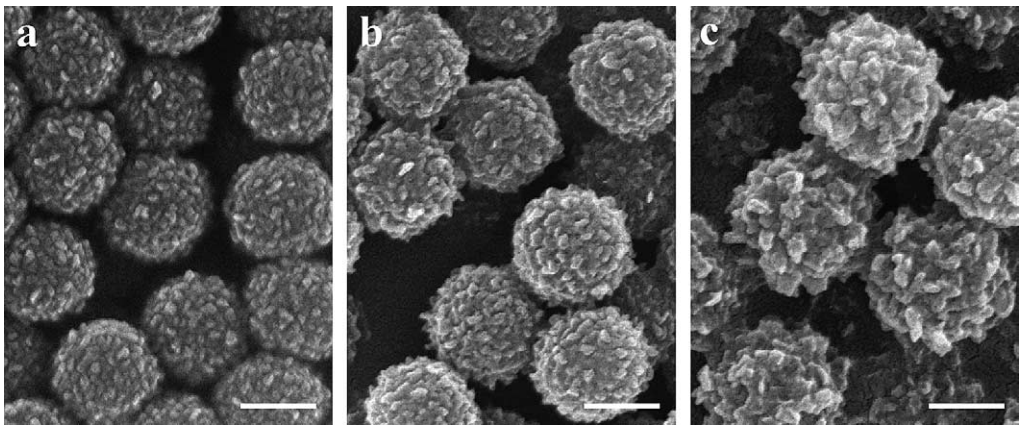

Fig. 1. FE-SEM micrographs of (a) PMMA/PAN-3; (b) PMMA/PAN-4; and (c) PMMA/PAN-5 composite latex particles. The scale bars are 300 nm.

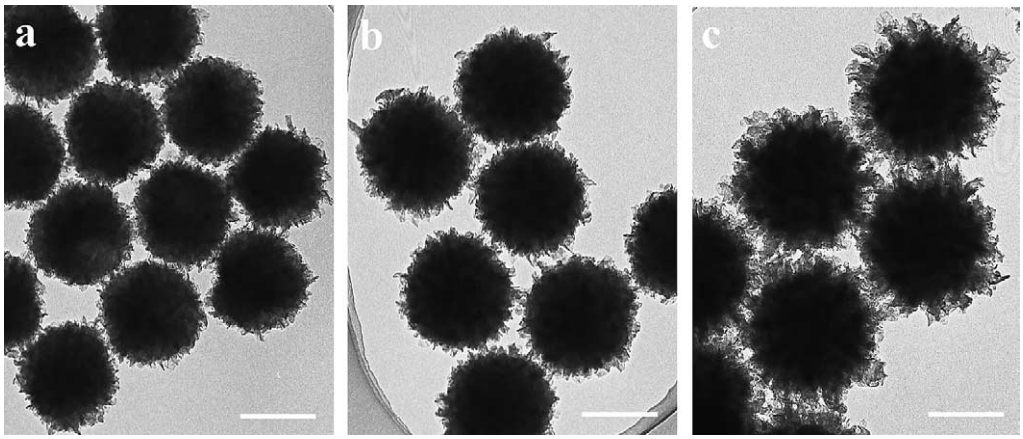

Fig. 2. TEM micrographs of (a) PMMA/PAN-3; (b) PMMA/PAN-4; and (c) PMMA/PAN-5 composite latex particles. The scale bars are 300 nm.

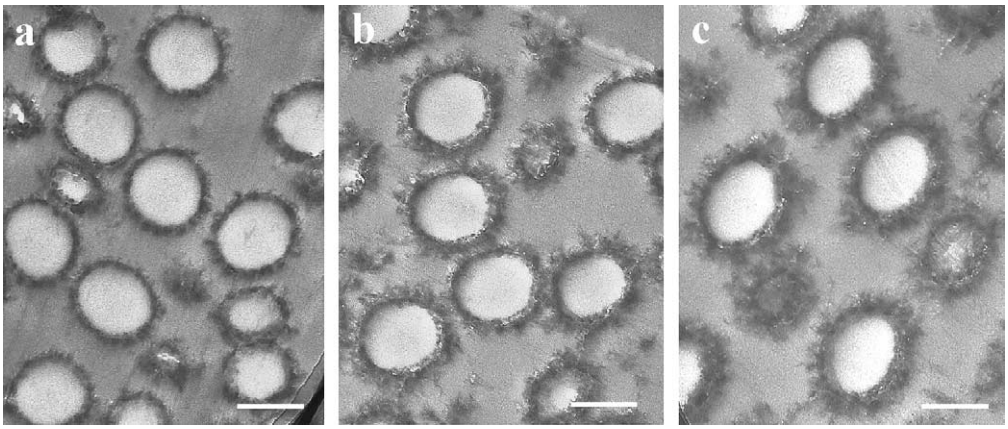

Fig. 3. TEM micrographs of ultrathin cross-sections of (a) PMMA/PAN-3; (b) PMMA/PAN-4; and (c) PMMA/PAN-5 composite latex particles. The scale bars are 300 nm.

in aqueous phase; (ii) propagation to a critical chain length and collapsing to a globular structure; and (iii) precipitation from aqueous phase onto PMMA seed particles. In the electron microscopical studies, no by-produced PAN particles were observed. This result indicated that the polymerization proceeded in the absence of secondary nucleation of new particles. PAN is a well-known polymer which has actually zero co-solubility with both the AN monomer and water. Therefore, the further propagation of deposited PAN globules occurred primarily on their surface, which may contribute to the generation of composite particles with a rough surface. On the other hand, PAN is known to form crystallites during radical polymerization [17]. In the wide-angle X-ray diffractograms (Rigaku RINT 2100 V, Cu K_α) shown in Fig. 4, a distinct diffraction peak centered around 16.7° was observed for all PMMA/PAN composite particles. This value is consistent with that reported in the literatures [18,19] and corresponds to a *d*-spacing of 5.30 Å. The crystalline nature of PAN polymer was believed to be responsible for the formation of the highly uneven particle surface.

It should be emphasized that it is possible to synthesize the core/shell PMMA/PAN composite latex particles with an almost smooth surface by decreasing the amount of the second-stage AN monomer relative to the PMMA seed polymer. These particles were employed to prepare carbon nanotubes by a polymer blend technique [20]. On the other

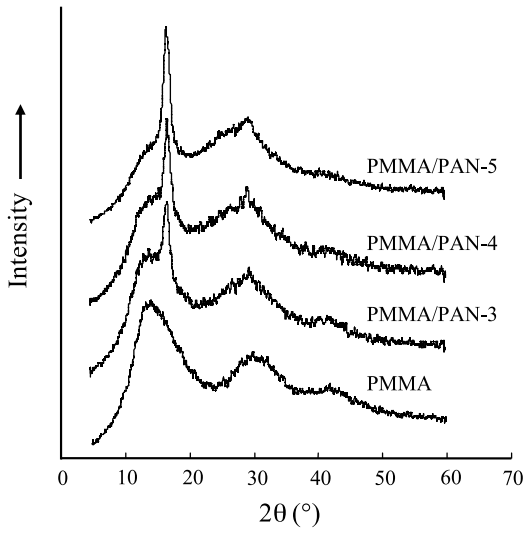

Fig. 4. Wide-angle X-ray diffractograms of PMMA seed particles and PMMA/PAN composite latex particles.

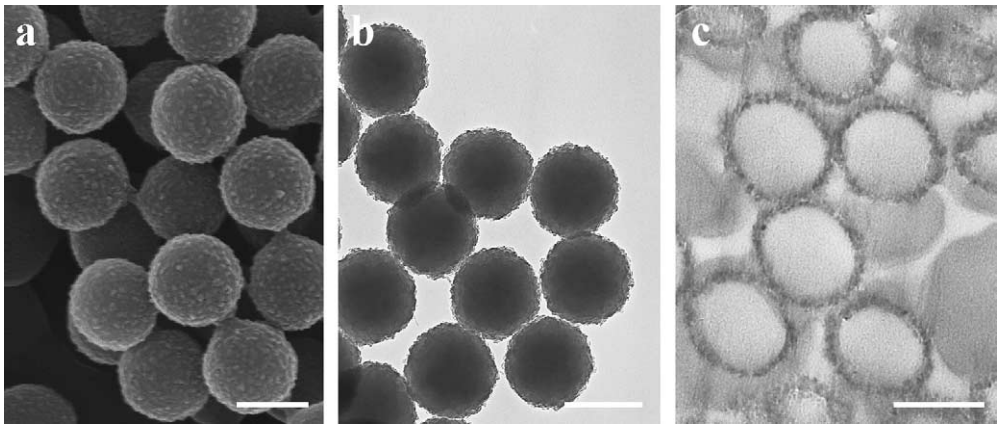

Fig. 5. Micrographs of PMMA/PAN composite latex particles prepared using VA-086 initiator: (a) FE-SEM; (b) TEM; and (c) TEM for ultrathin cross-sections. The polymerization conditions were otherwise the same as for the preparation of PMMA/PAN-4 composite latex particles using KPS initiator. The scale bars are 300 nm.

hand, we also carried out the second-stage polymerization using a water-soluble non-ionic azo-initiator, 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (VA-086). This initiator resulted in the PMMA/PAN composite particles having a core/shell internal morphology but a 'raspberry-like' surface morphology (Fig. 5). The interpretation of this morphological difference is still under investigation.

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