

The Formation of Asymmetric Polystyrene/Saponite Composite Nanoparticles via Miniemulsion Polymerization

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ABSTRACT: The synthesis of asymmetric spherical nanoparticles has attracted great interest because their anisotropic structure can be used as unique building blocks for constructing advanced materials. In this article, we report the formation of hemispherical or truncated polystyrene/nanosaponite composite particles via one-pot miniemulsion polymerization. It was found that the morphology of final composite latex particles strongly depends on the size of the nanoclay and its surface properties. Hemisphere or truncated sphere is the dominant morphology if the size of the nanoclay is larger than 100 nm. With the increase of the nanoclay content (up to 30 wt %), the fraction of hemispherical or truncated polystyrene/nanosaponite composite latex particles increased accordingly. The formation of hemispherical particles is possibly attributed to either the asymmetric growth of polymer chains on one side of the hydrophobically modified clay or the mechanical peeling-off of large spherical particles between polymer and saponite. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

The control of the particle morphology of a polymer is important for controlling the properties of coating, adhesives,¹ ink,² drug delivery, medical diagnostics,³ and other applications.^{4–7} Recently, there has been a focus of interest in the synthesis of particles or microbeads with nonspherical⁸ or asymmetrical shapes.⁹ Particles with an asymmetric shape could be used as the anisotropic building block for the advanced materials' construction. Physical methods such as capillary liquid break-up,¹⁰ microfabrication,¹¹ and the uniaxial stretching of spherical polymer beads¹² were developed to prepare asymmetrical particles. However, these methods require special substrates and facilities, and most of them can only be used for small-scale preparation. Furthermore, the particle size obtained from above methods is usually in micrometer-scale but not nanometer-scale.

Several methods for synthesizing unsymmetrical particles, such as hemispherical,¹³ bowl shape,¹⁴ and core shell¹⁵ have been reported. Phase separation in the composite spherical particles is the most common method for synthesizing hemispheres. Okaniwa reported a method of synthesis hemispheres poly

(butadiene) (PB).¹³ Experimentally, they synthesized spherical particles of poly(dimethylsiloxane) (PDMS) and PB composite particles using emulsion polymerization. They found that, by decreasing the cross-linking degree of PDMS, the PB could be segregated from PDMS to form hemispheres. Phase separation of two or three different polymers in one spherical particles from emulsion polymerization has been used for other polymeric hemispheres. Du et al.^{16,17} and Han et al.¹⁸ prepared micron and submicron-sized polymer particles with different morphologies by seeded dispersion or emulsion polymerization. The produced latex exhibited a wide variety of particle morphologies such as core-shell, hemispherical, and inverted core-shell structures. The mechanism of forming these asymmetrical particles was the microscale or nanoscale phase separation of two or more different types of polymers in a same particle after polymerization. Final particles usually contained two or more immiscible polymers.

In this article, one-pot miniemulsion polymerization method was used to synthesize hemispherical or truncated nanoparticles of polystyrene nanosaponite composites. It was found that in

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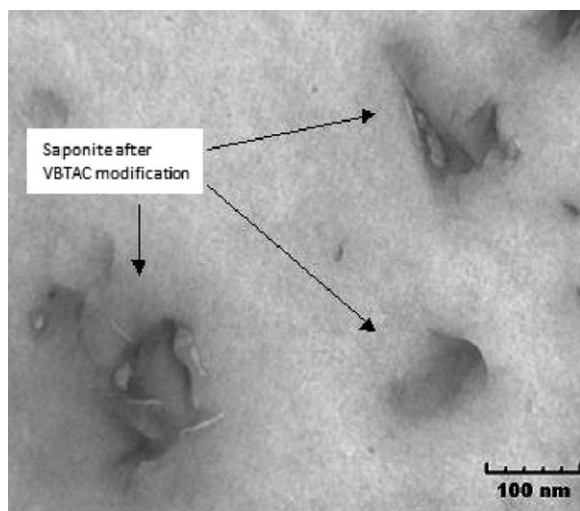


Figure 1. TEM of saponite after VBTAC modification.

the presence of the modified nanoclay, asymmetric polystyrene nanoparticles (hemispherical or truncated particles) with a size about 100–500 nm could be synthesized. The SEM analysis in combination with energy dispersive spectrometer (EDS) provided the evidence that the nanosaponite was attached to the truncated phase of the hemispherical nanocomposite particle. With the increase of the nanoclay content up to 30 wt %, the probability of forming hemispherical particles increased. The architecture of polymer composite particles strongly depends on the particle size and the morphology of nanoclay platelets. It is believed that either the asymmetric growth from one side of the nanoclay surface or the mechanical peeling-off of the polymer from large spherical particles is the possible mechanism for forming these asymmetric particles.

EXPERIMENTAL

Materials

Na-saponite clay was supplied by Kunimine industries, Japan. It was synthesized by a hydrothermal reaction with an ideal formula of $(\text{Na}_{0.49}\text{Mg}_{0.14})^{0.77+} [(\text{Si}_{7.20}\text{Al}_{0.80})(\text{Mg}_{5.97}\text{Al}_{0.03})\text{O}_{20}(\text{OH})_4]^{0.77-}$. The cationic exchange capability of the Na-saponite is 0.997 eq/kg. The average particle size of the Na-saponite is 50 nm (measured by a light scattering) when it was dispersed in water. 2,2'-Azobisisobutyronitrile (AIBN) was a product of Waco Chemicals and used as received. (*ar*-Vinylbenzyl) trimethylammonium chloride (VBTAC, 99%, a free radical polymerizable cationic surfactant), nonionic surfactant Triton 405 [TX-405, 4-(C_8H_{17}) C_6H_4 (OCH_2CH_2) $_{40}$ OH, 70 wt % solution in water], hexadecane (99%), and styrene (99%), were purchased from Aldrich Chemical. Styrene was purified by washing with 5 wt % NaOH solution followed by deionized water until pH was about 7, and then was distilled under reduced pressure and stored in the refrigerator prior to use. All other reagents were used as received.

Procedures

Surface Modification of Saponite Clay by VBTAC. In a typical procedure, a suspension of 5 g of saponite in 400 mL water was continuously stirred at room temperature for 2 h until a trans-

parent aqueous solution was obtained. Then, a solution of 1.2 g VBTAC (cationic vinyl polymerizable surfactant) in 100 mL water was added to the saponite suspension. After continuous stirring of the suspension overnight at room temperature, a white precipitate was collected by centrifugation and washed with water first and then ethanol to remove the excess VBTAC until no chloride could be detected by silver nitrate. The sample was then dried in a vacuum oven at room temperature. The modified saponite was examined with transmission electron microscope (TEM), and the image of modified saponite particles are given in Figure 1, which indicates the plate size of the saponite is about 10–100 nm. The amount of VBTAC on the clay saponite was measured by thermogravimetric analysis. When temperature was up to 463.8°C, 78.6 wt % of total weight of organophilic clay remained in the system, which agrees well with the maximum cationic exchange capability of saponite (99.7 meq/100 g equals to 21.1 wt % VBTAC for complete exchange).

Miniemulsion Polymerization of Styrene in the Presence of the Modified Saponite.

In a typical run, as indicated by the recipe shown in Table I, oil phase A composed of 1.2 g of costabilizer hexadecane and 0.24 g of AIBN, 12 g of the monomer styrene, and the varied amount of saponite (4–30 wt % of the weight of monomer styrene), was subjected to magnetic stirring at room temperature for 30 min. The mixture was then exposed to ultrasonification for 4 min. Following that, oil phase A was poured into an aqueous phase B comprising of 1 g of TX-405 in 100 mL of water under vigorous mechanical stirring in an ice bath for 30 min. The miniemulsion composed of A and B was thus prepared by homogenization using a homogenizer for another 3 min and ready for subsequent polymerization. The miniemulsion polymerization was carried out by degassing with N_2 at room temperature for 30 min first, and then increasing temperature to $80 \pm 2^\circ\text{C}$ and keeping at this temperature for >6 h under continuous mechanical stirring (600 rpm). The reaction was terminated by adding one drop of 2% 4-methoxyphenol solution into the miniemulsion.

Characterization

The TEM observation was conducted on a JEOL 100C machine at an accelerating voltage of 100 KV and a beam current of 70 mA. The SEM analysis was carried out on a LEO 1530 thermally assisted field emission scanning electron microscope in combination with a thin window EDS for microanalysis at an

Table I. The Basic Recipe for the Miniemulsion Polymerization

Mixtures	Component	Amount added (g)	Percentage in total (wt %)	Percentage to monomer (wt %)
Mixture A	Styrene	12.0	10.4	100.0
	Modified-saponite	0.48–6.0	0.4–5.0	4.0–50.0
	Hexadecane	1.2	1.0	10.0
	AIBN	0.24	0.2	2.0
Mixture B	TX-405	1.0	0.9	8.3
	D.I. Water	100.0	87.0	833.3

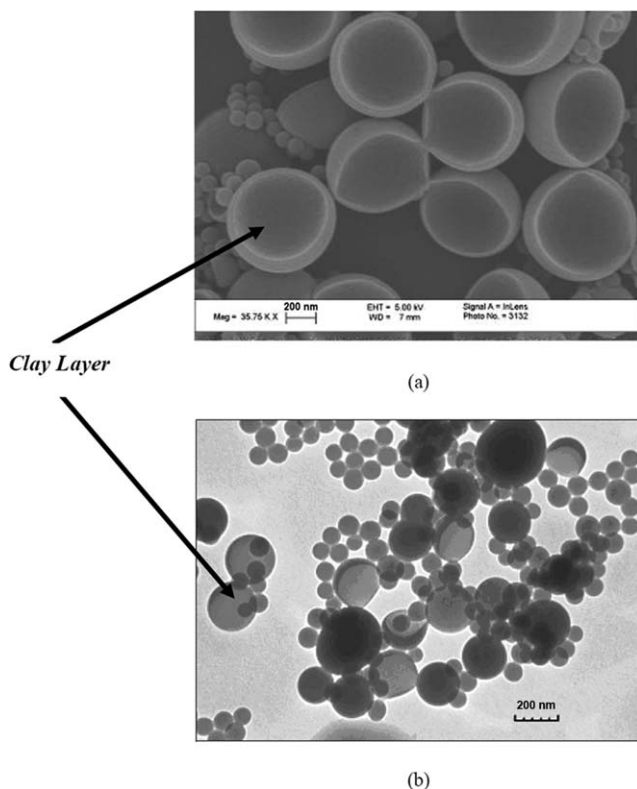


Figure 2. Hemispherical particles of polystyrene latex with the addition of 30 wt % VBTAC-modified saponite (a) SEM and (b) TEM.

operating voltage of 3 KV and a working distance from 6 to 10 mm. The ultrasonication was conducted on a W-385 sonicator from the Heat System-Ultrasonics at an output power level of 5 with a continuous mode, and a duty cycle of 70%. Centrifugation was conducted using Beckman 20 centrifuge at 10,000 rpm for 30 min at room temperature.

RESULTS AND DISCUSSION

The Formation of Hemispherical Particles using a VBTAC-Modified Nanoclay Platelet as the Template

Hemispherical polystyrene/nanosaponite composite latex particles were found by first premodification of the pristine saponite clay with the cationic monomer surfactant VBTAC, and subsequently followed by a miniemulsion polymerization with the monomer styrene. Figure 2(a, b) shows that the morphologies of polystyrene/nanosaponite composite latex particles with an addition of 30 wt % (based on the weight of the monomer) of the modified organophilic saponite clay. Final latex particles mainly consisted of truncated or hemispherical particles with a size ranging from 100 to 1000 nm. The EDS spectrum as shown in Figure 3 confirmed the existence of clay residues on the truncated surface of hemispherical polymer particles, with a weight ratio of Si/Mg/Fe/Al = 0.5/0.06/1.21/0.1 (Table II). The existence of these inorganic elements provided the evidence that the truncated layer was composed of the inorganic saponite clay and surrounding components were constituted by the polystyrene.

To track the shape evolution of a hemispherical particle formation during a reaction process, the samples were taken out from the reactor at different time during polymerization, and then their morphologies were investigated by the transmission electron microscopy (TEM) analysis. Figure 4(a) shows that only dispersed saponite plates (dark lines) are seen after 15-min polymerization, which indicates that no remarkable polymerization occurs in the beginning of the reaction. However, after 30-min reaction, the polystyrene/styrene component that attached on one or both sides of the planar clay saponite is observed as illustrated in Figure 4(b). The TEM images of the latex after 45- and 90-min reactions [Figure 4(c, d)] indicate the formation of spherical polystyrene particles (possibly some saponite clay core/polystyrene shell particles too), hemispherical, and truncated spherical particles. The irregular clay platelets attached on the asymmetric particles are clearly observed for those particles larger than 100 nm. However, regarding the latex particles smaller than 100 nm, no clay is directly observed from TEM images. It is believed that some small-sized clay can be fully encapsulated inside polystyrene particles and is not able to be directly observed in TEM images.¹⁹ These TEM images also indicate that the morphology and the particle size of final composite products can be greatly affected by the presence of the nanoclay. This relationship will be discussed in detail later.

The Effect of the Saponite Clay Content on the Stability and the Morphology of Final Polystyrene Nanosaponite Composite Latex

TEM images of Figure 5 show the morphologies of final latex particles formed with different contents of the modified clay. Figure 5(a) illustrates that the morphology of the polystyrene nanosaponite composite latex particles with an addition of 4 wt % of the modified organophilic saponite clay. Two groups of particles were observed. One group of particles consisted of the spherical particles <100 nm, which is believed to be either pure polystyrene or polystyrene encapsulated nanosaponite composites. Because the final size of latex is <100 nm for this group,

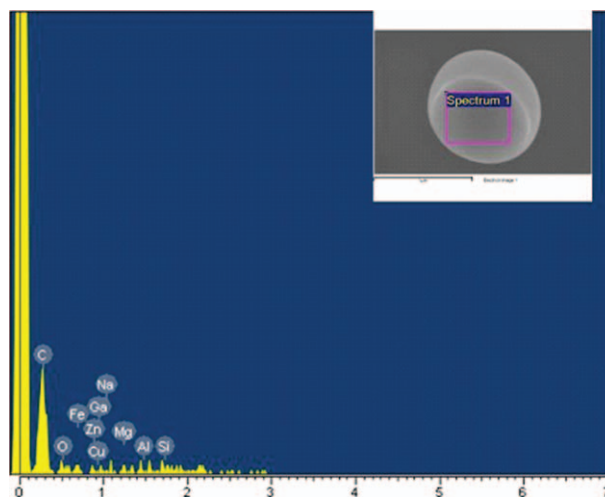


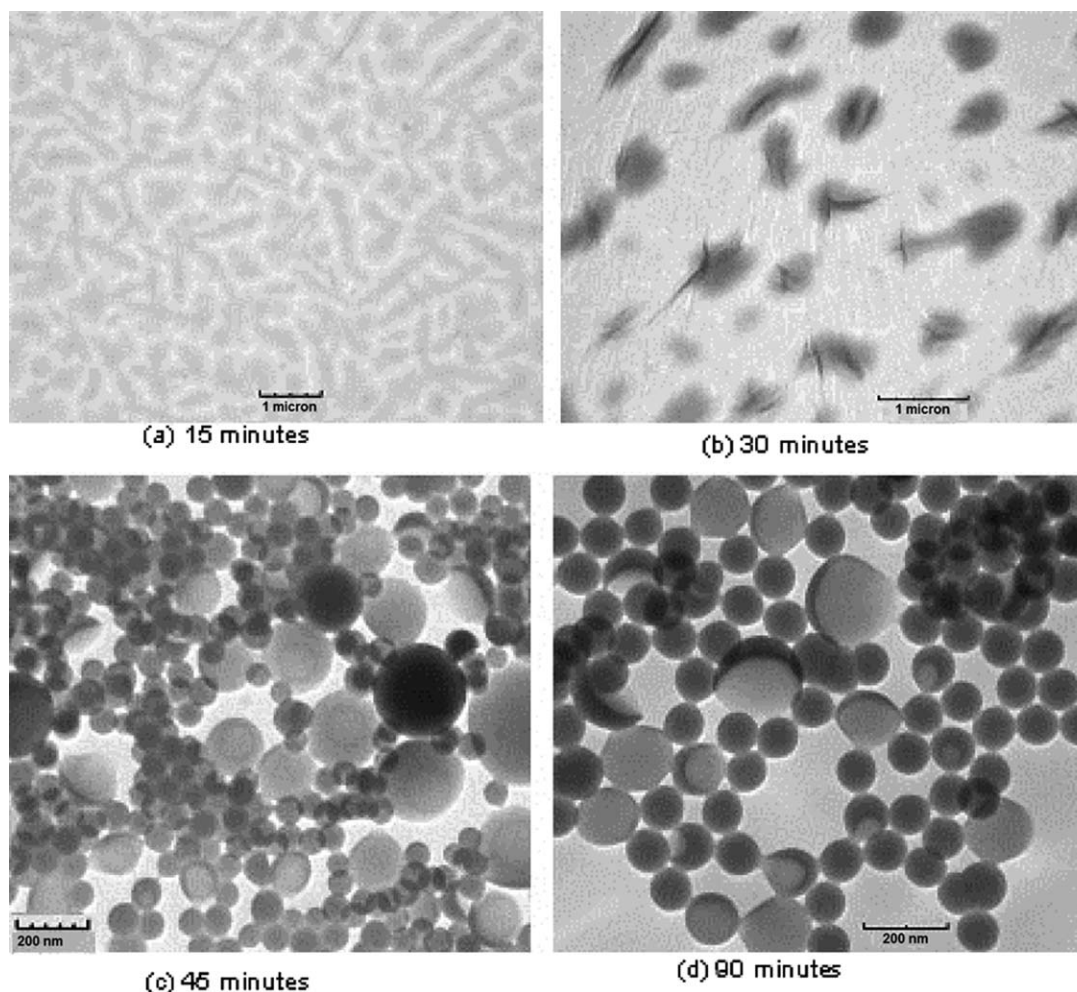
Figure 3. The EDS spectra of hemispherical polystyrene nanosaponite composite latex particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Elemental Analysis Results of EDS at the Truncated Area of the Polystyrene/Clay Nanocomposite Latex Particles

Element	App. Conc.	Intensity Corr.	Weight (%)	Atomic (%)	Compd. (%)	Formula	Number of ions
C K	3.05	2.0816	1.47	27.26	5.37	CO ₂	3.33
Na K	0.15	1.9136	0.08	0.77	0.11	Na ₂ O	0.09
Mg K	0.08	1.3041	0.06	0.60	0.11	MgO	0.07
Al K	0.12	1.1819	0.10	0.86	0.20	Al ₂ O ₃	0.10
Si K	0.56	1.1046	0.50	4.00	1.08	SiO ₂	0.49
Fe L	0.79	0.6472	1.21	4.85	1.56	FeO	0.59
O			4.69	65.47			8.00
Totals			7.00				
						Cation Sum	4.22

only very small saponite nanoplatelets could be encapsulated. Our previous research indicated that the dimension of the saponite nanoplatelet should be less than the equilibrium size (~ 100 nm) of polystyrene miniemulsion droplet to be encapsulated by polystyrene latex.²⁰ It is interesting to note that hemispherical or truncated particles are dominant in the fraction of the particles with a size >100 nm. With the increase of the addition of the organophilic saponite, the number of hemi-

spherical or truncated spherical particles was increased. It was also found that the latex with an addition of 4–30 wt % (based on the monomer styrene) nanoclay was stable even it was treated by 10,000 rpm centrifugation for 30 min. However, when the organophilic nanoclay was further increased up to 50 wt % (based on the monomer weight), final latex was not stable and the fraction of large-sized hemispherical and truncated spherical particles precipitated to the bottom rapidly. The

**Figure 4.** TEM images of the morphologies of polystyrene/VBTAC-saponite composite latex particles at different reaction time.

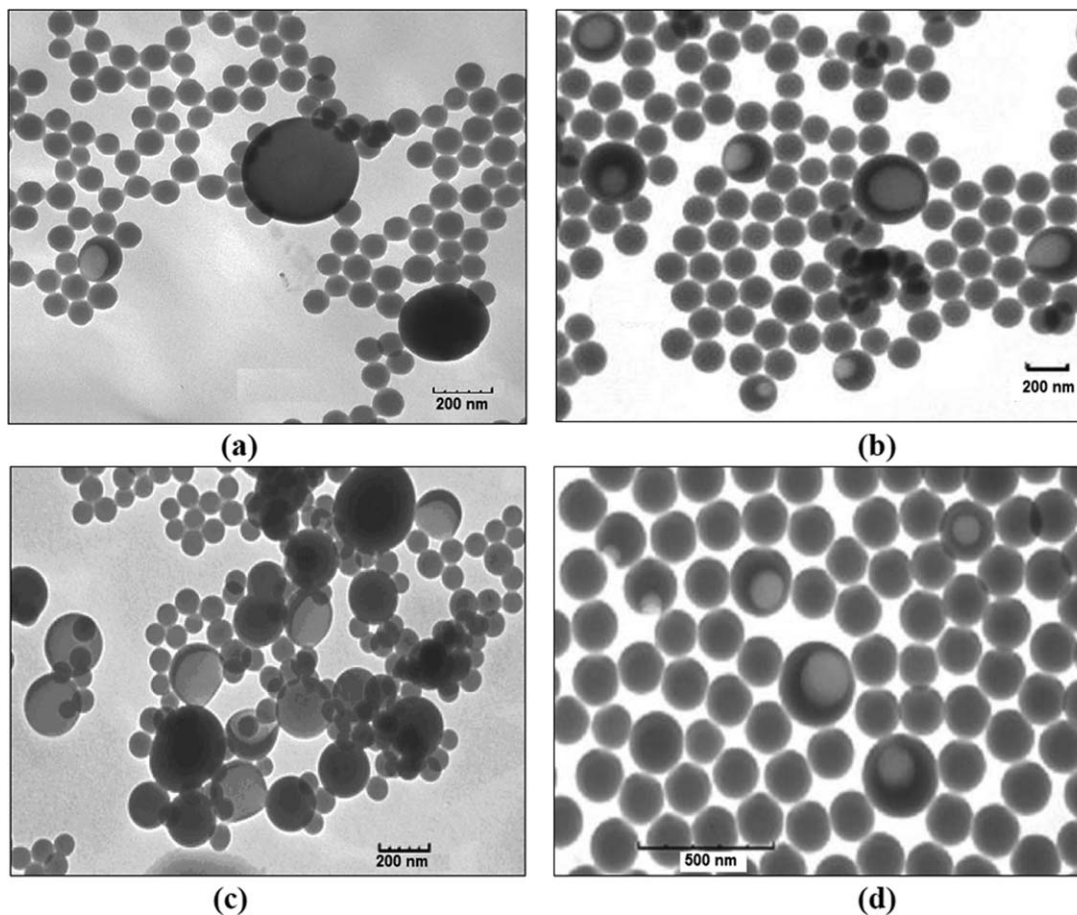


Figure 5. TEM images of polystyrene/nanosaponite composite latex prepared by miniemulsion polymerization in the presence of (a) 4 wt % modified saponite, (b) 10 wt % modified saponite, (c) 30 wt % modified saponite, and (d) 50 wt % modified saponite.

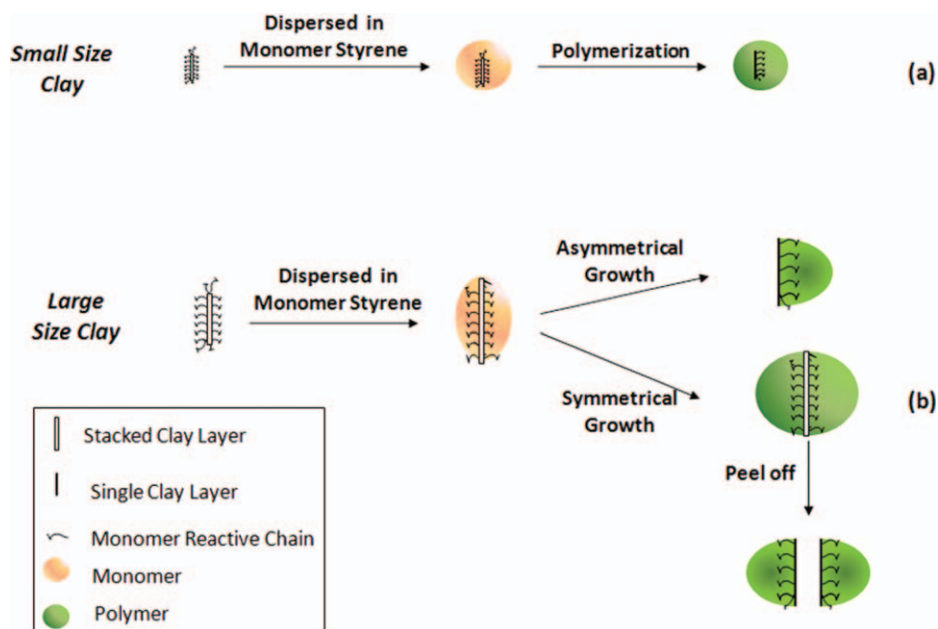


Figure 6. The scheme of the possible mechanism for the formation of hemispherical or truncated polystyrene nanocomposite particles. (a) Small-sized clay (<100 nm); (b) large-sized clay (>100 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amount of the organophilic nanoclay not only affects the final product stability, but also significantly affects the viscosity of the monomer before polymerization. With an increase of the organophilic nanoclay in the styrene monomer phase, the viscosity of the dispersion before the polymerization increased remarkably. If the organophilic nanoclay was >30 wt % (based on the monomer styrene), the monomer-saponite mixture could not form a stable emulsion in water, so miniemulsion polymerization could not be conducted.

The Possible Mechanism for the Formation of Hemispherical or Truncated Particles During Miniemulsion Polymerization

Figure 6 illustrates the scheme of the possible mechanism for the formation of a variety of morphologies (core-shell, hemispherical, and truncated morphologies) of polystyrene nanosaponite composite particles. The aforementioned TEM and SEM images clearly show that the final product includes two groups of particles: spherical particles with a particle size <100 nm and hemispherical or truncated particles with a particle size larger than 100 nm. As illustrated in Figure 6, at the first step in miniemulsion preparation, the cationic monomer, hexadecane (costabilizer), and the hydrophobically modified saponite clay are homogeneously dispersed in the styrene monomer phase with the aid of ultrasonification to form intercalated nanoclay particles. Because the nanoclay surface is less hydrophilic than the original clay by modification of cationic monomer VBTAC, the saponite has a higher affinity with styrene monomer. As a result, a homogeneous saponite-in-styrene suspension was obtained. The oil phase was then mixed with an aqueous phase containing surfactant TX-405 under vigorous mechanical stirring to form a miniemulsion before polymerization. When the small-sized clay existed in the system, as shown in Figure 6(a), the droplets with the monomer-encapsulated nanoclay inside were formed before the polymerization. Following a typical miniemulsion polymerization mechanism, spherical particles with the polymer encapsulated exfoliated nanoclay were formed after the polymerization. It is reasonable to believe that some pure polystyrene particles without nanoclay inside existed in the systems as well. Figure 6(b) illustrates the possible mechanism for the formation of hemispherical particles when the particle size is >100 nm. First, it should be noted that the saponite clay used in this research has a broad size distribution. When the large-sized clay dispersed in the styrene phase, the saponite platelet could not be fully encapsulated by the monomer to form a stable spherical droplet because of its large dimension (the droplet of miniemulsion is usually <100 nm). As a result, wetted saponite plates with styrene monomer covered on both sides were formed in the water phase. Different from conventional emulsion polymerization, the final particle size of miniemulsion polymerization is determined by the monomer droplet size before the polymerization. If the clay particle size is larger than the size of the equilibrium droplets of the miniemulsion, the droplets cannot be spheres, and these non-spherical shapes of the droplets will be directly copied into final latex particles, resulting in the formation of the hemispherical or truncated spherical particles. In the case of the monomer drop absorbs on only one side of saponite particles, hemispheres will be formed after polymerization. It is also possible that, even if the poly-

merization occurs symmetrically on both sides of the saponite in a large droplet, a peeling-off of the large sphere between the polymer and the clay is still possible under mechanical agitation during the miniemulsion polymerization, as shown in Figure 6(b), hemispherical particles with the saponite clay attached to the truncated surface were formed. The particles with this morphology were observed in the aforementioned SEM and TEM images. Finally, it should also be noted that small aggregates of saponite might also exist in the system. When polystyrene grows to certain size on the surface of the aggregates, the aggregates could be separated into two or more parts, resulting in broken of the polymer-saponite composite to form hemispheres. Therefore, it is believed that both the segregation of polymer from saponite surface and the segregation of aggregated saponite particles are the main reason of hemisphere formation. The segregation of PB from inorganic PDMS to form hemispheres has been reported before (see Ref. 17). We believe both systems have a similar mechanism.

CONCLUSIONS

This article presents the formation of a variety of morphologies (core shell, hemisphere, truncated sphere) and a broad size distribution of polystyrene latex particles via one-pot miniemulsion polymerization. In the presence of small amount of the nanoclay (4 wt %), the polystyrene/nanosaponite composite particles primarily consisted of two groups of particles: one of spherical particles with a diameter <100 nm and another of hemispheres with a large particle size (100–500 nm). With the increase of the nanoclay content (up to 30 wt %), the fraction of large hemispherical or truncated particles increased. Both the particle size and the surface hydrophobicity of the clay are important in determining the morphology and the particle size of final latex. We present two possible mechanisms for the formation of hemispherical or truncated particles. In the first possible mechanism, the formation of asymmetric particles is attributed to the asymmetric growth of polymer chains on one side of the organophilic nanoclay surface. In the second mechanism, we suggest that the formation of asymmetrical particles maybe results from a mechanical peeling-off of the large spherical particle between the interface of the polymer and the nanoclay.

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