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Poly(divinylbenzene-*alt*-maleic anhydride) Nanoparticles as a Novel Stabilizer for Pickering Polymerization of Styrene

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Pickering polymerization, presented by Ramsden and developed by Pickering, is an attractive strategy in the polymerization field, for which interest is booming.[1,2] This process has not only led to the development of fascinating avenues for polymerization methods, including emulsion,[3–5] suspension,[6,7] miniemulsion,[8,9] and even inverse emulsion[10,11] polymerizations, but has also enriched the range of functional polymer particles with complex morphologies,[12–16] thanks to introduction of various nanoparticles,[17–23] and has further broadened their application alternatives in the fields of bioscience, fuel cells, and environment treatment.[24–26]

However, for a typical Pickering polymerization system, the inorganic particles used as the stabilizer always need to be chemically modified due to the difference in surface properties between inorganic materials and polymers. The long-term mobility of these inorganic particles remains a big issue. To overcome these disadvantages, polymer-modified inorganic nanoparticles were developed through surface grafting modification or the assembly of block copolymers, and these hybrid particles served as efficient stabilizer particles. However, their fabrication process is very complex and time consuming. In order to simplify the synthetic route and reduce cost, polymeric nanoparticles have been specially designed and utilized as stabilizer particles, and recent research work has been devoted to Pickering emulsion and Pickering emulsion polymerization[27,28] stabilized with polymeric nanoparticles. But most of these polymeric stabilizer particles can only act as surfactant particles to immobilize on the oil/water interface, rather than being applied in Pickering polymerization.

Recently, a novel poly(divinylbenzene-*alt*-maleic anhydride) nanoparticles (PDMNPs) with a narrow distribution and a diameter of 30 nm were obtained through self-stable precipitation polymerization,[29–31] which was developed in our group. These nanoparticles were of highly crosslinked structure with hydrophilic anhydride groups (easily to be hydrolyzed to improve the water affinity) and pendant reactive vinyl groups (potentially to copolymerize with other vinyl groups) on the particle surface. In the present work, these PDMNPs were firstly applied as the only stabilizer for a Pickering polymerization of styrene (St), and it was surprisingly found that, the oil-in-water-type (see Supporting Information Figs. S1 and S2) PDMNPs were indeed very effective. Based on the experimental results, the influence of salt effect and PDMNP concentration on the polymerization was investigated in detail and a plausible mechanism was proposed to explain the particle formation process for this novel reaction system.

Salt plays an important role in determining the morphology and stability of the amphiphilic polymer nanoparticles in aqueous solution.[32] When different salts were added in the reaction system, the size and yield of the resultant polystyrene (PS) particles exhibited distinct features. Table 1 shows the influence of salts effect on the polymerization process (typical polymerization process is described in Supporting Information). When NaCl was used as the salt, 384 nm PS microspheres were obtained with a yield of 67%. While NH_4Cl was used instead of NaCl, the yield of PS particles decreased somewhat and the size increased to 460 nm. For $NaHCO_3$, the yield of resultant PS microspheres was about 94% (it could reach 100% with the increasing reaction time) and the diameter also increased to 494 nm.

From the zeta potential of PDMNPs dispersed in different aqueous solutions (see Supporting Information Fig. S4), it can be inferred that the dispersion state of the PDMNPs was largely affected by pH value of the solution (the hydrolysis of

Additional Supporting Information may be found in the online version of this article.

TABLE 1 Salt Effect on the Resultant PS Particles Obtained by Pickering Polymerization Stabilized by PDMNPs

Entry	Salt	PS yield (%)[a]	$\overline{D}_n$ (nm)[b]	Diameter Distribution Index (U)
1	NaCl	67.2	384	1.07
2	NH$_4$Cl	51.1	460	1.19
3	NaHCO$_3$	93.7	494	1.13
4	NaHSO$_3$	77.3	677	1.18

The reaction systems consisted of 0.1M salt aqueous solution, 10% (vol/vol) St, 0.6 wt % ammonium persulphate (APS), and 0.5 wt % PDMNPs (the percentages of both APS and PDMNPs were relative to St), and these polymerizations were all carried out with 300 rpm mechanical agitation at 75 °C for 7 h.

Hereby the average diameter $\overline{D}_n$ and distribution index were calculated based on the scanning electronic microscopy images (see Supporting Information Figure S3 and the dynamic light scattering result was shown in Table S1).

the anhydride groups was inhibited under acidic condition while being promoted under alkaline conditions). Furthermore, the influence of salt concentration (ion strength) and the type of counter-ion had also been evaluated [see Supporting Information Fig. S4(c,d) and S5, respectively], the results indicated that the salt concentration also had some influence on the dispersion state of the PDMNPs, however, it was not a substantial factor and not as important as that of pH value.

Specifically, when NaCl was used as the salt (pH = 7), only a small amount of PDMNPs was hydrolyzed and the dispersion state of PDMNPs was affected by the salt through electric double layer, so that the emulsion could not be stabilized effectively, and consequently the yield of PS particles was not too high. When NH$_4$Cl was used in the polymerization system (pH < 7), the hydrolysis of anhydride groups of the PDMNPs was inhibited and agglomeration of the un-hydrolyzed PDMNPs was driven by this acidic salt. This way, the PDMNPs could not be homogeneously dispersed nor could the emulsion be stabilized effectively. As a result, the yield of PS particles decreased slightly while their diameter increased. In contrast, when NaHCO$_3$ was employed as the salt (pH > 7), the anhydride groups could be easily hydrolyzed by this alkali salt, which dramatically improved the water affinity of these PDMNPs. Additionally, it was obvious that ion strength indeed had an important influence on the dispersion of the PDMNPs. According to the zeta potentials of PDMNPs colloids with different NaHCO$_3$ concentration, there should be

a suitable concentration range for NaHCO$_3$, in which the Pickering emulsion reaction system could be effectively stabilized and high yield of PS particles could be obtained.

The situation was much complex when NaHSO$_3$ was used as the salt. On the one hand, NaHSO$_3$ could affect the dispersion state of the PDMNPs through compressing the electric double layer as mentioned above (pH < 7); on the other hand, certain part of NaHSO$_3$ participated in the initiation process due to the redox reaction with APS. Hence, the experimental results were different with NaHSO$_3$ as the salt. It can be seen from Table 1 that the average diameter of the resultant PS particles was much bigger and the size distribution was also very broad.

Based on the above discussion, the alkalescent NaHCO$_3$ with suitable concentration was helpful for well dispersion of PDMNPs by promoting hydrolysis of the anhydride groups in the PDMNPs and providing suitable ion strength. The well dispersed PDMNPs could in return facilitate the emulsification process and improve the stability of the emulsion.

The Pickering polymerization of St was then carried out at different PDMNPs concentrations. It was found that the PS particles presented different morphologies with increasing amounts of PDMNPs (as shown in Fig. 1). When the PDMNPs content was only 0.5 wt % relative to St, the resultant PS particles exhibited a typical raspberry-like morphology with granules located evenly on the particle surface. The size of these granules was almost the same as that of the original PDMNPs (around 30 nm). With an increasing concentration of PDMNPs, the raspberry-like shape of the PS particles became more evident, and the size of the granules was found to be slightly larger (about 50 nm or 60 nm) than that of the PDMNPs, indicating an aggregation of PDMNPs. As the content of PDMNPs further increased to 2.5 wt %, they aggregated to form even bigger nanoparticles and these aggregates might play the role of stabilizer instead of the separated PDMNPs. As a result, the granules were too big to distinguish their own edges from each other.

Figure 2 shows the Fourier Transform infrared spectroscopy (FTIR) spectra of the original PDMNPs, the hydrolyzed PDMNPs, and the resultant PS particles fabricated through Pickering polymerization and stabilized with PDMNPs. For the pure PDMNPs, the peaks around 1854 cm^{-1} and 1774 cm^{-1} were assigned to the stretching vibration of C=O and the peak at 1073 cm^{-1} was attributed to the C—O
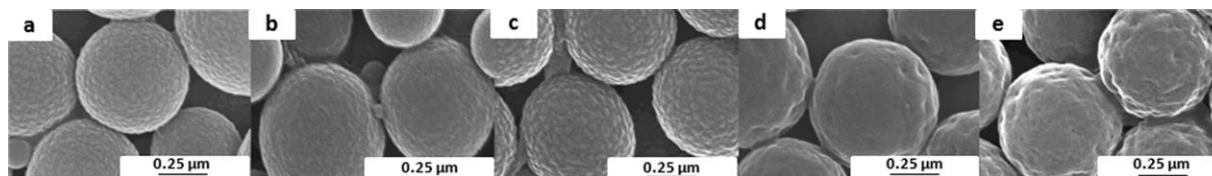
FIGURE 1 SEM images of the raspberry-like PS particles obtained through Pickering polymerization of St stabilized with different low concentrations of PDMNPs (wt % relative to St): (a) 0.5; (b) 1.0; (c) 1.5; (d) 2.0; (e) 2.5.
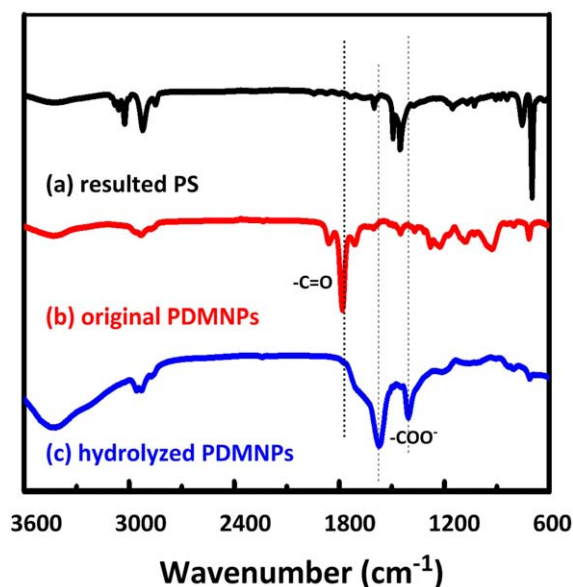
FIGURE 2 FTIR spectra of (a) the resultant PS, (b) the original PDMNPs, (c) PDMNPs hydrolyzed from a NaHCO$_3$ aqueous solution (PS was the final product of Entry 3 in Table 1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stretching vibration. For the hydrolyzed PDMNPs, the intensity of the characteristic peaks at 1854 cm^{-1} and 1774 cm^{-1} was markedly decreased, while two other strong absorption peaks appeared at 1540–1600 cm^{-1} and 1464–1360 cm^{-1}. These new peaks were ascribed to the homogenization of C=O and C—O as a result of the formation of COO$^-$ when the H atom (or H$^+$) was substituted by Na$^+$. This result was in good agreement with the fact that the PDMNPs could be easily hydrolyzed by an alkali salt.

The IR spectrum of the resultant PS particles exhibited characteristic peaks attributed to the carboxyl groups in addition to the absorption bands from 1650 cm^{-1} to 1450 cm^{-1} and 695 cm^{-1}, which were typical absorption bands of PS, indicating the presence of hydrolyzed PDMNPs. As mentioned above, the PS products were thoroughly washed with deionized water before IR characterization. Hence, the IR spectrum provided further evidence that the PDMNPs were attached to the PS particles through chemical bonds rather than simply being mixed together.

Additionally, the water contact angle (CA) value of the resultant PS particles were measured to be 78.5°, which was much larger than that of the film of PDMNPs (21.0°) but smaller than that of the pure PS (130.5°). The water CA measurements are shown in the Supporting Information Figure S6. The results illustrated that the hydrophobicity of the raspberry-like PS particles decreased dramatically compared with that of pure PS, owing to the presence of hydrophilic PDMNPs (which were in fact hydrolyzed) on the surface of the raspberry-like PS particles. This corroborated the SEM and FTIR results.

To evaluate the role of PDMNPs, a control experiment was carried out in the absence of PDMNPs, it was found that the yield of PS product was only about 5% and no particles were formed (see Supporting Information Fig. S7). The experimental result confirmed that the PDMNPs could serve as an effective Pickering stablizer during the emulsion polymerization. To assess the Pickering polymerization process stabilized with PDMNPs, the polymerization kinetics were fully investigated. The reaction system consisted of 10% St ($V_{St}/V_{solvent}$) in 0.1M NaHCO$_3$ aqueous solution, 0.6 wt % water-soluble initiator APS relative to St, and 0.5 wt % PDMNPs relative to St. The surface activity of the PDMNPs can be found in the Supporting Information.

As shown in the optical images of Figure 3, it is obvious that the PDMNP suspension and the St separated from each other at the beginning of the reaction, and a well-dispersed Pickering emulsion was gradually formed as the polymerization proceeded (without being pre-emulsified). The reaction system became a turbid dispersion with a St-rich upper layer after 1 h. This St-rich upper layer was consumed gradually, and a stable milky dispersion was formed after 3 h. The resultant milky emulsion could be stable for more than one week. This result demonstrated that the PDMNPs could act as effective stabilizers in the Pickering emulsion polymerization of St.

It is worth noting that PDMNPs are remarkably efficient as emulsifier, and that a stable PS emulsion was obtained even when the concentration of PDMNPs was only 0.5 wt % relative to the monomer. This concentration was much lower than that of inorganic nanoparticle stabilizers (10–30 wt % relative to the monomer) in a conventional Pickering emulsion polymerization process, which is even lower than that
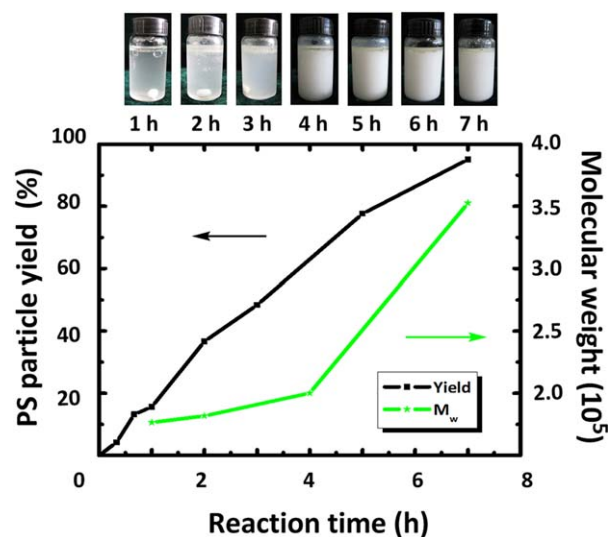
FIGURE 3 Optical images of the St latexes stabilized by PDMNPs as a function of the polymerization time and plots of the PS particle yields and molecular weights as a function of the polymerization time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
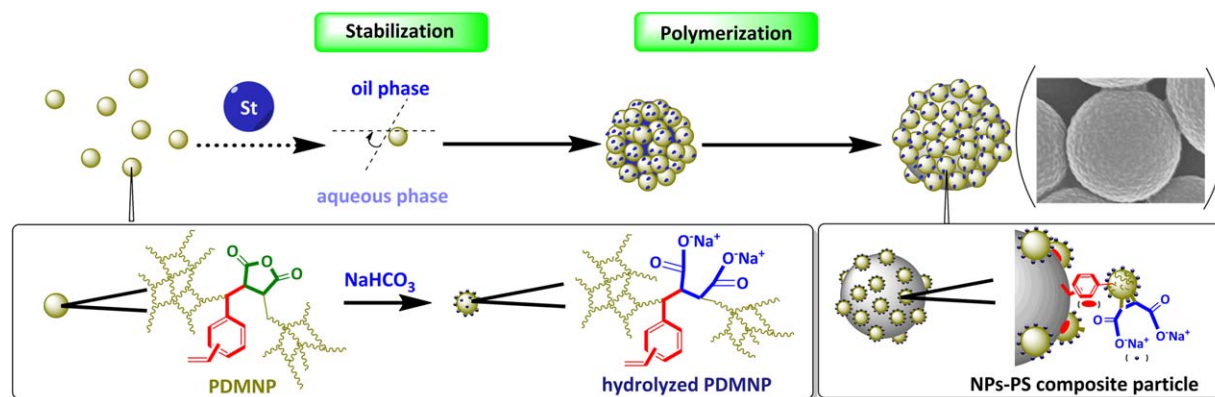
SCHEME 1 A possible formation process of the raspberry-like PS particles through Pickering emulsion polymerization of St stabilized with PDMNPs and initiated by APS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of recent polymeric nanoparticles stabilizer (with a content of 2 wt % relative to monomer) for novel Pickering emulsion polymerization.[33] With a content as low as 0.5 wt %, the PDMNPs could efficiently stabilize the emulsion system. The exceptionally high stabilization efficiency could be rationally explained based on two distinctive features of the PDMNPs, including low density and micro-gel-like structure. Firstly, different from the conventional inorganic Pickering particles with high density, the usage of PDMNPs could dramatically decrease due to its low density. On the other hand, the micro-gel structure endowed PDMNPs with certain deformability, which increased the contact area between PDMNPs and the PS micelle. In details, the hydrate size of hydrolyzed PDMNPs (about 70 nm, see Supporting Information Fig. S8) was much larger than that of solid one (about 30 nm, based on SEM result), indicating that hydrolysis could immensely improve the contact area for stabilization of emulsion. The atomic force microscopy (AFM) analysis further confirmed the derformability of wet PDMNPs (see Supporting Information Fig. S9). The AFM images of the wet PDMNPs indicated that the micro-gel could transform to flattened ellipsoid particle rather than keeping spherical shape. The larger hydrate size and deformability supplied much more contact area, which dramatically improved the stabilization efficiency of these PDMNPs. Besides, hydrolyzed PDMNPs particles could be easily anchored onto the micelles surface through covalent bond (pendant vinyl groups), which contributed additional immobilization effect.

The dependence of the monomer conversion and the molecular weight of the polymer product on the reaction time can be also seen in Figure 3. It is evident that the polymerization rate exhibited three standard stages, namely, a growth phase, a constant phase, and a phase of slowing down. The $\overline{M}_w$ of PS was only 170k in the early stage and increased to about 350k at the end of the polymerization process. The molecular weight was determined by gel permeation chromatography (GPC) with a Waters 2414 Refractive Index Detector. The system was equilibrated at 30 °C with THF as eluent with a flow rate of 1.0 mL min^{-1}. The calibration curve was obtained with PS standards.

The variation of the $\overline{M}_w$ of PS with the polymerization time can be rationally based on the typical feature of emulsion polymerization. Specifically, the water-soluble APS was decomposed to form primary radicals firstly, and these primary radical reacted with St in water phase to generate the propagating radicals. Then the propagating radicals diffused into the Pickering micelles to initiate the polymerization of St, and the polymerization proceeded until termination occurred at the entry of another free radical into the micelle. The termination of propagating radicals was very fast at the beginning and slowed down gradually as the polymerization proceeded, and consequently, the molecular weight of the PS product increased with the polymerization time.

In the former discussion on chemical structure, St was confirmed to be polymerized through Pickering emulsion polymerization with PDMNPs as an effective stabilizer in the NaHCO$_3$ aqueous solution, and the hydrolyzed PDMNPs remained in the resultant PS particles throughout the reaction of the residual pendant vinyl groups. It was also implied, based on the analysis of the water affinity, that the stabilizer PDMNPs anchored on the PS particles through chemical bonds.

Based on the above experimental results, a simple mechanism was proposed to describe the formation process of the PS particles through Pickering emulsion polymerization stabilized with PDMNPs and initiated by APS. As shown in Scheme 1, during this novel Pickering emulsion polymerization process, the PDMNPs was dispersed in the aqueous salt solution and the hydrolyzed PDMNPs acted as surfactant like conventional inorganic particles in a typical reaction system initiated by a water-soluble initiator. Mechanical agitation was used to make the reaction system a homogeneous emulsion during the polymerization process. However, the PDMNPs were chemically attached to the surface of the resultant PS microspheres, and it put them apart from the traditional surfactant particles.

In summary, we developed a novel type of oil-in-water Pickering emulsion polymerization system with PDMNPs as very effective stabilizers. The effect of salt was investigated in

detail, and an alkali salt $NaHCO_3$ with pH > 7 and advisable charge interaction was employed to hydrolyze and disperse the PDMNP colloids. PS particles of different morphologies were observed with varying PDMNP concentration: the surface of the raspberry-like PS particles became gradually smooth when the PDMNP concentration increased from 0.5 wt % to 2.5 wt %. However, further studies were still required to explain that the size of the as-formed PS particles remained unchanged with increasing PDMNP concentration. The polymerization kinetics and the microscopic morphology of the resultant raspberry-like PS particles confirmed that St was polymerized through a Pickering emulsion polymerization process. Moreover, FTIR and CA analysises provided further evidence that the PDMNPs were hydrolyzed and subsequently attached to the surface of the resultant PS particles through chemical bonds. The present work not only develops a novel Pickering polymerization technique, but also provides a new method for the fabrication of various organic–organic composite polymer particles whose surface is modified with functional polymeric nanoparticles. Due to the anhydride group of the functional polymeric nanoparticle on the particle surface, these raspberry-like particles could be applied in the fields of functional coating and biomedical applications, such as tracer and carrier.

ACKNOWLEDGMENTS

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