NJC

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

Journal Name
RSCPublishing

PAPER

Synthesis and Properties of Hybrid Core-Shell Poly(alkyltrialkoxysiloxane) Latex

Cite this: DOI: 10.1039/x0xx00000x

Bo Liu, Shiqiang Huang*, Zushun Xu, Feng Gao and Jie Zhu

Received 00th January 0000,
Accepted 00th January 0000

DOI: 10.1039/x0xx00000x

www.rsc.org/

We synthesized hybrid poly(alkyltrialkoxysiloxane) (PATOS) core-shell latex via emulsion polymerization under the alkaline environment using n-propyltrimethoxysilane (PTMS), methyltriethoxysilane (MTES)/PTMS, n-octylmethoxysilane (OTMS)/PTMS. We put forward the model of core-shell structure formation mechanism in emulsion polymerization. This nucleation mechanism model and progress of these hybrid core-shell latex particles were investigated by transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersion spectrum (EDS) and dynamic laser scattering. We found that the core-shell particles were formed during the chemical bonds reconstruction, shrinkage and rotation in the hydrolysis and condensation reaction process; the particles had three change stages during the emulsion polymerization; the shell of PATOS hybrid particles was organic layer (alkyl), and their core of those was inorganic layer (Si-O-Si-).The hybrid core-shell latex could be stored more than 6 months, and the latex centrifugal stability was excellent. The polymerization coagulum content ranged between 0.09wt% and 0.31wt%. The weight percentages of PATOSs are above 90% when the temperature is 400℃ in nitrogen atmosphere. The hydrophobility of OTMS/PTMS (1:4) latex (WCA≈110.8 °) was much more durable than others for its long alkyl chain.

1 Introduction

Hybrid core-shell particles have attracted tremendous interest in material science in the past decades as the combination with inorganic and organic components. They can be applied in many fields of material science, such as functional and protective coatings, textiles, catalysis, optics, micro-electronics, medicine and biotechnology, etc.[1-8]

Generally, Hybrid core-shell particles are typically prepared by heterophase polymerization techniques, such as emulsion, dispersion or precipitation polymerization,[6,9,10] and emulsion polymerization is the most frequently used. In the emulsion polymerization, hybrid core-shell particles are usually fabricated using inorganic materials and polymer, which are based on inorganic core and organic shell or organic core and inorganic shell.[2] However, in order to strengthen the interaction and promote the compatibility between inorganic materials (mainly silica) and carbon chain polymers, some functional monomers have been used to modify the surface of the silica before fabricating hybrid core-shell particles, such as the silane coupling agent(methacryloxy-propyl-trimethoxysilane(MPS), vinyltrialkoxysilane et.al) [11-17], N-carboxyanhydride (NCA)[18] and so on.

Compared with inorganic materials, silicone is a kind of inorganic-organic compound, such as alkylalkoxysilane. The hybrid core-shell particles can be synthesized directly during copolymerization of silicone (alkylalkoxysilane, PDMS) and organic monomer. For this reason, the additional modification steps for inorganic particles could be avoided. PS/silicone core-shell latex particles have been synthesized by emulsion polymerization using (MPS) as a functional co-monomer. MPS as a functional monomer in the emulsion polymerization, it reacts in free radical polymerization and undergo hydrolysis and polycondensation reactions in the aqueous phase.[19-22] Apart from those, silicone-acrylic core-shell hybrid latexes have been prepared via miniemulsion polymerization using PDMS with vinyl terminated and acrylate.[23] Our group has synthesized silicone- acrylic core-shell latexes by conventional seed emulsion[24,25] and microemulsion[26] copolymerization of acrylic monomers and vinyltrialkoxysilane. Polysiloxane containing Si-O-Si inorganic segment and organic groups is a kind of excellent hybrid materials. Li et al have synthesized polymethacryloxypropylsilsesquioxane latex nanoparticles using MPS.[27,28] The chemical activity of trialkoxysilane with large organic groups is lower, such MPS. Nevertheless, the reaction activity of alkyltrialkoxysiloxane is very high, especially in the non-neutrality water environment. On the other hand, the reaction activity of trialkoxysilane with a short alkyl chain is so high that it is hard to control in the emulsion polymerization process.

In this paper, we synthesized hybrid core-shell PATOS latex particles via emulsion polymerization using n-propyltrimethoxysilane (PTMS), Methyltriethoxysilane (MTES)/PTMS, n-octylmethoxysilane (OTMS)/PTMS. Unlike hybrid core-shell latex particles prepared using inorganic materials and carbon chain polymer, the as-obtained hybrid core-shell latex particles were composed of inorganic polysiloxane core and organic components shell depending on hydrolysis and condensation reactions of alkoxy groups. The seed emulsion of alkyltrialkoxysilane is formed in the process of hydrolysis and condensation reaction rather than a separate preparation. The nucleation mechanism and progress of these hybrid core-shell latex particles are investigated. The thermal properties, stabilities and the effect of alkyl chain on the hydrophobicity of core-shell latexes are also discussed.

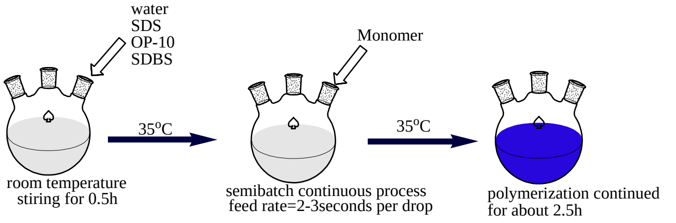
2 Experimental

2.1 Materials

Methyltriethoxysilane (MTES) (99.2%), n-propyltrimethoxysilane (PTMS) (99.2%) and n-octylmethoxysilane (OTMS) (97.7%) were purchased from Jingzhou Jianghan Fine Chemical Co., Ltd. (China). Sodium dodecylsulfate (SDS) (CP) was purchased from Shanghai Maxam Co., Ltd. (China). Sodium dodecylbenzesulfonate (SDBS) (CP) was purchased from Nanjing Tianxi Fine Chemical Co., Ltd. (China). Polyoxyethylene octylphenol ether (OP-10) (CP) was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Deionized water was used throughout experiments.

2.2 Synthesis of PATOS hybrid core-shell Latexes

The different kinds of PATOS core-shell hybrid particles were synthesized via emulsion polymerization. In a typical experiment, SDS(0.57wt%), SDBS(0.33wt%), OP-10(0.73wt%) and H_2O(67.84wt%) were mixed in a 250ml four-neck flask at room temperature for 0.5*h*. The pH value of system is about 9 because SDBS aqueous solution is alkaline. The mixture was heated to 35°C at a stirring rate of 300rpm and then PTMS(30.53wt%) was added into the reactor using semicontinuous process (feed rate=2-3seconds per drop). The polymerization was continued for about 2.5h after the monomer dripping off. When PTMS was replaced with MTES/PTMS =1:1, 1:4 or OTMS/PTMS= 1:4(molar ratio), the different kinds of PATOS core-shell hybrid particles were prepared respectively. (Scheme. 1) (see S1)



Scheme 1 Semi-batch continuous emulsion polymerization preparation of PATOS hybrid core-shell latex particles.

2.3 Characterization

The morphology and structure of hybrid core-shell particles were observed by transmission electron microscopy (TEM, Tecnai G20) and scanning electron microscopy (SEM, JSM6510LV), field emission scanning electron microscopy (FESEM, JSM7100F). SEM samples were gold-coated before analysis. TEM 200 mesh-sized Cu grids were supplied by Beijing Xinxing Braim Technology Co., Ltd (China). Element composition of hybrid core-shell particles was characterized through elemental EDAX/EDS line scan spectrometer map analyses.

Particle sizes and distributions were determined by dynamic laser scattering using Malvern Zetasizer (Nano-ZS90). Thermal gravimetric analysis (TGA) was carried out with DIAMOND TG/DTA at a heating rate of 10℃ min^{-1} from 30℃ to 800℃ in a nitrogen atmosphere (gas flow = 80 ml min^{-1}). Water contact angle (WCA) measurements were carried out on the sample at three different positions and the droplets were fixed at 5μL.[29]The mean value was taken as the final result. After the completion of the emulsion polymerization, the latexes were filtered, and the precipitates were washed with water and dried in a vacuum oven to constant weight. The coagulum content σ of emulsion polymerization process was calculated as follows:

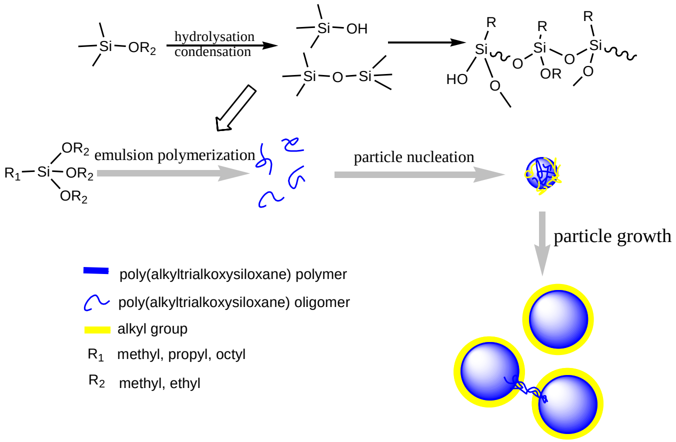
$$\sigma = \omega 1/\omega 2 \times 100\%$$

Where ω1 and ω2 are the weights of the precipitate and monomers, respectively.[24]

The measurements of the centrifugal stability of emulsion were done with the samples through a centrifugal machine from Shanghai Anting Scientific Instruments Plants TDL-4 (China). The centrifugal stability of emulsion is excellent, if there is no hierarchical or floating oil phenomenon after centrifuging at the speed of 3,000rpm for half one hour. The storage stability of emulsion was evaluated via seal storage at room temperature. If there is no obvious demulsification and sedimentation phenomenon after being stored 6 months or more than, the storage stability of emulsion is excellent.

3 Results and discussion

3.1 Nucleation mechanism of PATOS hybrid core-shell latex particles



Scheme 2 Schematic procedure of formation of PATOS hybrid core-shell latex particles.

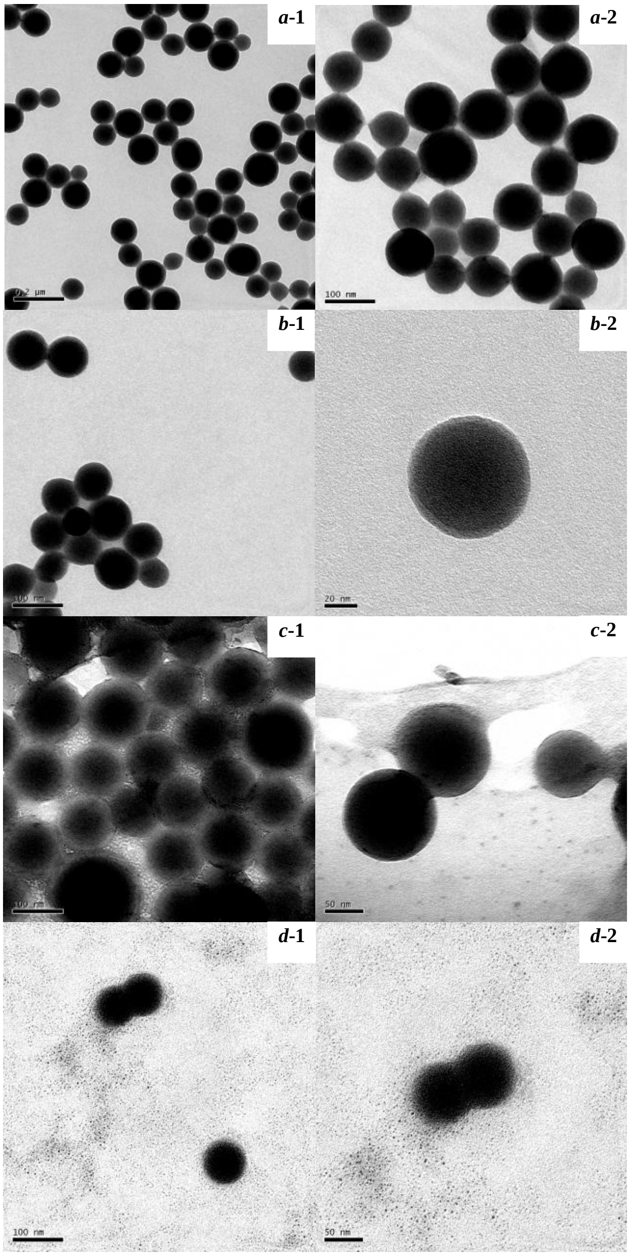


Fig. 1 Typical TEM images of the hybrid PATOS core-shell particles: *a*-1 and *a*-2 (PTMS:MTES=1:1), *b*-1 and *b*-2 (PTMS:MTES=4:1), *c*-1 and *c*-2 (PTMS), *d*-1 and *d*-2 (PTMS:OTMS=4:1).

We synthesized hybrid core-shell PATOS latex particles via emulsion under the alkaline environment using n-propyltrimethoxysilane (PTMS), Methyltriethoxysilane (MTES)/PTMS, n-octylmethoxysilane (OTMS)/PTMS. Compared with the classical free radical emulsion polymerization reaction, the trialkoxysilane emulsion polymerization reactions are hydrolysis to silanols, and condensation of the silanols with each other and with methoxy groups to polysiloxanes in the acid or alkaline catalyst.[30,31](see S2) It is atypical that there is inexistence of seed emulsion during hybrid core-shell latex particles formation process. It is easy for alkyltrialkoxysilane to hydrolyse and condensate in the presence of water and acid or alkaline catalyst. On the other hand, the simultaneous hydrolysis and condensation reactions of the alkoxysilyl groups make both the microstructure and morphology of the particles difficult to control.[20]On this account, semi-batch emulsion polymerizaiton method was selected to prepare PATOS because of easy to control polymerization.[5]

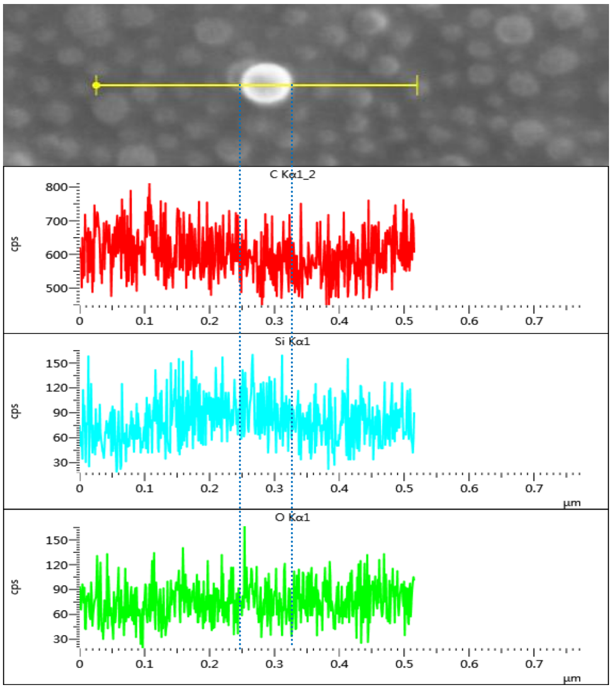


Fig. 2 FESEM/EDS linescan compositional analysis of PATOS hybrid core-shell particles (PTMS): **C**: red line, **Si**: blue line, **O**: green line.

The progress of formation mechanism of hybrid core-shell structure is illustrated through the model, as shown in Scheme 2. Si-OR firstly hydrolyzed into Si-OH after alkytrialkoxysilane was contacted with water in the alkaline condition. The silanols are metastable and self-condense in the water phase to yield cyclic molecules and higher molecular weight Polytrialkoxysiloxane oligomers. Polytrialkoxysiloxane molecular chain segments would folded and rotated during formation of Si-O-Si bonds through reaction between Si-OH and Si-OR, and the alkyl chain would be outward to reduce interaction between the silica chains and surface tension.[32-35] The alkoxide groups hydrolysed to produce primary nuclei. These small nuclei then aggregate to form seed particles during the first stage of the reaction.[36,37] With the increase of polymerization degree, the number of alkyl chain outward can increase to form shell, and the cross-linking of the core through siloxane bounds formation prevents of the movement of polytrialkoxysiloxane chain segments and stabilizes therefore the core-shell morphology. The core-shell particles are formed because of the chemical bonds reconstruction, shrinkage and rotation in the hydrolysis and condensation reaction process.

Unlike conventional radical core-shell emulsion, the seed emulsion of alkyltrialkoxysilane is formed in the process of hydrolysis and condensation reaction rather than a separate preparation. Fig. 1 shows a TEM photograph of PTMS/MTES (1:1, 4:1), PTMS, PTMS/OTMS (4:1) polymer latex particles. It reveals that the PATOS hybrid core-shell latex particles have been prepared. This result is in accordance with the model discussed above which PATOS hybrid core-shell latex particles can be synthesized directly through hydrolysis and condensation reaction of alkyltrialkoxysilane in the emulsion system. Because of the core-shell particle forming as the chemical bonds reconstruction, shrinkage and rotation in the hydrolyzation and condensation reaction process (discussed previously, scheme 2), the boundaries of core-shell structure is not very obvious and the thickness of the particle shell is not large as- shown in the Fig. 1. In order to further understand the core layer and shell layer composition of hybrid particles, we analyzed the element of core-shell particles via FESEM and energy dispersion spectrum (EDS) analyser using elemental EDAX/EDS line scan spectrometer map. High resolution SEM microphotographs and compositional (EDS) line scan analyses of resulting composite material are shown in Fig. 2. It can be seen from the mark area in the Fig. 2 that the carbon curve has a weak downward trend while the silicium and Oxygen curves have a weak fluctuation trend. Thus, combined TEM graph, it can be drawn a conclusion that the shell is mainly organic part and the core is inorganic part.

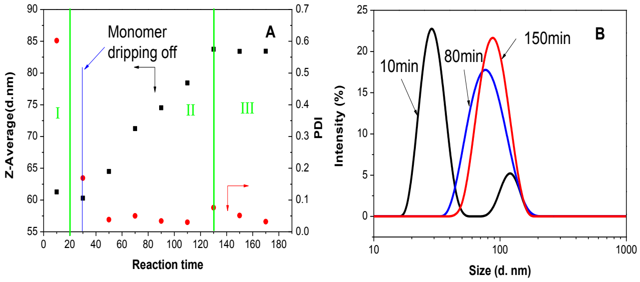


Fig. 3 A: variation of the particle size with the reaction time (I, initial reaction stage; II, middle of reaction stage; III, the end of reaction stage); **B**: variation of particle size distribution with the reaction time. MTES: PTMS=1:1(molar ratio).

Furthermore, we analyzed the change of the particles in the process of emulsion polymerization. Fig.3 showed that hydrolysis-condensation emulsion polymerization of MTES: PTMS=1:4(molar ratio) also had three stages in relation to the particle size change. We calculated the reaction time since the monomer started to be dripped. In the initial reaction I (Fig.3 A), the particle size was smaller but the particle size polydispersity index (PDI) was larger. Fig.3 B showed that the particle size distribution was bimodal. The oligomer could be formed through the hydrolysis and condensation of trialkoxysilane at pH 8~10. Although hydrolysis and condensation of trialkoxysilane monomer occur concurrently,[30] the polymerization degree of oligomers was low for little amount of monomers in this stage, and these oligomers might exist in the aqueous phase, monomer droplets. With the continuous monomer dripping and the degree of polycondensation of polysiloxane oligomers continuing to grow in the water phase until the formation of water insoluble clusters and/or nanoparticles,[20] the blue-fluorescence would be appeared in the emulsion reaction system at 10min, and the nucleation sites which composed of oligomers had been formed. In the middle of the reaction II (see Fig.3 A), the nucleation sites would grow gradually through their surface Si-OH or Si-OR groups condensed with monomer or low molecular oligomer. The mean particle size at 80min was larger than its size at 10min, and there was single peak. (see Fig. 3 A) The appearance of emulsion became milky white with blue fluorescence in this stage. At the end of the reaction period III (see Fig.3 A), the size change of PATOS would be not obvious. After 6 months, the Z- average particle size of latex (MTES: PTMS=1:4) increased. (see S3) This change is possibly caused by coalescence process and condensation of silicon hydroxyl on the surface particles.

Based on these results and discussion, we assume that: (i) the PATOS hybrid core-shell particles can be obtained by emulsion polymerization with PTMS/MTES, PTMS, PTMS/OTMS; (ii) the shell of PATOS hybrid particles is organic layer (alkyl), and the core of those is inorganic layer (Si-O-Si-); (iii) there are three stages of particles change during the emulsion polymerization.

3.2 Effect of monomer mole ratio on PATOS hybrid core-shell latex particle size

Table 1 The synthesis conditions, particle size of PATOS hybrid core-shell latex.

Monomer(molar ratio)	Z-Average (d.nm)	PDI	Monomer contents(wt%)*
PTMS:MTES=1:1	87.6	0.016	30.58
PTMS:MTES=4:1	119.9	0.014	30.54
PTMS	167.5	0.009	30.53
PTMS:OTMS=4:1	125.3	0.014	30.32

*****: mass fraction in the system (monomer weight/ system weight×100%)

Table 1 suggested that the particle size increased as the increase of monomer ratio (PTMS/MTES). Trimethoxysilanes are much more sensitive to hydrolysation than triethoxysilanes and more easily to form gels during polymerization.[20,38] Therefore, combining with nucleation mechanism as-introduced above, the larger the monomer ratio of PTMS/MTES was, the more quickly they reacted, and they were more prone to form highly cross-linked polymers capable of forming larger hybrid core-shell particles. In addition, table 1 also showed that the latex particle size of PTMS/OTMS was smaller than that of PTMS. Monomers with small organic groups (propyl groups) are more reactive toward hydrolysis than those with bulkier substituents (octyl groups) because of charge and steric effects. Therefore, the particle size of hybrid PATOS core-shell latex increases with the increase of the monomer ratio of

PTMS/MTES, and the long alkyl groups of monomers lead to the particle size smaller.

3.3 Properties of PATOS hybrid core-shell Latex

(1) Stability of PATOS hybrid core-shell latex. The stability property was very important for emulsion. We investigated stabilities of PATOS hybrid core-shell latex in polymerization stability (σ), storage stability and centrifugal stability. The σ of emulsion polymerization was shown in Table 2. The σ did not exceed 0.5 percent with the different alkyltrialkoxysilanes molar ratio in the condition that monomer concentration was around 30wt%. It indicated that the stability of alkyltrialkoxysilanes emulsion polymerization was good. The change of latex was no obvious after centrifugation, and there were no sediments after stored 6 months. (Table 2) Thus, the storage stability and centrifugal stability of hybrid emulsion were excellent.

Table 2 Polymerization Stability, Storage Stability and Centrifugal Stability of PATOS hybrid core-shell latex.

Material	σ （wt%）	centrifugal stability	Storage stability(months)
PTMS:MTES=1:1	0.23	No change	6
PTMS:MTES=4:1	0.31	No change	6
PTMS	0.09	No change	6
PTMS:OTMS=4:1	0.29	No change	6

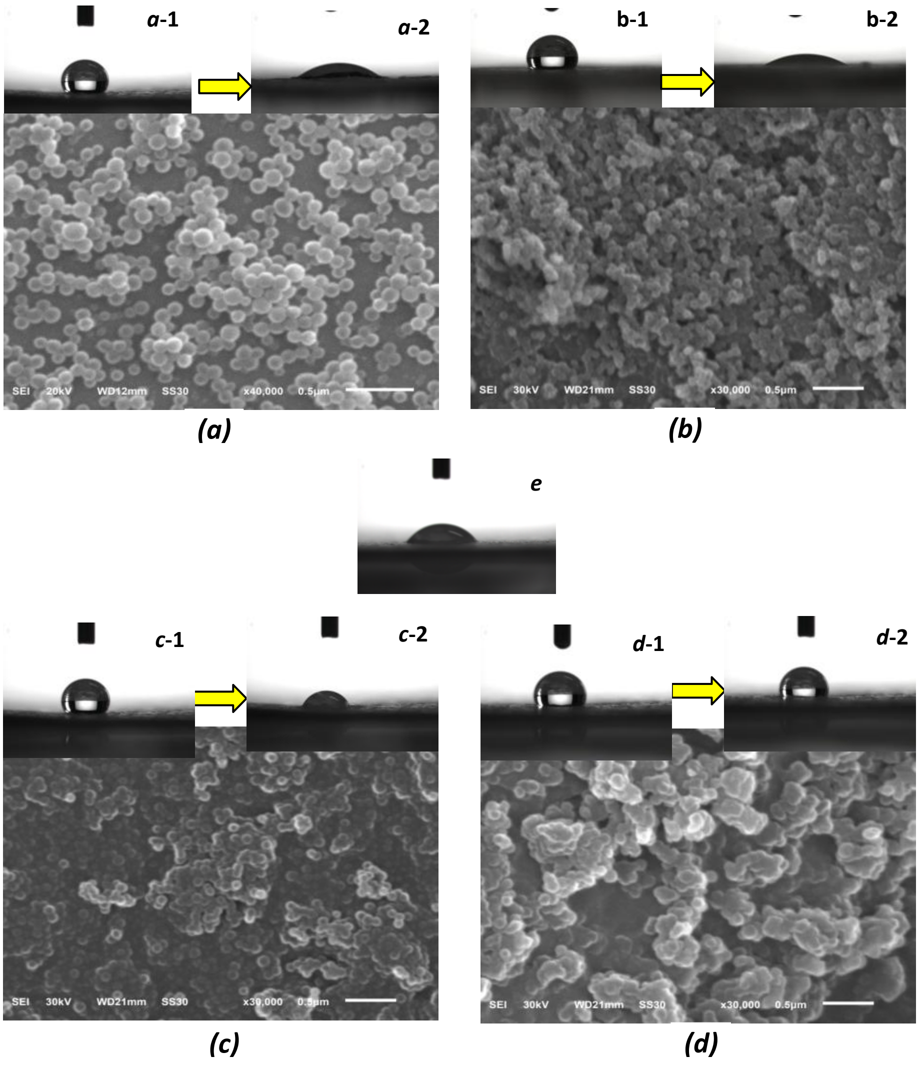


Fig. 4 Typical SEM images of the hybrid PATOS core-shell particles: ***(a)***, PTMS:MTES=1:1; ***(b)***, PTMS:MTES=4:1; ***(c)***, PTMS; ***(d)***, PTMS:OTMS=4:1 and hydrophobicity of the paper ***e*** untreated, ***a*-1**, ***b*-1**, ***c*-1**, ***d*-1** treated by ***(a)*** latexes, ***(b)*** latexes, ***(c)*** latexes, ***(d)*** latexes, respectively. The paper treated with water remaining for 0 and 5minutes (0minute: ***a*-1**, ***b*-1**, ***c*-1**, ***d*-1**; 5minutes: ***a*-2**, ***b*-2**, ***c*-2**, ***d*-2**).

(2) Wettability of the PATOS hybrid core-shell particles. The as-prepared hybrid core-shell particles are constructed by inorganic core and organic shell structure, it is reasonable that their surface wettability will be special. The property was studied by water contact angle (WCA) measurement. As shown in Fig. 4, by contrast, the WCAs of the samples (*a*-1, *b*-1, *c*-1, *d*-1) are similar, which are

122.2°, 121.3°, 123.2°, and 120.2°, respectively. The WCA of the blank space group contrast of the paper untreated is 61.3° (Fig. 4, *e*). However, after remaining for 5minutes, the WCAs decreased remarkably (Fig. 4, *a*-2, *b*-2, *c*-2). Subsequently, the water was absorbed by the paper. Fortunately, the WCA of the sample *d*-2 was 110.8° after remaining 5 minutes, and even more remaining for 10 minutes, the water was not absorbed by the paper but evaporated slowly. This result suggested that the hybrid core-shell latexes had the excellent hydrophobicity. It might be related to the alkyls in the surface of hybrid core-shell particles. It is well known that alkyls as a kind of non-polar groups are hydrophobic. The volume of methyl or propyl group is smaller than that of octyl group so that the roughness and thickness of shell for the core-shell particles with methyl or propyl groups were inferior to those of core-shell particles with octyl groups. That is to say, the inorganic hard core is coated much more compactly by the shell which is constituted by the long alkyl chain.

After the latex samples demulsification, purification, drying and grinding, the white powder was characterized with SEM. The SEM graphs of PATOS hybrid core-shell latex are shown in the Fig. 4. It can be observed that all of samples contained sphere particles (consistent with the TEM results), and also found some continuous irregular aggregates from the graph (*c*) and (*d*). In addition, we found that when the PATOS hybrid core-shell latex with methyl/propyl or propyl was coated on the paper, after curing the coating become white powder instead of film. However, the coating of the PATOS hybrid core-shell latex with octyl/propyl turned into thin film after curing. This might be due to the length of alkyl having an effect on the soft hardness of hybrid particles. Long chain alkyl groups have certain flexibility, thus it can reduce the internal stress during film forming for the cross-linked PATOS hybrid core-shell particles latexes. Therefore, the hydrophobility of the particles are much better as the increase of the length of alkyl chain. Meanwhile, it shows that there is rationality of the core-shell structure previously discussed.

(3) TGA. We measured the thermal properties of the products. The TGA curves of the hybrid PATOS core-shell particles with different molar ratio of trialkylalkoxysilane monomer are shown in Fig. 5. The weight percentages of samples are above 90% when the temperature is 400℃. It indicated that the hybrid core-shell particles had good thermal stability. The molecule of polyalkyltrialkoxysiloxane mainly contains three kinds of covalent bonds Si-O, Si-C and C-C which possess its bond energy 460.5 KJ/mol, 326.4 KJ/mol and 304 KJ/mol.[39,40] Polytrialkoxysiloxanes are polymers with highly branched 3-dimensional structures, and the number of Si-O bonds is the largest. Thus, the TG and DTG curves show that the degradation stage (Si-O), from 450℃ to 550℃, is the dominant in the curves. The DTG curves show that the degradation between 250℃ and 300℃ is mainly caused by the cleavage of Si-C and C-C bond. The FTIR spectra shows that the methyl and methylene absorption peaks decrease significantly after heat treatment in nitrogen atmosphere at 300℃. (see S4-S7)

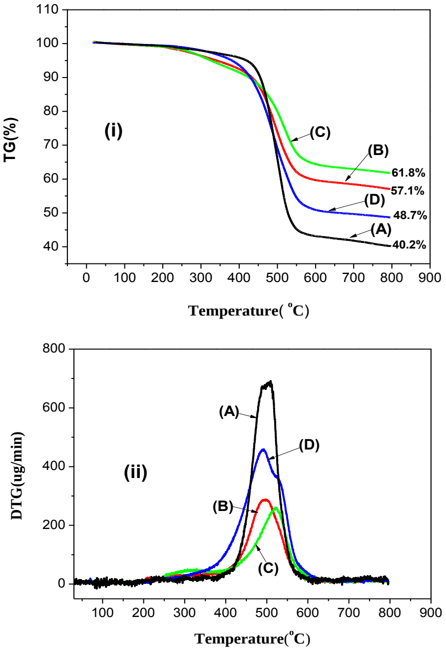


Fig. 5 TGA results of the final obtain hybrid PATOS core-shell particles with different molar ratios of trialkylalkoxsilane during the emulsion polymerization process: **(A)** PTMS:MTES=1:1, **(B)** PTMS:MTES=4:1, **(C)** PTMS, **(D)** PTMS:OTMS=4:1.

The residues of the samples at 800℃ increase from 40.2% to 61.8% from (A) to (C). For (D) (PTMS: OTMS=4:1), the residues are 48.7%. The DTG curves suggest that the order of degradation rate is (A) > (B) > (C) between 450℃ and 550℃. The reason may be that the long alkyl in the backbone of polysiloxanes could cause a chain branching reaction in the degradation process.[39,41] The degree of the cross-linking in the residues would be greater, and the degradation of the residues would be much more difficult. Due to that, the degradation process is further retarded.

4 Conclusions

In summary, we synthesized hybrid poly(alkyltrialkoxysiloxane) (PATOS) core-shell latex via emulsion under the alkaline environment using n-propyltrimethoxysilane (PTMS), Methyltriethoxysilane (MTES)/PTMS, n-octylmethoxysilane (OTMS)/PTMS. The nucleation mechanism and progress of these hybrid core-shell latex particles were investigated. We discussed the nucleation mechanism of hybrid PATOS core-shell particles through modelling, transmission electron microscopy and energy dispersion spectrum. The core-shell particles are formed during the chemical bonds reconstruction, shrinkage and rotation in the hydrolysis and condensation reaction process. The shell of PATOS hybrid particles is organic layer (alkyl), and the core of those is inorganic layer (-Si-O-Si-). The latex particles have three change stages during the emulsion polymerization. The particle size of hybrid PATOS core-shell latex increases with the increase of the monomer ratio of PTMS/MTES, and the long alkyl groups of monomers lead to the particle size smaller. The stability of alkyltrialkoxysilanes emulsion polymerization, the storage stability (6 months) and the centrifugal stability of hybrid emulsion are excellent. The thermal property of the particles is good. The hybrid core-shell latexes had the excellent hydrophobicity (Water contact angle, 110 °-125 °), and this hydrophobility is much more durable as the increase of the length of alkyl chain.

Notes and references

*Ministry of Education Key Laboratory for the Green Preparation and Application of Functional Materials, Hubei University, Wuhan 430062, PR. China. E-mail: Huangsq@hubu.edu.cn(Huang)

Electronic Supplementary Information (ESI) available: Alkyltrialkoxysilane hydrolysis-condensation reaction mechanism. See DOI: 10.1039/b000000x/

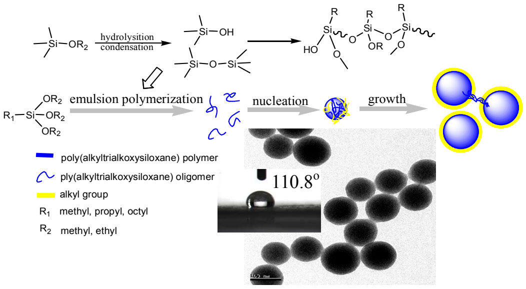
1 M. Álvarez-Paino, G. Marcelo, A. Muñoz-Bonilla, J. Rodríguez-Hernández and M. Fernandez-García. *Polym. Chem.*, 2013, **4**, 986-995.
2 E. Bourgeat-Lami and M. Lansalot. *Adv. Polym. Sci.*, 2010, 233, 53-123.
3 M. Karg and T. Hellweg. *J. Master. Chem.*, 2009, **19**, 8714-8727.
4 G. L. Li, H. Mŏhwald and D. G. Shchukin, *Chem. Soc. Rev.*, 2013, **42**, 3628-3646.
5 R. A. Ramli, W. A. Laftah and S. Hashim. *RSC Adv.*, 2013, **3**, 15543-15565.
6 M. Agrawal, S. Gupya and M. Stamm. *J. Mater.Chem.*, 2011, **21**, 615-627
7 A. V. Jovanoic, R. S. Underhill, T. L. Bucholz, and R. S. Duran. *Chem. Master.*, 2005, **17**, 3375-3383.
8 X. B. Li, Y. Yang and Q. H. Yang. *J. Mater. Chem. A*, 2013, **1**, 1525-1535.
9 A. Peled, V. Kotlyar and J. P. Lellouche. *J. Mater. Chem.*, 2009, **19**, 268-273.
10 H. Xu, L. L. Cui, N. H. Tong, and H. C. Gu. *J. Am. Chem. Soc.*, 2006,**128**, 15582-15583.
11 A. Schmid and S. P. Armes. *Langmuir*, 2009, **25**, 2486-2494.
12 E. L. Bourgeat, M. Insulaire, S. Reculsa, A. Perro, S. Ravaine, E. Duguet. *J. Nanosci. Nanotechnol*, 2006, **6**, 432-444.
13 L. A. Fielding and S. P. Armes. *J. Mater. Chem.*, 2012, **22**, 11235-11244.
14 V. Monteil, J. Stumbaum, R. Thomann, and S. Mecking. *Macromolecules*, 2006, **39**, 2056-2062.
15 J. Fickert, P. Rupper, R. Graf, K. Landfester and D. Crespy. *J. Mater. Chem.*, 2012, **22**, 2286-2291.
16 L. A. Fielding, J. Tonnar, and S. P. Armes. *Langmuir*, 2011, **27**, 11129-11144.
17 D. M. Qi, Y. Z. Bao, Z. X. Weng, Z. M. Huang. *Polymer*, 2006, **47**, 4622-4629.
18 T. Borase, M. Lacono, S. I. Ali, P. D. Thornton, and A. Heise. *Polym. Chem.*, 2012, **3**, 1267-1275.
19 E. Bourgeat-Lami, I. Tissot, and F. Lefebvre. *Macromolecules*, 2002, **35**, 6185-6191.
20 K. F. Ni, G. R. Shan, Z. X. Weng, N. Sheibat-Othman, G. Fevotte, F. Lefebvre, and E. Bourgeat-Lami. *Macromolecules*, 2005, **38**, 7321-7329.
21 K. F. Ni, N. Sheibat-Othman, G. R. Shan, G. Fevotte, and E. Bourgeat-Lami. *Macromolecules*, 2005, **38**, 9100-9109.
22 S. L. Yang, C. F. Song, T. Qiu, L. H. Guo, and X. Y. Li. *Langmuir*, 2013, **29**, 92-101.
23 R. Rodríguez, C. H. Alarcón, P. Ekanayake, P.J. Mcdonald, J. L. Keddie, M. J. Barandiaran, and J. M. Asua. *Macromolecules*, 2008, **41**, 8537-8546.
24 S. Q. Huang, D. Q. Fan, Y. Q. Lei, H. Huang. *J. Appl. Polym. Sci.*, 2004, 94, 954-960.
25 Z. G. Sun, D. Q. Fan, S. Q. Huang. *J. Appl. Polym Sci.*, 2009, **111**, 185-188.
26 J. Zhu, X. Y. Zhang, F. Gao, M. Chen, S. Q. Huang. *J. Polym. Res.*, 2011, **18**, 1991-1997.
27 R. Q. Bai, T. Qiu, M. Duan, G. Ma, L. He, X. Y. Li. *Colloids and surfaces A: Physicochem. Eng. Aspects*, 2012, **396**, 251-257.
28 R. Q. Bai, T. Qiu, C. Xu, L. F. He, X. Y. Li. *Colloid. Polym. Sci.*, 2012, **290**, 769-776.
29 R. Gao, M. Chen, W. Li, S. X. Zhou and L. M. Wu. *J. Mater. Chem. A*, 2013, **1**, 2183-2191.
30 F. D. Osterholtz, and E. R. Pohl. *J. Adhesion. Sci. Technol.*, 1992, **6**, 127-149.
31 J. ŠefčíK, A. V. McCormick. *Catalysis Today*, 1997, **35**, 205-223.
32 X. Y. Su, S. Y. Guang, C. W. Li, H. Y. Xu, X. Y. Liu, X. Wang, and Y. L. Song. *Macromolecules*, 2010, **43**, 2840-2845.
33 H. W. Ro, E. S. Park, C. L. Soles and D. Y. Yoon. *Chem. Mater.*, 2012, **22**, 1330-1339.
34 C. Chen, M. Chen, S. Q. Huang. *J macromol sci A*, 2011, **48**, 478-481.
35 F. Gao, B. Ku, S. Q. Huang. *J Appl. Polym. Sci.*, 2011, **122**, 798-803.
36 T. Matsoukas and E. Guilari, *J. Colloid Interface Sci.*, 1988, **124**, 252.
37 A. Arkhireeva and J. N. Hay. *J. Master. Chem.*, 2003, **13**, 3122-3127.
38 D. A. Loy, B. M. Baugher, C. R. Baugher, D. A. Schneider and K. Rahimian. *Chem. Mater.*, 2000, **12**, 3624-3632.
39 Z. Z. Yang, S. Han, R. Zhang, S. Y. Feng, C. Q. Zhang, S. Y. Zhang. *Poly. Degrad. Stabil.*, 2011, **96**, 2145-2151.
40 Z. Z. Yang, L. Feng, S. Diao, S. Y. Feng, C. Q. Zhang. *Thermochim. Acta*, 2011, **521**, 170-175.
41 N. Grassie, S. R. Beattie. *Poly. Degrad. Stabil.*, 1984, **7**, 231-250.

Synthesis and Properties of Hybrid Core-Shell Poly(alkyltrialkoxysiloxane) Latex

Bo Liu, Shiqiang Huang*, Zushun Xu, Feng Gao and Jie Zhu

Ministry of Education Key Laboratory for the Green Preparation and Application of Functional Materials, Hubei University, Wuhan 430062, PR. China. E-mail: Huangsq@hubu.edu.cn.

Graphic abstract:



We discussed the nucleation mechanism and progress of the hybrid core-shell poly(alkyltrialkoxysiloxane) latex particles.