Colloid Polym Sci (2008) 286:283–291
DOI 10.1007/s00396-007-1767-9

ORIGINAL CONTRIBUTION

Raspberry-like polymer/silica core-corona composite by self-assemble heterocoagulation based on a hydrogen-bonding interaction

Junyou Wang · Xinlin Yang

Received: 28 July 2007 / Revised: 18 August 2007 / Accepted: 20 August 2007 / Published online: 12 September 2007

Abstract Raspberry-like poly(ethyleneglycol dimethacrylate-*co*-4-vinylpyridine)/silica (poly(EGDMA-*co*-VPy)/SiO_2) core-corona composite was prepared by a self-assemble heterocoagulation based on a hydrogen-bonding interaction between the pyridyl group of poly(EGDMA-*co*-VPy) core and the active hydroxyl group of silica corona. The raspberry-like composite was stable near the neutral environment with pH ranging from 5.0 to 8.0. The effects of the solvent and the mass ratio of silica to polymer microsphere on the coverage of the silica corona on poly(EGDMA-*co*-VPy) core were investigated in detail. The resultant core-corona heterocoagulates were characterized with scanning electron microscope and the nature of the interaction between the polymer core particle and silica corona particle was identified as hydrogen bonding with Fourier Transform Infrared spectroscopy.

Keywords Self-assemble heterocoagulation ·
Organic–inorganic composite ·
Hydrogen-bonding interaction

Introduction

During the last two decades, the combination of the properties of inorganic and organic building blocks within a single material has attracted increasing attention for material scientists due to their possible combination of the various functional groups of organic components with the advantages of a thermally stable and robust inorganic substrate [1, 2]. These composite materials can exhibit novel and excellent properties, such as mechanical, electrical, rheolgical, magnetic, optical, and catalytic by varying the compositions, dimensions, morphologies, and structures, which have promised diverse applications as drug delivery system, diagnostics, coatings, and catalysis [3–9]. Several techniques have been reported for the preparation of organic/inorganic composite particles with various interesting morphologies such as silica core/organic shell [10], organic core/silica shell [11], raspberry like [12], snowman like [13], daisy shaped and multipod like [14], and raisinbun like [15]. The silica/polymer composite particles can be generally afforded by two categories: the self-assembly of the resultant silica and polymer particles via physical or physicochemical interaction and the direct polymerization of monomer on the surface of silica particles. Raspberry-like particles have been electrostatically self-assembled by positively charged polyferrocenylsilane microspheres and negatively charged silica particles [16, 17]. Layer-by-layer (LbL) deposition [18–22] has been utilized to prepare a range of polymer-core/inorganic-shell particles via subsequential adsorption of polyelectrolytes (PEs) with opposite charges onto silica particles with the aid of electrostatic interaction. Fleming et al. [8] prepared raspberry-like composites from silica microspheres and polystyrene nanospheres by either the reaction of amine and aldehyde groups or the biochemical interaction between avidin and biotin. Bourgeat-Lami et al. [21–23] synthesized silica/organic hybrid particles by dispersion polymerization and emulsion polymerization [24, 25] in which it was difficult to control the morphology of the resultant silica/polymer particles, and the encapsulation efficiencies of the polymer on the silica core were very low.

J. Wang · X. Yang (✉)
Key Laboratory of Functional Polymer Materials,
Ministry of Education, Institute of Polymer Chemistry,
Nankai University,
Tianjin 300071, China
e-mail: xlyang88@nankai.edu.cn

Well-defined silica/polymer hybrids have been synthesized by surface-initiated atom transfer radical polymerization with the initiator-modified silica as macroinitiators [26–28] in which the synthesis needed long reaction time and conversion of monomer to silica/polymer hybrids was low.

Hydrogen bonding is essential to the very basic process of life as protein recognition or DNA duplication, which has been widely used to induce supramolecular ordering in synthetic polymer systems [29–31]. Multilayer films of weak PEs have been fabricated by LbL self-assembly [32, 33], in which the hydrogen-bonding interaction has played a key role as a driving force for such construction. All these results suggest the possibility of using hydrogen-bonded multilayer films based on PEs in various applications as micropattering and drug delivery due to their stimuli-response to pH changes in the presence of electrostatic repulsion between layers within the films, in which the control of de-construction rate of the hydrogen-bonded films is desirable.

In our previous work, we reported the preparation of anomalous core-corona polymer composite with a raspberry-like structure having uneven surfaces by a self-assembled heterocoagulation based on a charge compensation mechanism between the carboxylic acid group and pyridinium group [34], a hydrogen-bonding interaction between the carboxylic acid group and pyridyl group [35], and a synergic hydrogen-bonding interaction between the carboxylic acid group and amide group [36]. In the present work, we describe the self-assembled heterocoagulation of polymer/silica composite with a raspberry-like structure via a hydrogen-bonding interaction between the pyridyl group of poly(ethyleneglycol dimethacrylate-*co*-4-vinylpyridine) (poly(EGDMA-*co*-VPy)) core and the hydroxyl group of silica corona. The core-corona polymer/silica composite with novel characteristics may be expected to extend its application in a wide variety of fields as the functional fine particles, and as the chemical, biological, pharmaceutical, and hydrophobic materials.

Experimental

Materials Ethyleneglycol dimethacrylate (EGDMA) was obtained from Aldrich Chemical Co. and utilized without any further purification. 4-Vinylpyridine (VPy) was purchased from Acros and distilled under vacuum. 2,2′-Azobisisobutyronitrile (AIBN, Chemical Factory of Nankai University) was recrystallized from methanol. Tetraethyl orthosilicate ($Si(OC_2H_5)_4$, TEOS) was available from Aldrich and used without any further purification. Acetonitrile (analytical grade, Tianjin Chemical Reagents II) was dried over calcium hydride and purified by distillation before use. All the other reagents were of analytical grade and used without any further purification.

Synthesis of silica particles

Silica particles were prepared according to the classical Stöber method [37]. TEOS of 11 ml was added to the mixture of 20 ml of deionized water and 200 ml of ethanol, in which 4 ml of 25 wt% ammonium aqueous solution was added with vigorous stirring at room temperature, and the reaction was continued further for 24 h with stirring. The resultant silica particles were then purified by three cycles of centrifugation, decantation, and resuspension in ethanol with ultrasonic irradiation. The silica particles were dried in a vacuum oven at 50 °C until constant weight was reached.

Preparation of poly(EGDMA-*co*-VPy) microspheres

The synthesis of poly(EGDMA-*co*-VPy) microspheres by distillation precipitation copolymerization of EGDMA and VPy in neat acetonitrile was reported in detail in our previous paper [38]. A typical procedure for such copolymerization was as follows: EGDMA (1.2 ml, 1.26 g, 6.3 mmol), VPy (0.80 ml, 0.80 g, 7.2 mmol), AIBN (0.04 g, 0.24 mmol, 2 wt% relative to the whole comonomer) initiator were dissolved in 80 ml of acetonitrile in a dried 100-ml two-necked flask attached with a fractionating column, Liebig condenser, and a receiver. The flask was submerged in a heating mantle, and the reaction mixture was heated from ambient temperature until boiling state within 15 min, and the reaction mixture was kept under refluxing state for 5 min. Then the solvent was distilled off the reaction system, and the reaction was stopped after 40 ml of acetonitrile was distilled from the reaction system within 1.5 h. After polymerization, the resultant poly(EGDMA-*co*-VPy) microspheres were purified by vacuum filtration over a G-5 sintered glass filter with subsequent washing with tetrahydrofuran and acetone three times. The final poly(EGDMA-*co*-VPy) particles were suspended in a suitable solvent, and the solid concentration was adjusted to 10 mg/ml for the self-assembly.

Preparation of raspberry-like core-corona poly(EGDMA-*co*-VPy)/Silica composite by self-assembled heterocoagulation

Self-assembled heterocoagulation of small silica particles on poly(EGDMA-*co*-VPy) surfaces was performed as follows: 2 mg of cross-linked poly(EGDMA-*co*-VPy) (10 mg/ml suspended in ethanol) core particles were dispersed in 5 ml suspension of silica particles with different concentrations in ethanol on an SHA-B shaker. The self-assembled heterocoagulation was carried out with gentle agitation by rolling the bottles in a horizontal position at approximately 50 rpm for 20 h. The resulting heterocoagulates were purified by alternative centrifugation and resuspension in ethanol three times and then dried in a vacuum oven.

The effect of pH on the morphology of the composite particles was determined by using either 0.1 M HCl or 0.1 M NaOH aqueous solution to adjust the pH in the range of 1–13.

The effect of the solvent on the morphology of the raspberry-like composite was investigated by suspending the resultant core-corona composite in an ultrasonic bath in different solvents, including *N,N*-dimethylformamide (DMF), methanol, acetonitrile, and water.

Characterization

The morphology of the silica, poly(EGDMA-*co*-VPy) and the resultant poly(EGDMA-*co*-VPy)/silica core-corona composite heterocoagulates were studied by scanning electron microscope (SEM, Philips XL-30) and transmission electron microscope (TEM, Tenai G2 20 S-TWIN). The particle size and size distribution of the particles are determined by SEM and TEM as well.

Fourier-transform infrared (FTIR) analysis was performed with a Bio-Rad FT-135 FTIR spectrometer, and the diffuse reflectance spectra were scanned over the range of 400–4,000 cm^{-1}.

Results and discussion

The TEM micrograph of silica from a sol-gel process as shown in Fig. 1a indicated that the silica particles had a spherical shape with an average size of 116 nm and monodispersity index (U) of 1.006.

Distillation precipitation polymerization has been proven to be a useful and facile technique for the synthesis of monodisperse polymer microspheres with different functional groups with high accessibility on a gel-layer and surfaces [36, 38–40]. The TEM image of the poly (EGDMA-*co*-VPy) microspheres by distillation precipitation polymerization is illustrated in Fig. 1b, which shows that the polymer particles had a spherical shape with a smooth surface. The average size and size distribution of poly(EGDMA-*co*-VPy) microspheres were 1.28 μm and 1.02, respectively. The loading capacity of the accessible pyridyl group on the poly(EGDMA-*co*-VPy) surface by distillation precipitation polymerization was 1.28 mmol/g determined by acid-base titration [38].

Heterocoagulation behavior through self-assembly

It is crucial to work with the polymer microspheres and silica particles rather than small molecules with only one

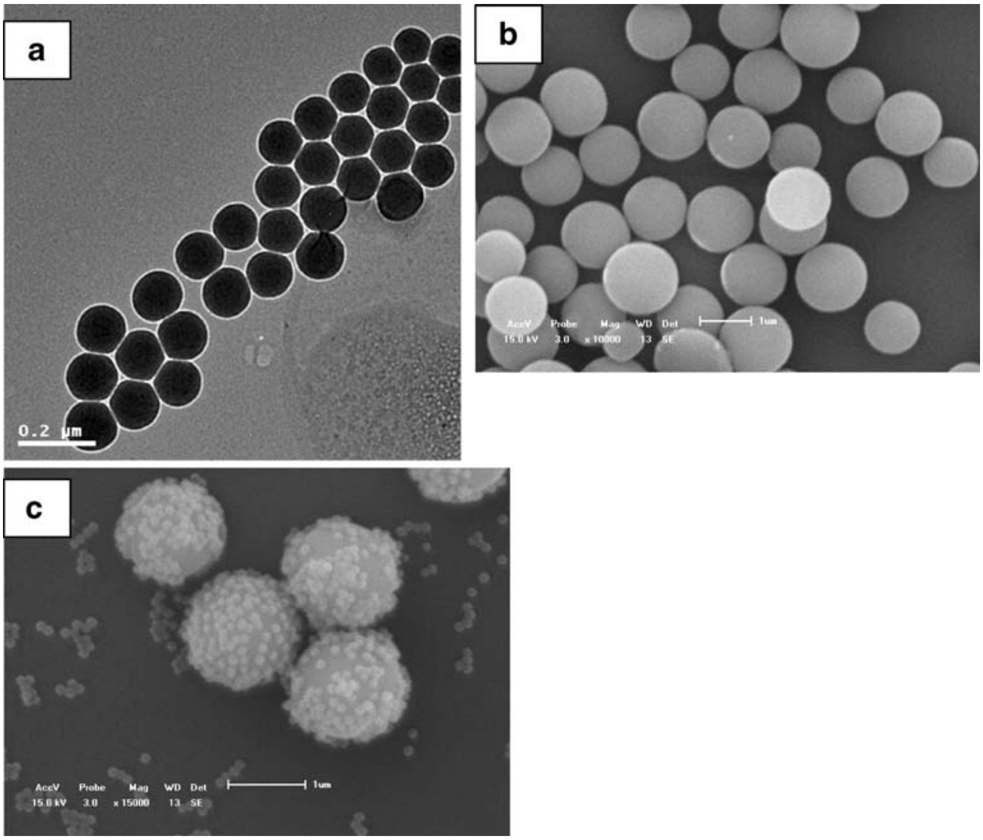


Fig. 1 Micrographs: **a** TEM for silica particles; **b** SEM for poly(EGDMA-*co*-VPy) microspheres; **c** SEM for self-assembled poly(EGDMA-*co*-VPy)/silica composite from ethanol with mass ratio of 1/2

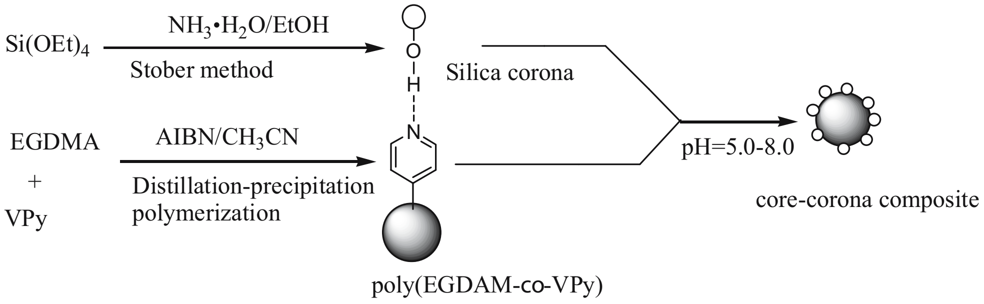
limited spot for interaction because the microspheres provide many spots for interparticle interaction for the construction of a single integral composite consisting of two different particles. The preparation of polymer/silica core-corona composite with a raspberry-like structure based on a hydrogen-bonding interaction via self-assembled heterocoagulation is illustrated in Scheme 1.

As is well known, pyridyl group and hydroxyl group on the silica surface were good hydrogen-bonding complementary partners, which were used to prepare currant-bun-like polymer-silica nanocomposite [3], and the nature of the hydrogen-bonding interaction has been investigated in detail by FTIR spectra [41]. In the present work, core-corona poly(EGDMA-*co*-VPy)/silica composite particles with a raspberry-like structure were produced by self-assembly based on an interparticle hydrogen-bonding interaction mechanism as shown in Scheme 1. The hydrogen-bonding complementary partners between the pyridyl group and hydroxyl group used were poly(EGDMA-*co*-VPy) microspheres and silica particles in which poly(EGDMA-*co*-VPy) acted as core and silica behaved as the corona. The typical SEM micrograph of the resultant poly(EGDMA-*co*-VPy)/silica core-corona composite from ethanol is shown in Fig. 1c, in which the efficient coverage of silica corona particles on the surface of poly(EGDMA-*co*-VPy) core microspheres was clearly observed.

The raspberry-like titania-silica (TS-SiO_2) composite was formed by the encapsulation of SiO_2 microspheres driven by heterocoagulation between the positively charged TS clusters and the negatively charged SiO_2 particles [42]. Composite particles with a core-shell structure have been obtained by self-assembly of oppositely charged silica particles and polymers [16–18]. The specific chemical (amine-aldehyde) and biological (avidin-biotin) interaction between a silica core and polystyrene shell have been used to afford the core-shell composite materials via self-assembly [8]. The core-shell composite particles were produced by heterocoagulation based on either hydrophobic [43] or electrostatic interaction between the large and small oppositely charged colloid particles [20]. Here, the raspberry-like poly(EGDMA-*co*-VPy)/silica core-corona particles were constructed by self-assembly with the aid of interparticle hydrogen-bonding interaction as illustrated in Scheme 1, in which the pyridyl group of poly(EGDMA-*co*-VPy) core microspheres acted as a lone-electron pair donor, and the hydroxyl group of silica having active hydrogen atom behaved as an electron acceptor. Such interparticle hydrogen-bonding interaction played the key role as the driving force for the heterocoagulation, which was different from those reported in the literature [8, 16–18, 20, 38–40, 42, 43]. It was evident that such driving force for the self-assembly of poly(EGDMA-*co*-VPy) core and silica corona competed favorably with the existed-interparticle association of hydroxyl groups of the silica corona particles.

The raspberry-like composites have provided characteristics uniquely different from those in homogeneous media and film states, such as uneven surfaces with a large area. To understand the hydrogen-bonding interaction mode between the host poly(EGDMA-*co*-VPy) microspheres and guest silica particles during the self-assembly, FTIR spectra were measured for these two particles and the raspberry-like composites as shown in Fig. 2. For silica particles, the FTIR spectrum in Fig. 2a had a middle peak at 1,166 cm^{-1} corresponding to the stretching vibration of Si-O-Si. For both the poly(EGDMA-*co*-VPy) microspheres and the raspberry-like composites, the FTIR spectra showed a strong peak at 1,596 cm^{-1} and a middle peak at 1,556 cm^{-1} assigning to the typical vibration of the pyridyl group, which were similar to the results in the literature [44]. The presence of a new peak at 1,108 cm^{-1} of the FTIR spectrum in Fig. 2c for the raspberry-like composites demonstrated that the interparticle hydrogen-bonding interaction occurred between the host and guest particles through the hydroxyl group and pyridyl group complementary partners. In other words, the interparticle hydrogen-bonding interaction between the hydroxyl group of the silica with the active hydrogen as electron-acceptor and the pyridyl group of poly(EGDMA-*co*-VPy) with a lone electron pair as electron-donor acted as a driving force for the construction of the organic/inorganic composites having raspberry-like structure in the present work.

Scheme 1 Preparation of core-corona poly(EGDMA-*co*-VPy)/silica composite with a raspberry-like structure



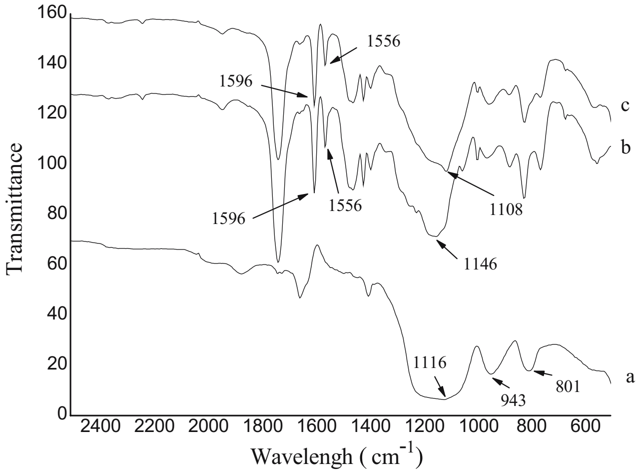


Fig. 2 FT-IR spectra: *a* indicates Silica corona; *b* indicates poly (EGDMA-*co*-VPy) core; *c* indicates poly(EGDMA-*co*-VPy)/silica composite

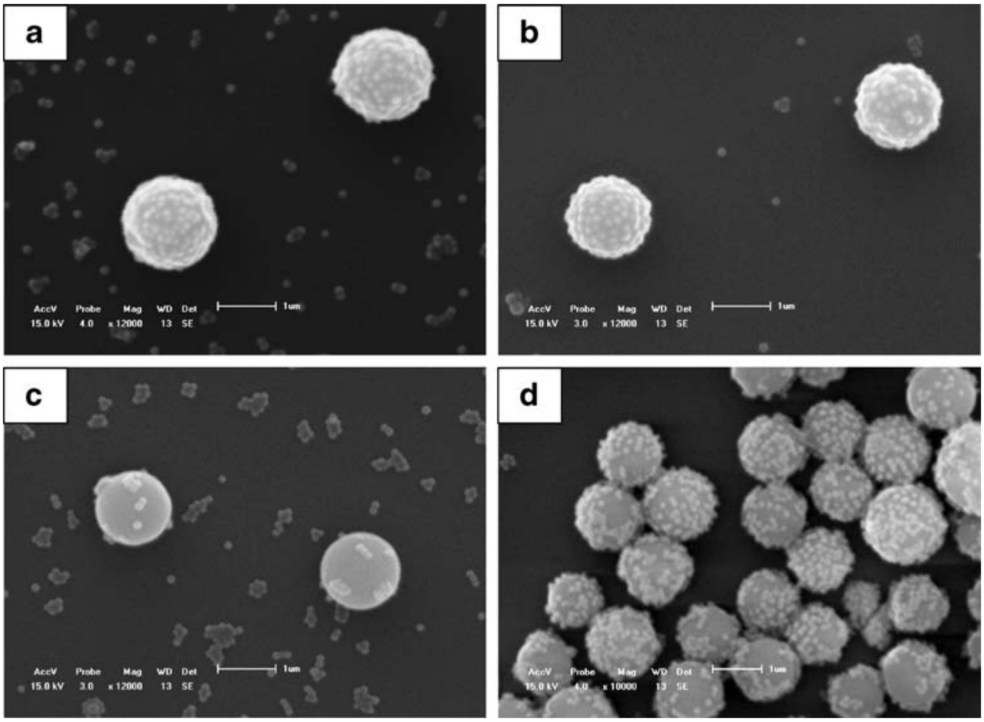
Effect of the ratio of corona to core particles on the morphology of the organic/inorganic composite

In the present work, the silica particles were adsorbed onto the surface of poly(EGDMA-*co*-VPy) microspheres via interparticle hydrogen-bonding interaction. To understand the effect of the resultant silica corona concentration on the morphology of the resultant composite particles, the mass ratio of the silica particle to poly(EGDMA-*co*-VPy) microsphere was varied from 1/1 to 1/8. The SEM micrographs of the prepared core-corona heterocoagulates with different silica particle loadings were illustrated in Fig. 3. The results indicated that the coverage of the silica corona particles on the poly(EGDMA-*co*-VPy) core surface was very high when silica/poly(EGDMA-*co*-VPy) was higher than 1/4 (mass ratio, Figs. 1c and Fig. 3a,b). While the mass ratio of silica particle to poly(EGDMA-*co*-VPy) microspheres was less than 1/8, the coverage of corona particles on the core surface was dramatically decreased as shown in Fig. 3c.

The mass ratio of silica corona particles to poly (EGDMA-*co*-VPy) core microsphere was kept at 1/2 for all the following experiments for the self-assembled heterocoagulation in the present work.

The organic/inorganic composites precipitated from the suspension after the self-assembly, while the residual silica particles were suspended in the system. The suspended silica particles can be readily removed from the self-assembled system with the aid of ultracentrifugation. The SEM images of Fig. 3d demonstrated that the coverage of the silica particles onto the poly(EGDMA-*co*-VPy) surface decreased slightly after the residual silica particles were removed from the system by ultracentrifugation. Such results indicated that the stability of the resultant silica/poly(EGDMA-*co*-VPy) composites were enough to support such removal, although the hydrogen-bonding interaction between the hydroxyl group of silica corona particle and the pyridyl group of poly(EGDMA-*co*-VPy) core particle was a kind of secondary weak interaction. This was much different from our previous work for the self-assembly of poly(EGDMA-*co*-VPy)/poly(EGDMA-*co*-acrylic acid) composites, in which the coverage of poly(EGDMA-*co*-

Fig. 3 Effect of mass ratio of silica corona particle to poly (EGDMA-*co*-VPy) core microsphere on the morphology of the raspberry-like polymer/inorganic composite: **a** 1:1, **b** 1:4, **c** 1:8, **d** composite after the removal of residual silica particle by ultracentrifugation



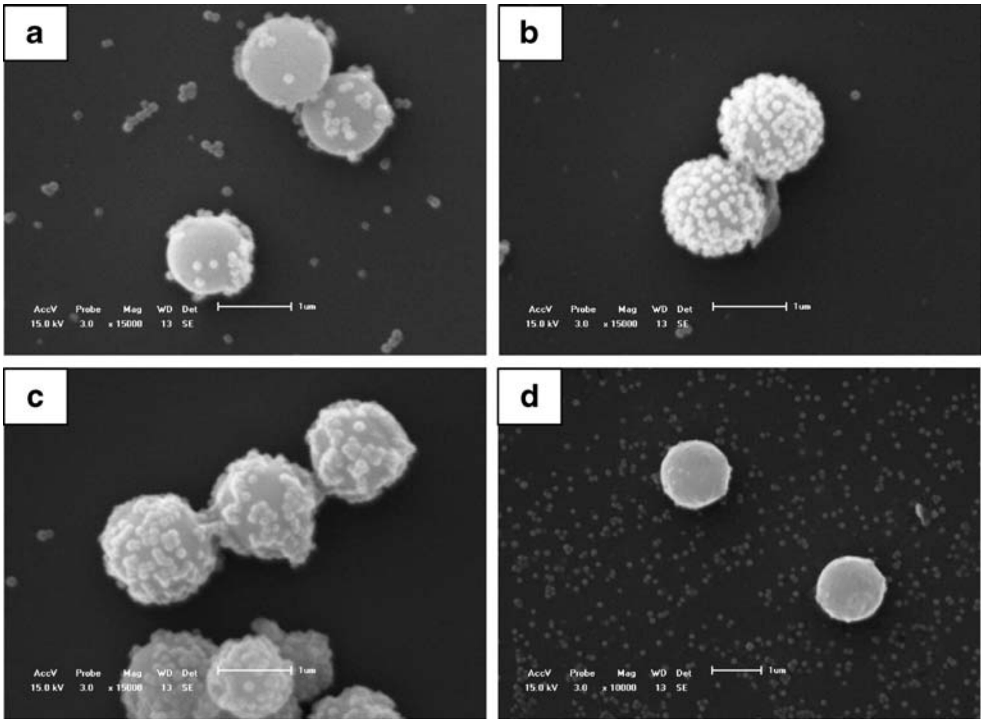
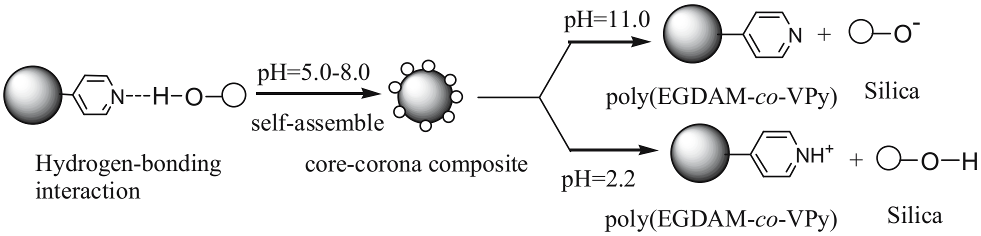


Fig. 4 Effect of pH on the morphology of the core-corona oly(EGDMA-*co*-VPy)/silica composite: **a** pH 2.2, **b** pH 5.1, **c** pH 8.2, **d** pH 11.0

acrylic acid) small particles was decreased significantly with the removal of the corona particles from the system in a dynamic equilibrium state [35]. These results demonstrated that the hydrogen-bonding interaction between the hydroxyl group of silica and the pyridyl group of poly(EGDMA-*co*-VPy) microsphere was much stronger than that between the pyridyl group of poly(EGDMA-*co*-VPy) microsphere and the carboxylic acid group of poly(EGDMA-*co*-acrylic acid).

Effect of pH on the morphology of the organic/inorganic raspberry-like composites

As the hydrogen-bonding interaction is pH sensitive, the pH of the self-assembled system should have crucial impact on the morphology of the poly(EGDMA-*co*-VPy)/ silica composite particles. The pH-sensitive deconstruction characteristics of hydrogen-bonded layers have been studied in detail for the heterogeneous multilayer films comprising alternate stacks of poly(4-vinylpyridine; PVPy) and poly(acrylic acid) via the LbL assembly technique [45]. Here, Fig. 4 showed the SEM micrographs of poly(EGDMA-*co*-VPy)/silica composites under different environmental pH conditions. The results indicated that the stable core-corona organic/inorganic composite particles can only be obtained near neutral conditions with pH in the range of 5.0 and 8.0 as shown in Fig. 4b and c. The heterocoagulates were mainly decomposed under acid environment with a pH value of 2.2 as shown in Fig. 4a and were completely destroyed when the pH was raised above 11.0 as illustrated in Fig. 4d. As pyridyl group of poly(EGDMA-*co*-VPy) microsphere was a weak base and the silica surface with active hydroxyl group was a weak acid, the pyridyl group was probably protonated in acid with the ethanol as solvent ($pH<5.0$) [41], and the hydroxyl group of silica was partially ionized under basic conditions [46]. In the present work, the silica corona particles cannot provide active hydrogen atom as the electron acceptor under basic condition with pH as high as 11.0 due to the partial ionization of the hydroxyl group, and the pyridyl group of poly(EGDMA-*co*-VPy) cannot act as the electron donor under acid condition with pH as low as 2.0 for the partial



Scheme 2 Mechanism of the construction of the core-corona poly(EGDMA-*co*-VPy)/silica composite

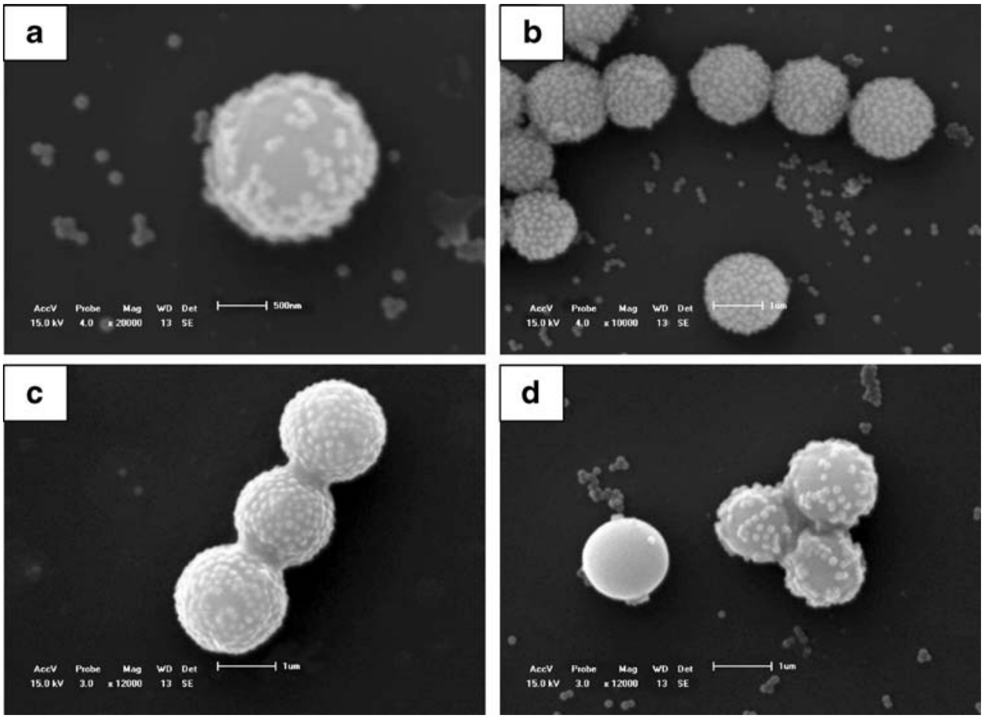


Fig. 5 Effect of the solvent on the morphology of the core-corona poly(EGDMA-*co*-VPy)/silica composite: **a** DMF, **b** Acetonitrile, **c** MeOH, **d** H_2O

protonation, which led to the deconstruction of the resultant organic/inorganic raspberry-like composite as illustrated in Scheme 2. While the pH of the environment ranged from 5.0 and 8.0, the stable raspberry-like composites could be obtained via the efficient interparticle hydrogen-bonding interaction between the hydroxyl group of silica corona particle and the pyridyl group of poly(EGDMA-*co*-VPy) core microspheres as shown in Scheme 1. In other words, a unique aspect of the present self-assembly technique was reversibility: the organic/inorganic heterocoagulates can not only be formed but can also be destroyed by the convenient control of the pH of the environment. Practical applications of such organic/inorganic composites may be suggested as the drug-delivery vehicle because of the sharp structure transition according to the pH change of the environment.

Solvent-induced morphology transition of organic/inorganic composite

The effect of the solvent conditions on the morphology of the raspberry-like organic/inorganic composites was investigated by means of transferring the self-assembled composites to various solvents with different polarities and the hydrogen-bonding parameters. The SEM micrographs of the resultant poly(EGDMA-*co*-VPy)/silica composites from different solvents were shown in Fig. 5.

The three-dimensional Hansen parameters describe the whole interaction between a solute and a solvent as disperse, polar, and hydrogen-bonding interactions [47] (Table 1). Particularly, the hydrogen-bonding parameter (δ_h) and the polar parameter (δ_p) correlate with the key polymer-solvent interactions and should have a large influence on the morphology of the resultant organic/inorganic raspberry-like composites. The effect of the solvent on the morphology of the core-corona polymer composites of poly(EGDMA-*co*-VPy)/poly(EGDMA-*co*-acrylic acid) was investigated in various solvents having different polarities and hydrogen-bonding parameters in our previous work [35]. In this study, the results indicated that the coverage of the silica corona on poly(EGDMA-*co*-VPy) microsphere was much higher with little change in the solvents with low and moderate values of the hydrogen-bonding parameters, δ_h=6.1–22.3 MPa$^{1/2}$, such as in acetonitrile (Fig. 5b), methanol (Fig. 5c) and ethanol (Fig. 1c). The coverage decreased drastically in the solvent with high hydrogen-bonding parameters such as water (δ_h= 6.1–22.3 MPa$^{1/2}$, Fig. 5d), which may be due to the strong

Table 1 Three-dimensional Hansen parameters describing the whole interaction between a solute and a solvent as disperse, polar, and hydrogen-bonding interactions [47]

Solvent	δ_d (MPa)$^{1/2}$	δ_p (MPa)$^{1/2}$	δ_h (MPa)$^{1/2}$
MeOH	15.1	12.3	22.3
EtOH	15.8	8.8	19.4
DMF	17.4	13.7	11.3
CH_3CN	24.3	18.0	6.1
H_2O	15.5	16.0	42.4

δ_d Disperse Hansen parameter, δ_p Polar Hansen parameter, δ_h Hydrogen-bonding Hansen parameter.

complete hydrogen-bonding interaction between water and hydroxyl group of silica particle. The core-corona composite partially decomposed in DMF with only intermediate parameters (δ_h=11.3 MPa$^{1/2}$, Fig. 5a), which may be due to the strong synergic hydrogen-bonding interaction between the amide group of DMF and the hydroxyl group of silica corona. The strong synergic hydrogen-bonding interaction between the amide group and the hydroxyl group of silica core has been successively utilized as a driving force for the preparation of monodisperse silica/poly(*N,N′*-methylene bisacrylamide) core-shell composite materials in our previous work [48]. All these results demonstrated that acetonitrile and alcohols with low and intermediate hydrogen-bonding parameters are appropriate solvents for the formation of inter-particle hydrogen-bonding interaction between the pyridyl group of poly(EGDMA-*co*-VPy) core and hydroxyl group of silica corona to construct an organic/inorganic core-corona composite with a raspberry-like structure. The preparation of the other core-corona structure polymer/inorganic composites with raspberry-like morphology via interparticle interaction, such as titania oxide/polymer and zirconia oxide/polymer, is in progress, which would present construction as a general technique for the other composite systems.

Conclusion

Silica small particles were efficiently self-assembled on the surface of poly(EGDMA-*co*-VPy) microsphere to form an organic/inorganic composite with a raspberry-like structure with the aid of interparticle hydrogen-bonding interaction. The results demonstrated systematically that the core-corona composite was formed through the hydrogen-bonding interaction mechanism between the lone electron pair of the pyridyl group of poly(EGDMA-*co*-VPy) core as electron donor and the hydroxyl group of the silica corona as electron acceptor. The stable raspberry-like composite particles with a high coverage were obtained when the silica/poly(EGDMA-*co*-VPy) was higher than 1/4 as mass ratio near neutral conditions with pH ranging from 5.0 to 8.0. The resultant heterocoagulates decomposed under acid condition due to the protonation of the pyridyl group of poly(EGDMA-*co*-VPy) core microsphere and under basic condition for the partial ionization of the hydroxyl group on the surface of silica corona particle. The solvent had a significant effect on the morphology of the resultant core-corona polymer/inorganic composites, which can be well interpreted by three-dimensional Hansen solvent parameters.

Acknowledgement This work was supported in part by the National Science Foundation of China (Project no. 20504015) and the Opening Research Fund from the State Key Laboratory of Polymer Chemistry and Physics, Chinese Academy of Sciences (Project no. 200613).

References

1. Zhang YD, Lee SH, Yonessi M, Liang KW, Pittman CU (2006) Polymer 47:2984
2. Strachotova B, Strachota A, Uchman M, Slouf M, Brus J, Plestil J, Matejka L (2007) Polymer 48:1471
3. Percy MJ, Barthet C, Lobb JC, Khen MA, Lascelles SF, Vamvakaki M, Armes SP (2000) Langmuir 16:6913
4. Chen M, Zhou SX, You B, Wu LM (2005) Macromolecules 38:6411
5. Caruso F, Lichtenfeld H, Giersig M, Möhwald H (1999) J Am Chem Soc 120:8523
6. Tiarks F, Landfester K, Antonietti M (2000) Langmuir 17:5775
7. Ming W, Wu D, van Berrithem R, de With G (2005) Nano Lett 5:2298
8. Fleming MS, Handal TK, Walt DR (2001) Chem Mater 13:2210
9. Hu YQ, Wu HP, Gonsadves KE, Merhari L (2001) Microelectron Eng 56:289
10. Zhang K, Chen HT, Chen X, Chen ZM, Cui ZC, Yang B (2003) Macromol Mater Eng 288:380
11. Tissot I, Novat C, Lefebvre F, Bourgeat-Lami E (2002) Macromolecule 34:5737
12. Reculusa S, Poncet-Lagrand C, Ravaine S, Minogotaud S, Dauget E, Bourgeat-Lami E (2002) Chem Mater 14:2354
13. Dero A, Reculusa S, Bourgeat-Lami E, Doguet E, Revaine S (2006) Colloid Surf A 284–285:78
14. Reculusa S, Mingotaud C, Bourgeat-Lami E, Duguet E, Ravaine R (2004) Nano Lett 4:1677
15. Barthlet C, Hickey AJ, Larins DB, Armes SP, (1999) Adv Mater 11:408
16. Kulbaba K, Resendes R, Cheng A, Bartole A, Safa-Sefat S, Coombs N, Stöver HDH, Greedan JE, Ozin GA, Manners I (2001) Adv Mater 13:732
17. Kulbaba K, Cheng A, Bartole A, Greenberg S, Resendes R, Coombs N, Safa-Sefat A, Greedan JE, Stöver HDH, Ozin GA, Manners I (2002) J Am Chem Soc 124:12522
18. Caruso F, Caruso RA, H. Möhwald (1998) Science 182:400
19. Caruso RA, Susha A, Caruso F (1999) Chem Mater 11:3309
20. Caruso F, Lidenfeld H, Giersig M, Möhwald H (1998) J Am Chem Soc 120:8523
21. Bourgeat-Lami E, Lang J (1998) J Colloid Interface Sci 197:293
22. Bourgeat-Lami E, Lang J (1999) J Colloid Interface Sci 210:281
23. Corcos F, Bourgeat-Lami E, Novat C, Lang J (1999) Colloid Polym Sci 277:1142
24. Tiarks F, Landfester K, Antonietti M (2001) Langmuir 17:5775
25. Lula-Xavier JL, Guyot A, Bourgeat-Lami E (2001) J Colloid Interface Sci 250:82
26. von Werne T, Patten TE (1999) J Am Chem Soc 121:7409
27. Perruchot C, Khan MA, Kamitsi A, Armes SP (2001) Langmuir 17:4479
28. Harrak AE, Carrot G, Oberdisse J, Jestin J, Boue F (2005) Polymer 46:1095
29. Ruokolainen J, Brinke GT, Ikkala O, Torkkeli M, Serimaa R, (1989) Macromolecules 29:3409
30. Bondzic S, Wit JD, Polushkin E, Schouten AJ, Brinke GT, Ruokolainen J, Ikkala O, Dolbnya I, Bras W, (2004) Macromolecules 37:9517
31. Stockron WB, Rubner MF (1997) Macromolecules 30:2717
32. Zhang HY, Wang ZQ, Zhang YQ, Zhang X (2004) Langmuir 20:9366
33. Sukhishvili SA, Granid S (2000) J Am Chem Soc 122:9550
34. Li GL, Yang XL, Bai F, Huang WQ (2006) J Colloid Interface Sci 297:705
35. Li R, Yang XL, Li GL, Li SN, Huang WQ (2006) Langmuir 22:8127

36. Li GL, Song YY, Yang XL, Huang WQ (2007) J Appl Polym Sci 104:1350
37. Stöber W, Fink A (1968) J Colloid Interface Sci 26:62
38. Li SN, Yang XL, Huang WQ Chin J Polym Sci in press
39. Bai F, Yang XL, Huang WQ (2004) Macromolecules 37:9746
40. Liu GY, Yang XL, Wang YM (2007) Polym Int 56:905
41. Agarwal GK, Titman JJ, Percy MJ, Armes SP (2003) J Phys Chem B 107:12497
42. Han J, Kumacheva E (2001) Langmuir 17:7912
43. Yamaguchi K, Ito M, Taniguchi T, Nagai K (2004) Colloid Polym Sci 282:366
44. Zhang HY, Wang ZQ, Zhang YQ, Zhang X (2004) Langmuir 20:9366
45. Cho J, Caruso F (2003) Macromolecules 36:2845
46. Stookron WB, Rubner MF (1997) Macromolecules 30:2717
47. Brandrup J, Immergut EH, Grulke EA (1999) Polymer Handbook, Vol. II, 4th edn. Wiley, New York
48. Liu GY, Yang XL, Wang YM (2007) Polymer 48:4835