Fabrication of pH-sensitive poly(2-(diethylamino)ethyl methacrylate)/palygorskite composite microspheres via Pickering emulsion polymerization and their release behavior

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ABSTRACT: The poly(2-(diethylamino)ethyl methacrylate)/palygorskite (PDEAEMA/PAL) composite microspheres were prepared via Pickering emulsion polymerization using palygorskite (PAL) as an emulsifier. The morphology, chemical structure, and content of PDEAEMA/PAL composite microspheres were investigated by polarizing optical microscopy, scanning electron microscopy (SEM), Fourier-transform infrared (FT-IR) spectroscopy, and thermal gravimetric analysis (TGA). The pH-responsive behavior of composite microspheres was studied by measuring their size at different pH values. Furthermore, their release behavior was investigated using rhodamine B (RhB) as a model molecule. It was proven that the release properties of RhB from PDEAEMA/PAL composite microspheres could be controlled by adjusting the pH values. The study of release kinetics found that Higuchi model was fit for RhB release from PDEAEMA/PAL composite microspheres at pH 5.0, 7.4, and 10.0. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42179.

INTRODUCTION

Organic–inorganic composite microspheres have become more and more widely applied in a variety of fields, such as conducting materials,[1] catalysts,[2] photonic crystal,[3] and drug vehicles,[4] etc., on account of their excellent performance out of both organic materials and inorganic materials. Recently, Pickering emulsions (i.e., solid particle-stabilized emulsions) have been developed as novel polymerization vessels for the fabrication of organic–inorganic hybrid microspheres because of the advantages of quick and convenient synthesis, excellent stabilization, and low toxicity compared to using small surfactants. Moreover, inorganic particles are introduced into the system to enhance the mechanical and thermal properties of polymeric materials.[5] Due to these own superiority, Pickering emulsion polymerization has attracted extensive attention. Bon and his co-workers prepared polystyrene latex particles armored with Laponite RD clay particles by Pickering miniemulsion polymerization.[5] Wang's group prepared magnetic polymer microspheres that have polymer cores enveloped by shells of magnetic nanoparticles via Pickering suspension polymerization.[6] Yin et al. syn-

thesized hollow microspheres with covalently bonded colloidal and polymeric shell by Pickering emulsion polymerization.[7] Wang et al. obtained a magnetic Fe_3O_4/polyamine hybrid microsphere using $O/W/O$ Pickering emulsion droplet as the polymerization microreactor.[8]

Palygorskite (PAL) is a kind of clay composed of rod-like crystals of 20–70 nm in diameter, and from several hundred nanometers to several micrometers in length.[9] The investigation of using fibrous palygorskite particles as a Pickering emulsifier has just been started.[10–12] There are merely several reports on preparation of Pickering emulsion using PAL or modified PAL as emulsifier, not to mention the polymerization via Pickering emulsions stabilized by fibrous PAL particulates. Only recently, Pan et al. reported the synthesis of magnetic/hollow double-shelled imprinted sorbents by Pickering emulsion polymerization using attapulgite (a synonym for palygorskite, PAL) particles as stabilizers and studied their selective adsorption behaviors for model pollutant λ-cyhalothrin.[13] Li et al. used the modified PAL as the sole stabilizer of the suspension polymerization of methyl methacrylate.[14]

Nowadays, stimuli-sensitive polymers have been studied extensively in a myriad of fields, such as drug and gene delivery systems.[15–18] Poly(2-(diethylamino)ethyl methacrylate) (PDEAEMA) is a kind of pH-sensitive polymer,[15,16] which exhibits pH-dependent swelling/collapse behavior in aqueous solutions. Sun and his co-workers prepared the hybrid poly(2-(diethylamino)ethyl methacrylate)-coated mesoporous silica nanoparticles via surface-initiated atom transfer radical polymerization (SI-ATRP) for pH-responsive controlled release.[15] Wang et al. synthesized the pH-responsive ethyl cellulose graft poly(2-(diethylamino) ethyl methacrylate) (EC-g-PDEAEMA) copolymers through atom transfer radical polymerization (ATRP) and investigated controlled release of rifampicin (RIF).[16] However, both of their syntheses involved tedious, toxic labor of immobilization of ATRP initiator moiety.

Previously, our group has prepared stable oil-in-water (O/W) Pickering emulsion stabilized by PAL particles without any chemical modification. Palygorskite has been demonstrated as an effective emulsifier with long-term stability, which can be stored at least 3 months.[11] We have also furthered our investigation on offering a novel water-in-oil (W/O) Pickering emulsifier by grafting PDEAEMA polymer brushes from the surface of PAL particles via Cu(0) mediated radical polymerization. A reversible Pickering emulsion system switched by pH was resulted.[12] Distinctively from above works, in this paper, pH-sensitive PDEAEMA/PAL composite microspheres were facilely prepared from Pickering emulsion polymerization using PAL as a sole emulsifier. The pH response and release behavior of the as-synthesized composite microspheres in aqueous solutions of various pH were discussed. Besides, the release kinetic of diffusion mechanism of composite microspheres was also investigated. To the best of our knowledge, this kind of investigation has not been reported.

EXPERIMENTAL

Materials
The raw PAL was supplied by Xuyi Zhongyuan Minerals. The clay was milled and collected through a 200 mesh ($<74~\mu m$) sieve. Toluene and ethanol (all AR) were bought from Jiuyi Chemical Reagent. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) (all AR) were obtained from Sinopharm Chemical Reagent. 2-(Diethylamino)ethyl methacrylate (DEAEMA, 99%), methyl methacrylate (MMA, 99%), ethylene glycol dimethacrylate (EGDMA, 98%), 2,2'-azobis-isobutyronitrile (AIBN, 99%) and rhodamine B (RhB, AR) were all purchased from Aladdin Reagent. MMA and EGDMA were passed through an activated aluminum oxide column to remove inhibitor before use. The rest of the chemicals were used without further purification. Water was prepared with a Milli-Q Direct 8 water system.

Preparation of PDEAEMA/PAL Composite Microspheres
PDEAEMA/PAL composite microspheres were fabricated via the Pickering emulsion polymerization using PAL as a Pickering emulsifier. A representative preparation procedure was described as following: 0.15 g of PAL particles were first dispersed into 10.0 mL of deionized water using a high-intensity ultrasonic vibracell processor (Jeken Ultrasonic Cleaner Limited, PS-40A) with an ultrasonic power of 240 W for 5 min. Secondly, the oil

phase containing DEAEMA (0.922 g, 4.98 mmol), MMA (0.468 g, 4.67 mmol), EGDMA (0.525 g, 2.65 mmol) and toluene (4.0 mL), in which 0.020 g of AIBN (0.122 mmol) had been dissolved, was mixed with the PAL dispersion. A stable Pickering emulsion was obtained using a homogenizer (rotor-stator, FSH-2A, Jintan Langbo Instrument) with a 12 mm head operating at 10,000 rpm for 5 min. Finally, the resulted emulsion was purged with nitrogen gas for 30 min and then polymerized at 80°C for 6 h. The obtained product was filtered and washed with water and ethanol for three times, and dried at 50°C under vacuum for 12 h.

pH-Responsive Behavior of PDEAEMA/PAL Composite Microspheres
pH-response studies were performed by dispersing the as-prepared PDEAEMA/PAL composite microspheres in the aqueous solutions with different pH values (pH 2.0, 5.0, 7.4, 10.0) under ambient temperature for 12 h and measuring their size and distribution till equilibrium was reached.

Determination of Loading Capacity of PDEAEMA/PAL Composite Microspheres
The PDEAEMA/PAL composite microspheres were loaded with RhB which was selected as a model molecule. 0.2 g of composite microspheres was added into 20 mL of ethanol solution containing RhB (25 mg mL^{-1}) with constant magnetic stirring at 40°C for 24 h. After being filtered and washed with ethanol to get rid of the free RhB, the composite microspheres were dried at 40°C under vacuum for 12 h. The amount of entrapped RhB was determined from the difference between the concentrations of the initial and final RhB solutions. The concentration of RhB was calculated by interpolation from a standard curve. RhB loading efficiency was computed from the following equation.

$$\text{Loading efficiency} \quad (\%) = \frac{W_0 - W_t}{W} \times 100\% \qquad (1)$$

where W_0 and W_t are initial and residual weight of RhB, respectively; W is the weight of PDEAEMA/PAL composite microspheres.

Studies of Release Behavior from PDEAEMA/PAL Composite Microspheres
The release profiles of RhB-loaded PDEAEMA/PAL composite microspheres were determined as follows: 0.1 g of RhB-loaded PDEAEMA/PAL composite microspheres were placed into a dialysis bag and immersed in 50 mL aqueous solution of different pH namely 2.0, 5.0, 7.4, and 10.0 at 37 ± 1°C, respectively. After each predetermined time interval, 5 mL of solution was acquired from the release medium. Meanwhile, the same volume of fresh solution having same pH and temperature was added into the release medium to keep its volume constant. The concentration of released RhB was measured at 554 nm by a UV–Vis spectrophotometer (UV-2401PC). Cumulative release was expressed as the released total percentage of RhB.

Characterization
The conductivity of the emulsions was determined using a DDS-307 digital conductivity meter with Pt/Pt black electrodes (INESA Scientific Instrument). The type of emulsions was differentiated according to their conductivities. A high
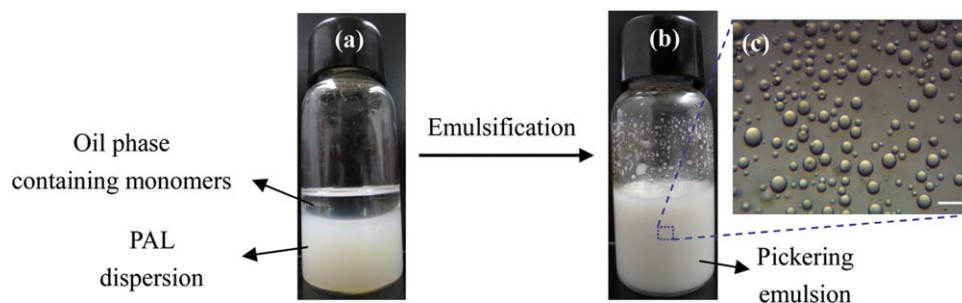
Figure 1. Digital photos of oil phase and PAL dispersion (a), as-prepared Pickering emulsion (b), and optical micrograph of Pickering emulsion (c). The scale bar is 100 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conductivity (>10 μs cm^{-1}) indicated an *O/W* emulsion, and a low or immeasurable conductivity indicated a *W/O* emulsion. Emulsion type was also inferred by observing what happened when a drop of each emulsion was added to a volume of pure oil or pure water. Oil continuous (water continuous) emulsions dispersed in oil (water) and remained as drops in water (oil).

Photographs of the palygorskite-stabilized emulsions were taken with a digital camera (DMC-LX5GK, Panasonic).

Fourier-transform infrared (FT-IR) spectra of the samples were recorded in KBr disks using a Nicolet-5700 FTIR spectrometer (Thermo Fisher Scientific) in the range of 4000–500 cm^{-1} for 32 scans.

Thermal gravimetric analysis (TGA) was conducted on a thermal analysis instrument (STA 449F3, NETZSCH) under nitrogen atmosphere at a balance purge flow rate of 20 cm^3 min^{-1} and a sample purge flow rate of 25 cm^3 min^{-1}. Temperature was elevated from 25 to 800°C at a rate of 10°C min^{-1}.

Optical microscopy (OM) of the samples was analyzed by a PH100-DB500U digital microscope (Phoenix Optical). Images were taken on the connected computer and processed using Nano Measure 1.2 Software to acquire composite microspheres size and its distributions. The mean size was calculated from at least 100 individual measurements of microspheres diameters.

Polarizing optical micrographs of the samples were obtained using a DM 2500P polarizing optical microscope (POM). The PAL particles are birefringent. In polarizing microscope images, birefringent domains are bright, while nonbirefringent ones are shown dark under any circumstance.

The chemical compositions of external surface of the samples were determined by an INCA X-Max 20 energy dispersive X-ray spectrometer (EDS, Oxford Instruments).

The morphologies of the samples were observed using an S-3000N scanning electron microscopy (SEM, Hitachi) operating at 20 kV.

RESULTS AND DISCUSSION
Preparation and Characterization of Pickering Emulsion
In our previous work,[11] we found that the PAL particles could be employed as a Pickering emulsifier to stabilize toluene/water (*O/W*) emulsion. Herein, polymeric monomers were chosen as a part of oil phase. Figure 1 showed photographs of oil phase,

PAL dispersion, and as-prepared Pickering emulsion, respectively. From Figure 1(a), the transparent oil phase was located at the top of the bottle. Due to the discontinuity of the silica sheets of PAL, abundant silanol groups (Si–OH) are presented on the surface of the rods and make the surface of PAL hydrophilic.[19] The uniform PAL aqueous dispersion after ultrasonic processing was located at the bottom of the bottle. After homogenization, a PAL particle-stabilized Pickering emulsion was obtained [Figure 1(b)]. The as-formed Pickering emulsion showed a long-time stability, which could be stored for at least 3 months with trace change.[11] According to the results of conductivity value (75 μS cm^{-1}) and drop test for as-prepared emulsion, the type of emulsion was *O/W*. This is consistent with the description of Aveyard *et al.* that hydrophilic particles tend to form *O/W* emulsions.[20] The morphology of the Pickering emulsion was characterized by an optical microscope, as shown in Figure 1(c). The average diameter of emulsion droplets containing monomers was 47 ± 13 μm.

Synthesis Process of PDEAEMA/PAL Composite Microspheres
A brief procedure of the fabrication of PDEAEMA/PAL composite microspheres was depicted in Figure 2. The PAL dispersion was emulsified with oil mixture, in which DEAEMA, MMA, EGDMA, AIBN were dissolved in toluene. Since the glass temperature of PDEAEMA is low (around 16–24°C),[21] a small amount of MMA was added to be copolymerized with DEAEMA. As indicated above, an *O/W* emulsion with the droplets stabilized by PAL was formed. As the reaction temperature elevated, oil-soluble initiator (AIBN) was thermally decomposed to generate primary free radicals in oil droplets. Monomers would capture the radicals and grow to polymer chains. A crosslinked polymer network would be formed in the oil droplets in the presence of the crosslinker (EGDMA). The PAL particles adsorbed at the interface were anchored into the surfaces of the polymer network as the polymerization reaction progressed, which enhanced the mechanical properties of composite microspheres.[5,13] After washing and drying, PDEAEMA/PAL composite microspheres were obtained.

### Characterization of PDEAEMA/PAL Composite Microspheres
Figure 3 showed the morphologies (POM and SEM images) and EDS analysis of PDEAEMA/PAL composite microspheres. From Figure 3(a), it was seen that there was a light halo surrounding the composite microspheres, which was attributed to the existence of PAL particles having the characteristic birefringence.
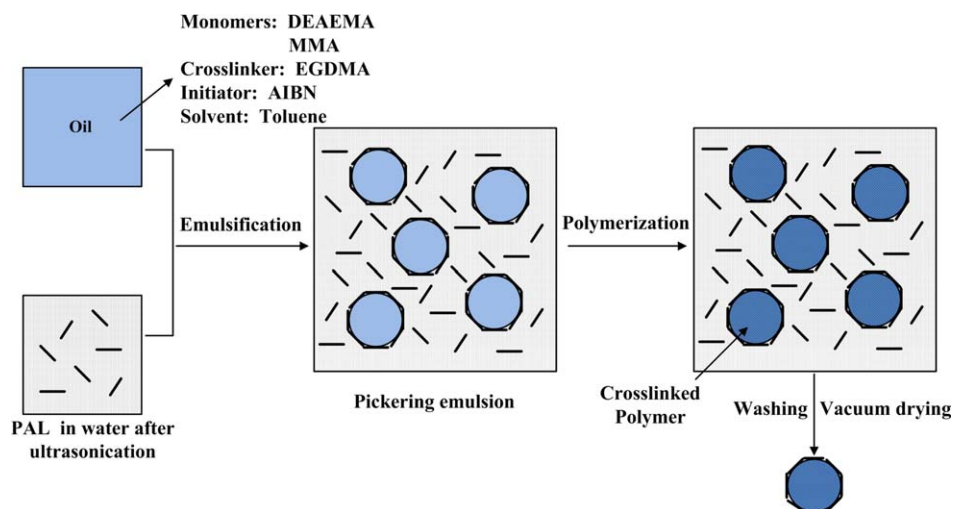
Figure 2. Schematic illustration of the fabrication of PDEAEMA/PAL composite microspheres via PAL-stabilized Pickering emulsion polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

This indicated that the PAL particles were attached to the surface of composite microspheres, as expected [Figure 3(b)]. According to statistically analyses, the average size of composite microspheres was about 50 μm, which was also consistent with aforementioned average diameter of emulsion droplets. It dem-

onstrated that PDEAEMA/PAL composite microspheres were prepared from the droplets of the Pickering emulsion stabilized by PAL particles as templates. Close-up SEM image of composite microsphere's surface was given in Figure 3(c). The fibrous PAL particles showed random arrangement in its surface. The
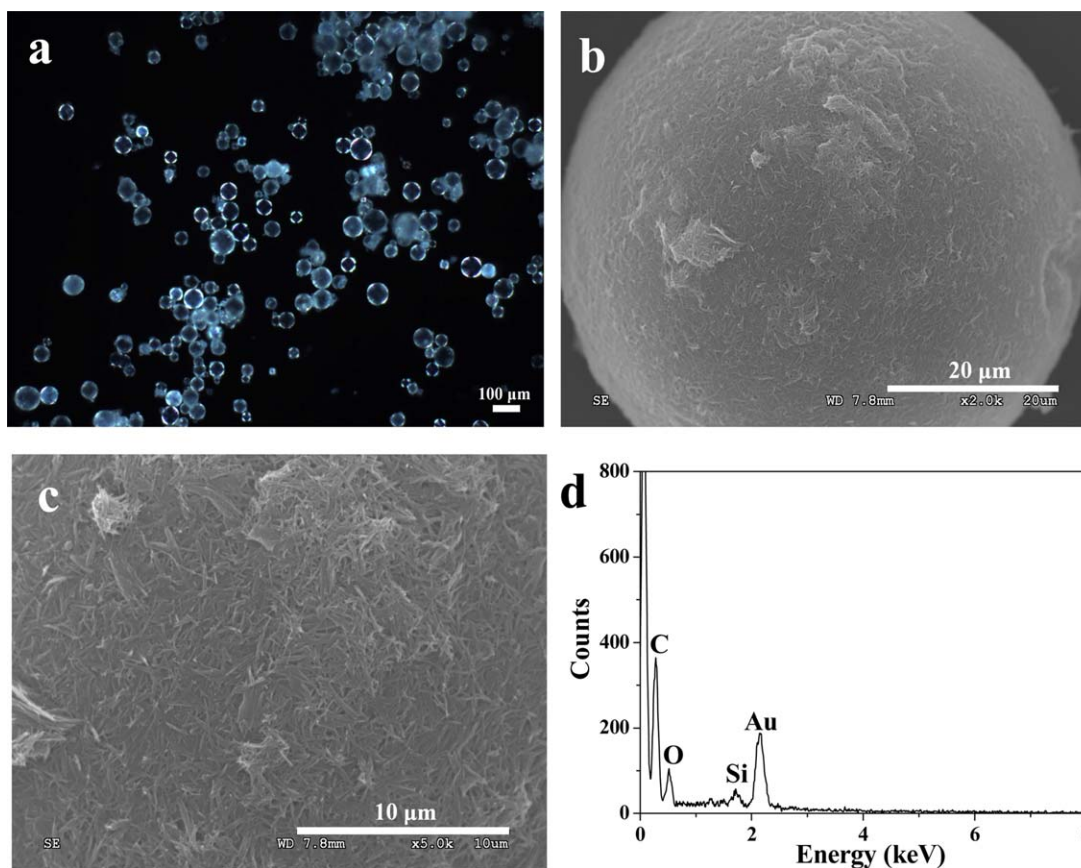
Figure 3. (a) POM image of PDEAEMA/PAL composite microspheres, (b) SEM image of composite microspheres, (c) close-up SEM image of composite microsphere's surface, and (d) EDS spectrum of the ektexine of composite microspheres. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
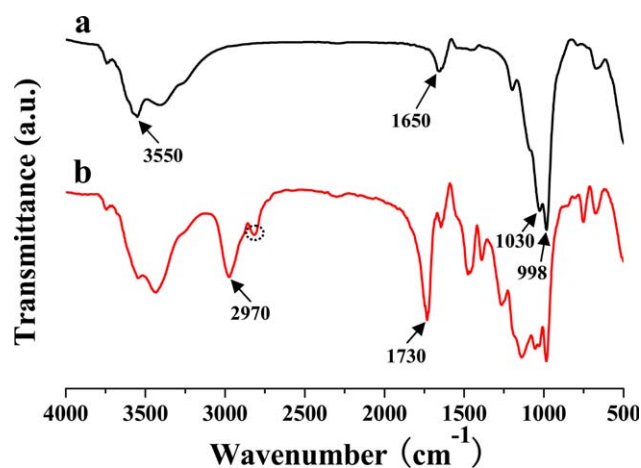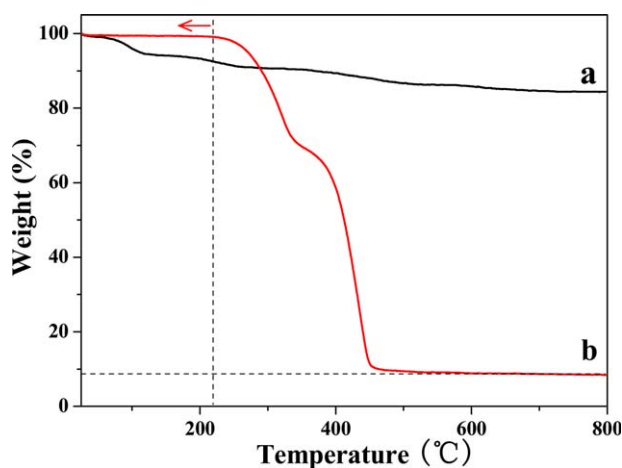
Figure 4. FT-IR spectrum of (a) PAL and (b) PDEAEMA/PAL composite microspheres. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. TGA curves of (a) PAL and (b) PDEAEMA/PAL composite microspheres. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EDS spectroscopy of external surface of composite microspheres was presented in Figure 3(d). Peaks for the elements of C, O, and Si were observed together, which proved that the composite microspheres wall was built up by the PAL particles and the formed polymer. The Au peak was due to the electrically conducting material that was deposited using a sputter coater.[13]

The FT-IR spectroscopy was further employed to provide direct identification of main functional groups on PAL particles and PDEAEMA/PAL composite microspheres (Figure 4). As shown in Figure 4(a), for PAL particles, the band at 3550 cm^{-1} had been attributed to the symmetric stretching mode of molecular water coordinated to the magnesium at the edges of the channels of PAL.[22] The band at 1650 cm^{-1} was attributed to zeolitic water. The band at 1030 cm^{-1} had been assigned to the asymmetric stretching mode of Si—O—Si. The Si—OH bending band appeared at 980 cm^{-1}. From Figure 4(b), the prominent peak at 1730 cm^{-1} was attributable to C=O stretching vibration of ester group. The absorption bands occurring from 2750 to 2950 cm^{-1} were attributed to symmetric stretching vibrations of —NCH$_2$— (for PDEAEMA) of the tertiary amine groups.[23] The C—H stretching vibration of alkyl occurred at 2970 cm^{-1}. Besides, the bands around 1000 cm^{-1} appeared the same absorption peaks of PAL. All of these supported the viewpoint that the composite microspheres were composed of PAL particles and the formed polymer.

In order to determine the content of PAL particles and inner polymer in the PDEAEMA/PAL composite microspheres, the thermo-gravimetric analysis (TGA) was carried out. The results in Figure 5(a) showed that when being heated, the weight losses of PAL particles were about 15%, which would be assigned to the contribution of water in PAL particles, including interparticle adsorbed water, zeolitic water, and structural water.[24] In Figure 5(b), the loss of composite microspheres was almost zero within the initial temperature range (<220°C), showing a fine thermal stability. At the temperature range of 250–500°C, the significant weight losses (about 90%) could be attributed to the decomposition of the inner polymer. After 600°C, the remaining mass for composite microspheres was approximately 10%,

which may be ascribed to the thermal resistance of PAL particles and little residual carbon by calcining the polymer.[25]

pH Response of PDEAEMA/PAL Composite Microspheres

As a kind of functional polymers, the pH-sensitive polymers have been studied extensively.[26–28] Herein, the swelling of PDEAEMA/PAL composite microspheres was investigated for the understanding of its pH-responsive behavior. The morphologies and average diameters of PDEAEMA/PAL composite microspheres at powder state and at different pH values, namely 2.0, 5.0, 7.4, 10.0, were shown in Figure 6. It was clearly found that the size of composite microspheres got minimum at powder state (without any outside stimulation) and its size increased with the decreasing pH value. There was an obvious increase in diameter of about 30% obtained by tuning the pH value from 10.0 to 2.0. The enhancement of the size of PDEAEMA/PAL composite microspheres was induced by the change in the environmental pH values. At low pH values, the amino groups of PDEAEMA/PAL composite microspheres were protonated and the inner polymer network may be swelled and become loose owing to the charge repulsion between the positive ions. Water molecules easily went into inner network structure, resulting in a volumetric expansion. These amino groups were deprotonated at high pH values and the collapse of PDEAEMA segments lead to the little change in size, indicated by comparing the data of pH 10 with that of powder [Figure 6(B)].
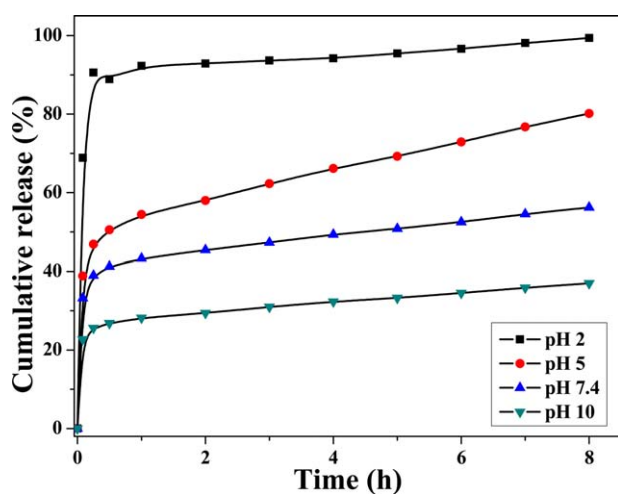
Release Behavior of PDEAEMA/PAL Composite Microspheres

The PDEAEMA/PAL composite microspheres were swollen by RhB–ethanol solution in order to load RhB into them. By calculation, RhB loading efficiency of PDEAEMA/PAL composite microspheres was about 13.5%. The release profile of RhB-loaded PDEAEMA/PAL composite microspheres in different pH solutions (pH 2.0, 5.0, 7.4, and 10.0) was described in Figure 7 with the same initial loading efficiency. From Figure 7, it was found that the release rates of RhB were dependent on the pH values. RhB was released much faster at lower pH value, and slower RhB release was achieved by increasing the pH value.
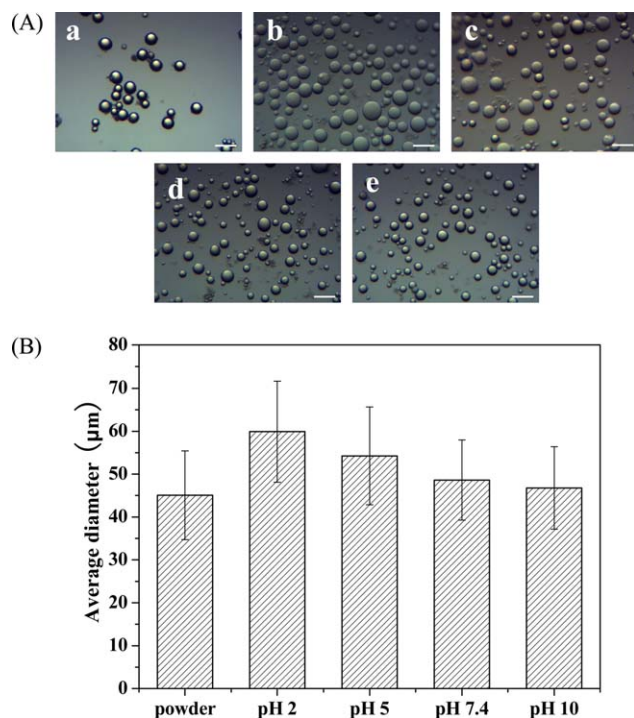
Figure 6. (A) Optical micrographs of PDEAEMA/PAL composite microspheres at (a) powder state and different pH values: (b) pH 2.0, (c) pH 5.0, (d) pH 7.4, (e) pH 10.0. The scale bar is 100 μm. (B) Average diameter of composite microspheres as a function of pH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The release rates of RhB were also consistent with the swelling behavior of PDEAEMA/PAL composite microspheres (Figure 6). As mentioned above, at different pH levels, there were different mesh sizes of inner polymer network induced by the charge repulsion interaction. At low pH, the large mesh size of the microsphere matrix network allowed an easy diffusion of the RhB out of the matrix.[29,30] In the first 30 min, about 50, 41, and 27% of loaded RhB were released at pH 5.0, 7.4, and 10.0,

Figure 7. Release profile of RhB from PDEAEMA/PAL composite microspheres at different pH values. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Correlation Coefficient R and Slope of Fit Line k of RhB Release at Different pH Values for Higuchi Model

Model	Kinetic equation		pH 2.0	pH 5.0	pH 7.4	pH 10.0
Higuchi	$Q = kt^{1/2}$	R	0.596	0.984	0.967	0.983
		k	–	14.45	7.71	4.98

respectively. At pH 2.0, the release rate of RhB was very fast and the released amount was up to 90% with 30 min. After 8 h, the release of RhB at pH 2 was almost completed. While at pH 5.0, 7.4, and 10.0, following a typical sustained release pattern, RhB was diffused out slowly and the release amount after 8 h was about 80, 56, and 37%, respectively. This demonstrated that the release rate of the RhB could be well controlled by regulating the pH value of the solution.

In order to understand the release kinetic of PDEAEMA/PAL composite microspheres, above experiment data (cumulative release shown in Figure 7) was used to fit to mathematical model based on diffusion consideration. Higuchi model has commonly been applied for the diffusion controlled release of drug from a homogeneous planar matrix or from a porous matrix, from which a drug is leached by the fluid that penetrates the matrix through pores and capillaries.[31]

$$Q = \sqrt{\frac{D\varepsilon}{\tau}(2A - \varepsilon C)C_t} \qquad (2)$$

where Q is the amount of drug released after time t, D is the diffusivity of drug in the permeating fluid, τ is the tortuosity factor of the capillary system, A is the total amount of the drug present in the matrix, C is the solubility of the drug in the permeating fluid, and ε is the porosity of the matrix.[31,32]

The above eq. (2) can be simply expressed as

$$Q = kt^{1/2} \qquad (3)$$

$$\text{and } k = \sqrt{\frac{D\varepsilon}{\tau}(2A - \varepsilon C)C} \qquad (4)$$

According to the Higuchi model, the percentage of RhB released was plotted as a function of the square root of time. The correlation coefficient R and slope of fit line k of RhB release at different pH values for Higuchi model were given in Table I (the slope of fit line k at pH 2.0 was not shown and not discussed due to its bad linear correlativity). At pH 5.0, 7.4, and 10.0, the correlation coefficients were all close to 1, suggesting that Higuchi model was well fit for RhB release from PDEAEMA/PAL composite microspheres at these pHs. It also demonstrated that the release process was supposed to be diffusion controlled.

The parameters D, A, C, and τ in the eq. (4) can hardly change only by altering the pH values of the release fluid.[33] Only the porosity of the matrix, ε, should change the slope of fit line (k).[33] As mentioned before, the polymer network in PDEAEMA/PAL composite microspheres may become looser with the decreasing pH value because of the charge repulsion among the protonated amino groups. From Table I, it was indeed in accord with the change that the slope of straight line k increased with the decline of pH values.

CONCLUSIONS

PDEAEMA/PAL composite microspheres were successfully one-step fabricated via the PAL particles-stabilized Pickering emulsion polymerization. The average diameter of composite microspheres was about 50 μm which was in good agreement with that of initial emulsion droplets. It was demonstrated that PDEAEMA/PAL composite microspheres were prepared directly from the droplets of the Pickering emulsion stabilized by PAL particles as templates. The size of composite microspheres was dependent on the environmental pH values and the release rate of RhB could be well controlled by regulating the pH value of the solution. The RhB release process from PDEAEMA/PAL composite microspheres at pH 5.0, 7.4, and 10.0 was well fitted by Higuchi model, suggesting a mainly diffusion-controlled process. This kind of pH-sensitive materials may have potential applications in the controlled release of dyes, drugs, and farm chemicals.

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