

Polymer hollow particles: Encapsulation of phosphoric acid partial esters and morphology manipulation

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ABSTRACT

The present work demonstrates the possible use of emulsion polymerization for fabricating structured-polymer particles which can store active materials. The hollow polymer particles were synthesized by multi-stage emulsion polymerization consisting of four main stages, (1) the preparation of alkali-swelable core latexes containing active materials, (2) first core-shell polymerization of a monomer mixture of methyl methacrylate (MMA), butyl acrylate (BA) and methacrylic acid (MAA), (3) second core-shell polymerization of styrene and (4) a neutralization stage. The morphology of synthesized capsules was observed by transmission electron microscopy (TEM). The size of the capsule prepared by standard recipe was around 300 nm and the polydispersity index was 0.024 representing that size distribution was highly monodisperse. The specific target material of encapsulation was the phosphoric acid partial ester. The amount of phosphoric acid partial ester encapsulated was determined by thermogravimetric analysis (TGA). From studies of encapsulation behaviors, it was found that the encapsulation efficiency and location of phosphoric acid partial ester in the interior of the particles were mainly dependant on its partition coefficient. In addition, the morphology of polymer capsule was manipulated by varying process parameters. The morphology changes, such as those of pore size and roughness of polymer shell, were characterized by scanning electron microscopy (SEM) and analysis of nitrogen adsorption and desorption isotherm. When neutralized with N,N'-dimethylethanolamine simultaneously during the styrene polymerization, the surface area of polymer capsule was increased drastically by about 5 times due to the formation of mesopores and the roughening of the surface on the hollow polymer shell.

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1. Introduction

Functionalized hollow polymeric microspheres have attracted a great deal of interest because of their potential applications, which range from controlled release of drug to advanced functional materials [1–7]. Because of their hollow polymer structure, they can store large quantities of functional guest materials and protect these from the environment until needed for fulfilling appropriate applications [8–15]. Thus, the fabrication of uniform hollow spheres in the nanometer-to-micrometer scale range with a tailored structure has been intensively pursued – by layer-by-layer deposition of polyelectrolytes onto a template core followed by subsequent removal of the template [16], polymerizing monomers in lipid vesicles [17], pH-induced micellization of a grafted copolymer [18], by the heterocoagulation of opposite charged latexes [19], in-situ heterogeneous polymerizations [20].

One important area for the application of this encapsulation technology is the development of self-healing anticorrosion coatings in which polymer capsules act as a sensitive reservoir for corrosion inhibitors [21–24]. The key point in the elaboration of a self-healing corrosion protection is the development of the functional nanocapsules which are able to effectively encapsulate corrosion inhibitors, successfully maintaining them in the interior and releasing them on demand, for instance, when triggered by pH changes due to onset of corrosion reaction. The realization of a self-healing anticorrosion performance requires a system for storage and release of corrosion inhibitors. Therefore, several aspects should be taken into account when designing nanocapsules for a self-healing coating: a good compatibility with the other coating components, the ability to up-take and release the corrosion inhibitors, and a suitable particle size. In addition, such multifunctionality of the nanocapsule characteristics requires a composite structure of the capsule wall which should be mechanically stable and possess the capability to release encapsulated corrosion inhibitors in a controlled way. Therefore, sub-micrometer sized capsules composed of rigid mesoporous polymer

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shell seemed most appropriate for application in anticorrosion protection coatings.

Many strategies have previously been suggested to incorporate the corrosion inhibitors into the polymeric capsules [25]. However, most of the methods were relatively laborious and inefficient, and limited possible applications and up-scaling. Oftentimes, it is impossible to apply in protective coatings in a thin layer due to the large size of the employed carriers.

Because the emulsion polymerization technology has many advantages such as easy manipulation of polymer composition, thickness of shell, particle morphology, and low cost scale-up, it has been explored extensively to make latex particles with desired structural characteristics. In the present work, the multi-stage emulsion polymerization, consisting of three main stages - two core-shell polymerizations and a neutralization stage - was employed to make mesoporous nanocapsules carrying corrosion inhibitors inside, in which hydrophobic styrene was polymerized around the acid-containing core particles. In principle, thermodynamic equilibrium would favor particles with hydrophobic cores encapsulated with hydrophilic alkali-swellable shells because the surface energies would favor the formation of a more polymer material contacted with a polar medium such as water [26]. In the present work, the hydrophobic polymer was formed on the hydrophilic acid-containing core through lower monomer partition in the core particles, a higher instantaneous conversion, monomer-starved condition. This hollow polymer capsule was synthesized to load the active materials and corrosion inhibitors via their preferred distribution into a polymer layer with similar partitioning coefficient, during the emulsion polymerization in their presence.

Phosphoric acid partial esters (PAPes), which have been known to form a stable anticorrosive protective film on metallic substrates

such as iron, aluminum and zinc [27,28], were used as target materials to be encapsulated. To investigate the effect of characteristic attributes of PAPE, such as alkyl chain length and degree of esterification, on the encapsulation behavior, four different kinds of phosphoric acid partial esters (PAPes) were employed in the present work.

2. Experimental

2.1. Materials

Phosphoric acid partial esters (PAPes) were employed as target materials for encapsulation. Four different phosphoric acid partial esters (PAPes), phosphoric acid monobutyl ester (Daihachi chemical industry Co., Ltd.), phosphoric acid dibutyl ester (Tokyo chemical industry Co., Ltd.), phosphoric acid 2-ethylhexyl ester (mono- and di-ester mixture) (Tokyo chemical industry Co., Ltd.) and phosphoric acid di-(2-ethylhexyl) ester (Tokyo chemical industry Co., Ltd.), were used as received in the present work. Reagent grade monomers such as methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA) and styrene were supplied by Samchun pure chemical Co. Ltd. and purified by vacuum distillation before use. Ammonium nonylphenol ether sulfate (Rhodapex® CO-436; Rhodia) was used as an emulsifier and sodium persulfate (Samchun pure chemical) was used as a radical polymerization initiator. Three different bases, ammonia (Samchun pure chemical), triethanolamine (TEA; Samchun pure chemical) and N,N-dimethylethanolamine (DMEA; ACROS organic), were used to neutralize the carboxylic acid group-containing core polymer and to swell polymer particles. Throughout the polymerization process, deionized water (DIW) with a conductivity of less than $3 \mu\text{S cm}^{-1}$ was used.

Table 1
Standard recipe for multi-stage emulsion polymerization.

Core forming stage			Intermediate shell forming stage	
1) DIW	24.38 g		15) DIW	15 g
2) Surfactant	0.04 g		16) Sodium persulfate	0.5 g
3) Sodium persulfate	0.092 g		17) Butyl acrylate	4.2 g
4) Butyl acrylate	0.9 g		18) Methyl methacrylate	51 g
5) Methyl methacrylate	0.4 g		19) Methacrylic acid	1.8 g
6) Methacrylic acid	0.018 g		Outer shell forming stage	
	↓		20) DIW	38 g
7) DIW	16.65 g	⇒	21) Surfactant	0.33 g
8) Surfactant	0.184 g		22) Sodium persulfate	0.5 g
9) Sodium persulfate	0.083 g		23) Styrene	99 g
10) Butyl acrylate	0.745 g		Neutralization stage	
11) Methyl methacrylate	11.32 g		28 % aqueous ammonia	10 g
12) Methacrylic acid	5.18 g		or	
Contacting PAPes with the core			20 % aqueous DMEA	40 g
13) DIW	435 g		or	
14) PAPes	0.037 mol		20 % aqueous TEA	40 g

2.2. Preparation of latex particles loaded with PAPes

The core-shell polymer particles containing phosphoric acid partial esters were prepared through multi-stage semi-continuous emulsion polymerization which was performed in a 1000 ml, four-necked, round-bottom flask equipped with a paddle stirrer, a thermometer, a nitrogen gas inlet, a reflux condenser and inlet tubes for the continuous feed of materials. As described in Table 1, the core polymer latex was prepared by a seeded emulsion polymerization in which the monomer mixture of 0.745 g of BA, 11.32 g of MMA and 5.18 g of MAA was fed into the flask at the rate of 0.3 g min⁻¹ at 85 °C after the seed latex composed of 68.3 wt.% BA, 30.0 wt.% MMA and 1.4 wt.% MAA was formed. 0.037 mol of phosphoric acid partial ester and 435 g of deionized water added to the core latex emulsion and then emulsion was heated to 85 °C in the flask under a nitrogen atmosphere with a 200 rpm of agitation rate. The emulsion was held at the temperature for about 30 min to allow the phosphoric acid partial ester to be absorbed into the core polymers. The solution containing 0.5 g of sodium persulfate dissolved in 15 g water was added into the flask slowly. A monomer mixture consisting of 4.2 g of BA, 51 g of MMA and 1.8 g of MAA was fed to the flask at the rate of 0.95 g min⁻¹. After the completion of the monomer feeding, latexes were stirred at 85 °C for an additional 60 min. In the subsequent polymerization of outer shell stage, styrene pre-emulsion consisting of 38 g of water, 0.33 g of ammonium nonylphenol ether sulfate, 0.5 g of sodium persulfate and 99 g of styrene monomer was fed into the flask at the rate of 2.3 g min⁻¹ at 85 °C, and latexes were held at 85 °C for the 30 min afterward.

2.3. Swelling of the latex particles

Two different neutralization methods were used in the present work as follows;

- 1) *Swelling of the latex particles by neutralization after styrene polymerization*: the core-shell structured latexes were neutralized with an aqueous basic solution after the completion of polymerization of styrene in the outer shell formation stage. The base used for the neutralization was 10 g of 28% aqueous ammonia, 40 g of 20% aqueous N,N-dimethylethanolamine or 40 g of 20% aqueous triethanolamine. All neutralizations were conducted during the 30 min period at 93 °C, which is close to the glass transition temperature of polystyrene. After the completion of the neutralization, the latexes were held at the same temperature for additional 30 min, and then cooled to the room temperature and filtered to remove coagulum.
- 2) *Swelling of the latex particles by simultaneous neutralization and styrene polymerization*: the core-shell latexes were neutralized by adding an aqueous basic solution as the styrene monomer stream was being fed into the flask. The neutralization was conducted during 30 min of the initial stage of styrene monomer feeding at 85 °C. Total feeding time for styrene was 60 min and, after completion of styrene feeding, the latexes were held at 93 °C for additional 30 min.

2.4. Characterization

The morphology of the capsule was observed by transmission electron microscopy (TEM, Philips CM 200). The latex specimens were prepared by drying dilute samples on a polyvinyl formal-coated TEM grid. Generally, negative staining with a 2% phosphotungstic acid (PTA) aqueous solution was used for both the highly carboxylated latexes and the composite latexes comprised of

methyl methacrylate or acrylate copolymers in order to prevent any deformation of the particles during the TEM observation. From the TEM analyses two different average diameter values (number average, D_n ; weight average, D_w) and polydispersity index (U) were calculated according to the following equations:

$$D_n = \frac{\sum n_i D_i}{\sum n_i}, D_w = \frac{\sum n_i D_i^4}{\sum n_i D_i^3}, U = D_w/D_n$$

where n_i is the number of polymer particles with diameter D_i . Dynamic light scattering (DLS) measurement was also performed on a Malvern Zetasizer Nano-ZS to determine the intensity weighted average hydrodynamic size (Z-average diameter) and the polydispersity index (Pd_{DLS}) which was derived from a cumulants analysis of the intensity autocorrelation function. The surface morphology was observed using scanning electron microscopy (SEM, Hitachi SU-6600). Before observation, the samples were coated by 10 nm of Pt/Pd. Nitrogen adsorption/desorption isotherm was performed with a BELSORP-minianalysis system with the sample degassed at 50 °C for 6 h. Surface areas were determined using the Barrett-Emmett-Teller (BET) method and the average pore diameter was calculated using the Barrett-Joyner-Halena (BJH) method. The amount of phosphoric acid partial ester encapsulated was determined by thermogravimetric analysis (TGA, Mettler-Toledo 851E). For the TGA analysis, polymer capsules were recovered by centrifugations after being coagulated by adding equiweight of 5 wt. % CaCl₂ solution to the latex and then washing with water to remove the residual phosphoric acid partial esters on the outer surface of capsules. Small amounts of the capsule (10–20 mg) were heated from 25 °C to 700 °C at the rate of 10 °C min⁻¹ in a nitrogen environment.

3. Results and discussion

3.1. Preparation of hollow polymer capsule containing PAPes

The polymer capsules were synthesized by multi-stage emulsion polymerization: (1) the preparation of acid-containing core latex particle (the core forming stage); (2) contacting PAPes with the core latex; (3) encapsulating the core particles with a shell layer of copolymerized methyl methacrylate, butyl acrylate and methacrylic acid (the intermediate shell forming stage); (4) second encapsulation with a shell layer of polystyrene (the outer shell forming stage); (5) the neutralization with a base for the osmotic swelling of the polymer particles. The core of the present hollow polymer particles is a copolymer which comprises high concentration of carboxylic acid monomer in order to generate capsule-structured particles with the addition of aqueous basic solution and be hydrophilic enough to absorb PAPes preferentially. Styrene was selected as the monomer for the outer shell because the shell should be rigid enough for mechanical stability and hydrophobic enough for preferred distribution of hydrophilic PAPes into the hydrophilic core polymer. However, it is difficult to encapsulate the well-defined hydrophobic shell around the core in aqueous medium because the core polymer in this system has a high affinity for water. In the first set of experiments, multi-stage emulsion polymerization without the addition of PAPes was conducted to figure out the process parameters for obtaining the desirable concentric core-shell particle morphology. It was found that the introduction of the so-called intermediate shell polymer having the intermediate hydrophilicity between the core and the outer shell polymer, and monomer-starved conditions during the semi-continuous polymerization of the shell forming stages were necessary as was reported previously [29]. The standard recipe for multi-stage emulsion was shown in Table 1. First, the acid-containing core polymer composed of 62 wt. % MMA, 7 wt. % BA and 31

wt. % MAA was prepared by a seeded semi-continuous emulsion polymerization process for the better control over the particle size, more monodispersed composite particles and minimizing the probability of the formation of a water-soluble polymer. In addition, methyl methacrylate was used instead of acrylic acid as an acid functional monomer because acrylic acid has a greater tendency to remain in the aqueous phase where it can form water-soluble, acid-rich polymer fractions that can have deleterious effects on the emulsion stability, compositional homogeneity and the particle size distribution [30]. The TEM micrograph of the core polymer particles is shown in Fig. 1 (a), which indicates that the average diameter of polymer particles was 130 nm and the polydispersity index (D_w/D_n) was 1.031 as summarized in Table 2. The formation of monodisperse hydrophilic polymer latex seemed to be due to the seeded polymerization process and the use of MAA. In the second stage, the core polymer particle was wrapped by an intermediate shell copolymer layer of 89 wt. % MMA, 8 wt. % BA and 3 wt. % MAA. Fig. 1 (b) shows the micrograph of the composite particles after the intermediate shell formation, which indicates that the average diameter of the particles was around 210 nm and their size distribution was highly monodisperse (PDI of 1.023). These particles were subsequently encapsulated with hydrophobic polystyrene. Fig. 1 (c) shows TEM micrograph of the composite polymer particles after the outer shell formation. Weight-average particle diameter of 284 nm closely coincided with the calculated value of 285 nm and PDI value was more reduced down to 1.007. It indicated that there was no generation of a new crop of polystyrene particles. In addition, the very low PDI values (less than 0.03) measured by dynamic light scattering further supported the continuous growth of core-shell polymer particles. Low concentration of emulsifier and instantaneous conversion higher than 90% were the most important parameters for avoiding the generation of new crop of secondary particles in the shell forming stages. Unexpectedly, most of the composite particles showed a region of low electron density at the center of the particle. One possible explanation is that it may have been due to the reflection of the inner morphology of these

Table 2
Particle size and size distributions of polymer particles.

Samples	TEM			DLS
	D_n (nm)	D_w (nm)	U	PdI
Core	130	134	1.031	0.022
Intermediate shell	210	215	1.024	0.030
Outer shell	282	284	1.007	0.021
Neutralized capsule	301	303	1.007	0.024

composite particles with a highly carboxylated acrylate copolymer core, poly (MMA-co-BA-co-MAA) intermediate shell and polystyrene outer shell. This argument is indirectly supported by the fact that the average size of the low electron-density regions roughly matched that of the core latex particles.

Composite latex particle with acid-containing cores become swollen when it is neutralized by bases. The bases permeate the shell polymer layer and form polyelectrolyte salt that builds up osmotic pressure which in turn causes water to be imbibed into the particle. A void will be formed during the drying process at ambient temperature in which water is dried out from the capsule. Considering that some degree of enlargement of the shell polymer occurs during expansion of the core, the neutralization was carried out close to the T_g , 93 °C, of the shell polymer for 30 min. The transmission electron micrograph of the neutralized latex particles was shown in Fig. 1 (d) in which the expansion of composite particle and formation of void interior after neutralization was clearly demonstrated. Average wall thickness of the polymer capsules was about 47 nm and aspect ratio of inner void diameter to outer diameter was about 0.75. The fact that there was no collapse of hollow polymer particles during TEM measurement indicates that the recipe and polymerization condition were well designed for obtaining concentric core-shell composite particle with appropriate mechanical stability for loading of target chemicals in this case – PAPE used.

In the second set of experiments, polymer capsules loaded with PAPEs were prepared through multi-stage polymerization, in

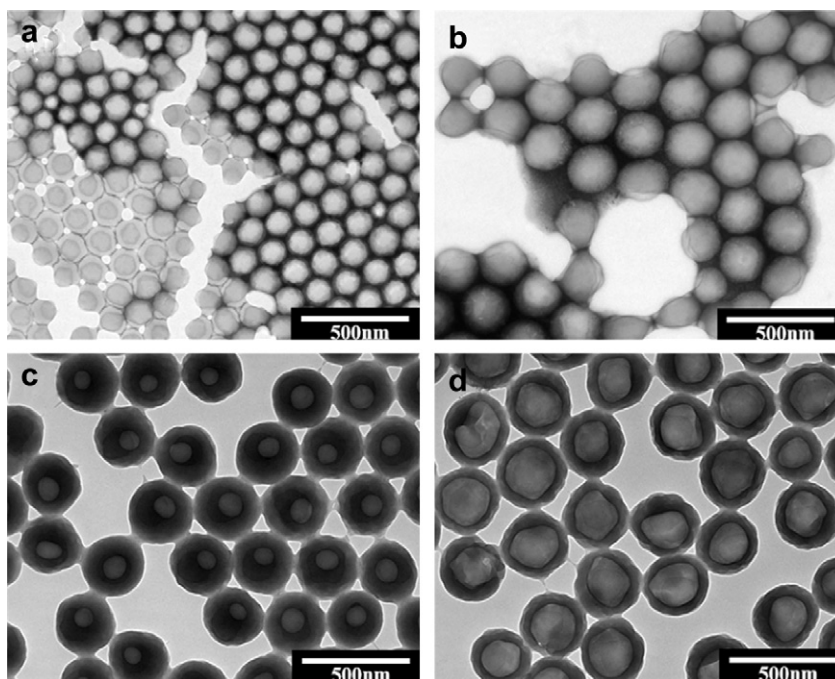


Fig. 1. TEM micrographs of the polymer particles. (a) The core polymer particles containing carboxylic acid groups in large quantities; (b) the core-intermediate shell particles; (c) the core-intermediate shell-outer shell particles with outer polystyrene; (d) the expanded hollow polymer particles after neutralization with 28% aqueous ammonia.

which PAPEs were contacted with the hydrophilic core polymer prior to the subsequent shell forming stage. Four different kinds of PAPE - monobutyl ester, dibutyl ester, mono-(2-ethylhexyl) ester and di-(2-ethylhexyl) ester - were selected as the target materials for encapsulation. The distinct encapsulation behaviors were expected due to the difference of the alkyl side chain length and degree of esterification of PAPEs. In case of phosphoric acid monobutyl ester, the preparation of homogenous polymer capsule was not successful because of unstable emulsion. It seems that phosphoric acid monobutyl ester interacted with the emulsifier, which lowered the emulsion stability due to its high water solubility. However, when other phosphoric acid partial esters were added, the emulsion was stable during the whole polymerization process. Fig. 2 shows TEM micrographs of the resultant composite polymer particles. When phosphoric acid dibutyl ester or mono-(2-ethylhexyl) ester was encapsulated, the center of the capsule was somewhat darker than the outer shell of the polymer as shown in Fig. 2 (a) and (c). While, the core polymer was brighter than the outer shell in case of phosphoric acid di-(2-ethylhexyl) ester, as shown in Fig. 2 (e), similar to the capsules that contain no PAPE as shown in Fig. 1 (c). In the TEM micrograph, acrylate polymers absorbed with phosphoric acid partial esters appeared darker because PAPE has higher electron density compared to the

neat acrylate polymers. Thus, it was concluded that phosphoric acid dibutyl ester and mono-(2-ethylhexyl) ester would exist preferentially within the relatively hydrophilic core polymer, while phosphoric acid di-(2-ethylhexyl) ester would exist within the intermediate shell layer. This preferred location of each PAPE can be explained by using the partition coefficients ($\log P_{\text{Octanol/Water}}$) and water solubilities ($\log S$) as shown in Table 3. They were calculated by using the ALOGPS 2.1 program which has been widely used to predict $\log P$, $\log S$ and pK_a of chemical compounds for drug design and environmental chemistry studies [31]. $\log P$ values of dibutyl ester and di-(2-ethylhexyl) ester are 1.64 and 5.15, respectively, which indicates that dibutyl ester is more polar than di-(2-ethylhexyl) phosphate as expected from their chemical structures. It was confirmed that the specific PAPE was located preferentially in the polymer layer with a similar polarity, which can be quantified by $\log P$ value.

The composite particles loaded with PAPE were neutralized with 28% aqueous ammonia solution at 93 °C. As explained above, the core polymer of the composite particles was swollen when the particles were neutralized by the base. The expansion may involve partial merging of the outer periphery of the core into the inner periphery of the shell and partial enlargement of the shell. When the swelling agents were removed by drying, the shrinkage of the

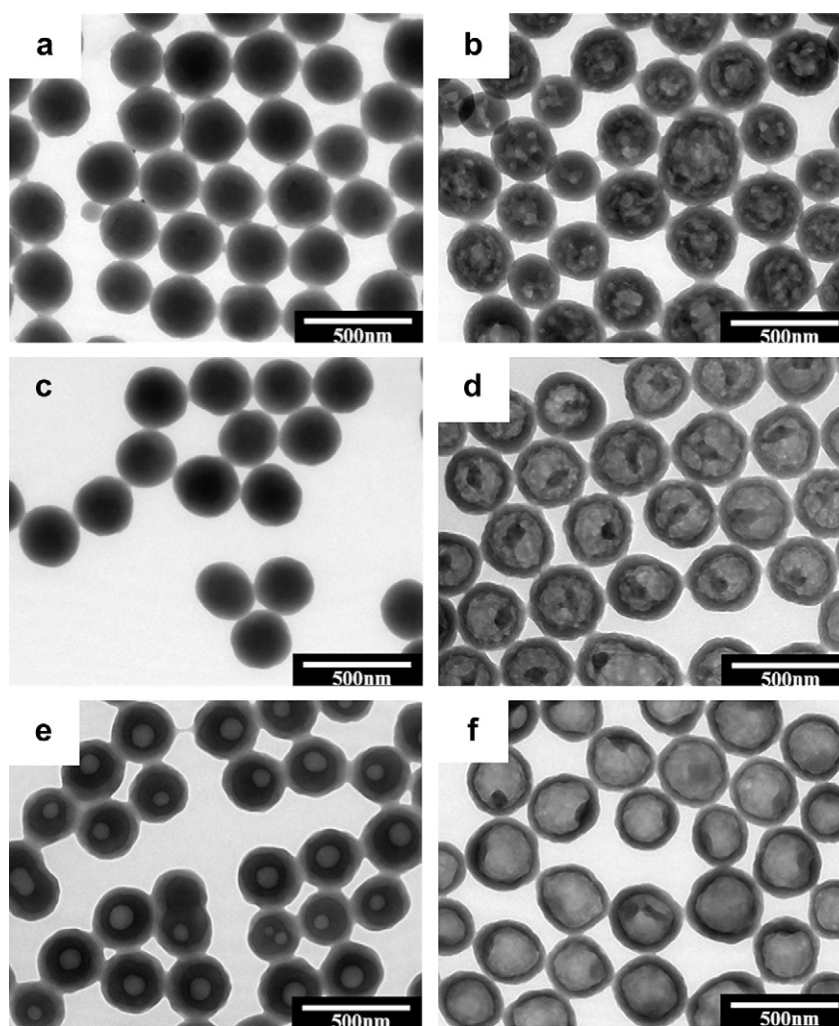


Fig. 2. TEM micrographs of the resultant polymer capsules before (a, c, e) and after the neutralization (b, d, f) using 10 g of 28% aqueous ammonia solution when (a, b) phosphoric acid dibutyl ester, (c, d) phosphoric acid 2-ethylhexyl ester (mono- and di-ester mixture) and (e, f) phosphoric acid di(2-ethylhexyl) ester were added to the emulsion at the initial stage of the polymerization.

Table 3
Partition coefficients and water solubilities of PAPEs and each stage of polymers.

	logP	logS
<i>PAPE</i>		
monobutyl ester	0.44	-0.78 (25.08 g L ⁻¹)
dibutyl ester	1.65	-1.20 (13.2 g L ⁻¹)
mono(2-ethylhexyl) ester	1.64	-1.48 (6.97 g L ⁻¹)
di(2-ethylhexyl) ester	5.15	-3.75 (57.74 mg L ⁻¹)
<i>Polymer</i>		
Core	2.35	-4.84
Intermediate shell	4.02	-5.36
Outer shell	10.82	-8.79

core would develop a void and then restore itself to its previous original state of spherical shape provided that there was no severe merging of the core into the shell and PAPE does not induce heterogeneous swelling of the core as is the case in Fig. 2 (d) and (f). Since dibutyl ester exists mostly in the hydrophilic core polymer, however, the core polymer experienced disintegration during the drying after being neutralized with a base as shown in Fig. 2 (b). This finding also supports the predicted distribution of PAPEs in each polymer layers based on the logP consideration.

3.2. Amount of encapsulated PAPEs

Thermogravimetric analysis (TGA) was performed to determine the relative amounts of phosphoric acid partial esters in polymer capsule. As a representative example, DSC scan of phosphoric acid di-(2-ethylhexyl) ester and TGA scans of various types of capsules prepared with different neutralization processes are shown in Fig. 3 (a). The DSC plot showed an endothermic peak around 280 °C, representing the evaporation of phosphoric acid di-(2-ethylhexyl)

ester. The relative contents could be estimated from the weight loss in TGA scans of the various type of capsule containing di-(2-ethylhexyl) ester between 230 °C and 330 °C. Other PAPEs contents were determined with the same method and were arranged in Fig. 3 (b). About 11 wt. % (verse input) of dibutyl ester was encapsulated when it was not neutralized by ammonia. Di-(2-ethylhexyl) ester and 2-ethylhexyl ester (mono- and di-ester mixture) were encapsulated about 35 wt. % (verse input) when it was not neutralized by ammonia. The contents of di-(2-ethylhexyl) ester within the capsule when it was neutralized by ammonia after styrene sell forming stage was 5 wt. % (verse constructing polymer). From the result, it was verified that substantial amount of PAPEs can be encapsulated. When the capsule was neutralized by ammonia subsequently or simultaneously, the content of PAPEs in the polymer capsule was slightly decreased with the exception to the subsequently neutralized capsule containing di-(2-ethylhexyl) ester. It is believed that the encapsulated PAPEs were released out from the capsule due to the decrease of distribution coefficient. Distribution coefficient of acidic material usually decreases with increase of pH in the aqueous phase [32]. Phosphoric acid di-(2-ethylhexyl) ester was most efficiently encapsulated by the polymer capsule. However, phosphoric acid dibutyl ester was not encapsulated in the capsule as much as di-(2-ethylhexyl) ester. The tendency of the encapsulation was in line with the partition property of PAPEs. It was concluded that encapsulation efficiency depends on the intrinsic characteristics, such as the partitioning coefficient of PAPE.

3.3. Morphology manipulation of the hollow capsule

The hollow polymer particle can be used as the control release apparatus for the encapsulated materials. The surface manipulation

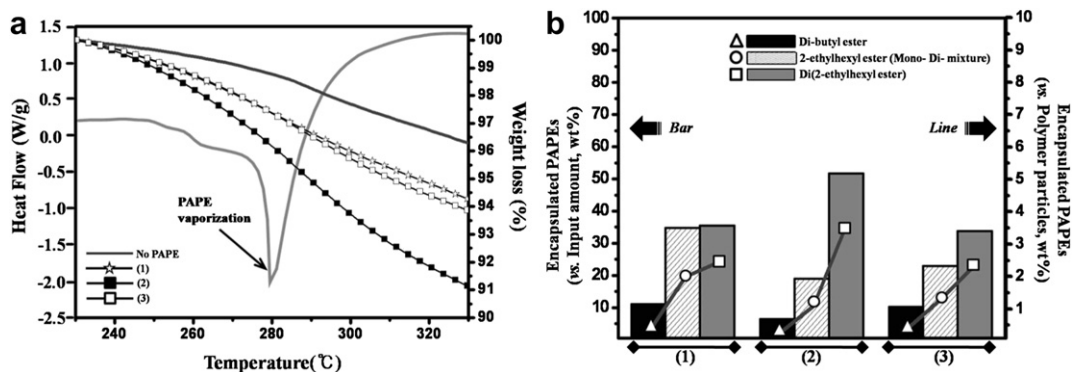


Fig. 3. (a) Representative DSC and TGA curves for the polymer capsules containing phosphoric acid di(2-ethylhexyl) ester. (b) Relative contents of phosphoric acid partial esters within the various capsules (1) un-neutralized, or neutralized by ammonia (2) during or (3) after the styrene polymerization.

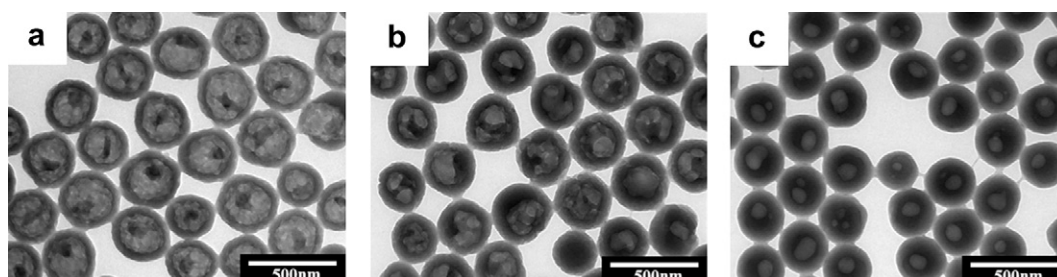


Fig. 4. TEM micrographs of polymer capsules containing phosphoric acid 2-ethylhexyl ester (mono- and di-ester mixture) when neutralized with (a) 28% aqueous ammonia, (b) 20% aqueous DMEA and (c) 20% aqueous TEA solution at 93 °C.

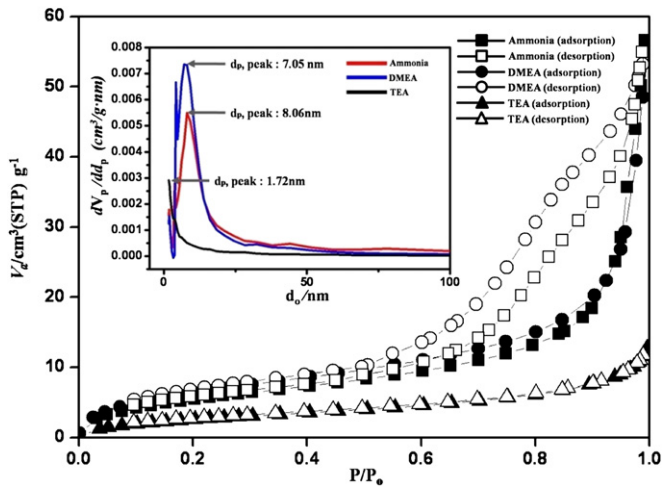


Fig. 5. Nitrogen adsorption-desorption isotherms and BJH pore size distribution plot (desorption branch) (inset) for the polymer capsules when neutralized at 93 °C with 10 g of 28% aqueous ammonia, 40 g of 20% aqueous DMEA or 40 g of 20% aqueous TEA after the styrene polymerization.

of polymer capsule is essential because the release kinetic of encapsulated materials is significantly dependent on shell morphology such as roughness and pore size. It was expected that the morphology of the polymer shell could be transformed by

varying the process parameters at the osmotic swelling stage. In the present work, various process parameters were manipulated at core expansion stage and the changes of the capsule morphology were investigated.

To investigate the morphology changes originating from the different types of the neutralization bases, the synthesized polymer capsule containing phosphoric acid 2-ethylhexyl ester (mono- and di-ester mixture) was neutralized with 28% aqueous ammonia, 20% aqueous DMEA and 20% aqueous TEA solution in the post-polymerization step at 93 °C. As shown in Fig. 4, the core polymer swelled up remarkably and the shell morphology was changed significantly when neutralized by ammonia and DMEA. Because ammonia and DMEA have a lower molar mass and relatively high basicity compared with TEA, these could diffuse easily through shell polymer layer and effectively neutralize the core polymer containing carboxylic acid groups. Due to the higher osmotic pressure generated by ammonia and DMEA neutralization, more water could subsequently imbibe into the core polymer from aqueous medium, which resulted in the expansion of the composite particles and formation of the substantial pore in the shell of the capsule as shown in Fig. 5. It is obvious that the nitrogen isotherm of the ammonia and DMEA neutralized composite particles exhibited hysteresis behavior, indicating that the walls of the polymer capsules were mainly mesoporous with average pore size of 7–8 nm. However, in case of TEA neutralized one, the polymer shell was virtually nonporous because of lower degree of diffusion through the shell due to their higher molecular weight and lower

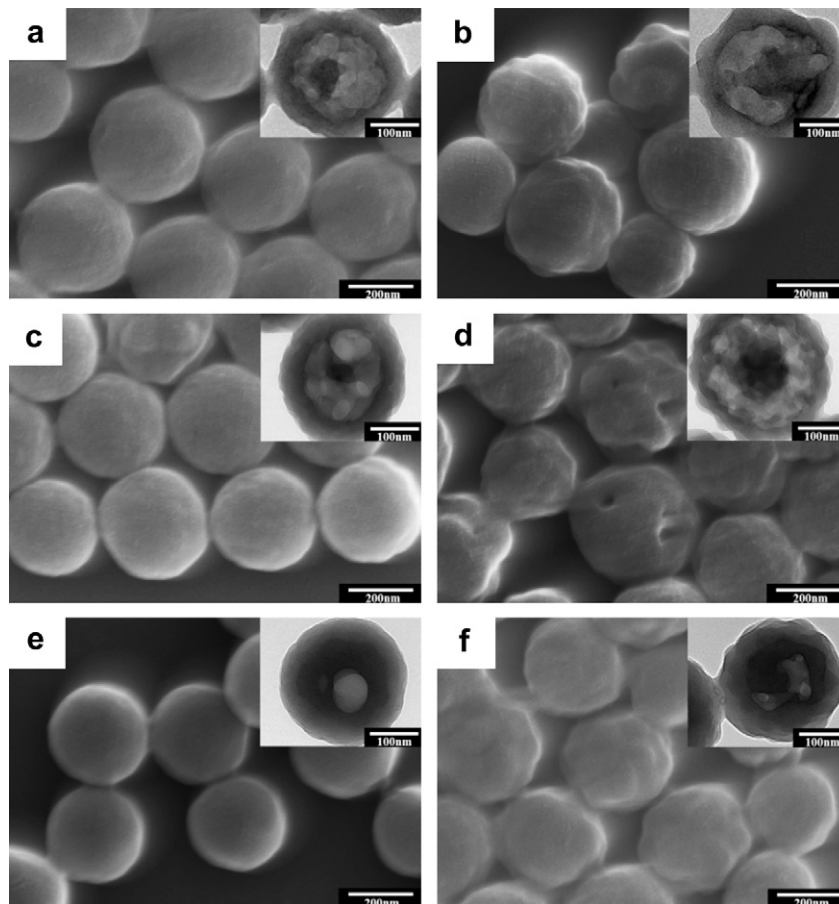
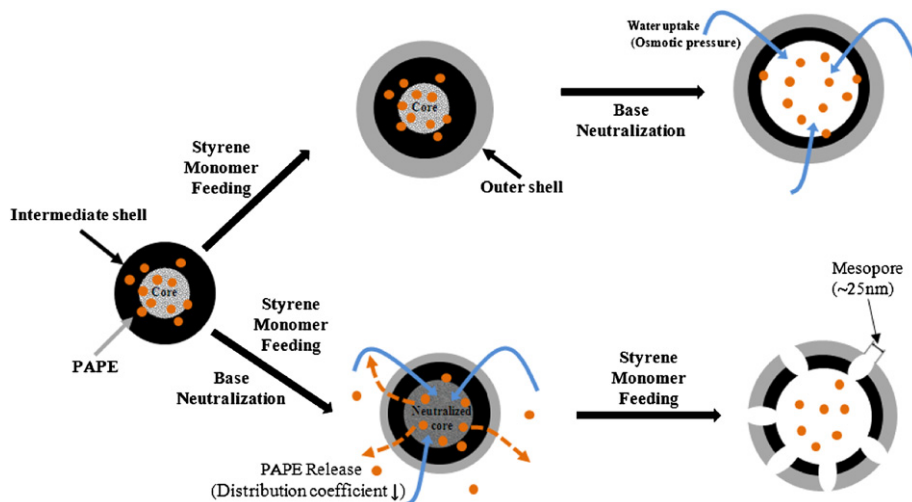


Fig. 6. SEM micrographs of the hollow polymer capsules containing phosphoric acid 2-ethylhexyl ester (mono- and di-ester mixture) when neutralized (a) after or (b) during the styrene polymerization with 28% aqueous ammonia; when neutralized (c) after or (d) during the styrene polymerization with 20% aqueous DMEA; when neutralized (e) after or (f) during the styrene polymerization with 20% aqueous TEA; insets are the corresponding TEM images.



Scheme 1. Schematic illustration of the formation of hollow particles with mesopores in their surfaces.

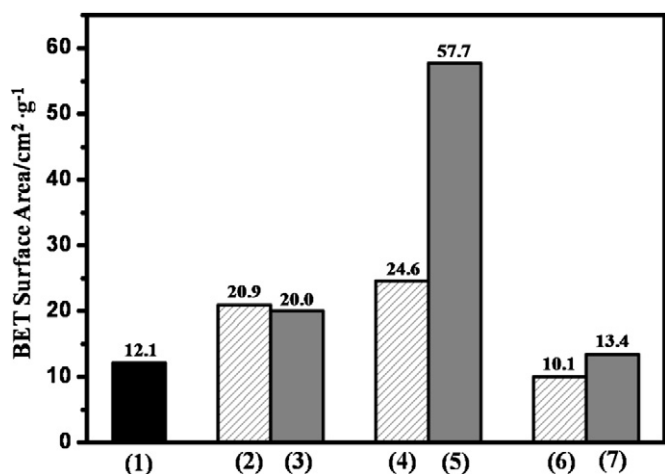


Fig. 7. BET surface area of the hollow polymer capsules which were (1) un-neutralized and neutralized with 28% aqueous ammonia (2) after and (3) during the styrene polymerization; with 20% aqueous DMEA (4) after and (5) during the styrene polymerization; with 20% aqueous TEA (4) after and (5) during the styrene polymerization.

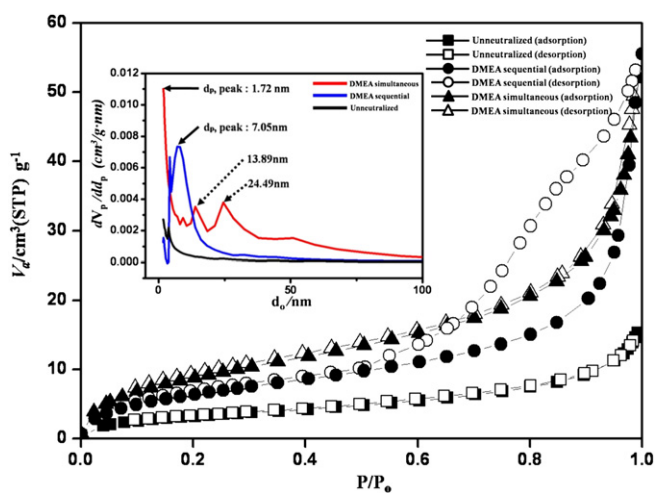


Fig. 8. Nitrogen adsorption/desorption isotherms and BJH pore size distribution plot (desorption branch) (inset) for the polymer capsules when neutralized with 40 g of 20% DMEA after or during the styrene polymerization.

basicity. Further investigations found that the sequence of neutralization stage, e.g., during or after polymerization of styrene, dramatically influenced the morphology of the swollen composite particles loaded with PAPEs. Fig. 6 shows TEM and SEM images of polymer capsules synthesized by simultaneous or sequential feeding of ammonia, DMEA or TEA with the styrene pre-emulsion feed at 85 °C. It was found that the core polymer was expanded more sufficiently when the neutralization base was fed into the reactor simultaneously with the monomer feed than when it was fed sequentially after the completion of the polymerization of styrene. Moreover, the polymer shell roughness was increased and the pore size was also enlarged when the polymer capsule was neutralized especially with DMEA during styrene polymerization. The neutralizing base could be easily diffused into the carboxylic acid group of the core polymer at the initial stage of styrene polymerization because there was only a thin PMMA polymer shell and the presence of monomer at the loci of polymerization of styrene will reduce viscosity of the polymer shell. Thus, the higher osmotic pressure was generated and more water could be imbibed into the core polymer. In addition, it was expected that the polyelectrolyte salts formed would leach out of the particle to aqueous medium because of their high water solubility or low $\log D_{\text{Octanol/Water}}$ value. To confirm the PAPEs transport during the neutralization stage, $\log D_{\text{Octanol/Water}}$ of di-(2-ethylhexyl) ester was measured in the similar pH condition of polymerization emulsion at neutralization stage. The calculated $\log D_{\text{Octanol/Water}}$ in the neat deionized water was 2.498. However, when the bases were added to the octanol-water system, $\log D_{\text{Octanol/Water}}$ significantly decreased; ammonia ($\log D_{\text{Octanol/Water}} = 1.255$ at pH = 11.05), DMEA ($\log D_{\text{Octanol/Water}} = 1.201$ at pH = 10.13), TEA ($\log D_{\text{Octanol/Water}} = 1.241$ at pH = 9.88). This bi-directional transport of chemicals, inward and outward flow through the particles, will increase the porosity of the polymer wall of the resultant hollow composite particles. Also, di-(2-ethylhexyl) ester preferentially existing in the intermediate shell layer will act as a so-called porogen during the formation of the hollow polymer capsules and also increase the hydrophilicity of polymer at the polymerization loci, which will further increase the deformation of the hydrophobic shell polymer and the formation of large pore in the shell as depicted in Scheme 1. When the capsule was neutralized simultaneously with DMEA, the surface area of the capsule was 57.7 m² g⁻¹, which was about five times that of un-neutralized one and about 2.5 times higher than that of other capsules as shown in Fig. 7. The fact that most mesopores formed were larger than 10 nm, as shown in Fig. 6 and Fig. 8, assist the

likely occurrence of such complicated morphology development during simultaneous polymerization of styrene illustrated in Scheme 1. It has been first reported in this paper that large mesopores in the 10~50 nm range can be introduced into the polymer wall having macroscopic hollow core loaded with functional chemical compounds in a tunable way. It is believed that such structured hollow composite particles may be applicable for drug and DNA delivery systems, biomolecular encapsulation, biomarker harvest and self-healing material designs.

4. Conclusion

We have demonstrated that the multi-stage emulsion polymerization could be used as the technique to encapsulate active materials, phosphoric acid partial esters, inside polymer particles. The resultant hollow polymer particles can be employed to store and release of active materials on demand, which is very important characteristic for smart materials design. From a series of studies for the encapsulation of phosphoric acid partial esters by emulsion polymerization, the conclusion is summarized as follows,

- (1) The hollow polymer capsule was successfully prepared by multi-stage emulsion polymerization. The key points for the recipe for hollow polymer particles are low monomer partitioning in the seed particles, introduction of intermediate shell forming stage and a higher instantaneous conversion of monomers during shell forming stages. The size of synthesized polymer capsules was around 300 nm with uniform particle size.
- (2) Phosphoric acid partial esters were encapsulated in hollow polymer capsules. The principal strategy for encapsulation was manipulation of the partitioning of active materials within the polymer matrix of the capsule. From studies of encapsulation behaviors, it was found that the encapsulation efficiency was mainly dependant on the partition coefficient of phosphoric acid partial esters. Furthermore, the encapsulated phosphoric acid was preferentially located in the specific polymer matrix which has a similar partition coefficient.
- (3) The morphology of polymer capsules was manipulated by varying the process parameter at the core polymer expansion stage. The surface area and pore size could be significantly changed at a certain synthesis condition. When N,N-dimethylethanolamine simultaneously added during styrene polymerization, the surface area of polymer capsule was increased drastically from $12.1 \text{ m}^2 \text{ g}^{-1}$ to $57.7 \text{ m}^2 \text{ g}^{-1}$ due to the formation

of mesopores of about 25 nm diameter and resultant roughened surface on the hollow polymer particles.

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References

- [1] Caruso F. *Advanced Materials* 2001;13:11–22.
- [2] Langer R. *Nature* 1998;392:5–10.
- [3] Bergbreiter DE. *Angewandte Chemie International Edition* 1999;38:2870–2.
- [4] Gill I, Ballesteros A. *Journal of the American Chemical Society* 1998;120:8587–98.
- [5] Oh JK, Lee DI, Park JM. *Progress in Polymer Science* 2009;34:1261–82.
- [6] Yang X, Chen L, Huang B, Bai F, Yang X. *Polymer* 2009;50:3556–63.
- [7] Jungmann N, Schmidt M, Maskos M. *Macromolecules* 2002;35:6851–7.
- [8] Guan G, Zhang Z, Wang Z, Liu B, Gao D, Xie C. *Advanced Materials* 2007;19:2370–4.
- [9] White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, et al. *Nature* 2001;409:794–7.
- [10] Cho SH, White SR, Braun PV. *Advanced Materials* 2009;21:645–9.
- [11] Yang J, Keller MW, Moore JS, White SR, Sottos NR. *Macromolecules* 2008;41:9650–5.
- [12] Blaiszik BJ, Caruso MM, McLroy DA, Moore JS, White SR, Sottos NR. *Polymer* 2009;50:990–7.
- [13] Xiao DS, Yuan YC, Rong MZ, Zhang MQ. *Polymer* 2009;50:560–8.
- [14] Jungmann N, Schmidt M, Ebenhoch J, Weis J, Maskos M. *Angewandte Chemie International Edition* 2003;42:1713–7.
- [15] Antonietti M, Förster S. *Advanced Materials* 2003;15:1323–33.
- [16] Caruso F, Caruso RA, Möhwald H. *Science* 1998;282:1111–4.
- [17] Deamer DW, Barchfeld GL. *Journal of Molecular Evolution* 1982;18:203–6.
- [18] Liu S, Weaver JNM, Tang Y, Billingham NC, Armes SP. *Macromolecules* 2002;35:6121–31.
- [19] Ottewill RH, Schofield AB, Waters JA, Williams NSJ. *Colloid and Polymer Science* 1997;275:274–83.
- [20] Schork FJ, Poehlein GW, Wang S, Reimers J, Rodrigues J, Samer C. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 1999;153:39–45.
- [21] Shchukin DG, Zheludkevich M, Yasakau K, Lamaka S, Ferreira MGS, Möhwald H. *Advanced Materials* 2006;18:1672–8.
- [22] Lamaka SV, Zheludkevich ML, Yasakau KA, Serra R, Poznyak SK, Ferreira MGS. *Progress in Organic Coatings* 2007;58:127–35.
- [23] Buchheit RG, Guan H, Mahajanam S, Wong F. *Progress in Organic Coatings* 2003;47:174–82.
- [24] Shchukin DG, Möhwald H. *Advanced Functional Materials* 2007;17:1451–8.
- [25] Yang H, van Ooij WJ. *Progress in Organic Coatings* 2004;50:149–61.
- [26] Durant YG, Sundberg DC. Washington. In: Glass E, editor. *Technology for waterborne coatings*, ACS Symposium series, 663; 1997. p. 44–56.
- [27] Kuznetsov YI, Andreeva NP, Kazanskaya GY. *Protection of Metals* 2000;36:351–5.
- [28] Müller B, Förster I. *Corrosion Science* 1996;38:1103–8.
- [29] Park JM. *Korea Polymer Journal* 2001;9:51–65.
- [30] Muroi S, Hosoi K, Ishikawa T. *Journal of Applied Polymer Science* 1963;11:1967–78.
- [31] Tetko IV, Tanchuk VY, Villa AEP. *Journal of Chemical Information and Computer Sciences* 2001;41:1407–21.
- [32] Scherrer RA, Howard SM. *Journal of Medicinal Chemistry* 1977;20:53–8.