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Facile Route to Synthesize and Morphology Control of Anionic Waterborne Polyurethane Hollow Microspheres via Self-Crosslinking Reaction

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Porous waterborne polyurethane （WPU） hollow microspheres were synthesized via self-crosslinking reaction of WPU prepolymer terminated by 3-Aminopropyltriethoxysilane (APTES). The microspheres with different morphologies were fabricated by changing the content of small molecules and hydrophilic groups.

Polymeric hollow microspheres have attracted intense research attention in recent years because of its unique properties, such as low density, high specific area, good flow ability and surface permeability. This class of polymeric hollow microspheres provides a new platform for applications in catalysts,[1-2] sensors,[3] controlled drug release,[4-6] microreactor[7-8] as well as nucleic acids transfection.[9] In addition to the applications mentioned above, polymeric hollow microspheres have also been found potential applications in several areas such as medical diagnosis, e-ink and photonics.[10-11] A variety of methods have been used for synthesis of the polymeric hollow microspheres, such as stepwise alkali-acid method,[12] template method,[13-15] self-assembly method,[16-18] precipitation polymerization and emulsion polymerization.[19-23] In order to obtain these unique properties, it is necessary to control their morphologies such as microsphere size, pore size and porosity.[19, 24]

Numerous reports have been devoted to synthesizing polymeric hollow microspheres with controllable morphology. Deng et al[19] synthesized polymeric hollow particle by seeded emulsion polymerization, the morphology of particle controlled by changing the size of carboxyl-containing core particles. Tavandashti et al[25] successfully prepared hollow polyaniline (PANI) structures with size controlled from nanotubes to microsphere by changing the synthesis conditions using a simple soft template method. Gao et al[26] fabricated Polymethylmethacrylate (PMMA) microspheres with porous and/or hollow structure via a nonsolvent assisted electrospraying, the most important factor for the formation of porous or hollow structure is that the nonsolvent induced phase separation.

Waterborne polyurethane (WPU) have attracted increasing research interests due to its excellent biocompatibility and unique soft hard segment structure, which have found tremendous application potential in polymeric hollow microspheres. The morphology of WPU hollow microspheres could be controlled by changing the molecular structure of WPU molecular chain. The methods have been reported to controlling morphology of polyurethane (PU) hollow microspheres were complicated. Li et al[11] fabricated PU hollow spheres with size-tunable single holes through self-assembly diffusion process, the hole size could be easily tuned from 75 to 210 nm. Hollow polyurea microspheres with uniform morphology prepared through a three-step process via precipitation polymerization were reported by Kong et al.[27] To the best of our knowledge, there have been no reports of self-crosslinking reaction to prepare polymeric hollow microspheres with controllable morphology.

Herein we synthesize anionic waterborne polyurethane (WPU) microspheres with porous and hollow structure through a facile route, of which the size of microspheres and cavities could be controlled by changing the content of small molecules and hydrophilic groups. The synthesis route is as illustrated in Scheme 1. In the first step, the WPU prepolymer were terminated by 3-Aminopropyltriethoxysilane (APTES), which is an organofunctional alkoxysilane monomer that can undergo the sol-gel reaction which involve the hydrolysis and polycondensation reactions of the alkoxy groups. Some water was then added, the $Si(OC_2H_5)_3$-terminated WPU prepolymer were subsequently self-crosslinked into microspheres with methylbenzene droplets encapsulated. The three-dimensional crosslinking structure of WPU microspheres were formed by the hydrolysis of ethoxy groups in WPU prepolymer, which leads to the formation of silanol groups (Si-OH), subsequently they condense to form siloxane (Si-O-Si) three-dimensional network structure. After the self-crosslinking reaction of WPU prepolymer was completed, the stable WPU microspheres encapsulate methylbenzene droplets were obtained. The

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cavity was formed by removal of methylbenzene droplets with heating. The diffusion flow of methylbenzene opened up the WPU microspheres and caused porous morphology.

In this paper, the WPU hollow microspheres were synthesized with different content of methylbenzene and carboxyl acid group, in order to obtain WPU hollow microspheres with different morphologies.

Figure 1 shows the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of WPU hollow microspheres. It can be observed that all the WPU microspheres with hollow and porous structure. The holes distributed on the surface of microspheres were inhomogeneous in distribution and size, one big hole and numerous small holes can be observed on the surface of microspheres, which were caused by the ununiformity in thickness of microspheres walls. Statistically, the average size of holes on the surface of WPU hollow microspheres was about 268nm. The big hole was preferred to be formed at the thinnest part of the microspheres walls where the methylbenzene droplets were biased, as shown in Figure 1A. Therefore, the size of big hole can be tuned by controlling the diffusion rate of methylbenzene droplets at different heating temperature, similar research have been reported by Li et al.[11] It is worth noting that the cavities were not exactly at the center of microspheres, they were biased toward on side of the microspheres due to the combining of Brownian motion and gravity action of methylbenzene droplets, as shown in Figure 1B.

Comparing with template method, methylbenzene droplets used in this research can be considered as template of hollow microspheres. The size of microspheres and cavities are strongly dependent on the volume of methylbenzene droplets. In order to verify this hypothesis, a series of TEM images of the WPU hollow microspheres with different mass ratio of methylbenzene and prepolymer were taken under the same condition. As shown in Figure 2A~E, with the mass ratio of methylbenzene and prepolymer increased from 0.6 to 1.8, the volume of methylbenzene droplets encapsulated by WPU increases, the microspheres size increased from 1.6 μm to 24.825 μm, the cavity ratio increases.

For WPU system, the concentration of hydrophilic groups was considered to be the most important factor in particle morphology. Figure 3 shows a series of optical microscope (OM) images of WPU hollow microspheres with different carboxyl concentrations under the same condition. The average size of microspheres is decreased along with the concentration of carboxyl groups increasing, as shown in Figure 3A~E. It can be observed that micropsheres had a shape of anomalous spherical when the concentration of carboxyl groups reached 1.4 wt%, as shown in Figure 3D and Figure 3E. With the increasing of carboxyl groups concentration, the water swelling degree of microspheres raised and stability of microspheres decreased, microspheres will deformed under shear stress at the process of self-crosslinking reaction.

In order to obtain the real sizes of WPU microspheres, 400 microspheres were investigated randomly in OM images and the diameter of microspheres were analyzed by statistics. As can be seen in Figure 4, the number average diameter of microspheres increased with increasing methylbenzene content and decreased with increasing carboxyl groups content. The increasing amplitude of microspheres diameter decreased from 1451.56 % to 540 % with carboxyl group content increases from 0.8 wt% to 1.6 wt%, while decreasing amplitude of microspheres diameter increased from 35.5 % to 74.22 % with the mass ratio of methylbenzene and prepolymer increases from 0.6 to 1.8.

In summary, a facile synthetic strategy to prepare WPU hollow microspheres with porous structure via a self-crosslinking reaction of prepolymer has been demonstrated. The microspheres size and cavity ratio were increased with the mass ratio of methylbenzene and prepolymer increasing. Microspheres had a shape of anomalous spherical when the concentration of hydrophilic groups exceeded 1.4 wt% due to the shear stress. There was different variation amplitude of microspheres diameter with different methylbenzene and carboxyl groups content. The methodology revealed in this study provided a unique synthestic route in WPU hollow microspheres, the morphologies of microspheres were various (such as nanometer to micrometer sizes, porou, single holes and closed-cell structures, rod-like structure and elasticity microspheres) by changing the ratio of reactants, reaction conditions and raw material types. The synthesized WPU microspheres with hollow and porous structure provided a new platform for applications in coating, leather retanning agent, flatting agent and as vehicles for sustained delivery of biologically active agents such as drug molecules, nutrients and growth factors. Ongoing work is underway.

Experimental section

Materials and Instrumentation

Isophorone diisocyanate (IPDI) was obtained from Bayer. 1,4-Cyclohexanedimethanol (CHDM) and 2,2-Bis(hydroxymethyl) propionic acid (DMPA) were obtained from Sigma-Aldric. 3-Aminopropyltriethoxysilane (APTES) was supplied from Alfa-Aesar. Methylbenzene, Acetone and Triethylamine （TEA） were produced by SCR. Prior to use, the IPDI and CHDM was purified by distillation under vacuum, acetone was treated with 4-Å molecular sieves for over one week.

The morphologies of the microspheres were measured with transmission electron microscope (TEM) (JEM-2100 from JEOL, Japan), cold field emission scanning electron microscope (SEM) (S-4800 from HITACHI, Japan) and optical microscope (OM) (BX-53 from OLYMPUS, Japan).

Preparation of WPU hollow microspheres

In a 250 ml three-necked, round-bottom flask fitted with reflux condenser, stirrer and mercury thermometer were used as reactor. A stoichiometric amount of IPDI, DMPA, methylbenzene and acetone were mixed and the reaction mixture was subsequently stirred for 1.5 h at 80 ℃. Then CHDM and Bismuth catalysts were added to the flask and reacted for 1.5 h at 80 ℃. After cooling the reaction mixture to room temperature, APTES was added drop by drop in the time of 5 min and reacted for 1 h at room temperature. After that,

TEA was added to the reactor and mixed thoroughly 5 min to neutralize carboxyl groups in prepolymer. Distilled water was added under vigorous mechanical stirring for 2 h to obtain WPU microspheres emulsion. Water and methylbenzene were removed by vacuum drying plants, WPU hollow microspheres were obtained.

Acknowledgements

The research was supported by the Ministry of Science and Technology of the People's Republic of China (863 Project, No. 2015AA033903).

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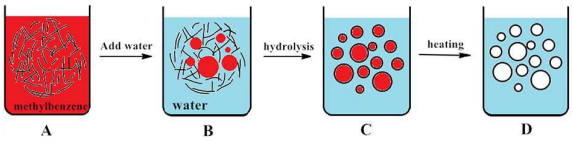
Scheme and Graphics



Scheme 1 Illustration of the synthesis route of WPU hollow microspheres.

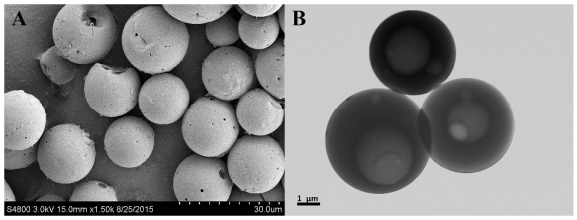


Figure 1 SEM and TEM images of the WPU hollow microspheres synthesized by the self-crosslinking route.

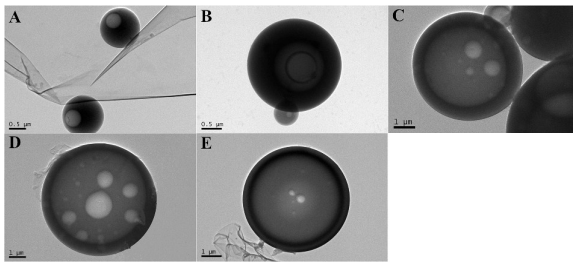


Figure 2 Series of TEM images of the WPU hollow microspheres with different mass ratio of methylbenzene and prepolymer: (A) 0.6; (B) 0.9; (C) 1.2; (D) 1.5; (E) 1.8.

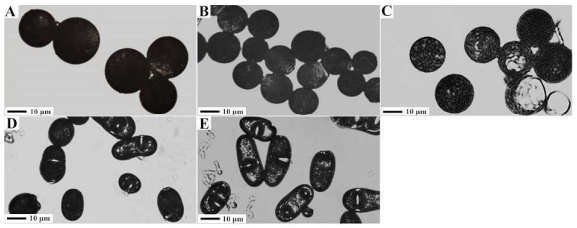


Figure 3 OM images of WPU hollow microspheres with different carboxyl concentrations: (A) 0.8 wt%; (B) 1.0 wt%; (C) 1.2 wt%; (D) 1.4 wt%; (E) 1.6 wt%.

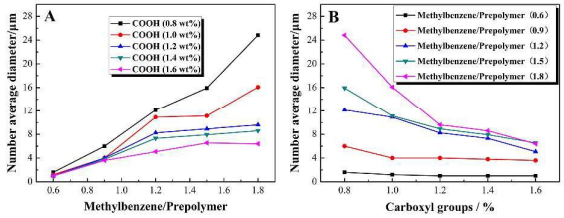


Figure 4 The effects of methylbenzene and carboxyl groups on the diameter of WPU microspheres.