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A novel approach to polymeric hollow nanospheres with stabilized structure†

Min Kuang, Hongwei Duan, Jing Wang, Daoyong Chen and Ming Jiang*

Department of Macromolecular Science and The Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China. E-mail: mjiang@fudan.edu.cn; Fax: 0086 21 65640293; Tel: 0086 21 65643919

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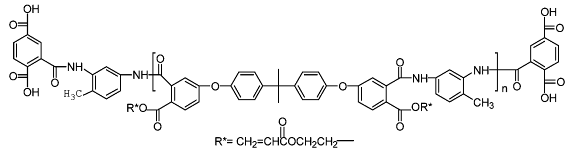
Polymeric hollow nanospheres with stabilized structure have been realized by self-assembly of crosslinkable rigid poly(amic acid) ester (PAE) oligomer and coil-like poly(4-vinylpyridine) (PVPy) *via* hydrogen bonding in their common solvent and subsequent photo-crosslinking of the PAE.

Polymeric hollow spheres with sizes ranging from nanometer to micrometer are particularly attractive functional materials due to their variety of potential applications.[1,2] Wooley *et al.*[3] and Liu *et al.*[4] produced such hollow spheres *via* self-assembly of block copolymers into core-shell micelles followed by crosslinking of the shell and degradation of the core. Meier *et al.* have prepared hydrophilic hollow spheres by polymerization of hydrophobic monomers in the template of lipid bilayer of liposomes followed by chemical modification or by self-assembly of amphiphilic ABA block copolymer.[5]

Our group has been following a *block-copolymer-free strategy* for making polymeric micelles and hollow spheres.[6–10] For example, non-covalently connected micelles (NCCM) with poly(4-vinylpyridine) as the shell and hydroxy-containing polystyrene as the core were formed in a selective solvent mixture for PVPy by inter-polymer hydrogen bonding. Then crosslinking the shell and removing the core by simple dissolution led to hollow spheres.[8]

When using carboxy-ended rod-like polyimide (PI) and coil-like PVPy as building blocks to fabricate NCCM, it was unexpectedly found that submicrometer-sized hollow spheres with a PVPy shell and a PI core formed directly in their common solvent.[10] The formation of the hollow spheres probably resulted from the propensity to parallel packing of the PI rods which were 'grafted' onto the PVPy chains through hydrogen bonding. This new way of forming hollow spheres is obviously much simpler and more straightforward than the existing methods mentioned above. However, due to non-covalent interactions connecting the core and shell, these hollow spheres are quite unstable, *i.e.* they will dissociate when the solvent or the temperature is changed.

Here we report that a crosslinkable rod-like polymer, *i.e.*, photosensitive and carboxy-terminated poly(amic acid) ester (PAE, Scheme 1),[11] and PVPy could self-assemble into hollow spheres, which could be structurally stabilized by subsequent crosslinking of the PAE. The PAE (Scheme 1) was produced by introducing photosensitive vinyl structure into PI prepolymer. (Supplementary Information†). The number-average molecular weight of the PAE was 7450, with M_w/M_n 1.23, and the molecular weight of PVPy was 1.38×10^5.



Scheme 1 Chemical structure of poly(amic acid) ester (PAE).

Upon mixing the PAE and PVPy in their common solvent THF, the blend solution turned faint blue, which indicated the formation of supramolecular aggregates in the solution. DLS studies (Table 1) showed the aggregates to have radii around 100 nm with a narrow distribution, as indicated by the low polydispersity index (PDI). Obviously, the size of the aggregates increases as the weight ratio PAE/PVPy decreases from 10.0 to 5.0, or as the chain number ratio of PAE/PVPy from 188 to 94: a low PAE/PVPy ratio corresponds to large aggregates. The relationship of aggregate size with 'graft density' is similar to that reported for the micelles of graft copolymer PAA-g-PS[12] and NCCM.[7] This dependence provides a simple way to adjust the dimensions of the supramolecular assemblies by changing the weight ratio of the component polymers.

As another way of changing the 'graft' density of PAE, we tried using a copolymer of styrene and 4-vinylpyridine SVP-32, (with a molar fraction of 4-vinylpyridine of 32%) to replace PVPy. The results showed that supramolecular aggregates could also be obtained but the micellar size was much larger and its distribution was broader compared to that of PAE/PVPy (Table 1). As the VP content in SVP decreases to 15 mol%, no aggregates with PAE are formed. In addition, the molecular weights of the two copolymers are of the same order, so the molecular weight effect on their self-assembly with PAE can be excluded. The results clearly show that there is a minimum value of the relative amount of the proton-accepting groups along the chain for forming supramoleculer assemblies.

The stabilized hollow spheres were fabricated by irradiation of the aggregate solutions in THF under a mercury lamp (365 nm, 300 W). As acrylate was not very sensitive to the irradiation, photosensitizer benzophone was used. The crosslinking reaction was more efficient than that reported in the literatures[4] as it was found that irradiation for 5 minutes at room temperature was enough to lock the structure. After the irradiation, an equivolume of dimethylformamide (DMF), which could cause dissociation of the interpolymer hydrogen bonding leading to decomplexation, was added into the solution. For a control solution without irradiation, adding DMF caused dissociation of the aggregates as monitored by DLS. For neither of the cases PAE/PVPy and PAE/SVP-32, did the integrity of the aggregates change, which meant that their structure had been successfully locked in by crosslinking. In addition, DLS showed that the crosslinked particles kept their monomodal distribution, which meant that there had been no

Table 1 Characterization data of the hollow sphere of PAE/PVPy measured by dynamic light scattering. A LLS spectrometer with a laser source of wave-length 514 nm and CONTIN analysis mode

Sample	C_{PAE} 10^3 g ml^{-1}	Before crosslinking		Crosslinked	
		$<R_h>$, nm	PD.I.	$<R_h>$, nm	PD.I.
PAE-PVPy	1.0	97.8	0.04	82.8	0.09
PAE-PVPy	0.8	114.6	0.07	89.9	0.02
PAE-PVPy	0.5	120.6	0.05	105.3	0.03
PAE-SVP32	1.0	265.0	0.12	154.3	0.18

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b210851h/

interparticle crosslinking. It was found that the size of the crosslinked sphere in THF/DMF had been significantly decreased (Table 1, Fig. 1). However, as reported in the literature, removing the inner moiety of the micelles causes a size expansion.[3,8] As discussed in our previous work,[10] the hollow aggregates of coil-rigid polymers would have a PI inner shell and a PVPy outer shell. We can reasonably assume that in the present case PVPy again will form the outer shell. In THF/DMF, the hydrogen bonding between the PAE and PVPy is disrupted and then the outer shell disappears, leading to a smaller size of the sphere. Note that we have not seen the peak associated with the individual PVPy molecules in DLS because they are too small to be detected when large aggregates are present.

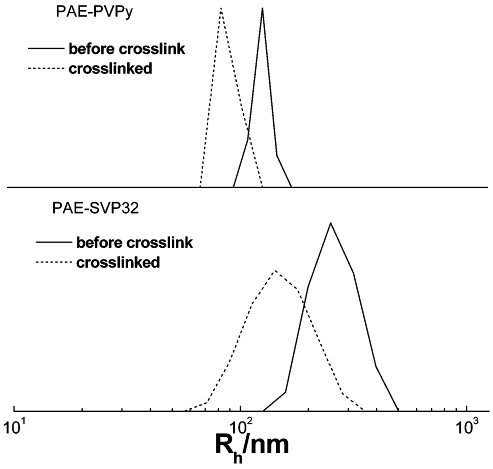

Fig. 1 Hydrodynamic radius distributions of the PAE/SVP32 (10:1, w/w) and PAE/ PVPy (10:1, w/w) hollow spheres in TIF, and the crosslinked products in solvent mixture DMF:THF = 1:1, v/v.

The three-dimensional morphology of the aggregates was studied by scanning electron microscopy (SEM) on silicon substrate. As shown in Fig. 2, most of the crosslinked hollow spheres of PAE and PVPy maintain their integrity. Further, they are relatively narrowly distributed, with the sizes comparable to the DLS results. The characteristically large cavity of the spheres can be clearly seen for the aggregates before crosslinking (Fig. 2 inset). Here some large aggregates are broken showing holes with shell thickness roughly estimated to be around 25 nm. The holes are believed to form under vacuum condition for SEM sample preparation, similar to the reports on hollow spheres from rod-coil block copolymers.[13]

The SEM images (Fig. 3) of the crosslinked hollow spheres of SVP-32 and PAE are similar to the case of PVPy and PAE.

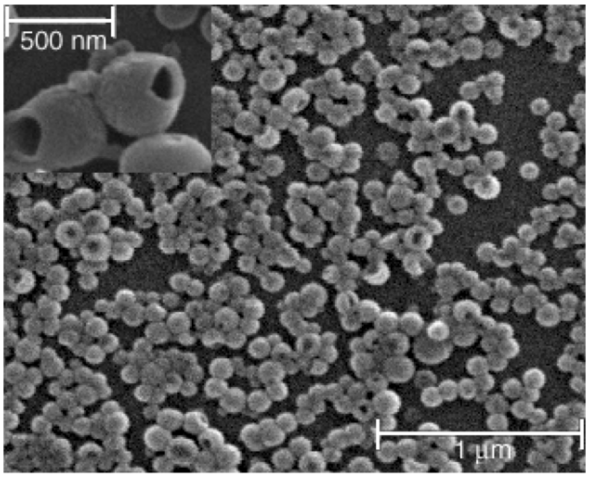

Fig. 2 Morphologies of discrete cross-linked hollow spheres of PAE/PVPy observed by SEM. The inset is for the hollow spheres before crosslinking.

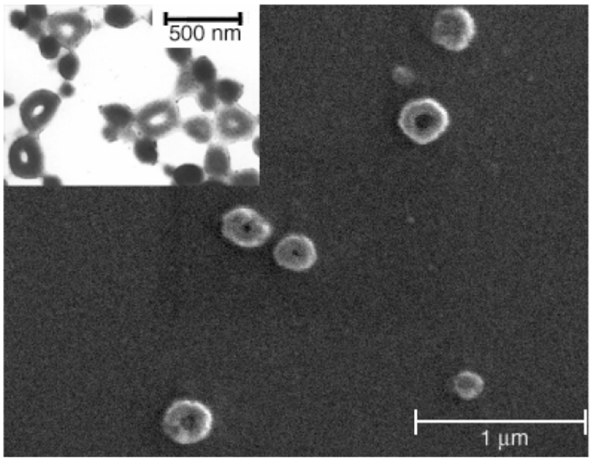

Fig. 3 Morphologies of discrete cross-linked hollow spheres of PAE/SVP32 observed by SEM and TEM (inset).

Furthermore, their TEM results (Fig. 3 inset) displayed clearly the hollow structure as evidenced by the obvious contrast between the central and surrounding part.

In conclusion, we presented a novel convenient approach to polymeric hollow nanospheres with stabilized structure. The fabrication rests on self-assembly of the rod-like PAE and coil-like poly(vinylpyridine) in their common solvent followed by a simple photo crosslinking reaction. A schematic illustration of this self-assembly process and dissolution of the outer shell is shown in Fig. 4.

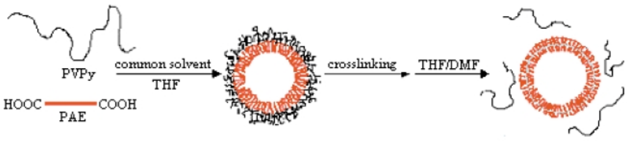

Fig. 4 A schematic illustration of the self-assembly process.

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