Stable ultrathin films and hollow spheres fabricated from P(DSS–VP) and porphyrin derivatives†

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Poly(4-diazosulfonate-styrene–4-vinylpyridine) (P(DSS–VP)), a new copolymer which possesses both photo-cross-linking and hydrogen accepting ability, was prepared and used to self-assemble (SA) with 5,10,15,20-tetrakis(4-aminophenyl) porphyrin (TAPP) or 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrin (THPP) on a quartz wafer (2D) or on submicrometre-sized spheres (3D) of styrene copolymer (or SiO_2) *via* H-bonding interactions. Under UV irradiation, the diazosulfonate groups ($-N{=}NSO_3Na$) of P(DSS–VP) decomposed resulting in the cross-linking of the film. Core–shell spheres with styrene copolymer (or SiO_2) beads as core and P(DSS–VP)/TAPP (or THPP) SA film as shell as well as the hollow spheres with cross-linked SA films as shell were prepared.

Introduction

Self-assembly (SA) techniques applied to fabricate ultra-thin films layer-by-layer have been developed rapidly.[1–3] Recently the substrate for SA has been expanded from planar (2D) to dimensional (3D) and many composite particles and hollow spheres have been prepared through SA method.[4,5] At the same time, the assembly components have also been extended from polyelectrolytes to colloidal particles, multi-functional small molecules, inorganic layer materials, biomaterials, proteins and DNA *etc.*[6a–g]

The main reason for TAPP (or THPP) being chosen as one of the SA components is that porphyrin derivatives are very important and interesting in both academic studies and practical uses. They have been widely utilized in photodynamic therapy,[7a,b] light harvesting and photocurrent generators,[7c] optical sensors,[7d] catalyst supporter for alkene epoxidation,[7e] anti-tumor agents[7f] and so on.

Although electrostatic interactions between polyelectrolytes plays a main role in SA, H-bond interactions have attracted more and more attention because of their crucial effect in biological and life sciences.[8] Many ultra-thin SA films and core–shell structures have been built up *via* H bonds in the recent decade.[9,10] However, the H-bonded SA films are not stable in strong polar solvents or high pH conditions and will be destroyed in rigid situations[10d,e] because H bonds are weak linkages. It is necessary to enhance the stability of H-bonded films through chemical cross-linking. Rubner and Yang reported that the stability of H-bonded SA films comprising polyacrylamide derivatives was enhanced *via* thermal or photo-induced cross-linking.[11a] Recently Sukhishvili and Rubner reported that the stable H-bonded SA films were prepared through the cross-linking reaction of carbodiimide.[11b,c] Both examples mentioned above need carboxyl containing polymer such as poly(acrylic acid) as one SA component and an acidic condition to limit the ionization of the carboxyl containing polymers. Although diazoresin (DR) has been used to build H-bonded SA films and those films can be stabilized by photo-cross-linking,[12a,b] unfortunately the diazonium group is not stable in basic conditions. To our best knowledge there is no example for fabrication of cross-linkable H-bonded SA film in basic conditions.

In this article, poly(4-diazosulfonate-styrene–4-vinylpyridine) P(DSS–VP), a new photosensitive copolymer was designed and synthesized. In this copolymer the pyridine group can form H bonds with amino or phenolic hydroxy group in weak basic conditions, and the photosensitive diazosulfonate group plays a cross-linking role under UV light. The photo-cross-linking degree and the density of H bonds can be efficiently controlled through the proportion of diazosulfonate and pyridine moieties. Herein we reported P(DSS–VP) self-assembled with 5,10,15,20-tetrakis(4-aminophenyl) porphyrin (TAPP) or 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrin (THPP) to build up SA films *via* H-bond interaction in basic condition on a quartz wafer (2D) and on the surface of polymer or SiO_2 particles (3D). The formed SA films were then stabilized under UV irradiation. In the case of 3D fabrication, stable hollow spheres were obtained after removing the core.

Experimental

Preparation of THPP and TAPP

5,10,15,20-Tetrakis(4-hydroxyphenyl) porphyrin (THPP) was synthesized according to the literatures[13a,b] with some modifications, and depicted briefly as follows: 5,10,15,20-tetrakis(4-methoxyphenyl) porphyrin (Fluka, 0.4 mmol) was reacted with BBr_3 (Aldrich, 1 ml) in CH_2Cl_2 at −20 °C for 1 h to transform the methoxy group into a hydroxy group. The rough THPP obtained then was purified chromatographically on a silica gel column using acetone-petroleum (bp: 60–90 °C, V : V = 1 : 1) as the eluate, yield: 70%.

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5,10,15,20-Tetrakis(4-aminophenyl) porphyrin (TAPP) was synthesized by reduction of 5,10,15,20-tetrakis(4-nitrophenyl) porphyrin (TNPP) with Sn–HCl.[14a,b] The product was precipitated from the reacted mixture by addition of NaOH. The TNPP was prepared from 4-nitro-benzylaldhyde and pyrrol in propanoic acid. The total yield of the TAPP calculated from 4-nitro-benzylaldhyde is ~21%.

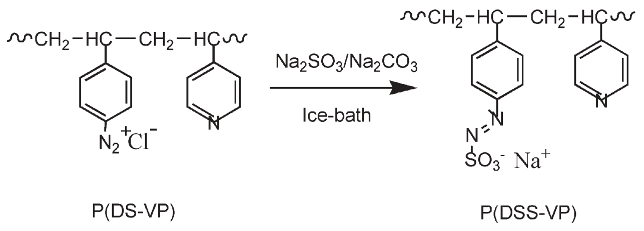
Preparation of P(DSS–VP)

P(DSS–VP) was synthesized from poly(styrene–4-vinylpyridine) (P(S–VP)) through nitration, reduction, diazotization and diazosulfonation. P(S–VP) was prepared with radical polymerization of styrene (S) and 4-vinylpyridine (VP) (2 : 1 mol) in acetic acid, $M_w = 7.3 \times 10^4$ g mol^{-1} and $d = 2.08$ (GPC, Waters). The nitration of P(S–VP) was proceeded as follows: a mixture containing 5 g P(S–VP), 15 mL concentrated sulfuric acid and 60 mL nitric acid was stirred at 0 °C for 24 h, then poured into 300 g of ice and filtered. The poly(nitro-styrene–4-vinylpyridine) (P(NS–VP)) was obtained as a yellow powder. The reduction of P(NS–VP) was carried out with HCl–Sn in DMF: 1g of P(NS–VP) dissolved in 40 mL DMF was quickly added into a mixture containing 25 mL HCl and 5 g Sn at 60 °C and refluxed for 12 h. The reactant was then poured into 500 mL ethanol to precipitate the product. The obtained poly(4-amino-styrene–4-vinylpyridine) (P(AS–VP)) was filtrated as a white powder which dissolved considerably in HCl solution. The nitration and the reduction degree were determined to be 85% and 95% respectively with elemental analysis.

Poly(4-diazonium styrene–4-vinylpyridine) (P(DS–VP)) was prepared with diazotization of P(AS–VP) carried out in $NaNO_2$–HCl aqueous solution at ~0 °C . The P(DS–VP) then reacted with aqueous solution of Na_2SO_3 and Na_2CO_3 (1 : 1, weight) to prepare poly(4-diazosulfonate styrene-4-vinylpyridine) (P(DSS–VP)) in weak basic condition (pH ~ 8–9). The ratio of benzene and pyridine moieties was calculated to be 2.4 : 1 from ^{1}H NMR (300Hz, [D$_6$]DMSO): $\delta = 6.6$ and 7.1 (benzene ring); $\delta = 8.2$, (pyridine ring)). The elemental analysis revealed that the molar ratio of C : N is 4.8 : 1, which is a little higher than the theoretical calculation (4.5 : 1) due to some side reaction occurring in the diazosulfonation reaction. The schematic reaction from P(DS–VP) to P(DSS–VP) is represented in Scheme 1.

Preparation of SA films

The quartz wafer was used as 2D substrate, which was treated previously in a mixture of 30% H_2O_2 and concentrated sulfuric acid (V : V = 3 : 7) at 80 °C for 0.5 h to give a hydrophilic surface. The treated wafer was immersed in an aqueous solution of P(DSS–VP) (1 mg mL^{-1}) for 5 min, washed with water thoroughly and air-dried; then it was dipped into a methanol solution of TAPP (1 mg mL^{-1}), washed with methanol and air-dried to complete an assembly cycle. In each cycle, a P(DSS–VP)/TAPP bilayer was fabricated on both sides of the wafer. [P(DSS–VP)/TAPP]$_n$ multilayer film was obtained by repeating fabrication for n cycles. The [P(DSS–VP)/THPP]$_n$ multilayer film was prepared in the same manner. All the work should be done in the dark.



Scheme 1 Schematic representation of the reaction from P(DS–VP) to P(DSS–VP).

Preparation of SiO_2 and styrene copolymer beads and core–shell spheres

Fig. 1 shows the TEM images of the SiO_2 and P(S–MMA–SPMAP) beads. The SiO_2 beads with average diameter of ~380 nm were prepared by Stöber method.[15] The copolymer beads (~300 nm in diameter) of poly(styrene–methyl methacrylate–3- sulfopropyl methacrylate, potassium salt) (P(S–MMA–SPMAP)) (19 : 1 : 1, weight) was prepared referring to our previous work[16] by soap free emulsion polymerization.

The core–shell composite spheres were prepared through following procedure: 1 ml of P(S–MMA–SPMAP) beads (1 mg mL^{-1}) dispersed in water was added into 2 ml of poly(diallyl–dimethyl ammonium chloride) (PDDA) aqueous solution (2 mg mL^{-1}), stirred for 30 min at room temperature. The PDDA modified polymer beads were obtained, followed by centrifugation at 20 000 rpm to remove excess PDDA and washed with water three times. Then 2 ml of P(DSS–VP) aqueous solution (2 mg mL^{-1}) was added, stirred and washed to obtain the P(DSS–VP) modified beads. Next 2 ml of TAPP (or THPP) methanol solution (2 mg mL^{-1}) was added to build up SA bilayer of P(DSS–VP)/TAPP (or THPP). The SA process was repeated n times to obtain [P(DSS–VP)/TAPP]$_n$ (or THPP) multilayer enwrapped beads (core–shell spheres). The core–shell sphere with SiO_2 beads as core was prepared in the similar manner.

Preparation of cross-linked SA films and hollow spheres

The SA films on quartz wafer were cross-linked under UV light for 10 min (irradiation density at 360 nm is 60 μw cm^{-2}). The core–shell spheres were dispersed in water and exposed with UV light for 10 min in the same condition to cross-link the shell of [P(DSS–VP)/TAPP]$_n$ (or THPP). The P(S–MMA–SPMAP) core then was dissolved out with tetrahydrofuran

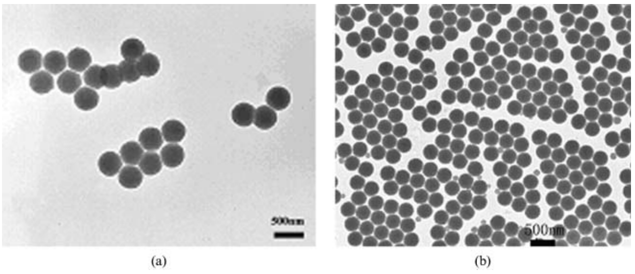


Fig. 1 TEM images: (a): SiO_2 beads (b): P(S–MMA–SPMAP) beads (scale bar: 500 nm).

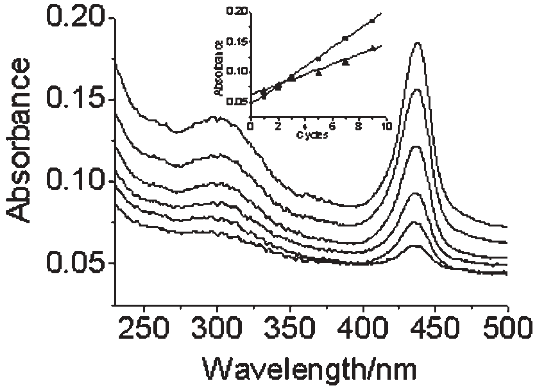


Fig. 2 UV–vis spectra of P(DSS–VP)/TAPP SA films with different fabrication cycles on quartz wafer, SA cycles (bottom to top): 1, 2, 3, 5, 7, 9. Inset plot: linear relation of the absorbance at 428 nm (square) and 303 nm (triangle) with SA cycles.

(THF, 12 h at ~25 °C) and the SiO_2 core was removed by 10% HF aqueous solution (pH = 5.5, 12 h at ~25 °C) to obtain the hollow spheres with cross-linked $[P(DSS–VP)/TAPP]_n$ (or THPP) film as shell.

Characterization

UV–vis spectra recorded on Shimadzu-2100 spectrophotometer and IR spectra recorded on the Bruker Vector 22- FTIR spectrometer were used to determine the formed films. Transmission electron microscopy (TEM, JEM200CX) was used to observe the size and morphologies of the core–shell and hollow spheres.

Results and discussion

Fig. 2 shows the UV–vis spectra of P(DSS–VP)/TAPP multilayer films prepared with different fabrication cycles. The band at 303 nm is assigned to the characteristic absorption of $–N{=}NSO_3$ group of P(DSS–VP) and 428 nm is assigned to the Soret band of porphyrin moiety. The linear relation (inset plot) between the absorbance (at 428 nm) and the cycles suggests that the alternate deposition of P(DSS–VP) and TAPP on the quartz wafer proceeds regularly. A similar result was obtained for the fabrication of P(DSS–VP) and THPP.

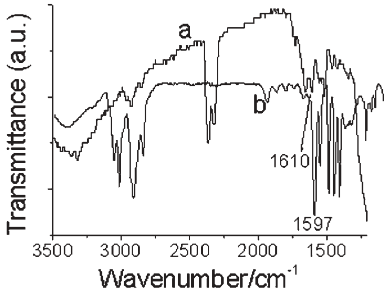


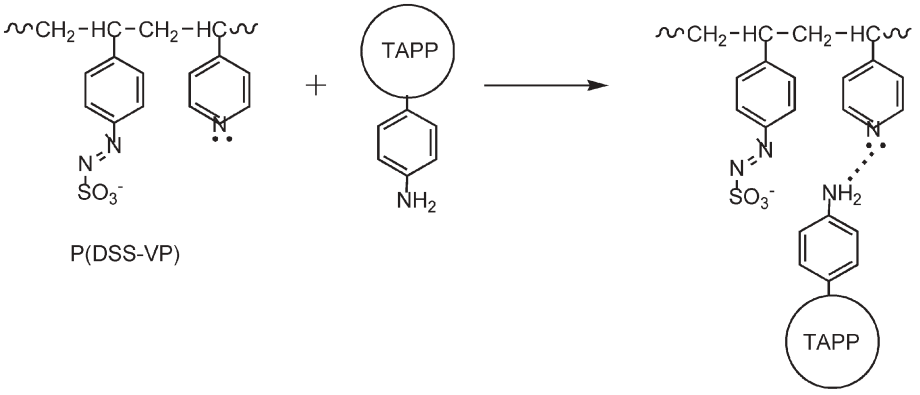
Fig. 3 IR spectra of P(DSS–VP)/TAPP SA film (line a) and the P(S-VP) copolymer (line b).

As the SA process was carried out in a weak basic condition (pH ~ 8–9) or methanol medium, the amino groups of TAPP are not protonated. The driving force between the P(DSS–VP) and TAPP, therefore, should be ascribed to the H-bond interaction between NH and pyridine groups rather than electrostatic interaction, which can be represented as Scheme 2:

In order to verify the H bond nature between P(DSS–VP) and TAPP, a 50-bilayer P(DSS–VP)/TAPP film was fabricated on a CaF_2 wafer to get IR spectra (Fig. 3). The stretching vibration of isolated pyridine ring appears at 1597 cm^{-1} in P(S–VP) coating (line b); but in $[P(DSS–VP)/TAPP]_{50}$ film it shifts to 1610 cm^{-1} (line a). It is well known that the stretching vibration of H-bonded pyridine group will shift to longer wave number.[9a,10e] So the vibration shifting 13 cm^{-1} toward longer wave number is an evidence of H-bond formation between pyridine and –NH groups.

The diazosulfonate group of P(DSS–VP) is photosensitive and will decompose under UV irradiation. Fig. 4 shows the absorption at 303 nm of $[P(DSS–VP)/TAPP]_{14}$ film decreases gradually under UV irradiation. The photoreaction of diazosulfonated compounds is rather complex and the most possible intermediate was considered to be phenyl free radical.[17] It then reacts with amino (or hydroxy) group or benzene nucleus of the TAPP (THPP) to form cross-linking structure.

Fig. 5 shows the UV–vis spectra of the irradiated and un-irradiated $[P(DSS–VP)/TAPP]_{14}$ film before and after immersion in DMF respectively. The absorbance at 423 nm and 305 nm decrease obviously for the un-irradiated film (line a and line b) after immersion for only 10 min. But there is no



Scheme 2 Schematic representation of H-bond interaction between P(DSS–VP) and TAPP.

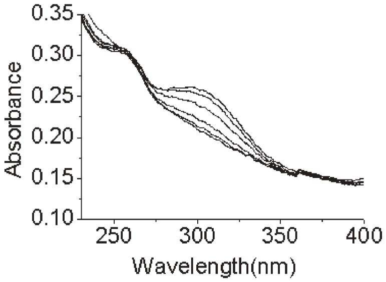


Fig. 4 UV spectra of a [P(DSS–VP)/TAPP]$_{14}$ film under UV irradiation at different time. Irradiation time (s, top to bottom): 0, 15, 30, 45, 60, 900; Irradiation density: 60 μw cm^{-2} at 360 nm.

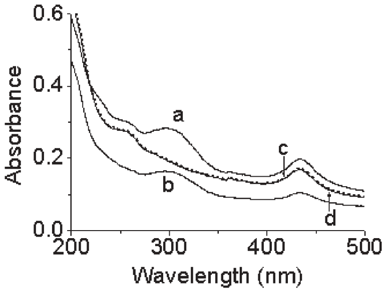


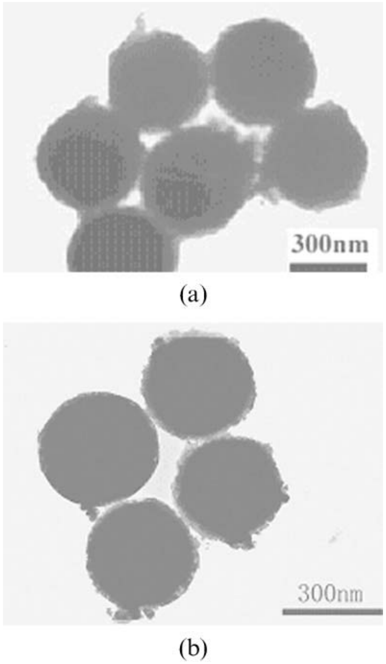
Fig. 5 UV spectra of [P(DSS–VP)/TAPP]$_{14}$ films before and after etching with DMF: Un-irradiated film before etching (a) and after etching (b) for 10 min; irradiated film before etching (c) and after etching (d) for 12 h.

considerable change for the irradiated film (line c and line d) after immersion in DMF for even 12 h. This means the irradiated P(DSS–VP)/TAPP films become very stable towards DMF etching due to the cross-linking structure by UV irradiation.

Fig. 6 shows the TEM images of the core–shell spheres with SiO_2 beads as core, cross-linked [P(DSS–VP)/TAPP]$_6$ films as shell (Fig. 6a) and P(S–MMA–SPMAP) beads as core, cross-linked [P(DSS–VP)/TAPP]$_4$ films as shell (Fig. 6b) respectively. The surfaces seem much rougher than the initial template beads. The diameter of the former composite particle increases from ~380 to ~410 nm and the latter increases from ~300 to ~320 nm. This means that the thickness of one bilayer of P(DSS–VP)/TAPP is ~2.5 nm.

Fig. 7 shows the TEM images of the hollow spheres with cross-linked [P(DSS–VP)/TAPP]$_6$ film as shell from removing the SiO_2 core with HF (Fig. 7b) and cross-linked [P(DSS–VP)/TAPP]$_4$ film as shell from removing P(S-MMA-SPMAP) core with THF (Fig. 7a). The hollow sphere surfaces show a little fold due to the shrinkage in the drying process.[18] The diameter of hollow spheres made from SiO_2 beads was measured to be ~410 nm with the shell thickness of ~15 nm, and those from polymer beads to be ~320 nm with the shell thickness of ~10 nm. Although the hollow spheres seem congregative, they can easily disperse in aqueous and non-aqueous mediums.

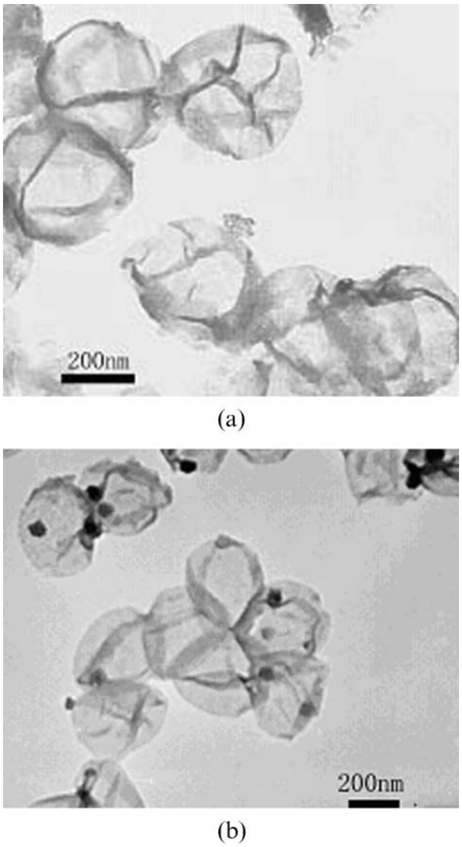
These cross-linked hollow spheres exhibit much higher stability in DMF than the un-cross-linked ones. Fig. 8a and 8b show the cross-linked and un-cross-linked hollow spheres



(a)

(b)

Fig. 6 TEM images of the composite particles (a) SiO_2 bead as core, [P(DSS–VP)/TAPP]$_6$ film as shell; (b) P(S–MMA–SPMAP) bead as core, [P(DSS–VP)/TAPP]$_4$ film as shell.



(a)

(b)

Fig. 7 TEM images of hollow spheres (a) made from removing P(S-MMA-SPMAP) core by THF; (b) made from removing SiO_2 core by HF.

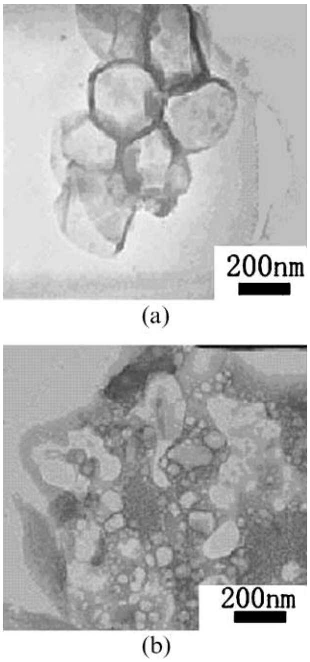


Fig. 8 TEM photographs of hollow spheres after immersion in DMF (a) cross-linked hollow spheres immersed in DMF for 24h; (b) un-cross-linked hollow spheres immersed in DMF for 30 min.

after immersing in DMF for 24 h and 30 min respectively. The shape of cross-linked spheres keeps perfectly but the un-cross-linked spheres collapse into the fragments fully. This result confirms the high stability of the cross-linked shell originated from photo-cross-linking reaction.

The porphyrin moieties of the hollow sphere are reserved after etching treatment with DMF. From the UV–vis spectra of the cross-linked hollow spheres after DMF etching, the obvious absorption peak at 424 nm indicates the reservation of porphyrin groups (Spectra can be found in the electronic supplementary information (ESI)†).

Conclusion

In conclusion, a new photosensitive copolymer P(DSS–VP) has been synthesized and used to self-assemble (SA) with TAPP (or THPP) on quartz wafer (2D SA) and on styrene copolymer (or SiO_2) beads (3D SA) in a weak basic condition. The core–shell composite spheres with $[P(DSS–VP)/TAPP (or THPP)]_n$ films as shell have been prepared. The driving force of SA between [P(DSS–VP) and TAPP (or THPP) is identified to be H-bond interaction. The photosensitive multilayer films can be stabilized by UV irradiation. The hollow spheres with cross-linked P(DSS–VP)/TAPP film as shell were prepared and demonstrated that they were very stable towards polar solvents.

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