Articles

Ion-Triggered Exfoliation of Layer-by-Layer Assembled Poly(acrylic acid)/Poly(allylamine hydrochloride) Films from Substrates: A Facile Way To Prepare Free-Standing Multilayer Films

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Received May 9, 2007. Revised Manuscript Received July 30, 2007

A facile way to prepare sheet- and tubelike free-standing films of poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH) was developed by exfoliating PAA/PAH multilayer films from substrates in acid aqueous solution containing copper ions. The exfoliation of the PAA/PAH film from the substrate was achieved by breaking the electrostatic interaction of the PAA layer with the underlying substrate while keeping the integrity of the resultant films. Further study shows that thermally cross-linked free-standing PAA/PAH film can be prepared by treating the film in acid aqueous solution with a pH of 2.0. The ion-triggered exfoliation of PAA/PAH multilayer film provides a simple and flexible way to prepare layer-by-layer (LbL) assembled free-standing multilayer films.

Introduction

Layer-by-layer (LbL) assembled multilayer films have attracted much attention in the recent decade because of their potential applications as separation membranes, sensors, optical and electronic film devices, and so forth.[1−5] The LbL assembled multilayer films are usually deposited on solid substrates which provide firm support but can meanwhile produce an influence on their properties. The preparation of LbL assembled free-standing multilayer films which exist without solid substrates is meaningful because of the following: (i) Free-standing films make it possible to investigate directly the elastomeric properties of the LbL assembled films.[6] (ii) Free-standing films are expected to broaden further the application of LbL assembled multilayer films, especially as separation membrances, sensors, catalytic film, micromechanical devices, or even artificial organs.[7] Several methods are being employed to fabricate LbL assembled free-standing multilayer films. The most frequently used and generally applicable method is using a predeposited sacrificial layer between the substrate and the LbL assembled films.[7−13] Free-standing films can be released from the substrate by dissolving the sacrificial layer in a selected solution. The sacrificial layer can be either a spin-coated polymeric film[9−11] or LbL assembled multilayer films.[7,8] Removal of the substrate is a straightforward method to prepare free-standing multilayer films. Besides the sheetlike free-standing films prepared by this method, typical examples include also LbL assembled capsules[14,15] and tubes[16−18] initially deposited on templates like colloidal spheres, anodic aluminum oxides (AAO), glass fibers, and so forth and finally released by removal of these templates. Additional methods which promise unique advantages in anticipated aspects but are not generally applicable, at least at present, include those reported by Hammond, Mallwitz, and Laschewsky. Hammond and co-workers demonstrated that free-standing hydrogen-bonded polymeric films with a thickness of several micrometers could be obtained by directly peeling the films away from the low-surface energy

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10.1021/cm071260j CCC: $37.00

substrate with tweezers.[6] This method is suitable for precursor multilayer films with extremely high mechanical strength and flexibility deposited on low-energy surface. By careful selection of a polyelectrolyte pair and the condition for film preparation, Mallwitz and Laschewsky successfully prepared free-standing polyelectrolyte multilayer films in the meshes of supports with pores of 100 μm × 100 μm.[19]

Although the combinations of the above-mentioned methods work well for most of the LbL assembled multilayer systems to prepare free-standing films, facile methods without the use of a sacrificial layer or complete removal of the substrate are still highly desirable. In this paper, we reported a facile way to prepare poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH) free-standing films by exfoliating PAA/PAH multilayer films from substrates in aqueous solution containing H^+ and/or Cu^{2+} ions. This work will open a new route to fabricate LbL assembled free-standing films by using an ion-triggered exfoliation method.

Experimental Section

Materials. Poly(acrylic acid) (PAA, M_w ca. 2000), poly(allylamine hydrochloride) (PAH, M_w ca. 70 000), and poly(diallyldimethylammonium) (PDDA, 20 wt %, M_w ca. 100 000−200 000) were purchased from Sigma-Aldrich. All chemicals were used without further purification. The concentration of polymer solutions used for all experiments was 1 mg mL^{-1} made from 18 MΩ Millipore water, and further pH was adjusted with either 1 M HCl or 1 M NaOH.

Preparation of PAA/PAH Multilayer Films. A substrate of a silicon wafer, quartz, or a glass tube was immersed in a slightly boiled piranha solution (3:1 98% H_2SO_4:30% H_2O_2 mixture) for 20 min and rinsed with copious amounts of water. In this way, the wafer was hydrophilized. ***Caution****: Piranha solution reacts violently with organic materials and should be handled carefully.* The LbL deposition of PAA/PAH multilayer films was conducted automatically by a programmable dipping machine (Dipping Robot DR-3, Riegler & Kirstein GmbH) at room temperature, as described in our previous work.[20] The substrate (includes silicon, quartz wafers, and glass tubes) was immersed in a PDDA aqueous solution for 20 min to obtain a cationic ammonium-terminated surface and was ready for PAA/PAH multilayer deposition. Next, the substrate was immersed into an aqueous PAA solution (pH 3.5) for 20 min to obtain a layer of PAA film. The substrate was then rinsed in four water baths for 1 min each before the next layer deposition. Next, the substrate was immersed into an aqueous PAH solution (pH 7.5) for 20 min to obtain a layer of PAH film. No drying step was used in the film deposition procedure. The adsorption and rinsing steps were repeated until the desired number of bilayers was obtained. The thermal cross-linking of the PAA/PAH film was conducted by heating the film at 180 °C for 2 h. Thermal cross-linking leads to the formation of amide bonds between the amine groups of PAH and the acid groups of PAA, as confirmed by the appearance of the amine I peak at ~1640 cm^{-1} in the corresponding Fourier transform infrared (FT-IR) spectra of the free-standing PAA/PAH film and PAA/PAH film deposited on the CaF_2 substrate.[21,22]

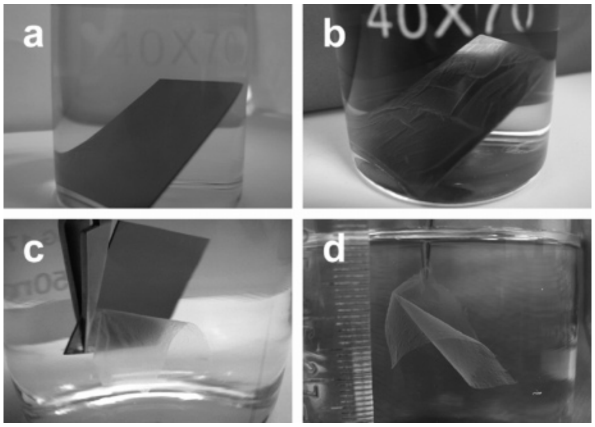

Figure 1. Photographs of a (PAA/PAH)*15 multilayer film (3 × 3 cm^2) deposited on a silicon wafer after immersion in the exfoliation solution (0.1 mol/L $CuCl_2$, pH=3.6) for different lengths of time: (a) 0, (b) 2, and (c) 4 min. (d) The free-standing (PAA/PAH)*15 film in water.

Characterization. Scanning electron microscopy (SEM) images were obtained on a JEOL JSM 6700F field emission scanning electron microscope. Atomic force microscopy (AFM) images were taken on a Nanoscope IIIa atomic force microscope (Digital Instruments, Santa Barbara, CA). The X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB250 (VG Microtech., U.K.). Digital camera images were captured by using a Canon camera (PowerShot S3 IS). Fourier transform infrared (FT-IR) spectra were collected on a Bruker IFS 66V instrument.

Results and Discussion

Multilayer films of PAA/PAH were deposited on substrates of silicon, quartz, and glass precoated with a layer of poly(diallyldimethylammonium) (PDDA) by a LbL assembly technique described in our previous work.[20] Because no drying steps were conducted during the deposition of the films, the thickness of PAA/PAH multilayer films increased exponentially with the number of film deposition cycles possibly due to the serious interpenetration of the polyelectrolytes in the neighboring layers.[20] A 15-bilayer PAA/PAH film (noted as (PAA/PAH)*15) deposited on a silicon wafer was proved to exfoliate rapidly and completely to form free-standing films with large lateral dimensions when immersed in an acidic aqueous solution of copper chloride (0.1 mol/L $CuCl_2$, pH=3.6). (The solution used here is called exfoliation solution if not specially stated.) To facilitate the exfoliation of the film, the edges of the sample were scratched or cut off with a knife. Figure 1 shows the photographs of a (PAA/PAH)*15 film deposited on a silicon wafer with a size of 3 × 3 cm^2 after being immersed in the exfoliation solution for different lengths of time. Taking the immediately immersed (PAA/PAH)*15 film as a reference (Figure 1a), ridges appear on the surface of the film after 2 min of immersion, indicating the partial separation of the films from the substrate (Figure 1b). When the length of the immersion time reaches 4 min, PAA/PAH films were released from the substrate by slightly shaking the substrate in the exfoliation solution, as shown in Figure 1c. Figure 1d shows the photograph of the (PAA/PAH)*15 free-sanding film transferred in deionized water (pH=6.2). The free-standing multilayer films keep their integrity in water over a

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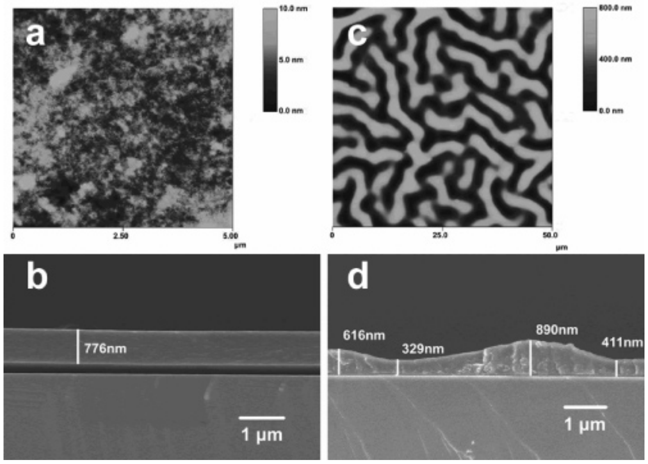

Figure 2. Microscopic characterization of (PAA/PAH)*15 multilayer films. AFM (a) and cross-sectional SEM (b) images of the as-prepared film on a silicon wafer. AFM (c) and cross-sectional SEM (d) images of the free-standing film transferred on a silicon wafer. The free-standing film was exfoliated by immersing the as-prepared (PAA/PAH)*15 film in the exfoliation solution of 0.1 mol/L $CuCl_2$ with a pH of 3.6.

period of 6 months and remain intact upon transferring to a solid substrate. Excitingly, thermal cross-linking of a (PAA/PAH)*15 free-standing film at 180 °C for 2 h turns the electrostatic interactions between carboxylate and amine groups into covalent amide bonds and enhances its robustness.[21,22] The thermally cross-linked (PAA/PAH)*15 film is stable in air.

Figure 2a shows the AFM image of the as-prepared (PAA/PAH)*15 film deposited on a PDDA-modified silicon wafer. The root-mean-square (rms) roughness of the as-prepared film is 1.7 nm. The cross-sectional SEM image (Figure 2b) reveals a uniform film with a constant thickness of 777.8 ± 5.1 nm. Figure 2c shows the AFM image of the (PAA/PAH)*15 free-standing film transferred onto a silicon wafer. Regular wavelike ridge structures appear on the surface. The width of the ridge structures is averaged to be ~3 μm. The rms roughness of the (PAA/PAH)*15 free-standing film increased to 244.0 nm. The typical cross-sectional SEM image of the (PAA/PAH)*15 free-standing film shows a wavelike profile (Figure 2d), with its thickness fluctuating in the range between ~320 nm to ~890 nm. The result of the cross-sectional SEM image is consistent with the corresponding AFM observation.

The evolution of the ridge structures is dependent on the length of immersion time of the PAA/PAH film in the exfoliation solution. Figure 3 shows AFM images of a (PAA/PAH)*15 film deposited on a silicon wafer with a size of 3 × 3 cm^2 when immersed in the exfoliation solution for different lengths of time. Within 10 s of immersion in the exfoliation solution, discontinuous ridge structures with low height appear on the surface although no exfoliation of the film from the substrate had taken place. After 30 s of immersion, continuous ridge structures can be observed. With elongating the immersion time, the ridge structures grow gradually and reach a constant within 5 min immersion. The rms roughness of the film after immersing in the exfoliation solution for 10 s, 30 s, 1 min, 5 min, and 30 min is 14.9, 115.8, 210.2, 247.5, and 244.0 nm, respectively.

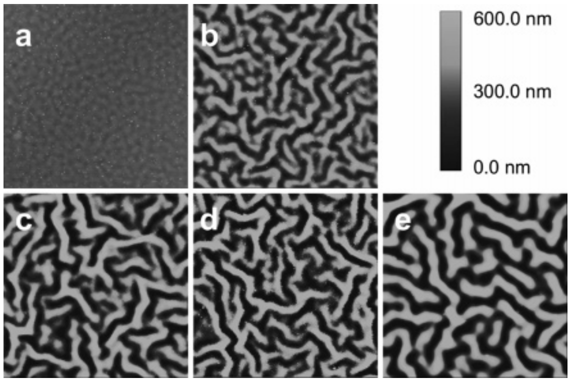

Figure 3. AFM images (50 × 50 μm) of a (PAA/PAH)*15 film deposited on a silicon wafer when immersed in an exfoliation solution (0.1 mol/L $CuCl_2$, pH 3.6) for different lengths of time: (a) 10 s, (b) 30 s, (c) 1 min, (d) 5 min, and (e) 30 min.

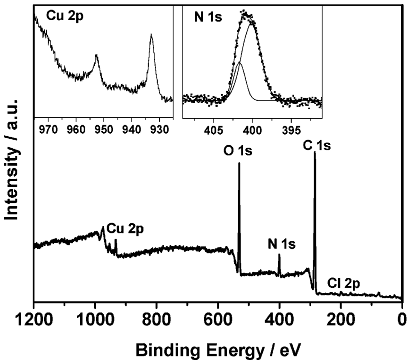

Figure 4. XPS spectra of a (PAA/PAH)*15 free-standing film released from an exfoliation solution of 0.1 mol/L $CuCl_2$ (pH 3.6).

The thickness of the PAA/PAH film takes an important role during the preparation of free-standing films. The PAA/PAH film with deposition cycles of 7, 10, and 12 has a thickness of about 102.4, 335.6, and 492.2 nm, respectively. When a (PAA/PAH)*7 film was immersed into the exfoliation solution, a cracked and incomplete free-standing film can be obtained. For a (PAA/PAH)*10 film, a continuous free-standing film scattered with holes can be obtained. When the number of film deposition cycles increased to 12, a continuous free-standing film which has the same size with the underlying substrate was finally obtained. It seems that a (PAA/PAH)*12 film is the thinnest film which can be exfoliated from the substrate by the present method to produce defect-free free-standing films.

Elemental analysis of the (PAA/PAH)*15 free-standing film was carried out by X-ray photoelectron spectroscopy (XPS). The XPS spectra (Figure 4) show the characteristic peaks of carbon (C1s 284.6 eV), oxygen (O1s 530.6 eV), and nitrogen (N 1s 400.6 eV), which is consistent with the elements of PAA and PAH. Meanwhile, the observation of the Cu 2p3/2 and Cu 2p1/2 peaks with the measured binding energy of 932.4 and 952.3 eV confirms the presence of Cu^{2+} in the PAA/PAH free-standing films. The N 1s can be deconvoluted to two peaks at 400.0 and 401.7 ev. The peak at 401.7 corresponds to the binding energy for amine groups coordinated with Cu^{2+} ions. The atomic ratio of Cu to N in the free-standing film is calculated to be 1:6.9 from their relative peak areas after correction of the sensitivity factors.

To elucidate the mechanism for the formation of PAA/PAH free-standing films in the exfoliation solution, the

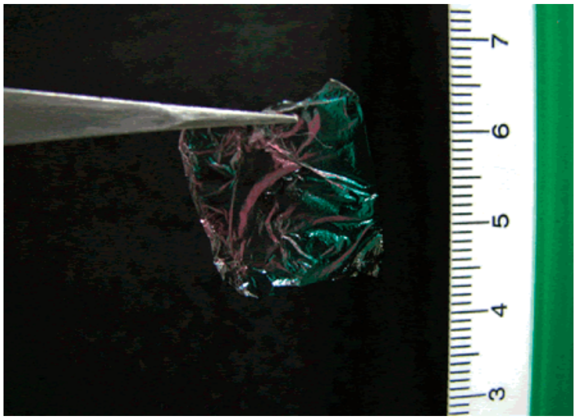

Figure 5. Photograph of a thermally cross-linked (PAA/PAH)*15 free-standing film (2 × 2 cm^2) in air. The free-standing film was obtained by exfoliating a thermally cross-linked (PAA/PAH)*15 in an aqueous solution with a pH of 2.0.

following parallel experiments were conducted. First, the as-prepared (PAA/PAH)*15 film was immersed in deionized water with its pH adjusted to 3.6 without the addition of $CuCl_2$. The PAA/PAH film adhered firmly to the substrate with partial dissolution of the film being observed, but no free-standing film was obtained. After immersing the (PAA/PAH)*15 film in 0.05 M aqueous $CuCl_2$ solution (pH 3.6) for 24 h, separation of the film with the substrate occurred only on the edges of the substrate. When the (PAA/PAH)*15 film was immersed into deionized water with a pH of 2.0 in the presence of 0.1 mol/L $CuCl_2$, the film decomposed immediately. When deionized water with a pH of 2.0 without the addition of $CuCl_2$ was used, fragments of PAA/PAH free-standing films were obtained. The free-standing (PAA/PAH)*15 film could be released in a 0.1 mol/L $CuCl_2$ aqueous solution with a pH of 4.0, but at a speed slower than that with a pH of 3.6. These results show that both H^+ and Cu^{2+} ions take important roles during the exfoliation of the PAA/PAH film from the substrate. The mechanism for the formation of the PAA/PAH free-standing film can be explained as follows: the interaction between the PAA/PAH film and the PDDA-modified substrate is mainly the electrostatic interaction between the carboxylate groups of PAA and the ammonium groups of PDDA. When the PAA/PAH film was immersed into the exfoliation solution, H^+ ions and Cu^{2+} ions break the interaction of the film with the substrate because H^+ ions can protonate the carboxylate groups of PAA, while Cu^{2+} ions can coordinate with carboxylate groups. In this way, the PAA/PAH film was exfoliated from the substrate. Meanwhile, H^+ and Cu^{2+} ions can diffuse into the PAA/PAH films where H^+ ions protonate the carboxylate groups of PAA, while Cu^{2+} ions coordinate with the carboxylate groups of PAA and the amine groups of PAH. The original interaction between the neighboring layers of the PAA/PAH film is mainly an electrostatic interaction, and hydrogen bonds between the carboxylate/carboxylic acid groups and the amine groups. The presence of H^+ and Cu^{2+} ions partially breaks the original interactions in the film and induces at the same time the rearrangement of the polyelectrolyte chains, which in turn leads to the formation of wavelike surface pattern structures.[23] Besides the role of breaking the interaction between the films with the substrate, the presence of Cu^{2+} ions in the film is believed to act as cross-linkers to stabilize the resultant free-standing films because of coordination interaction of carboxylate and amine groups in neighboring layers with Cu^{2+} ions.[22,23] The coordination of Cu^{2+} ions with the amine groups of PAH was confirmed by the XPS data shown in Figure 4. The coordination of Cu^{2+} ions with the carboxylate groups of PAA was recognized by the broadening of the $-COO^-$ asymmetric stretch in the FT-IR spectrum of Cu^{2+}-exfoliated free-standing films compared with that of the $-COO^-$ groups in the as-prepared PAA/PAH films.

The PAA/PAH free-standing films prepared by the present method were contaminated with Cu^{2+} ions, which will limit their application in biorelated aspects. Although the Cu^{2+} ions introduced into the free-standing films can be removed by treating the film with acidic aqueous solution or aqueous solution containing chelating agents such as ethylene diamine tetraacetic acid (EDTA),[22] it is necessary to examine if a free-standing film can be exfoliated from the substrate by H^+ ions without the participation of Cu^{2+} ions. The critical step to obtaining defect-free PAA/PAH free-standing films with a large lateral dimension by H^+ ions is to thermally cross-link the film to further enhance its robustness. After immersing the thermally cross-linked (PAA/PAH)*15 film into an aqueous solution with a pH of 2.0 for 1 min, the free-standing film of cross-linked PAA/PAH was obtained as shown in Figure 5. This result indicates that high concentration of H^+ ions is strong enough to exfoliate the PAA/PAH film from the substrate by breaking the electrostatic interaction between the PAA and the PDDA-modified substrate. The cross-linked PAA/PAH free-standing film is stable in air.

The LbL assembly technique enables the deposition of PAA/PAH multilayer films on nonflat surfaces. Herein, PAA/PAH multilayer films were further deposited into the inner walls of glass tubes to prepare tubelike free-standing PAA/PAH films. Figure 6 shows free-standing (PAA/PAH)*30 tubes released from glass tubes with an inner diameter of 6, 3, and 1 mm when an exfoliation solution of $CuCl_2$ was used. Because the PAA/PAH films can deposit on both the inner and outer walls of the glass tube to form a closed film, the films at the ends of the glass tubes must be removed to facilitate the release of the PAA/PAH films in the inner walls. The (PAA/PAH)*30 film has a thickness of ~2.74 μm, as measured from its cross-sectional SEM image. In all cases, defect-free free-standing PAA/PAH tubes could be released easily from the inner walls of glass tubes. We believe that the ion-triggered exfoliation method for the preparation of tubelike free-standing films will provide a possible way to prepare small-caliber artificial blood vessels in the future, especially those with inner diameters less than 3 mm, when biomaterials are used in film preparation.

Conclusions

In the present study, we demonstrate that free-standing PAA/PAH multilayer films with large lateral dimensions can be successfully prepared by ion-triggered exfoliation of the

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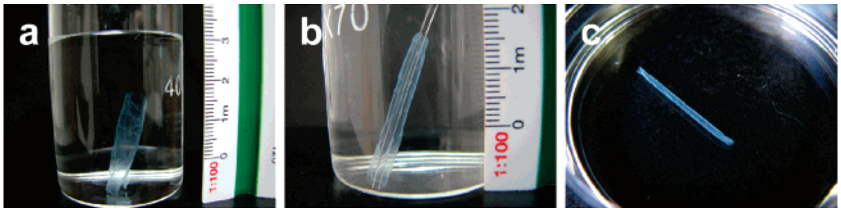

Figure 6. Photographs of tubelike (PAA/PAH)*30 free-standing films in water. The outer diameter of the free-standing films is 6 (a), 3 (b), and 1 mm (c), respectively. A glass rod was inserted into the (PAA/PAH)*30 free-standing tube in (b) to show that it really has a tube structure. The length of the tubes is 3 (a), 3 (b), and 2 cm (c), respectively.

film from the substrate. The exfoliation of the film was achieved by breaking the electrostatic interaction of the PAA layer with the underlying substrate. We believe that the types of ions capable of exfoliating PAA/PAH films is not restricted to H^+ and Cu^{2+} ions, and the present method can be further extended to prepare free-standing films comprising other types of materials prepared by the LbL assembly technique. For instances, we have already found that the ion-triggered exfoliation method was suitable to fabricate free-standing films of photocross-linked diazoresins/PAA, chitosan/PAA, and CO_2-cross-linked PAH gel/poly (4-styrene sulfonate), and so forth. Compared with the existing methods to prepare free-standing LbL assembled films, the present method is characterized by its simplicity and flexibility because no steps of dissolution of sacrificial layers or substrates are involved. Meanwhile, the present method is also suitable to prepare free-standing LbL assembled films with large lateral dimensions deposited on nonflat substrates.

Acknowledgment. This work was supported by the Foundation for the Author of National Excellent Doctoral Dissertation of P. R. China (FANEDD Grant No. 200323), National Natural Science Foundation of China (NSFC Grant No.20574029), National Basic Research Program (2007CB808000), Program for New Century Excellent Talents in University (NCET), and the Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT Grant No. IRT0422).

Supporting Information Available: Video of tubelike (PAA/PAH)*30 film exfoliation from a glass tube with an inner diameter of 3.0 mm. This material is available free of charge via the Internet at http://pubs.acs.org.

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