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Self-assembly ultrathin films based on dendrimers

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A photosensitive ultrathin film with G1.5 PAMAM dendrimers (carboxylate salts) as polyanions and NDR (nitro-containing diazoresin) as polycations was fabricated *via* sequential deposition and subsequent UV irradiation which causes the linkage between the layers to change from ionic to covalent.

The large size and globular shape of PAMAM dendrimers make them suitable building blocks for self-assembled monolayer or multilayer ultrathin films. Watenabe and Regen[1] used the procedure of repeated deposition of amine terminated PAMAM dendrimers onto a Pt^{2+} bearing surface, followed by reactivation with K_2PtCl_4, which yielded multilayer films. Wells and Crooks[2] reported the first covalently bound dendrimer monolayer, which resulted from linking PAMAM dendrimers to a mercaptoundecanoic acid self-assembled monolayer *via* amide bond formation. Tsukruk's group fabricated composite molecular films by self-assembly of dendritic macromolecules of two adjacent generations using electrostatic layer-by-layer deposition.[3] All these examples showed the potential application of mono- or multi-layer films as chemical sensors,[4] size selective heterogeneous catalysts or a basis for optical filters and optical devices.[5–7] Recently, Cao and coworkers reported the formation of a stable ultra-thin multilayer film by converting hydrogen or ionic bonds to covalent bonds under ultraviolet irradiation.[8,9] This conversion of the bonding increases the resistance of films to etching by polar solvents.

Here, we describe, for the first time, the preparation of multilayer films constructed from poly(amidoamine) dendrimers (PAMAM) and nitro-containing diazoresin (NDR) *via* a layer-by-layer technique and the conversion of the linkage bonds under UV irradiation.

The PAMAM dendrimers were synthesized according to the literature.[10] The methyl-ester-terminated dendrimer (G = 1.5) was hydrolyzed with stoichiometric amounts of KOH in methanol to obtain external carboxylate groups associated with potassium ions. NDR was prepared according to the method described in ref. 11. Surface-negatively charged mica was used as the substrate. The freshly cleaved mica was immersed in an aqueous solution of 2 mg ml^{-1} NDR for 5 min, rinsed with deionized water and then dried under a stream of air. After being totally dried, the mica was dipped into an aqueous solution of 2 mg ml^{-1} hydrolyzed G1.5 PAMAM dendrimer for 5 min, followed by rinsing and drying. Repetition of this procedure six times yielded a 12-bilayer self-assembled ultrathin film. All stages of growth were carried out at room temperature in the dark.

The absorbance of NDR on mica after each cyclic deposition was recorded using a UV–VIS scanning spectrophotometer (Shimadazu UV-2101 PC) to monitor the self-assembly process (Fig. 1). The peak at 383 nm is assigned to the absorption of the diazonium group of NDR and increases linearly with increasing bilayer number. From Fig. 1, it can be seen that the absorbance increases by *ca.* 0.016 every two bilayers, indicating smooth step-by-step deposition.

The twelve bilayer film was then irradiated with UV light for different times and the resulting absorbances determined (Fig. 2). From the inset plot it can be seen that the photodecomposition of the film follows the kinetics of a first-order reaction, where A_0 and A_t represent the absorbance of the film before and after irradiation for different times t, respectively. The absorbance at 383 nm (N_2^+ group absorption) decreases with irradiation, which indicates the formation of a covalent linkage. The conversion of the ionic bonds to covalent bonds is shown in Scheme 1. Before irradiation, the multilayer film is formed *via* electrostatic attraction between the diazonium groups and carboxyl groups. Under UV-irradiation, the diazonium groups decompose leading to phenyl cations, which combine with the carboxyl groups to produce covalent linkages.

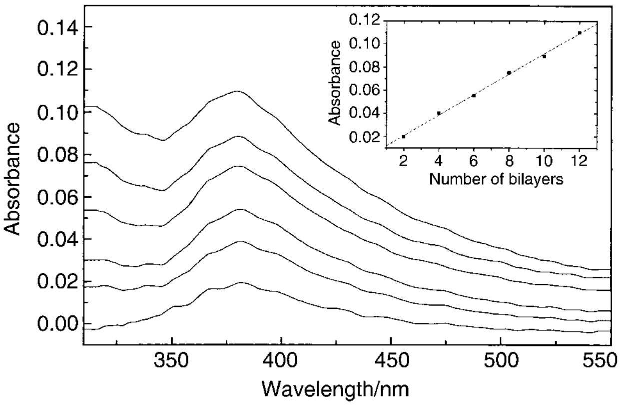

Fig. 1 Absorbance of multilayer films with different numbers of bilayers. Bilayer numbers (bottom to top): 0, 2, 4, 6, 8, 10 and 12. Inset: Relationship between the absorbance at 383 nm and the bilayer number.

The formation of covalent bonds was further verified by comparing the FTIR spectrum of the self-assembled film before and after irradiation. Distinct changes were the disappearance of the absorbances at 2162 and 1580 cm^{-1}, assigned to the stretching vibrations of the diazonium group and the carboxyl group, respectively. At the same time, the absorbance at 1738 cm^{-1} assigned to the carboxyl group of an ester bond increases.

From AFM measurements, the four-bilayer film (Fig. 3) is rather flat and the mean roughness only 1.4 nm which indicates

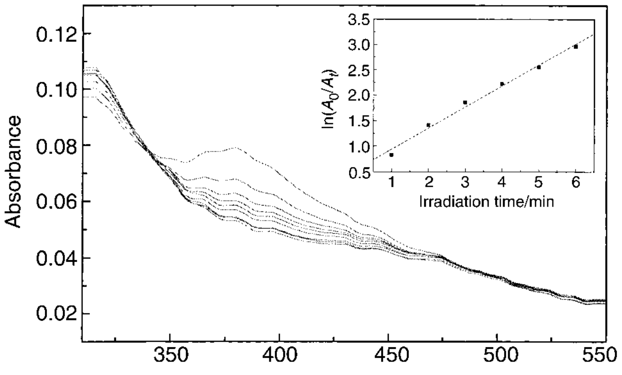

Fig. 2 UV–VIS spectra of a 12-bilayer film irradiated for different times. Irradiation intensity (360 nm): 230 μW cm^{-2}, irradiation time (top to bottom) 1, 2, 3, 4, 5, 6, 10, 20 and 30 min.

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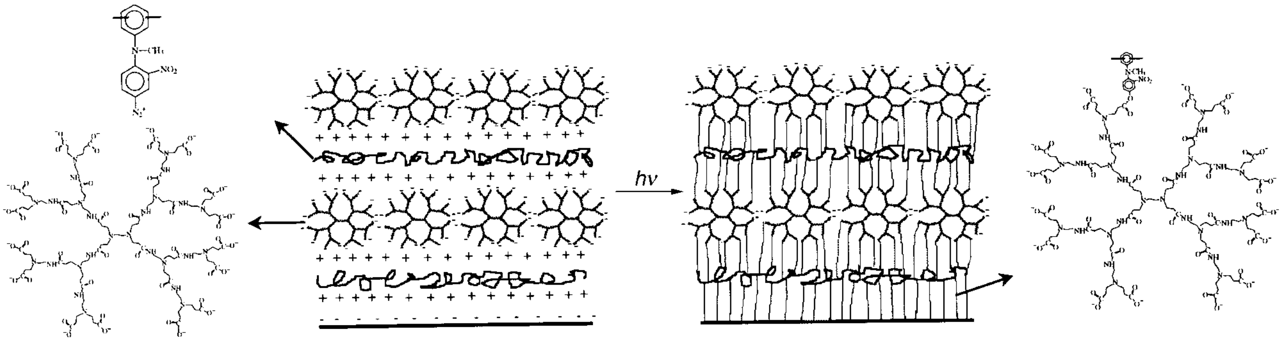

Scheme 1 The conversion of the linkage bonds from ionic to covalent in multilayer films fabricated from PAMAM and NDR.

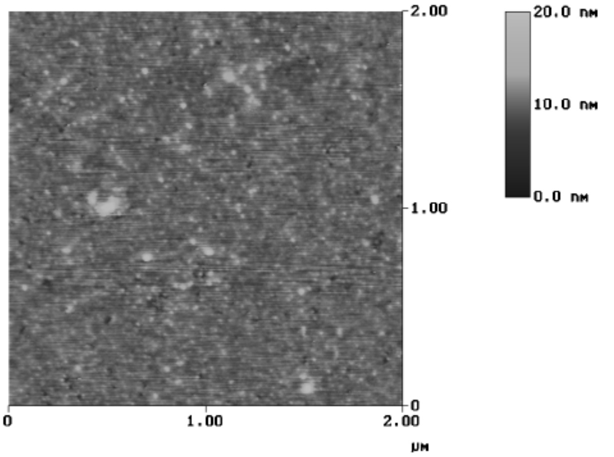

Fig. 3 Morphology of the 4-bilayer film fabricated from PAMAM and NDR. Mean roughness 1.4 nm.

the formation of a uniform multilayer film from PAMAM and NDR through the step-by-step technique.

The effect of UV irradiation on the stability of the film to polar solvents was also investigated. The absorbance of the unirradiated film decreases significantly after etching for 30 min in DMF, while the irradiated film showed no etching under the same conditions. This shows that the stability of the film towards polar solvents increases significantly after UV irradiation.

In order to determine the film thickness, X-ray diffraction measurements were performed on a Rigaku DMAX 2400 X-ray diffractometer. X-Ray data were collected within a scattering angle range of 1–8° using Cu-Kα radiation. A peak occurs at $2\theta = 2.500$ and 2.660 for the film before and after irradiation, respectively and suggests the film can be viewed as being ordered. According to the Bragg equation, the layer thickness of the film before and after irradiation is 3.5 and 3.3 nm, respectively. This change corresponds to the alteration in the bonding since the layers will become more compact when covalent bonds form.

In conclusion, an ultrathin multilayer film was fabricated from PAMAM dendrimers and NDR by a self-assembly technique. Under UV irradiation, the linkages change from ionic to covalent.

Studies in progress will focus on fabrication of the multilayer films by using different generation PAMAM dendrimers. We are also studying the characteristics of these unique films.

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