Articles

Self-Assembled Multilayer Films Based on Dendrimers with Covalent Interlayer Linkage

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Multilayer ultrathin films composed of nitro-containing diazoresin (NDR) as polycation and poly(amidoamine) dendrimers with carboxyl terminal groups (PAMAMC) ($G = 1.5$, 2.5, 3.5, and 4.5) as polyanion were fabricated on mica by electrostatic layer-by-layer deposition. Subsequent UV irradiation converted the interlayer linkage from ionic to covalent. The films were characterized with UV−vis, FTIR, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and X-ray diffraction (XRD). The results show that the uniform multilayer films were formed. All the films with dendrimers of various generations as building blocks have a very smooth surface with a mean roughness of about 0.8−1.1 nm. The thickness of the PAMAMC−NDR bilayer in the films increases with the generation number of the dendrimer, but the average thickness of the dendrimer monolayer is smaller than the diameter of the ideal spherical model of dendrimers with an extended conformation of all branches. They are significantly compressed in multilayer films. The conversion of the ionic to covalent linkage dramatically improved the stability of the films with respect to polar solvent, strong electrolyte, and surfactant solutions.

Introduction

To fabricate the layer-by-layer ultrathin films by the self-assembly technique has attracted more and more attention since the pioneering studies by Iler over 30 years ago.[1] Dendrimers are a novel class of well-defined macromolecules with three-dimensional architectures, varied surface functionality, and many unique properties, which make them promising candidates for self-assembly films. Regen and co-worker[2] used the procedure of repeating deposition of amine-terminated PAMAM dendrimers onto a Pt^{2+}-bearing surface, followed by reactivation with K_2PtCl_4, which yielded corresponding multilayer films. Crooks and co-worker[3] reported the first covalently bonded dendrimer monolayer that resulted from linking PAMAM dendrimers to a mercaptoundecanoic acid self-assembled monolayer. Tsukruk et al.[4] fabricated composite molecular films with dendritic macromolecules of two adjacent generations via electrostatic layer-by-layer deposition. The research of such mono- or multilayer films has showed the potential applications in chromatographic separations,[5−8] in multiple redox reactions,[9] and as chemical sensors.[3]

However, the joint force between layers of such films was based on coulometric interaction, which resulted in the films' lack of stability and poor resistance toward polar solvents. Therefore, their development and applications are limited. In 1999, Zhao et al.[10] reported the preparation of highly impermeable thin films using dendrimers as in situ thermosetting agents, and Cao and co-worker[11] prepared a family of stable ultrathin

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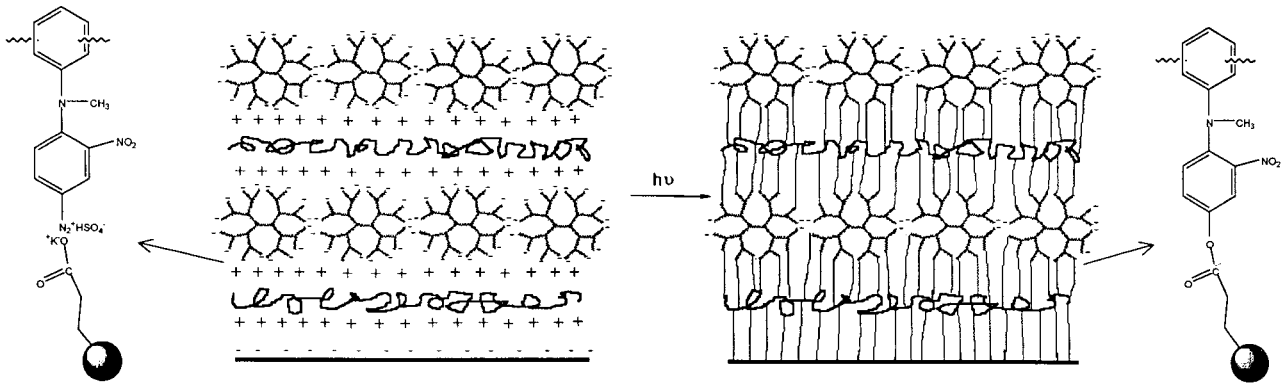
Scheme 1. Fabrication of Self-assembled PAMAM−NDR Multilayer Films and Conversion of the Interlayer Linkage from Ionic to Covalent upon UV Irradiation



multilayer films from conventional polymers. They reported the conversion of the ionic linkage nature of the films from the hydrogen or ionic bond to covalent bond under ultraviolet irradiation.

In this paper, we describe in detail the preparation of covalently attached multilayer ultrathin films based on dendrimers. The films were fabricated by sequential deposition using different generation poly(amidoamine) dendrimers (G = 1.5, 2.5, 3.5, and 4.5) with carboxylate end groups (PAMAMC) and nitro-containing diazoresin (NDR) as building blocks. Under UV irradiation, the linkage between layers of the films changed from ionic to covalent. (Scheme 1) The properties of the films such as surface morphology and resistance to solvent etching are also reported.

Experimental Section

Materials. PAMAM dendrimers (G = 1.5, 2.5, 3.5, 4.5) and NDR (η sp/c = 0.15 dL/g, $M_n \approx$ 2500 g/mol) were synthesized according to the literature,[11−14] respectively. Methyl-ester-terminated dendrimers were hydrolyzed with stoichiometric amounts of KOH in methanol to obtain carboxyl-terminated dendrimers (PAMAMC).[15] Dimethyl formamide (DMF), KOH, NaCl, and sodium dodecyl sulfate (SDS) were analytical agents and used as-received. All the apparatus were boiled in 50% sulfuric acid, then washed with distilled water, and dried before use. The PAMAM dendrimers were characterized with a Bruker-ARX400 NMR spectrometer. From the ^{1}H NMR spectrum of the G3.5 dendrimers, seven groups of peaks were clearly identifiable: δ (ppm) 2.19−2.21, 2.42−2.47, 2.50−2.56, 2.62−2.64, 3.0−3.2, 3.60−3.64, and 7.87−7.89, which are in agreement with those reported in the literature.[16] After hydrolysis of the PAMAM dendrimers, the peak that belongs to −COOC**H**$_3$ disappeared.[15] At the same time, in the FTIR spectrum the absorbance of −COOCH$_3$ $\nu_{C=O}$ at 1740 cm^{-1} disappeared and the absorbance $\nu_{C=O}$ at 1580 and 1400 cm^{-1} for the COO$^-$ group was observed.

Preparation of the Films. The deposition process was carried out at room temperature in the dark using mica as the substrate, which has a negative surface in water. The freshly cleaved mica was cleaned with deionized water at least three times. After being dried, it was immersed into a NDR aqueous solution (2 mg/mL) for 5 min. The positively charged NDR adhered on the negatively charged surface of mica, forming an ultrathin film. Having been carefully taken out, the film was rinsed with deionized water and dried, and then the mica was dipped into a PAMAMC dendrimer aqueous solution (2 mg/mL, G = 1.5, 2.5, 3.5, 4.5) for another 5 min, followed by rinsing and drying. One cycle of this procedure afforded a bilayer of the film. Repeating this procedure several times yielded a multilayer ultrathin film on both sides of the substrates.

Characterization. The UV absorbance of the films on mica after each cyclic deposition or after etching was recorded on an UV−vis scanning spectrophotometer (Shimadazu UV-2101 PC) with the selected scan range of 300−550 nm. The UV measurement was employed to monitor the self- assembly process and the stability of the films against etching by a polar solvent, strong electrolyte, and surfactant aqueous solutions. To obtain a flat baseline and reproducible results, carefully cleaved uniform mica was used to perform the UV−vis measurement. Each sample was measured 2−3 times to ensure the reliability of the results.

The surface morphology of the films was visualized by atomic force microscopy (AFM). For the AFM measurement, 4-bilayer films were fabricated on mica, which was glued to a glass slide. The measurements were carried out in air at ambient temperature on a Nanoscopy IIIA AFM (Digital Instruments, Inc.) in tapping mode. Commercial silicon probes (model TESP-100) were used to obtain the image with a typical resonant frequency around 300 kHz. All of the results were calculated from a randomly selected 4 μm^2 (2 × 21 μm) area on the samples.

X-ray diffraction measurements were performed on a Rigaku DMAX 2400 X-ray diffraction instrument with a 12-bilayer film composed of NDR and different generations of PAMAMC on mica. The data were collected within a 1−8° scattering angle range using Cu Kα radiation. X-ray photoelectron spectroscopy (Vgescalab 5 multitechnique electron spectrometer) was used to analyze the surface element composition of 3-layer and 4-layer films fabricated from PAMAMC (G1.5) and NDR.

The solvent etching experiments were performed following the literature procedure.[17−21] The films with 12 bilayers were immersed in DMF, NaCl (1 M), or SDS (5 wt %) aqueous solutions with different immersing times. Then, the UV−vis absorbance of the films was measured to examine the stability of the films toward etching. To confirm the formation of the interlayer covalent bonding, the spectra of 20-bilayer unirradiated or irradiated films fabricated on CaF_2 were recorded on a Nicolet Magna IR-750 spectrophotometer.

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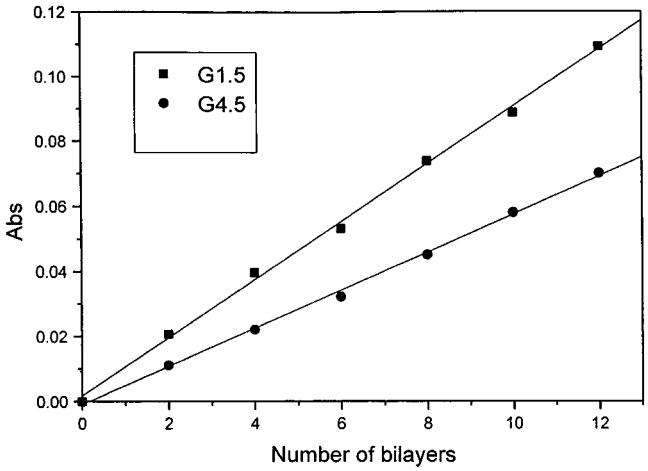

Figure 1. UV absorbance at 383 nm of the G1.5 PAMAM−NDR multilayer film and the G4.5PAMAM−NDR multilayer film with different numbers of bilayers.

Table 1. Element Ratios of 3-Layer (Top Layer Is NDR) and 4-Layer (Top Layer Is G1.5PAMAMC) Films at 60° and 90° XPS Takeoff Angles

ratio of elements	3-layer film takeoff angle		4-layer film takeoff angle	
	60°	90°	60°	90°
C/N	16.4	16.0	6.6	7.5
Na/N	0.0	0.0	0.15	0.23

The molecular models were simulated using Cerius[2] software. Molecular dynamics simulations were performed using a Cvff95 Force Field under constant NVE conditions. The total simulation steps were 200 000 in units of 1-fs simulation step at the simulation temperature of 300 K.

Results and Discussion

PAMAMC−NDR Multilayer Films. Multilayer films from PAMAMC dendrimers of various generations (G = 1.5, 2.5, 3.5, and 4.5) and NDR were prepared by the self-assembly technique. Monitored with UV−vis spectroscopy, the absorbance increases linearly with the bilayer number, indicating a smooth layer-by-layer film growth (Figure 1). The morphology of the four-bilayer films from PAMAMC dendrimers of different generations and NDR was examined with AFM. The films formed on mica are rather flat and the mean roughness is around 0.8−1.1 nm, which demonstrates that the uniform multilayer films have been obtained.

The results of XPS measurements are summarized in Table 1. It is quite clear that the surface of the 3-layer film does not contain sodium. Sodium cation is considered as the counterion of the extra carboxyl anion on the film surface. Therefore, sodium ions found on the surface of the 4-layer film further establish that the films are assembled in a layer-by-layer manner.

The thickness of the PAMAMC−NDR layer in the multilayer films was obtained from XRD data. The results are listed in Table 2. Chen et al.[12] has investigated the NDR monolayer formed on mica in detail. Their studies show that the average thickness of a NDR monolayer on mica is 2.1 nm. Therefore, the average thickness of a dendrimer monolayer in the multilayer films can be estimated and the values are given in Table 2. The average thickness of a dendrimer layer shows steady growth with the generation number increasing from 1.4 nm for low generation (G = 1.5) dendrimers to 4.6 nm for higher generation (G = 4.5) dendrimers. But these values are smaller than the diameter of ideal spherical models of dendrimers with an extended conformation of all branches as estimated from molecular dynamic simulations, which is 3.4 nm for generation 1.5 and 6.3 nm for generation 4.5 dendrimers.

There are a number of reports in the literature on the thickness of monolayer or multilayer films fabricated using the electrostatic layer-by layer deposition technique from oppositely charged PAMAM dendrimers themselves or with other compounds.[22−24] Bliznyuk and co-workers[4] prepared the monolayer of PAMAM dendrimers (G = 3.5 through G = 10.0) from aqueous solutions. They showed the thickness of all monolayers

Table 2. Average Thickness of the PAMAMC−NDR Bilayer and PAMAM Monolayer in the Multilayer Films

sample	2θ (deg)	R_b[a] (nm)	R_m[b] (nm)	R_s[c] (nm)	R_k[d] (nm)
G1.5PAMAM−NDR	2.521	3.5	1.4	3.4	
G3.5PAMAM−NDR	1.665	5.3	3.2	5.3	4.0
G4.5PAMAM−NDR	1.317	6.7	4.6	6.3	

[a] The thickness of the PAMAM−NDR in the 12-bilayer film obtained from XRD. [b] The thickness of the PAMAM dendrimer in the 12-bilayer film obtained from XRD. [c] The diameter of the half-generation PAMAM from the molecular simulation. [d] The dendrimer monolayer thickness from Karim's XRD results.[29]

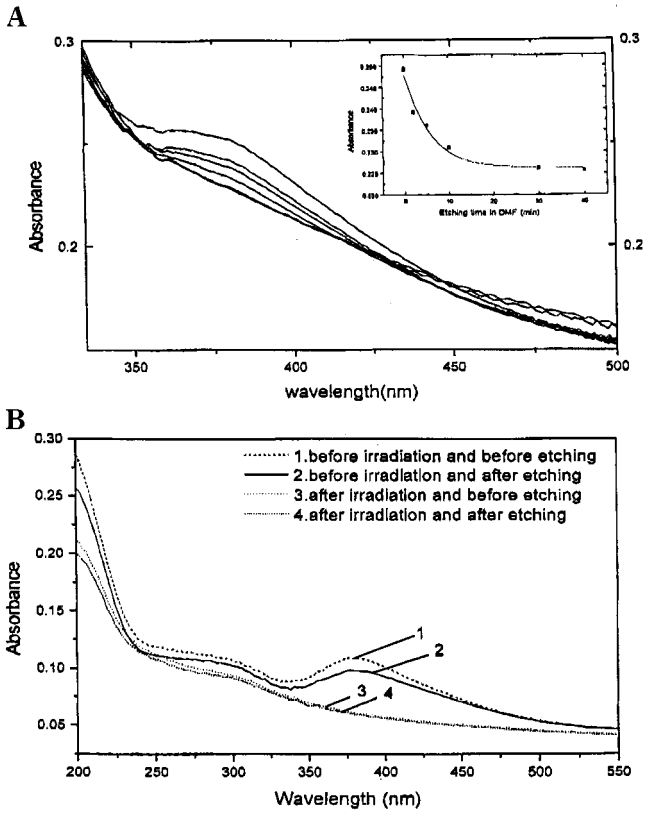

Figure 2. (A) UV−vis spectra of unirradiated 12-bilayer G1.5PAMAM−NDR film after etching in DMF for different time intervals: (top to bottom) 0, 2, 5, 10, 30, and 40 min. Inset plot shows the decrease in the absorbance at 383 nm with the increase of etching time. (B) UV−vis spectra of unirradiated or irradiated 12-bilayer film of G1.5PAMAM−NDR before or after etching in an SDS solution for 30 min: (top to bottom) before irradiation and etching, before irradiation and after etching, after irradiation and before etching, and after irradiation and after etching.

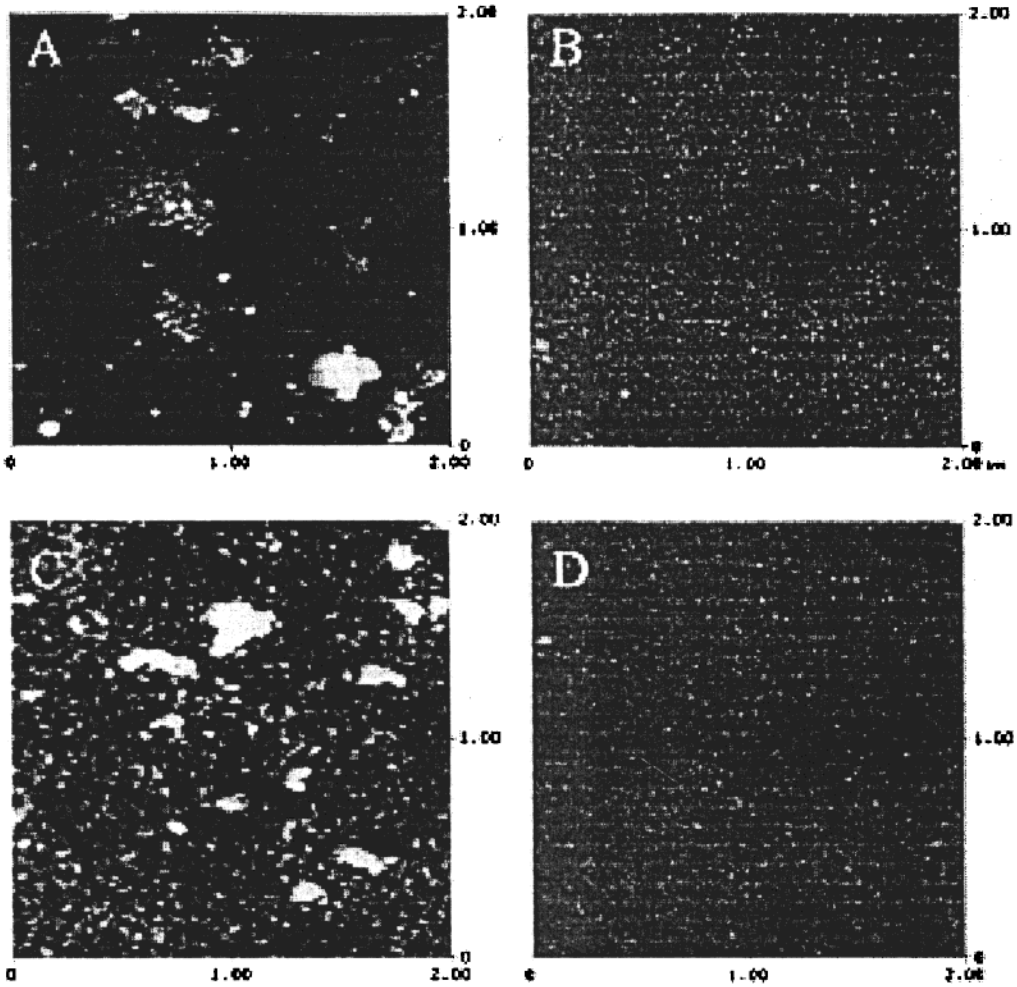

Figure 3. AFM images of irradiated and unirradiated multilayer films after etching in DMF. (A) 4-bilayer unirradiated GS.5PAMAM−NDR film etched in DMF for 30 min; (B) 4-bilayer irradiated GI.5PAMAM−NDR film etched in DMF for 30 min; (C) 4-bilayer unirradiated G4.5PAMAM−NDR film etched in DMF for 30 min; (D) 4-bilayer irradiated G4.5PAMAM−NDR film etched in DMF for 30 min.

studied is much smaller (by 60−70%) than the average diameters of dendritic macromolecules in "a contracted state". They noticed that the structure state of charged dendrimers in compact, complete monolayer differs from isolated islands of neutral dendrimers. A similar phenomenon has also been observed by Tsukruk and co-workers.[4,25,26] They found that the variation in multilayer film thickness with the number of deposited layers was linear with an incremental increase per layer of 2.3 for G4/3.5 and 3.8 for G10/9.5 films. These small increments indicated that the PAMAM macromolecules were significantly compressed in multilayer films. Crooks and co-worker,[27] on the basis of the ellipsometry studies, showed the flattened state of the dendrimers with the compression ratio close to those observed for PAMAM by Tsukruk et al.[4]

The experimental facts of our study are consistent with the above-mentioned results in the literature. There are several main reasons for this phenomenon. (1) Strong interactions between oppositely charged layers might be responsible for collapse and compression of the dendritic macromolecules within self-assembled films as revealed by computer molecular modeling.[28] (2) These dendrimers are soft molecules. When the films are formed, the feature of a dendrimer structure requires that the molecules be compressed by the closed neighboring branches so that oppositely charged surface groups could be suitable for the formation of organized multilayer films with alternating layers. The mutual interaction of terminal groups and the soft nature of the dendrimers contribute to the formation of a compact layer structure in which the dendrimer molecules should be deformed to an oblate shape.[29,30]

Stability of the Films. The films with 12 bilayers were fabricated on mica and then irradiated with UV light to convert the electrostatic to covalent interlayer linkage. The photodecomposition (as shown in Scheme 1) of the films, as monitored with UV−vis and FTIR spectroscopy, was found to follow the kinetics of a first-order reaction. After irradiation, the IR absorption

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bands of the diazo group at 2162 cm^{-1} and the carboxylate group at 1580 cm^{-1} disappeared and a new band around 1730 cm^{-1} mainly assigned to C═O stretching in the ester group was observed,[21,31] indicating the successful conversion of ionic diazonium carboxylate salt to covalent ester interlayer linkage.

The effect of UV irradiation on the stability of the films toward polar organic solvents, strong electrolytes, and surfactant aqueous solutions was studied. Both unirradiated and irradiated films were immersed in the solvents or solutions under the same conditions. After the films were washed with distilled water and dried, the UV−vis absorption spectra of the films were measured to examine the difference between the unirradiated and irradiated films. The unirradiated films were found to be etched significantly after immersion in DMF for 30 min, as evidenced by the decrease in the intensity of absorption bands (Figure 2a). In a sharp contrast, the irradiated films showed no decrease in absorbance after immersion in DMF for the same period of time (not shown in figure). The same results were obtained in the etching experiments with aqueous solutions of 1 M NaCl or 5 wt % SDS (Figure 2b). Figure 3 shows the surface morphology of the unirradiated and irradiated films after etching in DMF for 30 min. It can be seen that the unirradiated G1.5PAMAMC−NDR and G4.5PAMAMC−NDR films both have obviously etched areas up to 20 nm^2. When an irradiated film is compared to the sample before immersion in DMF, no appreciable etched area can be identified. The mean roughness of unirradiated films increases from 0.9 to 2.4 nm for G1.5PAMAMC−NDR and from 0.8 to 4.5 nm for G4.5PAMAM-NDR, whereas the irradiated films only changed to 1.3 and 1.0 nm for G1.5PAMAMC−NDR and G4.5PAMAMC−NDR, respectively. These results indicate that the stability of the films toward solvent etching increases significantly after exposure to UV irradiation. Such an increase in the stability could be attributed to the conversion from an ionic to covalent nature of the interlayer linkage.

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Conclusions

Multilayer ultrathin films were fabricated on mica using the self-assembly technique via layer-by-layer deposition, with NDR as the polycation and PAMAMC dendrimers (G = 1.5, 2.5, 3.5, and 4.5) as polyanions. The films have layered structures and the mean roughness of the film surface is around 0.8−1.1 nm. XRD results show the dendrimer layer in the multilayer films becomes thicker as the generation number of dendrimers is increased. The average thickness of dendrimers in the multilayer films is smaller than the diameter of the ideal spherical model of dendrimers with an extended conformation of all branches. The strong interactions between oppositely charged layers and the soft feature of dendrimer structures make the molecules compressed in the films. Upon exposure to UV irradiation, the interlayer linkage changes from ionic to covalent bonds. This makes the films very robust and stable toward polar solvents, strong electrolytes, and surfactant aqueous solutions.

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