

Note

COVALENTLY ATTACHED MULTILAYER ULTRA-THIN FILMS FROM DIAZORESIN AND CALIXARENES*

Zhao-hui Yang and Wei-xiao Cao**

College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Abstract A kind of photosensitive ultra-thin film was fabricated from diazo-resin (DR) and various calixarenes by using the self-assembly technique. Under UV irradiation both the ionic- and hydrogen bonds between the layers of the film will convert into covalent bonds. As a result, the stability of the film toward polar solvents increases dramatically.

Key words Calixarene, Diazo-resin, Self-assembly, Ultra-thin film

INTRODUCTION

Since Decher's pioneering work in 1991^[1] a technique named self-assembly (SA), which was used to fabricate ultra-thin films layer-by-layer, has attracted more and more attention^[2, 3]. The fabrication components have been expanded from oppositely charged polyelectrolytes to colloid particles, multi-functional small molecules, inorganic particles, proteins, DNAs *etc.*. The driving force of the SA film has also been enlarged from the original coulombic force to H-bonding attraction, coordinate force, charge-transfer interaction and so on. But almost all the films fabricated from these weak attractions are not strong enough toward polar solvents. Therefore, the solvent stability of the SA films has become a serious problem.

Calixarenes as a well-known host compound can form various host-guest complexes with organic and inorganic molecules^[4, 5]. Some of the water-soluble calixarenes are special surfactants and can act as "unimolecular" micelles in water solution^[6, 7]. In recent years, calixarenes have come to play a more and more important role as phase transfer catalysts, in sensor applications, photo-induced deprotection derivative, *etc.*^[8–10]. Therefore, calixarenes as a kind of variable synthetic hosts have attracted more attention in the area of bioorganic and biomimetic chemistry^[11].

Diazo-resin, a photosensitive polycation, has been used as a component to fabricate multilayer ultra-thin films via electrostatic^[12] or H-bonding^[13] attraction, in which the weak linkage will convert into a covalent bond under UV irradiation.

In this article, we report a kind of photosensitive ultra-thin film fabricated from diazo-resin (DR) and various calixarenes. Under UV irradiation, the weak bonds between the layers of the film will convert into covalent bonds and the stability of the film toward polar solvents increases dramatically.

EXPERIMENTAL

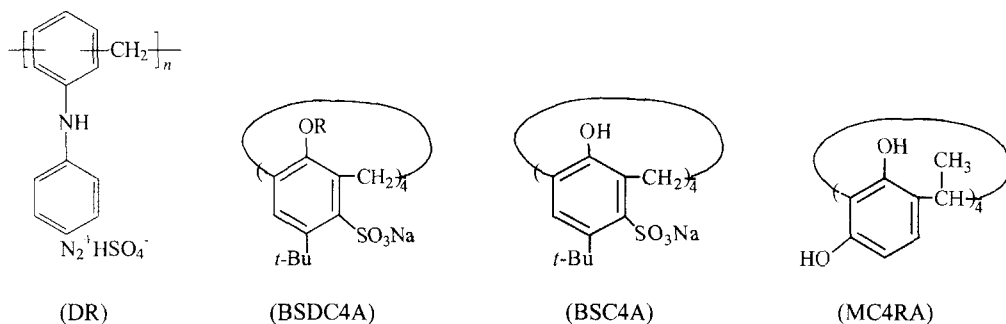
DR was prepared according to a method described elsewhere^[14]. Calixarenes, *i.e.* *t*-butylcalix[4]-arene(BC4A)^[15], *t*-butyl-*m*-sulfonatocalix[4]arene (BSC4A)^[16], *c*-methylcalix[4]resorcinarene (MC4RA)^[17] and *t*-butyl-*m*-sulfonato-dodecyloxy-calix[4]arene (BSDC4A)^[18], were synthesized according to the corresponding

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** Corresponding author: Wei-xiao Cao (曹维孝), E-mail: wxcao@pku.edu.cn

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references, respectively. The structural formulas of DR and calixarenes are represented in Scheme 1.



Scheme 1. The structural formulas of DR and calixarenes

Using DR/BSC4A film as an example, the film fabrication can be described as follows: a quartz wafer as the substrate was previously treated in a solution composed of 30% H_2O_2 and concentrated sulfuric acid (3:7 by volume) at 70°C for 0.5 h. The treated quartz wafer was immersed in an aqueous solution of 1 mg/mL DR for 5 min, washed thoroughly with deionized water and dried in air. Next, it was dipped into an aqueous solution of 1 mg/mL BSC4A for 5 min, washed and dried. In each fabrication cycle, a bilayer of DR/BSC4A was deposited on both sides of the substrate. DR/BSDC4A film was made in the same way. In the case of MC4RA, which does not dissolve in water but dissolves in methanol, the film of DR/MC4RA was fabricated in DR aqueous and MC4RA methanol solution. All these procedures should be done in the dark.

UV-spectra recorded on a Shimadzu-2100 spectrophotometer were used to monitor the process of the layer-by-layer deposition and the photoreaction occurring in the film when it was exposed to UV radiation. The IR spectrum was obtained from a 30-bilayer film fabricated on a CaF_2 wafer on a Bruker Vector-22 FTIR spectrometer.

RESULTS AND DISCUSSION

Figure 1 shows the increasing absorbance of DR/MC4RA film with increasing bilayer number. The peaks at 383 nm and 283 nm are assigned to the absorption of $-\text{N}_2^+$ group of DR and phenolic hydroxy group of MC4RA, respectively. A good linear relationship (see inset plot) between the absorbance and the bilayer number indicates that the layer-by-layer deposition is very regular and successful. The DR/BSDC4A or DR/BSC4A film exhibits a similar relation between the absorbance and the bilayer number (the figures were omitted in this note).

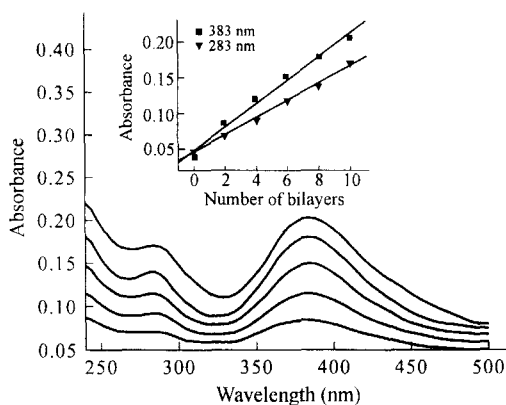
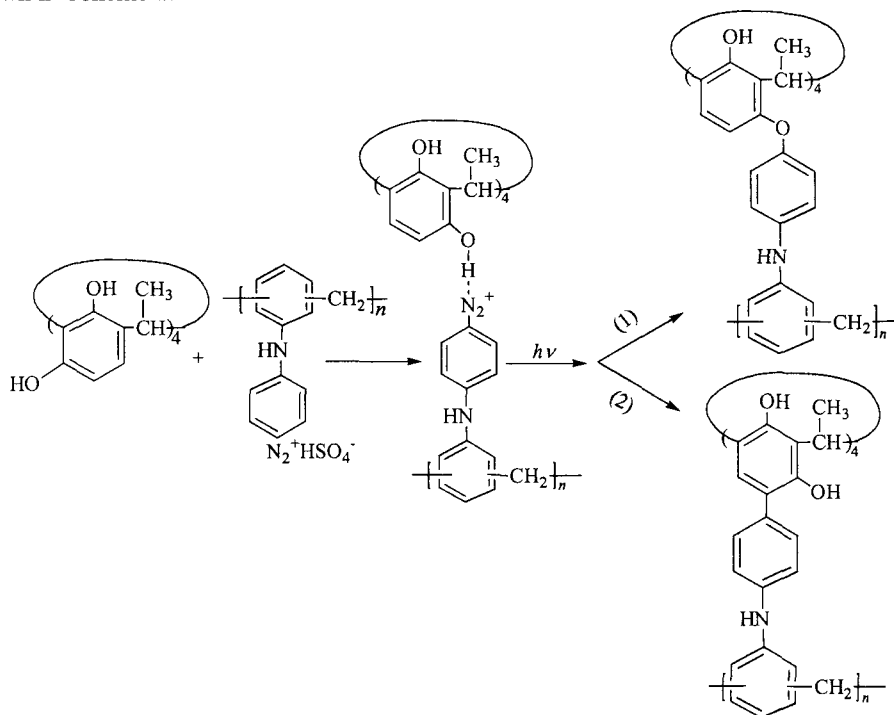
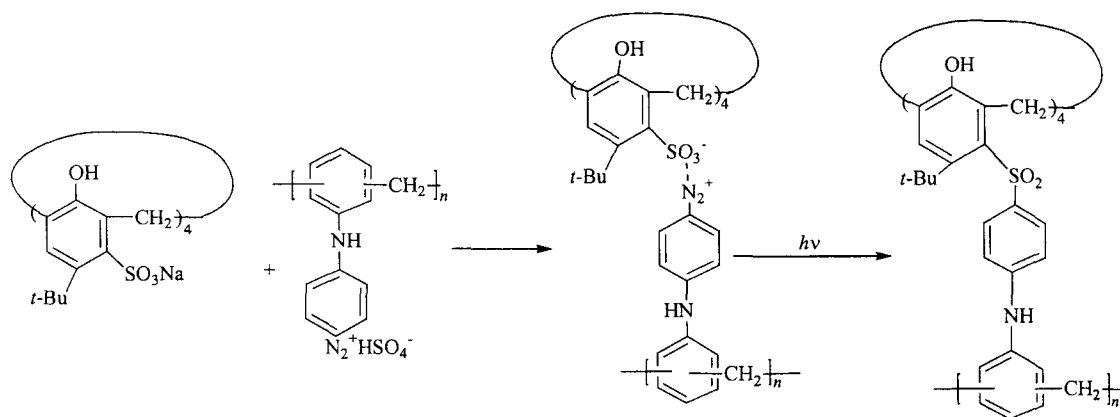


Fig. 1 Relationship between the absorbance and bilayer number for DR/MC4RA film

Unfortunately, all these films are unstable towards polar solvents because of their weak linkages. For example, when DR/MC4RA film was immersed in DMF for 10 min at 25 °C, the absorbance at 383 nm decreased by about 70%. That means that the film deteriorated extensively. However, after UV irradiation (230 $\mu\text{W}/\text{cm}^2$ at 360 nm), the stability of the film toward polar solvents increased significantly, *i.e.* when the irradiated DR/MC4RA film was immersed in DMF over 24 h at 25 °C, no significant decrease of the absorbance can be detected. This improved stability of the film could be ascribed to the conversion of H-bonds (Scheme 2a) or ionic bonds (Scheme 2b) into covalent bonds between the layers of film following the decomposition of $-\text{N}_2^+$ groups of DR, as shown in Scheme 2.



Scheme 2a Schematic representation of the conversion of H-bonds into covalent bonds between the layers of DR/ MC4RA film under UV irradiation



Scheme 2b Schematic representation of the conversion of ionic bonds into covalent bond between the layers of DR/BSC4A film under UV irradiation

For the calixarenes containing both sulfonate and phenolic hydroxyl groups such as BSC4A, the assembly with DR should be done under different driving forces. In order to verify that, various calixarenes were used to fabricate the films with DR on a CaF_2 wafer for determining their IR spectra. Figure 2 shows the IR spectra of DR/BSDC4A (containing sulfonate group) and DR/MC4RA (containing phenolic-hydroxyl group) films. The DR/BSDC4A film (curve 1) shows a normal stretching vibration of the $-\text{N}_2^+$ group at 2167 cm^{-1} as in DR itself, but in the case of DR/MC4RA film (curve 3), the stretching vibration of the $-\text{N}_2^+$ group shifts to 2156 cm^{-1} , lower by 11 cm^{-1} .

It is known that the wavenumber of the $-\text{N}_2^+$ vibration of DR decreases as it undergoes H-bonding with the phenolic-hydroxyl group of phenol-formaldehyde resin^[13]. Furthermore, MC4RA does not dissociate in methanol; therefore, we believe that the assembly driving force of the DR-MC4RA system comes from to H-bonding attraction.

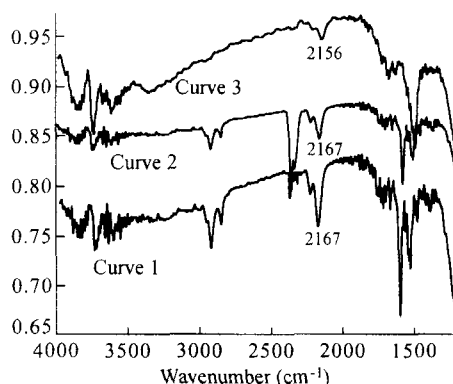


Fig. 2 IR spectra of DR/BSDC4A and DR/MC4RA films

Although $-\text{N}_2^+$ is a cation, its two nitrogen atoms are not equivalent: one is charge deficient and in equilibrium with the counter ion (such as HSO_4^-), and the other has a pair of non-bonded electrons that can form a H-bond with a strong H-donor, such as the phenolic hydroxyl group of the MC4RA.

BSC4A containing both sulfonate and phenolic hydroxyl groups in the structure is rather complex, because there is a possibility to form ionic and H-bonds at the same time. From its IR spectrum (Fig. 2, curve 2), the electrostatic rather than H-bonding attraction is dominant because only the normal vibration of $-\text{N}_2^+$ (at 2167 cm^{-1}) can be detected. It is reasonable to consider that the coulombic force is stronger than H-bonding attraction so electrostatic force plays the major role in the overall assembly process of the DR/BSC4A system.

CONCLUSION

In conclusion, a series of photosensitive ultra-thin films based on diazoresin and various calixarenes were fabricated by the self-assembly technique. A covalently cross-linking structure of the film was formed following the decomposition of $-\text{N}_2^+$ group. As a result, the stability of the film against polar solvent etching increases dramatically.

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