Polymeric nanostructured composite films*

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Abstract: This research news describes the construction of polymeric nanostructured composite film based on a variety of interactions, such as hydrophobic–hydrophilic effect, electrostatic interaction, hydrogen bonding, etc. The work focused on developing strategies to solve the basic problems in the area of ultrathin film research, such as stability, improving the interface quality, creating patterned interface, and techniques to construct nanolayered structure. With in-depth study of the relationship between the microscopic layered architecture and macroscopic function of supramolecular assemblies, it is anticipated that one could obtain miniature devices or machines of high efficiency through integration of the assembling process and device fabrication.

INTRODUCTION

Recently, self-assembled ultrathin films have received considerable interest because they allow fabrication of supramolecular assemblies with tailored architecture and properties [1]. Ultrathin films, including monolayer and multilayer films, is a branch of supramolecular system in which its structure and interfaces are easy to control and its function is currently used extensively. In general, the existence of ultrathin film must depend on a special interface. Meanwhile, it usually forms another interface with the neighboring layer or the circumstance in which it exists. In this sense, the interface properties could produce tremendous influences on the properties of the film. Up to now, a variety of materials, including charged and uncharged species, have been successfully assembled into nanolayered structures. Multilayers could be formed by using layer-by-layer assembly techniques based on electrostatic interaction [2], hydrogen bonding [3], coordination bonding [4], charge transfer [5], molecular recognition [6], and so on. Monolayers could be formed by exploiting the chemisorption of an active surfactant-containing material on a solid surface, e.g., the formation of gold thiolate resulting in self-assembled monolayers (SAMs) of organosulfur compounds [7] and the in situ formation of polysiloxane-directing SAMs of organosilicon derivatives [8].

Nanostructured composite film has its foundation in microelectronics, which provides the possibility of its miniaturization and integration. In these applications, "smaller" has meant better and less expensive, more components integrated per chip, fast operation, high performance, and lower power consumption [9]. It will continue to be the basis for microprocessors, memory, and other microelectronic devices for information technology and displaying industry in the foreseeable future. Moreover, nanostructured composite films are increasingly being applied in areas outside of microelectronics [10]. It is also clear that many interesting new phenomena occur at nanometer dimensions and have already provided and are currently providing challenges for scientists. Examples include electronic processes such as quantum size effect (QSE), coulomb blockade, and single-electron tunneling (SET). We have to accept the fact that nanolayered structures are of importance in both theoretical studies and practical applications because they connect the gap between the structure and the function of assembled

systems. With precise control of interface properties, the multilayer film can form symmetric or quasi-symmetric two-dimensional nanostructures. By exploiting the self-assembly characterization of some materials, nanosized patterns could be formed on special interfaces. The most appealing prospect of using self-assembly technique to fabricate patterned structure is that it can provide access to three-dimensional structures and circumvent the size limit determined by optical diffraction. All these above, i.e., both the symmetric/quasi-symmetric two-dimensional structures and the patterned structures, are essential to all the ultrathin film-based miniature devices. There is no doubt that it is necessary and urgent for chemists to investigate the structure-determined properties of ultrathin film-based devices.

Nanolayered multilayer structures mainly form at interfaces of gas/liquid or liquid/solid and are easily realized by means of layer-by-layer assembly techniques. In these systems, the neighboring layers are connected by either covalent or noncovalent bonds. Although noncovalent bonds are much weaker than covalent bonds, multiple weak bonds might add up to produce an association that is strong enough to maintain the stability of the structure formed. The interaction between the layers of different molecules could be an electrostatic interaction, hydrogen bonding, aromatic π–π^* stacking, charge transfer, coordination bond, hydrophobic effect, or the combinations of several interactions among them. It is the diversity of the interaction, as well as the fact that each interaction is weak, that makes it possible to produce different types of films and to tailor the structure of the films to realize a designed function at the same time. Some basic problems remaining in thin film research are as follows: (a) monolayer and multilayer architecture, including composite films, (b) diffusion-controlled interfaces, (c) control over the monolayer thickness, (d) patterning formation, (e) phase transition, (f) charge and energy transfer between layers, (g) stability, etc.

Polymeric nanostructured composite films, compared with other types of nanostructured ones, are meaningful in the sense of stability, diversity, and easy handling. In this research news, we describe some recent progress in the study of polymeric nanolayered structure in our laboratory that covers both layered nanoarchitecture and functional assemblies. The ultimate goal of our research is to find some key rules which control the structure of the ultrathin film so that the fabrication of functional devices through self-assembly and the integration of the material and devices into one unity will finally be realized.

"DUCKWEED" AND REVERSED "DUCKWEED" LB FILM BASED ON HYDROPHILIC–HYDROPHOBIC EFFECT

Self-assembled ultrathin films are mainly formed at interfaces, e.g., gas/liquid or liquid/solid interfaces. We have found that the amphiphilic polymer consisting of hydrophobic styrene–divinyl benzene microgel and hydrophilic polyacrylic acid grafting chains was able to self-rearrange at the air–water interface and to form a so-called "duckweed" monolayer. By controlling the grafting reaction, some residue double bonds could be left unpolymerized in the microgel. Although this kind of "duckweed" is not highly ordered, it can be further polymerized to enhance its thermal stability after it has been transferred onto a solid substrate using the Langmuir–Blodgett (LB) film technique [11]. We also found that the amphiphilic polymer composed of hydrophilic ethylenediamine–epichlorohydrin slightly cross-linking network and hydrophobic stearoyl chains could self-organize at the air–water interface to form a so-called "reversed Duckweed" monolayer. For an amphiphilic polymer with Mn = 7840, alkyl chains content = 75.8%, cross-linking degree ≈ 25%, it can be readily transferred onto a solid substrate as an LB multilayer with a transfer ratio of unity (Fig. 1A). More than three orders of sharp diffraction peaks (with odd–even alternate peak intensities) were observed for the polymeric LB film containing 48 layers. Combined with Fourier transform infrared (FTIR) measurements, we could conclude that the hydrophilic network was flexible enough and could reform its configuration to result in a thin, flat shape at the air–water interface on which hydrophobic alkyl chains were closely packed with a highly ordered orientation [12].
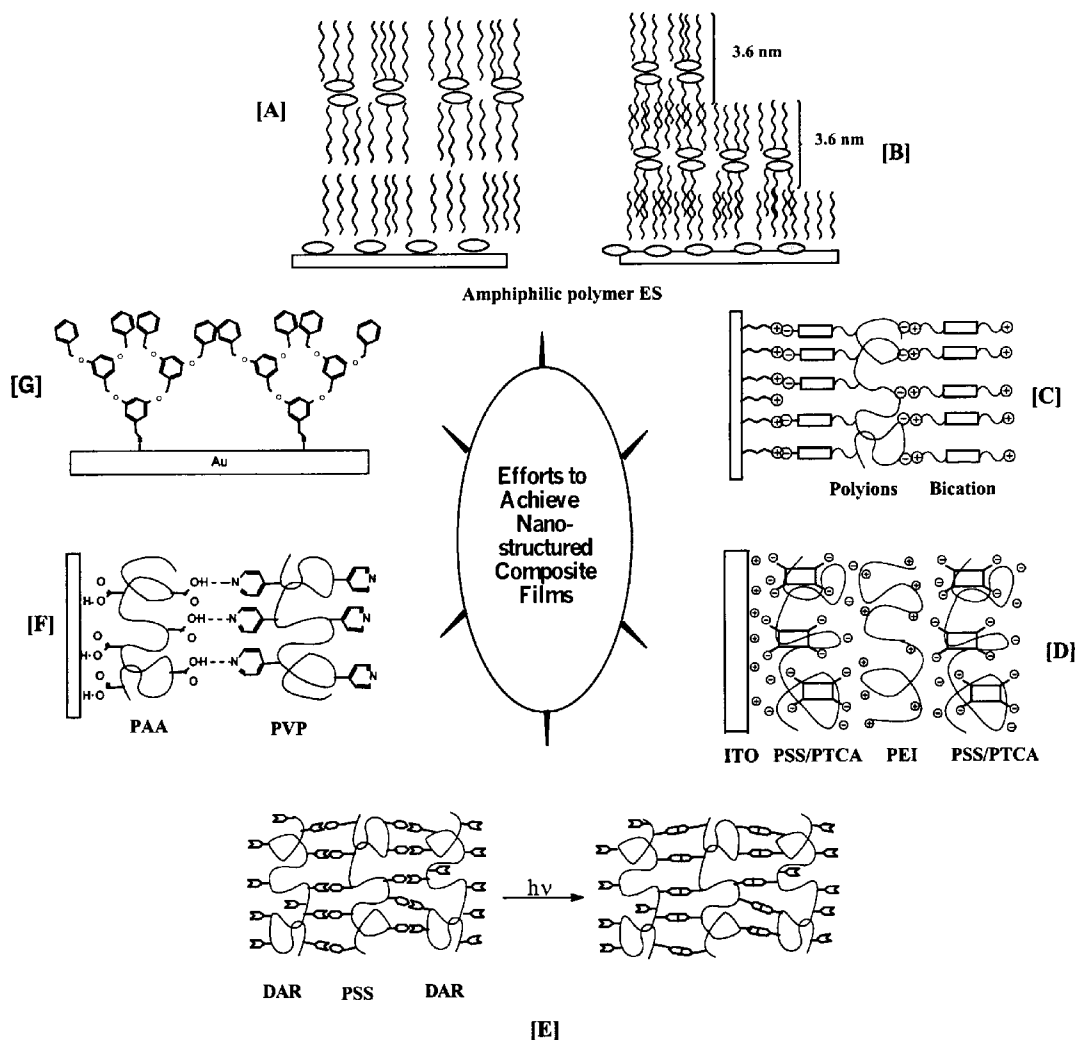
Fig. 1 Illustration of building blocks used in the assembly process: (A) reversed "duckweed" LB film, (B) self-organizing film with interdigitated structure, (C) electrostatic multilayer assemblies of polyelectrolyte and bication, (D) electrostatic multilayered assemblies of PEI/(PSS+PTCA) on ITO substrate, (E) conversion of the DAR/PSS film from ionic to covalent structure, (F) multilayer assemblies of PAA and PVP based on hydrogen bonding, (G) self-assembled monolayer of dendron thiol (D2) on gold surface.

The self-organization of the amphiphilic polymer-bearing hydrophobic alkyl side chains can be accelerated either by heating or by slow evaporation of organic solvents. The structures of the thermotropic mesophases were characterized as a function of the grafting content of long alkyl chains by differential scanning calorimetry (DSC), temperature-dependent X-ray diffraction [13]. It is inferred that some hydrophobic semi-rigid rods formed due to the strong interaction between the long alkyl chains, and thus thermotropic mesophases formed from these amphiphilic polymers although they contain no mesogenic groups. Cast film from aqueous bilayer membrane is another alternate route to multilayer films as proposed by Kunitake [14]. We found that an ordered self-organizing film of the amphiphilic polymer could be formed on solid substrates, such as Si single crystal or mica sheet, by

slow evaporation of organic solvents [15]. We believe that supramolecular organization in the macro-molecular system leads to the ordered film with partially interdigitated layer structure different from the corresponding bulk materials (Fig. 1B).

MULTILAYER BASED ON ELECTROSTATIC INTERACTION

Alternating physisorption of oppositely charged polyions at liquid/solid interface, first proposed by Decher in 1991 [16], is one of the layer-by-layer assembly techniques. Due to many advantages of this method, such as easiness in fabrication, independence of substrate size and topology, good mechanical and chemical stability of the resulting film, it has been proven that this technique is a rapid and experimentally very simple way to produce complex layered structures with precise control of layer composition and thickness. Small angle X-ray diffraction/reflectivity experiments showed that there are no Bragg peaks except one or several Kiessig fringes. This result indicates that the interfaces are usually interpenetrated in the typical polycation/polyanion system. For example, in the poly(allylamine hydrochloride)/poly(4-styrene sulfonate) assemblies, the interpenetration reached the order of 1.2 nm [17]. As an attempt to improve the interface quality, we have used anionic poly(maleic acid monoester) and bipolar quaternary ammonium salt bearing biphenyl mesogenic group to produce assembled multilayer films [18]. The driving force in this case is electrostatic attraction between polyanions and bications, combined with Van der Waals interaction among mesogenic groups of bications. In multilayer system of bication/polyanion (the structures are shown in Schemes 1A, 1B, and 1C), we found there are broad Bragg diffractions, probably indicating the suppression of the interfacial interpenetrating to some extent. As there is strong acid of sulfonate groups in side chains and weak acid of carboxyl groups in main chains, adjustment of pH value of cationic solution has a remarkable effect on the supramolecular structure of multilayer assemblies. Two types of ultrathin film were therefore fabricated with either symmetric or quasi-asymmetric structures (Fig. 1C).

Some dyes or pigments can not be easily assembled by directly exploiting electrostatic interaction as driving force, in some extent due to the low number of binding sites in small molecules. Taking the 3,4,9,10-perylenetetracarboxylic acid (PTCA) as an example, it is a four carboxylic acid group containing pigment and a very interesting material with good luminescence property. In experiment, we found that the assembly of PTCA with poly(ethyleneimine) (noted PEI) was not successful [19]. The already adsorbed PTCA would desorb in the next dipping in PEI solution, as evidenced by UV–vis absorption spectroscopy which showed a zigzag curve of its characteristic absorbance versus the number of layers deposited. So it is unsuccessful to assemble multilayer in this system. To resolve this problem, we mixed the solution of PTCA pigment with poly(4-styrene sulfonate) (noted PSS) first, and thus the mixed solution was used to alternately assemble with PEI (Fig. 1D). In doing so, stable multilayer assemblies containing PTCA were successfully fabricated. This kind of structure was interesting because, on the one hand, it realized the stable assembly of PTCA due to the physical entanglement between PSS and PTCA, although the content of PTCA was low; on the other hand, the incorporation of pigment into PSS matrix as well as PEI inert layer can partially eliminate the luminescence quenching in the inter- and intra-layer at the same time. We can also imagine a simple model for this type of assembly as PSS/PEI multilayer acting as a matrix to entrap small molecular pigments of PTCA. This, additionally, showed the advantage of polymeric assembly. A light-emitting device comprising 20 layers of PEI/(PSS+PTCA) as emitting layer was fabricated on ITO electrode (as anode), and then covered with aluminum cathode. A green light was observed with turn-on voltage about 4.7 V.

Another example discussed briefly is the alternate assembly of boladication form olig(*P*-phenylene vinylene) (OPV) (Scheme 1D) with two types of polyanions—poly(4-styrene sulfonate) and poly(aniline-*co-N*-propane-sulfonic acid aniline) to fabricate OPV-based light-emitting diodes [20]. By selecting different polyanions, the properties of the devices could be well tailored in some extent.
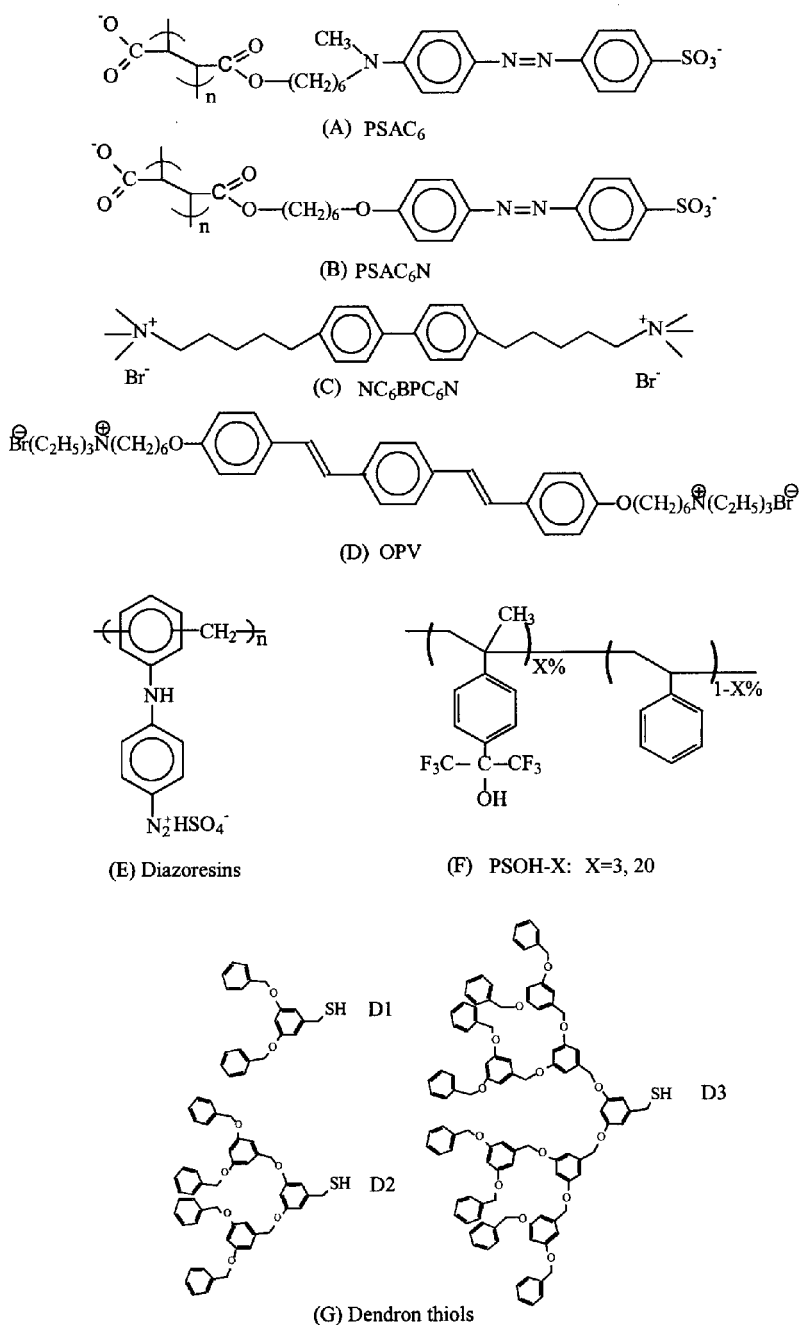
Scheme 1 Illustration of part of materials used in the assembly process: (A) poly(maleic acid monoester) of PSAC6, (B) poly(maleic acid monoester) of PSAC6N, (C) bipolar quaternary ammonium salt of NC6BPC6N, (D) boladication form olig(*P*-phenylene vinylene) (OPV), (E) polycation of diazoresins (DAR), (F) copolymer of *p*-(hexaflouro-2-hydroxyisopropyl)-*a*-methylstyrene and styrene (PSOH), and (G) dendron thiol of D1, D2 and D3.

IN SITU PHOTOREACTION TO FABRICATE COVALENTLY ATTACHED MULTILAYER FILM

As mentioned before, although electrostatic-interaction-directed assembly technique has so many advantages, it has disadvantages, too. The noncovalently attached films are not robust enough and can be etched by solvents, which limits application of this type of film in an extended range. A way we designed to solve this problem is to combine the simplicity of the layer-by-layer assembly technique with post photoinduced reaction in the restricted area [21]. We first selected the diazonium group containing polycation of diazoresins (note DAR) (Scheme 1E) and sulfonate containing polyanion of poly(4-styrene sulfonate) (PSS) as building blocks. In general, the process to fabricate covalently attached multilayer films involves two steps. First, the fabrication of layer-by-layer assembled films was based on electrostatic interaction as driving force. Second, this well-fabricated film was exposed under UV irradiation for a given time to ensure the reaction proceeded completely. The ionic attached film of DAR/PSS was irradiated with UV light, and UV–vis spectroscopy was employed to monitor the process. In experiment, we observed that under UV irradiation, the absorbance at 380 nm, which originated from the π–π* transition of the diazonium groups, decreased dramatically due to the decomposition of the diazonium groups; concomitantly, the absorbance at the vicinity of 290 nm increased gradually. At the same time, an isosbestic point at 332 nm appears. The change of the structure of the film from ionic to covalent after UV irradiation (Fig. 1E) was confirmed by two independent means. FTIR spectroscopy showed the existence of the asymmetric stretching vibrational mode of the sulfonate ester at 1 160 cm^{-1}. Solvent etching in a ternary mixture of H_2O–DMF–$ZnCl_2$ (3:5:2, w/w/w) showed that the stability of the films after UV irradiation could be improved greatly compared with the one without UV irradiation.

The UV-irradiated DAR/PSS film was characterized in details by means of X-ray diffraction measurements. A series of well-ordered Kiessig fringes could be observed which showed the homogeneousness of the films. The absence of Bragg peaks indicated an interpenetrated structure which is the property of the typical polycation/polyanion system but can not be determined by the photoreaction-induced covalent structure. The monolayer thickness of the film can be easily tuned in nanometer scale, which assures the fabrication of thickness-tunable covalent film. Atomic force microscopy (AFM) analysis showed no roughness change took place after UV irradiation when taking a 1-bilayer DAR/PSS film on mica for example. This result indicated that the roughness changes produced by the reaction—if they actually exist—are too little to be detected with the resolution of the characterizing technique.

It also found that oligo-charged molecules such as sulfonated porphyrins and phthalocyanines can be assembled well in the same way, and stable layered nanoarchitectures bearing functional species are formed by post-photoreaction [22]. We further extend this method to the acrylic acid-containing polyanion of poly(acrylic acid) and stability-improved DAR/PAA film has been already achieved [23]. So it is a general way to produce stable covalently attached films with different film thickness. This concept is the further development of the electrostatic-interaction-directed assembly technique and has made it more practicable.

HYDROGEN-BOND-DIRECTED MULTILAYER FILM

The electrostatic-interaction-directed assembly requires charge-containing materials that are usually dissolved in polar solvents, usually water. But there still exist a large amount of neutral organic polymers that can not dissolve in water, but in organic solvents. As an alternative method, we can take advantage of hydrogen bonding to realize nanolayered assembly of these materials. Hydrogen-bonding-based assembly for multilayer film was first reported by Rubner's group and ours at almost the same time [3]. It is shown that it is possible to deposit a thicker layer by using hydrogen bonding than by using

electrostatic interaction. As we know, the amount of charged polymers adsorbed onto a surface depends, among other factors, on the level of segmental repulsion of the charged groups along the chain. In polyelectrolytes, repulsion among the charged groups is larger; the polyion chain usually adopts an extended configuration in solution, so a thinner layer is deposited. Whereas in the case of hydrogen-bonding-based assembly, the polymers are usually neutral, and the repulsion among the groups is less; the chain adopts a coil structure in solution, so a thicker layer is deposited. So another property of the hydrogen-bonding-based assembly technique is that it is prone to construct thick film.

In the case of the poly(vinyl pyridine)/poly(acrylic acid) (PVP/PAA) assembly we investigated (Fig. 1F), we found that the time needed to reach a saturation adsorption of PVP is independent of its concentration and molecular weight (M_w). But the thickness of the film is sensitive to the change of the concentration and M_w. The film thickness increases with either the increase of the concentration of PVP or its M_w. This meant that the thickness of the layer could be controlled in the range of nanometer scale by either changing the concentration of the polymer solution or its molecular weight. The structure of the PVP/PAA assembly was further investigated by SAXD measurements. The appearance of a series of well-ordered Kiessig fringes suggested a good and smooth film with constant thickness and low surface roughness. The mean roughness (R_a) is calculated from AFM result to be 0.64 nm with a given area 1×1 square micrometer.

A copolymer of *p*-(hexaflouro-2-hydroxyisopropyl)-*a*-methylstyrene and styrene (noted PSOH, in Scheme 1F) was selected as another hydrogen bonding donor. Its acidity is weaker than that of PAA, so the hydrogen bonds forming between PSOH and PVP will be weaker than that between PAA and PVP. However, we still successfully prepared an alternating multilayer film of PSOH and PVP in chloroform on the basis of hydrogen bonding between hydroxy and pyridine groups.

DENDRIMER-BASED NANOPATTERNING STRUCTURE

Since Nuzzo and Allara first showed that self-assembled monolayers (SAMs) of alkane–thiolates on gold could be prepared by adsorption of di-n-alkyl disulfides from dilute solutions [7], this field has gained tremendous growth over the past decades [24]. Scientists devoted themselves not only to structural characterization, but also to functionalization of SAMs. Dendrimers, as a type of regular-branched molecule, have attracted extensive scientific interest because of their unusual architecture behavior and many unique properties [25]. These spherical polymers, whose structures could be precisely controlled at molecular level, have been hailed as promising nanoscopic building blocks in the fabrication of supramolecular architectures and devices. We combined the SAMs concept with the special properties of dendrimers to synthesize a polyether dendron with a thiol group at the focal point (Scheme 1F) and to study the self-assembly behavior on gold surface [26]. We employed scanning tunnel microscopy (STM) to study the SAMs of dendron thiol on gold surface. After annealing D2 (the second generation) on gold surface, we can obtain one-dimensional ordered strips with width of ca. 3.1 nm in long range. From the results of molecular dynamics (MD) simulation, the size of D2 is about 1.4 nm, so we infer that the ordered stripes should be the co-adsorption of two dendrons in a shoulder-to-shoulder manner (Fig. 1G). We think the molecular interaction, mainly π–π^* interaction in this case, should be responsible for the packing of the dendron molecules in long range. Before annealing, D2 only forms ordered stripe patterns in some regions, instead of long range. By increasing the voltage between STM tip and the annealed D2 sample, we can observe some defects induced on the strips, which provides a further proof that the ordered strips are formed by the dendron thiol, not by artifact of the gold substrate itself.

As for other sizes of dendrons, D1 (the first generation) can only form ordered stripes in some regions, and it is influenced slightly by annealing. D3 (the third generation) can form ordered stripes even before annealing. The widths of stripes of D1 and D3 are about 2.3 and 4.0 nm, respectively, which is also the double size of MD simulation results (D1: 0.9 nm and D2: 2.3 nm) when considering the

difference between the real size of the strips with the one obtained by STM technique. From the discussion on D2, we know that the molecular interaction, i.e., π–π* interaction, plays an important role in the packing of the dendron molecules. So with the increased size from D1 to D3, the molecular interactions among the dendrons become stronger, and the ability to form ordered stripes is enhanced.

At the end of this section, it is necessary to elucidate the relationship between dendron structure and ordered stripes from the point of molecular architecture. On the one hand, due to the large number of benzenes in dendron thiol, the intermolecular and intramolecular π–π* stacking interactions are strong enough to provide the driving force for its close packing. On the other hand, the insertion of a methylene unit could relax the rigidity of the thiol head group and lead to a stronger intermoleculer interaction [27]. At present, it is early to decide the real reason why one-dimensional ordered strips can be formed in these polyether dendron molecules. Now we are trying to synthesize dendron thiol with different functional groups at their periphery, and expect to establish the relationship of molecular structure and the ordered packing of their molecules at the interface.

The advantages of this concept-to-pattern construction are multiple. The pattern is formed completely based on self-assembly process of dendron on metal surface; therefore, the process is very simple. The size of the pattern can be easily adjusted by simply selecting the size of the dendrimer used, so the resolution of the pattern can reach a high level of several nanometers scale. It is anticipated that this method will provide a novel method to form patterns under 10 nm. Considering the extremely rich structural variation of dendrimers, various tailored surfaces would be available for pattern recognition and functional chips.

CONCLUSIONS AND OUTLOOKS

In summary, we have briefly discussed polymeric nanoarchitectures fabricated in our laboratory based on hydrophobic–hydrophilic effect, electrostatic interaction, hydrogen bonding, and self-assembly of thiol-containing dendrimers. The reversed "duckweed" LB film shows sharp Bragg diffraction peaks. The intensity of peaks showed odd–even alternation. By carefully selecting bication/polyanion system, which contains mesogen groups in bications, broad Bragg diffraction was observed, which indicated a better interfacial structure. In alternating deposition film with hydrogen bonding as driving force, no Bragg diffraction was observed, but well-resolved Kiessig fringes were observed with roughness of ca. 0.6 nm. Stable covalently attached multilayer film can be easily achieved by combining the layer-by-layer assembly technique and the in situ photoreaction. A special way to form patterns with sizes under 10 m has been achieved by self-assembly of thiol containing dendrimer. All these works are based on the motivation to look for and accumulate basic concepts for fully understanding the relationship between the structures and the future applications. There is still a long way to go to bridge the gap. The integration of nanoarchitecture and function in one self-assembling system is probably the way that will eventually solve the problems encountered in device fabrication. We believe that macromolecules-based thin films will enrich the diversity and provide stability of the resulting supramolecular assemblies. Development of polymeric nanostructures calls for theory and new experimental method, such as theory on intermolecular weak interaction, computational method of energy in supramolecular system, spectroscopy and method of nanometer and microdomain, spectroscopic theory and method of near-field optics, etc. Research in this regard has not only practical applications, but also fundamental interest.

ACKNOWLEDGMENT

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