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Preparation of Ultrathin Films of Molecular Networks through Layer-by-Layer Cross-Linking Polymerization of Tetrafunctional Monomers

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S *Supporting Information*

Various types of organic molecular networks, which consist of cross-links of molecular size, are promising materials for the development of energy-efficient and environment-friendly molecular separation or storage methods.[1−4] However, most of the organic network materials reported to date are produced as intractable solids. A new synthetic method allowing processing of the molecular networks into useful forms has to be developed. In particular, considering the potential of organic molecular networks as materials for size-based separation membranes,[5,6] it is of great importance to develop an effective method for producing thin films of three-dimensional molecular networks with nanometer scale thickness in a practically large area.

Here, we demonstrate the synthesis of nanometers-thick films of rigid organic molecular networks via layer-by-layer cross-linking polymerization, a type of molecular layer deposition method. Use of tetrafunctional monomers with rigid tetrahedral geometry enabled directional propagation of the network growth normal to the supported substrate surface under self-limiting conditions.

Ultrathin, conformal films of inorganic networks are grown by atomic layer deposition (ALD), a chemical vapor deposition technique that is capable of growing networks layer-by-layer.[7] In principle, a molecular version of ALD, namely, molecular layer deposition (MLD), may be performed to produce thin films of organic networks by employing rigid multivalent organic monomers. The resultant networks consist of molecular cross-links whose size is smaller than 1 or 2 nm. The network materials obtained from rigid monomers often possess micropores, which, by IUPAC definition, are smaller than 2 nm. Yet, the MLD method reported to date has been limited to the synthesis of the films of surface-grafted linear polymer chains via polymerization of bifunctional organic monomers[8−11] and never been used to produce films of molecular level organic networks from multifunctional monomers.

Typical organic monomers used for the synthesis of molecular-level networks are rigid aromatic compounds with multiple functional groups;[12,13] therefore, they usually have relatively high molar masses and boiling points, which would prevent complete removal of the excess adsorbed monomers on the surface in each cycle of vapor deposition process. A solution-based MLD method such as LbL deposition methods[14−16] needs to be developed.

For the network growth to be controllable on a molecular level in the solution-deposition method, the cross-linking polymerization of the multifunctional monomers must not extend beyond each molecular layer deposited on its underlayer. The monomer system must follow a self-limiting growth mechanism. Physically adsorbed excess monomers over the top molecular layer must be removed by rinsing with solvent so that the film can be dipped into the monomer bath for further network growth.

Our approach to the synthesis of thin film organic molecular networks is based on the use of the monomers with a rigid tetrahedral geometry. We employed a monomer system consisting of a pair of tetrakis(4-aminophenyl)methane (TAPM) and tetrakis(4-isocyanatophenyl)methane (TIPM) (Figure 1a), which were synthesized as reported previously.[17,18] When these rigid tetrahedral molecules react with the functional groups of the surface, at least one of the four vertices should remain intact and constitute the top surface of the growing film (Figure 1b), limiting the network growth only into two dimensions on each deposited layer. Alternating deposition of TIPM and TAPM onto the substrate surface produces thin films of a three-dimensional polyurea network, as shown schematically in Figure 1c. On each time of substrate-dipping into the bath, the covalent addition of the monomers to the surface ceases as the whole substrate surface becomes saturated with the grafted molecules. For example, an amino-functionalized surface immersed in TIPM solution will yield an isocyanate-saturated surface, and vice versa.

The first molecular layer (ML) was deposited onto silicon or quartz plate coated with a self-assembled monolayer (SAM) of 3-aminopropyltriethoxysilane (APTES). The amino-functionalized substrate was immersed in TIPM solution of 0.2% w/v in THF followed by rinsing successively with pure THF. The resulting 1-ML-coated substrate was dipped into TAPM solution of 0.2% w/v in THF and then rinsed with solvent to produce the 2-ML-thick (1 bilayer) film of the network (see Supporting Information).

Alternating the deposition steps of TIPM and TAPM multiple times yielded thicker films, where the film thickness was

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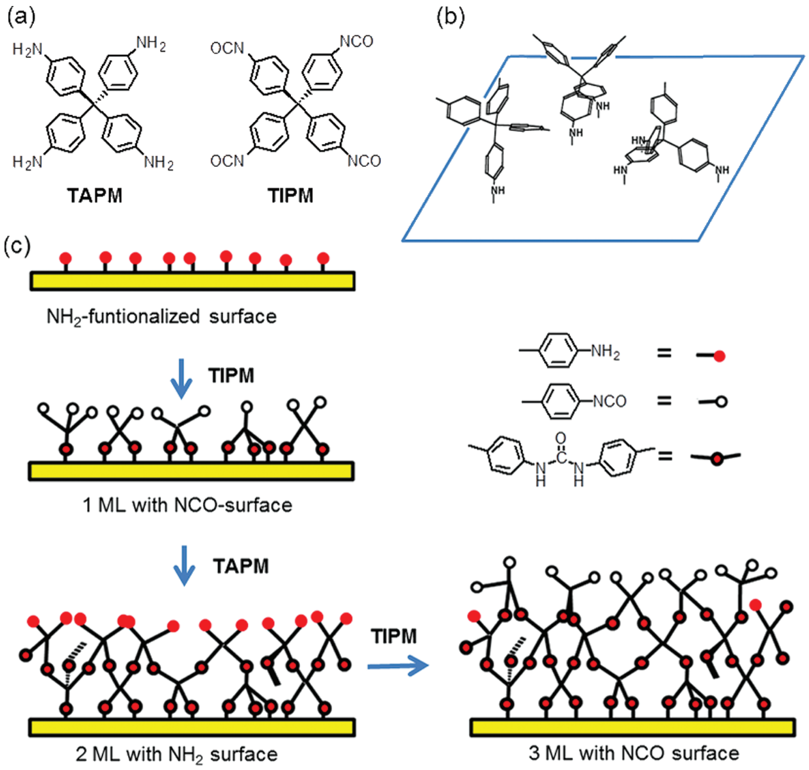

Figure 1. Molecular layer deposition process enabled by LbL cross-linking condensation polymerization. (a) Chemical structure of the two tetrahedral monomers. (b) Top view of the surface showing three different orientations of the tetrahedral monomers bonded to the underlayer. (c) Schematic representation of the deposition sequence to produce thin films of the networks with thicknesses of 1, 2, and 3 molecular layers (ML).

controlled by adjusting the number of deposition cycles. Figure 2a shows the UV spectra of the films deposited onto quartz plates as a function of the number of deposition cycles. The UV absorption maxima centered at 274 nm increased linearly with the number of deposition cycles, showing that the increment in film thickness per deposition cycle was nearly constant.

To achieve well-controlled film growth throughout the entire deposition process, the surface of the growing film has to be fully covered with a layer of monomers after finishing each half cycle. To optimize the deposition conditions to full surface coverage, various films were grown using different monomer concentrations of dipping solutions and varying the duration of substrate immersion in each dipping run. UV spectra of the films obtained from various concentrations indicated that a concentration greater than 0.2% w/v was needed for linear growth of the film. Irregular film growth at lower monomer concentrations may be attributed to insufficient surface coverage by the reactants and the formation of islands or aggregates. When the monomer solutions with concentrations higher than 0.2% w/v were used, the UV absorbance of the films produced by the same deposition cycle number reached nearly a constant value when the immersion time was greater than 20 s, as shown in Figure 2b. This indicates that covalent grafting of the tetrahedral monomers onto the growing film surface ceases after a critical immersion time for which the surface becomes saturated with the adsorbed countermonomers.

While the UV data indicate linear growth behavior of the network, it remains to be established that the network growth by the LbL method is controllable at the molecular level. The film thickness data were obtained using scanning electron microscope (SEM) images (Figure 3a) of fractured samples. Examination of a plot of film thickness as a function of deposition cycle number discloses a linear trend line (Figure 3b) of slope 1.94 nm/cycle, which is an approximate measure of the film thickness per deposition cycle. This means that the average thickness of 1 ML is 0.97 nm. Grazing incidence X-ray diffraction (GIXRD) of a sample grown onto APTES-coated quartz plates yielded the data in Figure 3c. No peak was observed in the q_{xy} direction, indicating that random molecular networks formed in two dimensions upon deposition of each layer. In contrast, a weak scattering peak appeared in the q_z direction near 6.5 nm^{-1}. The *d*-spacing corresponding to this peak is 0.96 nm, which is close to the SEM-measured thickness increment per half cycle and the height of a tetrahedron with four nitrogen atoms of TIPM or TAPM located at each vertex. The weakly periodic nature along the thickness direction is attributed to the segregation of urea bonds on the reaction front in the LbL process, i.e., the top surface of the growing film at each deposition run.

The microporocity of the molecular networks may be best estimated by the porosity measurement. However, currently available porosimeters cannot accommodate the ultrathin network samples produced in this study. In our previous study, bulk samples and nanoparticles of the TIPM/TAPM networks produced via the sol−gel method exhibited microporosity.[18] Although the current LbL-grown networks may have some structural discrepancy with the sol−gel-processed networks, the microporosity is likely to exist also in the materials produced in the current work because both materials consist of the repeating units of identical chemical structure. Furthermore, regardless whether the network is microporous or not, it is promising that the organic molecular networks can be easily processed into

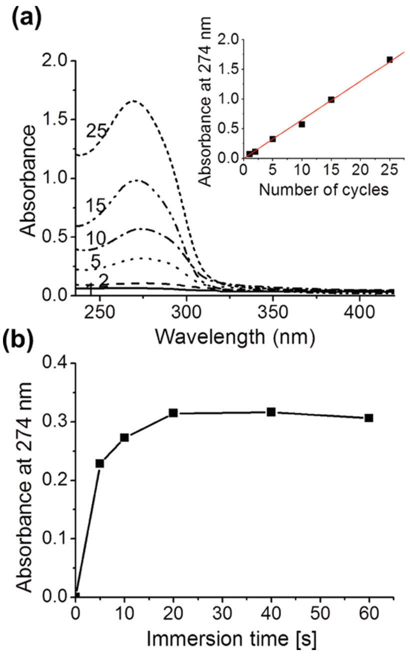

Figure 2. Growth of molecular network in thin films via the LbL-MLD process. (a) UV absorption spectra of the films on the quartz plates produced by varying the deposition cycle number (deposition condition: 0.2% w/v solution and 40 s of immersion time). Inset shows the absorbance at 274 nm plotted as a function of the deposition cycle number. (b) Absorbance at 274 nm of the films for 5 cycles of deposition plotted as a function of the immersion time of the substrate in 0.2% w/v monomer bath.

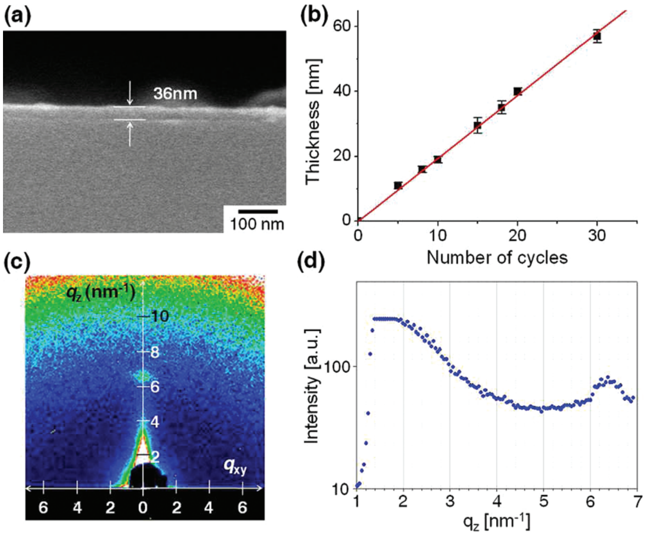

Figure 3. SEM and GIXRD data of the thin film molecular networks generated by LbL-MLD (0.2% w/v, 20 s, on Si wafer). (a) SEM image of the film prepared by 18 cycles. (b) Graph of the SEM-measured film thickness vs the number of deposition cycles. (c, d) 2-D and 1-D GIXRD data of the film prepared by 100 cycles of deposition.

ultrathin membrane by the LbL-cross-linking MLD method. We are currently studying for preparation of ultrathin membranes of the organic network on porous substrates that can be used for molecular separation.

An additional interesting aspect of the LbL-cross-linking MLD process is its micropatternability. In a preliminary study (Figure S1), we prepared a micropattern of the molecular networks on a silica substrate by microcontact printing of APTES using a PDMS stamp and subsequent LbL process with the TIPM/TAPM monomer pairs. Although the patterning method involving microcontact printing needs further optimization to establish conditions for uniform network growth, it is promising that the highly cross-linked molecular networks can be applied onto various solid substrates in a microscopic pattern.

In summary, we have presented a new solution-based method for producing ultrathin films of covalent organic molecular networks by alternating deposition of two monomers with rigid tetrahedral geometry. The thickness of the resulting thin film molecular network could be controlled on the molecular level by adjusting the number of deposition cycles. The LbL molecular network growth method may be conducted on various types of substrates such as porous or micropatterned substrates and may be readily combined with other conventional or advanced thin film or membrane fabrication techniques. Further studies on the synthesis of the ultathin organic networks using the LbL growth method from the monomers with different structures are also underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, an AFM image of micropatterned molecular network, XPS data of the network film, and a graph of AFM-measured thickness vs deposition cycle number. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Germain, J.; Frechet, J. M. J.; Svec, F. *Small* **2009**, *5*, 1098.
(2) Han, S. S.; Furukawa, H.; Yaghi, O. M.; Goddard, W. A. *J. Am. Chem. Soc.* **2008**, *130*, 11580.
(3) Li, J. R.; Kuppler, R. J.; Zhou, H. C. *Chem. Soc. Rev.* **2009**, *38*, 1477.
(4) Thomas, A.; Kuhn, P.; Weber, J.; Titirici, M. M.; Antonietti, M. *Macromol. Rapid Commun.* **2009**, *30*, 221.
(5) Striemer, C. C.; Gaborski, T. R.; McGrath, J. L.; Fauchet, P. M. *Nature* **2007**, *445*, 749.
(6) Vandezande, P.; Gevers, L. E. M.; Vankelecom, I. F. J. *Chem. Soc. Rev.* **2008**, *37*, 365.
(7) Puurunen, R. L. *J. Appl. Phys.* **2005**, 97.
(8) George, S. M.; Yoon, B.; Dameron, A. A. *Acc. Chem. Res.* **2009**, *42*, 498.

(9) Kim, A.; Filler, M. A.; Kim, S.; Bent, S. F. *J. Am. Chem. Soc.* **2005**, *127*, 6123.

(10) Lee, B. H.; Ryu, M. K.; Choi, S. Y.; Lee, K. H.; Im, S.; Sung, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 16034.

(11) Kohli, P.; Blanchard, G. J. *Langmuir* **2000**, *16*, 4655.

(12) El-Kaderi, H. M.; Hunt, J. R.; Mendoza-Cortes, J. L.; Cote, A. P.; Taylor, R. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2007**, *316*, 268.

(13) Weber, J.; Antonietti, M.; Thomas, A. *Macromolecules* **2008**, *41*, 2880.

(14) Quinn, J. F.; Johnston, A. P. R.; Such, G. K.; Zelikin, A. N.; Caruso, F. *Chem. Soc. Rev.* **2007**, *36*, 707.

(15) Hammond, P. T. *Adv. Mater.* **2004**, *16*, 1271.

(16) Jaber, J. A.; Schlenoff, J. B. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 324.

(17) Laliberte, D.; Maris, T.; Wuest, J. D. *Can. J. Chem.* **2004**, *82*, 386.

(18) Moon, S. Y.; Bae, J. S.; Jeon, E.; Park, J. W. *Angew. Chem., Int. Ed.* **2010**, *49*, 9504.