Fabrication of Large, Robust Nanomembranes from Diverse, Cross-Linked Polymeric Materials

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Ultrathin polymer membranes have been recognized as one of the most promising materials in science and technology of nanomaterials. They find applications in a variety of areas such as nano separation membranes,[1−3] nanosensors,[4,5] and functional nanosheets for electrochemical and photochemical applications.[6−8] Availability of robust, macroscopic nanomembranes is strongly desired in these applications. Unfortunately, fabrication of such membranes is quite difficult because the two often-incompatible characteristics—nanometer thickness and macroscopic size—have to be satisfied simultaneously. Macroscopic sizes are required for applications where quantity is intrinsic as in materials separation and energy conversion.

Recently, we reported that introduction of high-density cross-linking is a common element to attain sufficient robustness in order to satisfy the above two requirements. For example, a robust, large nanomembrane was prepared by taking advantage of densely cross-linked interpenetrating hybrid networks (IPN) of zirconia and acrylate.[9] More recently, we found a simple fabrication procedure for a large, free-standing nanomembrane from organic components of epoxy resin alone.[10] The epoxy nanomembrane was uniform and robust with a thickness of 20 nm, and an extremely high aspect ratio of size and thickness greater than 10^6 was attained. It is important to extend this concept to other densely cross-linked materials, in order to make it useful for diverse purposes.

The major purpose of this study is two folds. One is to demonstrate that fabrication of robust, free-standing nanomembranes is possible more generally from other cross-linked organic macromolecules such as melamine resin, urethane resin and phthalic resin. Typical chemical structures of these resins are shown in Figure S1. The other is development of useful underlayer polymer. This sacrificial underlayer must remain intact against various solvents employed during the spin-coating process, and additionally it should be readily dissolved in common organic solvents during the film detachment process. Such two conflicting properties are required for a general-purpose underlayer.

The general procedure of the nanomembrane fabrication is as follows (Scheme 1). A sacrificial layer is formed on a flat silicon wafer by spin-coating, and a thin layer of resin precursor is additionally formed with thickness of several tens of nanometer. The double layer is cured by heating on a digital hot plate at 120 °C for 5 min, and it is detached from Si wafer by dissolution of the sacrificial layer. In the present case, we need to use different solvents for different resin precursors, and the sacrificial underlayer should not be damaged by these solvents. Unfortunately, poly(4-hydroxystyrene) [PHS], which was used as the sacrificial layer in the previous study, does not have satisfactory tolerance toward these solvents, and nonuniform nanomembranes with a plenty of defects were formed. This solvent problem had limited our attempt to prepare robust nanomembranes from a wide range of cross-linked materials.

This problem is solved by the use of "thermally cross-linkable and photodecomposable" polymer mix[11] as the sacrificial layer. The polymer mix is composed of poly(4-hydroxylstyrene-*co*-methyl methacrylate) [poly(HS-MMA)], 4-divinyloxycyclohexane [CHDVE], and diphenyliodonium triflate [DPI-Tf] in this study. As shown in Scheme S1, thermal reaction of poly(HS-MMA) with CHDVE gives an insoluble and infusible cross-linked material. In fact, when the polymer mix was spin-coated and subjected to baking at 120 °C for 5 min, the sacrificial layer became resistant to most solvents, including 1-methyl-2-pyrrolidinone, *N*, *N*-dimethylformamide, and dimethyl sulfoxide. Therefore, most organic solvents can be used for preparing spin-coating solutions of the membrane precursor, since this underlayer is not damaged. The cross-linked structure of the underlayer is, however, decomposed by acid-catalyzed thermal reaction. Thus, photoirradiation at 254 nm (UVB-X; Sen Light Corporation) generated trifluoromethanesulfonic acid from DPI-Tf, and the additional baking at 120 °C for 5 min converted the insoluble underlayer to readily soluble underlayer. Details of the reaction mechanism of "thermally cross-linkable and photodecomposable" polymer mix is described in Supporting Information. At the same time, the upper resin layer was cured to form a hard, cross-linked material due to the baking, and it can be detached from the solid substrate.

Melanine resin (melamine acrylate resin), phthalic resin (polyol cross-linked with phthalic anhydride), and urethane resin (acrylurethane resin) were purchased from Nippon Paint (trade names: Orgaselect220, Unipak200, and Unipon200, respectively). These precursor resin solutions were diluted with toluene and spin-coated to form 20−40 nm thick films. All the nanomembranes were detached from solid substrate by immersion into acetone. The morphology of the isolated nanomembranes was affected by the solvent used. The melamine nanomembrane could not maintain extended morphology in ethanol, and it was crumpled into a ball. In the case of the urethane nanomembrane, it swelled considerably with ethanol solvent. This may be caused by the presence of soft segment and the relatively low cross-linking density in this resin. Swelling was scarcely observed when acetone was used as solvent, and the detached film was highly flexible with a size of over 25 cm^2. Figure 1a shows the melamine nanomembrane in acetone as an example. Although the membrane is thin enough, reflection of light clearly indicated the presence of nanomembrane. The silk-like nanomembrane swirled in acetone by gentle convection due to solvent evaporation (Movie S1). Figure 1b is a cross-section view of SEM observation for the nanomembrane attached onto anodized aluminum oxide (AAO) support. The nanomembrane is placed on the irregular AAO surface with uniform thickness of 25 ± 2 nm. Figure 1c gives a digital camera view of the melamine nanomembrane on a wire frame. The nanomembrane with 30 nm thickness was transferred to a wire frame of 0.8 mm diameter. It is clear that the nanomembrane of the melamine resin is stable even in the air.

Similar fabrication procedures were employed for phthalic resin and urethane resin, and free-standing nanomembranes were obtained from these thermosetting resins with about 30 nm

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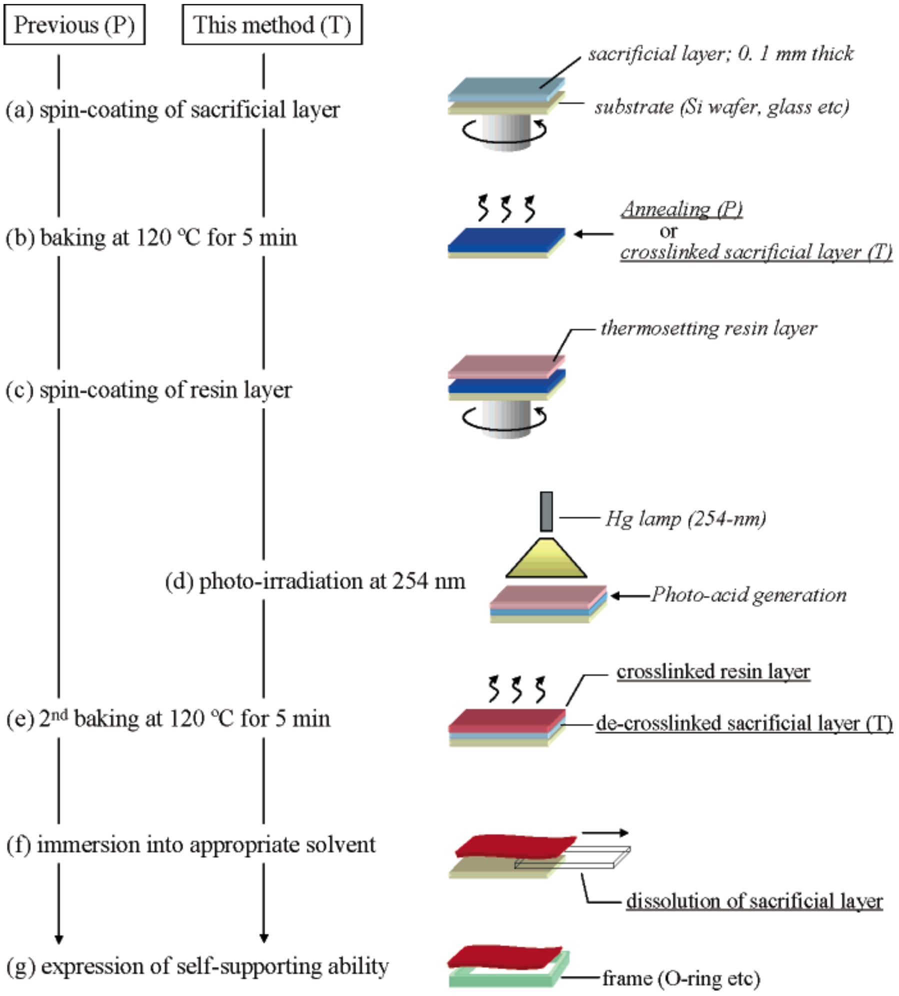
Scheme 1. Schematic Figure of the Preparation Procedure of Nanomembrane with and without Using a "Thermally Cross-Linkable and Photodecomposable" Photopolymer



thickness. No difference was found in their macroscopic observation. These results clearly indicate that the fabrication of large, nanomembranes is possible from diverse, highly cross-linked organic macromolecules.

The mechanical strength of nanomembranes was measured by the bulging test (Supporting Information).[9,12,13] The tensile stress (σ) and the ultimate elongation (ϵ) of the nanomembrane can be measured by applying air pressure to a membrane attached onto a small hole of a metal plate. The deflection of membrane was monitored by an optical microscope from the viewing angle as shown in Figure 2a. Parts b−f of Figure 2 show macroscopic pictures of the deflection. The melamine and

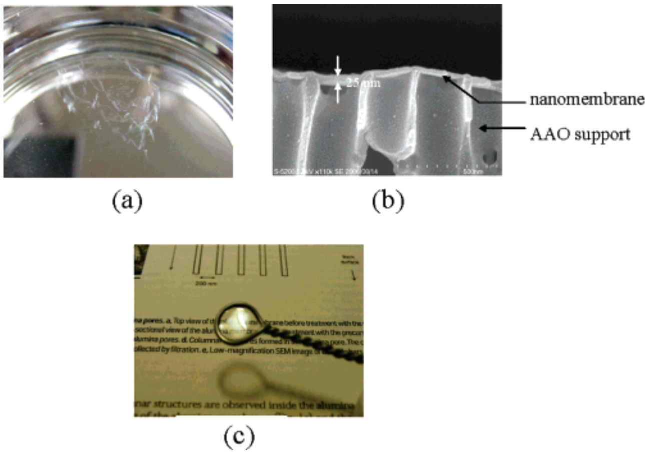


Figure 1. Macroscopic and microscopic images of melamine nanomembrane: (a) digital camera view in acetone solution; (b) SEM image on AAO support; (c) digital camera view of a free-standing nanomembrane on a wire frame of 0.8 mm diameter

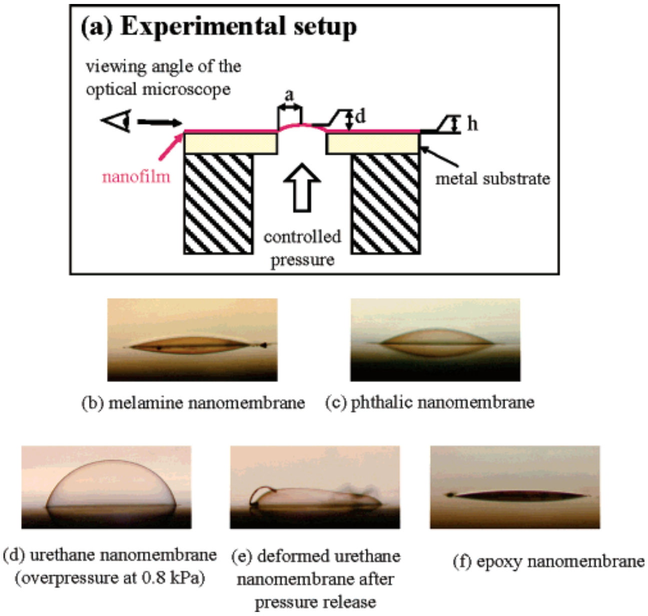


Figure 2. Bulging experiment: (a) experimental setup; (b−f) lateral views of deflected nanomembranes under overpressure; (e) deformed urethane nanomembrane after release of air pressure (over 1 kPa).

Table 1. Mechanical Properties of Nanomembranes

	nanomembrane				
material	thickness [nm][a]	ultimate tensile strength σ [Pa][b]	ultimate elongation ϵ [%][b]	Young's modulus [Pa][c]	conventional resins ultimate tensile strength σ [Pa][d]
melamine	25 ± 2	1.8×10^7	1.6	1.4×10^9	5.0×10^7 to 8.8×10^7
phthalic	19 ± 1	1.2×10^7	3.7	1.2×10^9	3.4×10^7 to 5.9×10^7
urethane	20 ± 3	$>1.0 \times 10^7$ [e]	>33.6 [e]	2.8×10^9	2.0×10^6 to 6.9×10^8
epoxy [f]	24 ± 2	2.2×10^7	0.2	3.5×10^8	3.5×10^7 to 8.8×10^7

[a] Determined by SEM observation. [b] Determined by the bulging test. [c] Determined by the buckling measurement. [d] From *Kagaku Binran Ouyo-hen*, 3rd ed. [e] Precise value not obtained due to plastic deformation. [f] From the separate study.[10]

phthalic nanomembranes give deflections somewhat greater than that of the epoxy membrane, and are broken before extensive deformation. In contrast, the urethane membrane gives nearly a semicircle deflection and regains the original flatness after removal of the pressure. However, overpressure greater than 1 kPa caused plastic deformation, and the membrane remained deformed even after the pressure removal (Figure 2e. The σ and ϵ values are summarized in Table 1.

Young's modulus of these membranes was determined separately by the "strain-induced elastic buckling instability for mechanical measurements (SIEBIMM)" technique (Supporting Information).[14−16] This technique utilizes buckling instability that occurs in a bilayer consisting of a stiff, thin nanomembrane layer and a relatively soft, thick substrate layer. Upon applying compression, the bilayer produces highly periodic wrinkles, and the elastic modulus can be calculated from the pitch of the periodic buckling wavelength. In our case, nanomembranes were transferred from Si substrate to the flat surface of diced PDMS. The PDMS was compressed by using digital vise, and the wavelength of the buckling was measured by optical microscopy. Young's modulus was calculated according to the published procedure and given in Table 1.

Generally speaking, the observed mechanical properties are in the same range as those of the macroscopic resins.[17] The large ultimate elongation of the urethane resin is unique. It will originate from the presence of the soft alkyl chain segment. We expected in the beginning to find unusual mechanical characteristics arising from quasi 2-dimensional cross-linking. However, this is apparently not the case, and we conclude that the mechanical property is essentially not affected by the current membrane thickness.

In summary, we demonstrated that macroscopically robust, free-standing nanomembranes became available from a variety of densely cross-linked organic polymers. Representative thermosetting resins belong to this class of polymers. The fabrication procedure is conducted by the solution process under ambient conditions, and precursor materials need to be compatible only with such moderate conditions except for final curing. In any case, it is apparent that the kind of macroscopic, defect-free membranes is now extended to a broad variety of chemical structures. This freedom of materials design is essential for its use in different functional applications that include, for example, biomedical applications, designed transport of ions and molecules, and separation purposes.

Supporting Information Available: Figures showing representative chemical structures of thermosetting resins and reaction mechanism of "thermally cross-linkable and photodecomposable" polymer mix, text giving the experimental details of the measurement of mechanical properties, and a movie of a swirling nanomembrane in acetone. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Zhang, Qi; Cussler, E. L. *J. Membr. Sci.* **1984**, *19*, 259−72.
(2) Hu, Q.; Marand, E.; Dhingra, S.; Fritsch, D.; Wen, J.; Wilkes, G. *J. Membr. Sci.* **1997**, *135*, 65−79.
(3) Shiflett, M. B.; Foley, H. C. *Science* **1999**, *285*, 1902−1905.
(4) Guizard, C.; Lacan, P. *New J. Chem.* **1994**, *18*, 1097−107.
(5) Wang, X.; Drew, C.; Lee, S.-H.; Senecal, K. J.; Kumar, J.; Samuelson, L. *Nano Lett.* **2002**, *2*, 1273−1275.
(6) Zhang, M.; Fang, S.; Zakhidov, A. A.; Lee, S. B.; Aliev, A. E.; Williams, C. D.; Atkinson, K. R.; Baughman, R. H. *Science* **2005**, *309*, 1215−1219.
(7) Ikeda, A.; Tsuchiya, Y.; Konishi, T.; Ogasawara, S.; Kikuchi, J. *Chem. Mater.* **2005**, *17*, 4018−4022.
(8) Gap, Y.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Li, X.; Kaliaguine, S. *Polymer* **2006**, *47*, 808−816.
(9) Vendamme, R.; Onoue, S.; Nakao, A.; Kunitake, T. *Nat. Mater.* **2006**, *5*, 494−501.
(10) Watanabe, H.; Kunitake, T. *Adv. Mater.* **2007**, in press.
(11) (a) Moon, S.; Kamenosono, K.; Kondo, S.; Umehara, A.; Yamaoka, T. *Chem. Mater.* **1994**, *6*, 1854. (b) Taguchi, T.; Yamashita, Y.; Suzuki, T.; Yamaoka, T. *J. Vac. Sci. Technol. B*, **1995**, *13*, 3026. (c) Watanabe, H.; Maeshima, K.; Aoai, T.; Kondo, S.; Naito, T.; Ohfuji, T.; Sasago, M.; Miyagawa, N.; Takahara, S.; Yamaoka, T. *J. Photopolym. Sci. Technol.* **1998**, *11*, 3, 537.
(12) Jiang, C.; Markutsya, S.; Pikus, Y.; Tsukruk, V. *Nat. Mater.* **2004**, *3*, 721−727.
(13) Markutsya, S.; Jiang, C.; Pikus, Y.; Tsukruk, V. *Adv. Funct. Mater.* **2005**, *15*, 771−780.
(14) Stafford, C. M.; Harrison, C.; Beers, K.; Karim, A.; Amis, E. J.; Vanlandingham, M. R.; Kim, H.-C.; Volksen, W.; Miller, R. D.; Simonyi, E. E. *Nat. Mater.* **2004**, *3*, 545−550.
(15) Wilder, E. A.; Guo, S.; Lin-Gibson, S.; Fasolka, M. J.; Stafford, C. M. *Macromolecules* **2006**, *39*, 4138−4143.
(16) Bowden, N.; Brittain, S.; Evans, A. G.; Hutchinson, J. W.; Whitesides, G. M. *Nature (London)* **1998**, *393*, 146.
(17) In *Kagaku Binran Ouyou-hen*, 3rd ed.; Maruzen: Tokyo, 1986 (in Japanese).

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