NOTE

Fabrication of Large Nanomembranes by Radical Polymerization of Multifunctional Acrylate Monomers

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Nanomembranes and naosheets are among the most interesting nanomaterials.[1,2] They are characterized by one nanometer dimension and two micro-to-macroscopic dimensions. This unique dimensional combination produces interesting features that are not attainable with other nanomaterials of different dimensionality such as nanocrystals,[3,4] nanoparticles,[5–7] and nanotubes.[8–10]

The macroscopic robustness is essential for application of such features particularly in case of giant nanomembranes. We have shown recently that high cross-linking density is effective for attaining sufficient robustness of nanomembranes with large aspect ratios (size/thickness).[11] For example, a hybrid membrane of cross-linked acrylate and zirconia/silica possessed superior robustness with a thickness of only 35 nm.[12,13] In the subsequent studies, we demonstrated that epoxy and other thermosetting resins similarly gave robust nanomembranes with equally large aspect ratios.[14,15] These results imply that robust nanomembranes become available only if high cross-linking density is introduced. In the above case of the hybrid nanomembrane,[12] however, it was not possible to obtain stable (*i.e.*, free-standing) nanomembranes from the organic component alone. This failure can result from insufficient cross-linking density and/or from insufficient robustness of cross-linked acrylate chains, since successful fabrication of robust nanomembranes is possible from thermosetting resins.

Here, we report fabrication of free-standing nanomembranes from acrylic components alone. According to the above supposition, we employed a precursor which contains a higher amount of the double-bond moiety on one hand and a precursor mixture which contains a rigid molecular backbone on the other. They are a tetra-functional acrylic monomer of pentaerythritol tetraacrylate (PETA, Aldrich) and a bisphenol A-functionalized acrylic oligomer (Kayarad R-280, Nippon Kayaku, with 20 wt% 2-hydroxypropylacrylate), respectively.

The fabrication procedure of nanomembranes is similar to that of our previous study.[14] Firstly, thin layers of poly(styrene-4-sulfonic acid) [PSS; $M_w = 1.0 \times 10^5$, Aldrich] or poly(4-hydroxystyrene) [PHS; $M_w = 4.5 \times 10^3$, Aldrich] were formed on Si-wafer by spin-coating. These layers act as water-soluble and ethanol-soluble sacrificial layers, respectively. Chloroform solutions (1 wt%) of acrylic precursors and a photo-initiator (Darocure4265, Ciba-Geigy, 5 wt% relative to the acrylic precursor) were then spin-coated, and UV irradiation was performed on the sample under vacuum. A high pressure mercury lamp (Hamamatsu, Lighteningcure LC5) was used as a light source, and irradiation was done through a slide glass as a filter. Chemicals used in this study together with the bi-functional aliphatic acrylate (hexanediyl diacrylate; HDODA) used in our previous study are summarized in Figure 1.

Figure 2 shows ATR-FT-IR (Thermo Nicolet, Nexus670 FT-IR) spectra of an R-280 film which was directly fabricated on a gold substrate under otherwise the identical conditions. Stretching vibration of acrylate ($CH_2=CH-$) at $810\,cm^{-1}$ disappeared completely after UV irradiation for 5 min under vacuum, indicating that free radical photo-polymerization took place by the UV irradiation. When irradiation was done in the air, the polymerization did not proceed, probably due to oxygen quenching of radicals.[16] On the other hand, consumption of the double bond, as confirmed by IR spectra was not complete in the case of PETA. Some of the double bond (roughly 50%) remained un-reacted, probably due to its very high content. Figure 3 shows digital camera views of the R280 nanomembrane. When PSS was used as the sacrificial layer, nanomembranes were detached as such onto water surface by careful immersion of the sample (Figure 3(a)). The detached nanomembrane was strongly spun, due to high surface tension of water. The detached films maintained the spin-coated size of over $5\,cm^2$. This R280 nanomembrane could be separated intact from substrate by ethanol solvent, even when ethanol-soluble PHS was used as the sacrificial layer, but the detached film immediately crumpled into a rubber-ball structure within a few seconds (Figure 3(b)). We observed a similar solvent-dependent change in the case of a urethane nanomembrane, and the use of acetone as solvent effectively alleviated the crumpling phenomenon.[15] However, common organic solvents were not effective for avoiding crumpling of the acrylate nanomembrane. When a spin-coated nanomembrane was detached before UV irradiation, it collapsed into small pieces during the detachment process. Polymerization is necessary for the fabrication of stable acrylate nanomembrane with large size.

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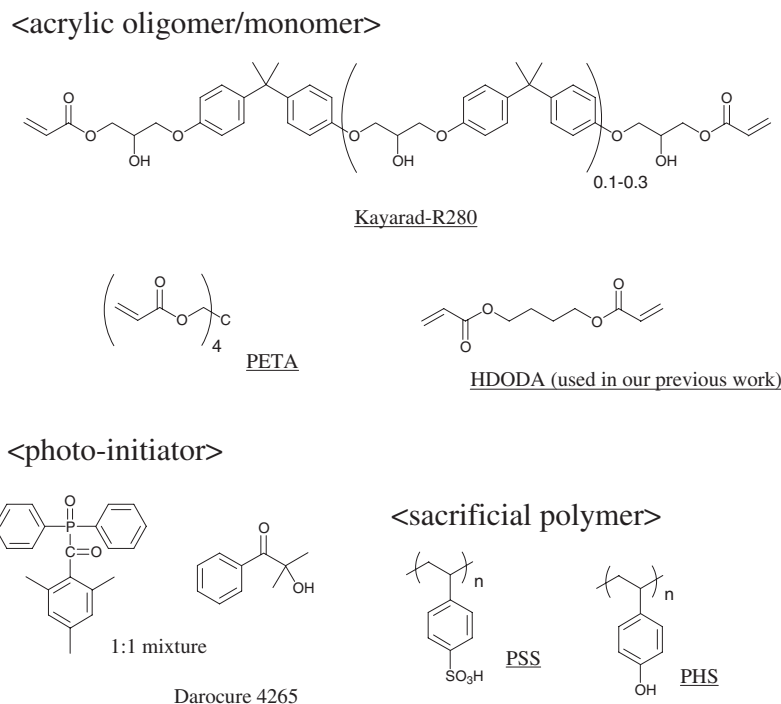
Kayarad-R280

PETA

HDODA (used in our previous work)

<photo-initiator>

<sacrificial polymer>

1:1 mixture

Darocure 4265

PSS

PHS

Figure 1. Molecular structures of acrylic precursors, photo-initiator, and sacrificial polymers.
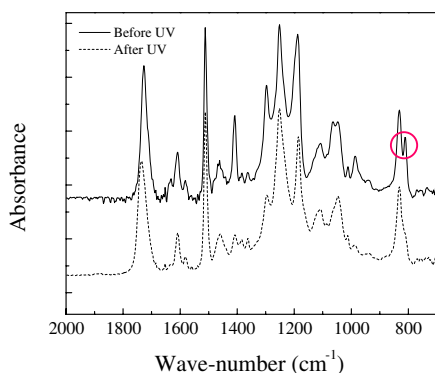

Figure 2. ATR-FT-IR spectra of R280 film before (solid line) and after (dotted line) irradiation of UV light.

Fabrication of acrylate nanomembrane was also conducted with tetrafunctional PETA monomer. The corresponding nanomembrane was fabricated successfully by a procedure similar to that for R280 nanomembrane. Unlike R280 nanomembrane, PETA nanomembrane possessed extended morphology even in ethanol. Radical polymerization of acrylate monomers is usually accompanied with volume shrinkage, often leading to a distorted shape of the polymeric product. The extended flat shape observed for the PETA nanomembrane suggests that the shrinkage, if any, does not affect the uniform morphology of nanomembrane.

Both of these acrylate nanomembranes are free-standing in air. The digital camera view of a free-standing R280 nanomembrane with 30-nm thickness is given in Figure 4. A nanomembrane on the water surface was scooped with a wire frame of 1-cm diameter. The picture is composed of the half membrane areas with lighting (left part) and without lighting (right part). Reflection of light by the nanomembrane is clearly seen on the left side. PETA nanomembrane was also stable in air with the same size.
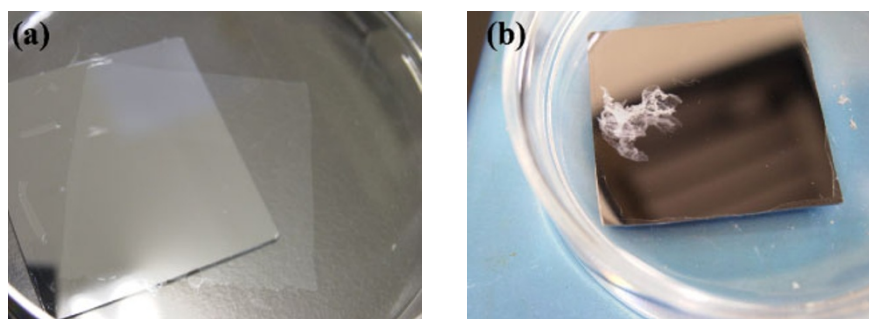

Figure 3. Digital camera view of R280 nanomembranes; (a) expanded on water surface by surface tension, and (b) crumpled morphology in ethanol.
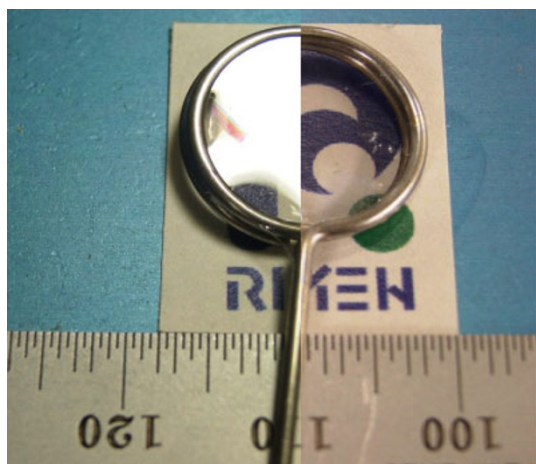
Figure 4. Combined photograph of a free-standing R280 nanomembrane on a wire frame; with lighting (left) and without lighting (right).

Table I. Mechanical properties of acrylate nanomembranes

material	Thickness [nm][a]	Ultimate Tensile Strength [Pa][b]	Ultimate Elongation [%][b]	Young's Modulus [Pa][c]
R280	22 ± 2	1.6×10^8	0.25	8.0×10^8
PETA	28 ± 3	7.8×10^7	1.8	3.9×10^9
Epoxy[d]	24 ± 2	2.2×10^7	0.2	3.5×10^8

[a]Determined by SEM observation. [b]Determined by the bulging test. [c]Determined by the buckling measurement. [d]From the separate study (ref. 11), 1:1 mixture (by weight) of poly[(o-cresyl glycidyl ether)-co-formaldehyde] and poly(ethyleneimine).

Microscopic morphologies were examined by scanning electron microscopy (Hitachi S5200 field emission scanning electron microscope) after transfer of the nanomembrane onto anodized aluminum oxide (AAO) substrate. Figure 5 shows cross-sectional and top views of PETA nanomembrane, as example. This nanomembrane shows a uniform thickness of 28 ± 3 nm, and no signs of cracks and other defects were observed on the membrane surface. The minute cracks observed in Figure 5(b) on the nanomembrane surface come from Pt cluster which were sputtered on the surface for SEM measurement. R280 nanomembrane showed a similar microscopic morphology without any cracks and defects.

Mechanical properties of the acrylate nanomembranes were evaluated by using the following two methodologies that have been used for other ultrathin films.[11] The ultimate tensile stress (σ) and the ultimate elongation (ε) were determined by using the bulging technique.[17] Young's modulus was determined by the "strain-induced elastic buckling instability for mechanical measurements (SIEBIMM)" technique.[18,19] The results are summarized in Table I, together with those of the epoxy nanomembrane as reference. The tensile strength (σ) of R280 and PETA nanomembranes were determined as 160 MPa and 78 MPa, respectively. These values were higher than that of the epoxy nanomembrane. Young's moduli of these acrylate nanomembranes were also higher than that of the epoxy nanomembrane. It is interesting that R280 showed superior mechanical strength. When complete consumption of the acrylate unit is assumed, the cross-linking density of R280 is simply one-forth of that of PETA, because the molecular weight of the whole monomer per number of the acrylate unit is 257 and 74 for R280 and PETA, respectively. Because R280 is a mixture of bi-functional and mono-functional acrylates, its superior mechanical property is not induced by high cross-linking density alone. We should note that HDODA itself did not produce a sufficiently robust nanomembrane. The rigid backbone of bisphenol A may contribute to the improved mechanical strength.

In summary, we demonstrated successful fabrication of nanomembranes from acrylic monomers alone. Together with our previous results, the present data indicate that robust nanomembranes are fabricated from a variety of polymer precursors including organic, inorganic and organic/inorganic components. In the case of organic polymers, thermosetting resins and acrylates are typical examples. These polymers are produced by the addition-condensation process and by the vinyl addition process, respectively. The major polymerization process not yet used for nanomembrane formation is the condensation reaction of esters and amides. Further efforts would expand the range of monomeric precursors to be used for formation of robust nanomembranes, and would facilitate chemical design of nanomembranes for specific uses.
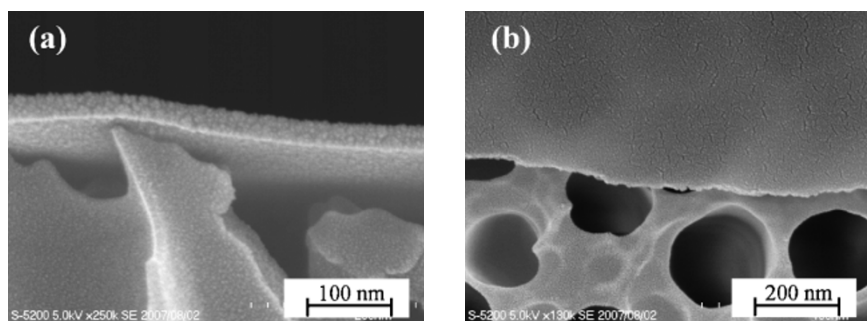
Figure 5. SEM images of the PETA nanomembrane on AAO support; (a) cross-sectional view and (b) top view.

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