

A Multilayered Film of an Ultrathin Siloxane Network

Kanji Sakata and Toyoki Kunitake*†

Molecular Architecture Project, JRDC, Kurume Research Park, Kurume 830, Japan

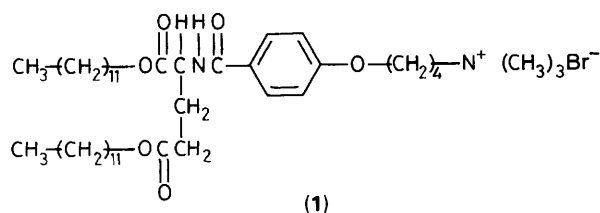
A multilayered film of an ultrathin siloxane network was prepared from $\text{MeSi}(\text{OMe})_3$ by using a multi-bilayer cast film of a double-chain ammonium amphiphile as a molecular template.

The siloxane skeleton has attracted much attention in organic and inorganic material sciences because of its very different

structures. The control of the siloxane skeleton on the molecular scale is a central problem in this field.¹ We report the preparation of siloxane networks with molecular-scale thickness.

Owing to their remarkable self-assembling properties, synthetic bilayer membranes can be transformed into free-

† *Permanent address:* Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan.



standing cast films with regular multilayered structures.^{2,3} The interlayer spaces of a cast film act as ideal molecular templates for formation of the siloxane network. A typical example follows.

The double-chain ammonium amphiphile (1)⁴ (Sogo Pharmaceutical Co., 50 mm) and MeSi(OMe)₃ (150 mm) were dispersed in water by sonication. The clear solution thus obtained was spread on a fluorocarbon polymer sheet and kept at 25 °C, 60% relative humidity for 3 days. The resulting cast film was exposed to gaseous NH₃ in a closed vessel for 10 days in order to complete the hydrolysis of the methoxysilyl group and its subsequent condensation.

X-Ray diffraction (Rigaku Denki Co., RAD R32, Cu-K_α, 50 kV, 200 mA) of the composite cast film showed a pattern similar to that of a cast film of amphiphile (1) alone, where diffraction peaks of more than one tenth order appeared with a long spacing of 40.5 Å. It is clear that the regular multi-bilayer structure is retained in the composite cast film. A differential scanning calorimetry (DSC) thermogram (Seiko Instrument Inc., SSC-5000) of the composite cast film showed an endothermic peak at 40.1 °C (ΔH 47.2 kJ mol⁻¹ of amphiphile). This is similar to the peak observed for the cast film without condensed MeSi(OMe)₃: T_c = 39.3 °C, ΔH 47.7 kJ mol⁻¹ of amphiphile. Therefore, the ordered side-chain packing in the bilayer remains intact after incorporation of the silicone polymer. The siloxane network appears to be uniformly separated by the molecular bilayers of the amphiphile.

Subsequently, the amphiphile component was extracted from the composite film by immersion in CHCl₃. A shiny white, self-supporting film (thickness, 15 μm) resulted. IR spectroscopy indicated that the ester carbonyl peak of the amphiphile at 1740 cm⁻¹ disappeared completely in the resulting film. At the same time, the methoxy peak at 1190 cm⁻¹ disappeared entirely and the δ_{Si-O-Si} bands at 1130–1030 cm⁻¹ predominated, indicating formation of a siloxane network.

Figure 1 shows scanning electron micrographs of the siloxane film; the overall multilayer structure of the cross

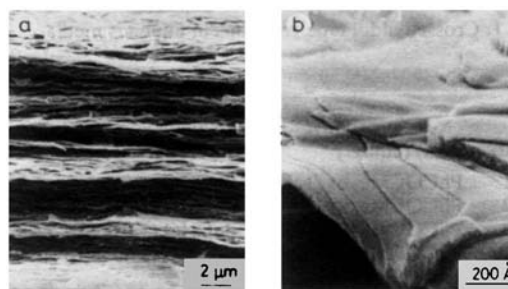


Figure 1. SEM micrographs of silicone polymer films (cross section). The specimens were coated with Pt in an ion sputter coater prior to SEM observation. (a) A whole view (original magnification, $\times 5000$); (b) an expanded view ($\times 150\,000$).

section is shown in Figure 1a. Very thin layers are placed parallel to the film surface. A closer look at the edge by high-resolution SEM (Hitachi S-900; theoretical resolution 8 Å) shows a one-layer thickness of approximately 20 Å (Figure 1b). In contrast, a polysiloxane film which was prepared from MeSi(OMe)₃ without amphiphile (1) gave a featureless, smooth cross section.

In conclusion, we have prepared an ultra-thin siloxane network using a multi-bilayer cast film as a molecular template. This network is by far the thinnest of all the siloxane polymers ever produced, and may be called a 2D network. The present methodology is readily applicable to the formation of two-dimensionally cross-linked organic polymers⁵ and siloxane networks of varied morphologies.⁶ It will be possible to develop a new concept of molecular ceramics, *i.e.*, ceramics with microstructures that are controlled on the molecular scale, from these observations.

We thank Hitachi Instrument Engineering Co. for the SEM results.

Received, 19th December 1989; Com. 9/05401D

References

- 1 *E.g.*, F. J. Feher, D. A. Newman, and J. F. Walzer, *J. Am. Chem. Soc.*, 1989, **111**, 1741.
- 2 N. Nakashima, R. Ando, and T. Kunitake, *Chem. Lett.*, 1983, 1577.
- 3 N. Shimomura, T. Kunitake, T. Kajiyama, A. Harada, K. Okuyama, and M. Takayanagi, *Thin Solid Films*, 1984, **121**, L89.
- 4 T. Kunitake, N. Nakashima, M. Shimomura, Y. Okahata, K. Kano, and T. Ogawa, *J. Am. Chem. Soc.*, 1980, **102**, 6642.
- 5 S. Asakuma and T. Kunitake, *Chem. Lett.*, 1989, 2059.
- 6 K. Sakata and T. Kunitake, *Chem. Lett.*, 1989, 2159.