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Siloxane Polymer Films with Varied Microstructures

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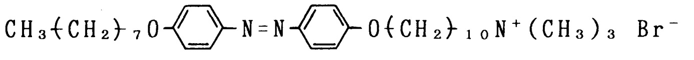
Cross-linked siloxane polymers were prepared by alkali treatment of composite films of $CH_3Si(OCH_3)_3$ and bilayer-forming amphiphiles. Dissolution of the bilayer matrices gave flexible, free-standing films with varied fine structures.

Formation of siloxane gels with controlled microstructures has attracted much attention due to their potentials in many practical applications. Forty years ago, Dickey prepared silica gels by using Methyl Orange as molecular template.[1, 2] The sol-gel method was very recently applied to mixtures of metal complexes and alkoxysilanes to obtain metal oxide catalysts with micropores.[3] Bilayer aggregates are highly stable in water and provide a rich variety of well-defined morphologies.[4] We thus thought that bilayer-based aggregates were suitable as molecular templates in the sol-gel method.



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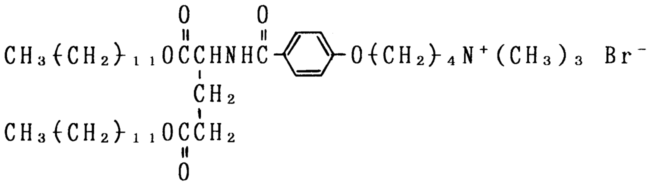

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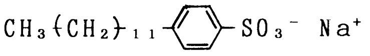

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Bilayer-forming ammonium amphiphiles **1**[5] and **2**[6] (Sogo Pharmaceutical Co.) were used for this purpose, in comparison with micelle-forming surfactant **3** (Tokyo Kasei Kogyo Co., 65% in water). Amphiphiles (0.05 mol dm^{-3}) and $CH_3Si(OCH_3)_3$ (Toshiba Silicone Co., 2.5 mol dm^{-3}) were dispersed in water by sonication (Ultrasonic Disruptor UD-201) for 3 min. Clear solutions were obtained probably due to partial hydrolysis of the alkyloxysilyl unit during sonication, and cast on petri dishes or on fluorocarbon polymer sheets for 3 days (25 ℃, relative humidity 60%). In order to accomplish complete hydrolysis

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and condensation, the cloudy cast films were exposed to gaseous ammonia in a closed glass vessel for 10 days at room temperature. The amphiphilic components were then extracted from the cast films by $CHCl_3$ or CH_3OH. Their complete removal was confirmed by the lack of IR peaks at 1500 cm^{-1} ($\nu_{N=N}$) for $\underset{\sim}{1}$, at 1740 cm^{-1} ($\nu_{C=O}$) for $\underset{\sim}{2}$, and at 1160 cm^{-1} (ν_{SO_3}) for $\underset{\sim}{3}$. The residual films gave IR peaks characteristics of the siloxane polymer. The polymer obtained in the absence of the amphiphilic component (bulk-polymerized siloxane) showed the identical IR spectrum.

A white film of the siloxane polymer (thickness, ca. 100 µm) was obtained by using amphiphile $\underset{\sim}{1}$. This amphiphile has been found to form cast films of the highly regular multi-bilayer structure.[7] In fact, a SEM photograph of the extracted cast film (Fig. 1A) clearly shows the presence of a multi-layered structure that is parallel to the film surface. The thickness of the individual layer is ca. 0.1 µm. This layer thickness can be reduced considerably by using smaller ratios of the siloxane component.[8]

A white siloxane film was similarly obtained when amphiphile $\underset{\sim}{2}$ was used as template. The microstructure of this film is represented by rods and complementary pores, as shown by Fig. 1B. Their diameters are 0.3-0.5 µm. It was shown previously that amphiphile $\underset{\sim}{2}$ produced helical superstructures (twisted tapes) upon appropriate aging of its aqueous dispersion.[9] The SEM micrograph appears to be a high-fidelity replica of this morphology. The rod-like siloxane polymers are formed by polymerization of $CH_3Si(OCH_3)_3$ which is incorporated inside the helical tape of amphiphile $\underset{\sim}{2}$. The helically wound rod and the complementary tubular pore remain after extraction of the amphiphile. Multi-layered microstructures were also obtainable from this amphiphile, when the molar ratio of $CH_3Si(OCH_3)_3$ / amphiphile was smaller. Preparation of a ultrathin siloxane film from this mixture will be reported elsewhere.[10]

A SEM micrograph of a semitransparent siloxane film obtained from $CH_3Si(OCH_3)_3$ and amphiphile $\underset{\sim}{3}$ indicates the presence of spherical pores distributed evenly in the siloxane polymer matrix (Fig. 1C). The pore diameter is 1 - 3 µm. Particle-like and fiber-like microstructures were obtainable from this system by changing the molar ratio of the two components. These varieties in the microstructure again reflect changes in the aggregate morphology, although they are coarser than those derived from bilayer aggregates.

In conclusion, we established a novel methodology for preparing siloxane polymer films that possess well-defined microstructures. A bulk-polymerized film of $CH_3Si(OCH_3)_3$ without amphiphile components displays a uniform cross-section that does not possess any microstructure (Fig. 1D). The microstructures shown in Figs. 1A - 1C are replicas of aggregate morphologies. The bilayer dispersion is characterized by a rich morphological variety such as vesicle, lamella, tube, rod, disk, helix, etc. The aggregate morphology is further affected by chemical structures of siloxane monomers and amphiphiles, molar ratios of the two components, and the preparative conditions (sonication time, casting temperature, aging conditions, etc.). Because of morphological

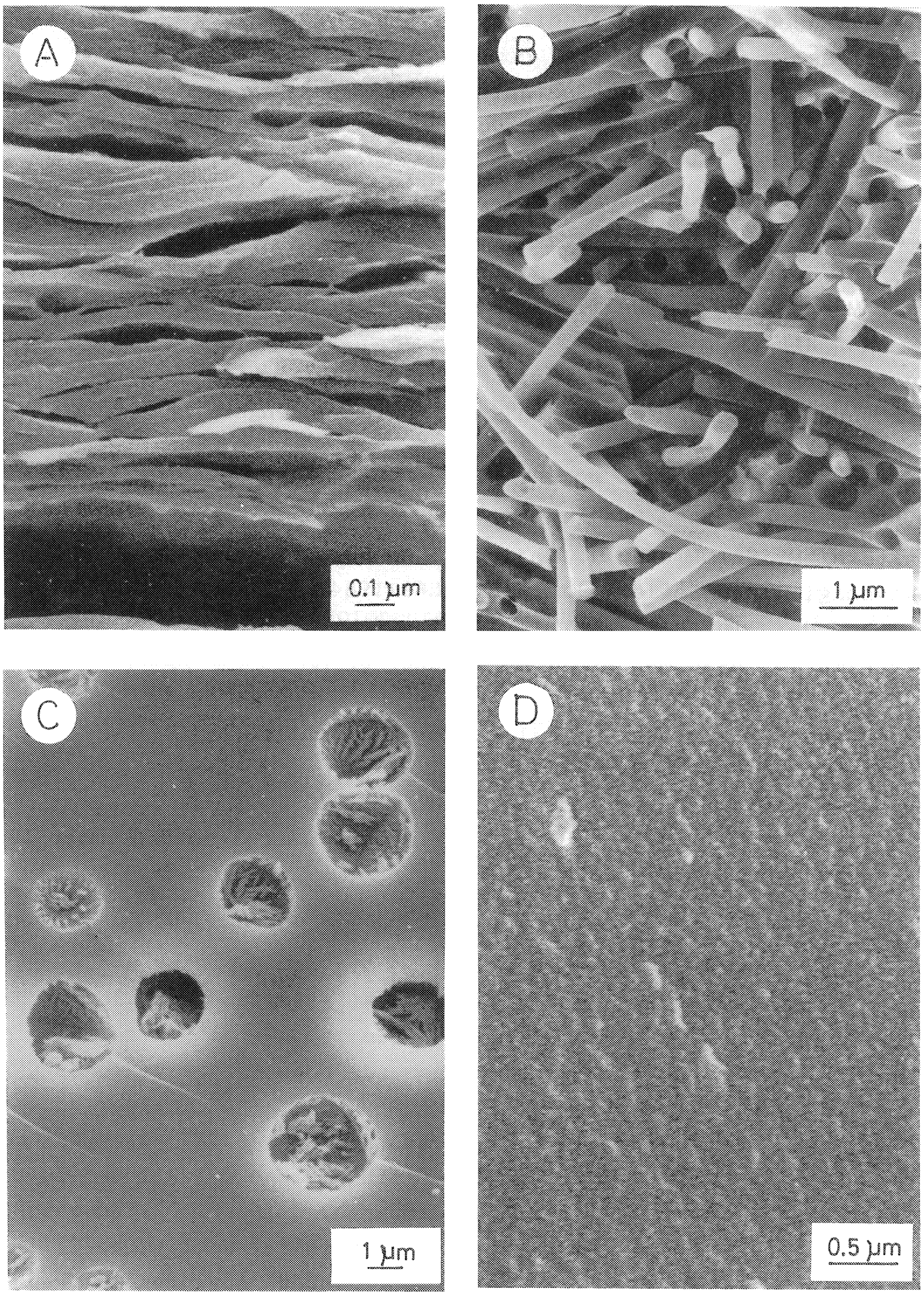

Fig. 1. SEM photographs of siloxane polymer films (cross section). Siloxane films were cleaved and coated with Pt-Pd in an ion sputter coater prior to the SEM observation (Akashi, DS-130).

variety and enhanced aggregate stability, synthetic bilayers can produce siloxane replicas in finer details, compared with those derived from conventional micelle-forming surfactants.

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