Polymerized gels and 'reverse aerogels' from methyl methacrylate or styrene and tetraoctadecylammonium bromide as gelator

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The low molecular mass gelator, tetraoctadecylammonium bromide, can be removed from polymerized gels of methyl methacrylate or styrene to leave mesoscopic channels with submicrometre diameters.

Recently, we observed that very small concentrations of several tetraalkylammonium salts, some containing a cholesteryl or aromatic unit[1] and others having four *n*-alkyl chains,[2] gel a variety of organic liquids in a thermo-reversible fashion. Subsequently, we discovered that methyl methacrylate (MMA) and styrene (STY) are among them. Here, we report (*i*) the polymerization of gels of MMA and STY in which the gelator is tetraoctadecylammonium bromide (TOAB),[2] (*ii*) a comparison of the gel properties before and after polymerization, and (*iii*) the successful removal of the gelator molecules, leaving the polymerized matrix with vacant submicron cross-sectional channels.

Typically, low molecular mass gelators organize into long, thin strands that assemble into colloids.[3] When the colloids fill the sample volume and are in contact with each other, the liquid component is immobilized on a macroscopic scale by surface tension, but remains isotropic on a microscopic (molecular) scale.[4] Gels can be converted to aerogels by evaporation of the liquid when the gelator strands have sufficient mechanical strength not to collapse under the force of gravity. This case is usually limited to high molecular mass (*i.e.* polymeric), inorganic gelators;[5] collapsed aerogels (*i.e.* xerogels) are usually obtained from gels with low molecular mass gelators.[6] The sizes of the channels created in an aerogel are dependent upon how extensive is the gelator network, but they are not uniform.[7]

If, instead, the gelator strands were removed and the liquid component were frozen in place, reverse aerogels, in which the cross-sections of channels are more uniform and less dependent upon the gelator concentration, would result. We report the formation of reverse organoaerogels from TOAB gels after polymerization of the liquid component.

The recipe for gels with monomeric liquid components is MMA or STY containing 8 vol% divinylbenzene (DVB, a cross-linking agent), 7 vol% ethylvinylbenzene, 1 mass% benzoin ethyl ether (the photoinitiator), and 0.1–2.0 mass% of TOAB.† The mixtures were flame-sealed under vacuum in 0.4 × 4.0 mm (id) × *ca.* 2 cm Kimax flattened-capillary tubes after being degassed by two freeze–pump–thaw cycles. The capillaries were heated in a hot water-bath (near 90 °C) until the solids dissolved. After agitating the solutions to homogenize the components, they were cooled either by quenching in an ice/water–bath or by placing them in the air; the cooling protocol was important in determining the sizes of the strands and their colloids (*vide infra*). Below *ca.* 1 mass% of TOAB, the samples were viscous, partially gelled materials that are better described as sols (or fracture gels). Polymerization was effected by irradiation of the capillaries in a water-bath (to maintain a near ambient temperature) at 320–360 nm for 5 h (MMA) or 14 h (STY). The stiff, solid samples were removed by breaking the capillary tubes with a metal object.

The unpolymerized and polymerized gels in the capillaries were examined by optical microscopy (× 50; *ca.* × 83 including photo to negative size ratio) between crossed polars using a full-wave plate for enhanced contrast. At 2 mass% TOAB, it is possible to detect colloids (*ca.* 500 µm in diameter) of the slower cooled MMA gels [Fig. 1(*a*)]. In general, their appearance was not affected markedly by polymerization [Figs. 1(*a*) and (*b*)]. Although the strands are less extensive in samples with lower concentrations of TOAB, there is no apparent concentration dependence on their cross-sectional dimensions when the same cooling procedure was followed [Fig. 2(*a*) and (*b*)]. The strand cross-sections are smaller and the strand lengths are shorter when samples are cooled more rapidly [Figs. 1(*a*) and 3].

Since the long axes of strands of other gels have been oriented by allowing gelation to occur in strong magnetic fields,[8,9] we reheated (unpolymerized) STY and MMA gels (with 0.5 or 1.0 mass% TOAB) to 87 °C, far above the gel–liquid phase transition temperature, in a 6.3 T magnetic field and allowed them to cool slowly to room temperature. By optical microscopy, the strand networks seemed more homogeneously dispersed (probably due to more careful and slower cooling), but there was no indication of alignment.
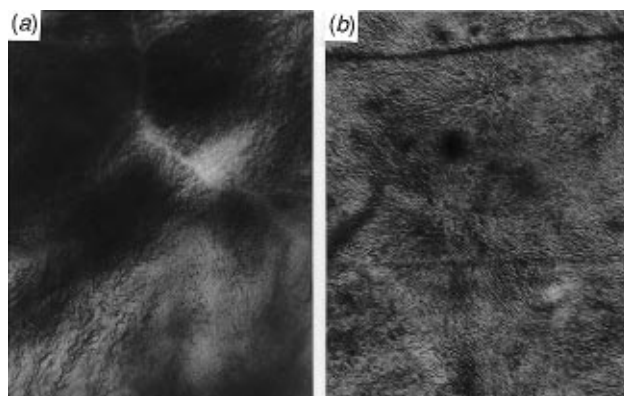

Fig. 1 Optical micrographs of a 2 mass% TOAB/MMA gel prepared by the slower cooling method before (*a*) and after (*b;*) polymerization
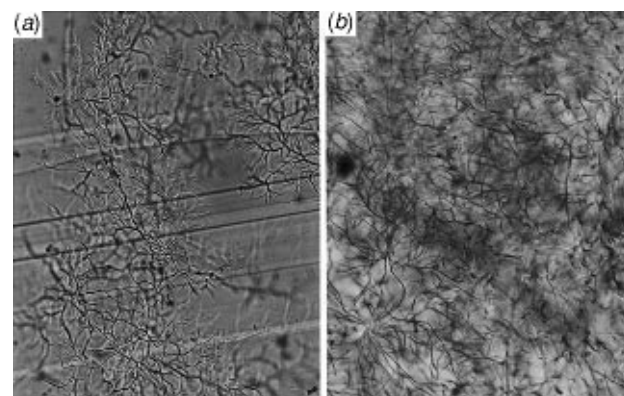

Fig. 2 Optical micrographs of 0.1 (*a*) and 2.0 mass% (*b*) TOAB/STY gels prepared by the slower cooling method and polymerized

Polymerized MMA and STY gels with 2 mass% TOAB were heated and cooled between crossed polars while being observed under an optical microscope. Since the glass transition temperatures (T_g) of non-cross-linked MMA and STY are $\geqslant 100$ °C,[10] and T_g of a polymerized cross-linked STY gel was found to be *ca.* 130 °C by DSC, the TOAB, mp 97–102 °C, should melt before its polymer matrix becomes malleable. The birefringence associated with the TOAB strands of the polymerized MMA gel was lost between 89 and 94 °C. Cooling from 100 °C resulted in reappearance of birefringence in most of the strands near 90 °C. During the second heating, the birefringence was lost at a slightly higher temperature range and only about half reappeared upon cooling. Very similar results were obtained with a polymerized STY gel. In both cases, we suspect that gelator molecules from some strands merge, leading to larger but fewer domains. Based upon the proximity of the melting points, we conjecture that TOAB molecules are packed in similar fashions in bulk crystalline and strand phases. This is not always the case with low molecular mass gelators.[11]

When refluxed in *tert*-butyl alcohol (bp 83 °C), a polymerized STY gel lost a large fraction, but not all, of the TOAB molecules in its strands. Residual TOAB strands were evident by optical microscopy, even when no more could be leached from the gel; refluxing with fresh aliquots of alcohol was continued until no precipitate was detected upon addition of $AgNO_3$. Thus, some of the strands are in environments that have no contact with the surface of the polymerized sample through other strands.

All of the TOAB was removed rapidly and at room temperature from 1 or 2 μm thick slabs of the polymer (cut from the bulk with a diamond knife) placed in *tert*-butyl alcoh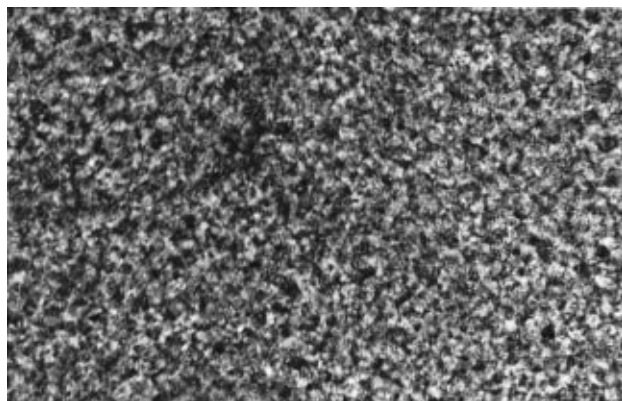ol. Cross-sectional diameters of the strands (before TOAB removal) appeared to be the same as the channels (after TOAB removal). However, when the slabs were refluxed in *tert*-butyl alcohol, the channels were slightly wider than the strands. Widening of the channels may be due to coincidental loss of some unpolymerized liquid-component molecules with the TOAB. The average strand sizes in MMA and STY polymerized gels as a function of TOAB concentration and cooling protocol (during initial gel formation) are shown in Table 1. The data, from optical microscopic observations ($\times$ 645) of the narrowest and widest strands in 1 μm slabs, demonstrate that the cross-sections are not uniform, but can be made to diameters that are within a small range. It is unclear as yet whether the strands are twined multiples of a smaller unit or are the result of stochastic nucleation processes. In other studies, we[4] and others[3] have found that the former is the norm. It is also possible that the strands were distorted somewhat during the sectioning into slabs or may have suffered much more severe changes due to friction of the knife (*e.g.* local heating to above the polymer T_g or tearing of the strand borders): even at 2 mass% TOAB, strands were not visible by optical microscopy in the faster cooled (polymerized) MMA gels before cutting; however, strands (or strand-like objects) were easily detected in the slabs. Since the MMA was gelled, strands must have been present, but may have been too small to be seen at the highest magnification of our optical microscope. Regardless, the data indicate that fast-cooling leads to somewhat narrower strands.

The slabs with vacated channels have potential applications as membranes, and the bulk polymers, even with partial removal of the gelator molecules, may be useful as selective adsorbers and complexing agents for chromatography[12] and selective guest reactions.[13] Future efforts will be directed to make reverse aerogels whose channels are narrower and have greater cross-sectional uniformity (*i.e.* organic zeolites).

Fig. 3 Optical micrograph of a 2 mass% TOAB/MMA gel prepared by the faster cooling method before polymerization

Table 1 Approximate range of strand cross-sections in 1 μm thick slabs of polymerized gels as a function of TOAB concentration and cooling protocol (see text) of the unpolymerized samples from the isotropic to the gel phase

TOAB (mass%)	Monomer	Cooling protocol	Cross-sectional range/μm
2.0	STY	Faster	0.24–0.5
2.0	STY	Slower	0.5–1.5
0.5	STY	Faster	0.5–1.0
0.5	STY	Slower	0.5–1.0
0.1	STY	Faster	0.5–0.7
0.1	STY	Slower	0.5–1.0
2.0	MMA	Faster	0.3–0.5
2.0	MMA	Slower	0.4–1.0
0.5	MMA	Faster	0.24
0.5	MMA	Slower	0.24–1.2
0.1	MMA	Faster	—[a]
0.1	MMA	Slower	0.24–1.4

[a] No objects clearly identifiable as strands were observed.

Footnote

† MMA, STY, and DVB (a mixture of *meta* and *para* isomers containing *ca.* 45% ethylvinylbenzene) from Aldrich were distilled under vacuum prior to use. Benzoin ethyl ether (99%) and TOAB (98%) from Aldrich were used as received.

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