lations. We have modeled the data appearing in Fig. 3A on the basis of a collection of noninteracting long, stiff cylinders, using just two levels of contrast. The associated core radii and polydispersities are relatively insensitive to these assumptions.
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Ordered Mesoporous Polymers of Tunable Pore Size from Colloidal Silica Templates

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Ordered mesoporous polymers have been prepared by replication of colloidal crystals made from silica spheres 35 nanometers in diameter. The pores in the colloidal crystals were filled with divinylbenzene (DVB), ethyleneglycol dimethacrylate (EDMA), or a mixture of the two. Polymerization and subsequent dissolution of the silica template leaves a polycrystalline network of interconnected pores. When mixtures of DVB and EDMA are used, the pore size of the polymer replicas can be varied continuously between 35 and 15 nanometers because the polymer shrinks when the silica template is removed.

Template synthesis is a commonly used tool in the preparation of porous materials. Zeolites and related molecular sieves are commonly crystallized around small molecule templates, and mesoporous molecular sieves are templated by supramolecular aggregates of surfactant molecules (*1*) or by block copolymers (*2*, *3*). However, the size of the pores is limited to the dimensions of the organic templates (3 to 100 Å) and to materials such as oxides, chalcogenides, and phosphates that can be processed hydrothermally or solvothermally. Inorganic materials with much larger pores, in the size range of hundreds of nanometers to micrometers, have been synthesized with the use of vesicle arrays (*4*) or polymer spheres (*5*, *6*) as templates. Recently, colloidal crystals of silica spheres 150 to 300 nm in diameter have been used to make three-dimensional (3D) porous replicas composed of graphite, amorphous carbon, and diamond (*7*). Replication and embossing have also been used to make a wide variety of polymer structures with micrometer- and submicrometer-sized pores, most generally as thin films and freestanding membranes (*8*). In the case of embossed polymer thin films, the minimum feature size that can be faithfully replicated appears to be on the order of 10 nm (*9*).

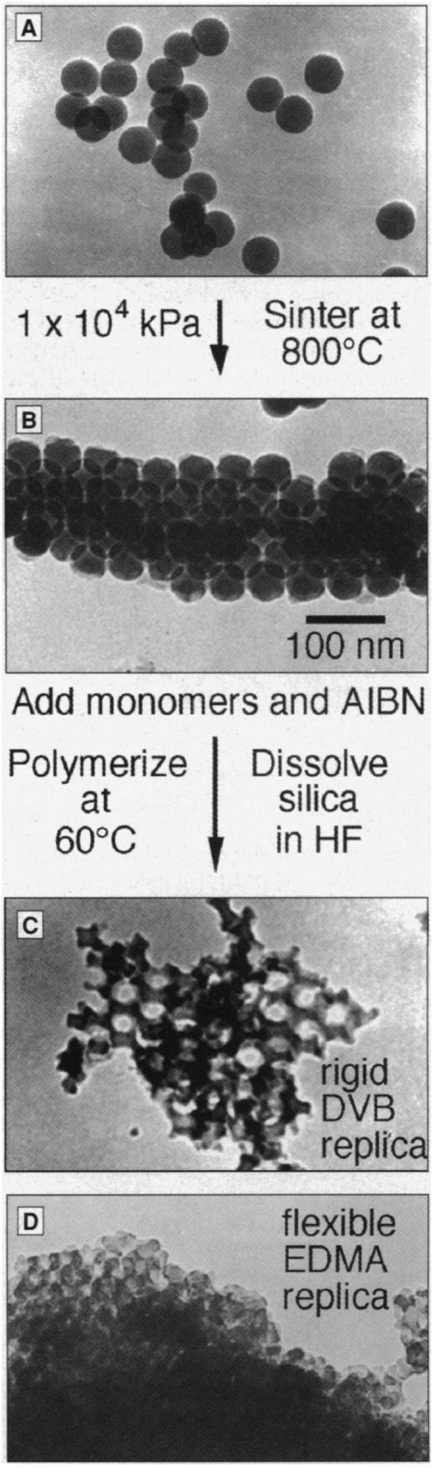

Fig. 1. TEM images of porous polymer preparation by replication. (**A**) Spherical silica particles as prepared. (**B**) Colloidal crystal of silica particles after pressing and heating. (**C**) DVB polymer replica. (**D**) EDMA polymer replica. The pore size in the flexible polymer is much smaller than the template diameter.

The mesoscopic regime of 10 to 100 nm represents a largely unfilled gap for three-dimensionally ordered porous materials. Block copolymer templating has been used to access the lower end of this range with porous silicates. Arrays of hexagonal channels up to 30 nm in diameter and cubic structures with pore diameters in the 5- to 6-nm range have recently been prepared (*3*). Three-dimensional materials with pores in the 10- to 100-nm size range are of immediate interest for certain fundamental problems, such as the study of diffusion and phase equilibria in restricted geometries (*10*). They also have potential applications in the preparation of mesoscopic devices, such as ordered arrays of metal or semiconductor quantum particles (*11*) and in various sorption and separation processes involving polymers and biological macromolecules. Replica polymers, metals, and semiconductors have been prepared from one- and two-dimensionally porous template materials, including zeolites, mesoporous silicates, porous polymer membranes, anodic alumina, and clays (*12*–*20*). Imprint polymers that retain the shape and size of macromolecular templates have also been reported (*21*). These techniques usually produce individual particles of controllable shape and size, rather than 3D polymer networks with characteristic pore sizes and repeat distances between 10 and 50 nm.

To create the inorganic template, monodisperse silica particles 35 nm in diameter were pressed into pellets at a pressure of 1 × 10^4 kPa (*22*). The particles were sintered slightly at their points of contact by heating the pellets to 800°C, in order to provide pore connectivity in the polymer replica. Transmission electron mi-

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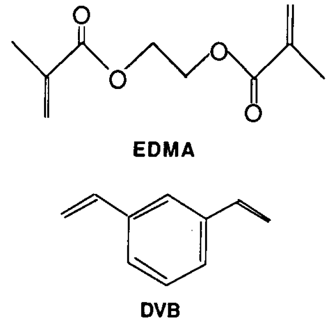
croscope (TEM) images revealed that the particles formed close-packed polycrystalline aggregates (Fig. 1). Because the volume fraction of space filled by close-packed spheres in such an arrangement is approximately 75%, it was expected that the polymer replicas would consist of pores 35 nm in diameter, separated by 20-nm-thick polymer walls, with a volume-filling fraction up to about 25%.

We prepared porous polymers from silica colloids, using divinylbenzene (DVB) to make a rigid polymer replica, ethyleneglycol dimethacrylate (EDMA) to make a flexible shrinkable replica, or mixtures of DVB and EDMA to vary the degree of shrinkage. A solution of the monomers (Scheme 1) and a free radical initiator, azobisisobutyronitrile (AIBN), which filled the void spaces between silica nanoparticles, was added to silica pellets. Dissolved oxygen was removed by several freeze-pump-thaw cycles, and the polymers were formed by heating to 60°C for 12 hours. The silica was subsequently dissolved in 48% aqueous hydrofluoric acid, and the resulting porous polymer pellets were washed with water and dried in air. Elemental analysis showed that there was <3% remaining silica in the replicas and that the C:H ratios were consistent with the homopolymer and DVB-EDMA copolymer compositions.



Scheme 1

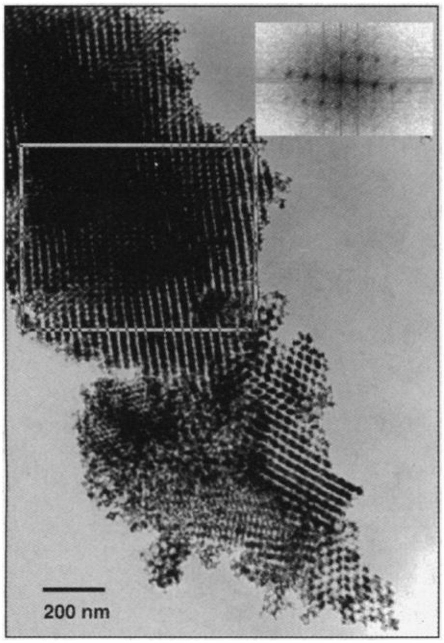


Fig. 2. TEM image of a 0.50 mole fraction DVB-EDMA copolymer replica, showing long-range ordering and several grain boundaries, as well as some regions of disorder. A Fourier transform of the image in the highlighted area is shown in the inset.

As synthesized, the polymer replicas retain the form of the silica pellets from which they were made. The polymers could be crushed or microtomed to make small particles for TEM imaging. Figure 2 shows a low-resolution TEM image of a DVB-EDMA copolymer replica along with a Fourier transform of the area outlined in the real space image. Regions of long-range order, separated by grain boundaries, are apparent in the image along with some regions of disorder. Higher resolution images (Fig. 1) show that the pores are close-packed, roughly spherical, and interconnected. These images show that the degree of order of the polycrystalline template is faithfully reproduced in the replica. Figure 3 shows TEM images of DVB-EDMA copolymers. All of the replicas have the same general structure. However, as the mole fraction of EDMA increases, the pore size becomes smaller. There is a linear relation (Fig. 4A) between the EDMA mole frac-

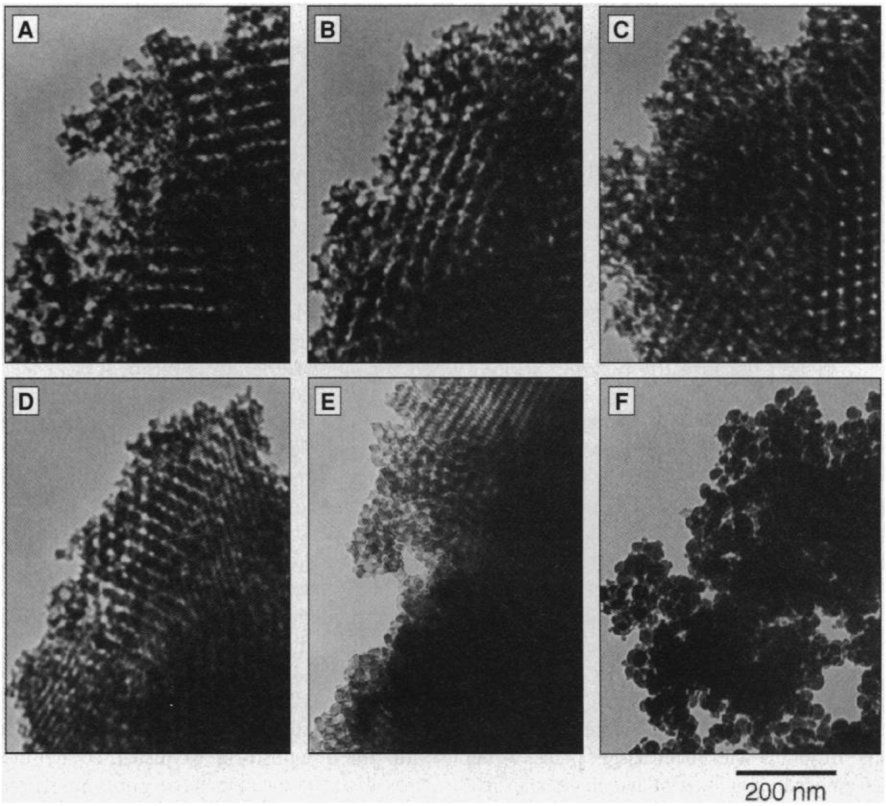


Fig. 3. Micrographs of the series of DVB-EDMA copolymer replicas. EDMA mole fractions are as follows: **(A)** 0.00, **(B)** 0.25, **(C)** 0.50, **(D)** 0.75, and **(E)** 1.00. **(F)** Silica replica of the porous polymer shown in (C).

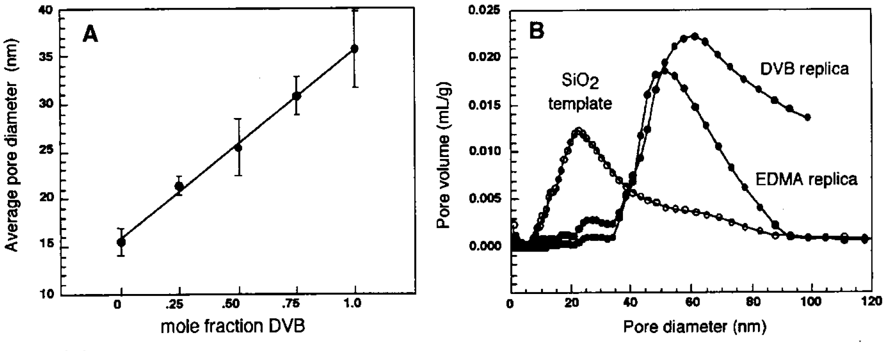


Fig. 4. **(A)** Pore size determined by TEM versus EDMA mole fraction for DVB-EDMA polymer replicas. **(B)** Pore volume plots of a sintered colloidal silica template and replica polymers, from nitrogen adsorption isotherms.

tion and the pore size, which allows one to prepare any desired pore size within the range of 15 to 35 nm.

Brunauer-Emmett-Teller surface areas, calculated from nitrogen adsorption isotherms, showed that the surface area of the silica templates was 80 m^2/g, which decreased to 50 m^2/g after the pellets were sintered. The DVB and EDMA polymer replicas had surface areas of 70 and 40 m^2/g, respectively. The near coincidence in the surface areas of the template and of the porous polymers is consistent with the faithful replication of one surface from the other. The lower surface area of the EDMA replica arises from its shrinkage. Pore volume plots (Fig. 4B) show that the replicas have larger pores than the colloidal silica template, as is expected from the fact that the fraction of space filled in the former is about 75% (*23*).

The replication process was taken one step further by using the porous polymers as templates themselves in which to grow silica particles. Figure 3F shows a TEM image of silica particles 15 nm in diameter that were obtained from the 0.50 mole fraction EDMA replica. The polymer pellet was filled with a mixture of tetraethyl orthosilicate and aqueous ammonia. After the hydrolysis reaction was complete, the pellet was calcined in air at 450°C to remove the polymer. The spherical shape and long range order of the pores were not retained in this second generation replica. Nevertheless, it was possible to produce smaller silica particles from large ones through the replication/shrinkage cycle. A control experiment carried out without the porous polymer shows that much larger (200 to 1000 nm) polydisperse silica particles are produced in the absence of a template.

The colloidal silica templates can be prepared inexpensively on a scale of hundreds of grams, so this is a viable route to the production of bulk mesoporous materials. Additionally, silica template particles with diameters up to 70 nm can be made by the same method (*22*), and thus we anticipate that the replication method could cover an even larger range of pore sizes. The polymerization reaction can incorporate a wide variety of vinyl monomers (for example, we have prepared porous DVB– and EDMA–methacrylic acid copolymers in this way), and so the possiblity exists that specific chemical functionality can be imparted to the pores in these materials.

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22. Silica colloids were made by a slight modification of the technique described by K. Osseo-Asare and F. J. Arriagada [*Colloids Surf.* **50**, 321 (1990)]. A microemulsion was prepared by rapidly stirring 150 ml of cyclohexane, 6 ml of *n*-hexanol, 19 ml of Triton N-101, 7 ml of water, and 1.7 ml of 28% aqueous ammonia. To this was added 10 ml of tetraethyl orthosilicate, and the mixture was stirred at ambient temperature for 2 days. Most of the solvent was removed by rotary evaporation, and 100 ml of ethanol was added. The mixture was stirred for 1 hour, then centrifuged. The product solid was resuspended in ethanol and centrifuged three times, then dried at 80°C. TEM images showed that the particle diameter was 35 ± 2 nm. Tablular pellets (0.7 cm in diameter; thickness, 0.3 cm) were made from the dry powder by means of a pellet press.
23. The pore size plots in Fig. 4B were calculated from adsorption isotherms with a model that is optimized for much smaller slit-shaped pores (*24*). The maxima are systematically shifted to pore diameters larger than are found by TEM (Figs. 1 through 3).
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Dislocations Faster than the Speed of Sound

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It is thought that dislocations cannot surpass the sound barrier at the shear wave velocity because the energy spent in radiation has a singularity there. Atomistic simulations show that dislocations can move faster than the speed of sound if they are created as supersonic dislocations at a strong stress concentration and are subjected to high shear stresses. This behavior is important for the understanding of low-temperature deformation processes such as mechanical twinning and may be relevant for the dynamics of tectonic faults. The motion of the dislocations at a speed of $\sqrt{2}$ times the shear wave velocity can be understood from a linear elastic analysis, but many of the peculiarities of the supersonic dislocations are dominated by nonlinear effects that require a realistic atomistic description.

The irreversible plastic deformation of crystalline materials is mainly carried by the motion of dislocations, which are line defects of the crystal lattice. The velocity of these dislocations is limited by the lattice friction and by drag effects from the interaction with lattice vibrations and mobile electrons (*1*). At low temperatures and high stresses, dislocation velocities can reach sizeable fractions of the transverse acoustic wave velocity c_T. Conventional wisdom, based on elasticity theory, is that dislocations cannot reach c_T because the energy required to drive a dislocation becomes infinite at this speed (*1*).

However, Eshelby noted that a singular radiation-free state exists for the motion of gliding edge dislocations at $\sqrt{2}c_T$ in an isotropic solid (*2*). Although this state is regarded as a mathematical curiosity rather than a physically relevant state of motion, it could in principle be accessible to dislocation motion if the dislocations could acquire this velocity. At all other velocities above c_T, elasticity theory shows that dislocations have negative energy release rates because they emit radiation (*1*, *3*). Steady mo-

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