predictions. The former solvolyzes very cleanly and rapidly to the trans diol **2a**, which is identical spectroscopically and chromatographically with allosamizoline. The latter is remarkably robust to acid solvolysis, forming a mixture of the two trans diols upon prolonged reaction times.

Synthetically, a solution of 5.4 M trifluoroperacetic acid in trifluoroacetic acid (prepared by adding 4 equiv of trifluoroacetic anhydride to 3.3 equiv of 90% aqueous hydrogen peroxide) at 0 °C is added carefully to the cyclopentene **5** at 0 °C (**CAUTION!**) and the mixture evaporated in vacuo and then solvolyzed in 10% aqueous trifluoroacetic acid at 40 °C. Direct hydrogenolysis (10% Pd/C, 40 psig H_2, methanol, room temperature) gives a 67% overall yield of pure (±)-allosamizoline (mp 203–5 °C) and 16% of the epoxide **9** (R = H). Thus, allosamizoline is readily available in 19% overall yield in six stages. The synthesis of all four diol diastereomers not only provides unambiguous establishment of the relative stereochemistry but also provides all of the diastereomers to evaluate structure–activity relationships when incorporated into pseudosaccharides and, more generally, the ability of these cyclopentane derivatives to function as pseudoglucosamine analogues. More generally, the utility of the Pd-catalyzed protocol for vicinal hydroxyamination and the novel exploitation of cyclodextrin as a temporary diastereochemical control element is highlighted.

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Supplementary Material Available: Spectral data for **1ab**, **2ab**, **3ab**, **4ab**, **5**, **6ab**, and **7** and table of NMR comparisons of synthetic diastereomers and allosamizoline (3 pages). Ordering information is given on any current masthead page.

Cross-Linked Polystyrene Incorporating Water Pools

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Past experience with polymer chemistry[1,2] and with microemulsion systems[3] led us recently to combine the fields. As will be described, new polymeric materials were prepared by rigidifying reverse micellar systems formed by adding water and a suitable surfactant to a polymerizable monomer.

Years ago the term "water pool"[4] was coined to depict aqueous microdroplets that form in apolar solvents containing a surfactant, AOT.[5] So effective is AOT that one can readily dissolve 10–20% water in octane to give optically clear solutions. The size of the resulting water pools depends on the $[H_2O]/[AOT]$ ratio, henceforth called R. For example, hydrodynamic radii of 3.6 and 14.5 nm in octane are obtained with R values of 11 and 56, respectively.[6] We now report on (a) the preparation of systems where styrene/divinylbenzene[7] (rather than octane) comprised the apolar continuous phase and (b) the subsequent conversion of these microemulsions into solids by photopolymerization.[8,9]

Table I lists 10 polymers, the first nine of which were produced from water pools of various sizes and concentrations. Scanning

Table I. Surface Areas of Water Pool Modified Polymers

polymer	[AOT], M	$[H_2O]$, M	R ($[H_2O]/[AOT]$)	surf. area,[a] m^2/g
1	0.10	1.39	14	1.4
2	0.20	2.78	14	19.4
3	0.50	6.95	14	1.2
4	0.20	1.83	9.2	26.9
5	0.20	1.11	5.6	18.0
6	0.30	2.78	9.3	24.0
7	0.40	2.78	7.0	11.6
8	0.50	2.78	5.6	2.2
9[b]	0.20	2.78	14	33.6
10	0	0		0.9

[a] BET adsorption analysis. Particle size of the polymer: 150–250 mesh. [b] Polymer made from 100% divinylbenzene.

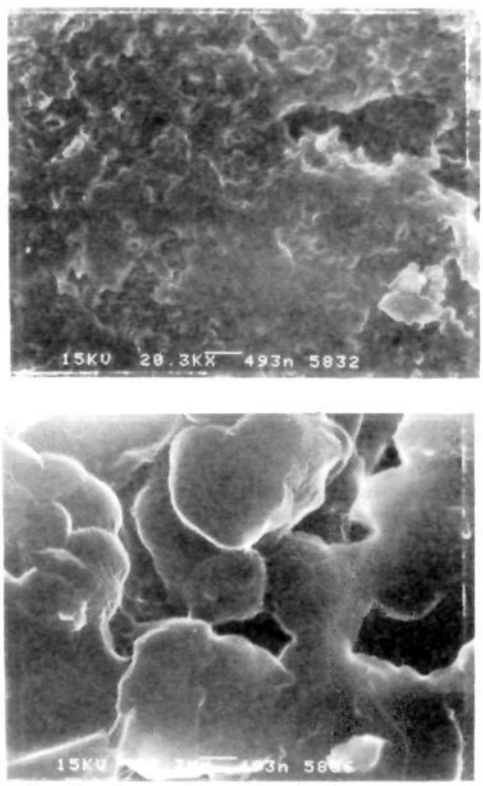

Figure 1. Scanning electron micrographs of polymer **4** (top) and polymer **8** (bottom) taken at 20 300 magnification. Scale bar is 493 nm.

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(7) Aldrich (55% purified by distillation) and abbreviated DVB.
(8) Polymerizations were carried out by irradiating for 10 h in a Rayonet reactor optically clear mixtures of the following: AOT (0.10–0.50 M) and H_2O (1.4–7.0 M, 2.5–12.5 vol %) in styrene/divinylbenzene (6:4 v/v) with 2% benzoyl peroxide initiator. Reacting systems (3 mL in 10-mL test tubes) became progressively more opaque with no apparent phase separation. The resulting porous polymer rods were either used as such or else ground into a powder with the aid of a Technilab Micro-Mill. Polymer particles were (a) sieved into two sizes (150–250 mesh and >400 mesh), (b) washed with methanol and hexane to remove any monomer and AOT, and (c) dried thoroughly under vacuum. IR data and elemental analyses indicated that no detectable AOT remained.
(9) Polymerization of acrylamide in microdroplets stabilized by AOT is described by Candau et al.: Candau, F.; Zekhnini, Z.; Durand, J.-P. *J. Colloid Interface Sci.* **1986**, *114*, 398. The system is totally different from ours in that they polymerized the dispersed phase within the pools whereas we polymerized the continuous phase external to the pools.

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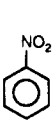
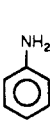
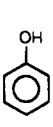
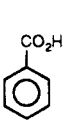
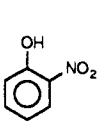
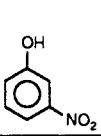
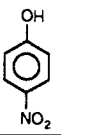
Table II. R_f Values from TLC Experiments[a]

polymer	developing solvent	R_f 						
2	MeOH	0.45	0.65	0.92	0.80	0.50	0.77	0.85
10	MeOH	0.70	0.84	0.92	0.90	0.68	0.93	0.95
silica	MeOH	0.94	0.88	0.80	0.72	0.88	0.81	0.93
2	hexane	0.45	0.30	0.19	0.53	0.45	0.0	0.0

[a] Experimental uncertainty, ±5%. Runs were carried out in triplicate.

electron micrographs (taken at 20 300 magnification) of polymers **4** and **8** are given in Figure 1. Both show porosity totally absent in polymer **10** prepared from styrene/DVB without AOT and water. Polymer **4** possesses a finer microstructure than polymer **8**, an observation consistent with BET adsorption analysis data giving surface areas for the polymer particles (150–250 mesh). Thus, as seen in Table I, polymers **4** and **8** have surface areas of 26.9 and 2.2 m^2/g, respectively. Note that the pores in the polymers are 1 order of magnitude larger than the radii of the original water pools at the monomer stage (<10 nm according to QELS data). Polymer porosity clearly reflects the propensity for pools to assemble as they become encased in polystyrene.

Although the polymerization process is complicated and not understood, three generalizations are possible from the BET data in Table I. (*a*) Polymers **2**, **4**, and **5**, made with pools of constant [AOT] but widely differing sizes (R = 14, 9.2, and 5.6, respectively), all have similar surface areas. Thus, initial pool size is, by itself, not critical to the porosity ultimately created in the polymer. (*b*) Polymers **1**, **2**, and **3**, made by using a constant pool size (R = 14) but with an increasing [AOT] and [H_2O], show a startling result; by far the largest surface area of 19.4 m^2/g was obtained with the intermediate concentration ([AOT] = 0.20 M) of the enclosed phase. A surface area of 1.3 ± 0.1 M^2/g was measured for samples made with lower ([AOT] = 0.10 M) and higher ([AOT] = 0,50 M) levels of dispersed water pools. (*c*) Polymers **6**, **7**, and **8** indicate that, at an increasing [AOT] with constant [H_2O] (and a consequent decrease in R), the area drops 10-fold from 24.0 to 2.2 m^2/g. Apparently, a small number of large microemulsion droplets are more effective than a larger number of small droplets in generating a high surface area.

TLC plates were prepared from powdered (>400 mesh) polymer **2** mixed with 10% $CaSO_4 \cdot 2H_2O$ as a binder. These plates were compared with those from polymer **10** (polystyrene made without water pools) and with commercial silica gel plates in their ability to separate the 7 compounds shown in Table II. Interestingly, the spread of R_f values is much greater for the plates based on polymer **2** than with plates made from polymer **10** or silica. Both methanol and heptane can be used with **2** to resolve the compounds although relative mobilities for the two eluting solvents are seen to be quite different. Selectivity in adsorption–elution characteristics could be extended to column chromatography. For example, the first four compounds in Table II were separated on a polymer **2** column with retention times of 6.2, 4.5, 3.7, and 4.2 min, respectively. In contrast, an identical column of polymer **10** gave retention times of 3.1, 3.0, 2.9, and 3.0 min, respectively.

Water pools in styrene/DVB were prepared by using water containing 6 mM $CuCl_2$. When the resulting polymer was dried, copper salt deposited on the walls of the pores. High-area polymer (no. **4**, 100–150 mesh) released 7% of $CuCl_2$ in 3 days and 80% in 0.5 days when extracted at 25 °C with water and methanol, respectively. Methanol must enter the pores much more efficiently than water. A similar experiment with low-area polymer (no. **1**) gave only 4% leaching in 3 days and 18% in 0.5 days with water and methanol, respectively.

We have shown that polymers prepared from reverse micellar systems can provide a variety of tailored porous surfaces. Such materials could find applications ranging from catalysis to separation science to controlled release of drugs.[10]

Acknowledgment. This work was supported by the Army Research Office. We thank Frank Horne (Georgia Pacific Corp.) for his help with the SEM studies and the Arakawa Chemical Co. (Osaka, Japan) for carrying out the BET measurements.

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Biosynthesis of Archaebacterial Membranes. Formation of Isoprene Ethers by a Prenyl Transfer Reaction

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Archaebacteria are a unique taxonomic group that diverged from eubacteria and eukaryotes at an early stage of evolution.[1] They inhabit environments characterized by high salt (halophiles), high temperature (thermophiles), low pH (acidophiles), or lack of oxygen (methanogens) hostile to most other life forms. Archaebacteria have several distinctive phenotypes at the molecular level, including characteristic sequences for their 5S and 16S RNAs,[2-4] unique metabolic cofactors,[5-8] and a novel architecture for the lipids in their cellular membranes.[9-12]

In contrast to the fatty acid ester motif found in other organisms, archaebacterial lipids are composed of *sn*-2,3-*O*-diphytanylglyceryl units bearing polar groups at the *sn*-C(1) position. A possible mechanism for formation of ether linkages between the glyceryl and fully saturated phytanyl moieties is a prenyl transfer reaction with an unsaturated C_{20} allylic diphosphate donor and a glyceryl acceptor with subsequent reduction of the double bonds. This hypothesis is supported by discoveries that gera-

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