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Cross-Linked Porous Polymer Resins with Reverse Micellar Imprints: Factors Affecting the Porosity of the Polymers

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ABSTRACT: Using styrene and divinylbenzene as the polymer matrix and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) as the surfactant, we have prepared highly cross-linked porous polymer resins with reverse micellar imprints. The pore size of the polymers was controlled by varying the amount of water in the AOT reverse micelles prior to polymerization. To study the factors that may affect the porosity of the polymers, several series of resins were prepared by systematically varying the surfactant concentration, the degree of cross-linking, and the amount of added cosurfactant. The BET gas adsorption experiments showed that the surface area and pore volume were influenced by the size of the micelles and the surfactant concentration, with maxima near an AOT concentration of 0.2 M. The degree of cross-linking was also found to have an effect on the surface area, pore volume, and even the pore size, but the addition of a cosurfactant, *n*-butanol, did not affect the porosity of the polymers. The porosity parameters of the polymer resins were found to remain stable after prolonged heating at elevated temperatures.

Introduction

The template-imprinting technique has been used in the preparation of cross-linked synthetic polymers with size- and shape-specific binding sites.[1−3] Since the size and shape of the molecules or molecular aggregates are important in the chemical processes,[4] these polymer materials with well-defined porous structures can be useful in various applications such as chemical catalysis[5,6] and selective binding and removal of drugs,[7−9] peptides,[10] proteins,[11,12] and nucleotide bases.[13]

Molecular aggregates such as reverse micelles can also be used as templates to make polymer resins with imprinted cavities of specific sizes.[14−16] The reverse micelles formed by sodium bis(2-ethylhexyl) sulfosuccinate (AOT) can solubilize large amounts of water. The size of the micelles can be controlled by varying the water content, expressed as the water-to-AOT molar ratio (W), which can attain a value of well beyond 20 in many apolar organic solvents.[17,18] The polymerization of styrene−divinylbenzene solutions of AOT reverse micelles was first reported by Menger et al.[14,15] The preparation of similar cross-linked polymers possessing positively charged[19] and negatively charged functional groups[5] was also reported. The structure and morphology of microporous methacrylate polymers prepared in the presence of microemulsions have been studied by Chieng et al.[20−22]

We have reported a systematic study of the effect of water content in the AOT reverse micelles on the size of the cavities inside the resulting polymers.[16] The average size of the cavities in the cross-linked polymers was found to be proportional to the amount of water added into the reverse micelles prior to polymerization.[16] In an effort to elucidate the relationship between the polymer porosity and the reverse micellar templates, we have prepared several series of polymer resins by varying systematically the concentration of AOT, the amount of the cross-linker (divinylbenzene) used, and the amount of an added cosurfactant (*n*-butanol). The effects of these factors on the porosity of the polymers and the thermal stability of the polymer resins have been studied, and the results are reported here.

Experimental Section

Styrene (S) and divinylbenzene (DVB) (Aldrich) were washed with a 10% NaOH aqueous solution and vacuum distilled to remove any added inhibitors. DVB was 55% pure, and the distillation did not change its apparent composition. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was purchased from Sigma and was used as received. The free radical initiator, 2,2′-azoisobutyronitrile (AIBN), purchased from Eastman Kodak, was recrystallized from methanol and stored in dark bottles in a refrigerator.

The preparation of the polymer resins was described previously.[16] The polymer resins used here were prepared with a fixed water-to-AOT molar ratio (W) of 12. Three series of polymers have been prepared by varying (1) the AOT concentration (0−0.4 M) to study the effect of the concentration of AOT micelles, (2) the volume fraction of divinylbenzene in the comonomers (20−100 vol %) to study the effect of cross-linking, and (3) the amounts of an added cosurfactant, *n*-butanol (*n*BuOH, 0−30 mol % of the amount of AOT used), to study its effect on the porosity of the resins. The reverse micelles formed when a desired amount of deionized water was added to an S−DVB solution of AOT under agitation or sonification in an ultrasonic bath. Polymerization started immediately upon the addition of 0.5−2 wt % AIBN followed by UV irradiation at a wavelength of 254 nm in a UV cross-linker (UVC-515 UV Multilinker, Ultra-Lum, Carson, CA) over a period of 6−12 h. Precautions should be taken to shine the UV light efficiently and uniformly on the entire sample to ensure the homogeneity of the sample and to avoid possible demixing and phase separation of the system. The polymers obtained were ground into powder with the aid of a Technilab micromill (Bel-Art, Pequanock, NJ) and then washed with toluene, ethanol, and ether successively in a Soxhlet extractor to remove any unreacted monomers and AOT. The ground resin particles were dried under vacuum and sieved into different sizes.

The infrared spectra were recorded on a Bomem Fourier transform IR spectrometer (model MB-100, from Hartmann & Braun). KBr pellets were prepared with the powder of the resins, and 30 scans were taken at room temperature. Solid-

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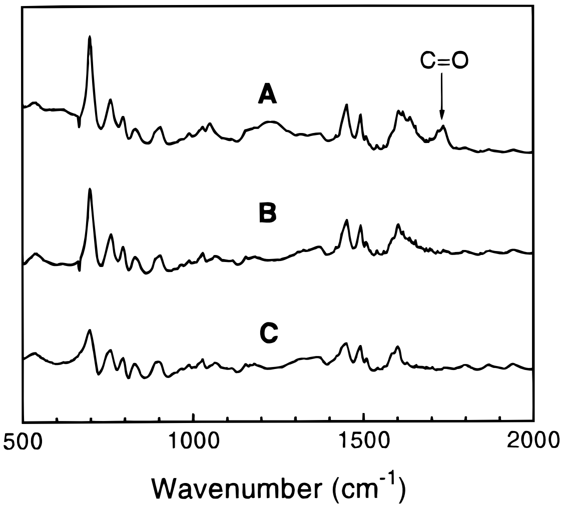

Figure 1. IR spectra of a polymer resin ([AOT] = 0.2 M, W = 12, S:DVB = 1:1, v/v) before (A) and after (B) Soxhlet extraction, showing the disappearance of the C=O stretching band at 1735 cm^{-1} belonging to the AOT molecules after washing. (C) IR spectrum of a nonporous polymer resin made without AOT reverse micelles (S:DVB = 1:1, v/v).

state NMR spectra were recorded at room temperature on a Varian VXR-300 NMR spectrometer equipped with a Doty CP/MAS probe operating at 75 MHz for ^{13}C and a spinning rate of ca. 4 kHz. The contact time (1.5 ms), relaxation delay (5 s), and other parameters were optimized for the comparison of the ^{13}C NMR spectra. The Brunauer–Emmett–Teller (BET) gas adsorption analyses were performed on a Coulter SA-3100 surface area and pore size analyzer (Coulter Scientific, Miami, FL) as described previously.[16] The pore size distribution was deduced from the desorption isotherm using the Barrett–Joyner–Halenda (BJH) method.[23,24] Polymer resins with mesh size between 60 and 100 (particle size 150–250 μm) were normally used for the BET measurements and for the thermal stability tests. The porous resin used in the thermal stability test was made with a AOT concentration of 0.20 M and W of 16. The resin was heated at 80, 100, and 120 °C for 12, 24, and 48 h, respectively, and each of the samples was analyzed by BET gas adsorption experiment.

Results and Discussion

The homogeneity of the polymer matrix can be ensured by a rapid polymerization with efficient and uniform UV irradiation. Demixing or phase separation can be observed when the water content is high (W > 18) for the samples.[16] The water content was kept relatively low in these samples (W = 12) to avoid any possible phase separation. Even though dynamic exchanges may occur between the reverse micelles, the micelles served as the templates for the formation of cavities in such polymers, as indicated by the variation of the pore size as a function of water content in the micelles and by the relative narrow distribution of the pore sizes in the resins.[16]

IR and NMR Spectroscopy. The IR spectra of a polymer resin before and after washing are shown in Figure 1. It can be seen that the C=O stretching band at 1735 cm^{-1} (Figure 1A) disappeared after washing (Figure 1B) along with the broader O=S=O stretching band close to 1250 cm^{-1}. Both groups belong only to the AOT molecules. The IR spectrum of the polymer after washing is comparable to that of a polymer resin made without AOT reverse micelles (Figure 1C). The IR spectra clearly indicate that most of the AOT molecules have been washed off during the Soxhlet extraction.

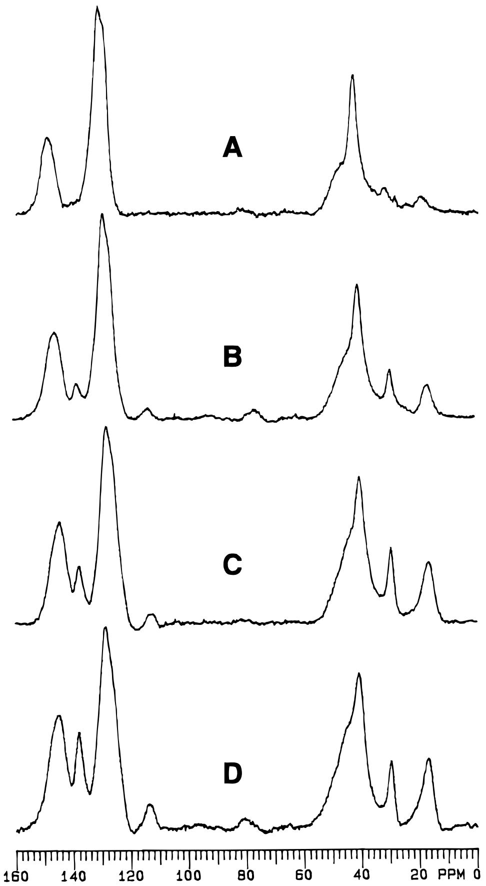

Figure 2. Solid-state CP/MAS ^{13}C NMR spectra of the polymer resins with various degree of cross-linking ([AOT] = 0.2 M, W = 12, after washing). Volume percentage of the crude DVB (55% pure, containing ethylvinylbenzenes) in the S–DVB copolymers: (A) 20%, (B) 50%, (C) 80%, and (D) 100%.

Solid-state ^{13}C NMR spectroscopy has also been used to verify the completion of the washing and extraction of the porous polymer resins.[16] The different chemical compositions of the polymers with different degrees of cross-linking are clearly shown in the solid-state ^{13}C NMR spectra in Figure 2. The NMR signals at about 16 and 30 ppm can be attributed to the carbons of the ethyl group of ethylvinylbenzenes, impurities contained in the DVB used. The NMR signal at 140 ppm is due to the carbons from the disubstituted aromatic rings. DVB itself may be made up of ortho-, meta-, and para-substituted isomers. In addition, the DVB sample is only 55% pure and contained also ethylvinylbenzene isomers. The intensities of all these NMR signals increased with increasing volume fraction of DVB in the resins (Figure 2), confirming the increasing degree of cross-linking of the polymers.

Effect of the Degree of Cross-Linking. The surface area and pore volume of the polymer resins were found to increase as a function of the degree of cross-linking, expressed by the volume percentage of pure DVB in the S–DVB mixture (Figure 3). The average pore diameter of the resins initially decreases with increasing degree of cross-linking until a certain point and then becomes more or less constant at ca. 18 m^2/g as the volume percentage of DVB varied from 30 to 55% (Figure 3C). The pore size distribution, on the other hand, remained more or less constant as indicated by the BJH analyses. Menger et al. also observed an increased surface area when only DVB was used in the preparation of the polymer resin.[14] It is possible that a lower degree of

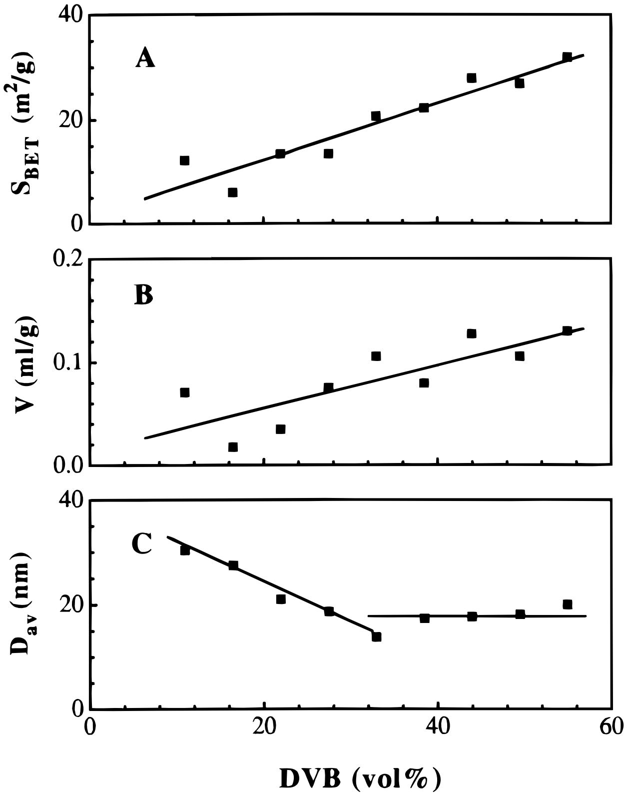

Figure 3. Specific surface area (A), pore volume (B), and average pore diameter (C) plotted as a function of volume percentage of pure DVB in the S−DVB mixtures ([AOT] = 0.2 M, $W = 12$).

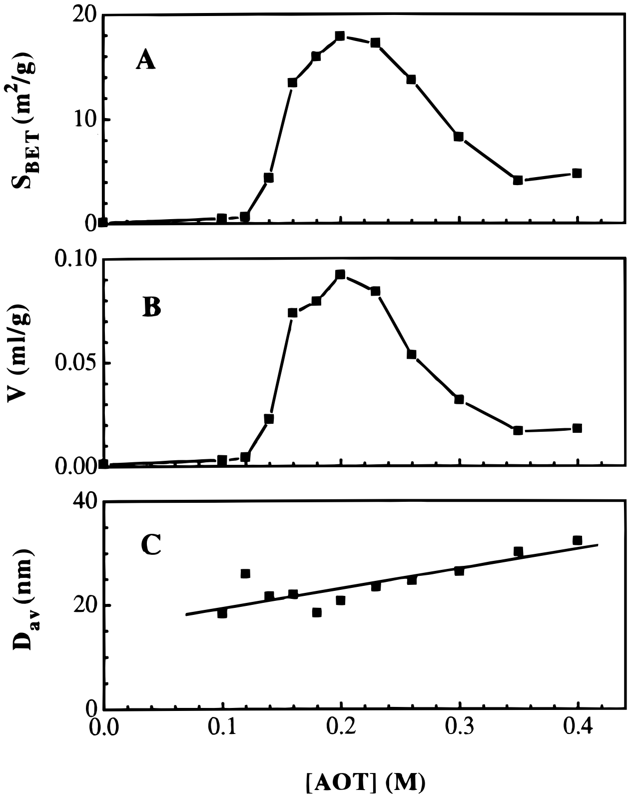

Figure 4. Specific surface area (A), pore volume (B), and average pore diameter (C) plotted as a function of AOT concentration. All samples: S:DVB = 1:1 (v/v), $W = 12$.

cross-linking may lead to more interconnected pores after washing and thus gives a larger apparent average size of the cavities. It is reasonable to expect that a decrease in pore sizes leads to an increase in the surface area. However, no obvious correlation can be found here between the cavity size and the pore volume of the resins. The pore volume increased with increasing surface area. The cylindrical pores assumed by the BJH model may not reflect the structure of the cavities in such polymers. One might expect a higher surface area than the measured values for such pore sizes, but it is possible that not all the cavities in the resins are exposed or accessible even though the washing was shown to be quite efficient. With a higher degree of cross-linking, the polymer resins became more rigid. It was noticed that the polymers became increasingly resistant to mechanical crushing (as in grinding) with increased degree of cross-linking.

Effect of the Surfactant Concentration. When the water-to-AOT molar ratio is kept constant, an increase in the AOT concentration should increase the number of reverse micelles per unit volume. The surface area and pore volume of the resins, in turn, are expected to increase accordingly while at the same time less effect is expected for changes in pore sizes. Figure 4 shows that all the porosity parameters were significantly influenced by the AOT concentration. The surface area and pore volume both show a maximum value (at 18 m^2/g and 0.09 cm^3/g, respectively) when the AOT concentration reaches about 0.20 M (Figure 4, A and B). This was rather unexpected, but the result on the surface area is also consistent with the observation of Menger et al. under different conditions.[14] On the other hand, the average pore diameter in the polymer resins varies in a more or less linear fashion as a function of AOT concentration (Figure 4C). BJH analyses showed that the increase in the pore diameter is also accompanied by an increasing pore size distribution. It is believed that the increase in the number of AOT reverse micelles facilitates collisions between the micellar aggregates, causing reorganization of the reverse micelles in the system, which includes both fission and fusion of the micelles. This should be similar to the aggregation of vesicles observed by Menger and Balachander.[25] The net result is an increased average pore size and its distribution. The change in the pore size does not have a direct correlation with the specific surface area and pore volume.

Effect of a Cosurfactant. The addition of cosurfactants such as alcohols may change the properties of the micelles by the formation of mixed micelles.[26] An advantage of using an alcohol cosurfactant would be to help the AOT reverse micelles to solubilize large amounts of water more rapidly. Cosurfactants would also be useful in the preparation of functionalized porous polymers.[5,15] A saturated alcohol, *n*-butanol, was added as a cosurfactant in the formation of AOT reverse micelles to study its influence on the porosity of the resulting polymers. As shown in Figure 5, the specific surface area, pore volume, and average pore diameter of the resins remained constant as a function of the added amount of *n*-butanol, expressed as the molar ratio of *n*-butanol to AOT. The BJH analysis showed that the distribution of the pore size was not affected either. We can conclude that the addition of various amounts of the cosurfactant in this concentration range does not have any significant influence on the porosity of the polymers.

Thermal Stability of the Porosity of the Resins. The possible change of the porosity parameters of these

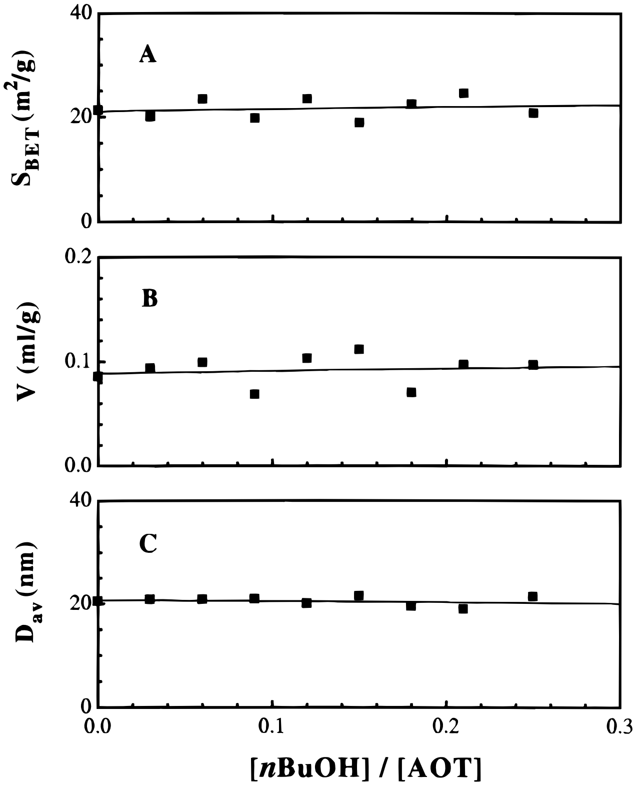

Figure 5. Specific surface area (A), pore volume (B), and average pore diameter (C) plotted as a function of the amount of an added cosurfactant, *n*-butanol (shown as the *n*BuOH to AOT molar ratio). All samples: S:DVB = 1:1 (v/v), [AOT] = 0.2 M, *W* = 12.

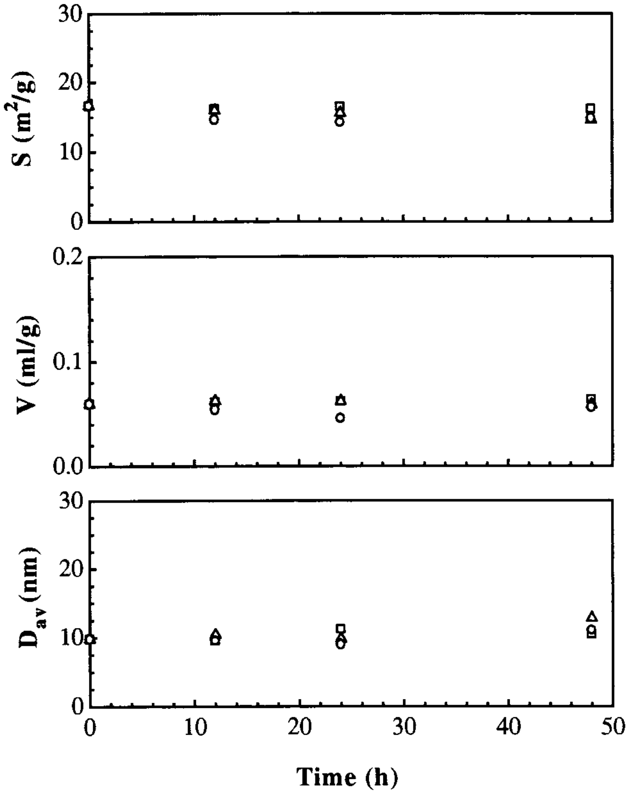

Figure 6. Specific surface area (A), pore volume (B), and average pore diameter (C) are shown to remain stable after being heated at elevated temperatures for 12, 24, and 48 h. Resin sample used: S:DVB = 1:1 (v/v), [AOT] = 0.2 M, *W* = 12. Squares, 80 °C; triangles, 100 °C; circles, 120 °C.

resins upon heating is a concern for the application of the materials. BET gas adsorption experiments were carried out after the cross-linked porous resins were heated for an extended period of time (up to 48 h) at elevated temperatures (up to 120 °C). An example of the resins is shown in Figure 6; it is clear that none of the parameters (specific surface area, pore volume, and average pore diameter) showed any significant changes. The small variations are within the normal range of experimental errors of the gas adsorption experiments. It can be concluded that the porosity of the resin remained stable under these experimental conditions. Polystyrene and PS-based resins are known to be stable over a large temperature range,[27] and its glass transition temperature (T_g) is in the range 85−100 °C, depending on the molecular weight of the polymer.[28] It is known that an increase in the molecular weight or cross-linking usually leads to an increased T_g. For these highly cross-linked polymer resins, no obvious T_g can be detected. We have observed, however, that during the grinding of the samples the normally brittle materials became difficult to break with rising temperature of the samples, especially when the cooling process was not efficient. Thermal analyses of the samples showed that the polymers were stable up to their decomposition temperature well above 300 °C.

Concluding Remarks

This work shows that reverse micelles can be used as imprints in the preparation of porous polymer resins. We have shown previously that the pore size of the polymer resins can be controlled within a certain range by adjusting the water content in the reverse micelles.[16] Due to the dynamic nature of the micelles, large concentrations of the surfactant led to an increased average pore size and its distribution, as a result of reorganization of the micelles. Since the porosity of the resins is not affected by the addition of a cosurfactant, polymerizable cosurfactants would be interesting candidates to be used for the formation of cavities with functional groups. The porosity parameters of the resins were found to remain unchanged over a large temperature range. Although only styrene−divinylbenzene-based polymers have been prepared in this work, other monomers and cross-linkers could also be used. The use of these resins as chromatographic materials has already been explored.[14,29] The elucidation of the factors that affect the porosity of the polymer resins should help in the establishment of a better correlation between the designed pore size in the polymers and the size of the targeted guest molecules in the application of the materials.

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