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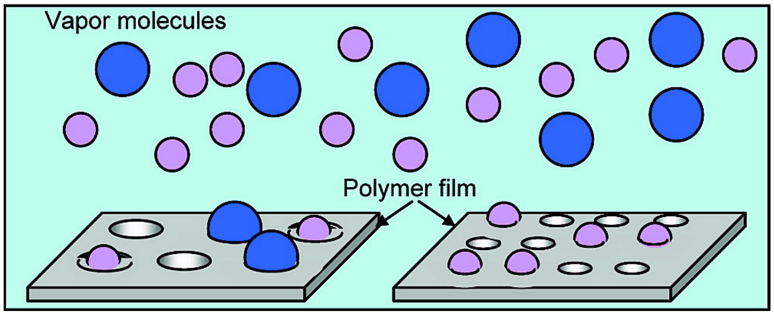

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Organic Zeolites from a Diolefinic Monomer

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Abstract: Submicrometer particles of diethyl *p*-phenylenediacrylate (EPA) with tunable molecular adsorption characteristics were produced by solid-state photopolymerization in the presence of template molecules. EPA monomer particles were produced by rapid expansion of supercritical solutions (RESS), and deposited directly onto surface acoustic wave (SAW) resonators. The EPA particles were photopolymerized directly on the SAW devices in the presence of molecular templates, and dynamic sorption isotherms of C_1- through C_9-alkanes were studied to characterize the particle−vapor interaction. The mass increase due to vapor uptake into the particulate coatings was measured by monitoring the SAW resonance frequency during vapor sorption. The vapor selectivity and molecular porosity of the particulate coatings were studied in situ on the piezoelectric substrate by measuring sorption isotherms. A gradual exclusion of smaller alkane molecules from the molecularly imprinted particulate coatings was observed with decreasing template molecule size. The observed selective and reversible adsorption of alkane analytes with different molecular sizes suggest that these imprinted polymers may be categorized as organic analogues of zeolites.

Introduction

Zeolites are inorganic microporous crystalline solids, which have well-defined network structures made up of silicon, aluminum, and oxygen. The tunnels and cages within the zeolite framework allow molecules small enough to pass through to be adsorbed while larger molecules are rejected. For this reason zeolites are also referred to as molecular sieves. Because of their precise and uniform molecular porosity and very high internal surface areas, zeolites are uniquely suited for a variety of applications, including petrochemical cracking, ion exchange (water softening and purification), and separation and removal of gases and solvents.[1,2]

Some types of zeolites occur naturally as minerals and are extensively mined in many parts of the world. Naturally occurring zeolites are the oldest known family of microporous materials. About 50 natural zeolites have been identified to date.[3] Others are synthetic and are produced commercially for specific uses. The interest in the synthesis of zeolitic materials started in the 1950s and was stimulated mostly by their efficacy as catalysts in the petrochemical industry.[4] Synthetic zeolites have a high impact on today's oil industry.[5]

In recent years, many researchers have tried to create organic analogues of zeolites.[6−11] Organic zeolites are non-silicious solids mimicking the physicochemical behavior of zeolites with respect to organic sorbate species.[3] The "zeolites" label was used to mark permanent porosity of these new materials, which is a characteristic of true zeolites.[12] The adsorption in zeolites is fully reversible and purely physical in nature. The structure of the zeolite stays intact during adsorption and its regeneration, which usually involves heating and purging with a carrier gas. The "organic" label was used to stress the hydrophobic nature of the interior pore surface[12] that can therefore selectively absorb nonpolar organic compounds. This is contradictory to the unique characteristic that distinguishes zeolites from other commercially available adsorbents: that is the highly polar surface within the pores is the main driving force for adsorption in zeolites.

The greatest advantage of organic zeolites over traditional zeolites is the greater control over the chemical nature of the accessible surface that is provided by organic components. There exists a huge multitude of organic building units and structural patterns into which they can be assembled to develop new and improved zeolites. Current efforts in the synthesis of organic zeolites has focused on glassy or semicrystalline polymers, crystalline organic materials, and metal−organic frameworks.[3,13] In particular, crystalline metal−organic frameworks that have been produced exhibit impressive levels of gas uptake.[14,15]

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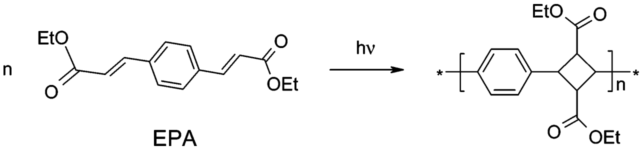
The variable pore dimensions and the large pore volume of traditional zeolites make them ideal candidates for sensor design with effective molecular size discrimination and high sensitivity.[16] For this very purpose, several strategies, including dip-coating of zeolite/silica sol suspension,[17] chemical attachment of zeolite crystals via molecular coupling,[18] embedding zeolite crystals into polymers,[19] covering with glazes,[20] and extruding into composite monoliths,[21] have been explored for thin-film formation. In order to enhance control of molecular selectivity in sensors, the pore sizes of the zeolite crystals in these films were controlled through in situ cation exchange.[16] The main concern in the above preparations is the potential blockage of the zeolitic pores and/or the formation of nondesirable additional affinity introduced by the matrix in the composites.[16]

In this contribution, we present the preparation and characterization of organic analogues of zeolites. The molecular sieving capability of diethyl *p*-phenylenediacrylate (EPA) submicrometer polymer particles is demonstrated by the sorption behavior of alkanes of different sizes. These *tunable* submicrometer EPA particles are prepared by rapid expansion of supercritical solutions (RESS), and the molecular size and shape selectivity is controlled by the introduction of a vapor template molecule during a solid-state photopolymerization reaction. Previously, we showed that when diolefinic monomers are polymerized in the presence of a template alkane vapor, the final polymer exhibits a molecular porosity that is related to the size of the template molecule.[22,23] Recently, these molecularly imprinted polymers were reported to be stable up to 3.8 years.[24] We now report on controlling and tuning the molecular porosity by using water and alcohols of various sizes. Dynamic sorption isotherms of alkane analytes were studied to characterize EPA particulate coatings on SAW devices. Although the molecular porosity was created using template molecules from a different chemical family, these coatings exhibited reversible sorption properties when tested against alkane analytes. A gradual exclusion of smaller analyte molecules from the molecularly imprinted particulate coatings is observed as the size of the template molecule is reduced. The observed reversible adsorption of alkane analytes with different molecular sizes suggests that these imprinted polymers may be categorized as *organic zeolites*. The high molecular porosity and controllable pore size, coupled with the versatility of organic synthesis, promise that these materials may be the initial step toward the preparation of key−lock structures that may perform like enzymes.

Scheme 1



Experimental Section

Materials and Equipment. HPLC-grade pentane, hexane, heptane, octane, isooctane, nonane, decane, and 1-butanol were obtained from Fisher Scientific. Methane (99.9995%), ethane (99.9995%), propane (99.99%), butane (99.99%) were obtained from BOC Gases. HPLC/spectrophotometric grade ethanol (dry) was obtained from Sigma-Aldrich. DI water was used for monomer synthesis and imprinting. Chlorodifluoromethane (Freon 22) was obtained from DuPont. The Diethyl *p*-phenylenediacrylate (EPA) was synthesized using a procedure described below. Nitrogen (Grade 5.5) was obtained from National Welders. SAW 250 MHz resonators were from Microsensors Systems, Inc. For polymerization of EPA particles, a UV lamp from American Ultraviolet was used. This lamp has 100-W power and emits UV within the range of 325−382 nm.

Diethyl *p*-Phenylenediacrylate (EPA). The monomer used in this study, EPA, was synthesized using the method described by Grinev et al. with some modifications.[25] Sodium ethoxide (14.9 mL of 21%; 0.04 mol) in ethanol was added to 8.97 g (0.04 mol) of triethyl phosphonoacetate in 30 mL of dry DMF, and the mixture was stirred for 1 h. A solution of 2.68 g (0.02 mol) of terephthalaldehyde in 12 mL of dry DMF was added dropwise with continuous stirring for 0.5 h, and the reaction mixture was left overnight. EPA was precipitated by adding water 3:1 by volume to the reaction solution. After 0.5 h the precipitate was filtered and rinsed by DI water and then ethanol. The resulting white powderlike crystals were obtained with 68% yield. After recrystallization from ethanol, the melting point of the EPA was 97 ± 1 °C (96 °C lit.[25]).

Preparation of EPA Particles. EPA was dissolved in supercritical Freon 22 at 340 atm and 120 °C. The solution was expanded through a capillary nozzle and sprayed directly onto SAW devices and glass microscope slides. The EPA particles obtained with this technique were 0.3−1 μm in diameter. The coated glass slides were used to investigate the particle size and morphology. The coated SAW devices were used to evaluate the selective vapor sorption property. A more detailed description of the apparatus and experimental procedure is provided in previous publications.[23,26]

Photopolymerization. The EPA particles were polymerized in the solid state directly on the various deposition substrates (i.e., SAW transducers, microscope slides). The EPA-coated substrates were placed in a sealed chamber filled with air. In order to facilitate polymerization, the samples were irradiated by the UV lamp through an optical filter (fused silica window by Mellis Griot) for 15 min from a distance of 22 cm. The optimization of these conditions was published previously.[23] The topochemical polymerization reaction of EPA is shown in Scheme 1.

Preparation of Organic Zeolites via Molecular Imprinting. The EPA coatings were photopolymerized in the presence of template vapors directly on the various deposition substrates (i.e., SAW transducers, microscope slides). The EPA-coated substrates were placed in a sealed chamber filled with air saturated with the selected template vapor. The chamber was kept in the dark for 40 min to allow EPA particles to absorb template vapors before polymerization. The monomer particles were polymerized in the presence of the template vapor as described in the section above. Upon photopolymerization, we obtained an

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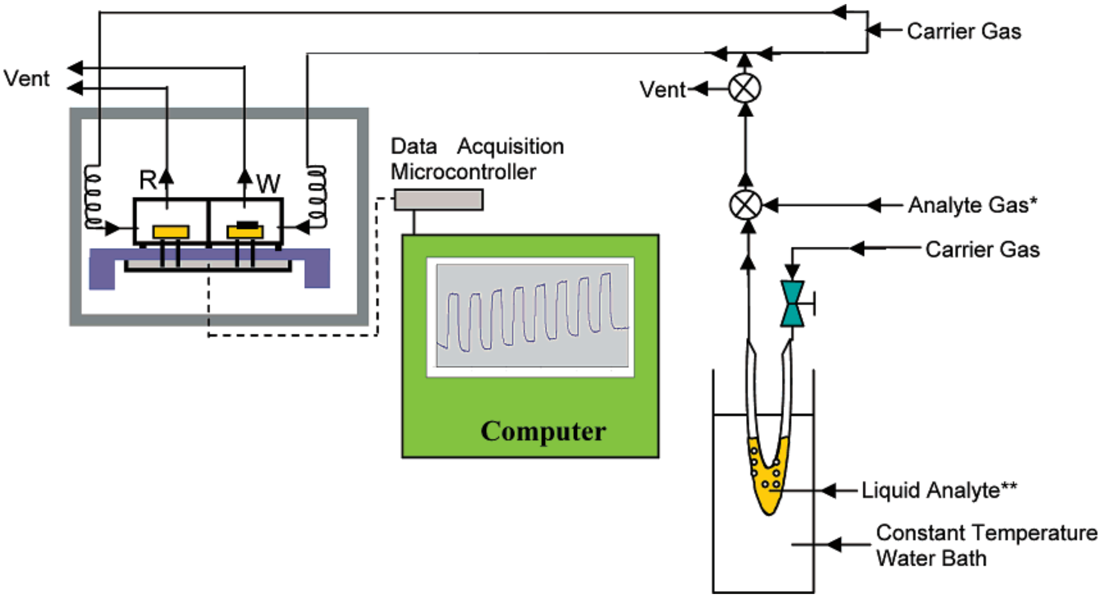

Figure 1. Dynamic sorption testing station for the characterization of coating porosity. *Gas analytes: C_1-C_4-alkanes. **Liquid analytes: C_5-C_9-alkanes.

inclusion compound in an atmosphere of the template sorbate. The coatings were then flushed with dry nitrogen for 20 min, and the inclusion compound converts into the microporous form by means of template sorbate removal.

Characterization of Coating Porosity via Dynamic Sorption Isotherms. An experiment designed to test the ability of these structures to exchange guest molecules with the environment was performed in order to confirm zeolitic behavior of the prepared particles.[3] The reversible sorption behavior of imprinted EPA coatings was evaluated by measuring the mass uptake of these particles when tested against C_1-C_9-alkane analytes using SAW resonators. For each analyte six different concentrations and for each concentration 10 sorption−desorption cycles were tested using a custom-built system. The system depicted in Figure 1 is the modified version of the system that was described previously[27] and is capable of introducing gas-phase analytes as well as liquid. Analyte vapors were generated by means of evaporation of liquid alkanes (C_5-C_9) at a temperature of 10 ± 0.1 °C, or by directly introducing the gas-phase analytes (C_1-C_4) from the cylinders through a regulator and a moisture trap (zeolite 3A). Analyte concentration adjustments were made by controlled dilutions with research grade nitrogen by means of mass flow meters. The analyte gas is then delivered to the unit that is equipped with a pair of SAW devices at a constant temperature of 30 °C. The pair of SAW devices includes one reference device (labeled "R" in the Figure 1) and one coated device (labeled "W" in the Figure 1), and the difference frequency is measured. The reference device is uncoated and is exposed to pure nitrogen at the same flow rate and temperature as for the analyte stream directed to the coated device. The frequency difference versus time data is recorded for increasing concentrations of each analyte gas.

Results and Discussion

Preparation of EPA Particles. Submicrometer-sized EPA particles were prepared via RESS. This technique consists of dissolution of the monomer in supercritical Freon 22 followed by expansion of this solution through a capillary nozzle. Upon expansion, the solvent (Freon 22) goes directly into the gas phase, and the micronized monomer precipitates are deposited on the target substrates. The main advantage of this technique is that the monomer particles are formed free of residual solvent contamination. Micronization of EPA such that the particle diameters are maintained at less than 1 μm is a crucial step in the preparation of organic zeolites with controlled molecular porosities. The optimization of RESS processing conditions yields particle sizes within the desired range.[26] Previously, we have shown that the unmicronized EPA monomer crystals undergo mechanical disintegration upon polymerization.[26] Stress release during the photopolymerization results in the formation of large cracks in the direction of chain growth. The main concern in the preparation of organic zeolites from EPA is the possible destruction of the molecular porosity during crystal disintegration caused by photopolymerization. The desired mechanical stability during polymerization can be achieved by micronization of the EPA monomer via RESS.[26]

Photopolymerization. EPA is a diolefinic monomer and can go through a four-center polymerization reaction in the solid state (see Scheme 1) and produce a linear polymer. The polymerization reaction is initiated by exposing the solid monomeric crystalline substance to UV radiation and converting it directly to the polymer without the use of external photoinitiators. Polymerization proceeds by the direct rearrangement of molecules from the monomer to the polymer without internal diffusion.[28,29] Photopolymerization of diolefinic monomers in the crystalline state has been studied extensively.[30] In general, topochemical polymerization is highly sensitive to the crystal structure of monomers. We have previously studied the photopolymerization of micronized EPA using FTIR spectrometry.[23] The kinetics for various samples was evaluated at different exposure times by measuring IR absorption of the double bond at 1630 cm^{-1}. It was concluded that 15 min of UV exposure was sufficient for complete polymerization of these particles.

Preparation of Organic Zeolites via Molecular Imprinting. Preparation of organic zeolites is very similar to molecular imprinting.[31−34] The monomer compound is polymerized in the

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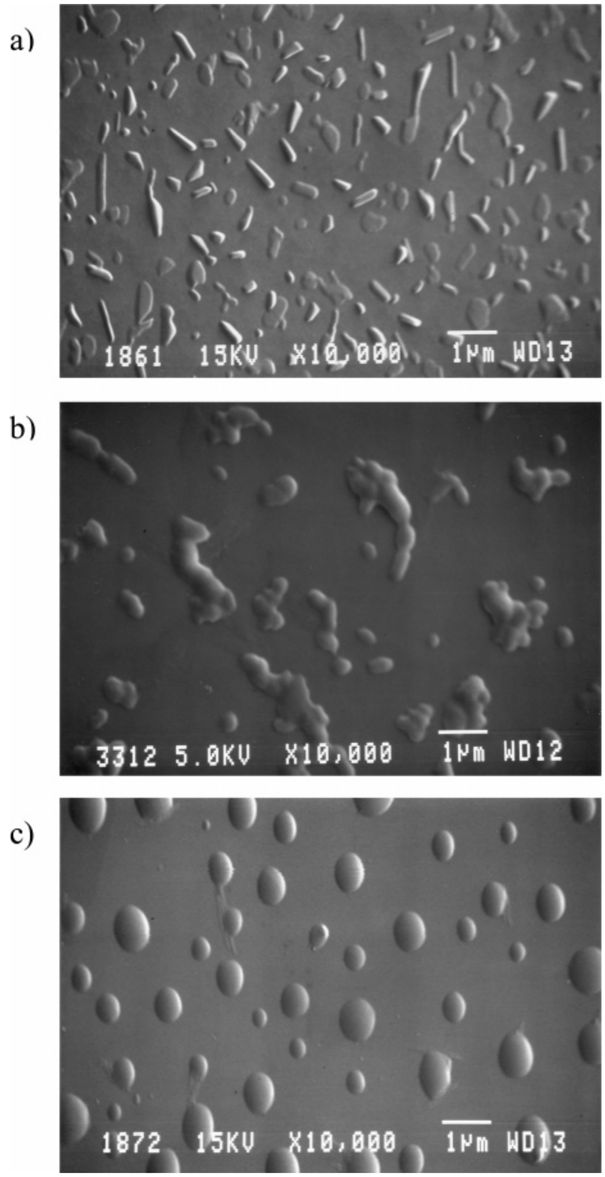

Figure 2. EPA particles (a) photopolymerized without template, (b) photopolymerized in the presence of water, (c) photopolymerized in the presence of butanol.

presence of a template molecule. Upon template extraction, cavities complementing the size and shape of the employed template molecule are obtained. Preparation of another polymer with the same technique, but without the introduction of the template molecule, and comparison of their sorption properties can be used to evaluate the porosity of the organic zeolite.

Previously, we have reported the selective sorption of heptane-imprinted EPA with respect to its nonimprinted counterpart that were prepared by a procedure similar to the one described above.[23] It was found that EPA polymer prepared in the presence of heptane vapor has preferential affinity to alkanes with molecular size equal to or smaller than that of a C_7-alkane.[23]

There are polymers and crystalline organic compounds with intrinsic angstrom-sized cavities that have previously been reported in the literature.[3,8,35] In our case, the fact that we are able to prepare cavities of different molecular sizes suggests that the porosity does not depend on the self-rearrangement of the building blocks, but rather, on templating.

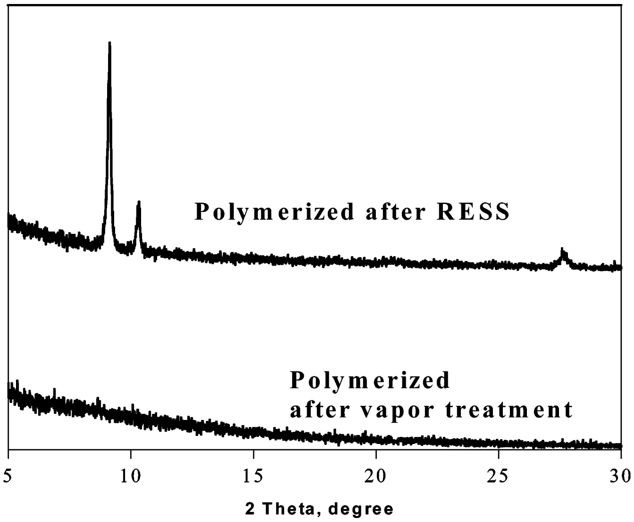

Figure 3. XRD scans of EPA polymer. The vapor used for the lower scan is butanol.

Obviously, there is a balance between rigidity of the polymer and its ability to be imprinted. Rigidity is needed in order to preserve the cavities upon removal of the template molecule. However, if the polymer is highly rigid, then it will not conform around the template molecule. We have found that EPA polymer maintains this balance by testing EPA particulate coatings imprinted to various template molecules against C_1-C_9-alkane analytes. For each imprinted polymer tested, reversible sorption experiments revealed that there was sufficient amount of vapor sorption for analytes of proper molecular size—sufficient enough to be easily detected by SAW devices. This result also suggests that the imprinting procedure used to prepare organic zeolites was an efficient process and that enough cavities were created for selective absorption of analytes for each template molecule tested. The template molecules used in this study are heptane, butanol, ethanol, and water. For template molecules with hydrogen-bonding ability, the imprinting efficiency was significantly higher.

We have also studied the morphology and the structure of the imprinted vs nonimprinted EPA polymers. Figure 2 shows SEM images of the nonimprinted, butanol-imprinted, and water-imprinted EPA polymers. The nonimprinted polymer seems to exhibit crystalline features, but both of the imprinted polymers look amorphous. This observation was confirmed by XRD (Figure 3). Crystallinity is not necessary for microporosity, and amorphous porous materials, such as activated carbons, are widely used in industry.[13] As such, all of these polymers exhibited high stability. They were all able to reversibly absorb analyte molecules and maintained their morphologies. Recently, we have reported that the nonimprinted and butanol-imprinted EPA polymer coatings were stable for up to 3.8 years.[24]

Characterization of Coating Porosity via Dynamic Sorption Isotherms. Zeolitic sorption implies the presence of significant and permanently available micropore space in a material. Any experiment designed to confirm zeolitic behavior

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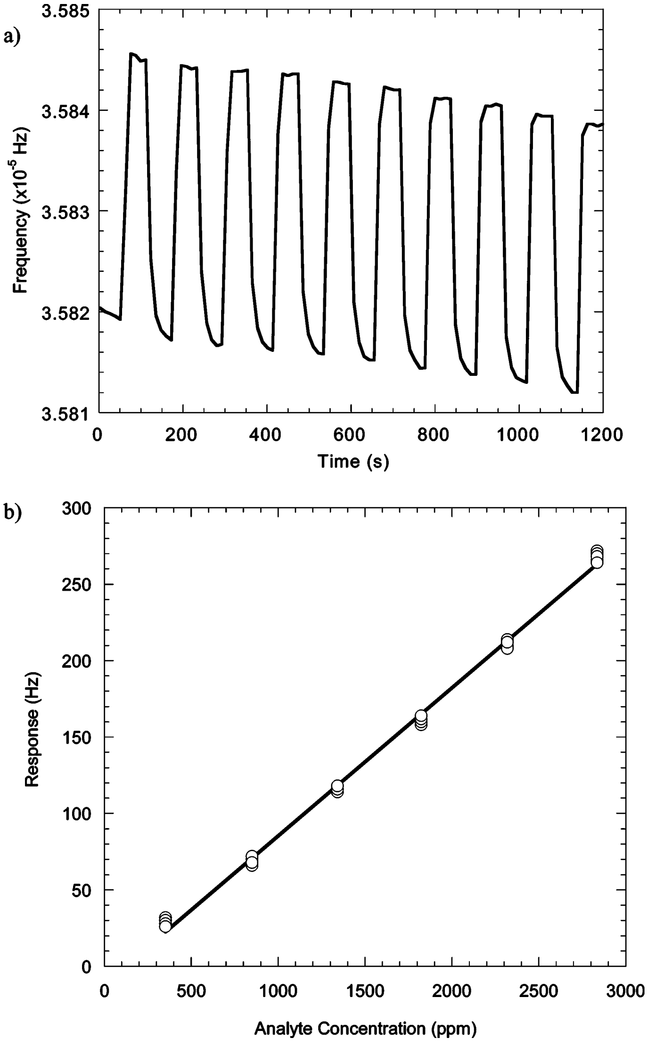

Figure 4. (a) Reversible sorption data for ethanol-imprinted EPA polymer tested against heptane at a concentration of 2836 ppm. (b) Frequency shift, which is proportional to mass uptake, as a function of heptane concentration for ethanol-imprinted EPA polymer.

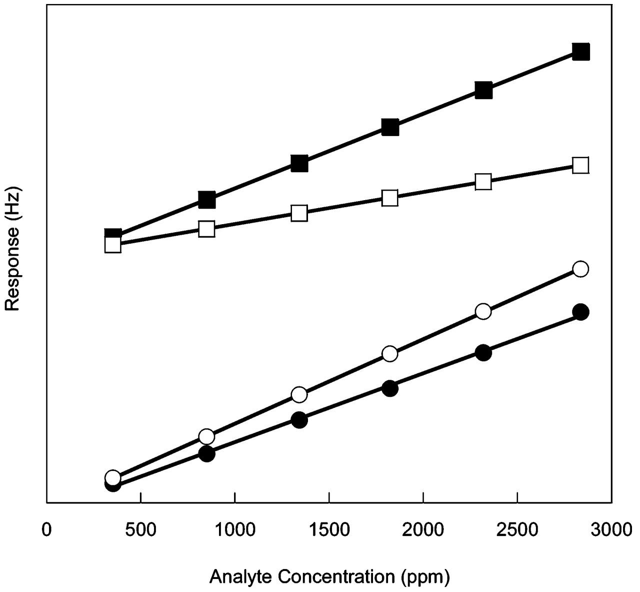

Figure 5. Frequency shift, which is proportional to mass uptake, as a function of (■) ethane concentration for ethanol-imprinted EPA polymer, (□) ethane concentration for nonimprinted EPA polymer, (●) heptane concentration for ethanol-imprinted EPA polymer, and (○) heptane concentration for nonimprinted EPA polymer.

of an organic or metal–organic material should test the ability of these structures to exchange guest molecules with the environment.[3] It was discovered that SAW and other acoustic wave devices can be used as mass-sensitive tools for the detection of even small mass changes in polymer coatings.[36–40] In this study, the reversible sorption behavior of the imprinted EPA polymers was evaluated by measuring the mass uptake of these particles when tested against analyte molecules of various sizes and concentrations using SAW resonators.

The experimental setup shown in Figure 1 was designed to test the ability of the imprinted EPA polymer coatings on SAW devices to reversibly absorb analyte molecules to confirm zeolitic behavior. EPA polymer imprinted to hydroxyl-containing molecules such as water, ethanol, *n*-butanol along with *n*-heptane, were tested against C_1–C_9-alkane analytes. Alkanes were chosen as analytes because they do not have polar functional groups and their sorption is based on Van der Waals forces, which leads to a fast sorption–desorption process.

For each concentration of analyte molecules tested, data for 10 reversible sorption cycles were collected. A typical adsorption–desorption cycle is depicted in Figure 4a. The amplitude of the sorption cycles is proportional to analyte concentration and increases with increasing concentration. The amplitudes for the 10 consecutive cycles are calculated and plotted as a function of analyte concentration. Representative data are given in Figure 4b.

SAW devices are mass-sensitive tools, and the difference in frequency during the sorption cycle and the baseline in Figure 4a is an indication of mass uptake by the imprinted coating.[36] Accordingly, Figure 4b represents the adsorption isotherm of heptane. The frequency increase and decrease that correspond respectively to the adsorption and desorption of the analyte molecule for each cycle are equal in magnitude. This may suggest that the analyte adsorbed is flushed out during desorption and that the imprinted EPA polymer is fully regenerated.

The sensitivity of the device to any given analyte is measured by the slope of the isotherm and will increase with increasing mass uptake. A comparison of the sensitivity of the SAW devices coated with imprinted vs nonimprinted EPA polymer revealed that the imprinted polymers preferentially adsorb analyte molecules with sizes that are equal to or smaller than the size of the template. This behavior is presented in Figure 5 with two sets of representative data collected for SAW devices coated with ethanol imprinted vs nonimprinted EPA polymer. In the first data set, both the ethanol-imprinted polymer (represented by solid circles) and the nonimprinted polymer (represented by hollow circles) are tested against heptane at various concentrations. Because the analyte molecule, heptane, is larger than the template molecule, ethanol, a significant difference between the sensitivities of these devices to the heptane analyte was not observed. In the second data set, both the ethanol-imprinted polymer (represented by solid squares)

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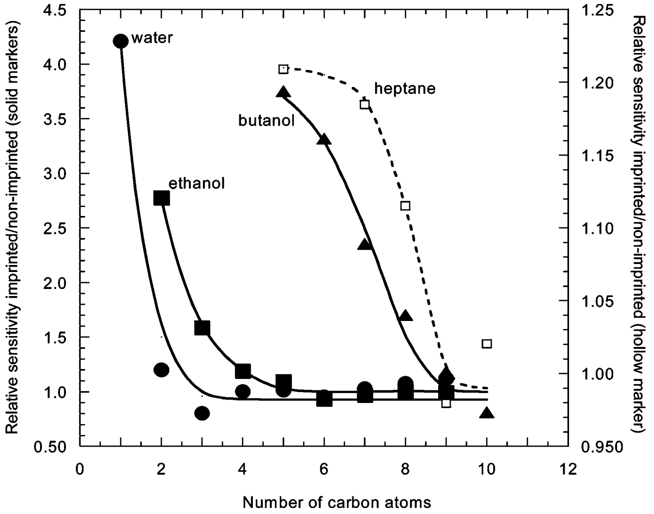

Figure 6. Relative sensitivity of polymers to C_1-C_9 *n*-alkane analytes, which are prepared by templated polymerization and characterized by mass loading response. The templates used for imprinting are H_2O, EtOH, BuOH, and heptane. The corresponding data are labeled accordingly.

and the nonimprinted polymer (represented by hollow squares) are tested against ethane at various concentrations. Because the analyte molecule, ethane, is smaller than the template molecule, ethanol, a significant difference between the sensitivities of these devices is observed.

The results of the systematic analysis of the isotherms for EPA polymer coatings imprinted to water, ethanol, *n*-butanol, and *n*-heptane tested against C_1-C_9-alkane analytes are depicted in Figure 6. Each data point in Figure 6 is the ratio of the slope of the corresponding analyte's isotherm for the imprinted EPA polymer to that of the nonimprinted. Therefore, they represent the sensitivity of the SAW devices with imprinted coatings relative to the device with the nonimprinted coating. This representation provides a comparison relative to a common reference. They also isolate the response based on the molecular porosity prepared by templated polymerization, eliminating the effect of the bulk polymer.

The selective adsorption of analyte molecules that have equal or smaller sizes than the template is clearly revealed in Figure 6. For example, the SAW device imprinted to butanol shows the highest affinity to the C_5-alkane since these two molecules have similar molecular sizes. The sensitivity difference between the "small" C_5 and the "big" C_9 is on the order of 400%. The relative sensitivity increase observed with heptane-imprinted coating as the molecular size of the analyte decreases from nonane to pentane is about 20%, which is plotted on the right ordinate for comparison. The sensitivity improvement observed in hydroxyl-containing template molecules may be attributed to intermolecular hydrogen bonding between these molecules and EPA during photopolymerization. The stronger bonding between the template molecule and the polymer yields a higher degree of molecular porosity.

Conclusions

In summary, the polymerization of micronized EPA particles in the presence of water and alcohol vapors result in polymers with molecular size porosity corresponding to the template vapors. The obtained material has amorphous structure with randomly distributed pores. Accordingly, they do not show any peaks in the XRD scans.

In addition, the described technique allows preparing polymers with zeolitic properties and hydrophobicity. The observed reversible adsorption of alkane analytes with different molecular sizes suggests that these imprinted polymers may be categorized as organic zeolites. We believe that this supramolecular-controlled templated polymerization and hydrophobicity offers an intriguing potential for the design of macromolecular systems with enzymelike catalytic activity.

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