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Vapor-phase testing of the memory-effects in benzene- and toluene-imprinted polymers conditioned at elevated temperature

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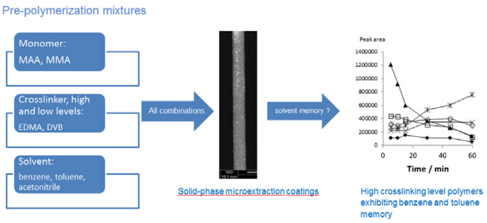
HIGHLIGHTS

- A diversity of imprinted copolymers was prepared in benzene and toluene.
- High crosslinking allowed for mesoporous structure and memory effects.
- Best solvation of monomers affected negatively the observed memory effects.
- Memory effects were lost with exposure to elevated temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

The preparation of polymers imprinted with common aromatic solvents such as benzene and toluene is an under-exploited subject of research. The present study was aimed at the understanding of whether true solvent memory effects can be achieved by molecular imprinting, as well as if they are stable at elevated temperature. A set of copolymers, comprising low and high cross-linking levels, was prepared from four different combinations of functional monomer and cross-linker, namely methacrylic acid (MAA)/ethylene glycol dimethacrylate (EGDMA), methyl methacrylate (MMA)/EGDMA, MAA/divinyl benzene (DVB) and MMA/DVB. Each possible combination was prepared separately in benzene, toluene and acetonitrile. The obtained materials were applied as coatings onto nickel–titanium (Ni–Ti) alloy wires which were incorporated into solid-phase microextraction devices and finally tested for their ability to competitively adsorb vapors from the headspace of an aqueous solution containing a few volatile organic compounds.

Porosity analysis showed that, regardless of the solvent used, only a high cross-linking level permitted the preparation of mesoporous copolymers (BJH radius typically in the range 13–15 nm), a requirement for providing accessibility to the targeted nanoscale-imprinted cavities. A noticeable exception was, however, observed for the MMA/DVB copolymers which exhibited much diminished BJH radius. The porosity data correlated well with the extraction profiles found, which suggested the presence of benzene-imprinted sites in all the highly cross-linked copolymers prepared in benzene, except for the MMA/DVB copolymers. Concerning the effect of an elevated conditioning temperature on the memory-effects created by the imprinting process, the results were clearly indicative that the tested copolymers, including the more robust highly cross-linked ones, are not suitable for high temperature applications such as solid-phase microextraction coupled to gas chromatography.

1. Introduction

The process of molecular imprinting relies on both shape and chemical complementarity for the target compound left in the

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imprinted cavities after removal of the template. Shape complementarity is achieved when a tri-dimensional network forms around the template. Chemical complementarity results from the formation of a non-covalent (most often) complex between the template and molecules bearing favorable functional groups for the formation of such complex which is stable to the process of network formation, generally a radical polymerization process [1,2].

The common organic solvents such as benzene, toluene and similar, are examples of quite small molecules that lack strongly interacting functionalities, and thus appear to be challenging templates for molecular imprinting procedures. But considering the concern with the potential exposure to these hazardous solvents, especially benzene, a carcinogen, the relevance of developing detection devices is high, and some imprinting attempts were reported. About a decade ago Fu and Finklea [3] studied molecularly imprinted polymers (MIPs) based on ethylene glycol dimethacrylate (EGDMA) as the cross-linker, methacrylic acid (MAA) as the functional monomer, and hydroquinone or phenol as the template. These MIPs were designed to bind benzene, toluene and similar compounds, and the choice of hydroquinone and phenol as templates was made because of their similar shape and the presence of hydroxyl groups capable of engaging in directional hydrogen bonds with appropriate functional monomers. The presence of size/shape selective cavities in the resulting MIPs was proven in vapor phase experiments where the MIPs, integrated in quartz crystal microbalance (QCM) devices, exhibited greater sensitivity and selectivity than the corresponding non-imprinted polymers (NIPs). The thus imprinted cavities have dimensions of a single molecule (several angstroms) and that poses technical difficulties for most of the porosity characterization techniques. A unique insight allowing the elucidation of microscopic behavior such as that related with the microporosity of MIPs was recently achieved by molecular dynamics simulations. Herdes and Sarkisov [4] performed simulations focused on MIPs based on MAA and EGDMA, chloroform as the solvent and templated with pyridine. The adsorption of pyridine, benzene and toluene was simulated so as to verify whether the model was able to recognize pyridine among these similar species and able to exhibit preferential adsorption of toluene over benzene as has been observed experimentally in similar systems [3,5]. The enhancement of adsorption in the MIPs over the NIPs for toluene and benzene found by simulation was comparable with that observed in experiments. Additionally this enhancement had similar values for all three adsorbates of similar size and shape, suggesting that the primary role of pyridine as template was to enhance porosity of MIPs compared to NIPs. Strictly speaking, it appears that these phenomena cannot be ascribed to molecular recognition.

Toluene and *p*-xylene were used themselves by Matsuguchi and Uno as templates of MIPs prepared with methyl methacrylate (MMA) and divinylbenzene (DVB) as cross-linker [6]. No porogen was added. In another study, by Sainz-Gonzalo et al. [7], toluene was the template used in the production of MIPs employing MMA, EDMA and chloroform as porogen and solvent. Less polar monomers like MMA and DVB were considered. However the adequateness of that choice was not discussed by the authors. In our view the less polar monomers should offer less polar micro environments and stronger dispersive interactions which together should favor the formation of recognitive sites. In the referred studies, a certain degree of selectivity was introduced with such small non-functionalized templates, but molecular recognition effects could never be clearly distinguished from macroscopic effects caused by the solvent (surface area, pore size, surface polarity, etc).

Clearly this constitutes an open subject of research and as such we were interested in understanding whether true solvent memory effects can be achieved by molecular imprinting, as well as if they are stable at elevated temperature.

Table 1
Hansen solubility parameter of polymers in poorly hydrogen bonding solvents and corresponding solubility parameters of solvents.

	δ [(MPa)$^{0.5}$]
Polymer	
p-MMA	18.2–26
p-MAA	0
p-Styrene	16–22
p-Styrene (10% MAA)	19.4–21.7
Solvent	
Benzene	18.8
Toluene	18.2
Acetonitrile	24.3

Knowledge about the solubility parameters (δ) for the porogen and the polymer allow an estimate of the heat of mixing per unit volume according to

$$\frac{\Delta H_m}{V} = (\delta_1 - \delta_2)^2 \Phi_1 \Phi_2 \qquad (1)$$

where δ is related to the energy of vaporization of species and Φ its volume fraction in the mixture (species 1 and 2 are assumed to be noninteracting) [8]. A minimum ΔG is obtained when $\delta_1 = \delta_2$ implying a maximum solvation of the growing polymer chains (good solvent). In Table 1 the solubility parameters of the poorly hydrogen bonding solvents used in the study as well as linear model polymers have been listed. A question we would like to address is whether crosslinking of the polymer chains in a good solvent favors solvent memory effects. We have therefore chosen solvents with both low and high parameter values and monomers leading to polymers covering a broad range of parameter values.

A set of 24 polymers were prepared, 12 with low cross-linker content (17%) and 12 with high cross-linker content (83%). Within each sub-set, four different combinations of functional monomer and cross-linker were used, namely MAA/EGDMA, MMA/EGDMA, MAA/DVB and MMA/DVB. Each possible combination was prepared separately in benzene, toluene and acetonitrile. The obtained materials were applied as coatings onto nickel–titanium (Ni–Ti) alloy wires which were incorporated into solid-phase microextraction (SPME) devices and finally tested for their ability to competitively adsorb vapors from the headspace of an aqueous solution containing a few volatile organic compounds.

2. Materials and methods

For the polymer synthesis, methacrylic acid (MAA), methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDMA) and divinyl benzene (DVB) were purchased from Sigma-Aldrich Chemie GmbH (Taufkirchen, Germany). MAA was dried over molecular sieves, and MMA over $MgSO_4$ prior to distillation under reduced pressure. EGDMA was washed consecutively with 10% NaOH, water, and brine, dried over $MgSO_4$, filtered, prior to vacuum distillation. DVB was simply dried over molecular sieves. Dry toluene and acetonitrile over molecular sieves were obtained from Acros Organics (Geel, Belgium) and benzene from Merck (Darmstadt) dried over molecular sieves prior to usage. The initiator azo-bis-isobutyronitrile (AIBN) was purchased from Acros Organics, recrystallized over dry MeOH and dried in a desiccator over P_2O_5.

For the fiber preparation and testing, hydroxy-terminated poly(dimethylsiloxane) (OH-PDMS), benzophenone, trifluoroacetic acid (TFA) and 2-octanone were obtained from Sigma–Aldrich Química (Sintra, Portugal), tetraethoxysilane (TEOS), vinyltriethoxysilane (VTEOS) and dichloromethane were purchased from Fluka (Buchs, Switzerland), and benzene, toluene, benzaldehyde and acetophenone from Merck (Whitehouse Station, NJ, USA). The Ni–Ti alloy wire used (Ni:Ti 56:44, 152 μm) was obtained from