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Detection and Extraction of PFOA and PFOS Using Molecularly Imprinted Polymers

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Abstract

Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are toxic and persistent compounds that result from the production and use of fluoropolymers in products such as Gore-Tex® and Teflon®. Their preclusion of environmental degradation leads to bioaccumulation in humans and animals and poses significant health risks such as decreased fertility and increased risk of cancer. Because of the persistence of these chemicals, it is essential that an effective method be developed for their identification and removal from the environment.

This project proposes the synthesis of novel fluorinated molecularly imprinted polymers (fMIP) (Scheme 3, 5) from two novel crosslinking monomers (Scheme 2). A non-imprinted polymer (NIP) will also be synthesized for comparison of analyte binding efficiency between the two polymers in batch rebinding studies. Quantification of analyte binding to the fMIP for each round of the binding assay will involve derivatization of free PFOA followed by GC/MS analysis.

Methods

The synthesis of the novel fMIP began with the synthesis and characterization of unusual monomer **1**. 4-aminobutanol was coupled with methacrylic acid to give cross-linking monomer **1**. Reactions were run for 48 hours in dichloromethane with DCC and DMAP as activators for the reaction. Work-up was achieved by filtering off the urea byproducts from DCC and washing the organic phase with saturated sodium bicarbonate. Removal of solvent *in vacuo* gave **1** with high purity without further purification (70-80%, 50 mmol). Molecular structure of **1** was confirmed by FTIR and ^{1}H NMR (Figure 1). Coupling of 4-aminobutanol with 2-(trifluoromethyl)acrylic acid was unsuccessful using multiple standard coupling conditions perhaps due to competing 1,4-addition. Polymerization of **1** in the presence of octanoic acid, PFOA, or no imprinting molecule was completed using UV-initiated radical induced precipitation polymerization (STH91 = OA imprinted, STH153 = OA imprinted, STH 155 = PFOA imprinted). Imprinting molecule and other chemical impurities were removed by washing and polymers were isolated by centrifugation. Initial polymer yields were moderate. Polymer was tested on both quartz crystal microbalance (QCM) and chemiresistor (CR) platforms to measure its binding specificity (via selectivity factor α) against aqueous solutions of PFOA, OA, and PFOS (Figure 3, 4). Binding efficiency was measured by imprinting factor (IF), which was calculated as fMIP vs NIP binding affinity, measured by constructing a binding isotherm.
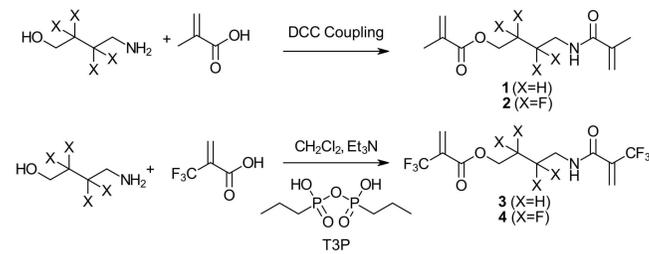
Scheme 1. Synthesis of cross-linking monomers 1-4 for fMIP **1** has been synthesized in 80% yield (50mmol scale)
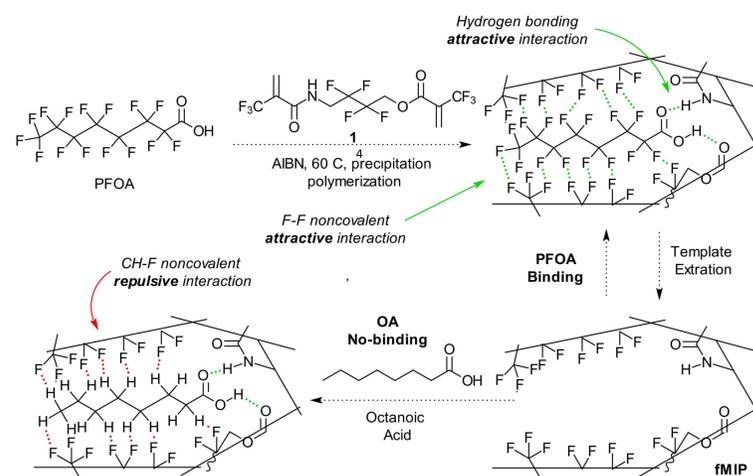
Scheme 3. General fMIP formation scheme

Scheme 4. Polymerization of **1**
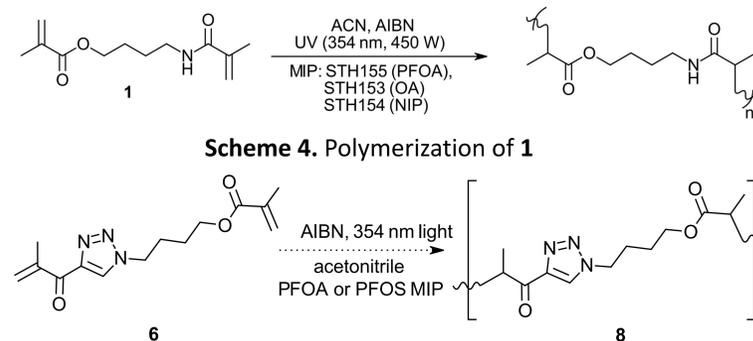
Scheme 5. Proposed polymerization of **6** to form MIP **8**
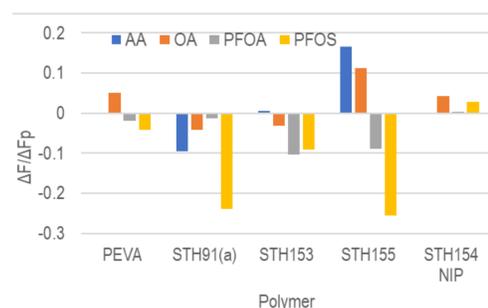
Figure 3. Normalized responses of the coated QCMs relative to mass of each polymer coating (ΔFp is the frequency shift of the polymer and is < 0)
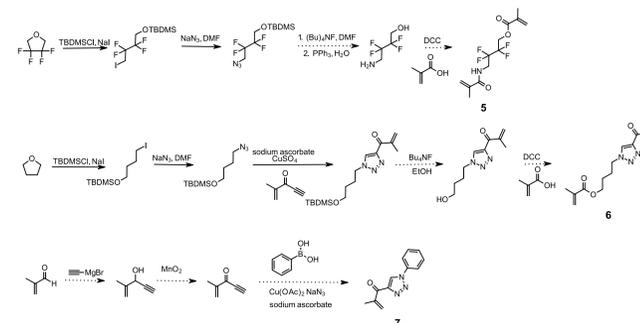
Scheme 2. Present synthesis of crosslinking monomers **5**, **6**, and **7**. Solid lines indicate completed synthesis, dotted lines indicate future work.
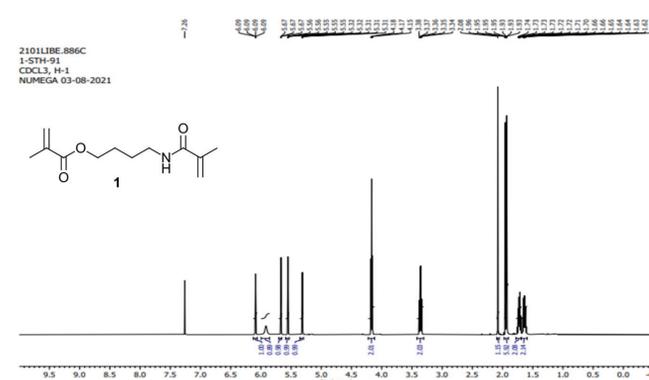
Figure 1. ^{1}H NMR Spectrum monomer **1**
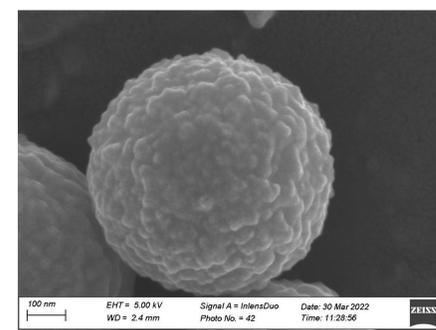
Figure 2. SEM Imaging for monomer **1** NIP
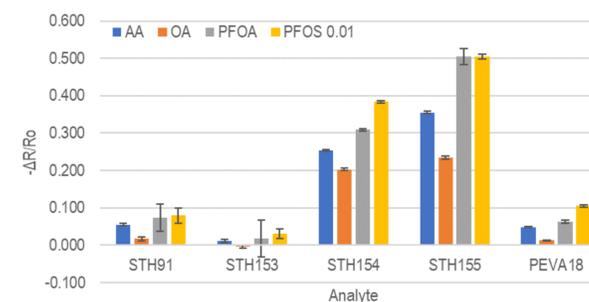
Figure 4. Relative resistance responses from four MIP/NIP blends and PEVA CR, to PFOS at various concentrations. (right, top) CR blends and PEVA to 0.01% of each analyte solution.

Results

- Synthesis and polymerization of **1** completed (OA MIP, PFOA MIP, NIP)
- Significant progress in the synthesis of **5** and **6** completed (Scheme 2).
- Analysis of MIP prepared from **1** with octanoic acid (**P1-OCT**) suggested preferential binding in QCM Sensor.
- Results with chemiresistor were opposite to QCM sensor

Future Work

- Complete synthesis of monomers **5**, **6**, and **7** (Scheme 2).
- Formation of molecularly-imprinted polymers (Scheme 5) against both PFOA and PFOS
- Batch rebinding studies with PFOA and fMIP with HPLC-MS
- Analysis of MIPs using QCM and resistive platforms

Acknowledgments and References

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