

# Studies on the Limitations of MIPs

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## 1. Introduction

Understanding molecularly imprinted polymers (MIP), and probing their limitations as sensors, in the hope of finding solutions has led me to Kyoto University, Uji Campus. There are three known limitations of MIPs, and these issues are preventing these materials from becoming commercially viable sensing systems. These limitations are difficulty of template removal, non-specific analyte binding, and non-homogeneous binding sites resulting to various values of rebinding constants.<sup>1</sup> Clearly, these are consequences of morphologic heterogeneity of the polymer matrix and the polymer surface morphology, and non-uniform dispersion of the template molecule in the polymer. Two studies were performed during my visit to Kyoto University. One was to probe the analyte dispersion in the polymer. This was performed using Raman and IR microscopy techniques. The other study was to test for the feasibility on the use of the Mid-IR FEL for template removal from the polymer matrix to create the MIP. Complexity in template removal using solvent washing, as shown in previous studies has led to this particular investigation.<sup>2</sup>

## 2. Methodology

The MIPs were prepared based on previous work.<sup>2</sup> The template molecule in this study is metronidazole purchased from Sigma-Aldrich, while the monomer used is methacrylic acid also procured from Sigma-Aldrich. The instruments used were a Nano Photon RAMANtouch raman microscope and a JASCO IRT-5000 Irtion Microscope infrared microscope. The mid-IR FEL facility used was the one situated in the Institute of Advanced Energy, Kyoto University, Uji Campus.

## 3. Results and Discussion

### Analyte Dispersion Studies

Inhomogeneous analyte dispersion was observed using Raman and IR microscopies. Images of the surface of the polymer film show pores on the polymer. These pores were observed to have varying degrees of aggregation. Some cavities are also larger than others implying solvent or porogen aggregation. Raman microscope studies have shown the tendency of the template molecules to occupy these cavities left by the porogen. Figure 1a shows the image of the polymer film showing these cavities at 20x magnification. Raman spectroscopic studies of these cavities indicate the presence of the template molecule metronidazole in these pores. Normal modes referring to the  $-\text{NO}_2$  functional group on the imidazolium ring of the metronidazole at around  $1367\text{ cm}^{-1}$  and  $1530\text{ cm}^{-1}$  are clearly observed in the spectrum. Figure 1b, is an example of these Raman spectrum corresponding to the crosshair on the image in Figure 1a.

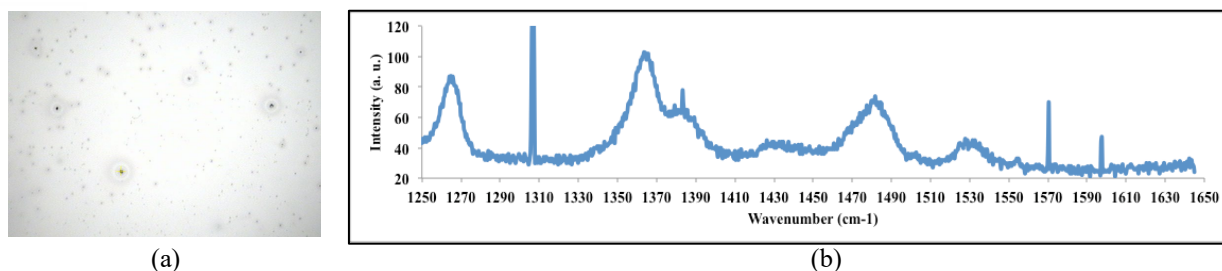


Fig.1. Raman results (a) optical image (b) Raman spectrum of area indicated by the crosshair on the image.

IR studies on the same polymer also exhibited the peak at around  $1367\text{ cm}^{-1}$ . In Figure 2a, the image of the polymer

film is also shown where at the center of the image, at the very pore, the IR spectrum was acquired. This is shown in Figure 2b. The background of the IR spectrum in this case was taken from the part of the polymers outside of the cavities.

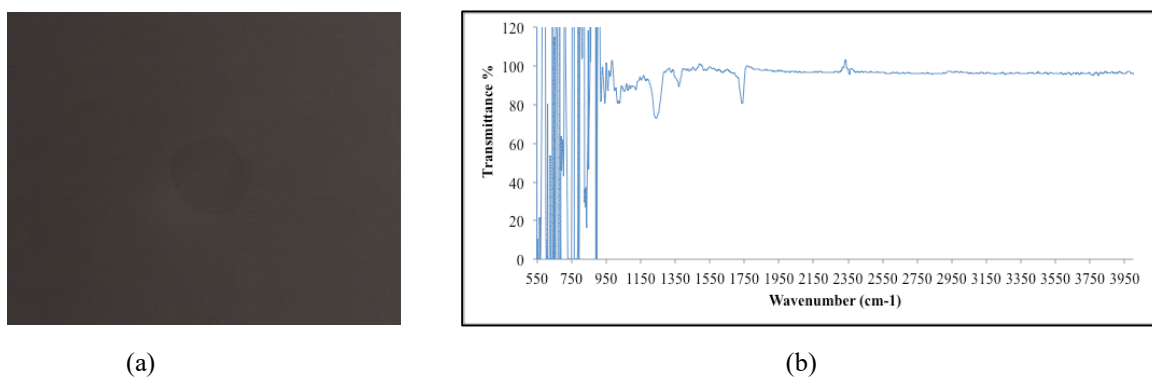


Fig.2. IR results (a) optical image (b) IR spectrum of the cavity.

From these results it can be seen that the dispersion of the analytes are not uniform throughout the polymer. They tend to aggregate based on the spaces occupied by the porogen or solvent material.

### Template Molecule Removal Studies

Subjecting the MIP to the FEL at a wavelength specific to the functional group  $-\text{NO}_2$  was performed in order to test whether this will lead to the removal of the vibrational modes coming from this functional group. This suggests bond breaking of the  $-\text{NO}_2$  moiety, which has implications in terms of template molecule removal from the polymer. Raman results indicate the disappearance of the peaks in consideration as shown in Figure 3. This disappearance is quite obvious particularly when compared to the parts of the MIP not subjected to FEL.

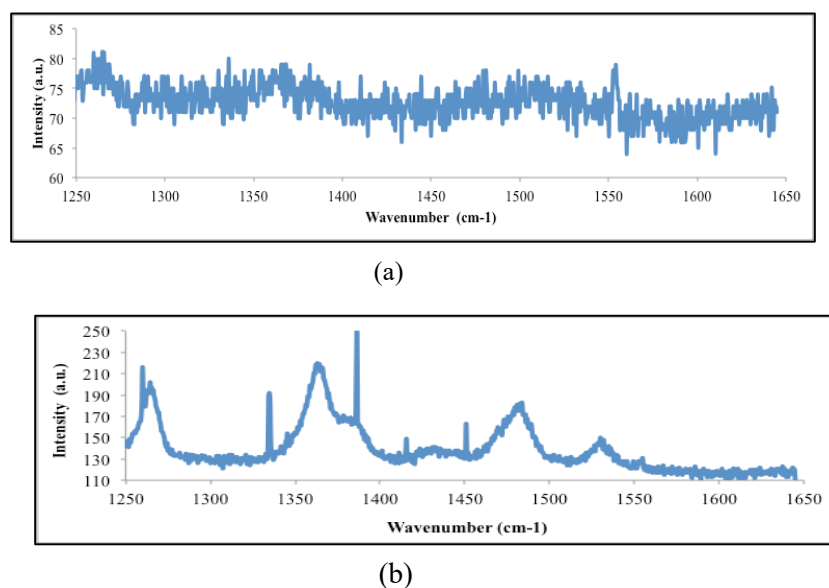


Figure 3. Raman studies of MIP after FEL exposure (a) exposed spot (b) unexposed spot

### Reference

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