

## Molecularly Imprinted Polymer for Recognition of *p*-Xylene in Organic Medium

(Polimer Bercetak Molekul untuk Pengecaman *p*-Xilena dalam Medium Organik)

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### ABSTRACT

*Molecularly imprinted polymer (MIP) based on acrylate monomer was prepared at 80°C for 5 hours using p-xylene and ethylene glycol dimethacrylate (EGDMA) as a template and crosslinking agent, respectively. The polymer obtained was washed with a mixture of acetic acid and methanol (1:4) and dried in the vacuum oven at 80°C. FTIR spectrum showed that all the templates were leached out from polymer during excessive washing and drying stage. The rebinding test result showed that the MIP was bonded with the analyte in the presence of organic solvents as shown by FTIR spectroscopy. The SEM micrograph showed that non-imprinted polymer (NIP) had no cavity as compared to MIP.*

*Keywords: Acrylate; FTIR; molecularly imprinted polymer; organic solvent; p-xylene*

### ABSTRAK

*Polimer bercetak molekul berasaskan monomer akrilat disediakan pada suhu 80°C selama 5 jam dengan menggunakan p-xilena dan etilena glikol dimetakrilat (EGDMA) masing-masing sebagai templat dan agen taut silang. Polimer yang diperolehi dibasuh dengan campuran asid asetik dan metanol (1:4) dan dikeringkan dalam oven vakum pada suhu 80°C. Spektrum FTIR menunjukkan semua templat telah terkeluar semasa peringkat pembasuhan dan pengeringan. Ujian pengikatan semula menunjukkan MIP dapat mengikat analit dengan kehadiran pelarut organik seperti ditunjukkan oleh spektroskopi inframerah. Mikrograf SEM menunjukkan bahawa polimer tidak bercetak molekul (NIP) tidak mempunyai liang kaviti berbanding dengan MIP.*

*Kata kunci: Akrilat; FTIR; pelarut organik; polimer bercetak molekul; p-xilena*

### INTRODUCTION

Molecularly imprinted polymers (MIP) are promising materials that have many applications in chemical and biological fields. It has been reported that the MIP can be applied as sensors, molecule separators, sorbents and column packing materials (Matsuguchi & Uno 2006). Different applications of MIP rely on the specific properties and configuration of the polymers such as polymer beads, monolith and membranes (Huai et al. 2005). The most special properties of MIP is the ability of the polymer for molecular recognition, thermal and chemical retention.

Many researchers have been using various types of MIP for detecting various kinds of analytes in air, aqueous solution and organic medium. Hirayama et al. (2006) reported the recognition of acetaldehyde in aqueous solution by using MIP layer on quartz crystal microbalance (QCM). Dickert and Tortschanoff (1999) studied molecular recognition of polyaromatic hydrocarbon (PAH) in aqueous solution using molecularly imprinted sensor layer.

There are two types of imprinting occurred between the template molecule and functional monomer; non-covalent and covalent imprinting. Generally, in non-covalent imprinting the interaction of analyte molecule in the MIP cavity includes several weak intermolecular forces such as dipolar interaction, hydrogen bond and Van der Waals. Specifically,  $\pi$  -  $\pi$  interaction has been shown to be highly suitable for the selective incorporation of analytes (Dickert & Hayden 1999).

There are a number of measurement methods which can be used for evaluating the analyte in MIP such as fluorescence, ultraviolet-visible absorption, infrared spectroscopy and gas chromatography. Infrared spectroscopy has often been used to elucidate structural features of organic materials. It is a valuable tool in the identification and confirmation of the interaction between template and functional entities before and after polymerization. In this study, the MIP samples were prepared and used to examine the effect of solvent in rebinding capability of the polymer. The FTIR spectroscopy was used as a method to confirm the template and analyte rebinding.

## MATERIALS AND METHODS

## MATERIALS

Materials used in this research were methyl acrylate (Aldrich), ethylene glycol dimethacrylate (EGDMA), benzoyl peroxide and p-xylene (BDH Laboratory), DMF and chloroform (System) and DMSO (Merck). The monomer (methyl acrylate) was first filtered through alumina prior to use to remove the inhibitor.

## PREPARATION OF MIP

The purified monomer (5 ml) was mixed with 2 ml of EGDMA in 25 ml of p-xylene which also acts as template. A total of 85 mg of benzoyl peroxide was added and the mixture was purged with nitrogen gas for 15 minutes to remove dissolved oxygen. The mixture was immersed in water bath at 80°C for 5 hours. In order to remove the template, the product of solid transparent polymer was extracted by Soxhlet apparatus with a mixture of 10% aqueous acetic acid and methanol (1:4) for 2 hours and followed with pure methanol for 2 hours. The white polymer was dried in the vacuum oven at 80°C overnight. The solid polymer was crushed and ground with mortar and pestle. Non-imprinted polymer was used in this study as a control and was prepared in the same way, but without the template.

## REBINDING TEST

The polymer particles (10 – 15 mg) were placed in cotton cloth and soaked in organic solvents containing 50% of p-xylene for 2 hours. The polymer was then removed and analyzed with NICOLET Nexus FTIR spectroscopy.

## RESULTS AND DISCUSSION

## MOLECULARLY IMPRINTED POLYMER (MIP)

MIP usually contains printed sites that can recognize the target molecules. The template used in the imprinting process may not necessary be the analyte itself, but it should be a molecule that is similar either in size or shape. Finklea and Fu (2003) have produced the recognition sites by using hydroquinone and phenol as the template for targeting toluene and benzene molecules. p-xylene is a compound with non polar molecule but the benzene ring is activated by the electron donating group ( $\text{CH}_3$ ). The binding sites inside MIP are printed by a crosslinking of functional monomers and co-monomer with the target molecule.

According to Matsuguchi and Uno (2006), when toluene and p-xylene are used as target molecules, the interaction between analyte and the functional group in the MIP is not hydrogen bonds or ionic interaction. Therefore, in this study, it is expected that the interaction will occur via additional  $\pi$  -  $\pi$  interactions in the imprinted sites. The carbonyl group in methyl acrylate and co-monomer (EGDMA) will interact with active benzene ring in p-xylene via  $\pi$  -  $\pi$  interaction and dipole-induced dipole interaction. Figure 1 shows the schematic illustration of the imprinting process. This is in accordance to what has been reported by Dickert et al. (1998), in which the imprinting of PAHs have been found to be due to the  $\pi$  -  $\pi$  interactions between the aromatic portions of PAHs and certain polymer components.

The powders of MIP samples were analyzed with FTIR spectroscopy to ensure all templates have been removed and the result was supported with  $^1\text{H}$  NMR spectra. Figure 2 shows the FTIR spectra of the MIP obtained before and

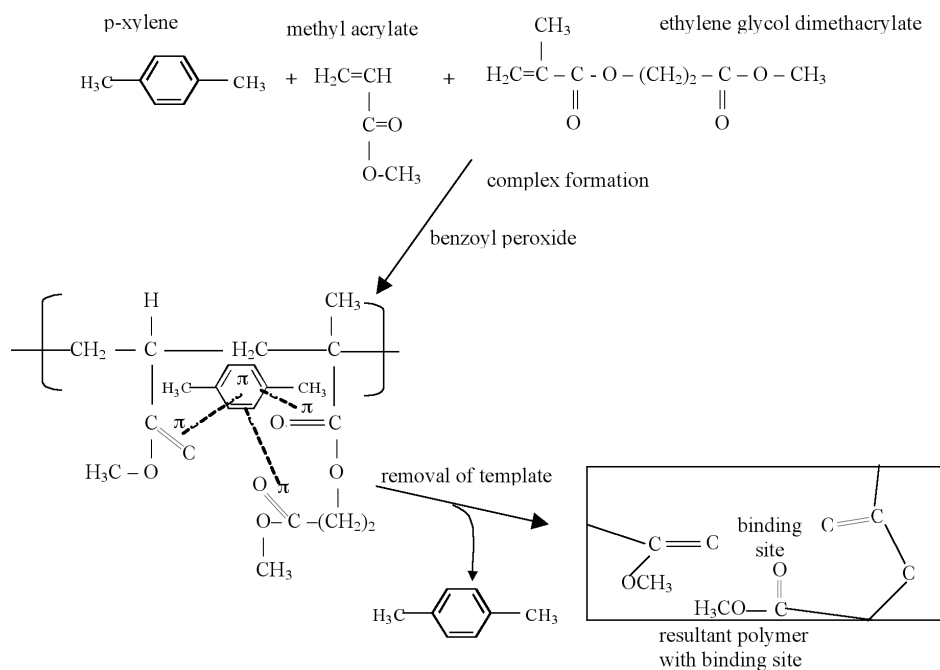


FIGURE 1. The schematic illustration on imprinting process

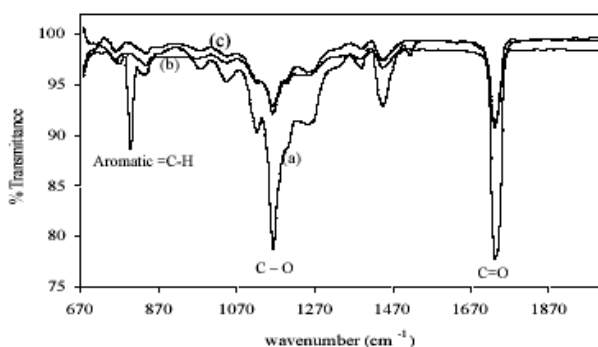


FIGURE 2. FTIR spectra of MIP (a) before and (b) after excessive washing and also (c) non-imprinted polymer

after excessive washing and also the non-imprinted polymer. The  $800 - 780 \text{ cm}^{-1}$  region in the FTIR spectrum of MIP before washing showed strong and sharp peak assigned to out of plane bending of aromatic  $\text{C} - \text{H}$  at para position. This peak indicates the presence of template (p-xylene) in the polymer, but the sharp peak vanished after excessive washing and drying. This observation implied that all template molecules may have leached out. This spectrum is similar to that of the non-imprinted polymer (NIP).

Figure 3 shows the  $^1\text{H}$  NMR spectrum that indicates the removal of template (p-xylene) during washing and drying stage. The spectrum shows that there are four protons which are directly attached to the benzene ring at

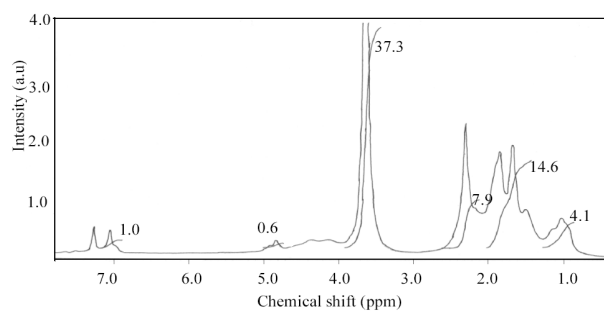


FIGURE 3.  $^1\text{H}$  NMR spectrum on molecularly imprinted polymer

$7.0 \text{ ppm}$  attributed to the presence p-xylene (Pavia et al. 1992; Skoog et al. 1997). This result indicates that the template molecule is not fully leached out. The percentage of remaining p-xylene in MIP has been found to be 5.77%. This value was obtained based on the integral ratio of p-xylene ( $7.0 \text{ ppm}$ ) with tertiary proton ( $1.0 - 1.5 \text{ ppm}$ ) in repeat unit of MIP (Wiles 2002).

The SEM micrograph of the non-imprinted polymer (NIP) and MIP before and after excessive washing is shown in Figure 4. After washing stage, it was observed that the MIP becomes more porous with cavity of smaller size. The SEM micrograph of non-imprinted polymer (NIP) was found to be more compact with rough morphology and no cavity was observed. The compact structure indicates no specific binding sites had been created by template (González et al. 2006).

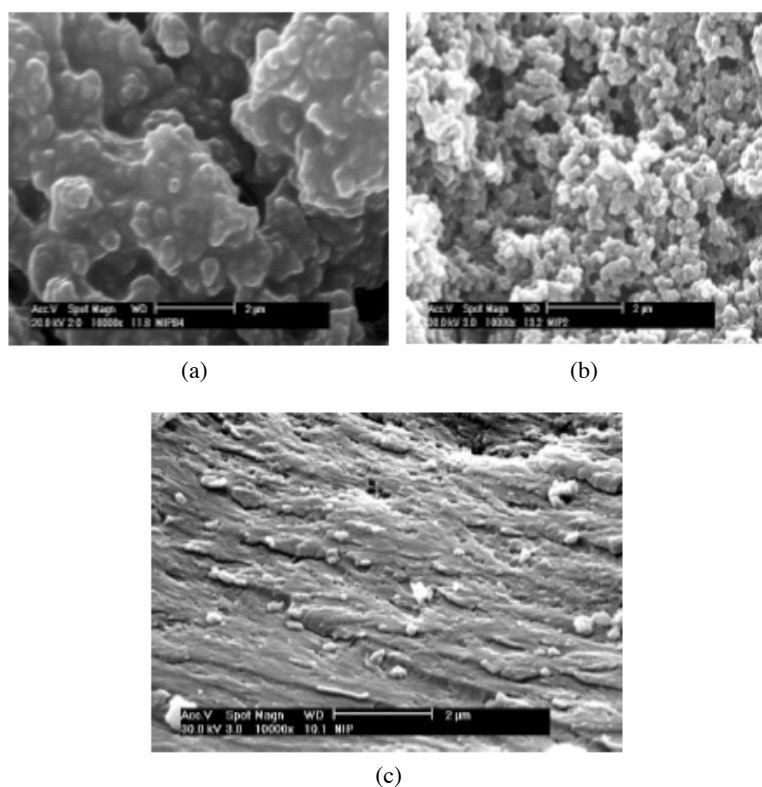


FIGURE 4. The SEM micrographs of MIP (a) before and (b) after excessive washing and (c) non-imprinted polymer

## REBINDING TEST

The rebinding test was carried out to determine whether the printed sites are tightly fitted with the analyte used. Figure 5 shows the FTIR spectra of MIP soaked in analyte with and without several selected solvent namely DMSO, DMF and chloroform. As can be seen, the spectra look quite similar to each other except for the peak that corresponds to the type of solvent used. There are sharp absorption peaks in the 780 – 900  $\text{cm}^{-1}$  region for the MIP soaked in solvent containing analyte, which clearly show the presence of out of plane bending of aromatic =C-H (Pavia et al. 1992, Skoog et al. 1997). However, no corresponding absorption peak was observed for MIP soaked in p-xylene alone. This indicates that solvent plays an important role in the rebinding mechanism. The interaction between

analyte molecule and functional group in MIP is  $\pi - \pi$  interaction (Dickert & Hayden 1999; Takeuchi & Haginaka 1999). However, the interaction is not strong enough so that the analyte evaporates easily.

Determination of transmittance ratio of out of plane bending aromatic =C-H to that of the carbonyl peak revealed that the MIP sample soaked in chloroform (a ratio of 0.25) was of better rebinding capability as compared to the one soaked in DMF (0.20) and DMSO (0.18). This result indicates that, the solvent of lower polarity could interact better with the MIP and so the analyte (p-xylene, 0.07 D) that dissolved in the solvent. The dipole moment of chloroform (1.08 D) is the lowest compared to DMF (3.82 D) and DMSO (3.96 D). Chloroform (1.08 D) and MIP (1.77 D) are of similar polarity and this might explain why the

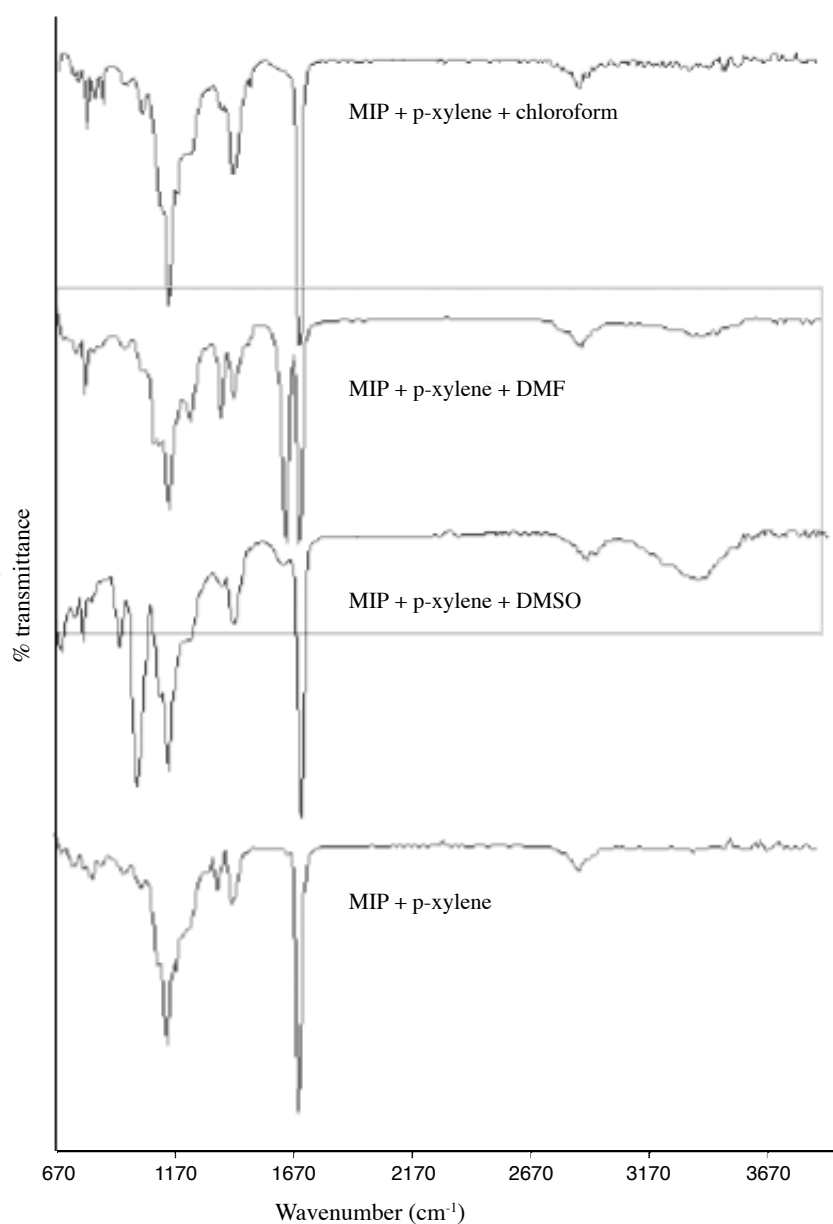


FIGURE 5. FTIR spectra of MIP soaked with p-xylene in several organic solvents

MIP sample soaked in chloroform exhibited better binding capability. Similar observation has also been reported by Huai et al. (2006).

#### CONCLUSIONS

It has been shown that the MIP obtained is capable of rebinding the analyte in the presence of organic solvents namely DMSO, DMF and chloroform. It was found that chloroform helps the most in the rebinding capability of the MIP towards analyte compared to DMSO and DMF. This has been assigned to the lower polarity of the chloroform that enhanced the interaction between MIP and the solvent as well as with the analyte.

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