

Synthesis and characterization of MAA-based molecularly-imprinted polymer (MIP) with D-glucose template

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Abstract. In this study, molecularly-imprinted polymer (MIP) was prepared by using a D-glucose template and a methacrylic acid (MAA) functional monomer. The obtained MIP was characterized using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy techniques to study the template imprinting results. For comparison, similar characterizations were also carried out for the respective non imprinted polymer (NIP). It was found that the polymer has semicrystalline structure, with crystallinity degree of the unleached-polymer, the NIP, and the MIP is 62.40%, 62.97%, and 63.47%, respectively. XRD patterns showed that the intensity peaks increases as D-glucose content decreases. The FTIR spectra of the MIP indicate the detail interaction of template and functional monomer.

1. Introduction

Molecularly imprinting polymerization is a polymerization technique to synthesize molecularly-imprinted polymers (MIPs), which are highly selective polymers containing recognition sites (cavities) that are generated artificially using molecular templates. As the template has a characteristic structure, thus the cavities in a MIP are also specific, i.e. similar with the template. As a result, the MIP can be used to recognize the presence of template molecules. Imprinting of template molecules typically occurs during the polymerization process. After the polymerization process, the template molecules were then removed from the polymer network. This produces recognition sites (cavities) that are similar to the template molecules in size, shape, and function [1-4].

Several advantages of MIPs are easy to synthesize, good physical strength, not easily degradable, excellent stability, resistance to pressure and temperature changes [5-7]. Due to the advantages of MIPs, many researchers have been exploring their diverse applications. Critical reviews have been given on technologies for imprinting recognition for targets in polymers and their incorporation with a number of transducer platforms for the preparation of MIP-based biosensors [8, 9], affinity separations [10, 11], electrochemical sensors [12], and drug delivery [13].



Recently, many different functional monomers have been employed in molecularly imprinting polymerization, as glucose recognition sites, such as (NIPAM-AAm-FPBA) [14], (VAA+AAm+AB+PA) [15], and (4-EPBA+NIPA+HEMA) [16]. However, these monomers were difficult to dimerize. Methacrylic acid (MAA) was proposed as the functional monomer for synthesis of this glucose imprint because MAA was demonstrated the great tendency to dimerize. MAA was considered to interact strongly with the template by providing multiple ways of interaction (H-bond donor, H-bond receptor, dipole-dipole interaction, and van der Waals interactions) [17]. In this study, the main goal was to prepare a MIP with glucose recognition sites and to evaluate its glucose-binding properties for potential applications in glucose sensing. D-glucose ($C_6H_{12}O_6$) was used as a template, methacrylic acid (MAA) as a functional monomer, ethylene glycol dimethacrylate (EGDMA) as a cross-linker, and chloroform as a solvent in synthesizing D-glucose MIP. XRD and FTIR characterizations have been carried out to examine the MIP. Experimental results will be discussed thoroughly.

2. Experimental

2.1. Chemicals and reagents

D-glucose (molar mass of 180.16 g/mol), methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), and benzoyl peroxide (BPO) were purchased from Sigma-Aldrich. All other chemicals and reagents were of the highest available purity. Chloroform, acetonitrile, methanol, acetic acid, and aquabidest were used without further purification.

3. Polymer synthesis

Initially, 29.5 mg D-glucose (template), 0.2 mL methacrylic acid (functional monomer), 0.62 mL EGDMA (cross-linker), and BPO (initiator) were dissolved in 3.1 mL of chloroform. The mixture was then stirred for 20 min. Next, the mixture was uniformly dispersed with sonication for 40 min. The mixture was then cooled for 1 h. to remove oxygen prior starting the polymerization. The polymerization was carried out at 60°C for 21 h. As a control polymer, a non-imprinted polymer was also synthesized using the same procedure without addition of the template molecules. The obtained solid polymer was then crushed into fine powders using a mortar and pestle. After crushing, the template molecules and the unreacted monomers were removed using consecutive solvents (acetonitrile, methanol, acetic acid, and aquabidest), and then dried at 40 °C for 2 h. A detailed procedure of the MIP preparation can be found in Ref. [18]. The scheme of D-glucose MIP formation is portrayed in figure 1. Recognition sites were formed after the template was removed.

4. Characterization

X-ray diffraction patterns were recorded with $CuK\alpha$ radiation, $\lambda = 1.54060 \text{ \AA}$, and 40kV/35mA (Bruker D8 Advance). Crystal structure, crystallite size, and crystallinity degree were calculated from the observed X-ray diffraction patterns.

The FTIR spectra were recorded with an ATR platinum diamond Fourier transform infrared spectroscopy technique (Bruker ATR FTIR Alpha) at the range of 500-4000 cm^{-1} and with 24 scans. The presence of molecular structure of polymer and functional groups of molecules in the polymer network were identified from the recorded FTIR spectra. To confirm the template removal, FTIR spectra of the polymer were taken before and after the template removal process.

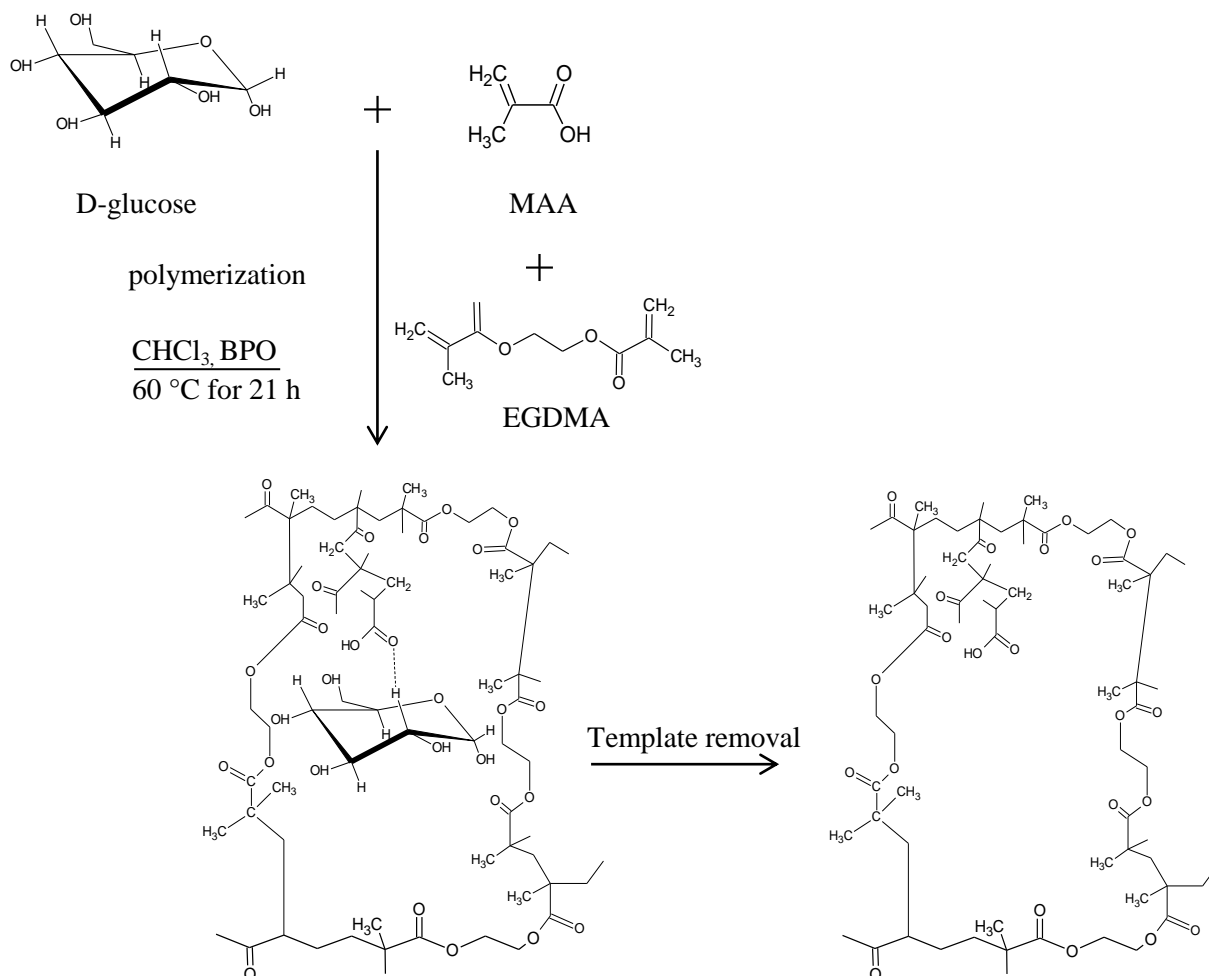


Figure 1. The scheme of D-glucose MIP.

4. Results and discussion

4.1. X-ray diffraction (XRD)

Figure 2 shows the XRD halo patterns of the NIP, MIP, and unleached-polymer in which each halo has a diffraction peak at 16.23°, 16.17°, and 16.15°, respectively. The shift of the diffraction peak to lower 2θ indicates that the interlayer spacing increases [19]. Moreover, the intensity of the diffraction peak decreases implying the presence of interaction between the monomer and template. Analysis of the crystal size in a polymer has been carried out in which the crystal size L is determined by equation (1) [20].

$$L = \frac{K\lambda}{B \cos \theta} \quad (1)$$

where K is the Scherrer constant (usually 0.9), λ is the X-ray's wavelength of, B is the full width at half-maximum (FWHM), and θ is the diffraction peak.

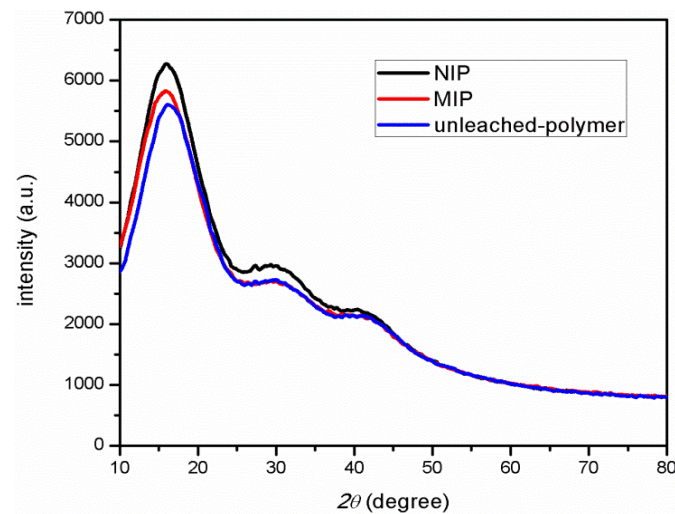


Figure 2. XRD patterns of NIP, unleached-polymer, and MIP.

From inspecting the diffraction peaks of the halo patterns, the obtained FWHMs of NIP, MIP, and unleached-polymer were 6.31° , 6.07° , and 6.63° , respectively. Smaller FWHM suggests that the polymer has better mechanical properties [21, 22] due to greater size of the crystal [23]. Larger crystal size leads to larger degree of crystallinity too [24-26]. The degree of crystallinity of the polymer was determined by assuming that the polymer is composed by a mixture of crystalline and amorphous domains [27, 28]. The crystallinity degree was determined by using equation (2). A summary of measured 2θ , calculated d -spacing, and calculated FWHM, crystal size and crystallinity degree is tabulated in table 1.

$$\text{Crystallinity (\%)} = \left(\frac{F_C}{F_C + F_a} \right) \times 100\% \quad (2)$$

where F_C is the domain of crystal and F_a is the domain of non-crystal.

Table 1. Analyses on XRD patterns of unleached-polymer, MIP, and NIP.

Sample	2θ ($^\circ$)	d -spacing (\AA)	FWHM ($^\circ$)	Crystal Size (\AA)	Crystallinity (%)
Unleached-Polymer	16.15	5.49	6.63	0.21	62.40
MIP	16.17	5.48	6.07	0.23	63.47
NIP	16.23	5.47	6.31	0.22	62.97

The diffraction patterns in figure 2 state qualitatively that the polymers (unleached-polymer, MIP, and NIP) are a mixture of crystal and amorphous phases. The crystallinity degree given in table 1 reveals quantitatively that the polymers are semicrystalline. Since the more the chain bonds, the smaller the degree of crystallinity presents in the polymer [29], then the unleached-polymer, NIP, and MIP have relatively less chain bonds.

4.2. Fourier Transform Infrared (FTIR) Spectra

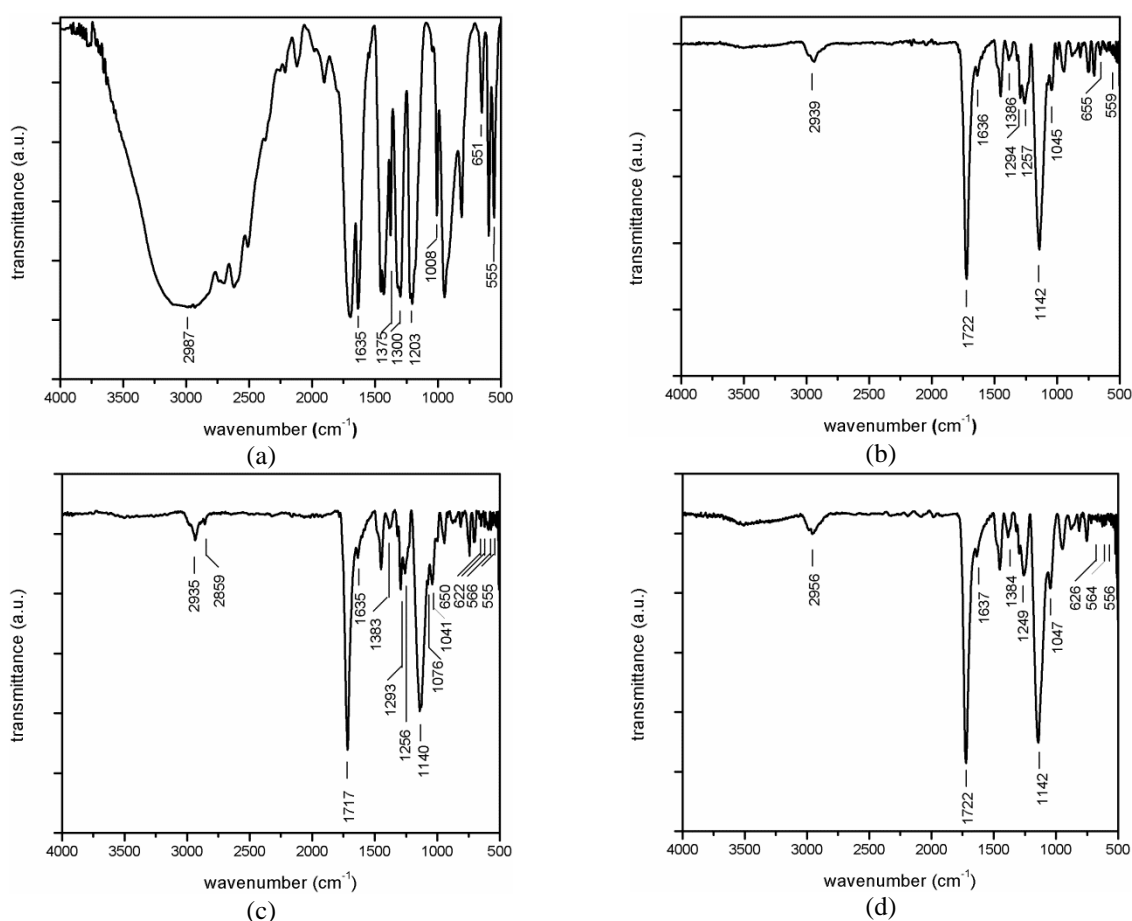


Figure 3. FTIR spectra of (a) MAA, (b) NIP, (c) unleached-polymer, and (d) MIP.

FTIR spectra of MAA, NIP, unleached-polymer, and MIP are shown in figures 3.(a), 3.(b), 3.(c), and 3.(d), respectively. The polymerization process is marked with the lower transmittance intensity of C=C double bond stretching (1635 cm^{-1}) and double bond C=O bending (555 cm^{-1}) in the unleached-polymer (figure 3.(c)) compared to the intensity of the double bond in the MAA monomer (figure 3.(a)). Moreover, in figure 3.(c), the O-H stretching at 2935 cm^{-1} and the O-H bending vibration at 1383 cm^{-1} confirmed the presence of carboxylic acid groups. The presence of two significant peaks at 1717 cm^{-1} (C=O stretching) and 1140 cm^{-1} (C-O stretching) show the existence of EGDMA cross-linker [30-32]. It is also shown the C-O-C asymmetric and symmetric groups at 1256 cm^{-1} and 1041 cm^{-1} , which are derived from the monomer chain. The peak at 2859 cm^{-1} corresponds to the vibration of C-H stretching confirming the presence of aldehyde functional groups. Three characteristic peaks (1076 cm^{-1} , 622 cm^{-1} , and 566 cm^{-1}) are possibly assigned to the absorption of C-O-C, C-O-H and C-C=O of the D-glucose ring [33]. Hence, the FTIR spectrum of MIP showed the presence of aldehyde and carboxylic acid groups. The peaks of unleached-polymer at 1293 cm^{-1} and 650 cm^{-1} are wider and higher than that of NIP. It may relate to the van der Waals interactions between monomer and template. Identification of the peaks of the aldehyde functional groups on the polymer FTIR spectra are shown in table 2. Evidence of D-glucose that has joined the polymer is strengthened with the shift of C-O stretching and O-C=O bending vibration. Vibration peaks of C-O stretching and O-C=O bending in the NIP appears at 1294 cm^{-1} and 655 cm^{-1} , whereas in case of unleached-polymer, it appears at 1293 cm^{-1} and 650 cm^{-1} . The presence of D-glucose seems causes the band shifts to

lower wave numbers. In FTIR spectrum of NIP (figure 3.(b)), aldehyde functional group was not appeared since no additional D-glucose was given during the synthesis of NIP. Therefore, the synthesized NIP is included to the carboxylic acid groups.

Table 2. Identification of the aldehyde functional group on FTIR spectra of polymer.

NIP	Wave Number (cm ⁻¹)		Functional Group
	MIP	Unleached-Polymer	
-	-	2859	C-H stretching vibration
1294	-	1293	C-O stretching vibration
-	-	1076	Asymmetrical C-O-C stretching absorption
655	-	650	O-C=O bending vibration
-	626	622	C-O-H bending absorption
-	564	566	C-C=O bending absorption

By comparing the FTIR spectra of MIP (figure 3.(d)) and unleached-polymer (figure 3.(c)), it can be seen that the washing process have been successfully carried out. This is indicated by the loss of C-H stretching, C-O stretching, C-O-C stretching, and O-C=O bending and the decreasing absorption intensity of C-O-H and C-C=O bending of the MIP after template removal process. This result explains that the washing process is able to reduce the D-glucose concentration significantly.

5. Conclusion

We have successfully synthesized molecularly imprinted polymer (MIP) using D-glucose as the template and MAA as the functional monomer. The XRD patterns of unleached-polymer, MIP, and NIP do not show any structural differences. The presence of D-glucose in the polymer causes the changes of intensity of peaks halo. The FTIR spectrum of polymer (MIP) showed the presence of carboxylic acid and aldehyde functional groups. All of those results show that the D-glucose MIP has been produced successfully.

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