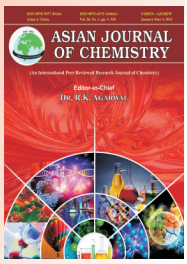
Asian Journal of Chemistry; Vol. 26, No. 8 (2014), 2285-2288

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.15699



Preparation and Characterization of Molecular Imprinted Polymer for Melamine Based on Methacrylamide and 9-Vinylcarbazole as Complexing Monomer

NOR AZAH YUSOF[1,2,*], WONG LING WEI[1], NOR AMIRAH MAAMOR[1] and NORHIDAYAH AZEMAN[2]

[1]Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[2]Institute of Advanced Technology, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

*Corresponding author: Fax: +60 3 89435380; Tel: +60 3 89466782; E-mail: azahy@upm.edu.my

Received: 27 April 2013; *Accepted*: 24 September 2013; *Published online*: 15 April 2014; AJC-15009

Molecular imprinted polymer (MIP) for melamine has been fabricated using precipitation polymerization method using methacrylamide and 9-vinylcarbazole. The molecular imprinted polymer was characterized using Fourier transform infrared spectroscopy, thermo gravimetric analysis, photon cross correlation spectroscopy analysis and scanning electron microscope. Both molecular imprinted polymer (metacrylamide and 9-vinylcarbazole based) have shown reasonable thermal stability. For molecular imprinted polymer of methacrylamide, the average particle size is 158.03 nm while the average particle size molecular imprinted polymer of 9-vinylcarbazole is 298.41 nm. From SEM result, molecular imprinted polymer shows a cloud like structure resulting form aggregated particles.

Keywords: Molecular imprinted polymer, Melamine, Methacrylamide, 9-Vinylcarbazole.

INTRODUCTION

Generally, melamine is described as harmful if swallowed, inhaled or absorbed through the skin. Chronic exposure may cause cancer or reproductive damage eye, skin and respiratory irritant. It is also an irritant when inhaled or in contact with the skin or eyes. Eventhough there are no direct human studies on the effect of melamine, but the data from the animal studies showed that melamine can cause bladder stones. If the melamine further reacts with the cyanuric acid which present in the melamine powder, it will form crystals which give rise to kidney stones. The crystals can block the small tubes in the kidney leading to kidney failure or the worse death. World Health Organization reported that the amount of melamine a person could stand per day without incurring bigger health risk is 0.2 mg per kg of body mass[1].

Molecular imprinted polymer (MIP) has attracted much attention due to their outstanding advantages, such as predetermined recognition ability, stability, relative ease and low cost of preparation and potential application for a wide range of target molecules[2-4]. In most common preparation process, monomers will form a complex with a template through covalent or non-covalent interaction and then join by using a cross-linking agent. After the removal of the template by chemical reaction or extraction, binding sites exposed are complementary to the template in size, shape and position of target molecules and consequently allow its selective uptake[5].

The most widely used technique for preparing MIP is non-covalent imprinting[1,6]. In this process, the complex of template and functional monomer is formed *in situ* by non-covalent interaction, such as hydrogen bonding, electrostatic forces, vander Waals forces, or hydrophobic interactions. There are several advantages of this technique including easy preparation of the template monomer complex, easy removal of the templates from the polymers, fast binding of templates to MIP and it is applicable for a wide range of target molecules[1,7].

In this study, precipitation polymerization has been used to prepare the MIP due to several advantages compared to other polymerization methods. Molecular imprinted polymer prepared through this process is more uniform in size and the process is much easier and less time consuming. The polymers obtained were characterized using thermo gravimetric analysis (TGA), photon cross correlation spectroscopy Analysis (PCSS) and scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FT-IR).

EXPERIMENTAL

Methacrylamide 98 %, 9-vinylcarbazole 98 %, ethylene glycol dimethacrylate 97 % and ethylene glycol 99.5 % from Sigma-Aldrich, benzoyl peroxide 98 % and tetrahydrofuran 99 % from R and M chemical.

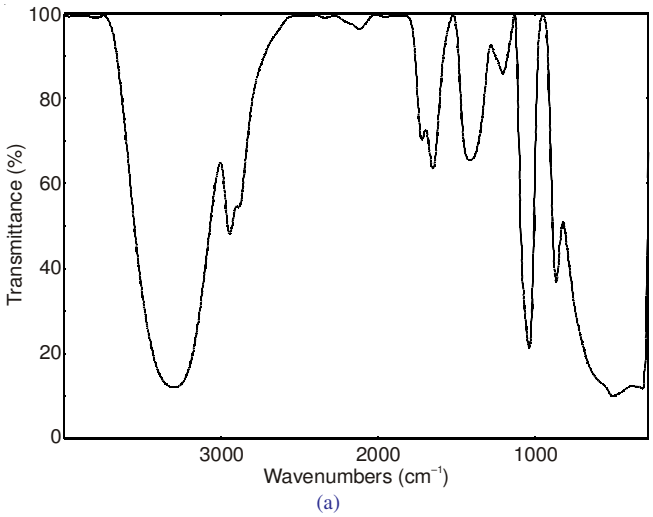
Synthesis of molecular imprinted polymer: In this study, MIP for melamine was prepared through free radical polymerization by using precipitation polymerization. Two types

of monomer were used in this study, which was methacrylamide and 9-vinylcarbazole. Firstly, 0.5 mmol or 0.063 g of melamine was dissolve in 30 mL of ethylene glycol. The mixture was heat up to 120 ºC with constant stirring to dissolve melamine. Later, 2 mmol or 0.170 g of methacrylamide was added to the mixture after it was cool down to room temperature. 10 mmol or 2 mL of cross-linker, ethylene glycol dimethacrylate (EGDMA) was then added to the mixture followed by initiator 10 mg of benzoyl peroxide. The mixture was sonicated for 20 min to get a homogeneous mixture followed by flowing nitrogen gas into the mixture for 5 min. Lastly, the mixture was sealed with aluminium foil and left for overnight in the water bath machine at 90 ºC. After the polymerization process, the polymer was collected by centrifugation at 4000 rpm for 5 min. The MIP was then filtered and washed with distilled water and dry at room temperature.

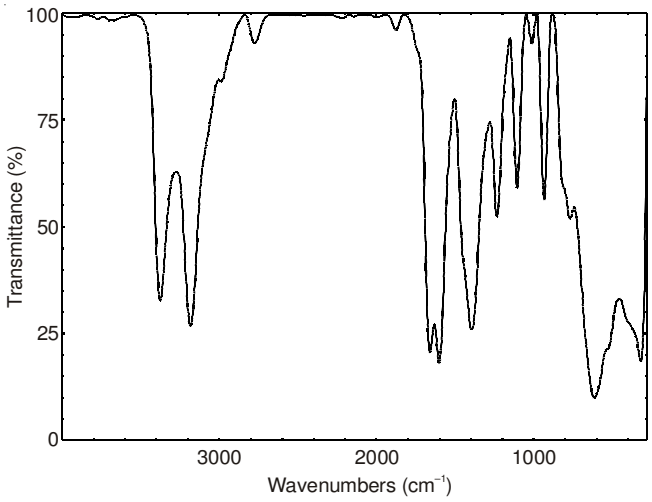
Mean while for 9-vinylcarbazole, 0.5 mmol or 0.063 g of melamine was dissolved in 15 mL of ethylene glycol at 120 ºC with constant stirring. The monomer, 9-vinylcarbazole was dissolved in the 15 mL tetrahydrofuran. This part is carry out due to the fact that in precipitation polymerization all the chemical compounds that involve need to be in the same phase before the polymerization was carry out. The other procedures are just the same as mention in preparation of MIP with methacrylamide.

RESULTS AND DISCUSSION

FT-IR spectrum for MIP prepared from methacrylamide is shown in Fig. 1. From the analysis of the spectrum obtained for MIP of methacrylamide, peaks at 3297, 2943, 1723, 1413, 1207 and 1040 cm^{-1} are observed. A broad peak is observed in the range of 3400-3200 cm^{-1}. Theoretically the vibration at this range belongs to the O-H group due to the hydrogen bonding which is due to interaction between melamine and carbonyl group in methacrylamide. The broad peaks at this range has been observed in our previous work[4,8-11] and also by other researchers[12-14]. The broad and strong band ranging from 3500-3000 cm^{-1} is attributed to the overlapping of O-H and N-H vibration which is consistent with peaks at 1207 and 1040 cm^{-1} assigned to C-O and C-N stretching vibration, thus showing the presence of hydroxyl and amide groups in MIP.



(a)



(b)

Fig. 1. FT-IR Spectra (a) MIP prepared from methacrylamide (b) methacrylamide monomer

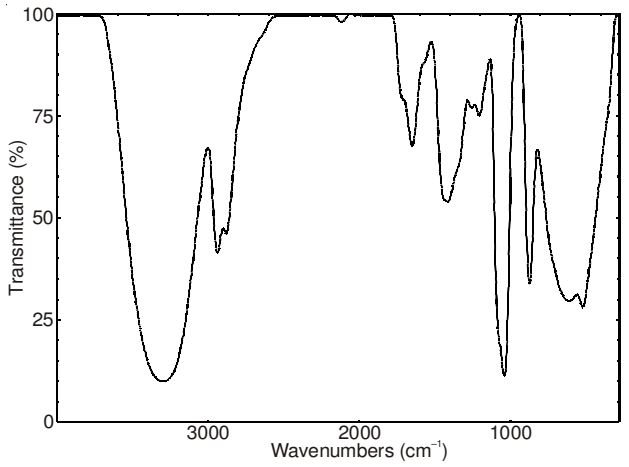
From the MIP spectrum it was observed that C-H stretching vibration occurs at 2943 cm^{-1} which indicate that C-H bond occur when the polymerization occurred. The C=O peaks appear at 1723 cm^{-1} but the peak intensity are not very sharp. This might due to the hydrogen bonds that lower the frequency.

From the analysis of the IR spectra obtained for MIP of 9-vinylcarbazole in Fig. 2, we can observe peaks at 3300, 2940, 1650, 1415, 1206 and 871 cm^{-1}. From the spectra, we can observe a broad absorption band of O-H at 3400-3200 cm^{-1} which is due to the hydrogen bond that forms between the polymerized MIP. This can be proved through observing the spectra of the monomer itself where there is no broad peak occurs at this range. Like the MIP spectra for methacrylamide, the broad band is due to the overlapping of O-H and N-H stretching vibration. Furthermore, the monomer shows splitting pattern in the range of 2000-1000 cm^{-1}, while the MIP shows a broad band in the same region indicating that the monomer have been successfully polymerized.

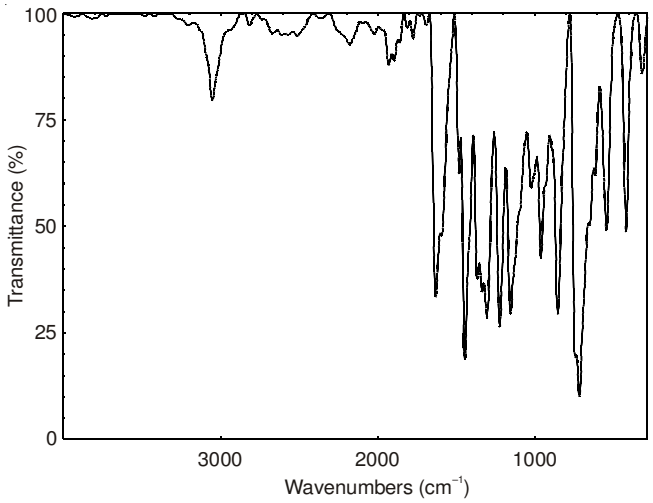
Figs. 3 and 4 show the decomposition curves of MIP of melamine prepared by methacrylamide. From the graph, it is clear that there are two stages of weight loss 79.9 and 18.7 %, respectively. The first stage of weight loss occurred around 190 ºC and complete degradation occur around 450 ºC. Almost the same pattern of degradation occurs for MIP prepared by 9-vinylcarbazole. It can be concluded that the prepared MIP are thermally stable for application with maximum temperature at around 150 ºC.

Photon cross correlation spectroscopy analysis: Particle size analysis of the prepared MIP was carried out using photon cross correlation spectroscopy from Sympatec GmbH. For each of the sample, three readings of the particle size were taken and the average of the particle size was calculated at the end of the analysis. For MIP of methacrylamide, the average particle size is 158.03 nm. Meanwhile the average particle size of MIP using 9-vinylcarbazole is 298.41 nm. The graph of average particle size of MIP of methacrylamide and 9-vinylcarbazole is shown in Figs. 5 and 6.

Scanning electron microscope: Morphology analysis was carried out using the SEM 1450 LEO. Fig. 7 showed the



(a)



(b)

Fig. 2. FT-IR Spectra (a) MIP prepared using 9-vinylcarbazole (b) 9-vinylcarbazole monomer

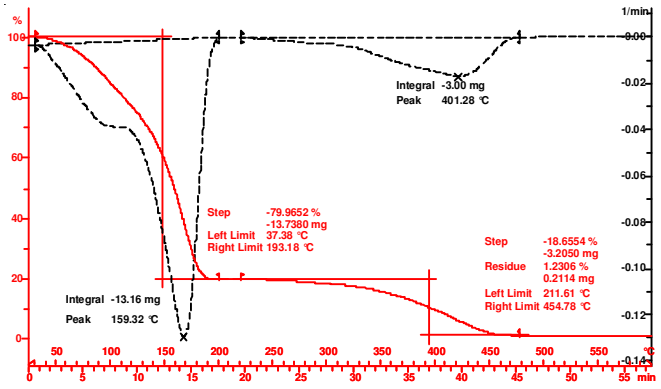


Fig. 3. TGA and DSC graph for MIP synthesize using methacrylamide

image of MIP of melamine prepared from methacrylamide and 9-vinylcarbazole. Both MIP particles seemed to agglomerate which might be due to electrostatic interaction between the particles. However it is clear from the picture that the particles obtained are round in shape and the MIP using methacrylamide has a much smaller size compared to MIP obtained using 9-vinylcarbazole. This support the observation made using particle size analyzer as discussed in previous section.

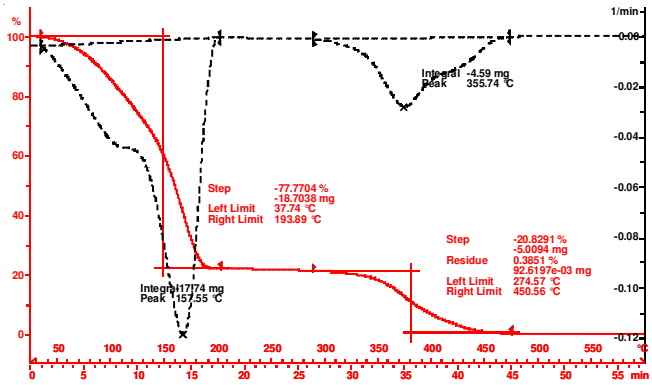


Fig. 4. TGA and DSC graph for MIP synthesize using 9-vinylcarbazole

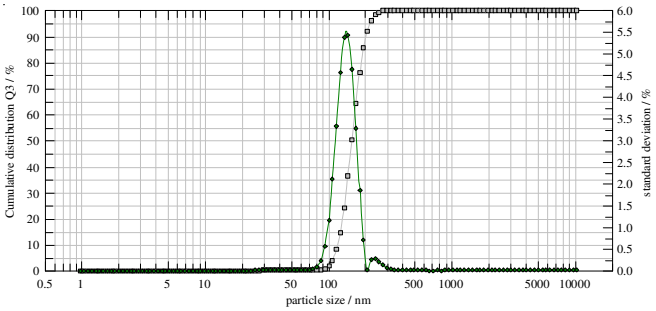


Fig. 5. Graph of average particle size for MIP using methacrylamide

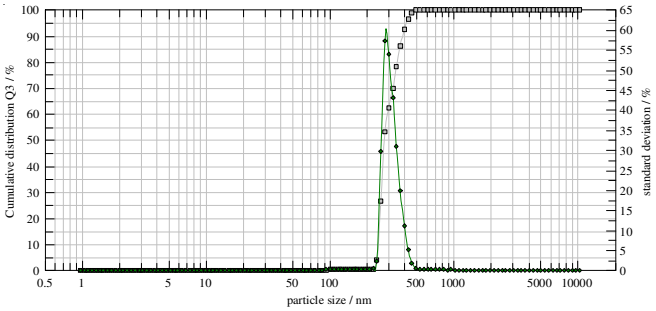
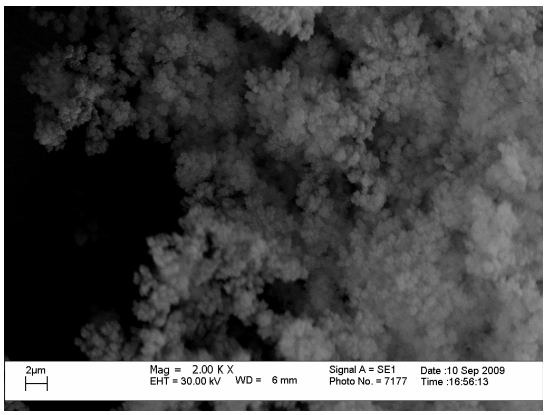


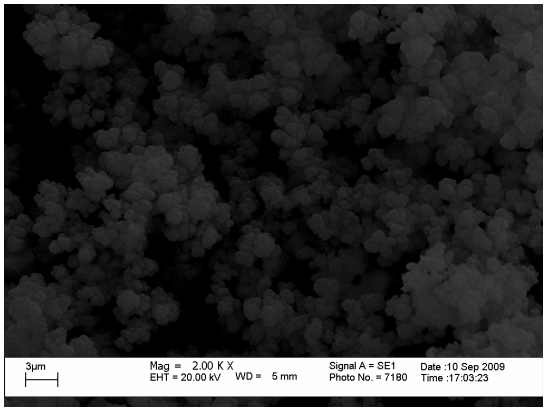
Fig. 6. Graph of average particle size for MIP using 9-vinylcarbazole

Conclusion

The synthesis of molecular imprinted for melamine has outlined many possible approaches. The approaches that been outlined has their own strengths and weakness and the resulting MIP will have the characteristics that might be considered advantageous or problematic. The MIP of methacrylamide and 9-vinylcarbazole for melamine was successfully synthesized for temperature of 90 ºC. Precipitation polymerization was proven to be easier compared to conventional bulk polymerization where the polymer needs to be ground and the MIP that can be used are only in a small amount. The results show that methacrylamide based MIP is thermally more stable and the particle size are smaller compared to the MIP synthesized from 9-vinylcarbazole. Thus methacrylamide are better monomer that can be used to synthesize MIP for melamine.



(a)



(b)

Fig. 7. SEM photograph of MIP synthesized using (a) methacrylamide and (b) 9-vinyl carbazole

REFERENCES

1. H. Yang, W. Zhou, X. Guo, F. Chen, H. Zhao, L. Lin and X. Wang, *Talanta*, **80**, 821 (2009).
2. B. Puschner, R.H. Poppenga, L.J. Lowenstine, M.S. Filigenzi and P.A. Pesavento, *J. Vet. Diagn. Invest.*, **19**, 616 (2007).
3. L. He, Y. Su, Y. Zheng, X. Huang, L. Wu, Y. Liu, Z. Zeng and Z. Chen, *J. Chromatogr. A*, **1216**, 6196 (2009).
4. N.D. Zakaria, N.A. Yusof, J. Haron and A.H. Abdullah, *Int. J. Mol. Sci.*, **10**, 354 (2009).
5. C. He, Y. Long, J. Pan, K. Li and F. Liu, *J. Biochem. Biophys. Methods*, **70**, 133 (2007).
6. C.Y. He, F. Liu, K.A. Li and H.W. Liu, *Anal. Lett.*, **39**, 275 (2006).
7. H.H. Yang, S.Q. Zhang, F. Tan, Z.X. Zhuang and X.R. Wang, *J. Am. Chem. Soc.*, **127**, 1378 (2005).
8. S. Asman, N.A. Yusof, A.H. Abdullah and M.J. Haron, *Molecules*, **17**, 1916 (2012).
9. Nor Dyana Zakaria, *Asian J. Chem.*, **23**, 2456 (2011).
10. S. Asman, *Asian J. Chem.*, **23**, 4786 (2011).
11. N.A. Yusof, *Sains Malaysiana*, **39**, 829 (2010).
12. J. Li, Z. Chen and Y. Li, *Anal. Chim. Acta*, **706**, 255 (2011).
13. J. Yu, C. Zhang, P. Dai and S. Ge, *Anal. Chim. Acta*, **651**, 209 (2009).
14. L. He, Y. Su, Y. Zheng, X. Huang, L. Wu, Y. Liu, Z. Zeng and Z. Chen, *J. Chromatogr. A*, **1216**, 6196 (2009).