

Towards the Development of Processable Molecular Imprinted Polymers

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Declaration

The thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to the final version of my thesis being made available worldwide when deposited in the University's Digital Repository, subject to the provisions of the Copyright Act 1968.

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Azrinawati Mohd Zin

Dedication

This thesis is dedicated to my beloved mom.

Acknowledgements

All my gratitude and praise goes to Allah, the Almighty, for giving me the strength and His blessing to accomplish this work. This thesis would not have been made possible without the great help of the following people.

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Abstract

The synthesis of processable core crosslinked star (CCS) polymers via iniferter and RAFT mediated radical polymerisation has been investigated for their potential application in the field of molecular recognition. Molecular imprinted CCS polymers have potential as delivery systems in solution and, by virtue of its improved processability, may be used to produce thin films with recognition capability for sensing applications.

Synthesis of CCS polymers, consist of poly(ethylene glycol dimethacrylate) core and polystyrene (PS) arms, via the arm-first method proved to be more straightforward than the core-first method. The length of the PS arm could be controlled by varying the ratio of styrene monomer to the iniferter or RAFT agent and polymerisation time. Although lower polydispersity (PDI) of PS arms were produced via RAFT (PDI values between 1.2 – 1.6) compared to those of the iniferter (PDI values between 1.8 – 12.2), synthesis of arm-first CCS polymers via iniferter was more successful than RAFT. Synthesis of CCS polymers via the core-first method was deemed more suitable for the preparation of molecular imprinted CCS since the imprinted core can be accessed for a more comprehensive characterisation and, unlike the CCS via arm-first, there is no contamination from unreacted PS arms.

CCS molecular imprinted polymers (MIPs) were synthesised employing the core-first method. The molecular imprinted microspheric cores were prepared using methacrylic acid as functional monomer and ethylene glycol dimethacrylate as crosslinker at various concentrations of iniferter/RAFT (i.e. 5, 10 and 20 mol % with respect to the total monomer) in the presence of benzylpiperazine (BZP) as template. The large difference in size between the MIPs and their NIP counterparts, which translated to a large difference in the specific surface areas of the microspheres, has implications on the assessment of binding efficiency generally normalised against NIPs with respect to mass. Therefore, the binding efficiency of the MIPs was also expressed with respect to specific surface area. Among the formulations, MIP microspheres prepared with 5% BDDC and MCEBTTC exhibited the best binding performance in their respective series,

with BDDC MIP cores exhibiting higher binding capacity and greater specific binding compared to the RAFT MIPs. Further investigation revealed that the 5%BDDC MIP exhibited higher maximum number of binding sites (N) and greater high affinity binding sites (about 90% and 2.5-fold higher, respectively) as well as stronger affinity towards the BZP template (lower K_d value) compared to those of the 5%RAFT MIP.

Selectivity studies were carried out on the 5%BDDC MIP against 1-phenylpiperazine (PHP) and (1R,2S)-(-)-ephedrine (EPH) having closely related structures to that of BZP. The MIP exhibited better selectivity towards BZP over PHP but better selectivity towards EPH over BZP in the non-competitive binding environment. In the competitive binding environments, the MIP exhibited better selectivity towards BZP over PHP but showed equivalent selectivity towards both BZP and EPH, which was attributed to the smaller size and stronger hydrogen bonding ability of EPH compared to BZP.

Several fractions of CCS MIPs, which differ in their degree of dispersibility in THF, were obtained when polystyrene (PS) arms were grafted to 5%BDDC MIP. Our results show that dispersibility improved with increasing arm length, although it did not necessarily contribute to better binding performance. The presence of PS arms around the imprinted core resulted in a decrease in binding capacity of the CCS MIPs compared to the core precursor in acetonitrile, a bad solvent for the arm. Similar results are obtained in THF, a good solvent for the PS arm. However, contrary to the binding results in acetonitrile where binding capacity seemed to decrease with increasing arm length, greater binding capacity was exhibited by the CCS MIPs with longer arms than those with shorter arms in THF. In this study, we have demonstrated that processability of MIP microspheres can be readily introduced by attaching linear polymeric arms. However, it was difficult to obtain comprehensive binding assessment using the conventional comparison of the MIP with the NIP due to the presence of difference number and/or arm length around the CCS polymers.

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