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Review

Recent applications of molecular imprinted polymers for enantio-selective recognition

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ABSTRACT

Molecular imprinted polymer (MIP) techniques have been increasingly used in a variety of fields including chromatography, sample pretreatment, purification, sensors, drug delivery, and catalysts, etc. MIP is a specific artificial receptor that shows favored affinity to the template molecule. The cavities of the template are produced by carrying out polymerization of a reaction mixture followed by eliminating the template molecules by washing. Various forms of MIP materials have been prepared for diverse applications including irregularly ground particles, regular spherical particles, nanoparticles, monoliths in a stainless steel or capillary column, open tubular layers in capillaries, membranes, surface attached thin layers, and composites, etc. When an enantiomer is used as the template, then the resulting MIP can show capability of enantiomeric recognition between the pair of enantiomers. In this review, progresses in applications of enantio-selective recognition by MIPs will be critically reviewed for the recent period since 2007.

Contents

Abbreviations: ACN, acetonitrile; AFM, atomic force microscopy; AIBN, 2,2′-azobis-isobutyronitrile; APS, ammonium persulfate; AM, acrylamide; AML, amlodipine; ATRP, atom-transfer radical polymerization; BMA, butyl methacrylate; Boc, *tert*-butoxycarbonyl; Boc-Trp, *tert*-butoxycarbonyl tryptophan; BP, brompheniramine; Cbz-L-Trp, carbobenzyloxy-L-tryptophan; CCD, charge-coupled device; CD, cyclodextrin; CDCA, chenodeoxycholic acid; CEC, capillary electrochromatography; CIT, citalopram; CL, chemiluminescence; CP-MAS, cross polaraization magic angle spinning; CP, chlorpheniramine; CS, camphorsulfoamide; CSA, camphorsulfonic acid; CTH, camphor-*p*-tosyl hydrazone; DA, dopamine; DCEE, 2,2′-dichlorodiethylether; DVB, divinylbenzene; DMAEMA, dimethylaminoethyl methacrylate; DMF, dimethyl formamide; DMSO, dimethyl sulfoxide; DPAP, 2,2-dimethoxy-2-phenyl acetophenone; EDMA, ethylene glycol dimethacrylate; ee, enantiomeric excess; EIS, electrochemical impedance spectroscopy; FE-SEM, field emission scanning electron microscopy; Glu, glutamic acid; HEMA, 2-hydroxyethylmethacrylate; IA, itaconic acid; ITO, indium–tin oxide; LC-MIP, liquid crystalline molecular imprinted polymer; LODs, limits of detection; L-THF, L-tetrahydropalmatine; L-Tyr, L-tyrosine; MAA, methacrylic acid; MAC, methyl-(*Z*)-a-*N*-acetamidocinnamate; MAM, 2-methacrylamidopropyl methacrylate; MBA, methyl benzylamine; Me_4Cyclam, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; MIP, molecular imprinted polymer; MIPCM, molecularly imprinted composite membrane; MIP-NOM, molecularly imprinted polymer nanoparticle-on-microspheres; MIP-SG, MIP on silica gel; MMA, methyl methacrylate; MISSM, molecularly imprinted self-supporting membrane; MPS, γ-methacryloylpropyl trimethoxysilane or 3-(trimethoxysilyl) propyl methacrylate; MQD, methacryloyl quinidine; MQN, methacryloyl quinine; *N*, number of theoretical plates; NEA, (1-naphthyl)-ethylamine; NHSG, nonhydrolytic sol–gel; NIP, non-imprinted polymer; NMMO, *N*-methylmorpholine-*N*-oxide; NMP, *N*-methyl pyrrolidone; NOM, nanoparticle-on-microspheres; NP, nanoparticle; o-PD, *o*-phenylenediamine; ONZ, ornidazole; OT, open tubular; PAA, phenylalanine anilide; pCEC, pressurized capillary electrochromatography; PCL-T, polycaprolactone-triol; PDMAEMA, poly(dimethylaminoethyl methacrylate); PEG, polyethyleneglycol; PFPS, perfluoro polymeric surfactant; Phe, phenylalanine; PIP, piperazine; PLOT, porous layer open tubular; PMC, perfluoro(methylcyclohexane); PO-CL, peroxyoxalate chemiluminescence; PPy, polypyrrole; PS, polystyrene; PSf, polysulfone; PVA, poly(vinyl alcohol); PVDF, poly(vinylidene fluoride); R, resolution; RSD, relative standard deviation; RTIL, room temperature ionic liquid; SBSE, stir bar sorptive extraction; SCC, 6-styrylcoumarin-4-carboxylic acid; SDS, sodium dodecyl sulfate; SEM, scanning electron microscopy; SPE, solid phase extraction; SSA, styrenesufonic acid; TCPO, bis(2,4,6-trichlorophenyl) oxalate; TEDMA, triethyleneglycol dimethacrylate; TEMED, *N*,*N*,*N*′*N*′-tetramethylethlenediamine; TFMAA, 2-(trifluoromethyl) acrylic acid; THF, tetrahydrofuran; THP, tetrahydropalmatine; TMC, trimesoyl chloride; TPD, temperature programmed desorption; TRIM, trimethylolpropane trimethacrylate; Trp, tryptophan; Tyr, tyrosine; UDCA, ursodeoxycholic acid; VCC, 6-vinylcoumarin-4-carboxylic acid; VPY, vinylpyridine

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1. Introduction

A MIP reaction mixture is commonly composed of a template, a functional monomer or monomers, a cross-linking monomer, a polymerization initiator, and a porogenic solvent. It is known that complex formation between the template and the functional monomer is very critical for fabrication of MIP, and the complex is surrounded by the surplus cross-linking monomer. A 3-dimensional polymer network with trapped template molecules is formed after completion of polymerization. The template molecules are taken off by exhaustive washing to give empty cavities complementary to the template in size, shape, and molecular interactions. The properties, physical appearance, morphology, and performance of the MIP are determined by polymerization conditions such as choice of functional monomer, cross-linking monomer, and porogen; mixing ratios of them; and reaction temperature and time, etc. The schematic illustration of MIP formation is given in Fig. 1.

There have been numerous review articles regarding MIPs. There have been several review articles on general and extensive introduction of MIPs [1–5]. Some of them are devoted to chiral recognition [2,3]. Reviews on characterization, evaluation and optimization of MIPs have also been published [6–10]. There have been many reviews on capillary electrochromatography (CEC) application of MIPs [11–19], an area of sharply increased attention. Most of them include discussion on enantiomeric separation. Reviews have also been made on specific forms of MIPs such as monoliths [18,19], particles [20–23], and membranes [6,24], etc. MIP has been incorporated in solid phase extraction (SPE), a powerful sample pretreatment/enrichment tool. Thus some reviews concerning SPE coupled with MIP have appeared in the literature [25–27]. The potential usefulness of MIPs in drug delivery has been examined in some review articles [28–30]. Application of MIPs as artificial enzymes or receptors for antibodies has also been reviewed in some articles [31–35]. There have been many reviews for MIP-based sensors [22,36–44] probably owing to their huge potential market. There are also some miscellaneous reviews on drug discovery with MIPs [45], MIPs incorporated with electrically conducting polymer [46], and template removal from the MIP matrix [47].

This review will focus on MIP applications only in enantiomeric recognition. Diverse studies of enantiomeric recognition by MIP methodologies in recent 5 years will be critically discussed. Applications in HPLC, CEC, SPE, sensors, and miscellaneous fields will be included in this review.

2. Enantiomeric recognition in HPLC

2.1. Bulk monolith MIPs

Monolithic MIP stationary phases have been simple and cost-effective compared to other types of MIPs [18,19]. Ou and Zou

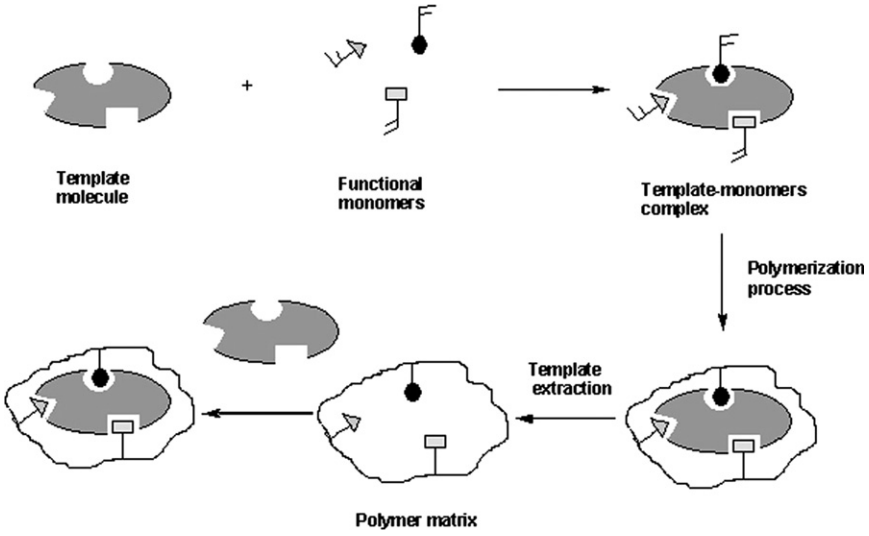

Fig. 1. The schematic illustration of preparation of molecule imprinted polymer (reproduced with permission from Ref. [1]).