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Chiral polymeric membranes: Recent applications and trends

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ABSTRACT

The development and marked growth of chiral compounds is primarily due to the increased demand for pharmaceutical applications, but it has been also extended to other sectors like agrochemicals, food, flavours, fragrances and material science. The pure enantiomers can present higher efficacy, potency and are considered safer than racemate or even achiral compounds. Enantiomerically pure compounds can be obtained by stereoselective synthesis and by post-synthesis separation through chiral separation methodologies. The use of solid polymeric membranes has become promising for enantiomeric separation, due to the low cost and energy consumption, continuous operability and variety of materials. This review aims to present the advances in research of chiral separation, using the enantioseparation technique based on solid polymeric membranes. Theoretical fundamentals and applications of solid polymeric enantioselective membranes in the last ten years is presented. The review also provides relevant information on the performance of this type of membranes for future applications and improvement in chiral separation field.

1. Introduction

Studies involving chiral compounds are increasingly attracting attention in academic research and industry, focusing mainly on their pharmacological, metabolic and toxicological activities in living systems [1-3]. Enantiomers can have different pharmacodynamic and pharmacokinetic properties, due to their three-dimensionality and arrangement in space [4,5]. Chiral recognition occurs when the enantiomers of a chiral molecule selectively interact with the biotarget, a common phenomenon in biological processes, leading enantiomers to present different biological responses (enantioselectivity) [6-9]. In this way, one enantiomer can produce the desired activity, while the other can be inactive or even result in unwanted effects that can be highly toxic [8-12]. On the other hand, due to the specificity in biological response of pure enantiomers, they can present higher efficacy and are considered safer than racemate or ev en achiral compounds, which have been boosted the market of chiral compounds.

The driving factors preferring chiral chemicals increased the demand for enantiomerically pure compounds in the life sciences and other pharmaceutical applications along with agrochemicals industries, flavors, fragrances interest and others in various developing markets. The pharmaceutical industry is the leader in chiral chemicals, comprising 72% of the chiral industry market. The agrochemical industry is also responsible for the growth of this market, it is estimated that in 2023 this industry will grow around 14%. The chemical chiral flavors and fragrances segment also boosted the growth of the chiral compounds market [13,14]. The global chiral chemicals market was valued at USD 50.762.5 million in 2018 an is expected to have a compound annual growth rate of 14% between 2019 and 2025 [14]. Worldwide, the market for chiral chemicals by 2024 is expected to be valued at over $ 96.8 billion [13,14].

Thus, methodologies to achieve enantiomerically pure compounds are essential and need improvements. There is still a wide range of chiral compounds being commercialized as racemate due to the difficulties in

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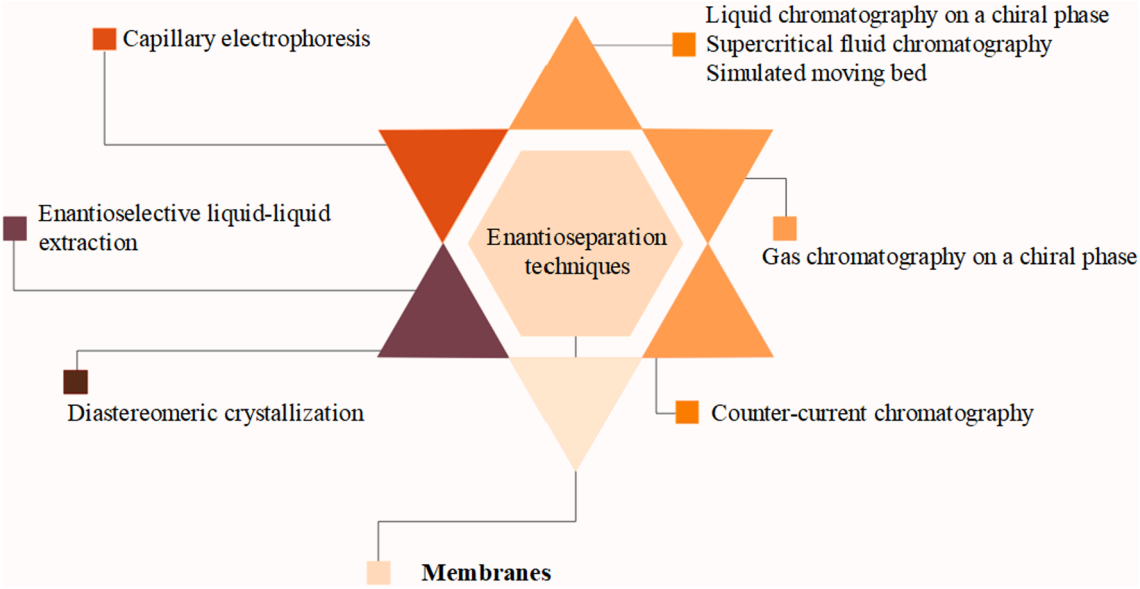

Fig. 1. Schematic of the enantioseparation techniques.

establishing a stereoselective synthesis [15] or a suitable enantioseparation process [16-18]. Enantiomers can be separated by several techniques, including capillary electrophoresis (CE), enantioselective liquid–liquid extraction (ELLE), diastereomeric crystallization (DC), liquid chromatography (LC), supercritical fluid chromatography (SFC), simulated moving bed (SMB), gas chromatography (GC), counter-current chromatography (CCC) and membranes (Fig. 1) [19].

DC or enantioselective precipitation process from the racemic solution, is a convenient and direct method that can be applied on a large scale, being widespread industrially [20,21]. However, it presented some disadvantages due to its limited flexibility, as it requires a conglomerate-forming racemate [22-24]. Chromatographic techniques are directly related to their high versatility in obtaining high enantiomerically pure compounds, resulting from instrumental improvements as well as in the development of highly efficient chiral stationary phases (CSPs) [25-27]. LC is one of the most important techniques for preparative resolution of enantiomers [24,27-30]. Nevertheless, LC presents same disadvantages as the need of large amount of organic solvents, the high cost of the CSPs for preparative scale and the difficulty to use on a large scale [31]. SFC is also emerged as a highly efficient technique for chiral separations, being associated to the advantage of reduced use of organic solvents [32-35]; however, it has the same limitations of LC concerning the cost of the CSPs and the large scale applications [27]. Chiral solid membranes can be a valuable alternative to preparative LC and SFC for industrial production due the simplicity in operation, the reduce use of solvents, which is the requirement for more sustainable methodologies, allied with the lower cost when compared to SFC and LC.

One strategy to reduce solvent use and obtain enantiomers on large scale involves SMB technology. Nevertheless, this technology requires more sophisticated concepts of continuous chromatography [36-38]. CCC, which is based on the liquid–liquid partition principle, is also used for preparative enantioseparation [27]. It has the advantages of low solvent consumption and cost, easy expansion, and complete recoverability. However, its major disadvantage is the low separation efficiency of some chiral selectors [39-41]. Currently, the use of GC with a CSP is very limited because this technique is used for volatile and thermostable compounds, and usually requires lengthy derivatization step [42,43]. ELLE is a technique that needs less solvent consumption than the chromatographic approaches mentioned above and can be applied continuously in several scales. The applied technology is relatively inexpensive, in addition to obtaining high transport rates and high flexibility. However, the main disadvantage is that the selectivity achieved is relatively low, due to the limited number of theoretical plates that are required [44-48]. CE has the advantages of using low amounts of reagents and samples, and presents high efficiency, resolution and simplicity, since chiral columns are not necessary. However, the CE has a disadvantage concerning its low sensitivity, due to the short optical path of detection, resulting from the small dimensions of the separation column [49-53].

Direct enantioselective adsorption by multifunctional materials, as well as membrane-based separation has attracted considerable attention in recent decades, as they are technically suitable for commercial applications [31,54-56]. They can provide high productivity with low emissions and energy use compared to alternative processes, such as crystallization and chromatography [10,56]. Membrane-assisted separation method has appeared as a promising alternative for large-scale chiral separation. The first chiral separation by membrane was successfully demonstrated by Peacock et al. [57], in 1980, which have elicited more researches on this separation technology. Commercial synthetic membranes are generally made of polymeric materials with different physicochemical characteristics. There are also membranes comprising inorganic materials, having a longer useful life and easy cleaning, but they are much more expensive than polymeric ones [58]. Stereoselective polymeric membranes have some advantages over other methods such as: low cost [59], continuous operation mode [60,61], large processing capacity [62] and, in most cases, processing at room temperature [63] and low energy consumption [64], due operational simplicity. The membrane operating units are modular and have smaller physical dimensions than conventional equipment, which guarantees a lower design cost, the membrane modules do not require intensive labor for the operation, which can be moved to more critical areas of operations. However, their successful applications are still restricted to enantioseparation at a small scale, mainly, for few pharmaceuticals and amino acids as exploratory projects. Nevertheless, tremendous efforts have been carried out to develop efficient chiral membranes to achieve enantiomers with high enantiomeric purity [27,65].

This review presents the theoretical background and applications involving polymeric membranes for enantiomeric separation and provide information on the performance of enantioselective membranes for future applications and development of chiral separation.

2. Separation membranes

A general definition of a membrane is an interphase that separates two phases and restricts the transport of various chemical species in a specific

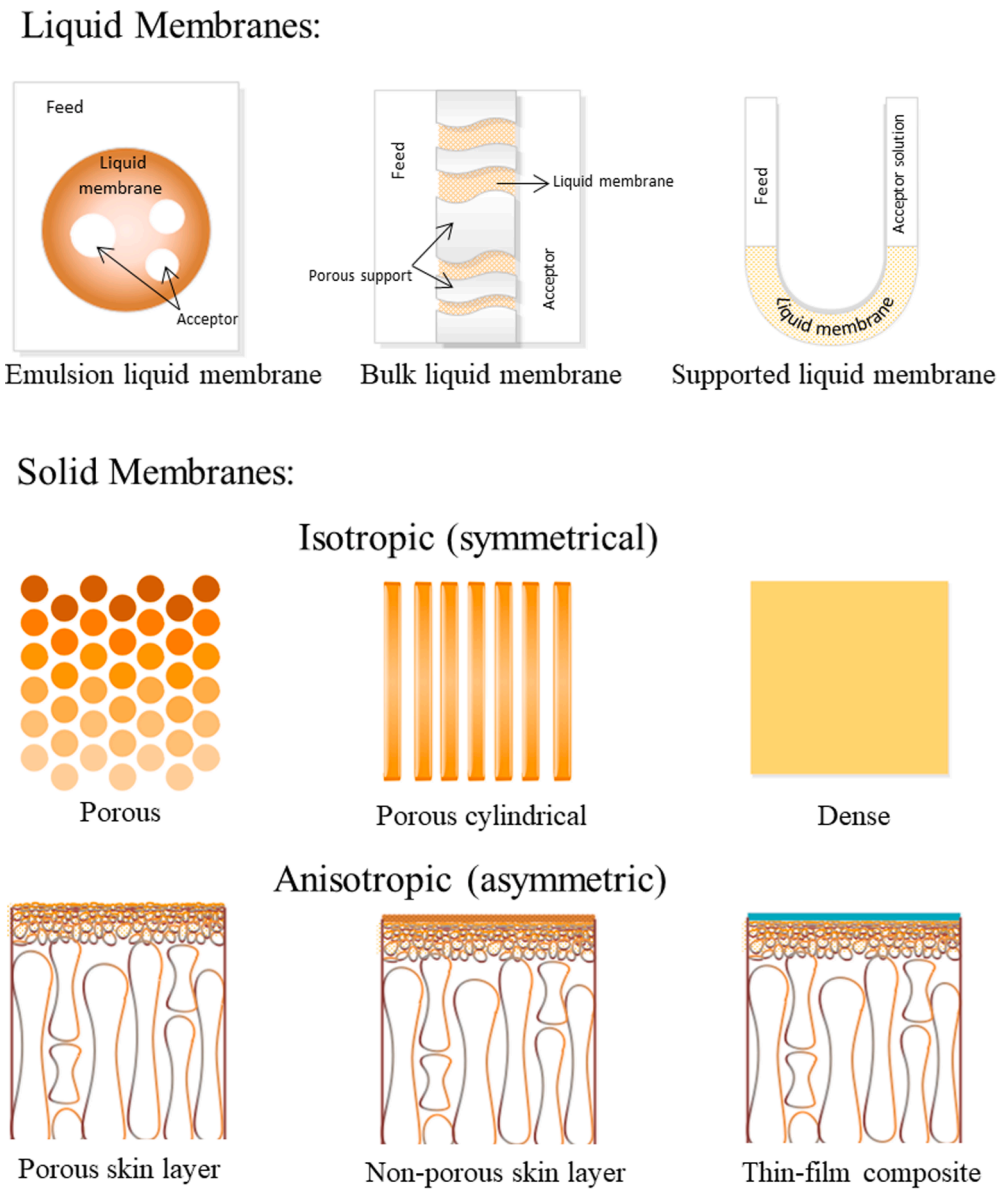

Fig. 2. Schematic presentation of the different types of membrane morphology Adapted from Ref. [25,67].

way [66]. This interface, depending on its chemical composition and physical structure, can be molecularly homogeneous or heterogeneous, containing pores or consisting of some form of layered structure [67]. Membranes can be classified into solid and liquid based on their physical nature [31,68]. A schematic representation of the principal types of membranes comprising different morphologies is presented in Fig. 2.

2.1. Liquid membranes

Liquid membranes are made up of two homogeneous miscible liquids (a feed solution and an acceptor solution), which are spatially separated by a third immiscible liquid, which acts as a membrane between the two liquids [10,25,69]. There are three basic types of liquid membranes: liquid emulsion membrane (ELM) [70,71], bulk liquid membrane (BLM) [72,73], and supported liquid membrane (SLM) [74,75]. The main disadvantage of the liquid membranes is the physicochemical instability of the carrier agent [67]. The advantages of liquid membranes over solid membranes are that molecular diffusion in the liquids, except in super-viscous ones, is faster than that in solids, and the transfer efficiency of the liquid membrane can be increased by means of swirl diffusion in some pertraction methods [76,77]. Despite the liquid membranes advantages, solid membranes are superior in the stability, durability and simplicity of the devices, being considered more suitable for enantio-separation [71].

2.2. Solid membranes

Solid membranes can be subdivided into organic (polymeric) and inorganic (ceramic, metal) membranes [62]. Unlike liquid membranes, solid membranes have good chemical, mechanical and thermal stability [65,78]. Solid membranes are characterized by parameters concerning their morphological nature and their transport properties. Accordingly, the solid polymeric membranes can be classified as dense or porous, and may be isotropic (symmetrical) or anisotropic (asymmetric) [58,67].

Anisotropic membranes consist of a thin polymeric film surface (skin-layer) containing pores with nanometric diameters, supported by a thicker porous layer with much larger diameters, on the order of microns. The polymeric film surface and its substructure can be formed in a single process or separately. In composite membranes, the thin film surface and the porous layer are generally made of different polymers. Isotropic

membranes can be porous or dense. Fig. 2 shows the two forms for porous isotropic membrane, in one type the pore size along the cross section is monodisperse. In another type of membrane it has cylindrical pores of the same diameter on both surfaces, but their application is limited, due to the fact that they get easily fouled, reducing selectivity [67,79].

In order to transport the penetrant across the membrane, driving force must acting on it, i.e. a gradient of chemical potential that can be expressed in terms of pressure, concentration and/or electric potential gradient [80].

The solid membranes are therefore categorized according to their mechanisms. The type of resolution mechanism in solid polymeric membranes depends on the dominant transport process. Transport can occur by convective mechanism or by diffusion, depending on the type of driving force used and the morphology of the membrane [58]. In processes that employ porous membranes, the selective capacity is related to the size of the species present and the size of the membrane pores. For porous membranes, the transport of species across the membrane can occur by convective and diffusive processes. The selective capacity in processes that use dense membranes depends on the diffusion of species across the membrane and the affinity of different species for the membrane material, the first stage being of kinetic nature and the other stage of thermodynamic nature [58,62,67].

In short, in the dense membranes, the main mechanism is the solution-diffusion model. In porous (asymmetric) membranes, the predominant model is the flow through pores. In dense and defect-free membranes, the species will permeate through the free volumes available in the polymer matrix. These free volumes have molecular dimensions, which makes dense membranes the most suitable for separating gases and vapors. The solution-diffusion model is based on three steps: 1) the sorption of species present on the membrane surface, on the higher concentration/pressure side (feed); 2) the diffusion of species along the thickness of the membrane, under the action of the potential gradient; 3) the desorption of species on the lower concentration/pressure side (permeate) [81]. In the solution diffusion mechanism, the flux through the polymer is proportional to a chemical potential gradient. This solution-diffusion mechanism can be described for enantiomers by [82]:

$$P_e = D_e.S_e \tag{1}$$

where, P is the permeability, S the sorption coefficient and D the diffusion coefficient. The subscript “e” indicates the D or L enantiomer, respectively.

The partition coefficient is defined as the ratio between the equilibrium membrane concentration (C_m) and the concentration in the bulk liquid (C_l), according to the following equation:

$$S=\frac{C_m}{C_l} \tag{2}$$

The basis of the solution-diffusion mechanism is diffusion, i.e., a mass transfer process due to the existence of a concentration gradient. In 1855, Fick formulated his results with the equation (Fick’s law)[67]:

$$J_i = -D_i\frac{dc_i}{dx} \tag{3}$$

where D_i is the diffusivity coefficient, J_i is the flux ($g.cm^{-2}.s^{-1}$) and dc_i/dx is the concentration gradient of component i.

In porous membranes, permeants are transported by pressure-driven convective flow through pores. The so-called pore-flow model can be described by Darcy’s law, according to the equation [67]:

$$J_i = K'c_i\frac{dp}{dx} \tag{4}$$

where dp/dx is the pressure gradient in the porous medium, c_i is the concentration of component i and K is a coefficient that reflects the nature of the medium. Darcy’s law comprises pores in the range of 5–10 Å in diameter.

Separation occurs through interaction with the inner membrane surface, however, the transport is not an intrinsic property of the membrane material and permeability in porous membranes is not normalized by membrane thickness [10,62]. The transport mechanism of dense membranes is an intrinsic property of the membrane material, whereas in porous membranes it depends on morphology, in addition to the membrane material.

Integral asymmetric membranes have two important characteristics that influence their permeation properties and selectivity for use in separation processes: the pores and/or surface defects, and the thin thickness of the surface layer. The transport mechanism in asymmetric membranes can be described by the Knudsen model, a pore flow model based on the mobility of the permeant and the average pore size [67,83]. The permeation rate of components through a membrane is inversely proportional to its thickness. Consequently, asymmetric membranes have higher permeability when compared to symmetric porous ones, since permeant transport is controlled by the dense surface layer.

Unlike conventional membrane separation, the enantioseparation will only occur in a chiral environment, therefore, it is necessary to introduce chirality into the polymeric membrane, either by intrinsic chirality of the polymers, or by adding chiral selectors, which will be described below.

2.3. Performance parameters of enantioseparation by solid membranes

To report the chiral separation process in enantioselective membranes, it is important to introduce membrane performance parameters for enantioseparation and verify which ones have proven to be effective for enantiomeric separations. The performance of membranes can be evaluated by permeating solutions of racemates, and it can be expressed by two more important parameters: permeability and selectivity [10,62]. For application on an industrial scale, membranes with high permeability and selectivity are expected [83].

The permeability is defined as the normalized flux in relation to the difference in concentration and thickness of the membrane. This parameter is, therefore, an intrinsic property of the membrane, being required by:

$$P = \frac{J.x}{C_i - C_f} \tag{5}$$

where, P is the permeation coefficient, J is the flux, x is the membrane thickness and C_i and C_f refer to the feed phase and stripping phase concentrations, respectively.

The flux of the enantiomers can be calculated by the following equation:

$$J = \frac{\Delta C.V}{\Delta t.A} \tag{6}$$

where, ΔC is the change in concentration, Δt is the permeation time, V is the volume and A is the effective membrane area.

The selectivity of a membrane over a mixture is usually expressed by retention (R) or separation factor (α). The solute is partially or fully retained as solvent molecules pass through the membrane [62].

Retention is given by:

$$R = \frac{c_f - c_p}{c_f} = 1 - \frac{c_p}{c_f} \tag{7}$$

where, C_p and C_f are concentrations of solute in permeant and feed, respectively. The R-value ranges from 0% to 100% (complete solute retention; i.e. an “ideal” semi-permeable membrane).

Membrane selectivity for racemates is usually expressed in terms of the α [84].

$$\alpha = \frac{c_p^D/c_p^L}{c_f^D/c_f^L} \tag{8}$$

If the concentrations on the feed side, c_f^R and c_f^S, are the same, the separation factor (α) can be calculated from the following equation:

$$\alpha = c_p^D / c_p^L \tag{9}$$

where, c_p^R and c_p^S are concentrations of D- and L-enantiomers in permeant.

So, if the permeation rate of the D-enantiomer across the membrane is greater than that of the L-enantiomer, the separation factor is denoted as $\alpha_{(D/L)}$; if the L-enantiomer permeates preferentially, then the separation factor is given by $\alpha_{(L/D)}$. If $\alpha_{(D/L)} = \alpha_{(L/D)} = 1$, no separation is achieved.

The enantioselectivity of membranes is also expressed by the preferential transport of one of the enantiomers over its analogue through membrane permeation and is calculated in terms of the percent enantiomeric excess (*e.e.*) of the permeates. The *e.e.* value is defined as the ratio of the concentration difference and the sum of the concentration of both enantiomers in the separation phase [10,84]:

$$e.e. = \frac{c_p^D - c_p^L}{c_p^D + c_p^L} \times 100 \tag{10}$$

or

$$e.e. = \frac{c_p^L - c_p^D}{c_p^L + c_p^D} \times 100 \tag{11}$$

3. Chiral polymeric membranes for enantioseparation

Enantioselective polymeric membranes allow a specific enantiomer to be adsorbed or diffused in a polymeric matrix [85-87]. They act as selective barriers in the resolution process and, preferably, transport an enantiomer due to the stereospecific interaction between it and the chiral recognition sites [88,89]. The chiral recognition occurs through several types of interactions, including van der Waals, hydrophobic, hydrogen bond, dipole–dipole, and steric effects [55]. The enantioselectivity of the membrane occurs through chiral recognition sites, such as chiral side chains, chiral backbones, and chiral selectors immobilized on polymeric membranes [83,84]. A variety of chiral selectors have been used in polymeric membranes, including derivatives of tartaric acid [90], cyclodextrins [63,91,92], amino acids [93], DNA [94,95], bovine serum albumin (BSA)[95,96], Pirkle type selectors [97], among others [56,98]. Chiral selectors can be immobilized on the pore surface or in the polymeric matrix by impregnation [99,100], grafting [101-104], transesterification [105] or molecular imprinting [106-108].

Chiral polymeric membranes can also be obtained by polymerizing chiral monomers or use natural polymeric material [64,109]. Polysaccharides are the most used natural polymeric materials, as chitosan [110-113] and cellulose [111,114]. Sodium alginate [113,114], poly (substituted acetylene)[115], poly (amino acids) as polyglutamates [113,114,116], and also lipids, such as polymerized diacetylene liposomes [117], among others, have also been used in membrane design and development.

Enantioselective polymeric membranes can be divided into two categories: diffusion-selective membranes and sorption-selective membranes [21,56].

Diffusion-selective membranes are usually made without adding a chiral selector, when the polymeric material is intrinsically chiral [118]. Chiral polymers normally bind to a reduced amount of enantiomers as they lack one-to-one interactions between the chiral recognition sites and enantiomers. The racemic penetrants can diffuse through the free volume between chains of the polymer matrix, reducing the effectiveness of the molecular interactions, what limits highly efficient chiral separation. The main disadvantage of these membranes is the proportionality of permeability and selectivity which is generally inverse [82,113]. However, many intrinsically chiral polymeric materials are described for ena ntioseparation by membrane. For example, Miao et al. [63] reported a dopamine-modified polysulfone (PSf) membrane prepared via mussel-inspired chemistry, which was subjected to polymerization in situ on the membrane substrate, and β-cyclodextrin (β-CD) was used as a chiral selector incorporated in the surface of the membrane. The pore size decreased with the deposition of β-CD and the narrower pores hinder non-enantioselective diffusion and increase the enantioselectivity at the expense of lower permeability, obtaining a diffusion-selective membrane with high enantioselectivity and low permeability. The *e.e.* value of the membrane for tryptophan (Trp) was close to 3.2% with the feed solution of racemic Trp of 5×10^{-5} mol/L and the operating pressure was 0.1 MPa. [63]. There is a great difficulty in obtaining diffusion-selective membranes with high enantioselectivity and high permeability. To solve this problem, studies indicate that dissolution selectivity should be added to diffusion selectivity, i.e. pendent groups can be introduced into the chiral membrane, which can interact more effectively during permeation, increasing the selectivity of dissolution [115,119]. Recently, Zang et al. [120] managed to simultaneously improve the permeability and selectivity of a chiral helical membrane of substituted poly (phenylacetylene) synthesized with the introduction of aldehyde groups by deprotection of dioxolane groups. They obtained an increase in both enantioselectivity and permeability for the membrane containing aldehyde groups. The simultaneous increase in permeability and selectivity was due to the facilitated transport caused by the enantioselective reaction of the aldehyde groups on the membrane with the amino groups in the permeant during permeation [120].

Regarding the sorption-selective membranes, they usually require a porous support and chiral selectors, having less diffusion-selective but show highly sorption-selective [121]. Unlike diffusion-selective membranes, sorption-selective membranes have stronger binding affinity between chiral recognition sites and enantiomers, allowing simultaneously high flow and enantioselectivity [82,83].

Since the review paper by Higuchi et al. [56], in 2010, about polymeric membranes, many improvements and applications have been reported concerning natural and synthetic polymers used in adsorption and membranes diffusion as well as the development of new molecularly-imprinted polymers (MIP). A review article by Moein [122], in 2021, presents an overview of the advances in the preparation and application of MIPs for the separation of chiral compounds in different analytical approaches, mainly in the sensor field. Some MIP applications based on membrane were also described [122]. Recently, Zhao Y. et al. [123] published a general review of the resolution of chiral molecules by chromatography and techniques based on membrane enantioseparation pointing out the intrinsic features of membrane-based for chiral resolution for large-scale industrial applications. However, since 2010 no systematic revision has been published about polymeric membranes for chiral separation. Herein, we summarized the development, applications and results of chiral polymeric membrane in the last ten years (Table 1).

3.1. Synthetic and natural polymers

This topic summarizes some examples of recent work with synthetic and natural polymeric materials used in membranes for enantioseparation. Yuan et al. [114] developed solid chiral membranes comprising natural polymers of cellulose, sodium alginate and hydroxypropyl-β-CD to discriminate the enantiomers of mandelic acid or *p*-hydroxy phenylglycine. When the feed concentrations solutions for the cellulose, sodium alginate, and hydroxypropyl-β-CD membranes were 0.5 mg/mL of mandelic acid, 0.8 mg/mL of p-hydroxy phenylglycine and 0.5 mg/mL of hydroxy phenylglycine the *e.e.* of 89.1 %, 42.6 % and 59.1 % were obtained, respectively. Higher concentrations of the racemates resulted in decreased enantioselectivity of the membrane. A mechanism for chiral selection of membranes in three stages, based on “adsorption - association – diffusion”, has been suggested [114].

In another study, Meng et al. [92] developed new membranes composed of L-glutamic-graphene oxide (Glu-GO), using cellulose

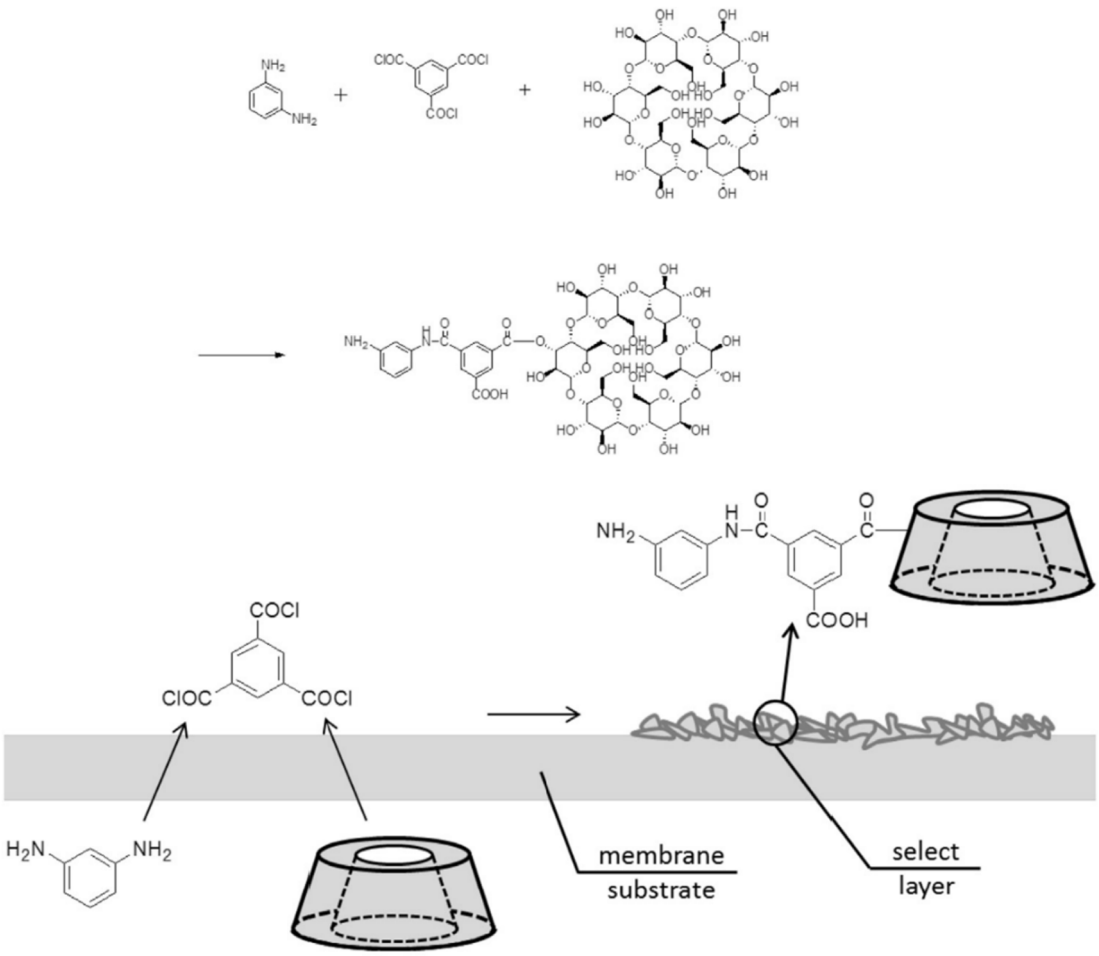

Figure 2 Schematic diagram of interfacial polymerization.

Fig. 3. Schematic diagram of IP (Reprint permission from Ref.[128]).

acetate membranes as a support layer, to evaluate the enantioseparation performance of the membranes for 3,4-dihydroxyphenylalanine (D,L-dopa). The Glu-GO membranes exhibit a great permselectivity for D,L-DOPA and the maximum selectivity was higher than 2.0. More recently, they managed to improve the enantioselectivity of the membranes using natural polymers based on polypeptides, reaching 1–2 orders of magnitude compared to the common chiral separation membranes. They used poly (L-glutamic acid sodium), PLGA, on the surface of GO leaves, the combination of GO-based materials and polypeptides can offer unusual control in the selectivity and flux of the corresponding composite membranes, achieved by regulating the interlayer spacing between the GO sheets and achieving composite membranes of the facilitated transport with high flux and high selectivity. The maximum α values was up to 2.8, which is higher than the membranes reported previously [92,124].

Takara et al. [110] prepared chiral membranes of chitosan by a technique of solvent casting/evaporation in order to study the enantiosorption process of L- and D-tyrosine (Tyr) in aqueous solutions. From computational calculations, they were able to evaluate the affinity of the enantiomers for two adsorption regions in the polymeric matrix. It was found that the absorption of Tyr reduced the crystallinity of the membranes and decreases the intercatenary spacing due to the rearrangement of the chains [110].

It is important to emphasize that there are many studies that use the process of interfacial polymerization (IP) in enantioselective membranes through the incorporation of chiral selectors. The IP is a technique used for preparing thin-film composite (TFC) membranes, widely used in nanofiltration, forward and reverse osmosis [125-127]. Zhou et al. [128] produced an enantioselective TFC membrane by using this technique. A PSf membrane was produced by the wet phase inversion method and the chiral selector - CD was used to synthesize the selective dense layer (Fig. 3). For evaluation of the enantioselective membrane performance, the racemic Trp was used as a model. The membrane performance was evaluated in two different modes of operation, conducted by the concentration gradient and pressure gradient; enantioselectivity of 1.55 and 0.6 were obtained, respectively. When the feed concentration was 0.1 mmol/L, the highest enantioselectivity ($\alpha = 1.55$) was achieved. The α values in both operating modes decreased with the concentration of racemic feed and increased with the CD content [128].

Gaálová et al. [129] produced membranes composed of three layers: a supporting layer composed of a commercial synthetic film (polyethylene/polypropylene), a nanofiber, forming the porous layer, and a selective layer of the thin film membrane containing the chiral selector *(S,S)*-1,2-iaminocyclohexane, which was prepared by IP. The enantioselectivity of the membrane was demonstrated through sorption tests, in which they were soaked in an aqueous solution of racemic Trp. The enantioselectivity of the membrane was increasing with the % of the chiral selector ($0\% < 10\% < 20\% < 30\% < 40\% < 50\%$). The corresponding final enantiomeric ratios were 50:50, 59:41, 70:30, 82:18, 91:9 and 99:1, respectively. The preferential sorption of L-Trp from the feed underlined the crucial importance of the selector in the active layer to achieve chiral recognition of enantiomers. Due to the exclusive membrane material, the retention of L-Trp in the membrane materials did not block the transport of D-Trp. In addition, an enantiomeric separation of

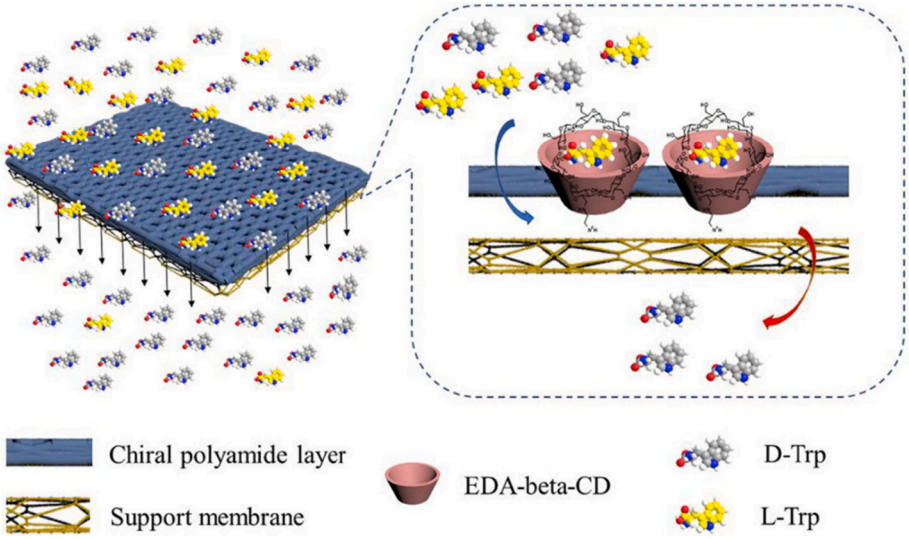

Fig. 4. Illustrations of molecular transport mechanism in the membranes for the enantioseparation of chiral drugs (Reprint permission from Ref. [91]).

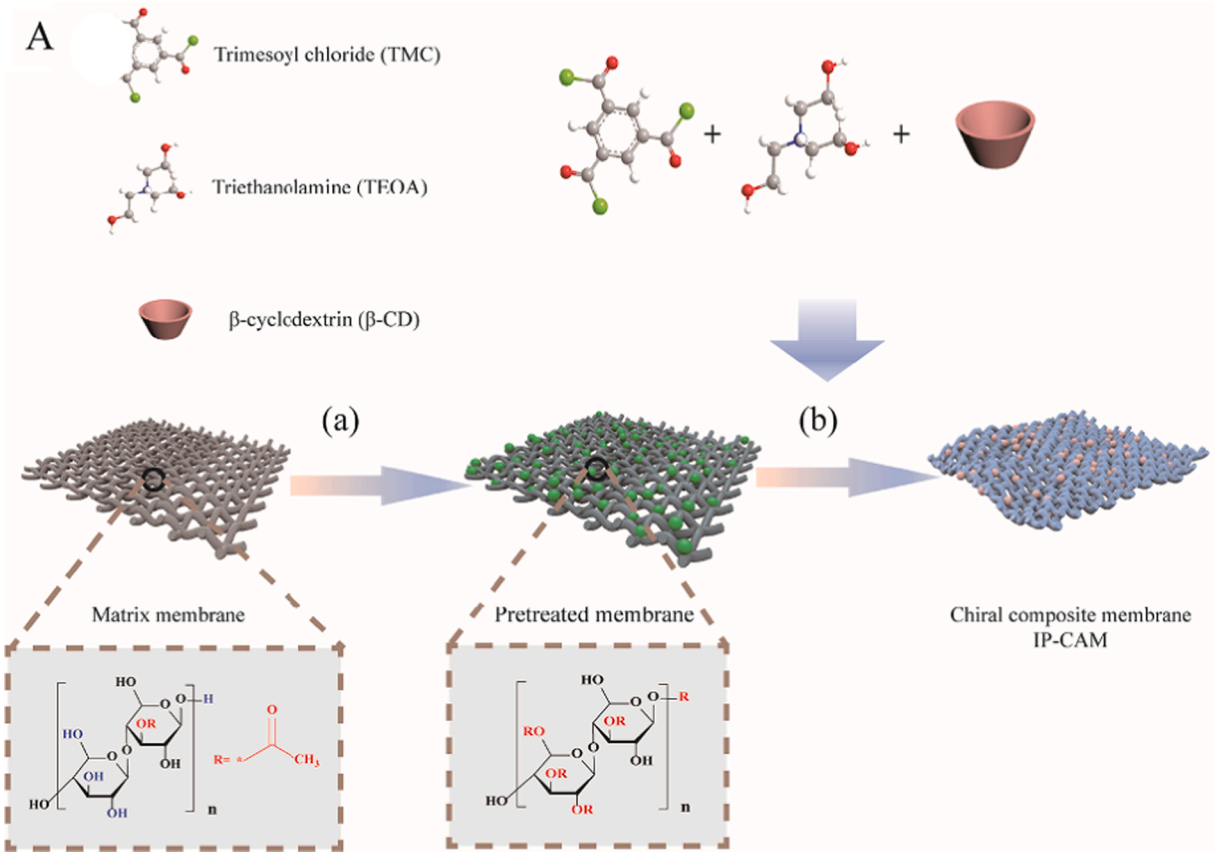

Fig. 5. Schematic diagram of the preparation process for a chiral composite membrane (Reprint permission from Ref. [130]).

the same model chiral drug was performed in by pertraction in diffusion cells. The result for the permeation was an excess of D-Trp in the permeate, where this excess was proportional to the amount of chiral selector in the membranes. Moreover, the presence of nanomaterial in the active layer assured the distribution of the selector in a part of the active layer, sufficient to achieve high enantioselectivity [129].

Another example of in situ IP, for development of a new chiral TFC polyamide membrane was reported by Ke et al. [91]. The diethylamino-beta-cyclodextrin monomer (EDA-β-CD) was used as chiral selector with trimesoyl chloride (TMC) to manufacture a TFC membrane on the commercial cellulose acetate membrane surface (Fig. 4). The enantio-separation of chiral compounds such as warfarin, ibuprofen, nefopam, ketoprofen and Trp were evaluated. The solutions of 25 mg/L were used for permeation using the membrane microdevice with a constant flow rate of 0.1 mL/min. The *e.e.* was 8.09% for warfarin, 3.65% for ibuprofen and 27.2% for Trp. In addition, it was suggested that the membrane can be used in industrial production and it was stable over a wide pH range [91].

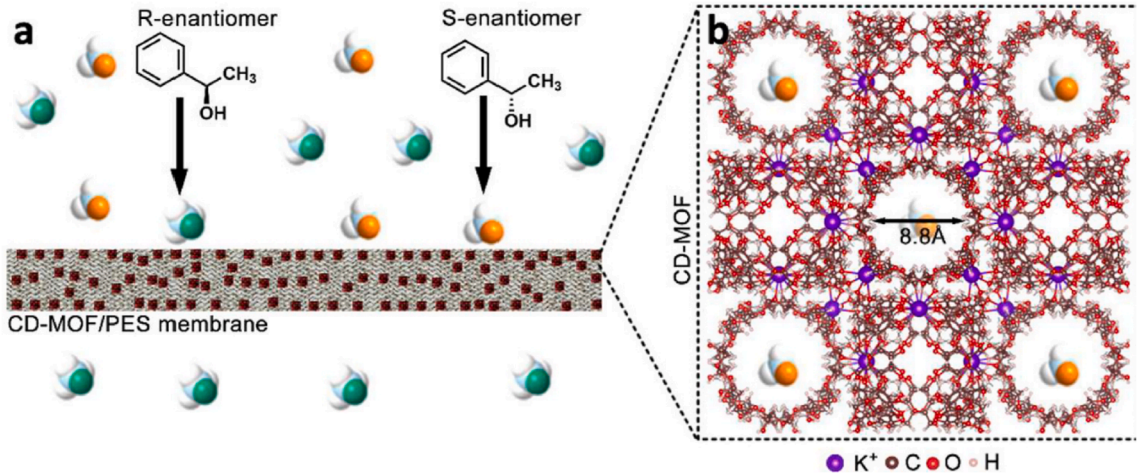

Fig. 6. Schematic diagram of CD-MOF/PES MMMs (a) CD-MOF/PES MMM for selective transport of *R*-(+)-1-phenylethanol molecules from racemic mixture. (b) 3D structure of CD-MOF (Reprint permission from Ref. [78]).

Recently, Ke et al. [130] used the IP method to prepare chiral polyester composite membranes, using CD as a chiral selector, commercial cellulose acetate membranes as support and TMC as a crosslinking agent. It was used Trp as a chiral model for IP. For the evaluation of the enantiomeric resolution of the membrane a lab-scale filtration apparatus with constant flow rate was used, and the permeate solutions was quantified by LC. The compounds tested were warfarin and nefopam, achieving *e.e.* values of 7.01 ± 0.41% and 6.74 ± 1.00%, respectively (Fig. 5). The chiral recognition mechanism was demonstrated employing molecular modeling with AutoDock [130]. However, when comparing with a previous work, in which the polymer acetate cellulose was used and both comprise a chiral selector based on CD, it was possible to observe that a greater enantioselectivity was achieved for the same compound. Regarding warfarin, for the membrane composed of cellulose acetate the value of *e.e.* was 8.09% and for polyester composite membrane the value of *e.e.* was 7.01% [91,130].

In a study by Lu et al. [78], mixed-matrix membranes (MMMs) composed of CD-homochiral metal–organic framework (MOF) as a chiral selector and polyethersulfone (PES) as a matrix were produced using the dry casting method. The racemate of 1-phenylethanol was used to evaluate the membranes enantioselectivity (Fig. 6). Racemic 1-phenylethanol was dissolved in n-hexane, ethanol or methanol to prepare a 0.008 mol/L feed solution. The enantioseparation of 1-phenylethanol was achieved with *e.e.* nearly 100% when non-polar n-hexane was the solvent. The enantioselectivity decreased with the permeation time with polar solvents such as methanol and ethanol. Although MMMs are highly attractive for continuous applications and efficient chiral resolution, in several studies, a decline in membrane enantioselectivity has been observed with the permeation time, being a common problem for its practical applications [78]. One of the possible causes for the permeation decline may be due to membrane fouling, the main problem associated to membrane filtration processes. There are several studies that approach this topic. Recently, Tian et al. [61], verified the relationship between membrane fouling and chiral purification, through several operational parameters, such as: chiral concentration, chiral selector ratio for chiral concentrations, pH, feed medium, and cross flow rate (CFV) in extent of chiral separation. PES ultrafiltration membrane with BSA as chiral selector, and phenylalanine was used to evaluate the enantioseparation. They checked that for high concentrations of phenylalanine both the α and the flow decreased, compared to CFV which the α increased with increasing flow and decreased when flux decline. They suggested that there is a weak correlation between chiral purification and flow decline. Thus, in order to obtain a high enantioselectivity, other means are needed to improve the binding of the chiral selector with the chiral species, not just using the conventional method to attenuate membrane fouling [61].

3.2. *Molecular imprinted*

The molecularly imprinted polymeric membranes are produced from a MIP, in which molecular recognition sites are created for a specific model molecule [131]. The model molecule can be covalently coupled to a monomer during polymerization, or they are mixed with functional monomers capable of interacting from intermolecular interactions with the printing molecules [56]. The physicochemical interactions between the polymer and the functional groups of the model molecule are memorized during molecular printing and after the crosslinking of the polymer, the printing molecules are removed from the polymer, leaving the recognition sites similar to the model molecules. The main advantages of MIPs are their high affinity and selectivity for the model molecule, with relatively low production costs [131,132]. In the last years many investigations involving MIPs with different applications have been reported [122,133]. However, when we approach MIP membranes for chiral separation there are only few studies.

One of the challenges for membrane separation processes is to obtain high flow and permeability. In 2010, Sueyoshi et al. [134] developed a molecularly imprinted nanofiber membranes using cellulose acetate as a support and *N*-benzyloxycarbonyl-D-glutamic acid (Z-D-Glu) or *N*-benzyloxycarbonyl-L-glutamic acid (Z-L-Glu) as printing molecules, simultaneously applying a print alternative molecular and electrospray deposition. It was found that membranes produced from molecularly imprinted nanofiber increased both selectivity and flow, being a potential to improve simultaneously flow and permeselectivity [134]. Afterwards, Sueyoshi et al. [135] produced molecularly imprinted membranes and molecularly imprinted nanofiber membranes using, this time, PSf with aldehyde (PSf-CHO-05 or PSf-CHO-10) as a support and used the same molecules as imprinting: Z-D-Glu and Z-L-Glu. It was verified that the membranes imprinted by the D-isomer, preferentially adsorbed the D-Glu isomer and the L- adsorbed the L-Glu isomer. As previously studied, it was found an increase in flow, without decreasing permselectivity, corroborating that molecularly imprinted nanofiber membranes have the potential to improve both flow and permselectivity (enantioselectivity). However, previously they achieved an enantioselectivity of $\alpha = 1.4$ in relation to this study, which was $\alpha = 1.2$ [135].

In another study, Zhou et al. [136] described a green method for the preparation of a composite membrane using sodium alginate as a functional natural polymer with D-Trp surface-imprinted, using water as solvent and calcium chloride as crosslinking agent. The performance of the chiral separation of molecularly imprinted composite membrane was studied, and a high *e.e.* of the filtrate D/L-Trp (>99%) was obtained. The permeation flux of D-Trp increased slightly and the permeation flux of L-Trp decreased sharply in higher temperature, increasing the *e.e.* The method, besides being green and low cost, was good for the significant increase in *e.e.*, compared to previous studies [136]. Afterwards, they applied the same green method, but used polyvinylidene fluoride (PVDF) membrane as a support, to achieve greater mechanical resistance and permeation flow, when compared to the previously developed molecularly imprinted self-supported membrane. Highly effective chiral resolution of the permeation solution within a range of mild conditions, feed concentration lower than 0.5 mmol/L, and pH higher than 5.89, was obtained in pressure-driven permeation experiments. The *e.e.* increased sharply with increasing the thickness of sodium alginate functional polymer layer. The permeation flux of D-Trp when the thickness was 0.02 mm was higher than that of L-Trp, the *e.e* was 99.13%. The obtained membrane was very stable at a temperature lower than 227 °C [137].

Gao B. et al. [107] proposed a MIP technique on the membrane surface using synchronized graft/crosslinking polymerization of monomer. The aminated PSf membrane was used as substrate and L-aspartic acid (L-Asp) as a template. After the formation of an initiation system on the membrane surface, the grafted/crosslinked polymerization of the functional monomer (dimethylaminoethyl methacrylate) and the crosslinking agent (*N*, *N*′-methylenebisacrylamide) occurred, at the same time, L-Asp molecules were incorporated into crosslinked networks (Fig. 7). The molecularly imprinted membrane (L-Asp-MIM) showed a high flux and a strong mechanical resistance with aminated PSf membrane. L-Asp-MIM obtained an excellent chiral recognition capacity ($\alpha = 7.52$) and in the permeation experiment of a racemate solution of Asp, the *e.e.* value of the penetrating fluid reached 82% [107].

Li H. et al. [138] produced a membrane composed of ZrO_2 and cellulose acetate with the molecular imprinting technique and the *(S)*-(+)-mandelic acid was used as the template. It was observed that the chiral polymer coating on the Al_2O_3 channel film modified with ZrO_2 increased permselectivity and flow, compared to the traditional membrane. Moreover, membranes with large pores can increase the cellulose acetate loading, thus increasing the sites for chiral recognition and leading to increased separation efficiency reaching an α value of 35 [138]. This research group also used an Al_2O_3 nanochannel modified with ZrO_2 and cellulose acetate with the molecular imprinting technique; however, the L-lactic acid was used as imprinted molecule. The enantioseparation of lactic acid was achieved with $\alpha = 8.7$ [139].

Recently, Ying X. et al. [140], processed a molecularly imprinted chromogenic membrane using the technique of electrospinning. Polyvinyl alcohol (PVA) was used as substrate and the molecule *p*-hydroxybenzene propanoic acid was the template, ninhydrin was used as a chromogenic agent to visualize the detection of the molecule- target L-Tyr. The authors found that the MIP membrane exhibited selectivity and specific adsorption capacity for L-Try. They also evaluated the influence of environmental factors such as reaction temperature, amount of ninhydrin and elution time [140].

A summary of the chiral polymeric membranes developed in the last ten years is shown in Table 1. The values of Flux (J), Permeability coefficient (P), Molar mobility (*u*), and the process for membrane preparation are also included, since the transport property of the polymeric membrane also depends on its morphology. Enantioselectivity is expressed in many studies by the α values and the enantiomeric purity by *e.e.* (Table 1).

Among the polymeric membranes presented in this review, it is evident that composite membranes both the obtained by IP and phase inversion (asymmetric membranes), based on PSf, as used by Ingole (>94% *e.e.*) [145], Gogoi (98.86% *e.e.*) [162] and by Singh ($\alpha = 17$) [146,147], among others, obtained a successful enantioseparation.

Synthetic membranes based on PSf are widely used in separation processes due to their physicochemical characteristics, as they are thermoplastic polymers with high glass transition temperature, high thermal and mechanical stability, in addition to high chemical stability [164-166]. Of course, other types of synthetic and natural polymers that have good chemical stability, a good enantioseparation was also achieved. The enantioselectivity of polymeric-based membranes can be increase when combined with chiral porous materials such as organic metal structures (MOFs) and modified graphene or GO. Furthermore, new trends suggest that other porous materials such as covalent organic frameworks (COFs) and MMMs can increase enantioseparation and mechanical strength.

4. Conclusions and future perspectives

The application of membranes for preparative enantioseparation is still restricted to academic research toward to a few pharmaceuticals and amino acids but has been pointed out as a promising green methodology for further industrial use. Polymeric membranes, natural or synthetic, are the most investigated type of membranes due to the easy access of polymeric materials, its relative low cost and easy operation.

Similar to LC, the porosity and the type of the support great affect the efficiency of the enantioseparation, but the resolution power of the chiral selector is the primary for the success in the enantioseparation of the membranes.

Regarding industrial application, membranes with high permeability, mechanical strength and enantioselectivity are required. The polymeric-based membranes when combined with chiral porous materials such as MOFs or modified graphene and GO can achieve high enantioselectivity. The use of porous materials in polymeric-based membrane consists in a new advance of chiral membranes. The COFs and MMMs with inorganic structures increase both the membrane performance and the mechanical strength as porous materials tends to increase the membrane flux and the separation factor. However, the number of chiral porous structures is still limited. Thus, the design and creation of new chiral porous materials with controllable pore size and chirality are required for the development of chiral membranes.

The MIP membranes have a high selectivity, but they do not have a wide selectivity like other types of membranes, in addition, in the process of preparing membranes with molecular printing can present high limitation for industrial production.

The predicted grow of chiral chemical market in pharmaceutical, agrochemicals, flavours and fragrances segments, among others, will demand the development and application of easy, low cost and environmental friendly methodologies for large scale enantiomeric separation. In that sense, new technologies to produce large-area membranes combining the fragile chiral porous materials, with the robust and well-known polymeric materials are an urgent need. Therefore, feasible, sustainable and low-cost methodologies for enantioseparation in preparative scale are transversal requirements to different field, from basic research to industry applications.

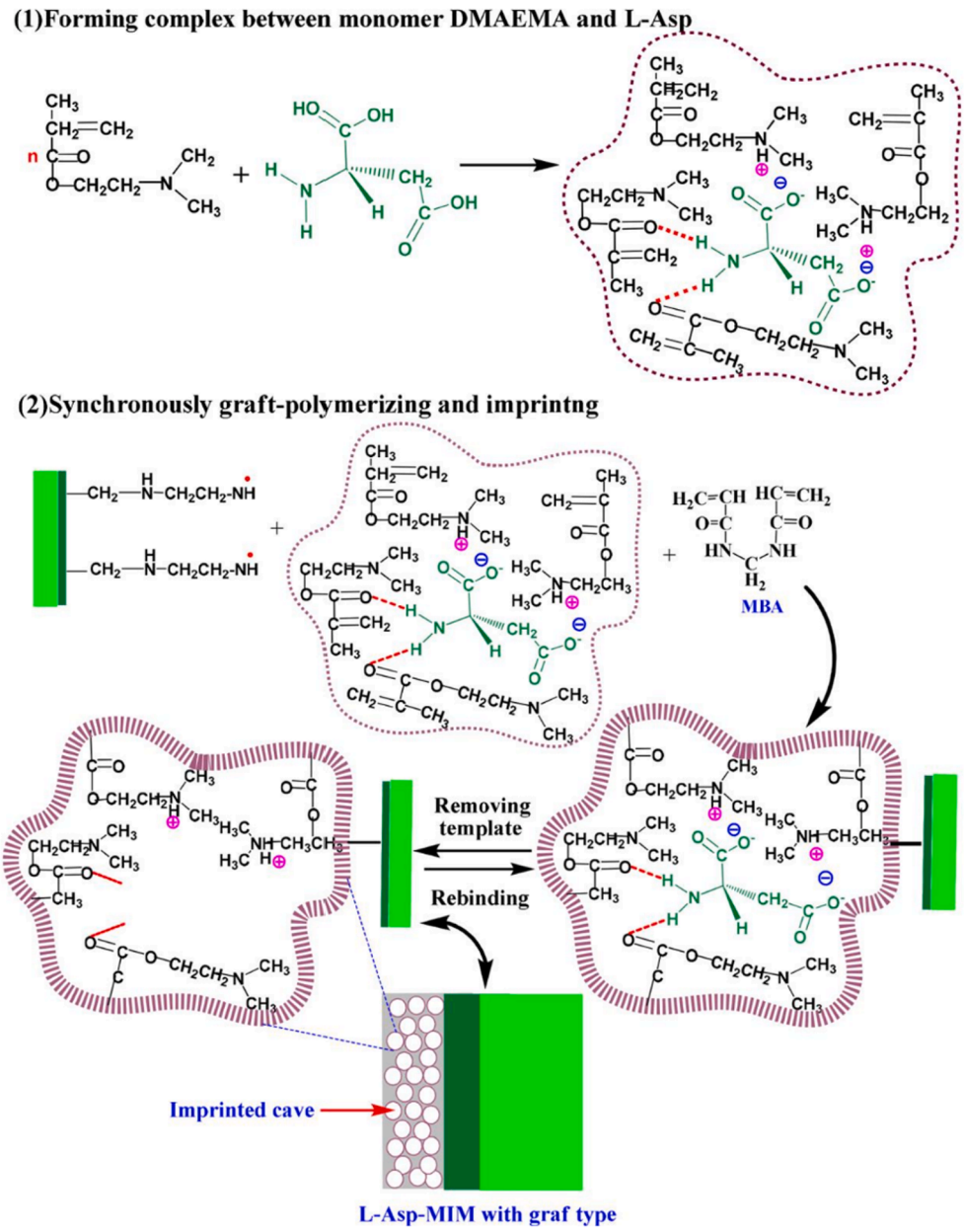

Fig. 7. Physical and chemical processes to prepare imprinted membrane L-Asp-MIM. *Note*: MIM, molecularly imprinted membrane (Reprint permission from Ref. [107]).

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 1
Chiral separation through polymeric membranes.

Membrane polymer[a]	Processing method	Separated substance	Flux (J)/Permeability coefficient (P)/Molar mobility (*u*) (method[b])	e.e. and/or α	Ref.
Polyethersulfone	Dry-jet wet phase inversion process	Tryptophan	$P_{(water)}$ = 74.79–116.27 $L.m^{-2}.bar^{-1}.h^{-1}$ (UF)	α = 5–7	[141]
Acrylamide/EGDMA	Molecular imprinting	UDCA	J = 3.5–9.5 $mL.h^{-1}$	$\alpha_{(UDCA)}$ = 3.24	[142]
		CDCA		$\alpha_{(CDCA)}$ = 1.93	
Cellulose acetate	Molecular imprinting	D-Glutamic acid	$u = 1.04_{\times}10^{-9}$ –$5.49_{\times}10^{-10}$ mol.cm.$cm^2.J^{-1}.h^{-1}$	$\alpha_{(D/L)}$ = 1.11–1.45	[134]
		L-Glutamic acid	$u = 1.32_{\times}10^{-9}$–$3.81_{\times}10^{-9}$ mol.cm.$cm^2.J^{-1}.h^{-1}$	$\alpha_{(L/D)}$ = 1.07–1.44	
Cellulose	Casting/solvent evaporation technique	D,L-Mandelic Acid	(UF)	90% e.e.	[143]
Poly (dimethylaminoethyl methacrylate) containing SiO_2 particles	Molecular imprinting	D,L -Glutamic acid	(Ad)	α = 3.3	[144]
Polysulfone containing chiral metal–Schiff base complexes	Phase inversion method	D- Lysine	J = 78,23–62.14 $L.m^{-2}.h^{-1}$ (UF)	> 94% e.e.	[145]
Polysulfone	Interfacial polymerization	D-Arginine	$P_{(water)}$ = 374 $L.m^{-2}.h$ (UF)	α = 17	[146]
Polysulfone	Interfacial polymerization	D- Lysine	(NF)	α = 17	[147]
Sulfonated polyetherketone (SPEK)	Phase inversion method	Tryptophan	$J_{(L)} = 1.04_{\times}10^{-7}$ –$8.3_{\times}10^{-7}$ mol.$cm^{-2}.s^{-1}$ (FFIEF)	α = 1.4–7.1	[148]
Polysulfone composite membrane	Interfacial polymerization	Lysine	(RO)	α = 8	[149]
Polysulfone nanofiber membrane	Electrospray deposition	D,L -Glutamic acid	$u = 5.02_{\times}10^{-9}$–$6.87_{\times}10^{-9}$ mol.cm.$cm^2.J^{-1}.h^{-1}$	$\alpha_{(D/L)}$ = 0.71–1.49	[150]
				$\alpha_{(L/D)}$ = 0.67–1.41	
Polysulfone	Interfacial polymerization	α-Amino acids	(UF)	α = 15–20	[151]
Cellulose acetate	Phase inversion method	D, L-Tryptophan	$J_{(D)} = 0.45_{\times}10^{-7}$–$8.5_{\times}10^{-7}$ mmol.$cm^{-2}.s^{-1}$	94% e.e. (conc. gradient)	[152]
			$J_{(L)} = 0.64_{\times}10^{-7}$–$8.4_{\times}10^{-7}$ mmol.$cm^{-2}.s^{-1}$	66% e.e (pressure)	
				19% e.e. (electric field)	
Polysulfone membrane and β-cyclodextrin glutaraldehyde crosslinked polysulfone membrane	Phase inversion method	D-Phenylalanine	J = 49.23 $L.m^{-2}.h^{-1}$ and 44.3 L.$m^{-2}.h^{-1}$ (UF)	>81% e.e.	[153]
		D-Tryptophan	J = 52.31 $L.m^{-2}.h^{-1}$ and 47.78 L.$m^{-2}.h^{-1}$ (UF)	>49% e.e.	
Polysulfone-aldehyde derivatized nanofiber membranes	Molecular imprinting	D -Glutamic acid	$u = 6.64_{\times}10^{-11}$–$1.15_{\times}10^{-9}$ mol.$cm.cm^2.J^{-1}.h^{-1}$	$\alpha_{(L/D)}$ = 1.12–1.25	[135]
		L -Glutamic acid	$u = 3.05_{\times}10^{-11}$–$2.20_{\times}10^{-9}$ mol.$cm.cm^2.J^{-1}.h^{-1}$	$\alpha_{(D/L)}$ = 1.16–1.20	
Chitin nanofiber membranes	Electrospray deposition	D,L -Glutamic acid	$J_{(D)} = 2.23_{\times}10^{-9}$–$2.67_{\times}10^{-9}$mol.$cm.cm^{-2}.h^{-1}$ (MS)	$\alpha_{(D/L)}$ = 1.10	[154]
			$J_{(L)} = 1.98_{\times}10^{-9}$–$2.40_{\times}10^{-9}$mol.cm.$cm^{-2}.h^{-1}$ (MS)		
		D,L -Phenylalanine	$J_{(D)} = 1.61_{\times}10^{-9}$–$2.27_{\times}10^{-9}$mol.$cm.cm^{-2}.h^{-1}$ (MS)	$\alpha_{(D/L)}$ = 1.16	
			$J_{(L)} = 1.45_{\times}10^{-9}$–$1.85_{\times}10^{-9}$mol.cm.$cm^{-2}.h^{-1}$ (MS)		
		D,L -Lysine	$J_{(D)} = 1.31_{\times}10^{-9}$–$2.12_{\times}10^{-9}$mol.$cm.cm^{-2}.h^{-1}$ (MS)	$\alpha_{(D/L)}$ = 1.13	
			$J_{(L)} = 1.11_{\times}10^{-9}$–$2.02_{\times}10^{-9}$mol.cm.$cm^{-2}.h^{-1}$ (MS)		
Polytetrafluoroethelene (PTFE)	Commercial membrane	D,L-lactic acid	$J_{(D)}$ = 0.0015 $mol.cm^{-2}.min^{-1}$ (F) (MS)	$\alpha_{(L/D)}$ = 4.43	[155]
			$J_{(L)}$ = 0.0066 $mol.cm^{-2}.min^{-1}$(F) (MS)		
Polysulfone composite membrane	Phase inversion method/ Interfacial polymerization	Lysine	J = 8.43–12.00 $g.m^{-2}.h^{-1}$ (UF)	$\alpha_{(D/L)}$ = 7–21	[156]
		Asparagine	J = 12.1–16.75 $g.m^{-2}.h^{-1}$ (UF)	$\alpha_{(D/L)}$ = 3.8–5.2	
Polyimide	Nanochannel by ion track-etching technique	Tryptophan	(BN)	–	[157]
(+)-PIM-CN membrane	Casting/solvent evaporation technique	*(R,S)*-Mandelic acid	P = $0.07_{\times}10^3$ $g.m.m^{-2}.h$	α = 1.92	[64]
		(R,S)-Binol	P = $0.019_{\times}10^3$ $g.m.m^{-2}.h$	α = 3.3	
		TTSBI	P = $1.65_{\times}10^3$ $g.m.m^{-2}.h$	α = 14.4	
(+)-PIM-COOH membrane	Casting/solvent evaporation technique	Fmoc-Phe	P = $0.073_{\times}10^3$ $g.m.m^{-2}.h$	α = 7	[64]
Terpolymer P(AN-AA-AAm)	Wet phase inversion method/ Molecular imprinting	Arginine	5.38– 12.76 $g.m^{-2}.h^{-1}$ (UF)	$\alpha_{(D/L)}$ = 5.56	[106]
		Asparagine	7.38–20.13 $g.m^{-2}.h^{-1}$ (UF)		
Sodium alginate	Molecular imprinting	Tryptophan	J = $8.0_{\times}10^{-5}$ $mol.m^{-2}.h^{-1}$	>99% e.e.	[136]
Cellulose	Casting/solvent evaporation technique	D,L-Mandelic acid	(UF)	80.9% e.e.	[114]
Sodium alginate			(UF)	16.6% e.e.	

(*continued on next page*)

Table 1 (*continued*)

Membrane polymer[a]	Processing method	Separated substance	Flux (J)/Permeability coefficient (P)/Molar mobility (*u*) (method[b])	e.e. and/or α	Ref.
	Casting/solvent evaporation technique	p-Hydroxy phenylglycine			
Hydroxypropyl-β-cyclodextrin/ Polysulfone membrane	Interfacial polymerization	p-Hydroxy phenylglycine	(UF)	23.2% e.e.	
Cellulose acetate membrane/ L-Glutamic acid-GO	Vacuum filtration method	L-DOPA D-DOPA	$J_{(L)} = 10.21$ nmol.cm^{-2}.h^{-1} $J_{(D)} = 21.01$ nmol.cm^{-2}.h^{-1}	α = 2.05	[92]
Polysulfone membranes/ polydopamine/ β-cyclodextrin	Mussel-inspired chemistry	Tryptophan	$P_{(water)} = 24.0$ L.m^{-2}.h^{-1}.bar^{-1} (UF)	3.2% e.e.	[63]
Sodium alginate/Polyvinylidene fluoride (PVDF) membrane	Molecular imprinting	D, L-Tryptophan	$J_{(D)} = 7.49_{\times}10^{-5}$ mol.m^{-2}.h^{-1} $J_{(L)} = 6.06_{\times}10^{-7}$ mol.m^{-2}.h^{-1}	> 98% e.e.	[137]
Polyvinylidene fluoride (PVDF)	Molecular imprinting	Amlodipine besylate	(CF)	α = 1.98	[158]
Poly(*L*-Glutamic acid sodium)-GO	Vacuum filtration method	L-DOPA D-DOPA	$J_{(L)} = 6$ nmol.cm^{-2}.h^{-1} $P_{(L)} = 1.5 \times 10^{-4}$ cm^2.h $J_{(D)} = 17$ nmol.cm^{-2}.h^{-1} $P_{(D)} = 3.7 \times 10^{-3}$ cm^2.h	α = 2.8	[124]
Cellulose acetate membrane/GO-IL-Glu	Vacuum filtration method	L-DOPA D-DOPA	$J_{(L)} = 8$ nmol.cm^{-2}.h^{-1} $P_{(L)} = 1.5 \times 10^{-4}$ cm^2.h $J_{(D)} = 25$ nmol.cm^{-2}.h^{-1} $P_{(D)} = 2.9 \times 10^{-2}$ cm^2.h	α = 3.13	[159]
Cellulose acetate composite membrane	Molecular imprinting	D,L-Lactic acid	$J = 0.070$ mg.cm^{-2}.min^{-1}	α = 8.7 79% e.e.	[139]
Cellulose acetate composite membrane	Molecular imprinting	*(R,S)*-Malic acid	$J = 0.1597$ mg.cm^{-2}.min^{-1}	α = 35 94.5% e.e.	[138]
Chiral membranes of chitosan	Casting/solvent evaporation technique	Tyrosine	(Ad)	15–68 % e.e.	[110]
MOF/Polyethersulfone MMM	Casting/solvent evaporation technique	1-Phenylethanol	$J = 25.21_{\times}10^{-5}$– $42.02_{\times}10^{-5}$ mol.m^{-2}.h^{-1}	100% e.e.	[160]
CD-COF/Polyethersulfone MMM	Phase-inversion method	D, L-Histidine	$J_{(L)} = 1.04$ μM.cm^{-2}.h^{-1} $J_{(D)} = 0$ μM.cm^{-2}.h^{-1}	$R_{(L)}/R_{(D)} = 34.0$	[161]
Polyethylene/polypropylene composite membranes	Interfacial polymerization	D, L-Tryptophan	$J = 3.25$–0.07 mmol.m^{-2}.h^{-1} (P)	99%	[129]
Nanocomposite polysulfone membrane	Phase inversion method	Tyrosine	$J = 3_{\times}10^{-6} - 5.9_{\times}10^{-4}$ mmol.m^{-2}.h^{-1}	98.86% e.e.	[162]
Composite cellulose acetate membrane	Interfacial polymerization	Warfarin Ibuprofen Tryptophan	$J_{(water)} = 35.7$ L.m^{-2}.h^{-1}	8.09 % e.e. 3.65 % e.e. 27.2% e.e.	[91]
Chiral-functionalized PSEBS membrane	Casting/solvent evaporation technique	Ibuprofen Tryptophan	(S)	peak ratio$_{(D/L)}$ = 43.7:56.3 peak ratio$_{(R/S)}$ = 60:40	[163]
Polysulfone	Wet phase inversion/ Interfacial polymerization	D, L-Tryptophan	$J_{(water)} = 4.4$ LMH/MPa $J_{(D)} = 17.48$–33.50 μmol.m^{-2}.h^{-1} $J_{(L)} = 20.10$–51.62 μmol.m^{-2}.h^{-1}	α = 1.55 (conc. gradient) α = 0.60 (pressure)	[128]
Polyester composite membrane	Interfacial polymerization	*(RS)*-Warfarin *(RS)*-Nefopam	(F)	7.01 ± 0.41% e. e. 6.74 ± 1.00% e. e.	[130]
CD-MOF/Polyethersulfone MMM	Dry casting technique	*R-(+)-1*-Phenylethanol *S-(-)-1*-Phenylethanol	$J_{(hexane)} = 2.48_{\times}10^{-3}$ mol.m^{-2}.h^{-1} $J_{(ethanol)} = 3.57_{\times}10^{-3}$ mol.m^{-2}.h^{-1}	100 % e.e.	[78]

[a] Ursodeoxycholic acid (UDCA), Chenodeoxycholic acid (CDCA), Ethylene glycol dimethacrylate (EGDMA), Amphiphilic polymer conetworks (APCN), Polymers of intrinsic microporosity (PIMs), 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (TTSBI), N-(9-fluorenylmethoxycarbonyl)phenylalanine (Fmoc-Phe), 3,4-dihydroxyphenylalanine (DOPA), Polyimide (PI), Terpolymer (Acrylamide (AAm) acrylic acid (AA) acrylonitrile (AN)) (P(AN-AA-AAm)), Graphene oxide (GO), Ionic liquid (IL), *L*-glutamic acid (Glu), polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (PSEBS), Cyclodextrin (CD), Homochiral metal–organic framework (MOF), Covalent organic frameworks (COFs), Mixed-matrix membranes (MMM).

[b] Method; Filtration process (F), Ultrafiltration (UF), Adsorption (Ad), Nanofiltration (NF), Ion-exchange membrane partitioned free flow isoelectric focusing (FFIEF), reverse osmosis (RO), Multi-stage separation (MS), Biomimetic single nanochannel (BN), Diffusion (D), Cross-flow filtration (CF), Pertraction (P), Sorption (S).

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