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Feature article

Advanced functional polymer membranes

Mathias Ulbricht *

Lehrstuhl für Technische Chemie II, Universität Duisburg-Essen, Essen 45117, Germany

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Abstract

This feature article provides a comprehensive overview on the development of polymeric membranes having advanced or novel functions in the various membrane separation processes for liquid and gaseous mixtures (gas separation, reverse osmosis, pervaporation, nanofiltration, ultrafiltration, microfiltration) and in other important applications of membranes such as biomaterials, catalysis (including fuel cell systems) or lab-on-chip technologies. Important approaches toward this aim include novel processing technologies of polymers for membranes, the synthesis of novel polymers with well-defined structure as 'designed' membrane materials, advanced surface functionalizations of membranes, the use of templates for creating 'tailored' barrier or surface structures for membranes and the preparation of composite membranes for the synergistic combination of different functions by different (mainly polymeric) materials. Self-assembly of macromolecular structures is one important concept in all of the routes outlined above. These rather diverse approaches are systematically organized and explained by using many examples from the literature and with a particular emphasis on the research of the author's group(s). The structures and functions of these advanced polymer membranes are evaluated with respect to improved or novel performance, and the potential implications of those developments for the future of membrane technology are discussed.

Keywords: Functional polymer; Polymer membrane; Membrane technology

1. Introduction

A membrane is an interphase between two adjacent phases acting as a selective barrier, regulating the transport of substances between the two compartments. The main advantages of membrane technology as compared with other unit operations in (bio)chemical engineering are related to this unique separation principle, i.e. the transport selectivity of the membrane. Separations with membranes do not require additives, and they can be performed isothermally at low temperatues and—compared to other thermal separation processes—at low energy consumption. Also, upscaling and downscaling of membrane processes as well as their integration into other separation or reaction processes are easy.

Abbreviations: 4Vpy, 4-vinyl pyridine; AAm, acrylamide; AFM, atomic force microscopy; ATRP, atom transfer radical polymerization; *-b-*, …block (copolymer); BP, benzophenone; BSA, bovine serum albumin; CA, cellulose acetate; CMR, catalytic membrane reactor; *-co-*, …(linear) copolymer; CVD, chemical vapor deposition; D, dialysis; DNA, desoxyribonucleic acid; ED, electrodialysis; EIPS, evaporation induced phase separation; EMR, enzyme-membrane reactor; *-g-*, …graft (copolymer); GMA, glycidyl methacrylate; GS, gas separation; HEMA, hydroxyethyl methacrylate; *i*, isotactic; LB, Langmuir–Blodgett; LBL, layer-by-layer; LCST, lower critical solution temperature; *M*, molar mass; MEA, membrane electrode assembly; MF, microfiltration; MIP, molecularly imprinted polymer; MPC, methacryloxyethylphosphorylcholin; NCA, *N*-carboxyanhydride; NF, nanofiltration; NIPAAm, *N*-isopropyl acrylamide; NIPS, non-solvent induced phase separation; PA, polyamide; PAA, polyacrylic acid; PAH, polyallylamine hydrochloride; PAN, polyacrylonitrile; PBI, polybenzimidazol; PC, polycarbonate; PDMS, poly(dimethylsiloxane); PEEKK, polyetheretherketone; PEG, polyethyleneglycol; PEGMA, polyethyleneglycol methacrylate; PEM, polymer electrolyte membrane; PEMFC, polymer electrolyte membrane fuel cells; PES, polyethersulfone; PET, polyethylene terephthalate; PFSA, perfluorosulfonic acid; PGMA, polyglycidyl methacrylate; PH, poly(1-hexene); PI, polyisopren; PL, polylactide; PP, polypropylene; PS, phase separation; PSf, polysulfone; PSt, polystyrene; PU, polyurethane; PV, pervaporation; PVC, polyvinylchloride; PVDF, polyvinylidenefluoride; PVP, polyvinylpyrrolidone; RhB, rhodamin B; RO, reverse osmosis; *s*, syndiotactic; SAM, self-assembled monolayer; SAXS, small angle X-ray scattering; SEM, scanning electron microscopy; SPSf, sulfonated polysulfone; SRNF, solvent-resistant nanofiltration; TEM, transmission electron microscopy; TFC, thin-film composite; TIPS, thermally induced phase separation; UV, ultraviolet; VIPS, vapor induced phase separation; VP, vinylpyrrolidone.

* Tel.: +49 201 183 3151; fax: +49 201 183 3147.
E-mail address: mathias.ulbricht@uni-essen.de

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After a long period of inspiration by biological membranes and scepticism about the ultimate technical feasibility, membrane technologies have now been industrially established in impressively large scale [1]. The markets are rather diverse—from medicine to the chemical industry—and the most important industrial market segments are 'medical devices' and 'water treatment'. The worldwide sales of synthetic membranes is estimated at over US $2 billion (in 2003) [2]. Considering that membranes account for only about 40% of the total investment for a membrane separation system,[1] the total annual turnover for the membrane based industry can be considered more than US $5 billion. The annual growth rate for most membrane products are more than 5%, in some segments up to 12–15%. For example, the market of the by far largest commercial membrane process, the 'artificial kidney' (hemodialysis), represents a turnover of US $1 billion, and >230 Mio m^2 membrane area are produced annually for that application. At the same time, the extremely high quality standards at falling prices[2] are only possible by a very high degree of automatization of the manufacturing process, integrating continuos (hollow-fiber) membrane preparation, all post-treatment steps and the assembly of the membrane modules into one production line [3].

In industrially established applications, some of the state-of-the-art synthetic membranes have a better overall performance than their biological counterparts. The very high salt rejections and water fluxes through reverse osmosis membranes obtained using transmembrane pressures of up to 100 bar may serve as an example for the adaptation of the membrane concept to technical requirements. However, relatively few of the many possible separation principles and processes have been fully explored yet. Consequently, a strong motivation for improving established membrane materials and processes is driving the current research in the field (cf. 3). Today this can be done on a sound technical and economical basis for the development and technical implementation of novel membrane materials and processes.

The membrane process conditions must be engineered very carefully, but the performance limits are clearly determined by the membrane itself. This will be briefly explained by giving an overview on the main membrane processes and separation mechanisms (cf. 2.1). Even when ceramic, metal and liquid membranes are gaining more importance, the majority of membranes are and will be made from solid polymers. In general, this is due to the wide variability of barrier structures and properties, which can be designed by polymer materials. Current (1st generation) membrane polymers are biopolymers (mainly cellulose derivatives) or (less than 20 major) synthetic engineering polymers, which had originally been developed for different purposes. The typical membrane structures and manufacturing technologies will be briefly summarized (cf. 2.2).

The development of synthetic membranes had always been inspired by the fact that the selective transport through biological membranes is enabled by highly specialized macromolecular and supramolecular assemblies based on and involved in molecular recognition. The focus of this feature article will be onto improved or novel functional polymer membranes (the 'next generation' of membrane materials), and important trends in this field include:

- the synthesis of novel polymers with well-defined structure as 'tailored' membrane materials
- advanced surface functionalizations, yielding novel barrier structures or enabling the combination of existing barrier structure with 'tailored' modes of interactions (from 'affin' to 'inert')
- the use of templates for creating tailored barrier or surface structures for membranes
- preparation of mixed matrix or composite membranes for the synergistic combination of different functions by different (polymeric) materials
- improved or novel processing of polymers for membranes, especially thin-layer technologies or the miniaturization of membrane manufacturing.

The main part of this article will be organized into two sub-chapters, the most comprehensive one will be concerned with syntheses and/or preparation methods and resulting membrane structures (cf. 4) and thereafter the functions and/or performance of the improved or novel membranes will be discussed organized according to the different membrane processes (cf. 5). An attempt had been made to cover most important trends (at least by mentioning them in the respective context). However, due to the wide diversity of the field, selections had to be made which also reflect the particular interests of the author.

2. Membrane technology—state-of-the-art

2.1. Membrane processes and separation mechanisms

Passive transport through membranes occurs as consequence of a driving force, i.e. a difference in chemical potential by a gradient across the membrane in, e.g. concentration or pressure, or by an electrical field [4]. The barrier structure of membranes can be classified according to their porous character (Table 1). Active development is also concerned with the combination of nonporous or porous membranes with additional separation mechanisms, and the most important ones are electrochemical potentials and affinity interactions.

For non-porous membranes, the interactions between permeand and membrane material dominate transport rate and selectivity; the transport mechanism can be described by the solution/diffusion model [5,6]. The separation selectivity between two compounds can be determined by the solution

[1] Because membrane processes are typical examples for enabling technologies, it will become more and more complicated to 'separate' the membrane units from large and complex technical systems where the membrane still plays the key role. The best example for a field with a very large degree of integration along the value chain is the hemodialysis segment of the medical industry, where membrane companies form the high-technology core of a business which also owns complete hospitals for the treatment of patients suffering from kidney failure and related diseases.

[2] The current market price of one high-end dialysis module, for example with up to 15,000 hollow-fibers yielding up to 2.2 m^2 membrane area, is 7–10 US$.