



Photo-irradiation for preparation, modification and stimulation of polymeric membranes

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ABSTRACT

The recent developments in combining photo-irradiation-based and membrane technologies are analyzed in this review. It is emphasized that the effects of photo-initiated reactions onto properties of polymeric membranes will largely depend on the nature of the membrane's barrier (i.e., porous vs. non-porous, uncharged vs. charged, or involving affinity interactions). For *de novo* preparation of membranes from low molar mass or soluble precursors, photo-initiated polymerization and photo-cross-linking are the main pathways, while photo-degradation for pore formation is only rarely applied. Membrane functionalization (modification) is described with many examples, organized into photo-cross-linking of membranes and photo-grafting of membrane surfaces, either via "grafting-to" or via "grafting-from" routes. Photo-stimulation of barrier properties is an attractive concept to create stimuli-responsive membranes, and various ways to use photo-chromic moieties for that purpose are discussed. Overall, photo-irradiation-based methods can be very versatile enabling technologies to improve the performance of polymeric membranes in technical separations (e.g., in gas separation, pervaporation, ultra- and microfiltration or as membrane adsorbers) and other processes (e.g., for controlled release or in sensor systems), and they will definitely also contribute to the development of entirely novel membrane-based materials.

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Abbreviations: AA, acrylic acid; AAm, acrylamide; ABMPEG, α -4-azidobenzoyl- ω -methoxy-PEG; AHBPE, aliphatic hyperbranched-polyester; BP, benzophenone; BSA, bovine serum albumin; BTDA, 3,3',4,4'-benzophenone tetracarboxylic dianhydride; CB, Cibacron Blue F3GA; D, dialysis; DG, degree of grafting; DHB, dihydroxybenzophenone; DMFC, direct methanol fuel cell; EC, ethyl cellulose; ED, electrodialysis; EDMA, ethylene glycol dimethacrylate; EIPS, evaporation-induced phase separation; EO, ethyleneoxide; GMA, glycidyl methacrylate; GS, gas separation; HEMA, 2-hydroxyethyl methacrylate; HFP, hexafluoropropylene; LEDs, light-emitting diodes; MBAA, methylene bisacrylamide; MC, membrane contactor; MD, membrane distillation; MF, microfiltration; MIP, molecularly imprinted polymer; NF, nanofiltration; NIPAAm, *N*-isopropyl acrylamide; NIPS, non-solvent-induced phase separation; NVP, *N*-vinyl-2-pyrrolidone; PA, polyarylate; PAA, poly(acrylic acid); PAEK, poly(aryl ether ketone); PAN, polyacrylonitrile; PB, polybutadiene; PC, polycarbonate; PCEMA, poly(2-cinnamoyl ethyl methacrylate); PDMS, polydimethylsiloxanes; PDPO, poly(2,6-dimethyl-1,4-phenylene oxide); PE, polyethylene; PEC, poly(ethylenecarbonate); PEG, poly(ethylene glycol); PEGDA, poly(ethylene glycol) diacrylate; PEGMA, poly(ethylene glycol methacrylate); PEO, poly(ethylene oxide); PEPP, poly[(4-ethylphenoxy)(phenoxy)phosphazene]; PES, poly(ether sulfone); PET, poly(ethylene terephthalate); PI, polyimide; Pls, polyisoprene; PMA, polymethacrylates; PP, polypropylene; PS, phase separation; PSf, polysulfone; PSt, polystyrene; PtBA, poly(*tert*-butyl acrylate); PtBMA, poly(*tert*-butyl methacrylate); PTFE, polytetrafluoroethylene; PV, pervaporation; PVA, poly(vinyl alcohol); PVC, poly(vinyl chloride); PVCin, poly(vinyl cinnamate); PVDF, poly(vinylidene fluoride); PVP, poly(2-vinyl pyridine); RO, reverse osmosis; SB, sodium benzoate; SPEEK, sulfonated poly(ether ether ketone); SPMMA, 1-[β -(methacryloyl)ethyl]-3,3'-dimethyl-6-nitro-spiro(indoline-2,2'-[2H-1]benzopyran); TIPS, thermally induced phase separation; tBIA, *tert*-butyl isophthalic acid dichloride; THO, theophylline; TMBA, tetramethyl bisphenol-A; TMPD, trimethyl-1,3-phenylenediamine; TPMLH, bis-[4-(dimethylamino)phenyl] (4-vinyl-phenyl)methyl leucohydroxide; UF, ultrafiltration; VIPS, vapour-induced phase separation.

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1. Introduction

Photo-irradiation has a special role for life on earth because it serves as an important source of energy; photo-synthesis is of crucial relevance for the global ecosystem. A more efficient use of solar energy is considered one of the key issues for sustainable development of mankind. Artificial sources of light have been used by men since very early days, and many more or less sophisticated versions are established nowadays. Light is used in information technologies for data transmission and storage. In many other technical applications, selective excitation with UV–vis irradiation is used to initiate chemical reactions which would not be possible via other pathways or which would be less efficient due to unwanted side reactions or effects. The synthesis, modification and controlled degradation of natural and synthetic polymers using photo-chemical methods are an important area.

Membranes are also essential for life; biological membranes form and define individual compartments on the cellular and sub-cellular levels. Any membrane is an interface between two adjacent phases acting as a selective barrier and regulating the exchange of substances between the two compartments. Synthetic membranes are nowadays established for a large variety of applications, and many more are targets of intense research and development. The main advantages of membrane technology as compared with other unit operations in (bio)chemical engineering are related to the 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 temperatures and – compared to other thermal separations – at low energy consumption. Also, upscaling and downscaling of membrane processes as well as their integration into other separations or reaction schemes are easy. Membrane technologies are considered as key technologies for process intensification. The majority

of technical membranes are made from polymers because a very wide variety of barrier structures can be realized with this group of materials.

It is the aim of this review to give an overview on the recent developments in combining photo-irradiation-based and membrane technologies. Because the rapid growth of membrane technologies has started only in the 1980s, there are only occasional papers on that topic in the earlier literature (and if so, more in side areas of membrane technology such as materials for coating, packaging or sensing). In agreement with the scope of this journal, we will focus on the work in the last decade. However, to our knowledge, such a comprehensive review on the topic has not yet been prepared before. Therefore, we will also include important examples from the earlier period. Brief introductions are given into the fields of photo-irradiation-based technologies (with focus on polymers; Section 2) and of polymeric membranes (with focus on concepts, preparation methods and functions of membrane systems; Section 3). The main part of this review is organized according to the three different ways, photo-irradiation can be used to create novel or improved membrane systems based on polymers (as already indicated in the title of this paper; Section 4). The conclusions part will also involve a brief outlook towards possible new developments in this interesting area (Section 5).

2. Photo-irradiation and technologies based thereon

2.1. General characteristics of photo-reactions

Photo-chemical reactions in the most general sense are reactions induced by ultraviolet ($\lambda = 100\text{--}400\text{ nm}$), visible ($\lambda = 400\text{--}760\text{ nm}$) and infrared ($\lambda = 780\text{--}20,000\text{ nm}$) radiation [1]. In this review we will focus on photo-chemistry based on excitation with light of wavelengths in the range

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