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Atom transfer radical polymerization (ATRP): A versatile and forceful tool for functional membranes

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ABSTRACT

The progress in atom transfer radical polymerization (ATRP) provides an effective means for the design and preparation of functional membranes. Polymeric membranes with different macromolecular architectures applied in fuel cells, including block and graft copolymers are conveniently prepared via ATRP. Moreover, ATRP has also been widely used to introduce functionality onto the membrane surface to enhance its use in specific applications, such as antifouling, stimuli-responsive, adsorption function and pervaporation. In this review, the recent design and synthesis of advanced functional membranes via the ATRP technique are discussed in detail and their especial advantages are highlighted by selected examples extract the principles for preparation or modification of membranes using the ATRP methodology.

Contents

Abbreviations: AEMs, anion exchange membranes; AGET, activators generated by electron transfer; ARGET, activators regenerated by electron transfer; ATRP, atom transfer radical polymerization; BSA, bovine serum albumin; CB, carboxybetaine; CTFE, chlorotrifluoroethylene; DMAEMA, 2-(dimethylamino)ethyl methacrylate; DP, degree of polymerization; FMA, 2*H*-perfluorooctyl methacrylate; FPAE, fluorinated poly(arylene ether); GMA, glycidyl methacrylate; GY, grafting yield; HEM, hydroxyethyl; HEMA, 2-hydroxyethyl methacrylate; HEX, hexagonally packed cylinder; HMA, hexyl methacrylate; HMTETA, 1,1,4,7,10,10-hexamethyl triethylene tetramine; HPL, hexagonally perforated lamellar; LAM, lamellar; MBR, membrane bioreactor; MeOEGMA, monomethoxy oligo(ethylene glycol)methacrylate; MF, microfiltration; NF, nanofiltration; NMDG, *N*-methylglucamine; NS, norbornenylethylstyrene; NSS, neopentyl-*p*-styrene sulfonate; NVP, *N*-vinyl-2-pyrrolidone; P(AA-Na), poly(acrylic acid sodium); P(VDF-*co*-HFP), poly(vinylidene difluride-*co*-hexafluoropropylene); PAAc, poly(acrylic acid); PAES, poly(arylene ether sulfone); PC, phosphobetaine; PEEK, poly(ether ether ketone); PEG, poly(ethylene glycol); PEMs, proton exchange membranes; PES, poly(ether sulfone); PESEKK, poly(ether sulfone ether ketone ketone); PET, poly(ethyleneterephthalate); PHMA-*b*-PS-PHMA, poly(hexyl methacrylate)-*b*-poly(styrene)-*b*-poly(hexyl methacrylate); PNIAAM, poly(*N*-isopropylacrylamide); PP, polypropylene; PPESK, poly(phthalazinone ether sulfone ketone); PPO, poly(2,6-dimethylphenylene oxide); PSF, polysulfone; PSSA, poly(styrene sulfonic acid); PtBA, poly(*tert*-butyl acrylate); PVC, poly(vinyl chloride); PVDF, poly(vinylidene); PVDF-*co*-CTFE, poly(vinylidene difluoride-*co*-chlorotrifluoroethylene); RC, regenerated cellulose; RO, reverse osmosis; SANS, small-angle X-ray scattering; SB, sulfobetaine; SBMA, sulfobetaine methacrylate; SI-ATRP, surface-initiated ATRP; SPM, 3-sulfopropyl methacrylate potassium salt; SPMA, sulfopropyl methacrylate; SSA, styrene sulfonic acid; Sty, styrene; TEM, transmission electron microscopy; TEOS, tetraethoxysilane; UF, ultrafiltration.

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1. Introduction

Functional polymeric membrane materials are the central component in different membrane applications, including fuel cells, stimuli-response, adsorption, and pervaporation. A long-standing goal is to synthesize polymers with well-defined architectures, compositions, and functionalities because precise design at the molecular level can achieve optimal macroscopic properties. Although conventional radical polymerization technique has been widely used in materials synthesis, it lacks effective control over the issues mentioned above. Atom transfer radical polymerization (ATRP), a living polymerization technique, shows promising prospective in designing well-defined polymeric materials.

ATRP is a versatile synthetic tool that enables the preparation of new (co)polymers with precisely controlled molecular weight, relatively low dispersities ($M_w/M_n < 1.1$), composition (block, graft, alternating gradient copolymers), and diverse functionalities [1–3]. As shown in Fig. 1, the essential characteristic of ATRP is the equilibrium between propagating radicals and dormant species, predominately in the form of initiating alkyl halides/macromolecular species (Pn-X) [4,5]. The radicals are generated through the dormant species periodically reacting with transition metal complexes in their lower oxidation state, $M_t{}^n/L$ ($M_t{}^n$ represents the transition metal species in oxidation state m and L is a ligand). The generated radical can then propagate with vinyl monomer (k_p), terminate by either coupling or disproportionation, or be reversibly deactivated [6,7]. Radical concentration is diminished in ATRP due to persistent radical effect and thus well-defined polymers can be prepared [8]. ATRP is a catalytic process and can be mediated by many redox-active transition metal complexes (Cu in Cu^I/L and $X\text{-}Cu^{II}/L$ is the widely used transition metal) [9]. With the deeper understanding of ATRP principles and higher requirements of materials for various advanced technologies, activators generated by electron transfer (AGET) ATRP using stoichiometric amounts of reducing agents were developed which permits the reaction without a rigorously deoxygenated process [10]. Furthermore, activators regenerated by electron transfer (ARGET) ATRP could decrease the amount of copper catalyst by 10^3 times from prior levels, and the procedure can contain a large excess of reducing agent [11–14].

In addition to the design of polymeric membranes with various architectures, ATRP has robust potential to place well-defined functional polymer brushes onto membrane surface for different applications, including antifouling, stimuli-responsive, adsorptive surfaces. Efforts have been devoted to develop functional membranes by employing the ATRP technique in academia, illustrated by the chronology of ATRP and membranes documented in Fig. 2. We herein summarize the role of ATRP in preparing functional membranes based on related literature papers. The following discussion is intended to provide a useful reference

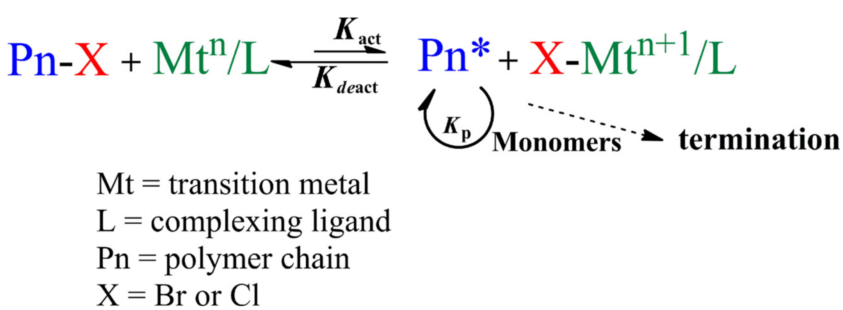

Fig. 1. The mechanism of transition metal-catalyzed ATRP.