Journal of Membrane Science 554 (2018) 109–116

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Controlling external versus internal pore modification of ultrafiltration membranes using surface-initiated AGET-ATRP

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ARTICLE INFO

Keywords:
Atom transfer radical polymerization
Grafting
Pore size
Rejection
Regenerated cellulose membrane

ABSTRACT

The activators generated electron transfer (AGET) method coupled with atom transfer radical polymerization (ATRP) is shown to be a simple and well controlled approach for surface-initiated polymerization of 2-hydroxyethyl methacrylate (HEMA) on regenerated cellulose (RC) membranes. The AGET-ATRP method has been optimized with respect to the initiator concentration, the polymerization reaction time and the reducing agent (activator) concentration. Control of polymer grafting on the external membrane surface versus the internal pore surface of RC ultrafiltration membranes was investigated using different pore filling solvents having a wide range of viscosity and reactivity during ATRP initiator immobilization via acylation of RC hydroxyl groups. The effectiveness of the pore filling solvent in limiting grafting inside the membrane pores was found to depend on both its viscosity and reactivity. Rejection of BSA and dextran was used to probe changes in pore size. Glycerol was found to be the most effective pore filling solvent, indicated by a significant degree of modification of the membrane surface with grafted polyHEMA but only a very minor increase in solute rejection.

1. Introduction

Chemical modification of membranes after fabrication allows established production methods to be utilized while enabling membrane properties such as permeability, selectivity, and resistance to fouling to be manipulated [1–6]. Membranes can be modified by a vast array of techniques, but attachment of polymer brushes is often used to introduce specific functional groups and offers additional control over the structure of the attached nanostructure [7–11]. Ideally, control over the brush chemistry, density, length, and spatial location will afford membranes with tailored macroscopic properties.

Polymer brushes can be attached to membranes in a *grafting to* or *grafting from* approach [12–14]. In the *grafting to* method, pre-fabricated polymers are covalently attached to the membrane, but steric repulsion may limit the grafting density and the reaction between the polymer brush and membrane can often be inefficient [15,16]. In a *grafting from* approach, polymer brushes are grown directly from the membrane surface at initiator-functionalized sites. These initiator sites can be generated in a number of different ways, but the most common include the formation of free radicals by UV or plasma treatment [11,17–19]. These straightforward free radical approaches are commonly used, but prevalent termination reactions between radicals limits control over polymer brush growth and free unbound polymer is also generated [10].

In contrast, controlled radical polymerization (CRP) techniques offer significant control over the polymerization reaction and the brushes can be easily tailored for a specific three-dimensional structure [9,20–23]. Atom transfer radical polymerization (ATRP) is an attractive CRP technique, since it works with a wide range of monomers and solvents, initiators and catalyst components are commercially available, and the technique is experimentally straightforward [24–26]. ATRP provides a platform for achieving complex macromolecular architectures with controlled topology. It includes precisely controlled linear chains, segmented as well as periodic copolymers, bi and multi-dimensional polymers and polymers with complicated structural arrangements [9,27–29].

Though membrane based separations have tremendous potential, a single bulk polymer or polymer blend as the membrane material rarely has all the desired characteristics for a given separation process. Consequently, surface modification is frequently used to enhance

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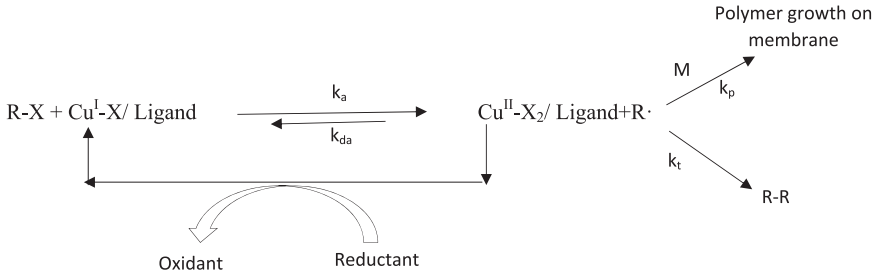
https://doi.org/10.1016/j.memsci.2018.02.066
Received 14 June 2017; Received in revised form 3 January 2018; Accepted 27 February 2018



Scheme 1. The simplified scheme for the AGET-ATRP [30].

surface properties such as hydrophilicity, surface charge and resistance to fouling. In most cases surface modification of ultrafiltration (UF) membranes leads to modification of the external membrane surface as well as the inner pore surface. While external surface modification is desirable, internal pore surface modification may lead to a decrease in the flux due to a decrease in pore size. Since CRP techniques can potentially offer control over the density and length of the grafted polymers, a modification procedure, that allows control over the location of grafting on the membrane surface, is developed here.

Recently, ATRP techniques have been simplified to an even greater degree by the development of activators generated by electron transfer (AGET). Conventional ATRP requires removal of oxygen present by drawing a vacuum. In the case of RC UF membranes this can lead to pore collapse especially for wet membranes [7]. AGET-ATRP provides a way around this problem because a small amount of Cu catalyst is generated by a reducing agent to account for the radical termination (Scheme 1) [30]. A variety of reductants, namely tin(II), 2-ethyl hexanoate, ascorbic acid (vitamin C), glucose, phenol, hydrazine, phenyl hydrazine and nitrogen containing monomers, have been reported as suited AGET reagents [31,32]. The nature of the ligands (cyclic, bridged, branched, nature of coordinating atoms) was reported to show a range of activities during ATRP [33]. In the present investigation, ascorbic acid (AA) was chosen as the reductant and bipyridine as the ligand for complexation of Cu ions. This AGET-ATRP procedure was found to be advantageous as it was not necessary to deoxygenate the solvents. Air sensitive copper (I) is not required, the reaction solution is simple to prepare and the reaction can be performed in any container with a good seal. Due to the decrease in the catalyst induced side reactions, AGET-ATRP also provides the possibility for the preparation of high molecular weight copolymers with appropriate chain end functionality [34]. Ultimately, this procedure does not require membranes to be dried. A complication is that since the membranes are never dried, the degree of grafting (mass grafted per membrane surface area) cannot be measured accurately.

In theory, the polymerization rate in ATRP only depends on the ratio of Cu^{2+}/Cu^{1+}, not the catalyst concentration. For AGET, the situation is more complicated. Enough ascorbic acid must be added to consume all the oxygen and generate the optimal amount of Cu^{1+}. If too much ascorbic acid is added, then all the copper is reduced and control is lost. It is easier to control the Cu^{2+}/Cu^{1+} ratio at higher catalyst concentrations. Since most oxygen in the system comes from the headspace, an argon flush is advisable.

The efficiency of polymerization can be expressed by the equilibrium constant for initiator or end group activation (K_{ATRP}) and it is governed by the ratio of rate constants for the forward reaction (k_a) and the reverse reaction (k_{da}), respectively, as follows

$$K_{ATRP} = \frac{k_a}{k_{da}} \quad (1)$$

Consequently, the initiator plays a significant role in controlling the rate of polymerization as the equilibrium constant K_{ATRP} largely depends on the equilibrium constant for homolytic bond dissociation of the initiators [35]. The structures of the alkyl group as well as the nature of halogens were found to affect the rate of ATRP significantly. Several studies provide the structure–activity correlation of the initiators, revealing the fact that alkyl bromide is more active than its chloride homologue and the stability of the alkyl radicals facilitates the ATRP process [36]. In view of these observations, α-bromoisobutyryl bromide (BIB) was chosen as the initiator for this study.

AGET-ATRP has only been utilized by a handful of researchers to grow polymer brushes from membrane surfaces [37,38]. Other variations of ATRP have also been used, but in general, all of this research has focused on tuning brush chemistry, density, and length [39]. Limited literature is available on manipulating initiator attachment to control regional growth of polymer brushes [40]. For porous microfiltration or UF membranes, this means polymer brushes could be selectively grown on the membrane surface or in the membrane pores [17,41], while maintaining control over the brush chemistry, density, and length. The present investigation deals with optimization of surface-initiated AGET-ATRP for regenerated cellulose (RC) UF membranes. A method to control the location of the grafted polymer by using a pore-filling solvent during initiator immobilization has been developed. Finally, the influence of controlled grafting on membrane separation performance has been investigated. Fig. 1 shows diagrammatically how initiator immobilization within the pores is suppressed using the method developed here. The method developed here allows us to, for example, graft polyHEMA to enhance fouling resistance while minimizing the effect on membrane performance.

2. Experimental

2.1. Materials

All reagents purchased were ACS reagent grade or higher unless specified otherwise. Methanol (MeOH), glycerol, and acetonitrile were purchased from EMD Millipore, Billerica, MA. Triethylamine (TEA), 4-dimethylaminopyridine (DMAP), and copper (II) chloride ($CuCl_2$, 99.999% trace metal basis) were purchased from Sigma-Aldrich, Munich, Germany. 2-hydroxyethyl methacrylate (HEMA, 97%, stabilized with 4-methoxyphenol), and α-bromoisobutyryl bromide (BIB, 98%) were purchased from Alfa-Aesar, Ward Hill, MA. Bovine serum albumin (BSA, biotechnology grade) and L-(+)-ascorbic acid (AA) were purchased from Amresco (Solon, OH). Basic aluminum oxide (Brockmann I) and 2,2′-bipyridine(Bpy) were purchased from BeanTown Chemical, Hudson, NH. Dextrans (40 kDa, 70 kDa and 100 kDa) were purchased from Amersham Bio-Sciences AB, Uppsala, Sweden. Deionized water was produced by Thermo Fisher 18 MΩ Barnstead Smart2Pure system (Schwerte, Germany). Commercially available regenerated cellulose (RC) membranes with a nominal molecular weight cut off of 100 kDa (Product code: PLCHK) were purchased from EMD Millipore, Billerica, MA. PEG 400, Pluronic L 64 and ethanol were procured from BroadPharm, San Diego, CA, Florham Park, NJ and EMD Millipore, Billerica, MA, respectively.