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Research Paper

Activator Generated Electron Transfer Combined Atom Transfer Radical Polymerization (AGET-ATRP) for Controlled Grafting Location of Glycidyl Methacrylate on Regenerated Cellulose Ultrafiltration Membranes

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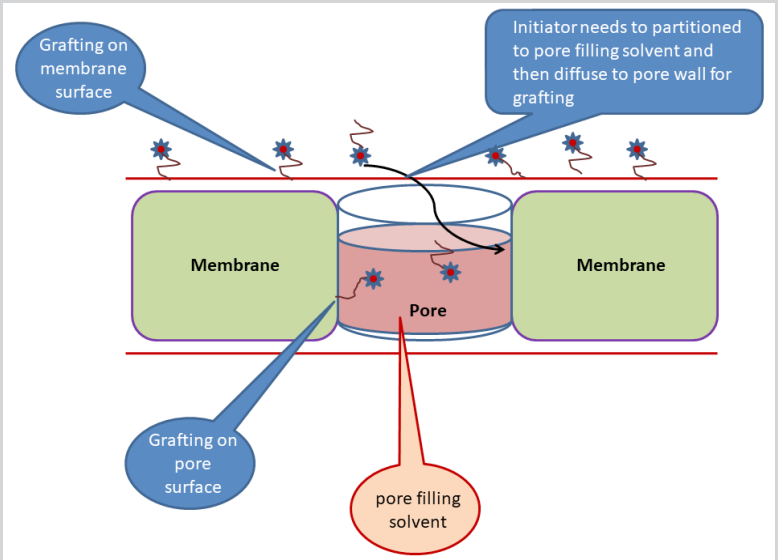
- Spatial control in ATRP
- Solvents induced grafting location
- Epoxy ring opening
- Solvents induced grafting location location

Graphical abstract



Abstract

This investigation indicates the ability to selectively graft glycidyl methacrylate (GMA) only from the external surface of regenerated cellulose (RC) ultrafiltration (UF) membranes using activator generated electron transfer (AGET) atom transfer radical polymerization (ATRP). This controlled polymerization resulted in epoxy functionalized polymer brush ends. Further reaction of the terminal epoxy groups provides a flexible platform to introduce desired functionalities either by electrophilic or nucleophilic epoxy ring opening. Selective grafting from the external membrane surface was achieved by using an appropriate pore filling solvent prior to modification. A high viscosity pore filling solvent that is immiscible with the reactive monomer solution used during surface modification was the most effective in supressing grafting from the internal pore surface. The effects of grafting on membrane performance were evaluated by determining water permeability and protein rejection.

1. Introduction

Surface modification is frequently used to impart unique properties onto the membrane surface [1-3]. Atom Transfer Radical Polymerization (ATRP) has been shown to be a flexible method for controlled polymer growth from the membrane surface, depending upon the associated chemistry and pore size [4-6]. Further ATRP provides a method for grafting specific polymer architecture [7,8]. Ultrafiltration membranes have pore sized in the range 1-100 nm. They are frequently used for size exclusion, pressure driven membrane-based separation for proteins, as well as concentration and buffer exchange. To date few publications have focussed on the use of ATRP to control the location of polymer grafting for the membrane surface [9]. Here

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we focus on grafting only from the external membrane surface and not the pore surface. This is particularly important for UF membrane where grafting from the internal pore surface can lead to pore plugging [10,11].

In this work we have grafted glycidyl methacrylate from the external membrane surface. Glycidyl methacrylate has been shown to be a versatile platform for introducing specific functionalities to the polymer brushes due to the presence of strained epoxy rings [12-14]. De et al. [15] grafted poly(GMA) brushes from a glassy carbon substrate by ATRP to introduce suitable chain end functionalities by either electrophilic or nucleophilic ring opening using azide, alcohols for post polymerization immobilization of ferrocene and nitrobenzene. They have exploited' thiol-epoxy click chemistry' to synthesize novel bi-functional polymeric chains.

AGET-ATRP has been used for grafting poly(GMA) from a PVDF membrane to improve its surface conductivity useful for its fuel cell application [16]. Surface initiated ATRP was used for grafting poly(GMA) on regenerated cellulose for fabrication of high capacity weak anion exchange membrane [17]. Redox initiated grafting of poly(GMA) on nylon membranes was reported for immobilization of antibodies by nucleophilic epoxy ring opening through amine functionality for the applications like:matrices/platform for biosensors, well-plates for enzyme linked immunofiltration, detection of various antigens including whole cell bacteria [18]. Poly(GMA) grafting on cellulose has also been exploited for efficient urease immobilization for urea detection, estimation, and degradation [19].Free radical grafting of poly(GMA) on solid polypropylene has also been reported to enhance the speed of crystallization [20].

Previous studies have tended to focus on controlling the length and density of the grafted polymer chains. Here we focus on the location of grafting, specifically the outer membrane surface. This is essential if it is to impart specific surface properties without modifying the membrane pore size due to grafting from the inner pore surface. Our previous investigation revealed that selectivity in grafting location can be introduced by suitable choice of a pore filling solvent. Here we continue our earlier work by investigating grafting of GMA from the outer surface of a RCUF membrane. The present investigation demonstrates not only the concept of site selectivity by use of a suitable pore filling solvent, but also provides an appropriate platform to introduce desired surface functionalities without compromising the nominal molecular weight cut and permeability of the membrane.

2. Experimental

2.1. Materials

All reagents purchased were ACS reagent grade or higher unless specified otherwise. Methanol (MeOH), glycerol, and acetonitrile were procured from EMD Millipore, Billerica, MA. Triethylamine (TEA), 4-dimethylaminopyridine (DMAP), and copper (II) chloride ($CuCl_2$, 99.999% trace metal basis) were procured from Sigma-Aldrich, Munich, Germany. Glycidyl methacrylate (GMA, 97%, stabilized with 4-methoxyphenol), and α-bromoisobutyryl bromide (BIB, 98%) were procured from Alfa-Aesar, Ward Hill, MA. Bovine serum albumin (BSA, biotechnology grade) and L-(+)-ascorbic acid (AA) were purchased from Amresco (Solon, OH). 2,2'-bipyridine(Bpy) were purchased from BeanTown Chemical, Hudson, NH while Dextran (70 kDa) was procured from GE Healthcare Biosciences, Pittsburgh, PA. Deionized water was obtained from ThermoFisher 18 MΩ Barnstead Smart2Pure system (Schwerte, Germany).

Commercially available regenerated cellulose (RC) membranes with 100 kDa molecular weight cut off were procured from EMD Millipore, Billerica, MA. The commercially available membranes were soaked in purified water for 30 min after washing three times with 25 mL of methanol for 30 min. This step was adopted to remove the preservatives used by the manufacturer.

2.2. Instrumentation

Fourier-transform infrared (FT-IR) spectroscopy was conducted using a Shimadzu IRAffinity-1 equipped with a PIKE single-reflection horizontal (attenuated total reflectance) ATR accessory (Shimadzu, Columbia, MD, USA). UV-vis measurements were taken using a Thermo Scientific GENESYS 10uv. The total organic content (TOC) was measured to determine dextran rejection using TOC analyser, Shimadzu TOC/TN vch. X ray photo electron spectroscopic (XPS) was carried out using an ultra-high vacuum XPS auger spectrometer, Chanhassen, MN.

2.3. Methods

2.3.1. Initiator immobilization

Washed membrane discs (25 mm diameter) were rinsed 3 times with dry acetonitrile (20 mL) for 20 min (acetonitrile was dried on a molecular sieve before use). Then 20 mL of acetonitrile containing 1 mM BIB, 1.25 mM TEA, and 0.05 mM DMAP was prepared. The washed membrane was transferred to the immobilization solution and allowed to react for 5 min followed by quenching with water. Finally, the membrane was washed in a 1:1 (v/v) MeOH/H_2O mixture.

The washed membranes were loaded into an 8050 Amicon stirred cell. 25 mL of pore filling solvent were added to the cell and it was gradually pressurized to 21.8 psi (1.5 bar). After collection of 2.5 grams of pore filling solvent as permeate, it was assumed that the pores of the RC UF membrane were filled with solvent. The membrane was then placed on a glass plate and an EPDM gasket with a circular cut-out 35 mm in diameter was centred on the sample. A piece of HDPE matching the gasket dimensions was set on top of the setup and everything was secured with binder clips. A solution containing 200 mM BIB, 250 mM TEA, and 10 mM DMAP in 5 mL of acetonitrile was prepared and poured on top of the membrane and allowed to react for 1 min followed by quenching with water. The membrane was washed in a 1:1 (v/v) MeOH/H_2O mixture 3 times. The modified region was cut out with a 25 mm punch.

2.3.2. AGET ATRP

Surface-initiated AGET ATRP was conducted next. The reactive monomer solution consisted of GMA (2 M), $CuCl_2$ (20 mM), and Bpy (50 mM) in a 1:1 (v/v) MeOH/H_2O mixture. A membrane disc was added to a 3-neck flask under argon flush along with 25 mL of the reaction solution. A 100 mM ascorbic acid solution in a 1:1 (v/v) MeOH/H_2O mixture was prepared. Under argon flush, 2 mL of this ascorbic acid solution was added. The flask was agitated for 30 seconds and allowed to settle for a 5 min. After reaction the membranes washed using a solution of 1:1 (v/v) MeOH/H_2O followed by washing with DI water. The chemical structures of the reagents used are shown in Figure 1.

2.4. Membrane performance

Prior to the measurement of water flux, membranes were soaked in DI water for 30 min. The membrane was loaded into an Amicon 8010 or 8050 stirred filtration cell. The cell was connected to a reservoir filled with DI water. Initially, a pressure of 0.5 bar (7.3 psi) of nitrogen gas was applied for 5 min for pre-compaction. The pressure was then reduced to 0.4 bar (5.8 psi) and the steady state flux was measured.

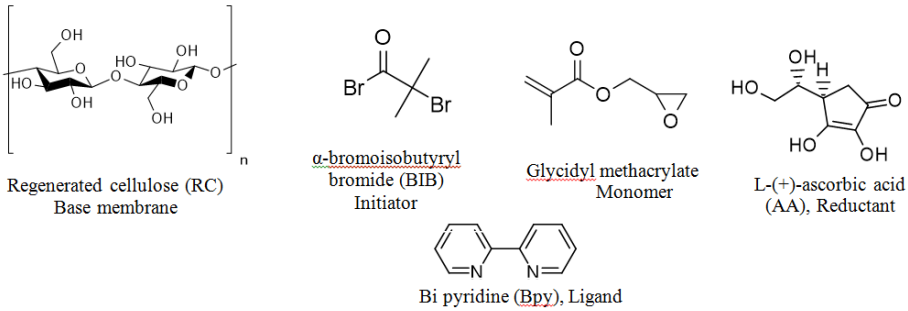


Fig. 1. The structure of the reagents used.

For BSA or dextran rejection measurements, feed solutions were prepared at a concentration of 1 mg. mL^{-1}. 100 mL of the feed was loaded into the reservoir and the pressure was set to 0.4 bar (5.8 psi) until 20 g of permeate were collected. For BSA, the relative concentration of the feed and permeate were measured by comparing the UV absorbance at 280 nm. For the BSA rejection test, the feed and permeate were analysed by UV-VIS spectrophotometer at a wavelength of 280 nm. The % BSA rejection was calculated as follows:

$$R = \left(1 - \frac{Absorbance\ of\ permeate\ solution\ at\ 280\ nm}{Absorbance\ of\ feed\ solution\ at\ 280\ nm}\right) x\ 100 \quad (1)$$

For dextran rejection experiments, 1 mg ml^{-1} of dextran solution (70 kDa) was used as feed. The permeate was collected for a constant time. The amount of dextran in the permeate relative to that in the feed solution was used for the determination of dextran rejection. The relative concentration of the feed and permeate was determined by TOC analysis.

3. Results and discussion

Successful ATRP depends on ensuring an oxygen free environment [21,22] in order to ensure all the Cu(1) ions present are not oxidised. The less stable Cu(1) is responsible for sustaining an ATRP reaction. By using surface-initiated Activator Generated Electron Transfer (AGET) ATRP one need not ensure an oxidant free environment [23-25].Moreover, it is a 'green' process since it utilizes only a ppm level of catalyst in the presence of suitable reductants such as: ascorbic acid [26],tin (II) 2-ethylhexanoate [27], glucose [28], phenol [29], hydrazine [30], trimethylamine [31] etc. A stable ratio of Cu ion concentration is maintained in both +1 and +2 oxidation states. AGET ATRP is also advantageous for the synthesis of copolymers with a higher molecular weight as it reduces catalyst induced side reactions. This living radical polymerization can be expressed as the following dynamic equilibrium between dormant and propagating species (Scheme 1).

Several reports are available in literature discussing the mechanistic as well as experimental aspects of ATRP to achieve desired topologies on membrane surfaces [32-35].Given the pore size range of ultrafiltration membranes, surface initiated AGET ATRP can lead to modification of the outer membrane and pore modification. Outer surface modification is desirable for attaching required functionality in order to either control the selectivity of the separation or improve basic performance. On the other hand, modification inside the pore surface may lead to reduction in pore size, which can decrease the fluid flux and modify the rejection properties of the membrane. Scheme 2 gives the reaction steps. In the first step, BIB initiator was allowed to immobilize on the RC-UF membrane.

Since subsequent polymer growth will be on the initiator sites only, spatial control should be attempted during the initiator immobilization step. During solution phase immobilization, no spatial control is achieved. The initiator molecules can attach to sites through the membrane surface (outer surface and inside the pores). However, if the membrane pores are first filled with a solvent that restricts initiator attachment within the membrane pores little grafting within the pores occurs. A variety of pore filling solvents were investigated in tuning the selectivity of initiator immobilization. In the next step, AGET-ATRP was used for controlled polymer growth. A longer ATRP time leads to longer polymer chains. In the present investigation, mono ethanolamine and sodium bisulphite were used to functionalize the polymer chain ends.

3.1. AGET ATRP

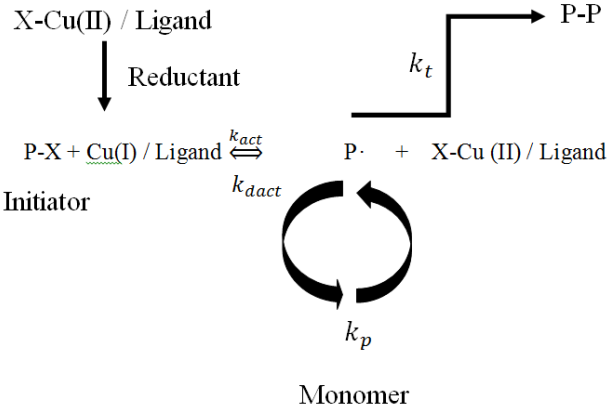
Careful control of any oxidants e.g. oxygen is required to sustain conventional ATRP. A trace of oxidant is sufficient to stop the ATRP reaction, as it leads to the oxidation of Cu^{+1} species to Cu^{2+}, which is the stable oxidation state of Cu. This constraint is not an issue for AGET ATRP due to the addition of a suitable reductant like ascorbic acid which maintains a constant Cu^{+1}/Cu^{2+} ratio. In this section we have optimized the experimental parameters for AGET-ATRP on RC-UF membranes using GMA. The membrane was modified using different relative concentrations of ascorbic acid to Cu for 1-hourpolymerization. Initiator immobilization was conducted for 1 min using 100 mM BIB. The water flux was measured using the resultant membranes and plotted as a function of ascorbic acid to Cu ratio (Figure 2 (a)). As the relative ascorbic acid concentration increased more Cu is converted to Cu^{1+}, which favoured the forward reaction and ultimately led to a higher degree of polymerization. Consequently, the flux after polymerization was found to reduce significantly. It was also noted that the flux reduction is enhanced beyond ascorbic acid to Cu ratio of more than 0.4. Therefore, the effect of ATRP time and initiator concentration on J_{ATRP}/J_{immob} were investigated at AA/Cu ratio 0.4.

Figure 2(b) shows the change in the ratio of J_{ATRP}/J_{immob} as a function of reaction time. The longer the reaction time, the longer the polymer chains. The rate of polymerization (R_p) is a function of the ratio of activator to deactivator while dead chain fraction (DCF) and time of ATRP can be quantified as follows [36].

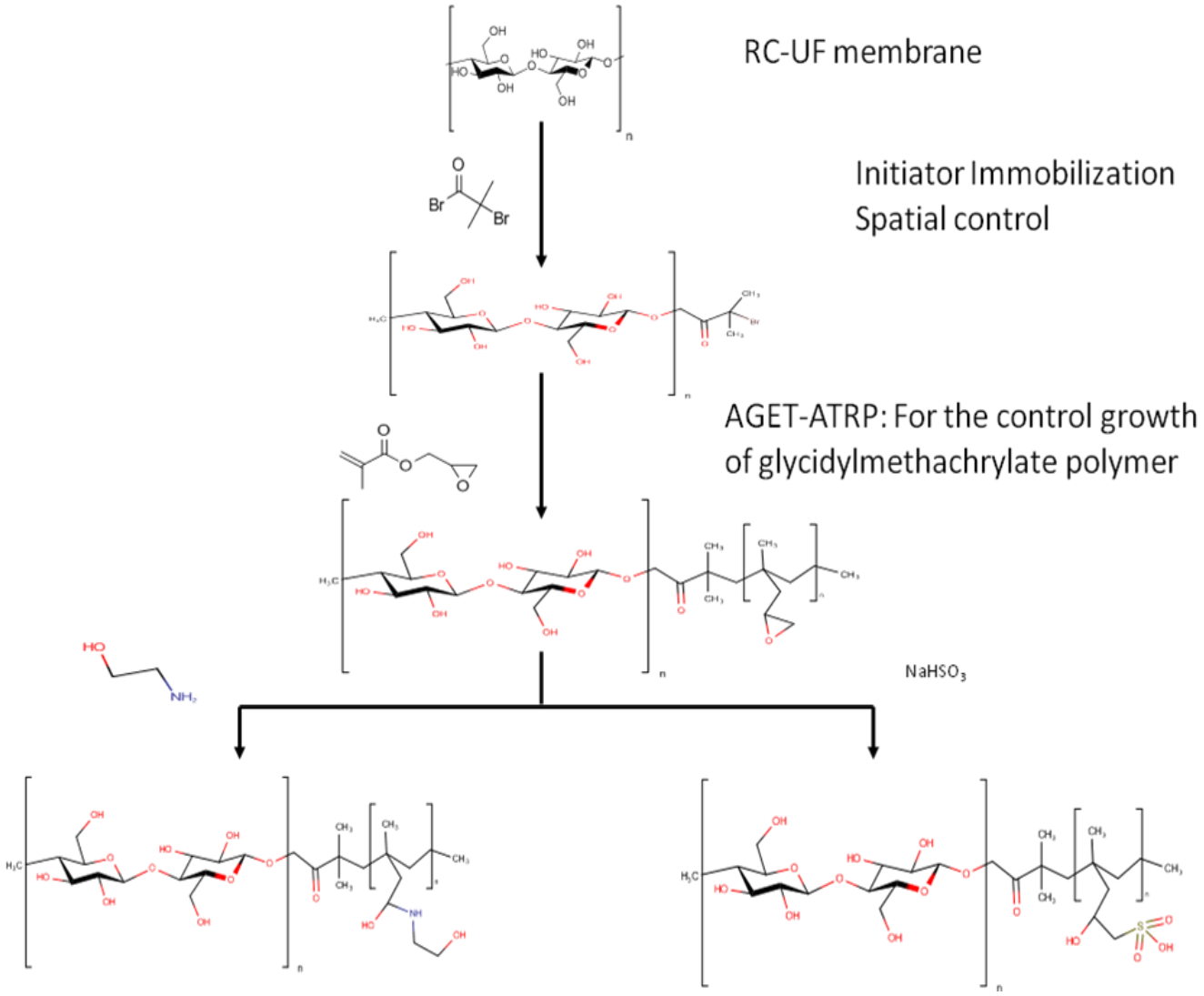
$$R_p = k_p[Cu][R^{\cdot}] = k_p k_{ATRP} \frac{[Cu][I]_0[Cu^I]}{[X - Cu^{II}]} \quad (2)$$

$$DCF = 2\ DP\ k_t \frac{[\ln(1-p)]^2}{[Cu]\ k_p^2\ t} \quad (3)$$

where, DP is the degree of polymerization, p is the monomer conversion, k_p is rate of polymerization, $[Cu]$, $[I]_0$, $[Cu^I]$, [X - Cu^{II}] and $[R^{\cdot}]$ are the concentration of Cu, initiator, Cu in +1 state, CuX_2 and the radical, respectively. The 't' is the time of ATRP. After 30 min of polymerization, the flux ratio was 0.93.Thisdecreased moderately with an increase in ATRP time, which is a sign of polymer growth. For 1 min of initiator immobilization, AA/Cu ratio 0.4, 100 mM BIB concentration; optimized ATRP time was evaluated as 60 min.



Scheme 1. Mechanistic representation of AGET ATRP.



Scheme 2. Modification of RC-UF by AGET-ATRP using GMA.

Polymer chains grow only by reaction with the immobilized initiator. Figure 2(c) depicts the variation of the flux ratio as a function of BIB concentration at AA/Cu ratio 0.4, 1 min initiator immobilization time, 1-hourpolymerization. There was a drastic decrease in the flux ratio with increase in initiator concentration up to 200 mM followed by a moderate decrease. The initial drastic decrease in water flux is an indication of the enhanced density of initiator immobilization and subsequent dense growth of polymer brushes. It is likely that above a BIB concentration of 200 mM, the membrane surface becomes saturated and hence the reduction in flux ratio is moderate. Based on this study, 100 mM BIB concentration was found to enable sufficient polymer growth without a significant decrease in water flux. Based on our results, 1 hour polymerization, an ascorbic acid / Cu ratio of 0.4 and 100 mM of initiator concentration were used further investigation.

3.2. Membrane performance

The spatial control of the modification was investigated by interfacial immobilization [37] using different pore filling solvents and compared with the solution mode of modification, where no spatial control was expected. Five different solvents having different viscosities (glycerol: 1414 Cp, 41.6 mol L^{-1}; L 64: 850 Cp, 0.7 mol L^{-1}; PEG 400: 101 Cp, 5.6 mol L^{-1}; ethanol: 1.1 Cp, 17.4 mol L^{-1}, acetonitrile: 0.4 Cp) were investigated as pore filling solvents during initiator immobilization.

The effectiveness of the pore filling solvent depends on its ability to supress initiator immobilization on the membrane surface. Thus, the solubility of the initiator should be minimal in the pore filling solvent. The higher the viscosity of the pore filling solvent lower the rate of diffusion of the imitator to the inner membrane pore surface. Figure 3 represents the flux ratio for ATRP to the initiator immobilization as a function of these pore filling solvents with 100 mM BIB, AA/Cu ratio 0.4, 1 min initiator immobilization, 1 hour ATRP. The ratio followed the order: glycerol > L 64 > PEG 400 > ethanol > acetonitrile ~ solution.

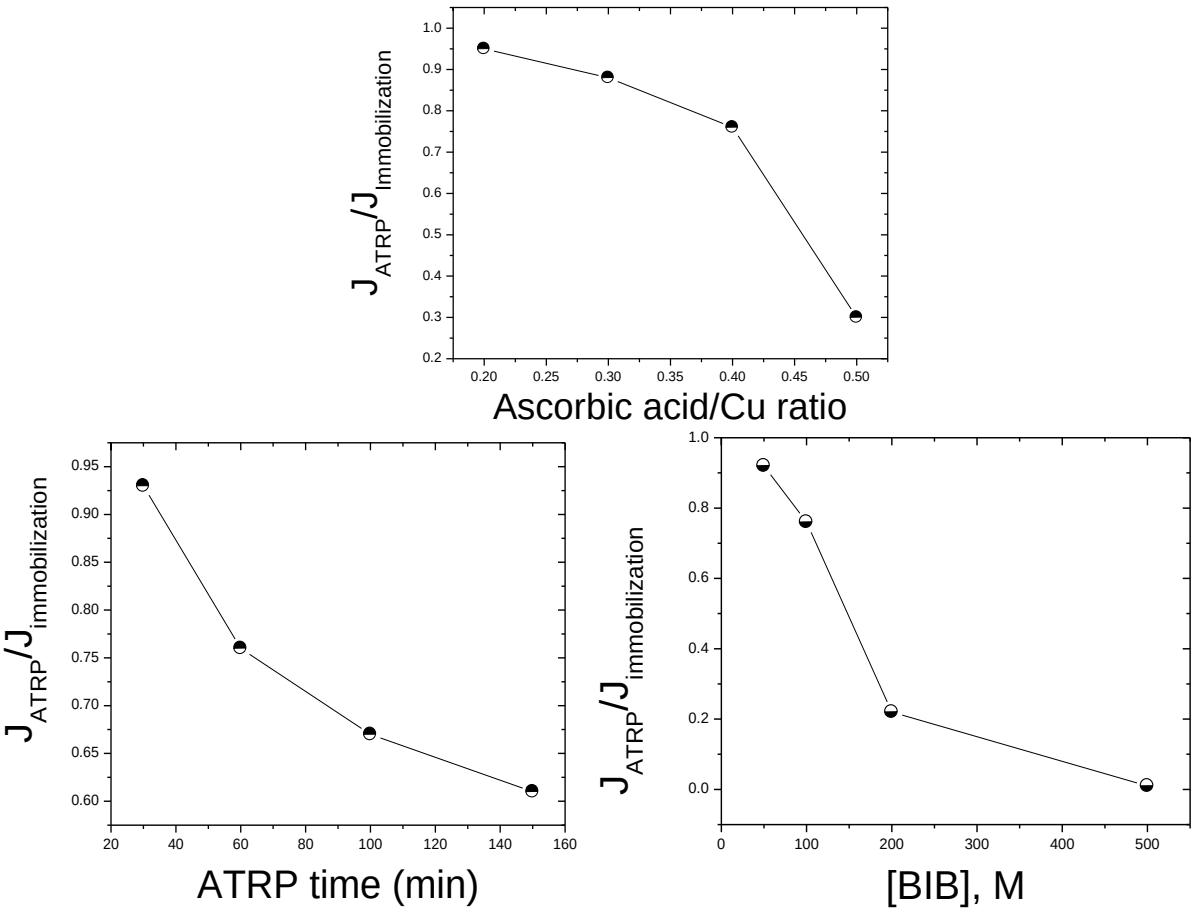


Fig. 2. Optimization of experimental parameters for AGET-ATRP; J_{ATRP}/J_{Immob} as a function of (a) ascorbic acid / Cu ratio; (b) ATRP time; (c) concentration of initiator, BIB.

Since acetonitrile is the solvent used for initiator immobilization, using it as pore filling solvent showed the similar scenario of solution phase immobilization and, hence, no spatial selectivity was observed. For glycerol, the ratio was 0.9 indicating the selective attachment of the initiator onto the external surface of the membrane but not on the surface of the pore. High immiscibility of glycerol and acetonitrile makes the partitioning of BIB into the glycerol difficult and again the high viscosity of glycerol diffusion of the BIB will be slow. In the case of other solvents, depending upon their miscibility with acetonitrile and viscosity there was selective initiator immobilization on the external surface over internal surface of the pore, as indicated by the flux ratio measurements.

3.3. Characterization of modified membrane using glycerol as pore filling solvent

Membrane surface characterization is an important tool for analysing the effectiveness of surface modification [38-42]. Figure 4(a) shows FTIR spectra for the base membrane and modified membrane after AGET ATRP for 1 hour with an ascorbic acid/Cu ratio of 0.4 and initiator immobilization for 1 min with initiator concentration at 100 mM. After AGET-ATRP, 2 clear peaks were observed in the modified membrane compared to the base membrane. The peak at ~ 1734 cm^{-1} was attributed to the stretching frequency of the carbonyl bond which was attached to the membrane during initiator immobilization [37]. The peak at 870 cm^{-1} was attributed to epoxy functionalization [36]. FTIR spectroscopic analysis were also done after treating the epoxy functionalized modified membrane with amine and sulphonate (Figure 4(b)). According to our expectation, the opening of the epoxy ring was confirmed by the depletion of the intensity of the 870 cm^{-1} peak, while the retention of carbonyl peak intensity after treatment with amine and sulfonate confirmed successful modification.

Figure 5 gives the XPS spectra for modified membranes after treatment with monoethanol amine and sodium sulfonate. There was growth of peak at ~ 396 eV, which is a signature of the N atom, (see Scheme 1) [43]. In a similar way, the XPS spectra of the modified membrane obtained after $NaHSO_3$ treatment showed growth of the S peak at ~ 150 eV which confirmed the attachment of the functional group of S onto the membrane [44]. The peaks for oxygen and carbon atoms were also identified from the XPS spectra of modified membrane after ring opening with monoethanol amine and sodium sulphonate [45].

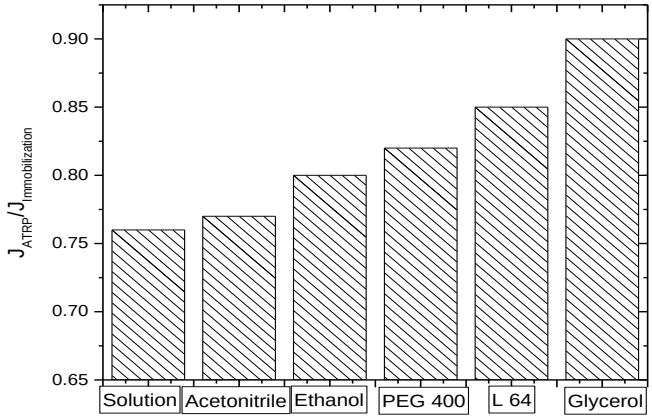


Fig. 3. The flux ratio for the modified membrane using interfacial modification by using different pore filling solvents and modified from solution phase (100 mM BIB, AA/Cu ~ 0.4, 1 min initiator immobilization, 1 hour ATRP).

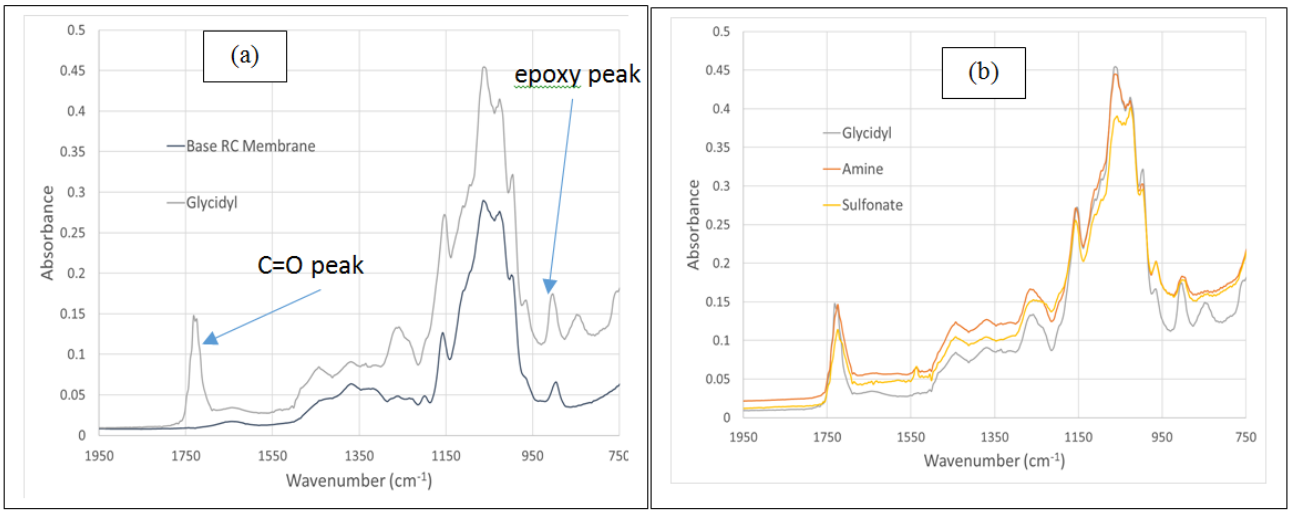


Fig. 4. FTIR spectra for the (a) base membrane and modified membrane after AGET-ATRP; (b) after treatment of the modified membrane with mono ethanol amine and sodium sulphonate.

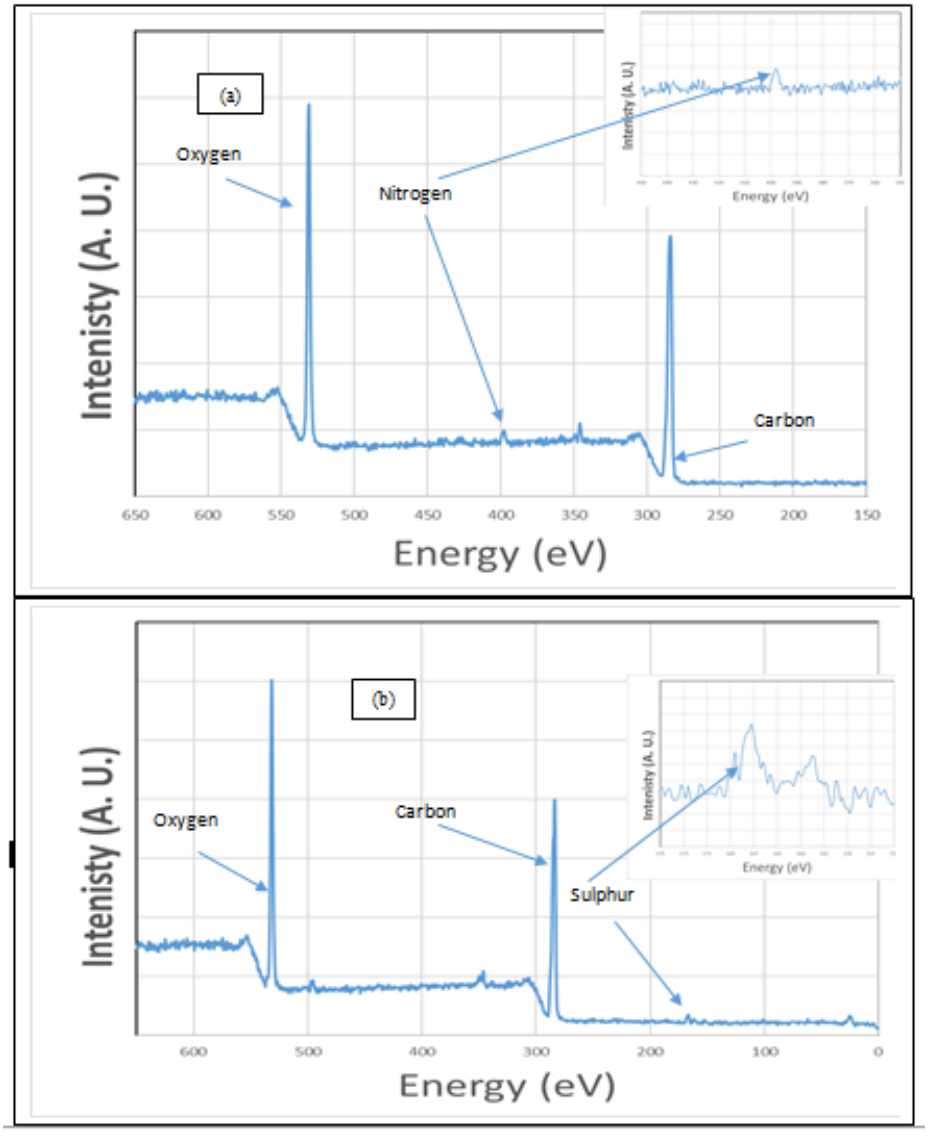


Fig. 5. XPS characterization of modified membranes after treatment with (a) mono ethanolamine and (b) sodium sulfonate.

Table 1
Change in flux (LMH) after each step of the modification including nucleophilic attack by $NaHSO_3$

ATRP time (min)	Solution			Interfacial with glycerol as pore filling solvent		
	Initiator imm.	ATRP	$NaHSO_3$ treatment	Initiator imm.	ATRP	$NaHSO_3$ treatment
30	402±20	375±21	320±20	331±21	320±20	225±18
60	400±25	303±27	281±19	333±20	301±18	211±16
100	401±27	270±22	258±17	330±23	296±15	193±15
150	398±26	242±24	124±11	335±22	290±17	170±16

Table 1 summarizes the changes in flux after modification using glycerol as the pore filling solvent and ring opening by $NaHSO_3$. A decrease in water flux was observed after polymerization. Further as the polymerization time increased the flux decreased significantly. Since longer ATRP times result in a longer polymer chains, more pore constriction is expected which results in a reduction in the water flux. Consequently, for membranes modified in the absence of a pore filling solvent the flux reduction after ATRP will be more significant as indicated in Table 1.

It was also observed that after treating the epoxy functionalized modified membrane with sulphonate, there was significant reduction in water flux which might be attributed to the interaction of the hydrophilic end of the modified membrane with the water molecules. Table 2 summarizes similar results obtained by treating the epoxy ring with another nucleophile, monoethanol amine.

Rejection tests for dextran and BSA were also carried out. UV-Vis spectrophotometry was used for the determination of BSA [46], while for dextran rejection TOC analysis was carried out [47-49]. The base membrane had 41 % BSA rejection, which increased upon modification. After 100 min or more ATRP, the membrane displayed 100 % BSA rejection, indicating a reduction in pore size (Table 3). Using acetonitrile as pore filling solvent led to almost similar results.

Changing the pore filling solvent, led to reduce BSA rejection. In the case of glycerol, only moderate enhancement in the BSA rejection was observed indicating the majority of the modification occurred on the external surface of the membrane. It can be argued that there may not be 100 % selectivity as there is an increase in BSA rejection compared to the base membrane. This can be explained on the basis of the extensive surface growth from the outer membrane surface. The extensive surface growth can be an obstacle for BSA molecules near the pore of the modified membrane, even though the pore itself is not modified.

Table 2
Change of flux (LMH) after each step of modification including nucleophilic attack by monoethanol amine.

ATRP time (min)	Solution			Interfacial with glycerol as pore filling solvent		
	Initiator imm.	ATRP	Monoethanol amine treatment	Initiator imm.	ATRP	Monoethanol amine treatment
30	408±22	382±20	329±19	435±26	428±20	415±20
60	410±20	308±17	261±20	430±28	421±21	385±18
100	399±25	281±18	220±20	427±27	411±19	380±19
150	405±27	232±20	174±15	432±22	392±17	367±19

Table 3
BSA rejection (%) for the epoxy modified membrane with solution phase and interfacial modification with different pore filling solvents.

Base membrane	ATRP time (min)	Solution phase immobilization	Interfacial immobilization with different pore filling solvent				
			Acetonitrile	Ethanol	PEG 400	L 64	Glycerol
41	30	96±3	96±3	95±3	80±4	74±3	53±5
	60	98±2	99±3	98±3	87±3	81±4	60±3
	100	100±3	100±2	99±4	93±4	86±4	75±4
	150	100±2	100±3	100±2	96±3	91±3	81±3

Table 4 summarizes the % rejection of dextran using different pore filling solvents as well; as in the absence of a pore filling solvent. The base membrane was found to display 69 % dextran rejection, which increases to 93 % in the absence of a pore filling solvent. An increase in ATRP time resulted in longer polymer growth, even inside the surface of the pore, therefore reducing pore size and enhancing dextran rejection in the case of solution phase modification. The outside surface of the membrane was selectively modified depending on the nature of the pore filling solvent in the interfacial polymerization, and the miscibility and viscosity coefficient. Pore size will be affected less by the modification only on the surface of the membrane and hence only a marginal increase in the % of dextran rejection is expected.

Table 3 indicates that the highest selectivity for outer surface modification is achieved using glycerol as the pore filling solvent, which can be attributed to its higher viscosity and immiscibility with the reaction medium solvent acetonitrile. Even after 150 min ATRP using glycerol as pore filling solvent, the % of dextran rejection only increased from 69 % to 77 %, confirming almost no modification on the internal surface of the pores of the membrane.

Table 4
The Dextran rejection (%) for the epoxy modified membrane with solution phase and interfacial modification with different pore filling solvents.

Base membrane	ATRP time (min)	Solution phase immobilization	Interfacial immobilization with different pore filling solvent				
			Acetonitrile	Ethanol	PEG 400	L 64	Glycerol
69	30	93±3	90±4	88±4	82±3	77±3	71±5
	60	97±3	92±3	90±3	84±4	80±4	72±3
	100	98±2	95±3	92±4	88±5	84±4	75±4
	150	99±2	98±2	95±3	91±3	89±3	77±3

Figure 6, compares dextran and BSA rejection after modification of 100 kDa RCUF membrane using 100 mM BIB, AA/Cu ratio 0.4, 1 min initiator immobilization, 1 hour of ATRP by GMA (with and without pore filling) followed by epoxy ring opening with nucleophile like monoethanol amine and $–SO_3Na$. The epoxy modified membrane was found to have higher protein rejection, when the modification is done conventionally (without any special control). This is due to the probable grafting inside the pores.

On the contrary, when the modification is conducted using glycerol as the pore filling solvent, protein rejection is only marginally modified. The ring opening with $–SO_3Na$ led to formation of polymer chain end having $–SO_3^-$ anionic group. This anionic group can induce repulsive interactions with BSA molecules at pH 7. As it is reported that above pH 4.5, the surface charge of BSA molecule is negative.

On the other hand, ring opening with monoethanol amine only enhanced protein rejection marginally. It is very interesting to check the fouling propensity of the modified membrane as compared to the virgin RC UF membrane. The modification led to increased hydrophilicity at the surface of the membrane, which decreased fouling tendency, while enhancing the permeability and protein selectivity properties of the membrane. In our earlier investigation on grafting PEGMA on RCUF membranes, we demonstrated improved fouling resistance [10]. Comparison of the atomic force microscopic images for PPEGMA-modified membranes pre- and post-rejection testing provides no evidence of fouling by dextran adsorption. This observation was found to be consistent with that reported in the literature [50].

ATRP is very successful in surface grafting polymers in a highly precise manner. It can provide the required architecture for fabrication of numerous functional materials. Matyjaszewski has indicated the wide variety of ATRP applications [37].

Development of commercial processes involving ATRP are limited. In classic ATRP the rate of polymerization is predominately determined inside the reactor without any chances of manipulation. The exothermic nature of this polymerization is significantly challenging when scaling up a process. By adjusting the feed rate, polymerization kinetics can be controlled, and thus the energetics and exothermicity. The growth of chains can be stopped promptly to attenuate any strong exothermic effect and then restarted with no loss of livingness. Recently, Jakubowski has reported Ultimate ATRP^{SM} Technology, demonstrating the adaptation of ATRP for commercial scale production [51].

4. Conclusion

A systematic investigation was carried out to limit surface grafting to the outer membrane surface only. The nature of the pore filling solvent in the interfacial mode of modification plays the most crucial role. The interactions of the pore filling solvent with the reaction solvent and initiator molecules were found to determine selectivity. This study revealed that glycerol, being a highly viscous liquid, limited BIB to the pore surface. The immiscibility of glycerol with acetonitrile, which was the reaction solvent, made the limited partitioning of BIB into the glycerol.

Optimization of the experimental parameters of surface initiated AGET ATRP revealed that an increase in relative concentration of the reductant (ascorbic acid) to Cu provided control of the ratio of the two oxidation states of Cu for sustaining the AGET-ATRP. Increased reaction time can lead to the formation of a longer polymer chain. With an increase in the initiator concentration, the density either on the outside surface of the membrane or on the inside surface of the pores resulted in a decrease in water flux. Dextran and BSA rejection were also carried out to evaluate the performance of the modified membranes. These rejection tests revealed the selective modification of the external surface of the RC-UF membranes.

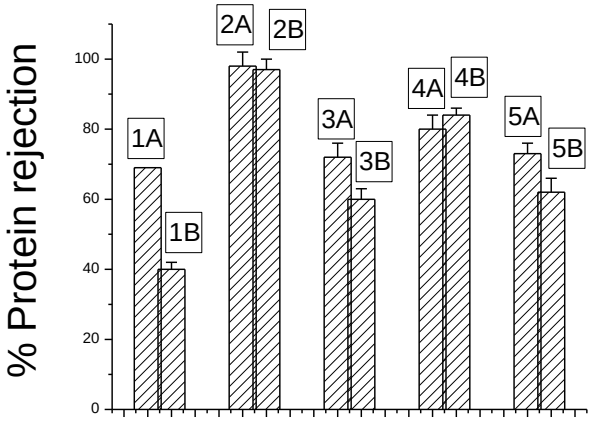


Fig. 6. The protein rejection test for 1: base membrane; 2: epoxy modification without spatial control; 3: epoxy modification with glycerol as pore filling solvent; 4: $-SO_3^-$ modification with glycerol as pore filling solvent; 5: Monoethanol amine modification with glycerol as pore filling solvent; A: Dextran rejection; B: BSA rejection

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