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Synthesis of the Poly(Methyl Methacrylate) Brush on the Poly(Vinylidene Fluoride) Membrane via the Surface Initiated Atom Transfer Radical Polymerization

Somayeh Fallahnejad[1], Behnaz MemarMaher[2*]

[1] Institute of Polymeric Materials and Faculty of Polymer Engineering, Sahand University of Technology, Tabriz, Iran

[2] Department of Chemical Engineering, Ahar Branch, Islamic Azad University, Ahar, Iran

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ABSTRACT

Polymer chains- tethered membranes exhibited a technic to improve membrane surface, and can be commonly used to change the inherent surface physico-chemical properties of materials. So, the grafting of poly(methyl methacrylate) (PMMA) chains onto poly(vinylidene fluoride) (PVDF) substrate was carried out via surface initiated atom transfer radical polymerization (SI-ATRP) at room temperature. Surface coverage and *grafting* density were controlled *by adjusting the* concentration of the initiator. The *attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and thermogravimetric analysis (TGA) results indicated that the PMMA brush was successfully synthesized on the substrates. The study examined the alterations in the physical characteristics of a the PVDF membrane modified with polymer brushes using the scanning electron microscopy. The results showed that PMMA brushes were attached not only to the outer surface of the membrane but also to the surfaces of its pores. Results from the atomic force microscopy and water contact angle measurements confirmed the homogeneous grafting of PMMA chains onto the substrate.*

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1. Introduction

PVDF is one of the most extensively used materials for the praparation of ultrafiltration and microfiltration membranes, because of its superior thermal and chemical resistances, well-controlled porosity, and good mechanical properties [1]. However, the fouling of the hydrophobic PVDF membranes declines the permeate flux by time and shortens the life of

*Corresponding author: be.maher@iau.ac.ir

the membrane. To improve the performances of membranes in their applications in biomedical and water treatment, many methods such as surface modification and blending have been proposed to enhance the hydrophilicity [2-3] and antifouling properties of PVDF membranes [4–5]. The surface of a membrane plays a crucial role in its performance. Accurate control of the surface topography at the nanoscale has a significant effect on separation applications [6]. Surface-initiated atom transfer radical polymerization (SI-ATRP) is one of the most useful and important methods for surface modification. It has been proven to be efficient in preparing high-flux and antifouling membranes [7]. Because in the ATRP method, the chain length and chain length distribution of the grafted polymer can be easily controlled by grafting conditions [8].

The ATRP of a wide range of monomers including methyl methacrylate (MMA) [9], 2-hydroxyethyl methacrylate (HEMA) [1, 10–11], ethylene glycol [12], and 2-(dimethylamino) ethyl methacrylate (DMAEMA) [1] was successfully carried out to fabricate polymer brushes on the PVDF membranes. The degree of the grafting of PMMA [9], PHEMA [10-11], and PDMAEMA [1] on the membrane exhibited an approximately linear increasing trend by the polymerization time. PVDF was also coated with 3,4-dihydroxyphenylalanine (DOPA). The hydroxyl groups on the surfaces of the poly DOPA-coated PVDF membrane and its pores were utilized to immobilize the alkyl halide ATRP initiator [1]. The antifouling property of a hydrophobic PVDF membrane was improved by using a PVDF-g-PHEMA copolymer as an additive prepared through ATRP [11]. PVDF membranes were grafted with the hydrophilic poly ethylene glycol methacrylate (PEGMA) polymer through SI-ATRP. The effects of the grafting time on the surface hydrophilicity, grafting weight, and uniformity of the grafted PEGMA layer on the PVDF membrane surface were studied [12].

In this study, PMMA brushes were synthesized using surface-initiated ATRP to enhance the hydrophilicity of PVDF membranes. The surface grafting density is a very important property of polymer brush-modified materials that plays a crucial role in the application of materials. The grafting density of the material surface was controlled by adjusting the concentration of the initiator. To validate the obtained results about the PVDF membrane, all experiments were also performed on silicon wafers (Si-wafer) using the same experimental conditions as those used for the PVDF membrane. Si-wafers differ from PVDF membranes since the atomic force microscopy and water contact angle measurement results obtained on the smooth surface of Si-wafers were more accurate compared to the corresponding data obtained from the rough surface of a PVDF membrane which confirm the formation of PMMA brush. As reported in the previous works [13–15], the initiator surface coverage and graft density of the tethered chains on the surface of the Si-wafer were tuned by adjusting the concentration of the ATRP initiator. The process of gas separation with brush polymers attached to membranes was a novel concept.

The polymer brush structure has attracted interests in gas separation due to the low polydispersity and well-controlled density of grafting on the selective polymer layer. In previous researches, grafting density was studied at a different polymerization time [16], and in other researches, the effect of the concentration of the initiator (initiator: 3-(chlorodimethylsilyl)propyl-2-bromoisobutyrate) immobilized on Mica surface on the grafting density is studied and the result indicated that the increase of the concentration of the initiator caused the rise of

the grafting density [17]. However, in this study the effect of the concentrations of the initiator on the grafting density on a silicon wafer was investigated and the results demonstrated that changing the concentration of the initiator was not very effective in controlling the initiator surface coverage and grafting density. We also explored the impact of the treatment time on the formation of the necessary hydroxyl groups on the substrates with the piranha solution .

2. Experiments

2.1. Materials

The following chemicals were purchased from Merck and used as received: sulfuric acid (>95%), hydrogen peroxide (H_2O_2, 30%), (3-aminopropyl)-trimethoxysilane (APTMOS, ≥98%), 2-bromoisobutyryl bromide (BIBB, 98%), *ethyl 2-bromoisobutyrate* (EBiB, >98%), N, N, N, N, N-pentamethyldiethylenetriamine (*PMDETA*, ≥98%), anisole (≥99%). Methyl methacrylate (MMA) (≥99%, Merck) was purified by calcium hydride and distilled under reduced pressure. Triethylamine (TEA, ≥99%, Merck), ethanol (≥99%, Merck), toluene (≥99%, Merck), dichloromethane (≥99.5%, Merck), acetone (≥99%, Merck), and tetrahydrofuran (THF, ≥99.8%, Merck) were distilled over calcium hydride (CaH_2, 95%, Merck). C*opper*(I) *chloride* (CuCl, ≥97%, Merck) and copper(I) bromide (CuBr, ≥98%, Sigma-Aldrich) were purified by being stirred in glacial acetic acid, filtered and washed with ethanol three times, followed by being driedunder vacuum at room temperature overnight. The water used in the experiments was purified using a Milli-Q water system. The PVDF membrane (the pore size of 0.45 µ, diameter = 47 mm) was purchased from Membrane-Solution Co. (Dallas, TX), n-type silicon wafers (resistivity = 0–100 Ωcm) were purchased from University Wafer Co. (Boston, MA).

2.2. Characterization

The **cross**-section and **surface** of dried neat PMMA chains-tethered PVDF were sputter-coated with gold and observed by a scanning electron microscope (SEM) (Tescan MV2300, Czech Republic) working at 5 kV. The cross-sections were prepared by fracturing the membranes in liquid nitrogen. Water contact angles were determined by a contact angle measuring system (Sahand University of Technology, Tabriz, Iran) equipped with a DV-3000 binocular (Bell, Italy). The Fourier transform infrared spectroscopy (FTIR) analysis was carried out on a Tensor 27 spectrometer (Bruker, Germany) equipped with an *attenuated total reflection* (ATR) unit. Atomic force microscopy was performed on a *Dual Scope* Probe Scanner (model DS 95-50-E, DME, *Denmark*) in tapping mode. Proton magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker DPX300 spectrometer operating at 300 MHz in chloroform-d ($CDCl_3$). The thermogravimetric analysis (TGA) was carried out using a TG 209 F1 Iris thermogravimetric analyzer (*Netzsch*, Germany).

2.3. Procedures

2.3.1. Synthesis of 3- (2-bromoisobutyramido) propyl (trimethoxy) silane (BrTMOS)

To a solution of APTMOS (5.25 mL, 30 mmol) and TEA (5.25 mL, 36 mmol) in 45 mL of anhydrous THF, BIBB (4.5 mL, 36 mmol) was added dropwise at 0 °C and under a nitrogen atmosphere. The solution was allowed to warm to room temperature and stirring was continued overnight. Next, triethylammonium bromide was removed by filtration through a glass funnel and the reaction mixture was evaporated to 1/3 of its initial volume. The

residual triethylammonium bromide that precipitated upon evaporation was removed by centrifugation. The resulting solution was then evaporated. The oily residue was stirred under a vacuum pump at 40 °C overnight and stored at 4 °C in nitrogen [18].

2.3.2. Pretreatment of substrates and the immobilization of initiators.

The fabrication of PMMA chain-tethered PVDF is outlined in Figure 1. This process was started with surface treatment followed by immobilizing the ATRP initiator. The PVDF membrane and Si-wafer were sequentially sonicated in acetone, ethanol, and deionized water for 5 min and dried under a stream of nitrogen. Before immobilizing the initiator, the substrates were immersed in the piranha solution (H_2SO_4/H_2O_2 = 7/3 v:v) for 60 min at 120 °C to remove any organic residues and to create hydroxyl groups on the substrate. The substrates were rinsed with acetone, ethanol, and deionized water, and then dried under a nitrogen stream. Next, the treated substrates were immersed in a mixture of the ATRP initiator (10 mM for the PVDF membrane and 5 mM for Si-wafer), toluene (50 ml), and TEA (2.87 mmol, 400 µl) for 20 h at 30 °C under nitrogen atmosphere. After that, the substrates were extracted with dichloromethane in a Soxhlet *apparatus* for 18 h to eliminate the physisorbed initiators. Then the substrates were sequentially rinsed with acetone, ethanol, and deionized water for 5 min. Finally, the initiator-functionalized Si-wafer was dried under a flow of nitrogen and the initiator-functionalized PVDF membrane was dried in an oven at 70 °C [19].

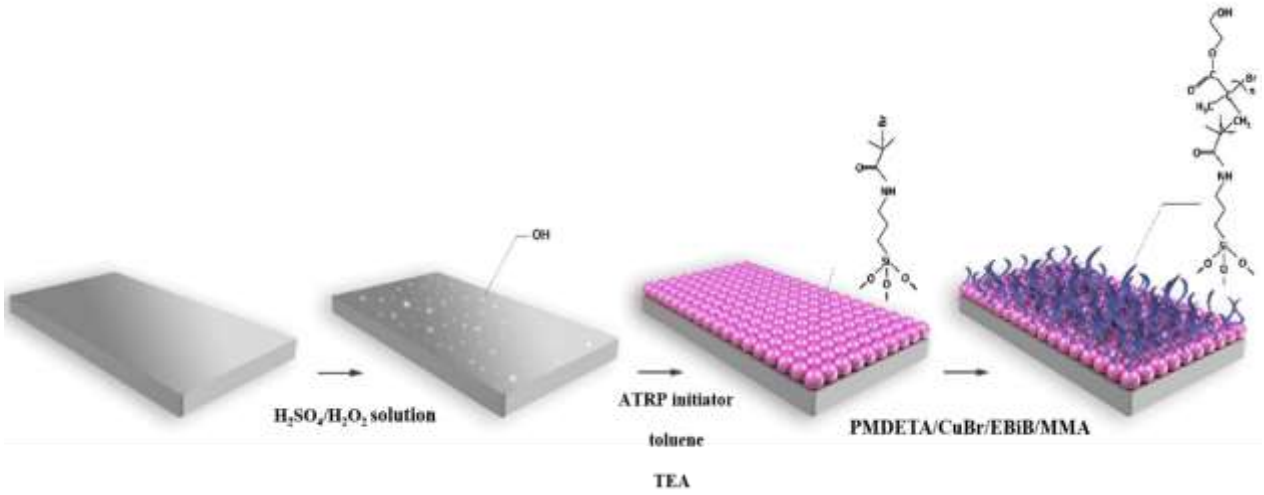

Figure 1. Schematically illustrating the principle of preparing PMMA chains-tethered PVDF.

2.3.3. Surface-initiated atom transfer radical polymerization of MMA

The surface-initiated ATRP of MMA was performed using a reaction system composed of PMDETA/CuBr/EBiB/MMA with a molar ratio of 1/1/1/1000. A separate vessel was charged with PMDETA (32 mg, 4.6 mmol), and CuBr (26 mg, 4.6 mmol), MMA (18.5 g, 4.62 mol), and anisole (MMA/anisole = 1/1 v:v). After degassing by bubbling nitrogen for 30 min, EBiB (35 mg, 4.6 mmol) was added to the mixture and then degassed by three freeze-pump-thaw cycles. After that, the resulting mixture was transferred, via cannula, to a nitrogen purged reaction vessel containing the initiator-functionalized substrates. The polymerization was done for 30 h at room temperature. After polymerization, the reaction mixture was removed and the PMMA chains-tethered substrates were extracted with

toluene in a Soxhlet *apparatus* for 18 h, and finally, the PMMA chains-tethered Si-wafer was dried under a flow of nitrogen and the PMMA chains-tethered PVDF membrane was dried in an oven at 70 °C [19].

3. Results and discussion

3.1. Synthesis of the initiator

The growth of polymer brushes via ATRP usually requires the introduction of an appropriate polymerization initiator on the substrate. Generally, in the surface modification process, this is accomplished by using chlorosilane or alkoxysilane initiators. During immobilizing the initiator on to the surface, alkoxysilanes undergo hydrolysis which initiates a complex cascade of reactions [20]. The ease of the hydrolysis of the $R_xSi(OR')_{4-x}$ type compounds decreases by increasing the size of both R and R′ [21]. Short-chain silane groups are the least stable, as the silane groups can be easily hydrolyzed. In this study, 3-(2-bromoisobutyramido)propyl(trimethoxy) silane was synthesized to minimize the hydrolysis of alkoxysilanes. This was done to introduce a suitable functional group for initiating ATRP, it need for a two-step initiator process of immobilization, which involves modifying the surface with the silane group and then immobilizing the initiator. The FTIR spectrum (Figure 2) confirms the formation of the initiator as it is evident from bands that appeared in the wave number range of 3100–3500 cm^{-1} (N–H stretching) [22], 650–800 cm^{-1} and 1534 cm^{-1} (N–H bending) [23]. Other absorption bands at 1113 cm^{-1} and 1654 cm^{-1} were observed, which were due to the C–N bond [24], and C=O group [25] respectively. An additional band because of the C–H bond was observed around 2940 cm^{-1}.

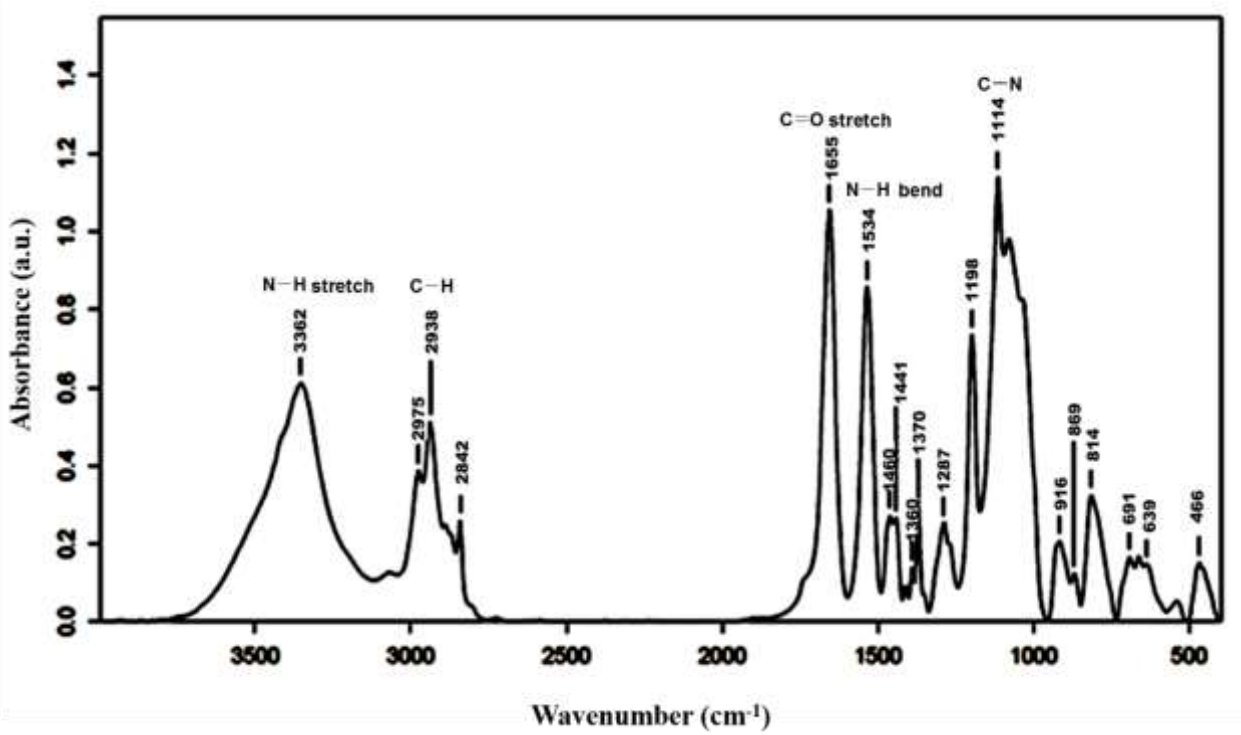

Figure 2. FTIR spectrum of the synthesized initiator.

The ^1H NMR spectrum of the initiator is shown in Figure 3. The signal for the methyl protons of $–OCH_3$ (a) in the BrTMOS initiator unit appeared at 3.54 ppm and the signal of $–SiCH_3$

protons (b) was seen at 0.66 ppm. The signals at 1.65 ppm (c), 3.27 ppm (d), 7.03 (e), and 1.95 ppm (f) correspond to the methylene protons of $–R_1CH_2R_2$, the methylene protons of $–CH_2–NH$, the amide proton of N–H, and the methyl protons of $–C(CH_3)_2Br$ respectively [26].

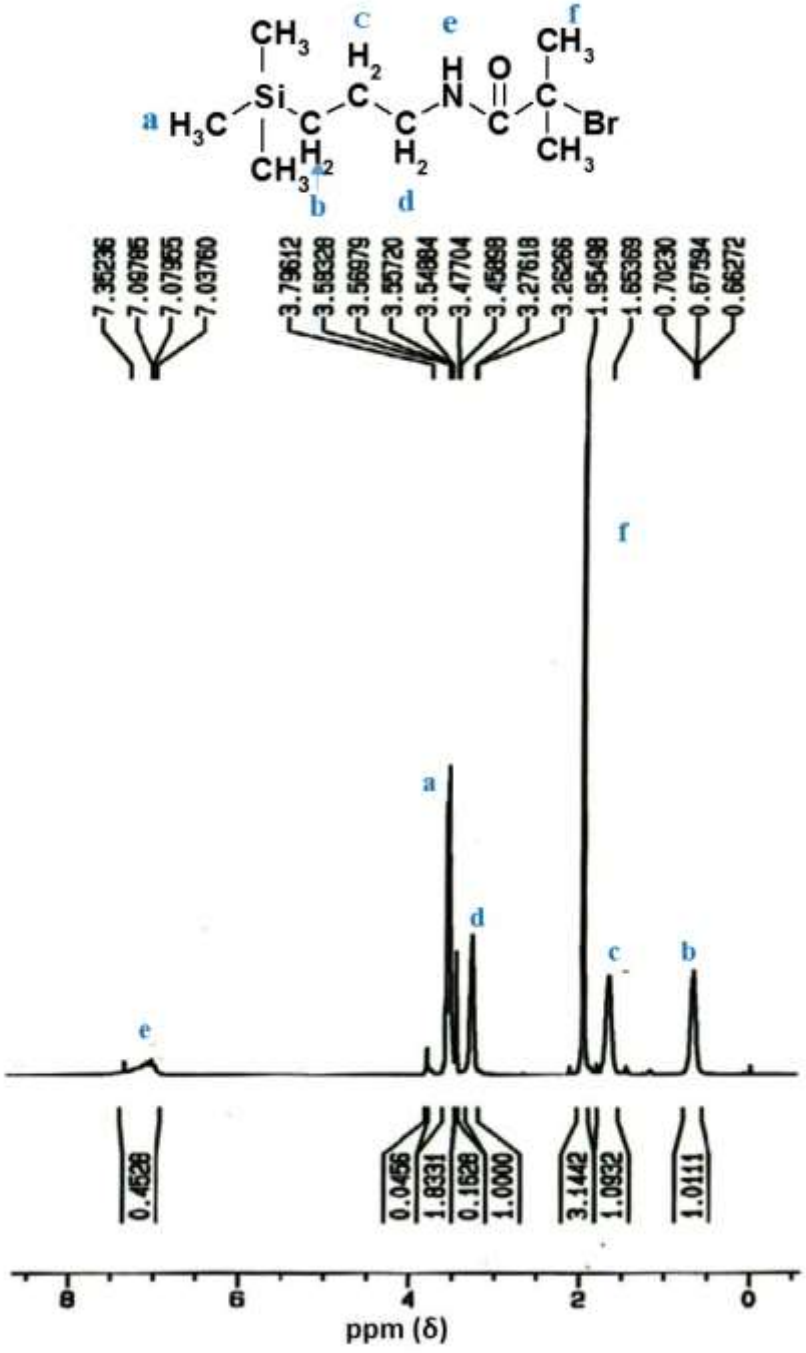

Figure 3. ^{1}H NMR spectrum and chemical formula of the synthesized initiator.

3.2. Surface characterization

3.2.1. ATR-FTIR spectroscopy

The ATR-FTIR analysis was used to characterize the chemical composition of modified surfaces. The spectra of the resulted pristine, treated, initiator-functionalized, PMMA chains-tethered Si-wafers and PVDF membranes are shown in Figures 4 and 5

respectively. The introduction of hydroxyl groups can be monitored with the ATR-FTIR spectroscopy. After the treatment of Si-wafer and PVDF substrates with the piranha solution, the absorption band of hydroxyl groups was appeared in the wave numbers between 3300 and 3500 cm^{-1} [27]. As illustrated in Figures 4 and 5, after the immobilization of the initiator, clear differences were observed at 1650-1750 cm^{-1} [28] and 1550 cm^{-1} that were assigned to the C=O stretching vibration of the amide group and NH bond respectively, that were associated with the ATRP initiator. Besides, the peak corresponding to the –OH groups in the spectral region of 3300-3500 cm^{-1} [29] became weaker indicating that the reaction between the hydroxyl and anchoring groups allowed the immobilization of the ATRP initiator onto the substrate. Compared to the spectrum of the initiator-functionalized substrate, the most obvious change for the polymer-brush-modified substrate was the presence of the adsorption band in the spectra region between 1650 and 1750 cm^{-1}[30]. This was attributed to the C=O stretching vibration of esters, which signified the grafting of PMMA onto the substrates.

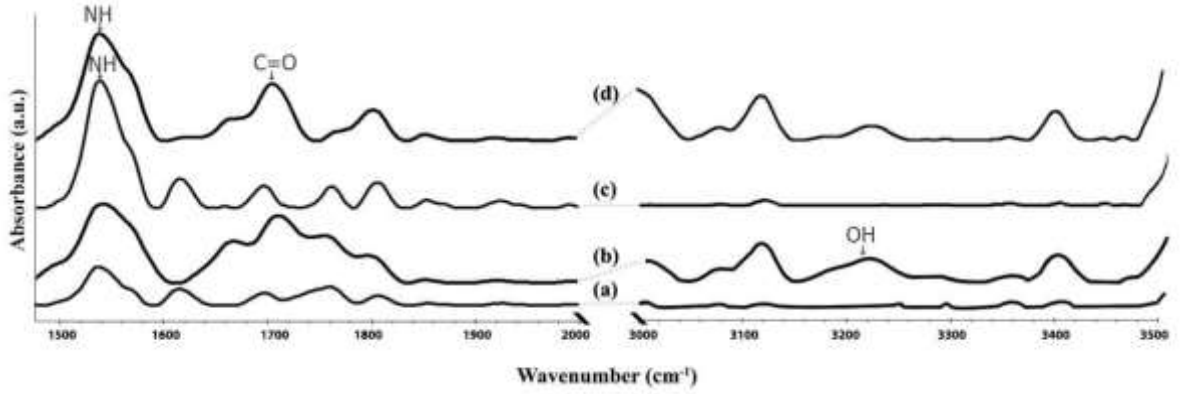

Figure 4. ATR-FTIR spectra of the pristine (a), piranha treated (b), initiator functionalized (c), and PMMA tethered (d) Silicon wafers membrane.

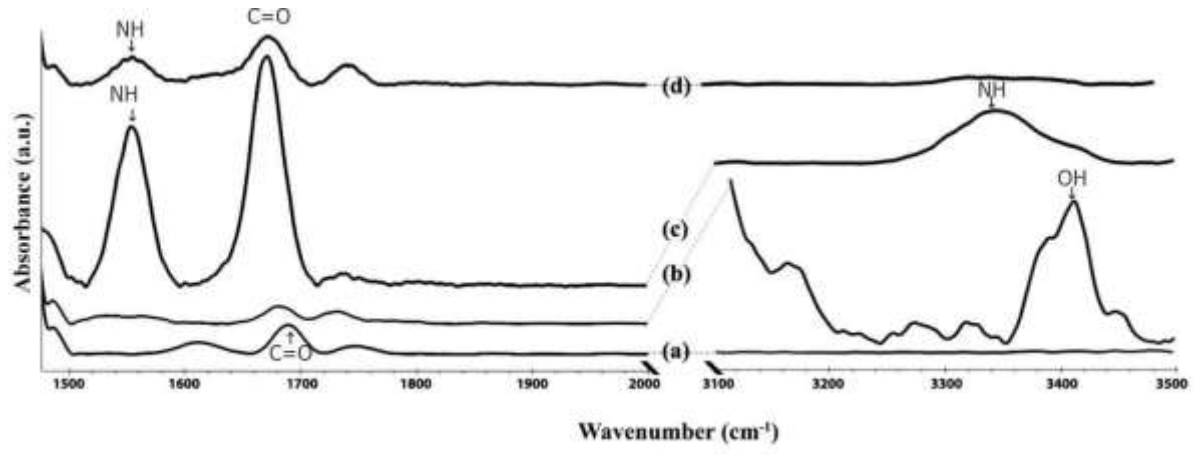

Figure 5. ATR-FTIR spectra of the pristine (a), piranha treated (b), initiator functionalized (c), and PMMA tethered (d) PVDF membrane.

3.2.2. Water contact angle (WCA) measurements

The changes in the water contact angles (WCAs) of the surfaces during the modification of the substrates were the

evidence of the formation of the required hydroxyl groups on the substrates (Table 1).

Table 1.
Water contact angle results for the piranha-treated silicon wafer as a function of the treatment time.

Time (h)	Contact angle (°)	
0	67.2 ± 0.5	
1	21.6 ± 0.8	
2	21.5 ± 0.8	
3	21.4 ± 1.0	
4	21.1 ± 0.9	
5	20.8 ± 0.9	
6	20.3 ± 1.4	

The introduction of hydroxyl groups, through the treatment with the piranha solution, provided a more wettable surface, as indicated by the decreased water contact angle from ~67 to ~20° and ~133 to ~93° for Si-wafer and PVDF substrate respectively (Figures A1, A2 respectively). The WCAs for the initiator-immobilized Si-wafers with different concentrations of the initiator (1, 5, 10, 20, and 40 mM) are reported in Table 2. The results for the various concentrations of the initiator showed that the initiator-immobilized substrates were more hydrophobic than the piranha treated Si-wafers. The increase of the concentration of the initiator led to higher water contact angle values due to the hydrophobic nature of the initiator. The immobilization of the ATRP initiator on the treated PVDF membrane led to an increase in WCA from ~93 to 126–132°. The WCA of the polymer-brush-modified substrate was 67.1° for Si-wafer, which could prove the introduction of hydrophilic PMMA chains on the substrates via SI-ATRP, and it was 127.8° for the PVDF membrane, because, the surface wetting behavior depends on not only the surface texture (roughness and particle shape) and surface chemistry (heterogeneity) but also on hydrodynamic conditions in the preparation route [31]. Therefore, the variation of WCA during the polymer brush tethering was not clearly distinguished on the PVDF surface. The WCA analysis of the modified surfaces was also in agreement with the ATR-FTIR results. For the PMMA brush-modified Si-wafer surface, the WCA data was in good agreement with the values reported before (62–70°) [32], which could indicate a high grating density of PMMA chains.

For the adjustment of the grafting density of the polymer brush prepared by SI-ATRP, one of the basic requirements is the control of the chemical composition and graft density of the immobilized ATRP initiator. The surface coverage of the ATRP initiator immobilized on the Si-wafer was calculated using the Cassie-Baxter equation [13, 14, 33]. In this equation, water contact angle values were used

to follow the surface coverage of the initiator. The surface of the initiator-functionalized Si-wafer was supposed to be covered by organoalkylsilane and Si-OH (silanol) groups. The equilibrium contact angle of a chemically heterogeneous surface, θ_{obs}, can be related to the fractions of the different chemical groups in terms of the Cassie-Baxter equation and the modified related equations [13]:

$$[1 + \cos \theta_{obs}]^2 = f_A [1 + \cos \theta_A]^2 + f_B [1 + \cos \theta_B]^2$$

$$f_A + f_B = 1 \quad (1)$$

where f_A and f_B are the fractions of organoalkylsilane and silanol groups respectively. The water contact angle of the surface, when it is covered with a maximum number of ATRP initiators, $f_A = 1$, is supposed to be $\theta_A = 90°$ [34, 35] and the water contact angle for a piranha treated Si-wafer surface containing only saturated OH groups, $f_B = 1$, is supposed to be $\theta_B = 20°$, as experimentally evaluated. The initiator grafting density on the substrate was dependent on the concentration of the initiator. To control surface coverage of the ATRP initiator, different concentrations, 1, 5, 10, 20, and 40 mM, of the initiator were deposited onto the piranha treated Si-wafers. For different concentrations of the initiator, the initiator grafting densities (σ, no./nm^2) were evaluated from the thickness of the initiator layer (h) using [13]:

$$\sigma = fA\rho hNA/M \quad (2)$$

where, ρ, M, and N_A are the density (1.3 g.cm^{-3}) and the molecular weight (328 g.mol^{-1}) of the initiator and the Avogadro's number respectively. According to theoretical calculations based on the normal bond angles and lengths, and assuming a 10° tilt angle for the initiator chain [36–37], the thickness of the initiator layer (h) on the surface was obtained at 1.5 nm. The surface coverage f_A and surface density for different concentrations of the initiator are presented in Table 2. The results of the composition of the initiator on the surface of the initiator functionalized Si-wafer confirmed that the ATRP initiator surface coverage was significantly large, even for the lower concentrations of the initiator. The results related to initiator concentration variation, reported in Table 2, revealed that the initiator surface coverage f_A was moderately affected by the concentration of the initiator. Moreover, the initiator grafting density increased from 2.81 to 3.17 (no./nm^2) when changing the concentration of the initiator from 1 to 40 mM. In summary, these results demonstrated that changing the concentration of the initiator was not much effective in controlling the initiator surface coverage and grafting density.

Table 2.
Water contact angle values, the calculated initiator surface coverage, and the initiator grafting densities for different concentrations of the initiator.

Initiator Concentration (mM)	Contact angle (°)	f_A (%)	f_B (%)	σ (no./nm^2)	
1	74.7 ± 1.6	79	21	2.81	
5	76.6 ± 1.3	81	19	2.88	
10	78.1 ± 1.0	84	16	2.99	
20	80.8 ± 0.6	88	12	3.13	
40	81.9 ±1.4	89	11	3.17	

3.2.3. Atomic force microscope (AFM)

Fig. 6(a–b) shows the AFM images of initiator-functionalized, and polymer-brush-modified Si-wafers. It could be seen that many dense lumps covered the surfaces of the initiator-functionalized Si-wafers (R_{rms}= 0.45 nm). The surface of the PMMA-brush-modified Si-wafer possessed an R_{rms} value of 0.37 nm confirming the formation of a smooth and homogeneous polymer film on the substrate.

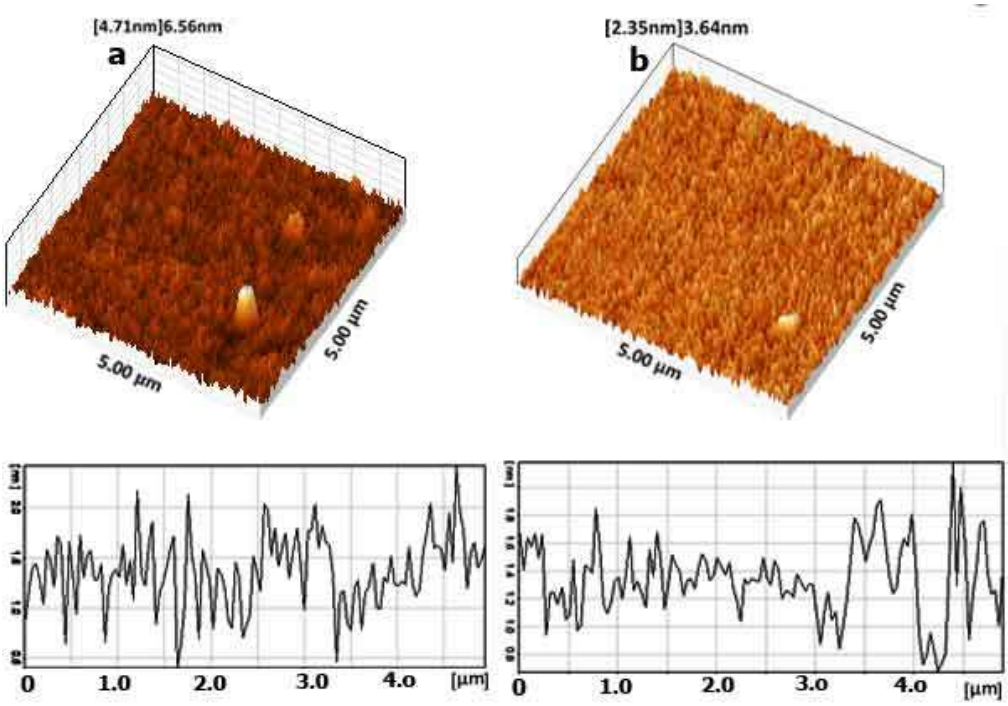

Figure 6. AFM images (top images) and height profiles (bottom images) of the initiator functionalized(a), and PMMA tethered (b), Silicon wafers.

3.2.4. Scanning electron microscopy (SEM)

The morphologies of the top surface and vertical cross-section for the pristine and polymer-brush-modified PVDF membranes were studied by SEM. Figures 7(a) and (b) suggested that the PMMA chains-tethered membrane had lower porosity, due to anchoring the PMMA chains on the pores in addition to the top surface of the membrane. It could be found from Figures 7(c) and (d) that, in addition to the top surface of the membrane, the PMMA chains were also grafted on the surface of the pores located at different heights of the membrane.

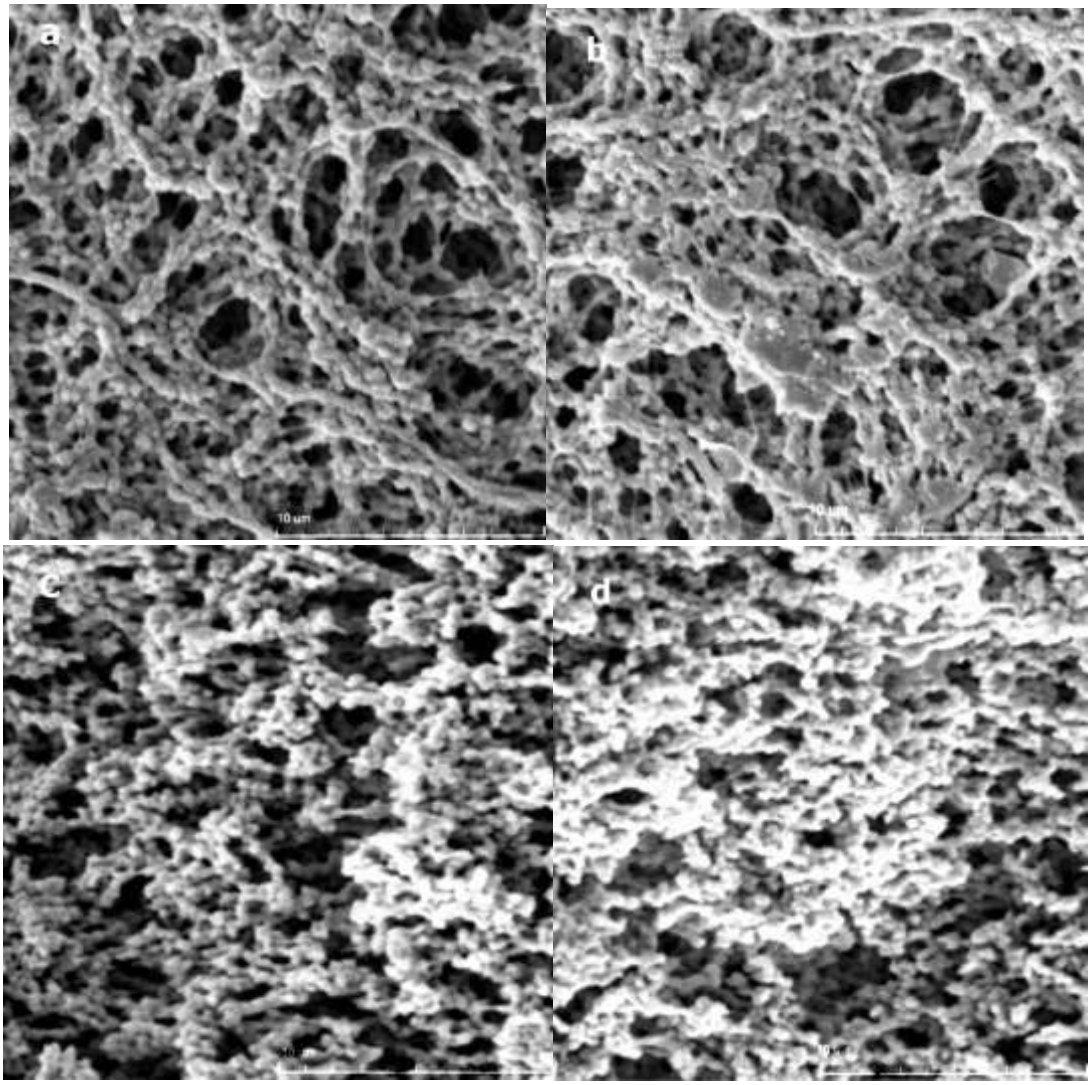

Figure 7. SEM images obtained from the surface of the pristine (a), PMMA-tethered (b), cross-section of the pristine (c), and PMMA- tethered (d) PVDF membrane.

3.2.5. Thermogravimetric analysis (TGA)

The thermogravimetric analysis was used to quantitatively indicate the PMMA grafting on the PVDF membrane. As shown in Figure 8, in the case of PMMA chains-tethered membrane, two different weight losses occurred in TGA thermograms, while the degradation of the pristine PVDF membrane proceeded in a single step that was identified with a peak at approximately 470 °C. The additional degradation in the case of the PMMA chains-tethered membrane was related to the degradation of the grafted PMMA that occurred at approximately 200 °C [38]. Because of the very small weight of the grafted PMMA, the observed reduction of PMMA was small. According to Figure 8, the PMMA weight loss was increased as the monomer/solvent volume ratio in the feed of MMA polymerization increased from 1:1 to 1.5:1.

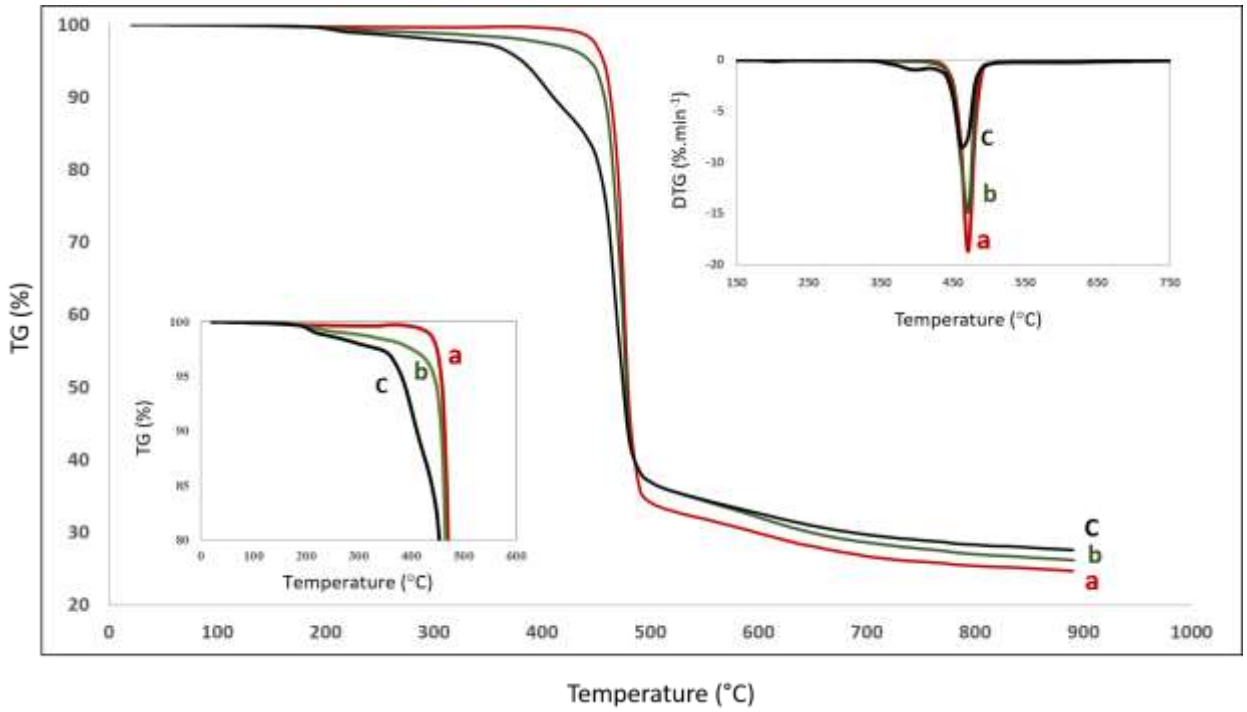

Figure 8. TGA thermograms of (a) the pristine, (b) PMMA-tethered (MMA/solvent = 1/1 v:v), and (c) PMMA-tethered (MMA/solvent = 1.5/1 v:v) PVDF membranes.

4. Conclusion

Surface-initiated atom transfer radical polymerization was used to tether poly(methyl methacrylate) brush on Si-wafer and PVDF membranes. The immobilization of the initiator and the anchoring of hydrophilic PMMA brushes on the substrates were proved by measuring water contact angles. The initiator surface coverage and grafting density were controlled by adjusting the concentration of the initiator. By changing the concentration of the initiator from 1 to 40 mM, ther were not considerable variations observed for the surface coverage and grafting density of the initiator. Because of the high grafting density of the initiator, even at a lower concentration of the initiator (1 mM), the surface coverage by the ATRP initiator was significantly high. Also, the results indicated that the grafted polymer could significantly alter the chemical and morphological properties of the PVDF membrane. The chemical and morphological changes for the PMMA brush modified PVDF membrane was confirmed by ATR-FTIR and SEM. Due to grafting PMMA brushes on the surfaces of the pores besides the top surface, the porosity of the polymer-brush-modified membrane was reduced compared to the that of the pristine PVDF.

Compliance with ethical standards

Funding: This study received no funding.

Conflict of interest: The authors declare that they have no competing interests concerning this article.

Appendix

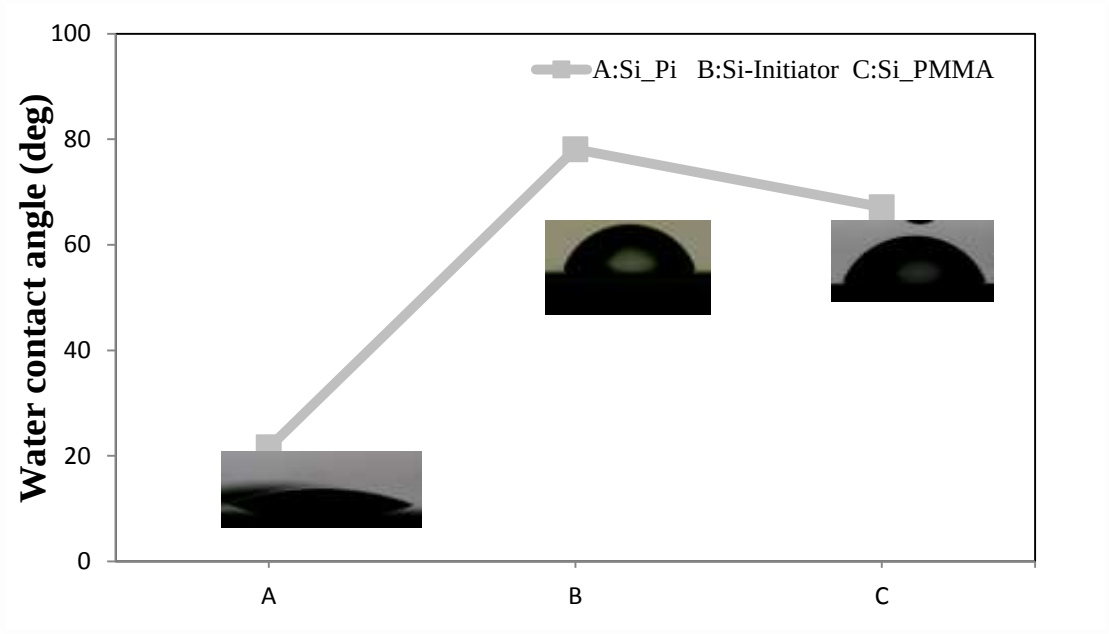

Figure A1. Trend of contact angle changes on the surface of the silicon wafer (A) after etching with the Piranha solution for one hour (B) after the immobilization of the initiator (C) after the synthesis of PMMA brushes.

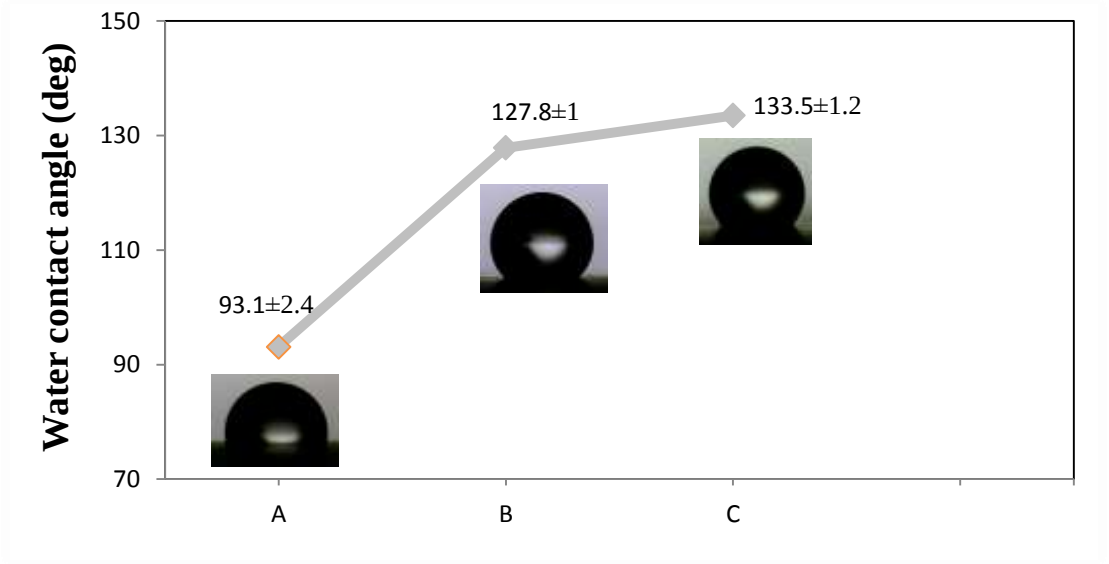

Figure A2. Trend of contact angle variations on the surface of the silicon wafer (A) after etching with the Piranha solution for one hour (B) after the synthesis of PMMA brushes (C) the the pristine PVDF.

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