SI-ATRP Polymer-Functionalized Graphene Oxide for Water Vapor Separation

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Graphene oxide is functionalized with poly(2-diethylaminoethyl) methacrylate (PDEAEMA), and the resulting material is used as a selective layer of a thin-film composite membrane (TFCM). The polymer synthesis is carried out by surface-initiated atom transfer radical polymerization (SI-ATRP) from bulk and also from single-layer graphene oxide (GO). The polymer brushes synthesized by the “grafting from” method are characterized by size exclusion chromatography (SEC), nuclear magnetic resonance spectroscopy (NMR), Fourier-transform infrared (FTIR) spectroscopy, thermal gravimetric analysis (TGA), and TGA-FTIR. The TFCMs are prepared by the deposition of the selective layer from a stable polymer solution. The molecular weight of the polymer is sufficiently high to obtain a continuous defect-free layer on a porous support. The thickness of the selective layer is ≈400 nm, as found in morphological investigations by scanning electron microscopy (SEM). The obtained membranes are utilized for gas and water vapor transport experiments in a wide temperature range. The water vapor permeability coefficient of the investigated materials is up to 4500 Barrer; this value increases threefold upon quaterization of the amine. The high permeance and selectivity for water vapor make this type of thin-film membranes a potential candidate for membrane distillation.

1. Introduction

Having a significant impact on CO₂ capture,[1] natural gas sweetening,[2] hydrogen purification,[3] and water vapor separation,[4] polymer-membrane-based gas separation has received considerable attention since 1980.[5] Despite the significant attention paid to the improvement of properties, most of the polymers studied did not exceed the Robeson upper bound, and none of them found use in the efficient separation system.[6] To obtain higher permeability and better selectivity, several approaches have been implemented, such as thermal rearrangement of the polymers,[7] formation of mixed matrix membranes (MMMs) by incorporation of metal-organic frameworks (MOFs),[8] covalent organic frameworks (COFs),[9] and other fillers into the polymer matrix.

Every year, the drinking water demand increases, and thus energy-efficient water separation becomes more and more significant in terms of safe water supply in the world. Since we need to supply the world population with drinkable water from salty ocean, seas, and brackish water, water needs to be separated from its constituents such as salts, organic compounds, and bacteria. The primary membrane separation methods used widely for this purpose are forward osmosis (FO), reverse osmosis (RO), ultrafiltration (UF), nanofiltration (NF), microfiltration (MF), and electrodialysis reversal desalination (ERD). As a robust and low-energy-consuming technique, membrane distillation (MD) has recently received extensive attention. For this purpose, hydrophobic microporous polymeric membranes based on polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polypropylene (PP), etc., are implemented. In MD, a hot water stream circulates on the surface of the hydrophobic membrane, while only water vapor can pass through the porous structure of the membrane. The separated water vapor afterwards condenses on cold surfaces. Lee et al. reported that an electrospun perfluorooctyloxybisilane-coated titanium dioxide/polyvinylidene fluoride-co-hexafluoropropylene (F-TiO₂/PVDF–HFP) membrane showed superhydrophobicity and a high water flux of 40 L m⁻² h⁻¹ compared to pristine PVDF membranes,[10] while the water flux of the PVDF nanofibrous hydrophobic membranes reinforced with fabric substrate was 49 kg m⁻² h⁻¹.[11]

Being a 2D material, graphene oxide (GO) has attracted extensive attention in membrane science as a potential material due to its mechanical strength,[12] the possibility for property alteration by covalent and noncovalent chemical bonding,[13] and its cost-effective production. Recent works[14] show how GO incorporation affects the selectivity of polyimide-
polydimethylsiloxane-based membranes. Membranes prepared from pure exfoliated GO dispersions showed high selectivity for H₂/CO₂ with a separation factor of 240, but low H₂ permeance.[10] The existence of high electron density in benzene rings of GO makes this material impermeable,[16] and the membranes are often formed as multiple layer structure, which serves as a sieving gallery in ~50 nm thick GO membranes.[17] The dense packing of the individual GO layers characterized by, e.g., d-spacing (~0.8 nm), provides a way for facile crosslinking in order to increase the membrane stability and dye rejection from water.[18]

Although it is a new type of material that is introduced into membrane science, such a kind of a membrane has several issues that prevent its application in the industry:

1) The preparation of the GO membrane with a smooth surface is a hurdle since GO wrinkles are formed on the support, which significantly affect the selectivity for specific gas molecules.

2) The GO membranes, as well as graphene membranes, struggle from the existence of pinholes or defect sites on the membrane that reduce the membrane performance.

3) Graphene itself facilitates a higher water contact angle than graphene oxide, which therefore would be useful for the MD process. However, the transfer of graphene onto the membrane support is another hurdle that renders graphene useless for several applications.

Graphene-based materials were investigated for gas separation and water purification even though there is little information for such kind of materials used in membrane distillation.

\[ \text{polymerization} \]

Leaper et al. successfully modified GO with 3-(amino-propyl)triethoxysilane (APTS) and incorporated it into a PVDF polymer matrix[19] for potential use in membrane distillation. They revealed that 0.3 wt% GO–APTS incorporation into the PVDF polymer matrix showed the best membrane performance with a flux of 6.2 L m⁻² h⁻¹ (LMH) and perfect salt rejection (>99.9%). It was described that the addition of GO nanosheets in a concentration of only 2 wt% boosts the selectivity of water vapor over nitrogen (α = 80 000) in a PEBAX layer.[20] Under direct contact membrane distillation (DCMD), the 0.5 wt% GO–NBA-incorporated PVDF flat composite membrane showed a flux of ~62 kg m⁻² h⁻¹ with a salt rejection of 99.9% (NBA stands for n-butylamine).[21] With an optimal graphene loading of 0.5 wt% prepared by the phase inversion method indicated a high water flux and salt rejection of ~21 L m⁻² h⁻¹ and 99.9%, respectively.[22] Another work describes the immobilization of GO on the permeate side of a commercial polypropylene-supported PTFE membrane and shows a water vapor flux of 64.5 kg m⁻² h⁻¹ under direct contact membrane distillation.[23]

Furthermore, having oxygen-containing functional groups such as phenolic hydroxyl, C=OH (tertiary alcohol on the basal plane), carboxyl, quinone, lactone, ketone, and epoxy[24] GO can be chemically modified. For example, GO can be modified into graphene initiators for the use in surface-initiated polymerization. Surface-initiated atom transfer radical polymerization (SI-ATRP) has opened up new avenues in material science, which were not accessible with conventional radical polymerization where the architectural control of the synthesized polymer is very limited. However, during radical polymerization, many free radicals are formed, and the dispersity index of the obtained polymers increases. This issue can be overcome by radical centers mounted on the substrate surface and different types of controlled polymer architectures (stars, combs, brushes, etc.) that might be synthesized, resulting in a low dispersity index.[25]

SI-ATRP on a solid substrate has a prominent role in the preparation of polymer nanocomposites and has been carried out on Au,[26] SiO₂,[27] clay,[28] mica,[29] cellulose,[30] multiwalled carbon nanotubes,[31] graphene oxide,[32] and other surfaces. A significant advantage of this method is a reasonable control of molecular weight, dispersity index, composition, and the end group functionality, which can be achieved with the polymerization of a wide range of the monomers.

As a versatile and robust method, SI-ATRP has a high impact on membrane preparation. By means of tuning the support, the selectivity and permeance of the gas molecules are controlled. Ultrathin (~50 nm) membranes, prepared by the polymerization of ethylene glycol dimethacrylate on porous alumina, showed a CO₂/CH₄ selectivity of ~20.[33] Wu et al. reported that GO with a surface tuned by epoxides increases the selectivity of PEBAX polymer membranes to a separation factor of up to 67 for CO₂/N₂ and 26 for CO₂/O₂.[34]

In this study, we used the method of SI-ATRP for the preparation of polymer brushes on the surface of graphene oxide nanoparticles. Although hydroxyl and carboxyl groups can be modified into an ATRP initiator, we focused on the modification of solely hydroxyl groups; the synthesized surface-initiator functionalized graphene oxide (SI-GO) was used for the polymerization of 2-diethylaminoethyl methacrylate (DEAEMA). In the polymerization procedure, two different approaches were implemented: a) bulk SI-GO initiators and b) dispersion of the exfoliated SI-GO initiators. Additionally, the effect of the exfoliated and bulk SI-GOs on the polymerization of the monomer was investigated in detail. On the base of the synthesized polymers, thin-film membranes were prepared on porous polycrylonitrile (PAN) support to explore single gas permeation, especially water vapor transport properties of the prepared membranes. Due to the presence of nitrogen in the polymer structure, the effect of quaternionization of the nitrogen group on water vapor permeance was investigated. During the rationalization of the work, we tried to disclose these questions:

1) Which effect does the “grafting from” polymer have on graphene wettability, surface smoothness, and pinhole formation?

2) Which effect do the polymers obtained by surface initiation have on gas transport?

3) Is quaternionization for the nitrogen beneficial for transport of water vapor?

The studies showed that the surface-initiated polymer (SIP) membranes prevent the flow of all gases, but favor permeance of water vapor. The results open up a new direction in the field of membrane distillation, which could be essential for the future safe water supply. The study shows the beneficial effect...
of the exfoliated SI-GO initiators on the polymerization and properties of the prepared membranes.

2. Results and Discussion

The surface-initiated poly(2-diethylaminoethyl) methacrylate (SI-PDEAEMA) polymers were prepared using the SI-ATRP method, and the standard polymerization procedure is shown in Figure 1.

In the first step, the hydroxyl groups of the graphene oxide layers were modified with 2-bromopropionyl bromide (BPrB) for the preparation of SI-GO layers (Figure S1, Supporting Information), and the structure was confirmed by Fourier-transform infrared (FTIR) and magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy (Figures S2 and S3, Supporting Information). Figure S2 (Supporting Information) shows the FTIR spectra of the surface-initiator functionalized graphene oxide layers. As it can be seen in the figure, bromide stretching vibrations of hydroxyl groups disappear after functionalization with 2-bromopropionyl and two alkane C–H stretching vibrations appear at 2975 and 2913 cm$^{-1}$. These were attributed to the $-\text{CH}_3$ and $-\text{CH}$ groups of the 2-bromopropionyl moiety covalently attached to graphene layers. The peak at 1724 cm$^{-1}$ corresponds to carbonyl groups of both graphene oxide, indicating the presence of carboxyl, ketone, quinone, and six-membered lactone functional groups and initiator moieties. The stretching vibration of conjugated benzene rings is observed at 1560 cm$^{-1}$. The $-\text{OH}$ bending and C–O stretching vibrations from the $-\text{COOH}$ group were observed at 1441 or 1379 and 1201 cm$^{-1}$, respectively. The peak at 1058 cm$^{-1}$ is corresponding to the epoxy group (C–O–C) stretching vibrations and is much broader than that of pristine graphene oxide. $^{13}$C {1H} MAS NMR (Figure S3, Supporting Information) confirmed the successful modification of graphene oxide into surface-initiator functionalized graphene oxide nanoparticles. A broad peak at $\approx$175 ppm belongs to carbonyl groups of graphene surface functionalities and initiator moieties. The peak at $\approx$6 ppm was attributed to $-\text{CH}_3$ groups of initiator moieties (Figure S3, Supporting Information), which confirmed the attachment of initiator moieties to the graphene.

Energy dispersive X-ray (EDX) analysis showed that 2-bromoisopropionyl bromide moieties were attached to the graphene surface after chemical reaction (Figure S4, Supporting Information). A characteristic band for bromine atoms is visible in Figure S4 (Supporting Information).

The SI-PDEAEMA polymers were prepared using varying concentrations of SI-GO with respect to monomer weight and varying the volumes of the exfoliated SI-GO dispersions in dimethylformamide (DMF) with the polymerization scheme described in Figure 1.

Since DEAEMA is a CO$_2$-triggered monomer,$^{[35]}$ our task was to synthesize a polymer–graphene nanocomposite with an affinity toward carbon dioxide. For this purpose, two methods were utilized for the synthesis of poly(2-diethylaminoethyl) methacrylate (PDEAEMA) using the SI-ATRP technique: a) the use of “bulk” SI-GO particles and b) exfoliated SI-GO dispersions in DMF. The composition and the characteristics of the polymers synthesized are given in Table 1.

Table 1 shows that during the polymerization of DEAEMA at the given conditions, the monomer conversion systematically increases with the increase of SI-GO contents (both bulk and exfoliated). The highest conversion of nearly 40% is achieved using 0.6 wt% SI-GO initiator in SI-PDEAEMA_GO_0.6 compared to the 24% conversion for SI-PDEAEMA-exf.GO_1, even though both results are much higher than those for PDEAEMA homopolymer synthesized via the ATRP method. The obtained 24% conversion degree is the best rate for the exfoliated samples. Interestingly, after 0.6 wt% addition of SI-GO, the conversion of the monomer decreases, and when 1 wt% SI-GO was added into the reaction, the precipitation of the synthesized polymer was impossible. This was attributed to the hydrophobic nature of SI-GO, implying that during the reaction, the initiator became less efficient with the catalyst–monomer complex,$^{[36]}$ which needs to be investigated further.
When it comes to the exfoliated SI-GO dispersions used as initiators with the low concentration of the exfoliated SI-GO (0.25 mL), the polymerization did not occur. It is explained by the low amount of initiator centers in the used SI-GO dispersion. When high amounts of the exfoliated SI-GO dispersions between 0.5 and 2 mL were used, polymerization was successfully accomplished. In the case of the SI-PDEAEMA_exf.GO_0.5 sample, it was not possible to dissolve the synthesized polymer; a gel is formed when mixed with tetrahydrofuran (THF). However, the other samples are completely soluble either in THF or in CHCl3. The polymerization of the SI-PDEAEMA_exf.GO_2 (2 mL exfoliated SI-GO dispersion was used during polymerization) sample was conducted within 5 days, suggesting that with the increase of the volume of the SI-GO dispersion, the initiator becomes inefficient and the possibility of polymer crosslinking increases.

For the molecular weight determination, the polymer chains were cleaved from the SI-GO surfaces. The cleavage was achieved by the attack of NaOH to the carbonyl bonds formed between graphene oxide layers and the polymer chains. For this purpose, the polymer solution was mixed with NaOH solution in a THF/water mixture. Unfortunately, this method did not work for SI-PDEAEMA_GO_X samples. It seems that during the cleavage procedure, the carbonyl groups of the side chains also degrade. In the case of SI-PDEAEMA_exf.GO_X samples, the cleavage procedure was possible in the samples that were soluble in THF. The molecular weight of the synthesized polymer from 0.75 mL exfoliated SI-GO dispersion (used as an initiator) was \( M_w = 39,500 \text{ g mol}^{-1} \) with a dispersity index of 1.25. The obtained SI-PDEAEMA_exf.GO_1 polymer is not soluble in THF; therefore, the sample was completely dissolved in CHCl3, and the cleavage reaction was conducted. The molecular weight of the cleaved polymer from SI-PDEAEMA_exf.GO_1 was \( M_w = 39,400 \text{ g mol}^{-1} \) with a dispersity index of 1.20. These data confirm that the usage of the exfoliated SI-GO dispersions is a new approach in terms of controlled polymerization. Thus, the controlled nature of the SI-ATRP is confirmed. However, further experiments are required to understand the kinetics of the polymerization. In Figure 2, the size exclusion chromatography (SEC) results for SI-PDEAEMA_exf.GO_0.75 and SI-PDEAEMA_exf.GO_1 are shown.

The structural characterization of the synthesized compounds using FTIR showed a sharp increase of stretching vibrations for C=H and –CH2 between 2727 and 2967 cm\(^{-1}\) compared to the FTIR spectra of the SI-GO particles (Figure S2, Supporting Information). A sharp peak at 1725 cm\(^{-1}\) represents the increase of the carbonyl group content, which can be attributed to the side chains of the synthesized polymers. C=H bending vibration of –CH3 is observed at 1450 and 1384 cm\(^{-1}\). The peaks at 1264 and 1146 cm\(^{-1}\) correspond to the C–O stretching vibration of carbonyl groups. C–N stretching vibration is seen at 1066 and 1022 cm\(^{-1}\). The C–Br stretching vibration of the unreacted initiator moiety is seen at 750 cm\(^{-1}\) (Figure 3). The results for other polymers are the same.

The FTIR analysis of the membranes on microporous PAN support (Figure 4) showed that after quaternization of the nitrogen, the spectrum has changed, and additional new peaks appear. The peak at 3450 cm\(^{-1}\) is attributed to the intermolecular bonded –OH stretching vibration, which could be explained that some methanol molecules are entrapped in the membrane, and it was impossible to remove them via the overnight vacuum drying process. Amine salt formation is seen at 2981 cm\(^{-1}\) and it confirms the quaternization procedure. The deformation vibration of the amine group is visible at 1623 cm\(^{-1}\), while the peak at 1400 cm\(^{-1}\) reveals the formation of amine salts. The C=I stretching vibration is detected at 500 cm\(^{-1}\).

To further confirm the structure of the polymers, \(^1\)H- and \(^{13}\)C-NMR spectra were recorded for the SI-PDEAEMA_exf.GO_0.75 and SI-PDEAEMA_exf.GO_1 polymers, respectively. The \(^1\)H-NMR spectra (Figures 5a,b) showed that the aliphatic region is shifted to the upfield region compared to the starting GO (Figure S1). The \(^{13}\)C-NMR spectra (Figures 6a,b) show characteristic peaks for the GO and the synthesized polymers.

### Table 1. Composition and characteristics of PDEAEMA nanocomposites synthesized via SI-ATRP and conventional ATRP.

| Sample name | SI-GO content [wt%] | Exfoliated SI-GO content [mL] | Conversion [%] | dMbpy/CuBr |
|-------------|---------------------|------------------------------|---------------|-------------|
| PDEAEMA\(^a\) | – | – | 0.50 | 1:1 |
| SI-PDEAEMA.GO_0.2 | 0.2 | – | 1.80 | 1:1 |
| SI-PDEAEMA.GO_0.4 | 0.4 | – | 11.8 | 1:1 |
| SI-PDEAEMA.GO_0.6 | 0.6 | – | 41.1 | 1:1 |
| SI-PDEAEMA.GO_0.8 | 0.8 | – | 25.8 | 1:1 |
| SI-PDEAEMA_GO_1 | 1.0 | – | – | 1:1 |
| SI-PDEAEMA_exf.GO_0.25 | – | 0.25 | – | 1:1 |
| SI-PDEAEMA_exf.GO_0.5 | – | 0.50 | 8.60 | 1:1 |
| SI-PDEAEMA_exf.GO_0.75 | – | 0.75 | 21.9 | 1:1 |
| SI-PDEAEMA_exf.GO_1 | – | 1.00 | 24.0 | 1:1 |
| SI-PDEAEMA_exf.GO_2\(^b\) | – | 2.00 | 9.00 | 1:1 |

Note: PDEAEMA—Poly(2-diethylaminoethyl) methacrylate; SI-PDEAEMA—Surface-initiated poly(2-diethylaminoethyl) methacrylate; dMbpy=4,4'-dimethyl-2,2'-dipyridyl.

\(^a\)2-diethylaminoethylmethacrylate was polymerized using 10 µL 2-bromoisobutyl bromide via ATRP; \(^b\)This polymerization took 5 days.
respectively. As can be seen from the figure, a sharp peak at 1.00 ppm belongs to the side chain –CH_{3} groups, while backbone –CH_{2} groups are located between 1.00 and 1.5 ppm. The chemical shift at ≈2 ppm belongs to the main chain –CH_{2} groups, while side chain –CH_{2} group of ethyl moiety is at ≈2.5 ppm. The characteristic resonance signal at ≈4.0 ppm corresponds to the –OCH_{2} groups. In addition, ¹³C-NMR spectra (Figure 6) showed that the SI-PDEAEMA_exf.GO_0.75 sample has a characteristic signal for the C=O bond. The other polymers did not show the characteristic signal of that double bond. This is explained by the assumption that the samples are in the crosslinked form (SI-PDEAEMA_exf.GO_0.5) or that termination occurred by the combination mechanism (SI-PDEAEMA_exf.GO_1 and SI-PDEAEMA_exf.GO_2).

Solid-state ¹³C cross-polarization (CP) MAS-NMR analysis (Figure 7) shows signals of COO groups at ≈176 ppm. The sharp peaks at ≈50 and ≈10 ppm belong to –CH_{3} and –CH_{2} groups of the N–CH_{3}CH_{3} side chains, respectively. Signals at ≈55 and ≈65 ppm can be attributed to the –CH_{2} groups attached to the nitrogen atom and carboxyl moiety of the side chain of the polymer, respectively. The –CH_{2} and C (quaternary) of the main polymer chain yielded signals are between ≈45 and ≈50 ppm. Solution and solid-state NMR results confirm the structure of polymeric methacrylate, demonstrating that the polymerization was successful both on the single-layer exfoliated SI-GO and on bulky SI-GO particles. The ¹³C-NMR analysis is an excellent technique for the stereochemistry of the polymers. A peak at ≈52 ppm shows that the polymer has isotacticity.²⁷

TGA results for the synthesized polymer, SI-GO, and GO nanoparticles are shown in Figure 8. There are two degradation steps for both SI-GO nanoparticles and SIPs; however, the weight loss of these systems occurs at significantly different temperatures. The curve of SI-GO shows that the synthesized surface-initiated nanoparticles are stable in the temperature range of 30–100 °C above, in which the pure GO starts to lose its weight. The first degradation step between 100 and 200 °C in an amount of ≈23% corresponds to the elimination of 2-bromoisopropyl bromide moieties from GO layers and the evolution of carbon dioxide and carbon monoxide from lactone and carboxyl groups of the layers themselves. This step is followed by another degradation step with ≈25% mass loss accompanied by the degradation of other oxygen functional groups such as quinone and ketone groups of the GO layers. Unlike GO and SI-GO, the synthesized polymers are stable up to 250 °C, meaning that GO layers are covered by polymer chains, which increases the thermal stability. The first weight loss occurs at 250–350 °C, with ≈60% weight loss. The TGA curve at this step for the polymers has a steep decline, which can be attributed to the degradation of polymer’s side chains. The second step is between 350 and 450 °C, with around 38% mass loss corresponding to the main chain destruction. The degradation of the oxygen functional groups of SI-GO coincides with the degradation of polymer chains, and it was not possible to differentiate.

To support this theory, TG-FTIR analysis was conducted, and the eliminated gaseous compounds were analyzed (Figure S5, Supporting Information). The experiments strongly support the idea that degradation starts from the side chains. The strong C–H stretching vibrations for the side chain –CH_{3} groups are recorded between 2820 and 2975 cm⁻¹. The peak at 1740 cm⁻¹ belongs to the C=O stretch vibration of methylformate, a possible degradation product of the polymer side chain. The experiment showed that during this degradation step, the bromine groups of the polymer end functionalities are eliminated, and the peaks at 1204 and 1164 cm⁻¹ correspond to the C–H wagging vibrations of CH_{3}Br. The C–N stretching vibration of the eliminated trimethylamine is seen at 1061 cm⁻¹.

It was proposed that the second step is accompanied by the degradation of the main polymer chains. A small peak at 3091 cm⁻¹ is attributed to the =C=H stretching vibrations of the degraded –C=CH–Br moiety. The peaks for sp³ type C–H...
vibrations are smaller in intensity than that for the first degradation step, which strongly supports the interpretation as degradation of \(-\text{CH}_3\) groups of the backbone. This method helped us to reveal that at this step, the degradation of graphene oxide layers starts. The increase of the peaks corresponding to CO$_2$ and CO gases suggests that those are the result of lactone, ketone, quinone, epoxy, and carboxyl groups’ elimination. The peak for \(\gamma\)-lactone is at 1775 cm$^{-1}$, while the peak at 1748 cm$^{-1}$ belongs to acetaldehyde, a thermal degradation product of the unreacted mounted initiator groups. The vibrations recorded at 1721 and 1690 cm$^{-1}$ are the C=O stretching vibrations of carboxyl groups (Figure S5, Supporting Information).

Figure 9 shows the water contact angle images of the exfoliated GO layers, SI-PDEAEMA_GO_0.6, and SI-PDEAEMA_exf.GO_0.75 polymer nanocomposites coated on the PAN porous membrane. The images show that the water contact angle for the exfoliated GO layers is 45°, which is smaller than the water contact angle of porous PAN support (54°). This phenomenon can be explained by the high degree of oxygen functionality, making graphene surface hydrophilic. In addition, pure graphene layers epitaxially grown on SiC showed a bad wettability with a water contact angle of 92° for single, bi-, and multilayer vibrations are smaller in intensity than that for the first degradation step, which strongly supports the interpretation as degradation of \(-\text{CH}_3\) groups of the backbone. This method helped us to reveal that at this step, the degradation of graphene oxide layers starts. The increase of the peaks corresponding to CO$_2$ and CO gases suggests that those are the result of lactone, ketone, quinone, epoxy, and carboxyl groups’ elimination. The peak for \(\gamma\)-lactone is at 1775 cm$^{-1}$, while the peak at 1748 cm$^{-1}$ belongs to acetaldehyde, a thermal degradation product of the unreacted mounted initiator groups. The vibrations recorded at 1721 and 1690 cm$^{-1}$ are the C=O stretching vibrations of carboxyl groups (Figure S5, Supporting Information).

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For the polymer films, the contact angle is higher than for exfoliated GO, however, smaller than that of epitaxially grown graphene. Thus, a water contact angle of 80° observed for SI-PDEAEMA_GO_0.6 and 77° for SI-PDEAEMA_exf.GO_0.75.

Scanning electron microscopy (SEM) images show the effect of SI-GO particles on the polymerization of the DEAEAMA monomer. As it can be seen in Figure 10, the SI-GO particles successfully polymerized DEAEAMA monomer due to the surface-mounted initiator groups. In Figure 10c, it is clearly seen that SI-GO particles are in agglomerated form, and we suggest that the graphene layers are connected to SI-PDEAEMA polymer chains. Transmission electron microscopy (TEM) image of the single-layer GO and the SEM image of bulk SI-GO are shown in Figure 10a,b, respectively. The cross section of the membrane (Figure 10d) shows that the polymers cover the PAN support without significant penetration into the porous layer. Due to the atom size thickness of graphene, it is not possible to detect the polymer-covered graphene layers by SEM. The image (Figure 10d) shows the SI-GO particles only in agglomerated form.

Pure single gas transport performance of SIP membranes for H2O vapor, H2, N2, O2, and CO2 was determined at 30 °C employing our home-build gas permeation facility. The data of the gas transport performances of the membranes prepared from surface-initiated polymers show an improved ideal selectivity in comparison to other amorphous polymer membranes. The membranes show high selectivity for water vapor, demonstrating that they are potential candidates for the dehumidification of various gases. Additionally, the experiments showed that when the amount of the SI-GO particles increases, the ideal selectivities decrease as it is demonstrated in Table 2.

Figure 8. Thermal gravimetric analysis results of the synthesized polymer nanocomposites.

Table 2. The ideal selectivities for gas mixtures are significantly influenced by choice of the type of SI-GO, i.e., polymer grown on single-layer exfoliated SI-GO layers showed higher selectivities in comparison to the polymer synthesized from the bulky SI-GO particle. The ideal selectivities for H2O/N2 and H2O/CO2 gas pairs are 1682 and 84, respectively, in the case of SI-PDEAEMA_exf.GO_0.75 thin-film membrane. The SI-PDEAEMA_exf.GO_1 thin-film membrane showed higher selectivities for the aforementioned gas pairs with a selectivity factor of 3158 for H2O/N2 and 113 for H2O/CO2. The ideal selectivity recorded for CO2/N2 is ≈28 in the case of SI-PDEAEMA_exf.GO_1.

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In order to understand the transport of water vapor through the prepared membrane, a series of experiments were conducted. Figure 11 represents the water vapor permeability versus water vapor activity in the temperature range of 30–80 °C. Metz et al. explained that when water vapor dissolves in polymer chain fragments that have interaction with the water molecule, the sorption isotherm shows a linear trend at low activities \( (p/p_0 < 0.4) \) and increases exponentially at higher activities.\(^{[46]} \) The same trend is seen in our research explaining that the polymer might have low solubility for water vapor at \( p/p_0 < 0.4 \) (see the curve at 40 °C, Figure 11), and with the increase of the vapor activity, water vapor solubility increases due to the clustering or multilayer formation.\(^{[43]} \) Since our polymer is completely in the amorphous state, it is possible that water vapor molecules form clusters at the “free” polymer chains. With the increase of temperature, the polymer–penetrant interaction becomes weak. Considering the recent work of Akhtar et al.,\(^{[48]} \) we can assume that at high temperatures where the vapor activity reaches \( \approx1 \), this kind of membrane could transport water vapor with more than 2400 Barrer at high temperatures. To support this approximation, we conducted Aspen Custom Modeling (ACM) in order to understand the water vapor transport through the prepared membranes. The results are shown in Figure 12.

Figure 9. Images of a water droplet on a PAN membrane surface coated with exfoliated graphene oxide, SI-PDEAEMA_GO_0.6, and SI-PDEAEMA_exf.GO_0.75.
The modeling showed that water vapor transport could be adequately described in terms of the Free Volume Model (Equation (3)). Due to experimental setup’s limitations, it was not possible to conduct vapor transport measurements at high water vapor activity on the feed side of a membrane. Since the Free Volume Model was found to be applicable for the description of water vapor transport through polymers under study, the estimation of permeability coefficient at \( p/p_0 = 0.99 \) was done. For data points obtained from this estimation at each temperature point, Arrhenius dependence showed a minor positive effect of temperature on water vapor transport. The calculated activation energy of water vapor transport was just 0.6 \( \text{kJ mol}^{-1} \) (Figure 13). Assuming water vapor permeance at 100 °C, vapor activity \( p/p_0 = 0.99 \) as 2800 Barrer, and transmembrane pressure 1000 mbar, for the studied membrane with the selective layer thickness of 400 nm one can calculate a permeation of \( \approx 13 \text{ kg h}^{-1} \) of pure water to the cold side of the 1 m² membrane.

The quaternized SI-PDEAEMA_exf.GO_0.75 membrane showed higher water vapor transport than the same nonquaternized SI-PDEAEMA_exf.GO_0.75 membrane. The experiments show that the introduction of the amine salts into the

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**Table 2. Ideal Selectivities for the SIP TFC membranes in comparison to results from the literature.**

| Membrane code | Selectivity | Ref. |
|---------------|-------------|-----|
| H\(_2\)/N\(_2\) | H\(_2\)/N\(_2\) | O\(_2\)/N\(_2\) | CO\(_2\)/N\(_2\) | H\(_2\)O/CO\(_2\) |
| Poly(methyl methacrylate) | – | – | 3.9 | 13.9 | [39] |
| Poly(ethyl methacrylate) | – | – | 3.0 | 20.5 | – | [40] |
| Cross-linked poly(ethylene glycol diacrylate) | – | 7.5 | 2.5 | 50.0 | – | [41] |
| Poly(ethylene glycol) dimethacrylate | – | 9.4 | 2.9 | 59.0 | – | [42] |
| Poly(acrylic acid) | – | – | 0.93 | 0.93 | – | [43] |
| Poly(tertiary-butyl methacrylate) | – | 75.0 | 5.6 | 13.0 | – | [44] |
| Poly(2-ethoxyethyl methacrylate) | – | – | 3.6 | 21.4 | – | [45] |
| Poly(2-(2-ethoxyethoxy) ethyl methacrylate) | – | – | 3.2 | 37.0 | – | [45] |
| SI-PDEAEMA_GO_0.6 | 1937 | 10.0 | 3.0 | 21.5 | 90 | This work |
| SI-PDEAEMA_GO_0.8 | 1148 | 7.5 | 2.3 | 14.0 | 82 | |
| SI-PDEAEMA_exf.GO_0.75 | 1682 | 9.0 | 3.0 | 20.0 | 84 | |
| SI-PDEAEMA_exf.GO_1 | 3158 | 12.0 | 4.0 | 28.0 | 113 | |

\(^{a)}\text{Selectivity at water vapor activity 90% obtained during the experiment; }^{b)}\text{Experiments have been done at 25 °C.}
structure improves the interaction between the polymer chain and water vapor. It seems that during quaternization, the polymeric chains of the graphene charge, and they dissolve much more vapor molecules than the nonquaternized compartment. Although quaternization leads to the formation of bulky structures with the alkyl groups that hinder the water vapor molecules to accessing the positive charge, the increase in the water vapor permeance can be explained with the effect of the improved hydrophobic surface and the dissolution of vapor molecules in the unreacted oxygen functionalities such as carboxyl, quinone, and ketone of the graphene oxide nanosheets. Due to experimental design of the gas transport equipment, we could reach 95% vapor activity at the feed side, and using the extrapolation based upon on our Free Volume Model we can judge that at low temperatures and high vapor activities, the permeability of water vapor is around 9000 Barrer (Figure 14), which at conditions described above up to 27 kg h\(^{-1}\) of pure water that can be obtained from 1 m\(^2\) of the membrane.

According to the activation energy calculation, we assume that this kind of membrane can be useful for the lowering of the distillation cost by reducing the temperature on the hot side of the membrane. Graphene oxide has exhibited an advantage in water purification even though the large scale GO membrane preparation suffers from damage to the membrane, which needs to be solved for better performances. To avoid this, Chang et al. prepared hierarchically assembled GO-MOF composite membranes to achieve better results.[49] Growing polymer chains from the single GO layers affect the orientation of graphene nanoparticles significantly during the membrane preparation, and it helps to reduce the thickness of the selective layer below 100 nm as a consequence of increasing membrane performance by a factor of at least 4 compared to the membrane under study.

Considering our results, we will further conduct experiments in this field to understand the water sorption, membrane distillation processes, and the synthesis of block-copolymers via SI-ATRP in order to get better results with this polymer.

3. Conclusion

In this study, graphene oxide layers were transformed into surface-mounted graphene initiators and were used for the polymerization of 2-diethylaminoethyl methacrylate. EDX, FTIR, and SSNMR analyses showed that the modification was successful. For the first time, an exfoliated graphene initiator dispersion was applied for polymerization. SEC results showed dispersity index of 1.25 and 1.20 for SI-PDEAEMA\(_{\text{exf.GO.0.75}}\) and SI-PDEAEMA\(_{\text{exf.GO.1}}\), respectively. The synthesized polymers were analyzed by FTIR, NMR, TGA, TG-FTIR, dynamic water contact angle measurement, and SEM analysis. Using the synthesized polymers, thin-film composite membranes (TFCMs) were prepared on porous PAN support, and their single gas and water vapor transport performances were investigated. Single gas transport experiments showed that the prepared amorphous polymer membranes are defect free and show high selectivities such as 3158 for \(\text{H}_2\text{O}/\text{N}_2\), 28 for \(\text{CO}_2/\text{N}_2\), and 113...
for H2O/CO2. According to the membrane water transport results, we can draw the following conclusions:

- Since the synthesized polymer is in the rubbery amorphous state, the polymer of the selective layer is in a fully relaxed, nonaging state.
- Single-layer surface-initiator functionalized graphene oxide gives us the opportunity to decrease the thickness of the membrane.
- Grafting polymer brushes on the GO surface eliminates the defect or pinhole formation in the selective layer, improving the performances of the GO membranes.
- The polymer brushes on the GO surface facilitate only the transport of water vapor, preventing the permeances of other gas molecules, which would be interesting for the air dehumidification and membrane distillation.
- The activation energy of the water vapor transport is low, which means the operational costs of the membrane distillation can be decreased by the optimization of separation process conditions.
- The obtained data open a new prospect for further development of the thin-film membranes for membrane distillation.

### 4. Experimental Section

**Synthesis of SI-GO:** Synthesized by the Hummers method,[50] GO was modified into SI-GO using the method initially reported in previous works.[35] In general, GO (1.0 g) was dispersed in DMF (100 mL, anhydrous, 99.8%, Sigma–Aldrich) in a 250 mL round bottom flask in the sonication bath for 1 h, and a brownish-black dispersion was obtained. After triethylamine (TEA, 10 mL, 0.072 mol, ≥99%, Sigma–Aldrich) was added to the dispersion, and the flask was immersed in an ice bath placed in the sonication bath and then, using a dropping funnel, which was mounted on the flask, BPrB (15 mL, 0.142 mol, 97%, Alfa Aesar) was added dropwise into the dispersion at 0 °C. After the addition, the resulting dispersion was stirred at room temperature for 24 h. The product was vacuum-filtered on a qualitative Grade 1 filter paper (Whatman, pore size 11 µm), washed with chloroform (200 mL), ultrapure water (100 mL, to remove Et3N·HBr) and methanol (300 mL) sequentially. The product was dried under high vacuum at 50 °C for 2 days.

**Exfoliation of SI-GO:** In order to use the single-layer SI-GO in SI-ATRP, the study on exfoliation was performed for the SI-GO nanoparticles. For the preparation of a calibration curve, ten different concentrations (between 0.002 and 0.1 wt% of SI-GO in DMF) were used. After sonication, the samples were investigated using a Genesys 10S UV–Vis spectrophotometer (Thermo Scientific, Ottawa, Canada) in absorbance mode with a 10 mm cuvette at a wavelength of 600 nm. Then, the samples were centrifuged on a Heraeus Biofuge primo centrifuge (Thermo Scientific, Ottawa, Canada) at the speed of 5000 rpm for 30 min to remove the large particles for obtaining only the single-layer SI-GO dispersion. The concentration of the single-layer SI-GO containing dispersion was calculated on the basis of the calibration curve (Figure S6, Supporting Information). The maximum concentration obtained for the single-layer SI-GO dispersion was 0.0015 wt% even though the dispersions were not stable in DMF after several hours.

**Polymerization of 2-Diethylaminoethyl Methacrylate from SI-GO:** Two approaches were applied for the polymerization of DEAEMA containing 1500 ppm 4-methoxyphenol (MEHQ) as an inhibitor (99%, Sigma–Aldrich) monomer. The first method, called “bulk” polymerization, was performed using the polymerization method reported by Rajender et al.[32b] In a typical SI-ATRP experiment, Cu(I)Br (~18 mg, ~0.1 mmol, 99.999% trace metals basis, Sigma-Aldrich) and 4,4’-dimethyl-2,2’-dipyridyl (~23 mg, dMbp, ~0.1 mmol, 99%, Sigma–Aldrich) were mixed in anhydrous DMF (0.6 mL) under argon flow in a round bottom flask with magnetic stirring until homogeneous solution was obtained. In another round bottom flask, after purification of the monomer through basic alumina-containing column (ICN Alumina B-Super I, VWR International, Germany), 2 mL DEAEMA was mixed with different concentrations of SI-GO (0.2, 0.4, 0.6, 0.8, and 1 wt% SI-GO, with respect to DEAEMA monomer weight) and sealed under argon, followed by 30 min sonication in a sonication bath. The polymerization was carried out in an oil bath at 70 °C for 48 h. In this procedure, the weights of the bulk SI-GOs were 3.69, 7.38, 11.1, 14.8, and 18.4 µmol, respectively. The synthesized polymer was dissolved in anhydrous THF (10 mL) and precipitated in water–methanol (250 mL, 4:1, v:v).
The synthesized polymers were labeled as SI-PDEAEMA_GO_X (X means the weight percentage of the SI-GO nanoparticles with respect to the monomer weight). In the second method, 0.0015 wt% exfoliated SI-GO dispersion in anhydrous DMF was used for the polymerization. Thus, under argon flow, DAEAMMA monomer (2 mL) was sealed in a round-bottom flask. After argon purge, homogeneous Cu(I)/Br/dmBpy solution in DMF (0.6 mL) was injected into the monomer-containing flask, and then the injection of different volumes of the exfoliated SI-GO dispersion in anhydrous DMF (0.25, 0.5, 0.75, 1, and 2 mL) was conducted. In this procedure, the weights of the single-layer SI-GOs were 0.0034, 0.0068, 0.0102, 0.0170 mg, respectively. It was assumed that the amounts of the initiator on the surface of GO were about 0.0034, 0.0068, 0.0101, 0.0135, and 0.0270 µmol, respectively. The polymerization and the polymer recovery procedures were the same as reported for the “bulk” polymerization. The synthesized polymers were labeled as SI-PDEAEMA_exf.GO_X (X means the added volume of the exfoliated SI-GO nanoparticles).

Cleavage of the polymer chains from SI-GO: Approximately 20 mg of SI-PDEAEMA_exf.GO_0.75 polymer was dissolved in THF (5 mL) and, after the addition of NaOH solution (0.1 M, 2 mL), the polymer solution was stirred for 24 h. The cleavage of SI-PDEAEMA_exf.GO_1 polymer was conducted in the interface of CHCl3/water after successful dissolution of polymer in chloroform. Then, the cleaved polymers were precipitated in water–methanol (5:1) mixture. The obtained polymers were analyzed by SEC to identify the molecular weight.

Thin-Film Composite Membrane Preparation: The thin-film membranes (TFM) from SI-PDEAEMA_exf.GO_0.75 were prepared on dry microporous PAN support (made in-house, the average pore size of 22 nm and 15% surface porosity, polyester nonwoven as mechanical stability provider) using a laboratory-scale membrane casting machine. The SI-PDEAEMA_exf.GO_1 polymer was dissolved in THF (10 mL) in order to prepare 1 wt% dispersions. The obtained dispersions contained some amount of graphene–polymer agglomerates, which were removed before the membrane casting. After the preparation of the black dispersions, they were kept for 30 min without stirring to settle down the large particles by gravitational forces, and the homogeneous part of the dispersion was taken for membrane casting. The concentration of the homogeneous dispersion was controlled by the UV–vis spectroscopy using calibration curves shown in Figures S7 and S8 (Supporting Information). The dispersions were stable during membrane casting, and no precipitation was observed.

The polymers synthesized from exfoliated SI-GO dissolved completely in THF, and the obtained solutions were used for membrane casting without the polymer–graphene agglomerates’ removal. The polymer solutions were transparent, and no agglomerates were seen. The selective layer deposition was done by a modified dip-coating method, where the porous support was first brought into contact with the polymer solution and then raised by 1–2 mm to form a meniscus of the polymer solutions. The selective layer deposition was done by a modified dip-coating method, where the porous support was first brought into contact with the polymer solution and then raised by 1–2 mm to form a meniscus of the polymer solutions. The selective layer deposition was reproducible coating. The evaporation of the solvent was not controlled or targeted. The evaporation of the solvent was not controlled or targeted. The formed membrane was allowed to dry at ambient conditions.

Quaternization of the SI-PDEAEMA_exf.GO_0.75 Polymer Membrane: Quaternization of the SI-PDEAEMA_exf.GO_0.75 membrane sample was conducted. Thus, methyl iodate (CH3I, ≥99.0%, 2 mL, Sigma–Aldrich) was dissolved in methanol (10 mL) in the sample container, and the SI-PDEAEMA_exf.GO_0.75 polymer membrane sample soaked into the container. After sealing the container, it was shaken overnight at 2.5 Hz in a shaking incubator (Incutec K30-300, EquipNet, Canton, MA, USA, at ambient temperature). On the next day, the polymer membrane was removed from the quaternization solution, washed five times with the excess of methanol, and dried in the vacuum oven overnight.

Characterization Techniques: FTIR spectra were recorded in attenuated total reflectance (ATR) mode on a Bruker ALPHA FT-IR spectrometer (Bruker, Ettlingen, Germany). The transmittance measurements were done at ambient temperature in a spectral range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹ and an average of 64 scans. Liquid-state NMR (LSNMR) experiments were conducted on a Bruker Avance 300 NMR spectrometer (Bruker, Ettlingen, Germany) operating at a frequency of 300 MHz using a 5 mm H2O/C13 triple resonance (TXI) probe at 298 K. 1H NMR spectra were recorded applying a 10 ms 90° pulse. 13C spectra measurements were done using dept-45 and dept-135 sequences, employing a waltz-16 decoupling scheme. The relaxation delay was chosen in that way that the samples were fully relaxed. SSNMR experiments were performed on a Bruker Avance II 400 spectrometer (Bruker, Rheinstetten, Germany) equipped with a 4 mm double resonance probe. Direct excitation 13C MAS-NMR spectra were obtained with a 45° pulse length of 2.05 µs and recycle delay of the 30 s at an operating frequency of 100.66 MHz. 13C{1H} CP MAS spectra were acquired using 1H spin-labeled 2.5 µs pulse in the H 2O pulse length of the composite membrane was soaked into a thermostated part of the membrane testing facility, and the single gas transport properties for H2, N2, O2, CO2, and H 2O vapor were determined at feed pressures of 100, 250, 250, 250, and 1000 mbar, respectively. The effective membrane area was 0.97 cm² during all experiments. The pressure of the water vapor was predetermined by the temperature of the thermostated part of the facility, was 95% of water vapor activity at a given temperature, and lowered during the experiments due to consumption by vapor transport through the membrane. The cell temperatures during the experiments were between 30 and 80 °C. The described feed pressures and permeate pressure of a maximum of 10 mbar give the possibility of considering all aforementioned gases as ideal for the calculation of membrane permeance. Water vapor was considered as other gases, even taking into account that vapor activity on the feed side of the membrane changed during the experiment significantly. No experiments on possible water vapor concentration effects on the diffusion coefficient were carried out. The gas permeation experimental facility is described elsewhere in more detail.[16] The membrane permeance (L) of a gas can be calculated using the following equation

\[ L = \frac{V \times 22.41 \times 3600}{RTA} \left( \frac{p_f - p_o}{p_f - p_{inj}} \right) \]

where \( L \) is the gas permeance (m³ (STP) m⁻² h⁻¹ bar⁻¹), \( V \) is the permeate volume (m³), 22.41 is the molar volume (m³ STP kmol⁻¹), 3600 is a conversion factor (s h⁻¹), \( R \) is the ideal gas constant (0.08214 m³ bar⁻¹ K⁻¹ mol⁻¹), \( T \) is the temperature (K), \( t \) is the time of measurement between permeate pressure points \( p_o \) and \( p_{inj} \) (s), \( A \) is the membrane area (m²),
and $p_0$, $p_a$, and $p_{p(0)}$ are the pressures at the feed, and permeate side at the start and at the end time of measurement, respectively (mbar). The ideal selectivity for a gas pair A and B ($\alpha_{A/B}$) can be calculated by the equation

$$\alpha_{A/B} = \frac{L_A}{L_B}$$

(2)

The equation oriented process simulator Aspen Custom Modeler was employed for the description of water vapor permeance through the SI-PDEAEAEXEF,GO,0.75 membrane using the Free Volume Model equation.

$$L_i = L_{0,i}^L \exp \left\{ \frac{-E_i}{RT} + \sum_{j=1}^{\infty} \frac{(\sigma_{ij}}{\sigma_j})^2 m_{w,i,j} f_{w,i,j} \exp(m_{T,i,j} T) \right\}$$

(3)

$$f_{w,i,j} = 0.5(f_{w,i} + f_{w,j})$$

(4)

where $L_i$ is the permeance, $L_{0,i}^L$ is the permeance at infinite temperature and pressure approaching zero, $E_i$ is the sum of the activation energy of diffusion and heat of sorption, $R$ is the universal gas constant, $T$ is the temperature, and $\sigma$ is the Lennard–Jones molecule diameter. $f_{w,i}$ and $f_{w,j}$ are the average, reactant, and permeate fugacities, respectively.

This model is allowed to predict the permeation of multicomponent gas mixtures based on the single gas experiments by accounting for the increase in flux of one component caused by the swelling induced by another. According to the model, these parameters were used: $E_0 = -174.266$, $L = 2.52415$, $L_0 = 14.0671$, $m_0 = 0$, $m_t = 0$, $\rho = 0.487239$ bar, $R = 8.31433$, $T_0 = 273.15$ for the no-swelling condition; $E_0 = -2087.48$, $L = 2.52415$, $L_0 = 5.66042$, $m_0 = 468.30$, $m_t = -0.0352701$, $\rho = 0.487239$ bar, $R = 8.31433$, $T_0 = 10.275 \, ^\circ C$, $T_0 = 273.15$ for the swollen condition. In case no swelling caused by a component, $m_0$ and $m_t$ are equal to 0 and the model becomes an Arrhenius-type relationship.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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gas separation, membrane distillation, poly(2-diyethylaminoethyl) methacrylate, surface-initiated atom transfer radical polymerization, surface-initiator functionalized graphene oxide

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