CO₂-Responsive Copolymers for Membrane Applications, Synthesis, and Performance Evaluation

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The urgent need to mitigate climate change has spurred research into innovative carbon dioxide (CO_2) capture materials. In this study, the design and synthesis of CO_2 -responsive diblock copolymers, poly (N-[3-(dimethylamino)propyl]-acrylamide)-*b*-poly(methyl methacrylate) (PDMAPAm-*b*-PMMA) are focused on via a two-step reversible addition—fragmentation chain-transfer (RAFT) polymerization as well as the application of the synthesized diblock copolymer as a membrane for CO_2 capture. The resulting diblock copolymer possesses distinct blocks with varying properties. The poly (N-[3-(dimethylamino)propyl]-acrylamide) (PDMAPAm) block provides CO_2 -responsive behavior, while the poly(methyl methacrylate) (PMMA) block contributes to mechanical stability. The gas transport properties of the fabricated thin-film composite membrane made of PDMAPAm-*b*-PMMA are measured. It is determined that the copolymer exhibits dual responsiveness towards CO_2 and can be tailored for use in fabrication of membranes for direct air capture (DAC).

1. Introduction

Carbon capture is one of the particular research fields that is currently desired to be applied as a technology^[1] in various industries such as power generation,^[2] chemical production,^[3] metal production plants^[4] etc., to reduce carbon dioxide (CO₂)emission. Apart from that, CO₂ existing in the atmosphere in a relatively small amount can be captured by the newly introduced principle called direct air capture (DAC).^[5] In DAC technologies, there should be a stronger binding between CO₂ molecules and adsorbent (solid), which means the process is more related to chemisorption than physisorption.^[5]

Diblock copolymers hold great potential to be used as an adsorbent for DAC due to their ability to form films with high

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porosity^[6-10] and scalability.^[11-13] Particularly, the diblock copolymers with amine functional groups can represent excellent performance in capturing CO₂, considering that the amine group has a great affinity for CO₂.^[14,15] Some acrylate polymers such as poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA),^[16-19] poly(N,N-dimethylallylamine) (PDMAAm),^[20-22] and polv(2aminoethyl methacrylate) (PAEM)^[23,24] with amine groups that behave CO2responsive, can be utilized as the first block for further chain extension to diblock or triblock copolymers. These polymers exhibit favorable characteristics suitable for CO₂ adsorption technologies, including a consistent, relatively high, and rapid CO₂ adsorption capacity, along with a low desorption temperature.^[25,26] The presence of amino acrylate polymers on the surface and pore walls of the membranes allows

them to exhibit CO_2 -responsive behavior, enabling tunable pore sizes through the ad- and desorption of CO_2 gas. Specifically, the polymer membranes showing better CO_2/N_2 selectivity adsorb CO_2 at room temperature and release it when the temperature is raised, demonstrating reversible adsorption.^[16]

The diblock copolymers can be synthesized using living polymerization techniques such as atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain-transfer (RAFT), ring-opening metathesis polymerization (ROMP) etc., which allows precise control over the polymer structure. Polymerization using these outstanding techniques allows good control over the reaction rate, dispersity and molecular weight distribution (MWD) of the potentially produced polymer.^[27-30] Compared to ATRP and ROMP, RAFT-mediated polymerization can be used for a wide range of monomer types such as butyl acrylate, (meth)acrylates, (meth)acrylamides acrylonitrile, styrene,[30] and its derivatives, butadiene, vinyl acetate and Nvinylpyrrolidone^[27] and vinyl-pyridines^[31,32] to synthesize complex and diverse architectures (block,^[33] branched, star,^[34] hyperbranched,^[34] surface-grafted copolymers,^[35] etc.). All these contributions and findings^[8,36,37] have provided a better insight into the control of the polymerization processes, making it a powerful and widely used technique to synthesize well-defined copolymers.

Depending on the application area (whether for liquid or gas separation), the pore size, porosity, thickness, selectivity, and permeability of membranes are considered crucial properties.^[38,39] Polymer membranes can be manufactured with different methods such as induced phase separation (NIPS),^[40–43] self-assembly

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with nonsolvent induced phase separation (SNIPS),^[32,40,44-46] film casting,^[47–50] melt extrusion,^[51,52] doctor blade.^[53–56] Among these methods, casting using a doctor blade is the one that is used the most. Isoporous membranes by casting the polymer solution with a doctor blade onto a flat substrate have been referred previously in literature.^[56] Similarly, using the doctor blade technique, Cao et al. has created magnesium/boronamide and magnesium-amide (LMBNH-TPX and LMNH-TPX) composite membranes by molding them with polymethylpentene (poly(4-methyl-1-pentene), TPXTM) onto a glass substrate for hydrogen storage applications.^[53] Apart from that, in several publications, blade casting is mentioned as a well-established method for the development of thin isoporous block copolymer membranes.^[31,45,57]

In this study, we focus on the development of a new diblock copolymer, namely poly(N-[3-(dimethylamino)propyl]acrylamide)-b-poly(methyl methacrylate) (PDMAPAm-b-PMMA) via RAFT polymerization, and perform a first approach on its application as a membrane for CO2 capture. N-[3-(dimethylamino)propyl]-acrylamide (DMAPAm) was selected as a CO_2 -responsive monomer for several reasons. Apart from the fact that this monomer has not yet been investigated in detail for the case of synthesis via RAFT polymerization, another reason is that the monomer contains both secondary and tertiary amines, which are more readily protonated by CO₂ compared to primary amines. This is because secondary and tertiary amines have more electron-donating alkyl groups, which increase the electron density on the nitrogen atom, making it more reactive toward CO₂.^[5,58] Additionally, the CO₂-induced transformations in secondary and tertiary amines are more easily reversible. This allows the polymers to switch between their hydrophilic and hydrophobic states more efficiently, enhancing their responsiveness.[58]

2. Experimental Section

2.1. Materials

N-[3-(Dimethylamino)propyl]acrylamide (stabilized with MEHQ) (DMAPAm, >98.0%, TSI, Zwijndrecht, Belgium) was first dissolved in 1,4-dioxane (>99.8%, Merck, Darmstadt, Germany) and percolated through a column of basic aluminum oxide (>98%, Sigma-Aldrich) prior to use to remove the inhibitor. Then, 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%, Sigma-Aldrich, Taufkirchen, Germany, stored at 4 °C) and 4-cyano-4-[(dodecylsulfanylthiocarbonyl)-sulfanyl]pentanoic acid (CDTPA, 97%, Sigma-Aldrich, Taufkirchen, Germany, stored at 4 °C) were added to the monomer and solvent mixture. Methyl methacrylate (MMA) (99%, stabilized with \leq 30 ppm MEHQ, Sigma-Aldrich, Steinheim, Germany) was also freshly percolated with the same procedure for the same reason. Nitrogen (N_2) , oxygen (O_2) , CO₂ gases were purchased by Air Liquide (Hamburg, Germany, 99.999% purity). The copolymer was precipitated in n-hexane (99%, Sigma-Aldrich, Taufkirchen, Germany). The proton nuclear magnetic resonance (¹H NMR) measurements were carried out in deuterated chloroform-d1 (CDCl₃, 99.8%, contains 0.03% (v/v) TMS, Sigma-Aldrich, Taufkirchen, Germany, stored at 4 °C). The gas permeation chromatography (GPC) measurements were

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carried out in N,N-dimethylacetamide (DMAc, ≥99.9%, Sigma-Aldrich, Taufkirchen, Germany).

2.1.1. Synthesis of PDMAPAm via Free Radical and RAFT Polymerization

For the synthesis of PDMAPAm via RAFT polymerization, CDTPA (44.4 mg, 0.11 mmol, 1.2 eq.), AIBN (14.93 mg, 0.09 mmol, 1 eq.), and percolated DMAPAm (2700 mg, 17.30 mmol, 200 eq) dissolved in 11.3 mL of 1,4dioxane (20 w% monomer content) were mixed and degassed with N₂ nitrogen on cold water bath (15 °C) for 20 min (for more see the detailed synthesis protocol in Table S1, Supporting Information). Following that, the polymerization was carried out in a 20 mL glass flask in a thermoshaker at 70 °C, 250 rpm, for 3 h. The reaction was stopped by exposing the reaction medium to air in an ice bath (0 °C). ¹H NMR and GPC samples were taken to determine the monomer conversion and molecular weight of the synthesized polymers, respectively. The final product was precipitated in n-hexane, which was followed by the filtration and drying of the product in a vacuum oven (1 mbar) overnight at a reduced pressure of 1 mbar at 35 °C.

The same procedure was applied for thesynthesis of PDMA-PAm via free-radical polymerization, but without CDTPA.

2.1.2. Synthesis of PDMAPAm-b-PMMA via RAFT Polymerization

Subsequently, in a typical synthesis for PDMAPAm-*b*-PMMA diblock copolymer, the dried PDMAPAm (2600 mg, 0.10 mmol, 1 eq.), which was the macro-RAFT/macro-stabilizer, MMA (1000 mg, 10 mmol, 100 eq.), and AIBN (17 mg, 0.10 mmol, 1 eq.) were dissolved in 15 ml of 1,4-dioxane (see in the detailed synthesis protocol in Table S2, Supporting Information). The mixture was degassed with nitrogen in cold water bath (15 °C) for 20 min. Afterward, the polymerization was carried out in a 30 mL glass flask in a thermos-shaker at 70 °C, 250 rpm, for 24 h. The experiment was stopped by exposing the reaction medium to air in an ice bath (0 °C). ¹H NMR and GPC samples were taken to determine the conversion of MMA and molecular weight of the synthesized diblock copolymer, respectively. The polymer was precipitated in n-hexane and dried again in vacuum (1 mbar) oven at 35 °C for 24 h.

2.1.3. Membrane Preparation

The PDMAPAm-*b*-PMMA polymer thin-film composite was prepared through a three-step process as shown in the **Figure 1** below. First, the polymer PDMAPAm-*b*-PMMA was dissolved in tetrahydrofuran (THF) to create a 40% concentrated polymer solution. Next, this solution was cast onto a thin-film composite membrane. The thin-film composite membrane consists of a cross-linked polydimethylsiloxane (PDMS) gutter layer that was cast on a porous polyacrylonitrile (PAN) film applied over a nonwoven substrate. The casting was done using a doctor blade, as depicted in Figure 1. The casting gap was set to 200 µm. In the

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Figure 1. Three steps of preparation of the PDMAPAm-b-PMMA polymer thin-film composite membrane.

final step, the cast film was dried under $\rm N_2$ for 24 h. After drying, a thin-film composite membrane coated with the PDMAPAm-b-PMMA polymer was obtained.

2.2. Characterization

2.2.1. ¹H NMR Spectroscopy

¹H NMR spectroscopy experiments were performed using a Bruker AV500 spectrometer (Bruker, Rheinstetten, Germany) and a Spinsolve Carbon 60 benchtop spectrometer (60 MHz, Magritek GmbH, Aachen, Germany). The spectra with the Bruker AV500 were recorded applying a 10 ms 90° pulse at a sample temperature of 298 K. Sixteen scans were recorded with a relaxation delay of 3 s. In a similar way, the experiments with the Spinsolve Carbon 60 were accomplished using the proton+ protocol with 4 scans, an acquisition time of 6.4 s, a repetition time of 1 min, and pulse angle of 90°. Sample concentrations were 20 g L⁻¹ in CDCl₃, respectively. The ¹H NMR spectra were analyzed with the software MestReNova 10.0 (Mestrelab Research, Santiago de Compostela, Spain). 1,3,6-trioxane was used as an intern standard. DMAPAm conversion from macro-RAFT synthesis was estimated by comparing the integration of double-bond proton areas in the sample before and after the reaction, which was \approx 90%. Using the same method, the conversion of methyl methacrylate in the second block synthesis, also measured in CDCl₃, was calculated from the decrease in the integral of the monomer peaks, which was also $\approx 90\%$ (see Figures S1 and S2, Supporting Information).

2.2.2. GPC measurement

The apparent molecular weight distributions of the PDMA-PAm homopolymers (macro-RAFT agents) and PDMAPAm-*b*-PMMA diblock copolymers were measured in a GPC at 50 °C with DMAc and the addition of lithium chloride (0.1 M) as eluent. A Waters 717 plus instrument (Waters, Milford, MA, USA) equipped with PSS GRAM columns (PSS GmbH, Mainz, Germany) [GRAM pre-column (dimensions 8–50 nm) and two GRAM columns of different porosity (3000 and 1000)] with dimensions of 8 × 300 mm and a particle size of 10 µm was used. The samples were measured at a flow rate of 1 mL min⁻¹ using a VWR-Hitachi 2130 pump (VWR Hitachi, Darmstadt, Germany) and a VWR-Hitachi L2490 RI (refractive index) detector (VWR Hitachi, Darmstadt, Germany). GPC was calibrated with narrow PMMA standards, and data were analyzed using PSS WinGPC UniChrom software (PSS GmbH, Mainz, Germany).

2.2.3. Thermogravimetric Analysis (TGA)

TGA was conducted using a TG 209F1 Iris (NETZSCH Gerätebau GmbH, Selb, Germany) to observe the thermal stability of polymers. A heating rate of 10 K min⁻¹ was used in a temperature interval of 25 °C to 800 °C under argon gas.

2.2.4. Differential Scanning Calorimetry (DSC)

DSC was carried out using a DSC 1 instrument from Mettler-Toledo (located in Gießen, Germany). The temperature range investigated was from -50 to 200 °C, with a heating and cooling rate of 10 K min⁻¹. N₂ was used as the purge gas stream at a 60 mL min⁻¹ flow rate. Each sample underwent two heating-cooling cycles, and the results were interpreted based on the second heating trace.

2.2.5. Scanning Electron Microscopy (SEM)

The scanning electron microscope Merlin (Carl ZEISS, Oberkochen, Germany) was used to investigate the morphology of the diblock copolymer samples and to measure the thickness of each layer of the thin-film composite membrane prepared from the synthesized diblock copolymer PDMAPAm-*b*-PMMA. The measurement took place at an accelerating voltage of 1.5 kV, while the detectors used were a high-efficiency secondary electron (HE-SE2) detector and an in-lens secondary electron detector. For cross-sectional imaging samples were cross-fractured using liquid nitrogen. Prior to examination, all specimens were sputter-coated with 1.5 nm of platinum using a CCU-010 coating device (Safematic, Switzerland).

2.2.6. Time-Lag Measurement

Time-lag and permeability of several gases through the PDMAPAm-*b*-PMMA polymer thin-film composite membrane were measured using a custom-made time-lag instrument (Hereon, Geesthacht, Germany) in order to obtain the gas transport properties of the membrane. The working principle and flowsheet of the device can be found in the literature.^[59]

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Figure 2. Reaction scheme for the synthesis via RAFT solution polymerization of a) PDMAPAm that serves as the macroRAFT agent and b) of poly(methyl methacrylate) (PMMA) using the macroRAFT agent synthesized in the first step for the synthesis of the PDMAPAm-b-PMMA.

3. Results and Discussion

The synthesis of PDMAPAm-*b*-PMMA involves a two-step polymerization of the two monomers. Initially, PDMAPAm was synthesized at 70 °C via RAFT solution polymerization in 1,4dioxane of the DMAPAm. Subsequently, PDMAPAm serves as a macroRAFT agent to synthesize a PDMAPAm-*b*-PMMA diblock copolymer by extending the chain through RAFT solution polymerization. **Figure 2** illustrates the pathway for the synthesis of PDMAPAm-*b*-PMMA.

Molar mass ratio (75:25) of the first block (PDMAPAm) to the second (PMMA) was aimed for the synthesis because the potential diblock copolymer should consist of high content of monomeric units with amine groups to enable stronger CO_2 responsivity,^[14,15] while the PMMA block contributes only to the mechanical stability more straightforward applicability via coating for the fabrication of the thin-film composite CO_2 adsorber membrane.^[60–62]

Altogether, six experiments were conducted to synthesize the PDMAPAm: five via RAFT, and one free via free radical polymerization. Three of the experiments via RAFT polymerization and one via free radical polymerization ran for 24 h, while the other two RAFT polymerization experiments were stopped after just 3 h. In addition, using the synthesized macroRAFT from the earlier stopped polymerization, the diblock copolymer of PDMAPAm-*b*-PMMA was synthesized.

3.1. RAFT and Free Radical Polymerization of DMAPAm

For the synthesis of PDMAPAm, in all experiments, the ratio of AIBN to DMAPAm was maintained at a constant value of 1:200 equivalents, while the equivalent amount of CDTPA was systematically reduced from 3 to 0 to synthesize polymers with varying molecular weights.

3.2. Characterization of Polymers via $^1\mbox{H}$ NMR Spectroscopy and GPC

The PDMAPAm was synthesized using both radical polymerization and RAFT polymerization techniques. The apparent and

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 Table 1. Apparent and theoretical number and weight average molecular

 weight, and dispersity of the synthesized PDMAPAm macroRAFT agents

 after 24 h of polymerization.

Polymerization type	CDTPA (eq.)	₩ _{n,app} [kDa]	M _{w,app} [kDa)]	$M_{n,th}[kDa]$	Ð
RAFT	3	12	18	11	1,5
	1,2	16	27	28	1,6
	0,7	19	37	48	1,9
Free Radical	0	23	89	-	3,8

theoretical molecular weights of the polymer synthesized within 24 h of reaction time can be found in the **Table 1**. By keeping the initiator to monomer ratio the same and varying concentration of the RAFT agent, the weight average molecular weight of the synthesized polymer was altered from 18 to 89 kDa.

Moreover, this is clear from the Table 1 and **Figure 3**, the qualities of macroRAFT, PDMAPAm, obtained from the RAFT and free radical polymerization distinguish significantly from each other. The difference can mainly be seen in weight average apparent molecular weight ($\bar{M}_{w,app}$) and dispersity values (\bar{D}). The dispersity indices of the prepared samples exhibited significant differences: the \bar{D} value for sample PDMAPAm from RAFT polymerization changes between 1,5 and 1,9, whereas for the sample synthesized via free radical polymerization, $\bar{D} = 3,84$, which means that the use of RAFT agent enabled the control of the reaction leading to lower polydispersity in the end. In addition, the dispersity of the polymer synthesized by RAFT polymerization remains within the range of the dispersity values of the amine acrylate polymers synthesized by the same method.^[63–65]

Furthermore, two additional reversible additionfragmentation chain-transfer (RAFT) polymerization experiments were carried out using the specified recipe but with a reduced reaction time of only 3 h. Subsequently, the end group fidelity of the macroRAFT polymer was compared to that obtained from a standard RAFT polymerization conducted over a 24 h period (Figure S3, Supporting Information).

Table 2. Apparent and theoretical number and weight average molecular weight, dispersity of the synthesized PDMAPAm-b-PMMA.

Polymer	Ū _{n,app} [kDa]	Ū _{w,app} [kDa]	Ð
PDMAPAm ₂₂₂	22	35	1,5
PDMAPAm ₂₂₂ -b-PMMA ₇₇	29	43	1,5
PDMAPAm ₁₉₈	19	27	1,4
PDMAPAm ₁₉₈ -b-PMMA ₁₂₀	23	43	1,8

It was determined that the chain end of the purified polymer obtained from RAFT polymerization after 3 h is more ultraviolet(UV)-active at 309 nm than the sample taken at the end of 24 h. This is due to the existence of trithiocarbonate group attached to the polymer chain within the first 3 h of the reaction time^[33,66–68]. This means that the polymer shows better fidelity in the first 3 h of the reaction in comparison to later. Considering this point, two more macroRAFTs were synthesized with the same recipe, but the reactions were stopped at the end of 3 h to increase their chain end fidelity. The conversion of DMAPAm monomer was determined again with ¹H NMR measurement to be \approx 87%, while the apparent number average molecular weight of the PDMAPAm was obtained by GPC, $\bar{M}_{n,app} = 22$ (kDa). Using the macroRAFT, diblock copolymers PDMAPAm-*b*-PMMA were synthesized with 90% conversion of methyl methacrylate.

Table 2 shows the molecular weight and dispersity values of the successfully synthesized PDMAPAm-*b*-PMMA polymer using the PDMAPAm as a macroRAFT. It can be clearly seen that the number average molecular weight ratio of the first block, PDMA-PAm, to the second block, PMMA, is \approx 75:25 and 80:20, meaning the polymer has a high block content with the amine group. As for dispersity, it agrees well with the values existing in other publications regarding the synthesis of diblock copolymers.^[8,36,37]

Figure 4 depicts the molecular weight distribution curve of the macroRAFT, PDMAPAm and diblock copolymer,



Figure 3. MWD of PDMAPAm synthesized via RAFT and Free radical polymerization after 24 h of reaction time. Three different CDTPA:AIBN ratios of 3:1 (---), 1.2:1 (---), 0.7:1 (---) and free radical polymerized (---).



Figure 4. MWD of PDMAPAm with 3 h of reaction time and MWD of PDMAPAm-b-PMMA with 24 h of reaction time synthesized via RAFT polymerization. PDMAPAm₁₉₈ (---), PDMAPAm₁₉₈-b-PMMA₁₂₀ (---), PDMAPAm₂₂₂ (---), and PDMAPAm₂₂₂-b-PMMA₇₇ (---).



Figure 5. DSC results of the synthesized homopolymer (PDMAPAm) and diblock copolymer (PDMAPAm-b-PMMA). PDMAPAm₂₂₂ (---), PDMAPAm₂₂₂-b-PMMA₇₇ (—), PDMAPAm₁₉₈ (---), and PDMAPAm₁₉₈-b-PMMA₁₂₀ (—).

PDMAPAm-*b*-PMMA, synthesized using the macroRAFT. It is clear from that figure that the chain extension of the macroRAFT with the methyl methacrylate shifted the MWDs to the right side, which clearly signs the growth of the second block.^[12,13,37] Apart from this, no second peak appears within the molecular weight distribution curve of the diblock copolymer,^[12,13,37] which can mean that all of the macroRAFT was consumed during the polymerization.

3.3. Thermal Properties of Polymers

Since the developed material is supposed to be used for fabrication of CO₂-reactive film membranes that will be implemented in DAC technology, in which application temperature can be different, the knowledge regarding thermal properties of the material is very crucial.^[69] Therefore, DSC and TGA analyses were performed to determine the thermal behavior of the diblock copolymer.

3.3.1. DSC of PDMAPAm and PDMAPAm-b-PMMA

DSC experiments were conducted to study the thermal properties of PDMAPAm-*b*-PMMA diblock copolymers over a temperature range from -50 to +150 °C. The **Figure 5** illustrates that the heat flow profile of the homopolymer (PDMAPAm) and diblock copolymer with respect to temperature. It can be clearly seen that two glass transition temperatures (T_g) were identified for the diblock copolymer, corresponding to each of the two blocks. Namely, T_g of the PDMAPAm was measured to be 55 °C, while the figure for PMMA is approximately double times higher, ≈ 110 °C, as also reported in literature.^[70] Another consideration is that the T_g of the homopolymer was switched around by 20 °C when the chain was extended with PMMA. Because the PDMAPAm block constitutes a substantial portion of the diblock copolymer, the alteration in heat flow near the



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Figure 6. TGA results of the synthesized the synthesized homopolymer (PDMAPAm) and diblock copolymer (PDMAPAm-*b*-PMMA). PDMAPAm₂₂₂ (---), PDMAPAm₂₂₂-*b*-PMMA₇₇ (---), PDMAPAm₁₉₈ (---) and PDMAPAm₁₉₈-*b*-PMMA₁₂₀ (---).

 $\rm T_g$ of PDMAPAm between 40 and 60 °C is notably greater than that observed for PMMA. The nearly 55 °C difference in the T_gs for the PDMAPAm-*b*-PMMA diblock copolymer suggests a microphase separation between the two blocks, as published previously.^[36,71,72]

3.3.2. Thermogravimetric Analysis (TGA)

TGA was performed for the homopolymer and diblock copolymer; the analysis results can be found in Figure 6 below. The data obtained from TGA shows three for homopolymer and four mass loss clicks for diblock copolymer for the given temperature range. The first mass loss appears at 60 °C for both PDMAPAm and PDMAPAm-*b*-PMMA, which is $\approx 1-2\%$, due to the trapped solvent or humidity. Regardless of extensive drying, the mass loss could not be avoided. This can be related to its hygroscopic properties because PDMAPAm is hydrophilic due to the presence of the methylamino group (-N(CH₃)₂) in its structure.^[73,74] Between 180 and 200 °C, there is 10% weight loss only for the homopolymer but this is not the case for the diblock copolymer, which means that the PMMA block provides thermal stability to the diblock to some extent, as described in recent publications.^[75,76] In the final stage, starting from 225 °C the critical mass loss can be observed, \approx 50–80% for both homopolymer and diblock copolymer, which means both blocks are thermally stable up to this temperature and then, they degrade if they are heated further up.

Another consideration is that within the examined temperature span (up to 500 °C), thermal decomposition of PDMAPAm*b*-PMMA copolymers and PDMAPAm-homopolymer results in a minor amount of leftover weight. In some publications regarding the synthesis of similar CO₂-responsive diblock copolymers such as PDMAEMA-*b*-PMMA, it was mentioned that PMMA homopolymer breaks down completely at that high temperature, while the decomposition of PDMAEMA homopolymer and PDMAEMA-*b*-PMMA copolymer left some remaining masses such as fragile carbon residue or ashes.^[77,78] Additionally, in

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Figure 7. SEM Images of the PDMAPAm-b-PMMA-coated thin-film composite membrane. a,b) Cross/section SEM images with two different magnifications. In 7b, 3. corresponds to PAN porous support, 2. to the cross-linked PDMS thin-film (gutter layer) and 1. to the layer of PDMAPAm-b-PMMA diblock copolymer. c,d) surface SEM images with two different magnifications indicating the amorphous feature of the diblock copolymer coating.

several publications, it was pointed out that the presence of amine groups in copolymers can lead to cross-linking during thermal decomposition. This cross-linking can produce more stable residues that do not volatilize easily, resulting in a higher remaining mass.^[79,80]

3.4. Characterization of Membrane

PDMS gutter layer thin-film membrane (on PAN porous support) was coated with the synthesized PDMAPAm-*b*-PMMA diblock copolymer, and the gas transport properties and surface structure of the PDMAPAm-*b*-PMMA polymer thin-film composite membrane were measured using time-lag instrumentation and SEM, respectively.

3.4.1. SEM Characterization of Membrane

The surface characterization of the prepared thin-film membrane coated with PDMAPAm-*b*-PMMA polymer was performed, and thickness of each layer was measured. **Figure 7** represents both cross-sectional and surface SEM images of the PDMAPAm*b*-PMMA polymer thin-film composite membrane. The crosssection images prove that the membrane has as expected three layers: at the bottom non-woven with a porous PAN layer, then the PDMS gutter layer, and on the top of it PDMAPAm-*b*-PMMA diblock copolymer. From this image, the thickness of the PDMAPAm-*b*-PMMA was determined to be $\approx 5 \,\mu$ m. Another consideration is that the top layer of membrane, consisting of the PDMAPAm-*b*-PMMA diblock copolymer is a non-porous and dense continuous phase. This means that the gas is transported through the membrane at the molecular level via the solutiondiffusion mechanism, in which separation is achieved by differences in the solubility of the gases and the difference in the gas concentrations between the feed and the permeate. As for surface analysis of the polymer layer of the membrane film, at 10 μ m, a predominant direction can be seen in the picture, which illustrates the direction of film casting. When the picture is magnified to 100 nm, some inhomogeneity appears, which can be related to the microphase separation mentioned based on the results of DSC-analysis,^[8] which is however very weak and no conclusions about structure can be drawn.

3.4.2. Gas Transport Properties

Time-lag and permeability of different gases through the thin-film composite membrane with and without coating of PDMAPAm-*b*-PMMA polymer were measured using the timelag machine described in the previous publication to characterize the gas transport properties of the membrane.

In **Figures 8** and **9** the permeabilities of H_2O (saturation vapor at a pressure of 10^{-6} mBar), CO_2 , O_2 , and N_2 gases are presented. Figure 8 corresponds to the data from the thin-film composite membrane without the PDMAPAm-*b*-PMMA diblock copolymer (only the gutter layer, which consists of the PAN porous support and the cross-linked PDMS film), while Figure 9 presents the permeability of the thin-film composite membrane of the PDMAPAm-*b*-PMMA diblock copolymer. **Figure 10** compares the selectivities of the PDMAPAm-*b*-PMMA thin-film composite membrane for the corresponding gases. It can be clearly observed from the Figure 8 that the PDMS gutter layer film membrane without the PDMAPAm-*b*-PMMA-coating shows too high



Figure 8. Permeability of gases from the porous PAN and gutter layer PDMS membrane without the PDMAPAm-b-PMMA coating.

permeability values, in other words, the membrane shows no "resistance" to any of the gases.^[81] Therefore, the contribution of the gutter layer to the measurement of the gas transport properties of the thin-film composite membrane is considered negligible.

In detail, for the diblock copolymer thin-film composite membrane of PDMAPAm-b-PMMA, CO₂ and H₂O gases show larger permeability through the membrane than O2 and N2, making the membrane more selective for H₂O and CO₂ than N₂ and O₂. This means that the membrane has the capability to separate H₂O and CO₂ from the rest two gases. The membrane performance can be compared to other types of amine containing polymers such as membranes based on poly(amidoamine) (PAMAM) that indicate CO_2 permeabilities in the range of 10^2 to 10^3 Barrer with CO_2/N_2 selectivities between 10 and $50^{[82]}$ while also polyamidebased membranes typically exhibit CO₂ permeabilities ≈100 Barrer with CO₂/N₂ selectivities in the range of 10-20.^[83]

Another consideration is that it can be clearly seen from the Figures 9 and 10 that the permeability and selectivity do not show any significant trend with the increasing molecular weight of the polymer. However, this occurs because the diblock copolymer with 40 kDa molecular weight exhibits the highest CO2-selectivity toward the N₂ and CO₂-permeability compared to the other two polymers.

Furthermore, as illustrated in Figure 11, by altering the PDMA-PAm block content of PDMAPAm-b-PMMA of the membrane, in other words, the ratio of the first block to the second block of the copolymer (PDMAPAm-b-PMMA), the selectivity of the PDMAPAm-b-PMMA thin-film composite membrane was customized. This is clear from the figure below that the selectivity of the membrane rises up to five times as the PDMAPAm proportion of the diblock copolymer is increased. This can be explained by the fact that more amine groups, that have affinity for CO₂ and



PERMEABILITY (Barrer)

Figure 9. Permeability of gases through the PDMAPAm-b-PMMA thin-film composite membrane.

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Figure 10. Selectivity of the PDMAPAm-b-PMMA thin-film composite membrane for different gas pairs.

 H_2O ,^[14,84] interact and make the polymer more selective for CO_2 in comparison to other gases.

Moreover, the thickness of the PDMAPAm-*b*-PMMA polymer layer was determined to be 5 μ m according to the SEM measurement. Knowing the time lag and permeability of each gas through the membrane, diffusion coefficients (D) and solubilities (S) of the gases can be calculated as described in literature.^[59]

In **Table 3** the calculated values of diffusion coefficients and solubility of H_2O , CO_2 , O_2 , and N_2 gases for the PDMAPAm-*b*-PMMA polymer film composite membrane are presented. Generally, the PDMAPAm-*b*-PMMA thin-film composite membrane shows diffusion coefficient and solubility values for gases that align with the literature for similar polymers. In detail, the diffusion coefficient of CO_2 , which is $\approx 6,42 \times 10^{-8}$ cm² s⁻¹, is two-fold higher than the ones of the rest gases, whereas the solu-



Figure 11. Effect of polymer (PDMAPAm-*b*-PMMA) content on the thinfilm composite membrane selectivity.

bility of CO₂ exhibits a lower value compared to the rest gases. Hyperbranched polymer membranes such as poly(amidoamine) (PAMAM)^[82] and also polyamide membranes containing PDMS groups^[85] show CO₂ diffusion coefficients in the range of 10^{-8} cm² s⁻¹ and solubility values $\approx 10^{-1}$ cm³ (STP)/(cm³ cmHg)), which agree well with the results in this study. Apart from that, water solubility appears to be the highest among all gases and according to the literature, high solubility values for water are common in hydrophilic polymers due to affinity for water.^[86] Also, diffusion coefficient value of H₂O was determined to be 5.74×10^{-8} cm² s⁻¹, which is similar to that of CO₂ and this value aligns well with the values in other publications, because typical diffusion coefficients for water vapor in hydrophilic polymers such as Nafion are reported to be in the range of 10^{-7} to $10^{-6} \text{ cm}^2 \text{ s}^{-1}$.^[87] As for the other two gases, the diffusion coefficients of O₂ and N₂ through the fabricated thin-film membrane follow the literature values for standard polymer membranes, being in the range from 10^{-8} to $10^{-7[88]}$ and 10^{-9} to 10^{-8} cm² s⁻¹,^[89] respectively.

From above mentioned, the fabricated PDMAPAm-*b*-PMMA copolymer thin-film composite membrane exhibits comparable gas transport properties compared to other polymer membranes. This indicates that PDMAPAm-*b*-PMMA copolymer could be a promising material for membrane applications which, however,

Table 3. Diffusion coefficients and solubilities of the $\rm H_2O,\,CO_2,\,O_2,$ and $\rm N_2$ gases through the PDMAPAm-b-PMMA polymer film composite membrane.

D [cm ² s ⁻¹]	S [cm ³ (STP)/(cm ³ cmHg)]
$5,74 \times 10^{-8}$	$1,17 \times 10^{2}$
$6,42 imes 10^{-8}$	$1,91 \times 10^{-1}$
$2,64 \times 10^{-8}$	$2,49 \times 10^{-1}$
$1,73 \times 10^{-8}$	1,00
	D $[cm^2 s^{-1}]$ 5,74 × 10 ⁻⁸ 6,42 × 10 ⁻⁸ 2,64 × 10 ⁻⁸ 1,73 × 10 ⁻⁸

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needs to be further advanced with improvement of the polymer synthesis and the membrane fabrication.

4. Conclusion

In this work a new CO_2 -reactive material, PDMAPAm-*b*-PMMA diblock copolymer was developed by two-step RAFT solution polymerization. In the first step, PDMAPAm was synthesized via RAFT solution polymerization, and in the second step, it was used as a macroRAFT to synthesize PDMAPAm-*b*-PMMA diblock copolymer again via RAFT solution polymerization. It was found that the conversion of DMAPAm reaches a high level already after 3 h of the reaction time and the chain end activity of the macroRAFT is one of the most critical points, which allows the extension of the polymer chain further using the second monomer, methyl methacrylate, that made polymer mechanically more stable.

Based on the DSC data, it was observed that the PDMAPAm*b*-PMMA diblock copolymers exhibit glass transitions from both microphases arising from the incompatibility between the covalently bonded PDMAPAm and PMMA blocks. Apart from that, the thermal stability of the homopolymer was determined to be 225 °C, and it was found that the addition of the PMMA block improved the thermal stability of the polymer.

Finally, the gas transport properties of the thin composite film membrane made of the PDMAPAm-*b*-PMMA polymer and PDMS with gutter layer were examined. According to the time-lag measurement of the gases, the membrane is more selective for CO₂ and H₂O than O₂ and N₂, which means the membrane can separate CO₂ and H₂O from the rest of the gases. Additionally, diffusion coefficient of the CO₂ through the membrane was calculated to be 2–3 times higher than the other three gases, $\approx 6.4 \times 10^{-8}$ cm² s⁻¹.

In the future, the material's properties can be customized by further simulating the polymerization process and kinetics of the system, which will enable the optimization of the properties of the polymer in the end and to scale the synthesis process up to a pilot scale. However, this can be a work that will be done as a next step to produce the CO_2 -responsive material in a large amount to implement in direct air capture (DAC) technology.

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.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

Block Copolymers, CO2, Direct Air Capture, Membranes, RAFT

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