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Article

Fabrication of CO_2 Facilitated Transport Channels in Block Copolymer through Supramolecular Assembly

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Abstract: In this paper, the molecule 12-amidine dodecanoic acid (M) with ending groups of carboxyl and amidine groups respectively was designed and synthesized as CO_2-responsive guest molecules. The block copolymer polystyrene-*b*-polyethylene oxide (PS-*b*-PEO) was chosen as the host polymer to fabricate a composite membrane through H-bonding assembly with guest molecule M. We attempted to tune the phase separation structure of the annealed film by varying the amount of M added, and investigated the nanostructures via transmission electron microscope (TEM), fourier transform infrared (FT-IR) *etc.* As a result, a reverse worm-like morphology in TEM image of bright PS phase in dark PEO/M matrix was observed for PS-*b*-PEO/M1 membrane in which the molar ratio of EO unit to M was 1:1. The following gas permeation measurement indicated that the gas flux of the annealed membranes dramatically increased due to the forming of ordered phase separation structure. As we expected, the obtained composite membrane PS-*b*-PEO/M1 with EO:M mole ratio of 1:1 presented an evident selectivity for moist CO_2 permeance, which is identical with our initial proposal that the guest molecule M in the membranes will play the key role for CO_2 facilitated transportation since the amidine groups of M could react reversibly with CO_2 molecules in membranes. This work provides a supramolecular approach to fabricating CO_2 facilitated transport membranes.

Keywords: block copolymer; supramolecular self-assembly; carbon dioxide; amidine; hydrogen-bond; facilitated transport membrane

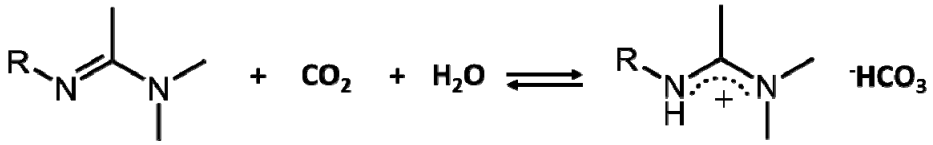
1. Introduction

Separation and utilization of carbon dioxide (CO_2) has been a traditional research topic in recent decades and attracted continual attention of material chemists [1]. Two of the main CO_2 separation methods are adsorption and membrane separation [2]. Membrane separation was considered one of the most promising high technology due to its high separation efficiency, energy saving and economic advantages. CO_2 separation membranes are usually classified into inorganic membranes, polymeric membranes and facilitated transport membranes [3]. Among them, facilitated transport membranes have been found more efficiency for gas separation and became more attractive in membrane scientific field [4]. A carrier of gas molecules in the facilitated transport membranes plays the essential role to accelerate gas molecule permeation over the membrane. To conduct the job, the carriers generally take place reversible chemical reaction with the characteristics gas molecules such as CO_2 in the mixed gas. As a result, CO_2 molecules have been transported from the side of high potential energy to the side of low potential energy in membranes [5–7].

It is well known that self-assembly of block copolymers exhibits varied phase nanostructures which provides excellent template for functional membranes. By adjusting the volume fraction of each block of copolymer and changing the strength of segmental interaction between the units, well-defined nanostructures can be tuned and obtained on purpose, such as from spheres to cylinders, from spheres to lamella morphology and so on [8–12]. Usually, guest functional groups are attached onto the main chain or side chain during either pre-polymerization or post-polymerization process. Supramolecularly assembling the guest functional molecules onto the specific block units through non-covalent bond such as hydrogen bond, has succeeded in increasing of the volume fraction of the certain as-assembled block in the whole system which is leading to the transition of the phase morphology in membranes. Based on this supramolecular assembly technique, numbers of interesting works have recently been reported to prepare composite materials containing block copolymer and functional guest molecules for various applications such as electric-optical material, magnetic quantum array, gas permeation membranes and so on [13–18].

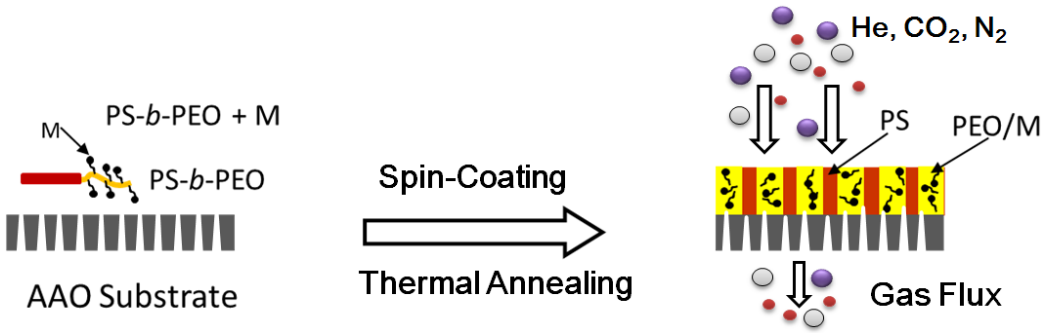
In this article, fabricating a CO_2-favored permeable composite membrane with inside oriented nanostructure inside via supramolecular assembly was proposed. As we know, amidine groups have reversible reaction with CO_2 in the presence of water forming the intermediate compound carbonate [19–23]. The intermediate compound can be delivered from the high potential energy side to the low potential energy side. Then the intermediate compound releases amidine molecules and CO_2 at the low potential energy side to finish the CO_2 transportation job. The reaction mechanism was shown in Scheme 1.

Scheme 1. Mechanism scheme of the facilitated transportation of CO_2 in PS-*b*-PEO/M film [1].



As shown in Scheme 2, the membrane was fabricated by spin-coating the polystyrene-*b*-polyethylene oxide (PS-*b*-PEO)/M solution in chloroform on porous anodic aluminum oxide (AAO) substrates. The morphology inside the annealed films was investigated by transmission electron microscopy (TEM). After controlling the amount of hydrogen assembled M, well-defined CO_2 permeable PEO/M channels were expected to be achieved after thermal annealing process.

Scheme 2. Schematic of fabrication of PS-*b*-PEO/M membrane and an ideal model proposed for the nanostructured membrane.



2. Experimental Section

2.1. Materials

PS-*b*-PEO (M_{PS} = 23 kg/mol, M_{PEO} = 7 kg/mol, PDI = 1.07) was purchased from Polymer Source Inc. (Dorval, QC, Canada). Here, the block copolymers we used in our work were selected based on the pre-design of our project. We proposed that the addition of the guest molecules/additive will lead to the morphological transformation of the diblock copolymer. Therefore, we started with PS-*b*-PEO (M_{PS} = 23 kg/mol, M_{PEO} = 7 kg/mol, PDI = 1.07) which has low volume fraction of PEO around 0.23 and is also commercial available. For example, we know the molecular weight of the small molecule M, so we can calculate the molar number of M we need add to assemble with EO units, in order to obtain different volume fraction ratios of EO/M to PS after hydrogen bonding assembly happened. Chloromethane was purchased from Beijing Chemical Reagents Co., Beijing, China. Anodic Aluminum Oxide (AAO) was purchased from Whatman International Ltd., Maidstone, UK. Silicon wafers were purchased from Beijing Zhongjingkeyi Technology Co. Ltd., Beijing, China. Molecule M was synthesized according to the former works [24–26]. The silicon substrates were first cleaned successively in chloroform and acetone respectively by 10-min ultrasonication before managed in piranha bath (70% H_2SO_4 and 30% H_2O_2) for 120 min at 77 °C, then rinsed by deionized water and dried under nitrogen gas.

2.2. Preparation of Membranes

Since chloroform is good solvent for both PS-*b*-PEO and M, we used it as solvent to make two chloroform solutions with 2 wt % of PS-*b*-PEO and 2 wt % of M, respectively. Then the two solutions were blended together to get a uniform mixed solution, in which the mole ratio of M to ethylene oxide (EO) units of PS-*b*-PEO was controlled. After stirred for several hours, the solution was kept for at least 12 h to complete hydrogen bonding formation. The solution was spin-coated on AAO substrate and silicon substrates at 500 rpm for 3 s and then at 1000 rpm for 30 s. The membranes were then thermally annealed in vacuum for hours.

2.3. Characterization

The hydrogen bonding between guest molecule M and EO units of block copolymer were assessed by Fourier transform infrared spectroscopy (FT-IR, Thermo Scientific, Waltham, MA, USA). The FT-IR spectra for solid composite samples were recorded in transmission model. Thermal behaviors of complexes were investigated using a differential thermal analysis (DTA). The samples were heated from 25 to 160 °C at the scan rate of 10 °C min^{-1}. The membrane thickness was measured on silicon substrates by a SENpro ellipsometer (SENTECH Instruments GmbH, Berlin, Germany) with visible spectrum at 70° angle of incidence. In order to analyze the phase-separated structure of the membranes, transmission electron microscope (TEM) measurements were carried out on JEOL-2100F electron microscope (JEOL Ltd., Tokyo, Japan) operated at 200 kV. The PS-*b*-PEO and PS-*b*-PEO/M solutions were respectively dipped onto carbon layer of copper mesh TEM grids which has supported carbon film, followed by thermal annealing in vacuum for hours. The TEM samples were obtained after staining the membrane in ruthenium tetraoxide (RuO_4) vapor for 15 min at room temperature.

2.4. Gas Permeation Measurement

The gas permeation measurement was based on our previous works and carried out with a home-built instrument [27–29]. The pure gases, He, N_2 and CO_2, which have different kinetic diameters, were studied in this work. A membrane spin-coated on AAO substrate was placed in the permeation cell with a support screen. The surface area of the tested membrane available for gas transport was 2.84 cm^2. The membrane was placed in the cell of the test system to conduct the gas permeation test. The gases, after passing through the membrane in the cell, was directed into a glass U-tube flow meter (A_{col} = 0.03 cm^2) to give the volumetric flow rate of the gas. It was measured by recording the time (t) that was required for a liquid column to travel a distance (X_{col} = 10 cm). All the measurements were taken at ambient temperature, and the values were obtained at steady-state (usually last for at least 2 h). The values were obtained from 6 independent measurements, and the mean value and standard deviations were determined. The error in each case was <5%. This procedure was repeated for the next tested gas. In general, the permeation properties were first measured for He, then for N_2, and finally for CO_2. The permeance, p (10^6 $cm^3 \cdot cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$), was calculated by Equation (1):

$$P = \frac{X_{col} \cdot A_{col}}{t \cdot \frac{76p}{14.7} A_{mem}} \times 10^6 \quad (1)$$

And the selectivity (α) of gas A, over gas B, was defined as Equation (2):

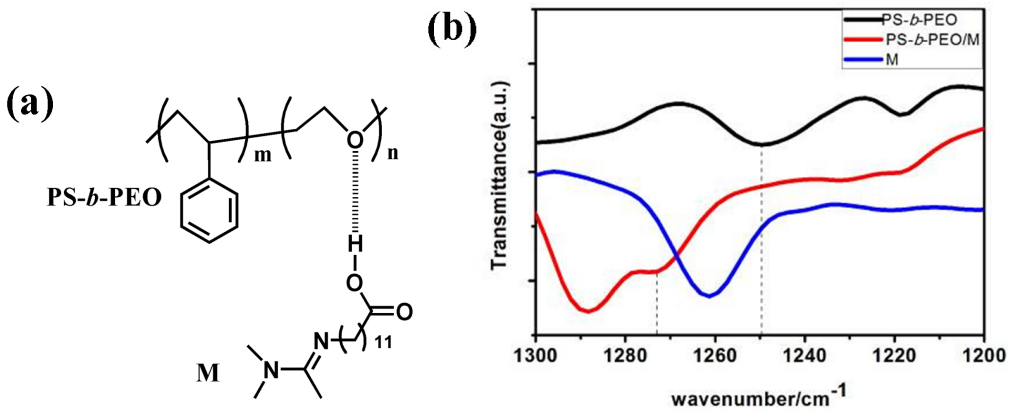
$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (2)$$

3. Results and Discussion

3.1. Structure and Morphology of Membranes

A series of membranes based on the supramolecular assembly of PS-*b*-PEO with guest molecule M were fabricated in this work. The supramolecular interaction between the EO units and the carboxylic acid group of molecule M was investigated using FT-IR spectrum. It has been known that the formation of hydrogen bond between the ethylene oxide and carboxylic acid group will shift the carbon-oxygen stretching band of the EO block [30,31]. As shown in Figure 1, the 1249 cm^{-1} (carbon-oxygen stretching) band of neat PS-*b*-PEO shifted to higher wavenumber of 1271 cm^{-1} of PS-*b*-PEO/M when hydrogen bond formed, which is in agreement with previous studies. The shift is attributed to the changes in the electronic distribution of ethylene oxide unit caused by H-bonding between EO and COOH.

Figure 1. (**a**) The chemical molecular structure of the PS-*b*-PEO and guest molecule M; and (**b**) FT-IR spectra of PS-*b*-PEO, M and PS-*b*-PEO/M membrane.



The phase separation of the block copolymer PS-*b*-PEO was facilitated by thermal annealing for 10 h at 90 °C which is above PEO blocks melting temperature (T_m) of around 60 °C based on differential thermal analysis (DTA) measurement (Figure 2) [32].The thermal annealing process allows the block copolymer film to have sufficient mobility to form oriented structure. To find optimized the thermal annealing condition, we attempted to anneal the polymeric membranes at different conditions and checked the film morphology by TEM (Figure 3). It should be noted that the nature of the substrate surface is seriously important for the microphase separation of the block copolymer [33]. In our work, we use copper grids with a supporting layer of carbon on the surface as the substrates. The PS-*b*-PEO and PS-*b*-PEO/M solutions were respectively dipped onto carbon layers of copper mesh. Restricted by the experimental condition, we study the morphology transformation of the block copolymer on carbon layer of TEM grids instead of AAO substrates [27]. It was indicated from

Figure 3d that the micro-phase separation of the membrane was completed after 10-h annealing process at 90 °C, worm-like domains of dark PEO dispersed in the bright PS matrix.

Figure 2. DTA curves of sample PS-*b*-PEO, PS-*b*-PEO/M0.5 and PS-*b*-PEO/M1 at a heating rate of 10 °C/min.

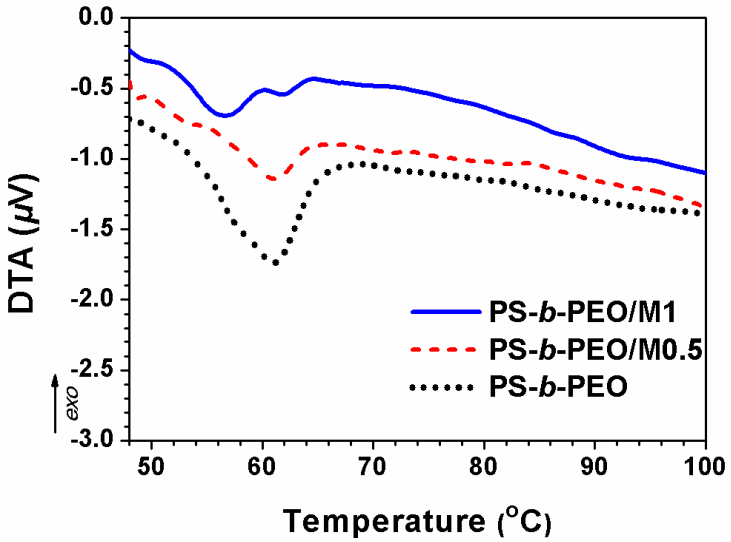
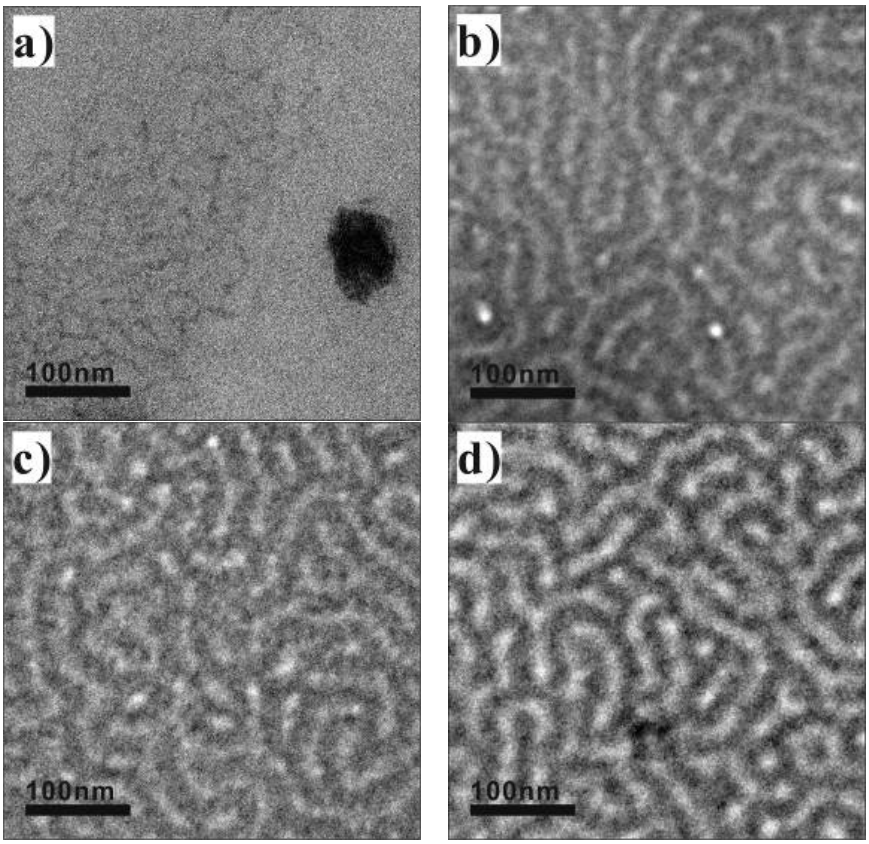
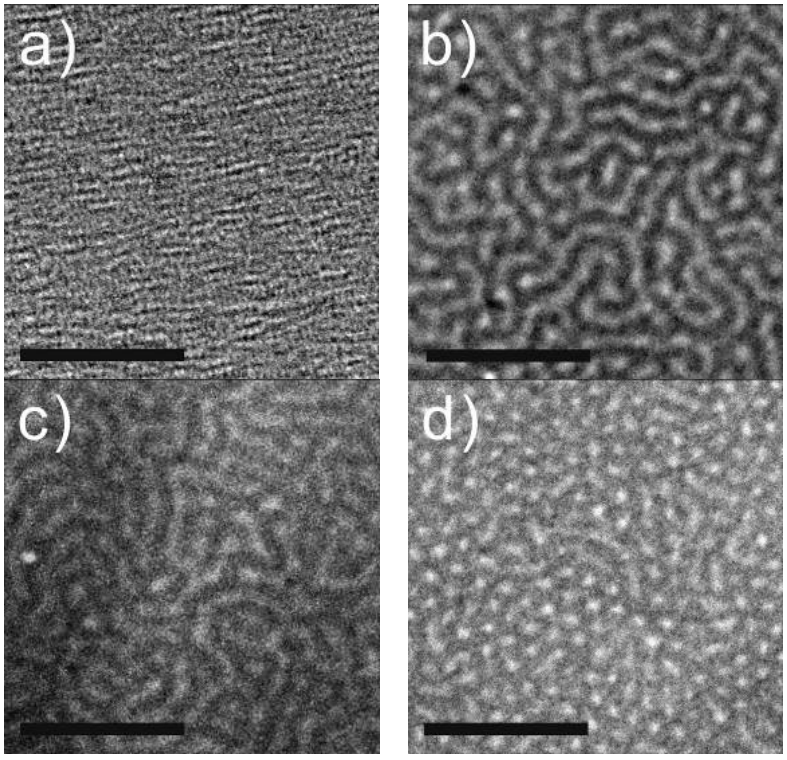


Figure 3. TEM images of PS-*b*-PEO membrane annealed at different condition. (**a**) 90 °C, 3 h; (**b**) 90 °C, 6 h; (**c**) 90 °C, 8 h; and (**d**) 90 °C, 10 h.



To have the insight of the transition of the phase structure in the membrane before and after hydrogen bonded with guest molecules, we compared and investigated the TEM morphologies of the neat block copolymer membrane PS-*b*-PEO, hydrogen assembled composite membrane PS-*b*-PEO/M0.5 which has 2:1 molar ratio of EO to M, and membrane PS-*b*-PEO/M1 with 1:1 molar ratio, respectively (Figure 4).

Figure 4. The bright-field TEM images of the membranes. (**a**) PS-*b*-PEO (unannealed); (**b**) PS-*b*-PEO (annealed); (**c**) PS-*b*-PEO/M0.5 (annealed); and (**d**) PS-*b*-PEO/M1 (annealed) (scale bar: 200 nm).



We started with a worm-like forming PS-*b*-PEO with PEO volume fraction of approximately 0.23 [32]. The as spun-cast PS-*b*-PEO membrane without annealing shows a disordered structure (Figure 4a). A worm-like morphology of dark PEO phase in bright PS matrix was formed after the thermal annealing process (Figure 4b). Due to the high interface energy between PS-*b*-PEO and the substrate, the revealed worm-like PEO phase was not perpendicular to the base plane. The supramolecular interaction of M with EO block through H-bond resulted in the volume fraction of PEO/M in PS-*b*-PEO/M reaching to 0.56, which brought a transitional morphology of bright PS domains in the larger area of dark PEO/M phase after thermal annealing (Figure 4c). Furthermore, when increased the amount of molecule M added until the EO:M mole ratio became 1:1, accordingly the volume fraction of the PEO/M in PS-*b*-PEO/M became approximately 0.69, a reverse worm-like morphology of bright PS phase in dark PEO/M matrix was observed after thermal annealing (Figure 4d).

3.2. Gas Permeability of Membranes

The following gas permeation measurements under dry and humid conditions revealed the correlations between gas permeability and varied micro-phase structures of polymeric membranes. The

results of gas permeation property were calculated using the Equation (1) and presented in Table 1. The membrane thickness was also determined by ellipsometry. For the untreated PS-*b*-PEO membrane with disordered structure, the gas permeance for dry He, N_2, CO_2 was respectively 140.31, 71.42 and 79.76 (10^6 $cm^3 \cdot cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$), and the permeation selectivity of He over N_2 was 1.96. As shown in Table 1, the permeability of untreated PS-*b*-PEO membrane did not change when using humid gases for measurement, which intimates that the membrane structure will hardly be affected by moisture. The similar result was also obtained for annealed PS-*b*-PEO membrane. It implies that the gas permeance over the neat PS-*b*-PEO membrane is still based on the molecular size difference of gases either in dry or humid conditions.

It is consistent with our previous reports that the gas permeance over annealed membrane which has ordered phase structure will increase dramatically due to the formation of larger and more continuously interface layers between the different domains as compared to the disordered phase structure [26].

It has been known that the gas permeation through the membrane obeys Knudson diffusivity which is determined by two main mechanisms, solubility selectivity (S) and diffusivity selectivity (D) [29]. The solubility selectivity is related to the favorable interactions of the membrane with CO_2, so the membrane containing M was expected to improve the CO_2 solubility selectivity due to the interaction between M and CO_2 with the presence of water. As shown in Table 1, for the composite membrane PS-*b*-PEO/M0.5, it has been found that the selectivity of CO_2 over N_2 was increased to 1.21 from 1.15, which can be attributed to the reversible reaction between functional molecule M and CO_2 under humid condition. The consistent but more improvement of $\alpha_{CO2/N2}$ was exhibited by PS-*b*-PEO/M1 membrane which has 1:1 molar ratio of EO to M. Under humid condition, $\alpha_{CO2/N2}$ of the annealed PS-*b*-PEO/M1 membrane was found improved to 1.46, which presented an evident selectivity for CO_2 permeance and meanwhile demonstrated that the guest molecule M plays the key role for CO_2 facilitated transportation in the membrane. In our case, since we focus on the roles of the guest molecule M supramolecularly assembled with block copolymer PS-*b*-PEO for the morphology transformation and for CO_2 gas permeation as well, it is difficult to compare the absolute values of selectivity in our work with others due to different experimental methods used. Comparing with properties of PS-*b*-PEO without M in Table 1, we can certainly draw a conclusion that complex membranes containing M showed improvement of CO_2 selectivity. To the best of our knowledge, the means of supramolecular assembly to fabrication of CO_2 facilitated transport channels in this work is innovative. We believe that this work provides a facile approach to fabricating CO_2 facilitated transport membranes and is going to make contribution to fabrication of gas permeation membranes. Further investigation is ongoing.

Table 1. Gas permeation of the membrane [a].

Membrane	Thickness(nm)	Condition	He	N_2	CO_2	$\alpha_{CO2/N2}$
PS-*b*-PEO (dry)	455	unannealed	140.31	71.42	79.76	1.12
PS-*b*-PEO (humid)		unannealed	139.62	69.05	80.00	1.15
PS-*b*-PEO (dry)	520	annealed	241.76	170.97	195.46	1.14
PS-*b*-PEO (humid)		annealed	242.85	164.61	188.49	1.15
PS-*b*-PEO/M0.5 (dry)	387	unannealed	169.49	80.68	87.21	1.08
PS-*b*-PEO/M0.5 (humid)		unannealed	163.41	82.64	87.09	1.05

Table 1. *Cont.*

Membrane	Thickness(nm)	Condition	He	N_2	CO_2	$\alpha_{CO2/N2}$
PS-*b*-PEO/M0.5 (dry)	350	annealed	366.04	242.99	278.33	1.15
PS-*b*-PEO/M0.5 (humid)		annealed	372.4	240.94	290.4	1.21
PS-*b*-PEO/M1 (dry)	358	unannealed	152.59	85.37	101.05	1.18
PS-*b*-PEO/M1 (humid)		unannealed	149.92	85.10	110.84	1.30
PS-*b*-PEO/M1 (dry)	373	annealed	231.07	149.30	201.71	1.35
PS-*b*-PEO/M1 (humid)		annealed	236.29	146.54	214.64	1.46

[a] PS-*b*-PEO/M0.5, the mole ratio between EO and M was 2:1. PS-*b*-PEO/M1, the mole ratio between EO and M was 1:1. Permeances at ambient temperature, 1×10^6 ($cm^3/(cm^2 \cdot s \cdot cmHg)$), were calculated by dividing the observed flow rate by the area of the membrane (2.84 cm^2) and the pressure gradient (10 psi) employed, using porous AAO substrate as supports. Values were obtained 6 independent measurements. The error in each case was <5%. All these measurements were made at ambient temperatures (20 °C).

4. Conclusions

We designed and synthesized the functional guest molecule 12-amidine dodecanoic acid (M) that has unique response to CO_2. A composite membrane PS-*b*-PEO/M was fabricated through H-bonding assembly of EO block with guest molecule M. Phase separation structure of the annealed film was tuned by varying the amount of M added. When the molar ratio of EO and M was 1:1, a reverse worm-like morphology of bright PS phase in dark PEO/M matrix was obtained by means of TEM measurement. Gas permeation measurement indicated that the gas flux of the annealed membranes dramatically increased due to the development of ordered phase separation structure after thermal annealing treatment. As we expected, the obtained composite membrane PS-*b*-PEO/M1 with EO:M mole ratio of 1:1 presented an evident selectivity for moist CO_2 permeance, which is believed ascribed to the existence of the guest molecule M who reacts reversibly with CO_2 molecules in membranes and is playing the key role for CO_2 facilitated transportation.

Acknowledgments

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Author Contributions

Y.S., X.L. and T.T. performed the experiments, analyzed the data and proposed the mechanism. Y.W. and X.L. wrote the text. L.G provided very helpful discussion. Y.W. and L.J. conceived the project and designed the experiments.

Conflicts of Interest

The authors declare no conflict of interest.

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