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Probe Into the Influence of Crosslinking on CO₂ Permeation of Membranes

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Crosslinking is an effective way to fabricate high-selective CO₂ separation membranes because of its unique crosslinking framework. Thus, it is essentially significant to study the influence of crosslinking degree on the permeation selectivities of CO₂. Herein, we report a successful and facile synthesis of a series of polyethylene oxide (PEO)-based diblock copolymers (BCP) incorporated with an unique UV-crosslinkable chalcone unit using Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT) process. The membranes of as-prepared BCPs show superior carbon dioxide (CO₂) separation properties as compared to nitrogen (N₂) after UV-crosslinking. Importantly, the influence of different proportions of crosslinked chalcone on CO₂ selectivities was systematically investigated, which revealed that CO₂ selectivities increased obviously with the enhancement of chalcone fractions within a certain limit. Further, the CO₂ selectivities of block copolymer with the best block proportion was studied by varying the crosslinking time which confirmed that the high crosslinking degree exhibited a better CO₂/N₂ ($\alpha_{\text{CO}_2/\text{N}_2}$) selectivities. A possible mechanism model revealing that the crosslinking degree played a key role in the gas separation process was also proposed.

The deteriorating environment caused by the global warming has become an immediate threat nowadays. Even though the excessive release of CO₂ is considered as a real threat for the global warming it is also regarded as a new energy resource which is attracting much attention nowadays. The conventional techniques for capturing CO₂ include “wet scrubbing” using alkaline solutions and membrane separation. However, “wet scrubbing” and traditional membrane separation process possess some drawbacks which include high cost, erosion of equipment and irreversible process^{1–4}. Recently, fabrication of CO₂-responsive materials is regarded as a new approach to solve such drawbacks^{2–6}. Meanwhile, invention of novel membrane separation technology has always attracted great interests in CO₂ capture from economic and environmental points of view due to its various advantages such as low energy cost, high-efficiency, high-stability, ease of fabrication^{7–15}. Literature reveals, according to the theory of gas separation, that there are several kinds of membranes including inorganic membranes¹⁶, polymeric membranes^{17–25} and facilitated membranes^{26–28} which are used for CO₂ capture²⁹.

It was observed that the polymers containing EO (ethylene oxide) units were widely used in the separation of CO₂ from other gases^{30–36}. It was found that EO units showed strong interactions with CO₂ compared with other gases such as N₂, CH₄, H₂, especially with the temperature increased, EO units became more favored to CO₂, which resulted in high CO₂ permeabilities and selectivities over other gases³⁷. A high content of EO segments was supposed to lead high CO₂ permeabilities according to the reported principles³⁸, however, it was explored that the PEO chains with high molecule weight was easy to crystallize, resulting in the decrease of the chain mobility, and hence exhibiting a reduction in the CO₂ permeabilities and selectivities. Therefore, in order to avoid such crystallization, several methods were proposed, such as mixing the liquid PEO with rigid polymers³⁹, doping PPO⁴⁰, building a network by crosslinking PEO^{37,41–47} and so on. The influence of crosslinking on gas permeation has always been the issues researchers concerned about. Lin *et al.* have studied the effect of crosslinking on gas permeabilities in crosslinked Poly(Ethylene Glycol) Diacrylate, notably, they found that crosslinking had negligible effect on the gas separation properties of Poly(Ethylene Glycol) Diacrylate³⁹. However, Our previous

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Figure 1. Photochemical Reaction of the chalcone under UV irradiation forming “Head to Head” and “Head to Tail” structures⁴⁹.

Figure 2. Photoreactions of the block copolymers with irradiation at 365 nm.

work reported that a kind of CO₂-selective membrane consisting of EO segments and commercially available UV-crosslinker coumarin achieved high CO₂ selectivities compared with N₂ and He after UV-crosslinking, which suggested that the impact of crosslinking on gas permeation properties existed⁴⁸. Based on this, it is our motivation in this work to have an insight on the role of crosslinking degree during the gas separation process of PEO-based membranes.

Chalcone was chosen by Iyoda and his coworkers as an UV-crosslinker to better control the crosslinking degree in their previous work^{49,50}. It was because that the chalcone could be crosslinked like “head to head” and “head to tail” and hence forming a higher crosslinking degree of membrane structure as shown in Fig. 1. Therefore, in this work, in order to better understand the correlation of crosslinking degree and CO₂ permeation properties, chalcone was selected as a unique crosslinkable segment instead of coumarin. In detail, chalcone was designed as a UV-crosslinker to study the regulation of gas permeation and crosslinking degree. For this, firstly, the chalcone segments and EO units were synthesized. Further, a series of block copolymers consisting of PEO (poly(ethylene oxide)) and PMA (poly(methacrylate) with chalcone mesogens) with different block ratios (PEO₁₁-*b*-PMA(rChal)₇, PEO₁₁-*b*-PMA(rChal)₉, PEO₁₁-*b*-PMA(rChal)₁₂, PEO₁₁-*b*-PMA(rChal)₁₆) were fabricated using Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT) method. The prepared copolymers were further investigated to examine the changes of gas permeabilities and selectivities of the membranes before and after UV crosslinking, respectively. Moreover, the variations of gas permeabilities and selectivities by changing the fraction of the crosslinkable block and crosslinking time were discussed. Based on the obtained results, a plausible mechanism between crosslinking degree and CO₂ permeation properties was also demonstrated.

Results and Discussion

Characterizations of crosslinking degree. The effect of UV-crosslinking time on the prepared membranes was examined by UV-vis absorption spectroscopy. Figure 2 exhibited the typical UV-Vis spectra of the prepared membrane UV-crosslinking for various time intervals. The UV-Vis spectral trend was monitored at

Temp (°C)	Condition	N ₂ Permeabilities (barrer)	CO ₂ Permeabilities (barrer)	$\alpha_{(CO_2/N_2)}$
30	Un-crosslinked	84.40	138.01	1.63
	Crosslinked	38.71	113.18	2.92
40	Un-crosslinked	85.16	178.91	2.10
	Crosslinked	31.79	155.30	4.89
50	Un-crosslinked	88.01	229.14	2.61
	Crosslinked	20.97	217.29	10.36
60	Un-crosslinked	90.67	250.46	2.76
	Crosslinked	19.89	249.87	12.56

Table 1. Pure Gas Permeabilities and Selectivities of PEO-*b*-PMA (rChal) (11:7) Un-crosslinked Compared with Crosslinked Membrane. Permeances at 1×10^6 (cm·s⁻¹·cmHg⁻¹), were calculated by dividing the observed flow rate by the area of the membrane (2.84 cm²) and the pressure gradient (10 psi) employed, using porous Al₂O₃ membrane supports. The values were obtained from 10 independent measurements and the mean value and standard deviations were determined. The error in each case was <5%. The membrane PEO-*b*-PMA (rChal) showed no difference of gas permeation in humid environment.

Figure 3. Graphical explanation of PEO-*b*-PMA(rChal) diblock copolymer thin film and CO₂ separation from N₂ gases (CO₂/N₂).

special chalcone absorption band appearing in the range of 300 to 450 nm. The observed UV-vis absorption spectroscopy revealed that the π - π^* transition of the chalcone unit had a decrease from the 340 nm absorption band. The observed photoreaction could be explained according to the dimerization of the chalcone moieties through the [2 + 2] cyclization of the double bond⁵¹. Interestingly, it was observed that with increasing the UV-crosslinking time, the change of absorption spectra tended to balance, which illustrated that the greatest degree of crosslinking reached at 40 min.

Comparison of CO₂ permeation properties of the membranes before and after crosslinking. Table 1 showed the gases permeation and CO₂/N₂ selectivities of the un-crosslinked film compared with crosslinked film with PEO₁₁-*b*-PMA(rChal)₇ at different temperature. The α_{CO_2/N_2} data for other films are demonstrated in Tables S1 and S2. As shown in Table 1, the α_{CO_2/N_2} of these two membranes were increasing with rising the temperature. Interestingly, α_{CO_2/N_2} of un-crosslinked membrane was 2.76 at 60 °C which was much smaller than α_{CO_2/N_2} of crosslinked membrane equal to 12.56. (Figure S1) The selectivities was mainly related to solubility selectivities and diffusivity selectivities which mainly depended on the interactions of EO unit with CO₂ and the free volume of EO, respectively. To explain this phenomenon, a probable mechanism model was proposed to interpret the increase of α_{CO_2/N_2} (Fig. 3). For un-crosslinked membrane, the EO units and the chalcone units had a large excess free volume and increased the mobility of the chain with the temperature rising, which led to higher gas permeabilities. Notably, differed from N₂, the CO₂ had a strong interaction with EO units, causing the PEO chains more flexible, which also contributed to the final α_{CO_2/N_2} . Referred to crosslinked membrane, for the diffusivity selectivities, crosslinking structure limited the free volume and hence the EO units were confined in the hard regions of crosslinked chalcone walls. With increasing the temperature, the crosslinked hard regions were hardly moved but EO units were more flexible in the limited domain. However, for N₂, the flexible EO units would lead to denser barriers in a limited area⁴⁸, and then the less N₂ molecules went through the free volume which produced a low gas permeabilities for N₂. For CO₂, the interactions between EO units and CO₂ increased with rising

Temp. (°C)	Block ratio (PEO:PMA)	N ₂ Permeabilities (barrer)	CO ₂ Permeabilities (barrer)	$\alpha_{(CO_2/N_2)}$
30	11:7	38.71	113.18	2.92
	11:9	32.43	108.65	3.35
	11:12	29.05	100.53	3.46
	11:16	26.13	72.62	2.78
40	11:7	31.79	155.30	4.89
	11:9	28.42	142.34	5.01
	11:12	21.40	123.35	5.76
	11:16	19.23	89.43	4.65
50	11:7	20.97	217.29	10.36
	11:9	17.01	216.41	12.72
	11:12	12.64	164.82	13.04
	11:16	11.15	106.71	9.57
60	11:7	19.89	249.87	12.56
	11:9	15.49	219.94	14.20
	11:12	11.19	165.69	14.79
	11:16	10.56	106.99	10.13

Table 2. Pure Gas Permeabilities and Selectivities of Different Block Ratio PEO-*b*-PMA (rChal) Crosslinked Membrane. Permeances at 1×10^6 (cm³·s⁻¹·cmHg⁻¹), were calculated by dividing the observed flow rate by the area of the membrane (2.84 cm²) and the pressure gradient (10 psi) employed, using porous Al₂O₃ membrane supports. The values were obtained from 10 independent measurements and the mean value and standard deviations were determined. The error in each case was <5%. The membrane PEO-*b*-PMA (rChal) showed no difference of gas permeation in humid environment.

Figure 4. α_{CO_2/N_2} with PEO:PMA = 11:7(black), 11:9(red), 11:12(blue) and 11:16(green) at different temperature.

the temperature and plasticized EO regions which lead to more flexible EO fraction, thus further increasing the CO₂ permeabilities⁵². Therefore, with such aforementioned discussion, it can be concluded that the crosslinked membranes showed a favored gas selectivities towards CO₂ with increasing the temperature.

Comparison of gas permeation properties of the membranes composed of various block ratio. In this study, four kinds of block copolymers with different block ratios, i.e. PEO₁₁-*b*-PMA(rChal)₇, PEO₁₁-*b*-PMA(rChal)₉, PEO₁₁-*b*-PMA(rChal)₁₂, PEO₁₁-*b*-PMA(rChal)₁₆ were prepared and consequently, four membranes were exposed to UV light (40 min) for complete crosslinking. Table 2 showed the data of crosslinked membranes with the block ratios of PEO₁₁-*b*-PMA(rChal)₉, PEO₁₁-*b*-PMA(rChal)₁₂ and PEO₁₁-*b*-PMA(rChal)₁₆ at different temperatures. It was clearly indicated that all of these block copolymers possessed same tendency with the block ratio of PEO₁₁-*b*-PMA(rChal)₇. At 60 °C, α_{CO_2/N_2} reached to 12.56 when the mole percentage of PMA (PMA%) was about 39%. Further, the α_{CO_2/N_2} reached to 14.79 when PMA% was approximately equal to 50%, however, the α_{CO_2/N_2} dropped to 10.13 when PMA% was greater than 60% (Fig. 4).

For solubility selectivities, the interactions between EO and CO₂ increased with rising the temperature. For diffusivity selectivities, the complicated crosslinking network led to the limited free volume. Moreover, crosslinking segments barely moved with the vary of temperature, so the N₂ denser barriers increased with the more crosslinking units⁴⁸. When the ratio of PEO:PMA varied from 11:7 to 11:12, the N₂ permeabilities decreased as

Figure 5. Robeson Upper Bound for CO₂/N₂ separation in 2008 with different block ratio copolymer membranes⁵³.

Temp(°C)	Crosslink Time (min)	N ₂ Permeabilities (barrer)	CO ₂ Permeabilities (barrer)	$\alpha_{(CO_2/N_2)}$
30	0	80.43	125.48	1.56
	5	46.24	119.31	2.58
	15	35.61	108.24	3.04
	40	29.05	100.53	3.46
60	0	97.78	237.62	2.43
	5	31.62	204.34	6.46
	15	17.21	176.84	10.28
	40	11.19	165.69	14.79

Table 3. Pure Gas Permeabilities and Selectivities of PEO-*b*-PMA(rChal) (11:12) Membrane under Different Crosslink Time. Permeances at 1×10^6 (cm³·s⁻¹·cmHg⁻¹), were calculated by dividing the observed flow rate by the area of the membrane (2.84 cm²) and the pressure gradient (10 psi) employed, using porous Al₂O₃ membrane supports. The values were obtained from 10 independent measurements and the mean value and standard deviations were determined. The error in each case was <5%. The membrane PEO-*b*-PMA (rChal) showed no difference of gas permeation in humid environment.

the data described. In contrast, CO₂ plasticized EO chain to be more flexible which resulted in higher CO₂/N₂ selectivities. However, the continuous increase of mole percentage of chalcone segments did not represent sustainable rising trend in α_{CO_2/N_2} but form a more rigid crosslinking framework instead. The rigid framework structure limited the mobility of EO segments in a large degree, which became obstacles for CO₂ transfer, representing a sharp reduction of α_{CO_2/N_2} . As shown in Fig. 5, the highest CO₂ selectivities of crosslinked membranes in this work was much closer to upper bound⁵³ than un-crosslinked ones. Taking account of these factors, the content of crosslinking segments after fully crosslinking played a key role in CO₂ gas permeable membrane.

Comparison of CO₂ permeation properties of a fixed block ratio BCP under different irradiation time. For this study, the PEO₁₁-*b*-PMA(rChal)₁₂ was treated as an example. (The data for other membranes are shown in Tables S3 and S4). Chalcone was an unique UV-crosslinker because of its easy crosslinking degree control by altering the UV irradiation time, which provided us a feasible way to verify the mechanism that crosslinking degree affected the ultimate CO₂ permeation properties. Table 3 presented the system data obtained under different UV irradiation time 0 min, 5 min, 15 min and 40 min (fully crosslinked) at 30 °C and 60 °C, respectively. The observed results (Figure S2) revealed that the α_{CO_2/N_2} was rising with the variation of UV irradiation time. Specifically, the data of α_{CO_2/N_2} was 2.43 without UV irradiation at 60 °C and the α_{CO_2/N_2} reached to 6.46 after 5 min UV irradiation. Further, the α_{CO_2/N_2} value was reached to the maximum of 14.79 after 40 min of UV irradiation, which revealed the full crosslinking. With increasing the irradiation time, the crosslinking degree in chalcone units increased which were minimizing free volume of the framework, resulting in the decreasing of N₂ permeabilities. Meanwhile, harder crosslinked PMA segments may also be contributed to the improvement of CO₂/N₂ selectivities. For diffusivity selectivities, CO₂ would make EO chains more flexible in the limited area surrounded by the crosslinked wall, which caused high CO₂ permeabilities. On the other hand, the confinement of free volume would result in denser barriers as explained above, leading to the low N₂ permeabilities. Thus, based on the observed results, one can conclude that the demonstrated mechanism is fully consistent with the obtained results.

Figure 6. The synthesis route of chalcone.

Conclusion

In summary, we have successfully synthesized a series of diblock copolymers incorporating a novel UV-crosslinkable chalcone based on PEO chains using a facile RAFT process. Interestingly, it was observed that crosslinked membrane exhibited high CO₂ permeabilities over N₂ and hence showing high selectivities of CO₂, in contrast with un-crosslinked membrane. Further, the detailed studies revealed that the diblock copolymers with different proportion displayed various selectivities. It was researched that the rising amounts of chalcone within certain limits enhanced the crosslinking degree by which the EO fractions become more flexible and thus exhibiting a higher CO₂ permeabilities and selectivities with temperature enhancement. However, excess crosslinking chalcone fragment formed an ultra-rigid framework and confined the transfer of CO₂ through the membrane, which resulted in low CO₂ permeabilities. Thus, tunable CO₂ selectivities could be achieved by monitoring the crosslinking degree of membranes. The presented work provided further applications of UV-crosslinking network for CO₂ separation.

Materials and Methods

Materials. All the chemicals were analytical grade and used as received without any further purifications. 4-hydroxybenzaldehyde, Methoxypolyethylene glycols, 2-(Dodecyl- thiocarbonothioylthio)-2-methylpropionic acid (DDMAT), 11-bromoundecan-1-ol, Azo-bisobutyronitrile (AIBN), Methacryloyl chloride, 4-butylphenylethylketone, N,N-Dimethylformamide (DMF), were all purchased from Sigma-Aldrich and Alfa-Aesar. Anisole was procured from Sigma-Aldrich with extra-dry grade purification.

Measurements. The prepared materials were characterized in detail using several techniques. The ¹H-NMR measurements were performed on Bruker AV-300 spectrometers in chloroform-d using tetramethylsilane (TMS; δ = 0) as internal reference. All copolymers were examined by gel permeation chromatography (Malvern, GPC 270) as reported in our previous work⁴⁸. The standard sample of GPC is Polystyrene(PS) and Mn = 99385, the measured solvent was THF. The DSC curve was measured in DSC(NETZSCH, STA449F3). Gas permeation measurements were carried out in the similar manner as reported in the literature by the authors; i.e. a home-made stainless steel permeation apparatus as described previously^{21,48}. The UV-crosslinking of the films was monitored by UV-Vis absorption spectroscopy. The average thickness of the tested film was examined by ellipsometry. Six sections on each membrane were measured respectively to calculate the average thickness of 1.8 ± 0.1 μm.

Synthesis of the monomer chalcone. The synthesis of monomer chalcone was done according to the Fig. 6 using organic synthetic procedure. The prepared material was purified with typical process and the purified product was characterized using ¹H-NMR spectroscopy.

Preparation of PM1. To prepare the PM1, in a typical reaction process, 4-hydroxybenzaldehyde (15.27 g, 125 mmol), 11-bromoundecan-1-ol (32.66 g, 125 mmol) and DMF (100 mL) were added in a 3-necked flask under continuous stirring. The mixture was stirred until the materials were completely dissolved. Consequently, 1.88 g NaI and 34.56 g K₂CO₃ were added in the resultant solution and stirred again for 30 min. After stirring, the resultant mixture was reflux for 24 h. After desired reaction time, the reaction was terminated and the mixture was cooled at room-temperature and the solvent was removed using rotary evaporation process. Subsequently, the residue was added to water and thus twice extracted with dichloromethane (DCM). Finally, the organic layer was separated and dried over MgSO₄ which was filtered. The obtained precipitate was then purified by column chromatography which finally provided a white solid (43.13 g). Yield: 90%. The ¹H NMR data measured in deuteriochloroform (CDCl₃; 300 MHz) solvent exhibited several chemical shifts at δ 9.87 (1H, s), 7.84 (2H, d, J = 8.7 Hz), 6.99 (2H, d, J = 8.7 Hz), 4.03 (2H, t, J = 6.5 Hz), 3.64 (2H, t, J = 6.6 Hz), 1.81 (2H, m), 1.59–1.29 (12H, m). The

Figure 7. The synthesis route of EO precursor.

Figure 8. The synthesis route of PEO macro-initiators.

Figure 9. The synthesis route of PEO-*b*-PMA(rChal) (11:7, 11:9, 11:12, 11:16) diblock copolymers.

typical ^1H -NMR spectrum is shown in Figure S3. ^{13}C -NMR (400 MHz, CDCl_3 , δ , ppm) 191.39, 164.26, 132.20, 129.73, 114.76, 77.15, 63.21, 32.92, 29.41, 26.28; TOF MS ($\text{C}_{18}\text{H}_{28}\text{O}_3$) m/z : calcd. for 292.410, found 293.212.

Preparation of PM2. To prepare PM2, in a typical process, PM1 (34.9 g, 100 mmol) and 3 namely, 4-butylphenylethylketone (21 g, 100 mmol) were mixed in alcoholic sodium hydroxide (50 mL, 10%) solution under continuous stirring. After 12 h stirring at room-temperature, the reaction mixture was poured into ice-water. The solid precipitate was formed which was collected by filtration and dried. The dried product was further purified by column chromatography and finally yellow solid was obtained (50.31 g). Yield: 90%. The ^1H -NMR data measured in deuteriochloroform (CDCl_3 ; 300 MHz) solvent exhibited several chemical shifts at δ (ppm): 7.90–7.81 (d, 4H, phenyl proton), 7.76 (d, 1H), 7.31–7.28 (d, 2H, phenyl proton), 7.19 (d, 1H), 7.00–6.97 (m, 2H, phenyl proton), 4.11 (t, 2H, CH_2O), 4.03 (t, 2H, CH_2O), 2.68 (t, 2H, CH_2Ph), 1.94 (s, 3H, CH_3), 1.82 (m, 2H, CH_2), 1.70–1.31 (m, 20H, $(\text{CH}_2)_{10}$), 0.94 (t, 3H, $-(\text{CH}_2)_3\text{CH}_3$) (Figure S4). ^{13}C -NMR (400 MHz, CDCl_3 , δ , ppm) 190.32, 161.43, 148.23, 144.33, 136.37, 130.45, 128.72, 127.64, 120.00, 115.12, 77.17, 63.22, 35.71, 33.27, 32.81, 29.49, 25.75, 22.34, 13.90; TOF MS ($\text{C}_{30}\text{H}_{42}\text{O}_3$) m/z : calcd. for 453.310, found 453.227.

Preparation of chalcone. To prepare the chalcone, in a typical reaction process, PM2 (42.8 g, 115 mmol), TEA (1.82 mL, 120 mmol) and 100 mL DCM were added in a dry round-bottom flask. Consequently, methacryloyl chloride (14.57 mL, 115 mmol) was added dropwise to the mixture at 0°C and the reaction was continued overnight. The obtained product was then added to the water and subsequently extracted with DCM twice. The organic layer was then separated and dried over MgSO_4 . Finally, the obtained product was filtered and purified by column chromatography which gives a light yellow solid (40.66 g). Yield: ~95%. The ^1H -NMR data measured in deuteriochloroform (CDCl_3 ; 300 MHz) solvent exhibited several chemical shifts at δ (ppm): 7.90–7.81 (d, 4H, phenyl proton), 7.76 (d, 1H), 7.31–7.28 (d, 2H, phenyl proton), 7.19 (d, 1H), 7.00–6.97 (m, 2H, phenyl proton), 6.10 (s, 1H, $\text{H}=\text{C}$), 5.54 (s, 1H, $\text{H}=\text{C}$), 4.11 (t, 2H, CH_2O), 4.03 (t, 2H, CH_2O), 2.68 (t, 2H, CH_2Ph), 1.94 (s, 3H, CH_3), 1.82 (m, 2H, CH_2), 1.70–1.31 (m, 20H, $(\text{CH}_2)_{10}$), 0.94 (t, 3H, $-(\text{CH}_2)_3\text{CH}_3$) (Figure S5). ^{13}C -NMR (400 MHz, CDCl_3 , δ , ppm) 190.32, 167.66, 161.43, 148.25, 144.30, 136.28, 130.14, 128.62, 127.63, 125.08, 119.80, 114.84, 77.00, 68.30, 35.71, 33.33, 29.57, 25.97, 22.56, 18.31, 13.89; TOF MS ($\text{C}_{34}\text{H}_{46}\text{O}_4$) m/z : calcd. for 518.630, found 519.281.

Figure 10. The ^1H -NMR and GPC of different block ratios of diblock copolymers.

Preparation of EO precursor. The synthesis of monomer was done according to the Fig. 7. In a typical synthesis process, solution of 10.5 g (100 mmol) methacryloyl chloride, in 30 mL DCM, was dropwise added to a mixture of 15.1 g (150 mmol) triethylamine and 35 g (100 mmol) methoxy polyethylene glycols ($M_n = 350$) in 100 mL of DCM at 0°C . The resultant mixture was then stirred overnight. After overnight stirring, the resultant mixture was filtered and the obtained crude product was added to 100 mL water and subsequently extracted with DCM twice. Finally, the solvent was dried by rotary evaporation which leaves oily liquid (43.23 g). Yield: 95%. The ^1H -NMR data measured in deuteriochloroform (CDCl_3 ; 300 MHz) solvent exhibited several chemical shifts at δ (ppm): 1.93 (s, 3H), 3.24 (s, 3H), 3.54 (t, 24H, $\text{CH}_2\text{CH}_2\text{O}$), 3.65 (t, 2H), 4.32 (t, 2H), 5.58 (s, 1H, $-\text{C}(\text{CH}_3)=\text{CH}_2$), 6.15 (s, 1H, $-\text{C}(\text{CH}_3)=\text{CH}_2$). (Figure S6); ^{13}C -NMR (400 MHz, CDCl_3 , δ , ppm) 167.32, 136.34, 125.56, 76.85, 70.50, 69.20, 63.55, 59.39, 18.31; TOF MS ($\text{C}_{20}\text{H}_{38}\text{O}_9$) m/z : calcd. for 422.510; found 422.277.

Preparation of PEO Macro-initiators. The macro-initiator was synthesized by the Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT) method. In a typical reaction process, 2.0 g (4.8 mmol) of EO precursor, 34.94 mg (0.096 mmol) of 2-(Dodecylthio-carbon-thiyl-thio)-2-methyl propionic acid (DDMAT) and 3.149 mg (0.0192 mmol) of Azobisisobutyro-nitrile (AIBN) were mixed in a 10 mL Shreck bottle with 1.5 mL anhydrous anisole. Consequently, the resultant mixture was degassed four times using the

freeze pump-thaw procedure and the bottle was sealed under vacuum. The sealed bottle was then placed in a preheated oil bath (90 °C) for 12 h. Finally, the solution was precipitated in hexane (Fig. 8). The obtained yield was 45.5% (0.91 mg). The observed Mn and PDI are 4600 and 1.13, respectively. The ¹H-NMR, measured in deuteriochloroform, exhibited several chemical shifts at δ (ppm): 1.25–1.34 (t, 23H, -C₁₂H₂₃), 3.36–3.42 (s, 3H, -OCH₃) (Figure S7); ¹³C-NMR (400 MHz, CDCl₃, δ, ppm) 216.01, 177.26, 174.59, 70.65, 68.34, 65.25, 52.46, 46.03, 43.37, 35.82, 33.37, 29.73, 29.62, 29.50, 29.27, 28.25, 26.23, 22.36, 13.94.

Preparation of PEO-*b*-PMA(rChal) diblock copolymers. A series of PEO-*b*-PMA(rChal) containing a chalcone mesogen with different content of polymerization were synthesized by RAFT method. The targeted material was prepared as presented in Fig. 9. As an example, a procedure to prepare PEO₁₁-*b*-PMA(rChal)₇ is described here. In a typical reaction process, 0.097 g (1 eqv) PEO macro-initiators, 0.24 g (30 eqv) chalcone and 0.0003 g (0.12 eqv) AIBN were mixed in a 10 mL Shreck bottle with 1.8 ml anhydrous anisole. Then, the mixture was degassed four times using the freeze pump-thaw procedure and sealed under vacuum. The sealed bottle was then placed in a preheated oil bath (90 °C) for 17 h. The solution was precipitated in diethyl ether and finally pure diblock copolymer was obtained. Figure 10 showed the typical ¹H-NMR (a) and GPC (b) results. The observed Mn and PDI of PEO₁₁-*b*-PMA(rChal)₇, PEO₁₁-*b*-PMA(rChal)₉, PEO₁₁-*b*-PMA(rChal)₁₂, PEO₁₁-*b*-PMA(rChal)₁₆ are 8200 and 1.13, 9200 and 1.11, 10800 and 1.16, 13200 and 1.19. The ¹H-NMR data measured in deuteriochloroform (CDCl₃; 300 MHz) solvent exhibited several chemical shifts at δ (ppm): 1.30–1.46 (t, 23H, -C₁₂H₂₃), 3.51–3.57 (s, 3H, -OCH₃), 1.19–1.23 (s, 22H, -O(CH₂)₁₁O-); ¹³C-NMR (400 MHz, CDCl₃, δ, ppm) 208.61, 189.94, 177.90, 169.84, 164.89, 162.11, 148.52, 144.46, 136.15, 130.23, 128.69, 127.78, 115.09, 70.80, 68.31, 65.17, 35.77, 33.33, 29.63, 28.35, 26.18, 22.42, 14.13. The DSC curve of un-crosslinked block copolymer PEO₁₁-*b*-PMA(rChal)₁₂ was measured at a rate of 2 °C/min from 40 °C to 140 °C and shown in Figure S8.

Preparation of thin membranes. The diblock copolymer membrane was made by spin-coating (1000 rpm) of 6 wt% chloroform solutions on Anodic Alumina Oxide (AAO) substrate. The prepared diblock copolymer membrane was placed in vacuum for 4 h at room-temperature. Consequently, the crosslinking of the block copolymer membrane was exposed to UV light (365 nm) for a desirable time and finally the UV-crosslinked membrane was obtained.

Gas permeation measurements. A home-built gas permeation measurement system was used to estimate the gas permeation as described in our previous work^{22,48}. The pure gases with different kinetic diameters such as N₂ and CO₂ were studied in this work. For this, a spin-coated membranes on AAO substrates were placed in the permeation cell with a support screen. The surface area of the tested membrane, available for gas transport, was estimated and found to be 2.84 cm². The membranes were placed in the test system cell to investigate the gas permeation test. The gases, after passing through the membrane in the cell, was directed into a glass U-tube flow meter (Acol = 0.03 cm²) 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_{column} = 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 10 independent measurements and the mean value and standard deviations were determined. The error in each case was <5%. The same experimental procedure was repeated for other targeted gas. In general, the permeation properties were sequentially measured for He, N₂ and CO₂, respectively. The permeance (P; 10⁶ cm³·s⁻¹·cmHg⁻¹) was calculated based on the equation (1)⁴⁸:

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

And the selectivities (α) of gas A, over gas B, was defined based on the below equation (2)⁴⁸:

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

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Author Contributions

J.L. and Y.W. initiated and designed entire project. J.L., Z.C., Y.S., X.Z. participated in the experiments and Y.L. supported the study. J.L., Y.W. and A.U. prepared and checked the manuscript. Y.W. conceived the research project and directed the study. All the authors reviewed the manuscript.

Additional Information

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