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1,3-Dioxolane 기반 CO_2 선택성 고분자막의 개발

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1,3-Dioxolane-Based CO_2 Selective Polymer Membranes for Gas Separation

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요 약: 1,3-다이옥솔란은 용매, 전해질 및 시약으로서 화학, 페인트 및 제약 산업에서 광범위한 관심을 받고 있는 화합물이다. 1,3-dioxolane은 주로 독성, 발암성, 폭발성, 자동 인화성이 없으며 다기능성을 가지고 있어, 대부분의 유기 및 수성 용매 조건에서 우수한 용해성을 가져 고분자 전구체로서 사용된다. 최근 몇 년 동안 이 물질은 배가스 및 천연 가스 혼합물에서 CO_2를 분리하기 위한 CO_2 선택적 고분자 전구체로서 점점 더 많은 관심을 받고 있다. Poly(1,3-dioxolane) (PDXL)은 폴리에틸렌 옥사이드(PEO)보다 높은 에테르 산소 함량을 가지고 있으며, 이는 극성 에테르 산소 그룹이 CO_2에 대해 강한 친화력을 나타내기 때문에 우수한 막 CO_2/N_2 분리 특성을 보인다. 따라서 PDXL 기반 분리막은 비극성(N_2, H_2 및 CH_4) 가스에 대해 탁월한 CO_2 용해도 선택성을 보인다. 그러나 PEO와 마찬가지로 PDXL의 극성기는 고분자 사슬의 밀집도를 증가시키고 고분자 결정화를 유발하여 기체 투과도를 감소시켜 이에 대한 개선이 필요하다. 이 논문에서는 기체 분리 응용 분야에서 PDXL기반 고분자막의 최근 발전과 한계에 대해 알아보고자 한다. 또한 CO_2 분리 공정에서 1,3-dioxolane 기반 고분자의 한계를 극복하기 위한 몇 가지 분자 설계방안에 대해 다루어 보기로 한다.

Abstract: 1,3-Dioxolane is an exciting material that has attracted widespread interest in the chemical, paint, and pharmaceutical industries as a solvent, electrolyte, and reagent because 1,3-dioxolane is not toxic, carcinogenic, explosive, auto-flammable, and multifunctional, and due to their excellent miscibility in most organic and aqueous solvent conditions. Recently, this material has received increasing attention as a CO_2-selective polymer precursor to separating CO_2 from flue gas and natural gas mixtures. Poly(1,3-dioxolane) (PDXL) possesses higher ether oxygen content than polyethylene oxide (PEO), which demonstrates superior membrane CO_2/N_2 separation properties owing to their polar ether oxygen groups exhibiting strong affinity toward CO_2. Thus, PDXL-based membranes displayed an outstanding CO_2 solubility selectivity over non-polar (N_2, H_2, and CH_4) gases. However, the polar groups of PDXL, like PEO, promote chain packing efficiency and cause polymer crystallization, thereby reducing its gas permeability, which should be improved. In this short review, we discuss the recent advancement and limitations of PDXL membranes in gas separation applications. To conclude, we provide future perspectives for inhibiting the limits of 1,3-dioxolane-based polymers in the CO_2 separation process.

Keywords: *1,3-dioxolane-based polymer, membrane, carbon dioxide separation*

1. Introduction

Polymer membrane-based gas separation technology has drawn significant attention during the last 40 years since 1979 due to its intrinsic advantages over conventional technologies (e.g., amine scrubbing, sorbent adsorption, and cryogenic distillation)[1-10]. The technology demands potentially less energy consumption since it does not require any phase changes compared to oth-

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er separations[5,11]. In addition, it is environmentally friendly because it does not require toxic and corrosive chemicals for separation, such as the chemical absorption process, where toxic mono-ethanolamine (MEA) is used. The lack of mechanical complexity in membrane systems is another advantage, and their modularity allows easy scale-up and results in significant flexibility[7].

Numbers of commercial polymers as membrane materials are in use today, such as cellulose acetate (CA), polyimide (PI, e.g., Matrimid), polyphenylene oxide (PPO), polycarbonate (PC), polysulfone (PSf), with far below separation performance than expected[7,12-14]. Current research in this area is focused on developing high-performance polymer membranes for efficient CO_2 separation. However, it is incredibly challenging because the performances of polymer membranes always suffer from an undesirable trade-off between permeability, P (how fast the penetrants pass through the membrane materials), and selectivity, α (the purity, to what extent the desired molecule is separated from the mixture)[5]. The sacrifice of selectivity attains the high permeability to the polymer (α) and vice versa, theoretically evaluated by the Robeson upper bound[15-17]. Moreover, the membrane process has some uncertainties in extreme conditions, such as temperature, pressure, and high flow rates[5].

Therefore, realizing the intrinsic nature of the materials being used and the critical parameters for membrane separation to develop high-performance polymers is crucial. The dense polymer membrane follows the solution-diffusion mechanism, where the permeability (P) is the product of the diffusivity (D) and solubility (S), i.e., $P_i = D_i \times S_j$, and the selectivity ($\alpha_{i/j}$) is the ratio of the permeability between two gases (i and j), and a product of solubility selectivity (S_i/S_j) and diffusivity selectivity (D_i/D_j), i.e., $\alpha_{i/j} = (S_i/S_j) \times (D_i/D_j)$ [5]. A highly efficient membrane can be obtained if the polymer displays high permeability and selectivity. Diffusivity selectivity is the size-sieving ability that depends on the difference between the kinetic diameters of two target penetrants, the polymer chain stiffness, and the degree of inter-segmental chain packing[5]. In contrast, the solubility selectivity is attained by the favorable/relative interactions of the desired gas (with a high level of condensability due to high critical temperature) to the polymer[5].

Therefore, flue gas (CO_2/N_2) separation selectivity is predominantly originated from the solubility selectivity because the CO_2 is polar and more condensable (high critical temperature, T_c = 305 K) than non-polar N_2 (low critical temperature, T_c = 126 K). Besides, only minor differences (0.34 Å) in kinetic diameter between N_2 (3.64 Å) and CO_2 (3.30Å), with the large critical volume of CO_2 than N_2, do not allow a high diffusivity selectivity to CO_2/N_2 pairs. Therefore, most of the state-of-the-art polymer materials with strong size-sieving ability, such as thermally rearranged (TR) polymers[18,19], polymers of intrinsic microporosity (PIMs)[11,20], perfluoro polymers[21,22] and KAUST-PIM[23], do not exhibit high CO_2/N_2 selectivity demanding for energy-efficient CO_2 separation processes.

In contrast, for the natural gas sweetening (CO_2/CH_4 separation), the most approach focuses on enhancing the size-sieving ability of above mentioned glassy polymers to increase the diffusivity selectivity because of the relatively sizeable kinetic diameter of CH_4 (3.8 Å) than CO_2 (3.3 Å). However, the high sorption tendency of hydrocarbon (CH_4 and heavy members) in these glassy polymers impedes CO_2 sorption and thus reduces CO_2 permeability. Moreover, adsorbed hydrocarbon allows the polymer to swell, reducing diffusivity selectivity. Finally, unstable separation performances of the glassy polymer due to the reduction of non-equilibrium free volume with time (well-known aging effect) make challenging their application for industrial uses. Therefore, researching the development of CO_2-selective materials (over N_2 and CH_4) with stable performance over time that can suppress competitive sorption is highly desired for flue gas and natural gas purification applications.

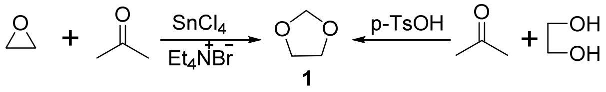
Poly(ethylene oxide) (PEO)-containing materials has established as leading materials for CO_2/light gas separation membranes with a balanced high CO_2 permeability and CO_2/light gas selectivity until 2018, such as

Pebax and Polyactive[24-26], crosslinked PEO[8,27] and PEO-based nanocomposites[28,29]. The polar ether oxygen in PEO repeating units exhibits a strong affinity towards CO_2 but not light gases (which leads to high CO_2 solubility and CO_2/light gas solubility selectivity) while retaining polymer chain flexibility and thus high CO_2 diffusivity[30]. Several reported examples displayed excellent CO/light gas separation performance, placing these materials beyond Robeson's upper bound for CO_2/light gas separation. Thus enhancing solubility selectivity is a unique approach to overcoming the trade-off relationship, and this strategy is renowned as very stable at high pressure and mixed hydrocarbon conditions. Therefore, designing polymers with higher ether oxygen content (O/C ratio) can enhance CO_2/light gas solubility selectivity.

In this regard, Prof. H. Lin and his co-workers have developed a unique polymer, 1,3-dioxolane-based materials, for the first time to accelerate the CO_2/light gas separation selectivity with robust performance to process flue gas and raw natural gas mixture[30,31]. It was evaluated that higher ether oxygen content in poly(1,3-dioxolane) (PDXL) (O/C ratio: 0.67) compared to that of PEO (O/C ratio: 0.5) demonstrates superior CO_2/light gases separation performance through joint experimental-computation studies. In this mini-review, we summarize all the Poly(1,3-dioxolane) (PDOL) based polymer, their properties, and the advancement of PDOL membranes in gas separation applications. Finally, we provide future perspectives for inhibiting the limits of 1,3-dioxolane-based polymers in the CO_2 separation process.

2. 1,3-Dioxolane, Synthesis and Applications

1,3-Dioxolane (DXL) is a five-membered, nonplanar, fully saturated oxygen heterocycle with two oxygen atoms at the 1,3-positions of the cyclic system. Its structure is similar to THF, except that an oxygen atom replaces the methylene group at position 3. It is also called five-membered cyclic acetal.



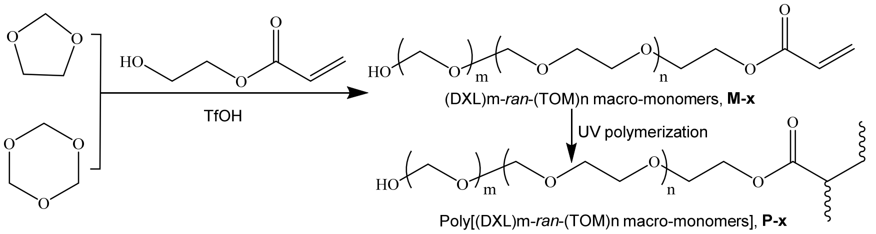
Scheme 1. Synthesis of 1,3-dioxolane.

Synthesis of parent DXL is very straightforward by treating formaldehyde with ethylene glycol in toluene using p-toluene sulfonic acid as a catalyst (Scheme 1). It can also be obtained from the reaction of formaldehyde with ethylene oxide using $SnCl_4$ or tetraethylammonium bromide as a catalyst. Some other catalysts and solvent systems are also reported in the literature for their synthesis.

DXL is a widely used compound in the laboratory as a solvent and a reagent[32-36]. The boiling point, polarity, density, and viscosity of DXL are 76°C 7.9, 1.06 g/cm^3, and 0.58 cP, respectively. It is known as a green chemical because it is non-toxic, non-carcinogenic, non-explosive, easy to evaporate, and multifunctional, and its excellent miscibility in most organic and aqueous solvent conditions finds application in formulations, in production processes[33,35]. It can be used as an alternative green solvent to chloroform, dichloromethane, methyl ethyl ketone, THF, and DMSO [35].

Besides, DXL is used in natural product syntheses as protecting group for ketones, aldehydes, and 1,2-diols, and represents essential intermediates and end-products in the pharmaceutical and fragrance[37,38]. It is also used in the paint industry as a substitute for toluene and xylene[35].

Derivative of 1,3-dioxolane is known as the precursor of numerous biologically and pharmacologically active molecules such as antiviral[39], antibacterial [40], antifungal[41], antineoplastic[42], anti-HIV, anesthetic[43] and anticonvulsant ones[44]. Besides, DXL is commonly used as an electrolyte solution in lithium-ion batteries[45,46]. The polymer of DXL, i.e., Poly (1,3-dioxolane) (PDXL), dramatically enhanced the electrode interface compatibility. It is used to synthesize polyacetals and polymer industries. Therefore,



Scheme 2. The synthetic procedure for the preparation of $(DXL)_m$-ran-$(TOM)_n$ macromonomers and their corresponding polymers[31].

the 1,3-dioxolane can successfully be used as a polymerizing agent for membrane-based gas separation as a CO_2 philic unit.

3. Dioxolane-based Polymer Membrane And Physical Properties

The polymer containing a higher ether content (O/C ratio) is expected to exhibit a higher CO_2/ light gas solubility selectivity, which can be rationalized for flue gas and natural gas separation applications with the robust performance of polymer membranes. Prof. H. Lin's group successfully applies this hypothesis through theoretical and computational studies using 1,3-dioxolane as an effective co-monomer[33-36].

In their first approach, a series of amorphous and rubbery copolymer-based membranes were prepared by the photo-polymerization of 1,3-dioxolane (DXL) and 1,3,5-trioxane (TOM)-based macromonomers (PDXL and PTOM) with varying ratios of O/C up to (0.66~0.80) as shown in Scheme 2[31]. These PDXL and PTOM were synthesized prior by cationic chain ring-opening polymerization of 1,3-dioxolane and 1,3,5-trioxane with chain transfer agent 2-hydroxyethyl acrylate (HEA) using trifluoromethane sulfonic acid (TfOH) as an initiator with various chain length of DLX and TOM. The UV-irradiated copolymers membrane was found to have a crosslinked structure, which originated from the polymerization of diacrylate produced as a byproduct during the preparation of macromonomers. The molecular weight of the PDXLA and PTOM precursors was controlled by manipulating the molar ratio of DXL (or TOM) and HEA. The length of these branches was controlled and kept low to avoid polymer crystallization. The structure /property relationship of these copolymers was thoroughly evaluated.

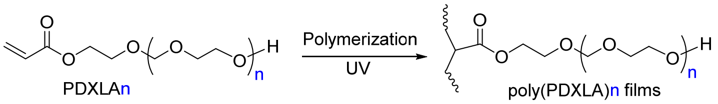
Table 1 summarizes some physical properties of 1,3-dioxolane-based polymer membranes used in gas separation membranes. All the copolymers obtained from PDXLA and PTOM are rubbery and amorphous at 21°C and show only a single glass transition temperature (T_g) ranging from -64 to -5°C, based on the DXL composition (Table 1)[31]. The DXL-containing homopolymer (PDXLA) membrane (P66) is flexible with a T_g of -65°C. The chain flexibility and fractional free volume decrease as the O/C ratio increase (with the increase of TOM content) in the polymer[31]. However, all polymers display similar d-spacing.

The number of repeating 1,3-dioxolane units in the branched chain of PDXLA-based polymer membranes significantly affects the morphology and other properties. Prof. Lin's group extended their studies by tuning the chain length (repeating unit, DXL) of poly(1,3-dioxolane) (PDXL) following the same ring-opening UV polymerization technique to yield PDXLAn polymer membranes and analyzed their various properties (Scheme 3)[47].

The polymer [poly(1,3-dioxolane) (PDXL)] membranes with various repeating units ranging from 4 to 12 are amorphous at 23°C, indicating that short branches can easily prohibit the crystallinity originating from polar interaction between them. Surprisingly, the density and T_g decreased with the increase in the chain length DXL units, which is attributed to the decrease of H-bonding (originating from the end OH of the polymer chain) by the increase of repeating units to the

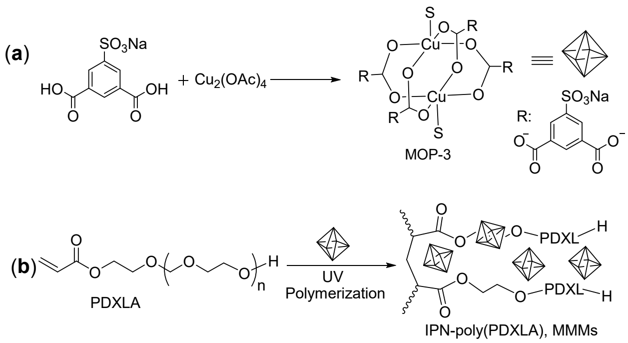
Table 1. Physical Properties of 1,3-dioxolane-based Polymer Membranesa

Membrane code	Composition	T_g (°C)	Density (g/cm^3)	FFV	Ref.
$(DXL)_m$-ran-$(OM)_n$.	P66	-64	1.1119	0.136	[31]
	P68	-54	1.225	0.124	
	P71	-48	1.223	0.091	
	P74	-36	1.289	0.087	
	P80	-5	1.345	0.084	
PDXLA-co-PDXLEA-xx	xx = 0	-66	1.210	0.139	[30]
	xx = 25	-67	1.199	0.145	
	xx = 50	-68	1.179	0.164	
	xx = 75	-69	1.114	0.178	
	xx = 100	-71	1.185	0.150	
PDXLAn (n)	n = 4	-46	1.235	0.116	[47]
	n = 6	-58	1.224	0.117	
	n = 8	-60	1.212	0.123	
	n = 10	-60	1.213	0.121	
	n = 12	-60	1.208	0.124	
PDXLA8 + PEGDME/PEG blend	DME-0	-59	1.212	0.123	[48]
	DME240-10	-68	1.183	0.136	
	DME240-30	-81	1.140	0.151	
	DME240-45	-88	1.118	0.155	
	DME240-50	-92	1.107	0.160	
	PEGDME240	-120	1.030	0.180	
	PEG400-40	-69	1.188	0.120	
	DME500-10	-63	1.206	0.121	
	DME500-20	-66	1.184	0.130	
	DME500-30	-63	1.165	0.138	
	DME500-40	-63	1.151	0.142	
	DME500-45	-63	1.148	0.141	
	DME500-50	-64	1.144	0.140	
	DME500-55	N/A	1.137	0.142	
	PEGDME500	-67	1.050	0.180	

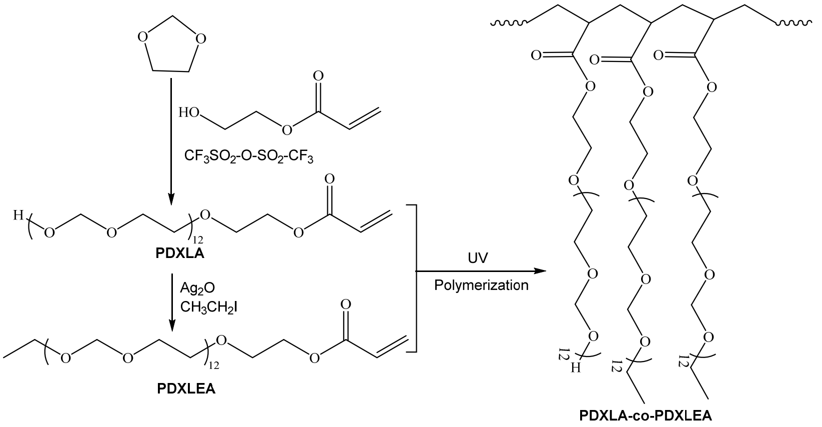


Scheme 3. Synthetic steps of the PDXLn macromonomers and corresponding PDXLAn films[47].

polymer structure[47]. However, the T_g of PDXLA does not affect by the chain length unit after a specific range of repeating units (8~12) because only a small mass % of OH is reduced, and the possibility of chain packing tendency increases. Thus the fraction of free volume increases with increasing repeating units of DXL. PDXLA8 with a chain length of 8 was found as an optimum membrane with a good combination of chain flexibility and free-volume elements because some crystallinity initiates once the DXL chain length becomes higher than eight (> 8) in the polymer. The properties of the corresponding membranes with varying repeating units of 1,3-dioxolane (4, 8, 12, and 20) are shown in Table 1. The 1,3-dioxolane-based poly-



Scheme 4. (a) Synthesis of MOP-3, and (b) development of IPN-MMMs by dispersing discrete MOP nanoparticles in the monomer solutions before polymerization[49].



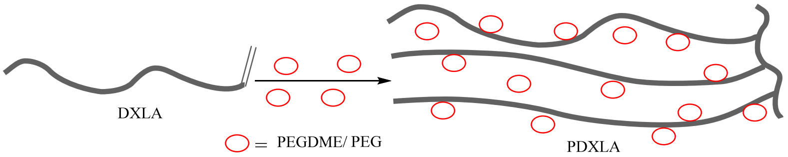
Scheme 5. The synthetic route of macromonomers (PDXLA and PDXLEA) and highly branched polymers.

mer membranes perform as auspicious CO_2-selective material.

The DXL-based rubbery polymer can also be used as an excellent compatible support matrix for mixed-matrix membranes (MMMs). A series of defect-free interpenetrated mixed-matrix membranes (IPN-MMMs) was fabricated by the same group by introducing metal-organic polyhedron (MOP-3) into poly(1,3-dioxolane) based polymer, and PDXL showed its potential as a matrix of MMMs as shown in Scheme 4[49]. We skip the discussion on this work as it is the out of context for the present studies. We cover only the effect of PDXL content on the polymer, not the MMMs, where the effect of filler loading is mainly evaluated.

The effect of the end group of branched-chain in the poly(1,3-dioxolane)-based copolymer is very significant for various properties, including flue gas (CO_2/N_2) separation performance[30]. To do so, the same group synthesized a series of highly branched copolymer membranes using poly(1,3-dioxolane) acrylate (PDXL) and its ethoxy chain ended version polydioxolane ethyl acrylate (PDXLEA) through UV polymerization as shown in Scheme 5[30]. The number of DXL repeating units in the PDXL controls the crystallization, and the ethoxy chain end groups increase the polymer fractional free volume (FFV) and transport property.

The ethoxy chain terminated copolymers is mechanically flexible enough. These rubbery copolymers (at room temperature) membranes displayed well-desired properties in T_g and density but were complex in crystallinity and free volume depending on the PDXLEA loading (Table 1). The T_g and density decrease and FFV_d increases with the increase of the PDXLEA content in the copolymer due to flexible ethoxy end groups, which is expected to enhance the diffusivity and permeability of the corresponding membrane.



Scheme 6. Preparation of PEGDME and PEG incorporated poly(PDXLA) membranes by UV-polymerization.

However, PALS analysis determined that even though the density/numbers of the free volume elements (FVE) increased, the size of the FVE decreased with the PDXLEA loading[30]. The increase of the FVE was explained by the presence of flexible ethoxy chain end groups, while the increased chain flexibility was suspected to improve chain packing efficiency and thus slightly decrease the FVE diameter[48]. The results of the PALS analysis reflect on gas separation performance.

H. Lin and his co-workers, in their recent work, incorporated the soft PEG/PEG dimethyl ether (PEGDME) into the PDXLA8 membrane to plasticize the highly selective membrane and thereby accelerate the transport properties by several orders (Scheme 6) [48]. The effect of additive (PEG/PEGDME) loading on various properties is investigated. All the blend membranes are amorphous at 23°C or above. The T_g and density of blend membranes decreased, and the FFV increased with adding both types of additives due to the plasticization effect. Both additives, PEG and PEGDME (m.wt. 240 and 500), are well miscible to PDXLA. However, PEGDME-240 was the best effective plasticizer due to its lower molecular weight (low T_g) and the lack of end hydrogen bonding between themselves.

4. PDXLA-based Membrane for CO_2 Separation

The polymer with a higher ether content (O/C ratio) exhibits a higher CO_2/light gas solubility selectivity, which can be rationalized for flue gas and natural gas separation applications with robust performance. The performance of CO_2 separation membranes is summarized in Table 2.

Table 2. The Gas Permeabilities and Selectivities of 1,3-dioxolane-based Membranes

Membranes	Permeability				CO_2 selectivity/gas				T (°C)	Ref.
	C_2H_6	N_2	CO_2	CH_4	C_2H_6	H_2	N_2	CH_4		
$(DXL)_6$-ran-$(TOM)_5$A	26.6	–	320	15	12	–	–	21[a]	50	[31]
PDXLA-co-PDXLEA 75	–	11.69	725	–	–	–	62[a]	–	35	[30]
	–	21.87	1400	–	–	–	64[b]	–	70	
polyPDXLA30	–	–	580	–	–	10	62	20		[49]
PDXLA8	–	4	220	–	–	–	56	–	35	[47]
	–	3.9	240	–	–	–	62	–	35	
	–	3.3	190	–	–	–	56[c]	–	35	
	–	3.4	190	–	–	–	56[d]	–	35	
	–	3.5	190	–	–	–	56[e]	–	35	
	–	8.7	300	–	–	–	35[d]	–	60	
DME240-45	–	32	1400	–	–	–	45	–	35	[48]

[a] Mixed gas, [b] humidified mixed gas, mixed gas with different compositions: [c](15:85), [d](20:80), [e](30:70).

The 1,3-dioxolane-based oxygen-rich polymers exhibit favorable CO_2/C_nH_{2n+2} (n = 1, 2) selectivity due to their solubility selectivity[30,31,48]. However, the addition of much O/C content by 1,3-trioxane into PDXLA membrane provides more beneficial CO_2 selectivity due to the combined product of solubility selectivity and diffusivity selectivity, and this perm-selectivity increased with the increasing order of O/C ratio[31]. The solubility-selectivity dominantly accelerates the overall perm-selectivity due to increased ether oxygen content in the copolymer structure. However, as expected, the CO_2 permeability decreases with increasing the O/C ratio, because of decreasing flexibility (increasing T_g) and decreasing FFV. These DXL-based polymers displayed even better CO_2/C_nH_{2n+2} (n = 1, 2) separation performance in the presence of other hydrocarbon mixtures with enhanced permeability and stable selectivity due to dominating the solubility selective separation behavior. It demonstrates the benefit of designing amorphous polymers with a high content of ether oxygen polar groups on the structures and gas transport properties.

The number of DXL repeating units (n) in the PDXL controls the crystallization and gas permeability [31,47]. The gas permeability gradually increases with the increase of the n value up to a specific limit of 8, followed by an unsettled performance above 8. The PDXLA8 membrane, with a chain length of 8, displayed the best combination of CO_2 permeability of 220 Barrer with excellent selectivity over other gases (such as CO_2/N_2 = 56 and CO_2/CH_4 = 22). The performance of the optimum membrane PDXLA8 displayed stable CO_2 separation results (over N_2 and short-chain hydrocarbon) concerning the time and pressure and mixed gas separation environment, demonstrating the benefit of using higher ether oxygen-containing polymer for gas separation membranes. Indeed, the ether oxygen content in the DXL-based polymer favorably enhances the binding energy with the CO_2 compared to other non-polar gases, indicating that increased ether oxygen content in the polymer facilitates the CO_2/N_2 solubility selectivity.

The PDXLA polymer also performs very well as a support in the filler-loaded mixed matrix membrane because of its flexibility and compatible nature with metal-organic polyhedra (MOP)[49]. The separation performance of PDXL-supported defect-free MMMs (IPN-MMMs) is near or above the upper bounds for CO_2/H_2 and CO_2/N_2 gas pairs separation with good MOP-polymer compatibility, indicating the potential of PDXL polymer for MMM-based CO_2 separation[49].

However, an excess amount of O/C content in the polymer resulted in crystallinity that reduced the FFV and flexibility, thereby decreasing the permeability and its capability to be used in gas separation applications [31]. Therefore, the flexibility of polymer is also essential for its actual applications. Moreover, the hydroxyl end group of ether oxygen-based polymer negatively affects its flexibility, FFV, and gas separation performance, due to their strong tendency to form H-bonding and compact structure[30]. Ethoxy and methoxy-chain termination in this polymer solve the intrinsic characteristics of these polymers because these groups inhibit H-bonding and enhance flexibility by reducing the T_g of the resultant polymer[30]. The ethoxy/methoxy chain end groups increase the polymer fractional free volume (FFV) and thus gas permeability.

The ethoxy chain termination in the PDXLA polymer dramatically affects the various properties, including gas separation performance by several orders. The permeability of the PDXLA polymer is significantly enhanced by incorporating an ethoxy end terminated version, PDXLEA, due to an increase of FFV and flexibility and a decrease of T_g. However, the permeability trend was unexpected and complicated above 75 % loading of PDXLEA (Fig. 1). H. Lin *et al.* explained this behavior by PALS analysis. They explain that the numbers of the free volume elements (FVE) increase with increasing PDXLEA loading due to the presence of flexible ethoxy chain end groups, while the size of the FVE decrease by the increased chain flexibility, which is suspected to improve chain packing efficiency, and thus slightly decrease the FVE diameter.

However, none of the orders of FVE was fitted

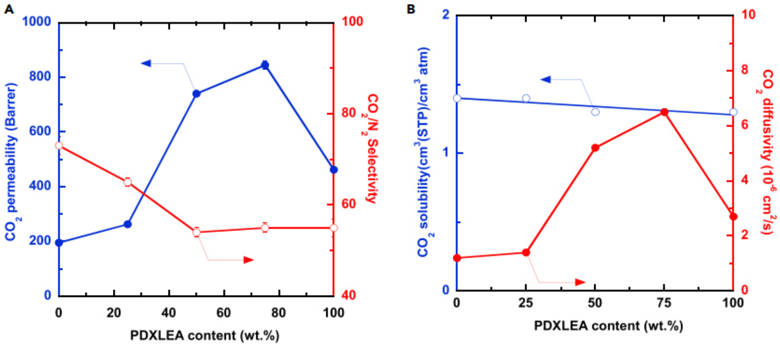


Fig. 1. Effect of PDXLEA content in the copolymers (a) CO_2/N_2 on gas separation performance and (b) CO_2 solubility and diffusivity at 35°C (Reproduced with Permission from H. Lin *et al.*,[30], copyright 2019, Elsevier).

enough to explain the trend of the gas separation performance of these copolymers, significantly above 75% loading of PDXLEA. For example, the increase in the number of FVE could explain the behavior of gas permeability until 75% loading of PDXLEA, and it did not follow beyond 75% PDXLEA loaded membranes, and vice-versa[30].

Nevertheless, the copolymer PDXLDA-*co*-PDXLEA75 displayed excellent CO_2 separation performance over N_2 and H_2 due to their superior selectivity originating from the higher ether oxygen content in the polymer structure and highly flexible chain end-oriented excellent permeability.

The polymer membranes obtained from 1,3-dioxolane-based acrylate displayed an excellent CO_2 selective gas separation performance due to the presence of a precious content of ether oxygen (O/C) with its flexible nature. However, the permeability of the PDXL homo polymer membranes is still low (180~220 Barrer) for the cost/energy efficient CO_2 separation application, which rationally demands collaboration with other materials.

It is well established that adding helping materials can accelerate the separation performance of PEG-based soft membranes. Therefore, incorporating highly flexible and CO_2-selective guest molecules such as PEG or PEGDME could significantly enhance the separation performance of 1,3-dioxolane-based membranes by their CO_2-facilitated transport nature. It was confirmed that the CO_2 permeability, solubility, and selectivity were increased with the increase of PEG/PEGDME loading in the blend membranes due to the increase of flexibility and FFV by the plasticizer[48]. The gas separation performance of blend membranes was enhanced dramatically by several orders compared to the pristine polymer membranes, keeping the selectivity of CO_2 (over other gases) sufficiently high. For example, the blend membrane above 45% loading of PEGDME, DME-45, and DME240-50 displayed superior CO_2/N_2 separation performance, having a permeability of 1540 and 1700 Barrer, respectively, remaining selective above 40 using model flue gas (CO_2/N_2) mixture with a stable long-term separation performance[48].

5. CO_2 Separation performance of 1,3-dioxolane at Challenging Conditions

5.1. High-temperature separation performance

The separation performance of membranes at high temperatures is also significant for industrial demand. The gas permeability of PDXLA membranes increases with increasing temperature due to increased diffusivity for all gases. Accordingly, the CO_2/N_2 selectivity decreased, and the CO_2/CH_4 selectivity remained unchanged due to a much decrease in the solubility of condensable gases. It is typical for most polymers because the gas activates more, and the mobility of polymer chains increases at higher temperatures, and both of these factors accelerate the transport of gases and enhance the fractional free volume of polymers. Thereby,

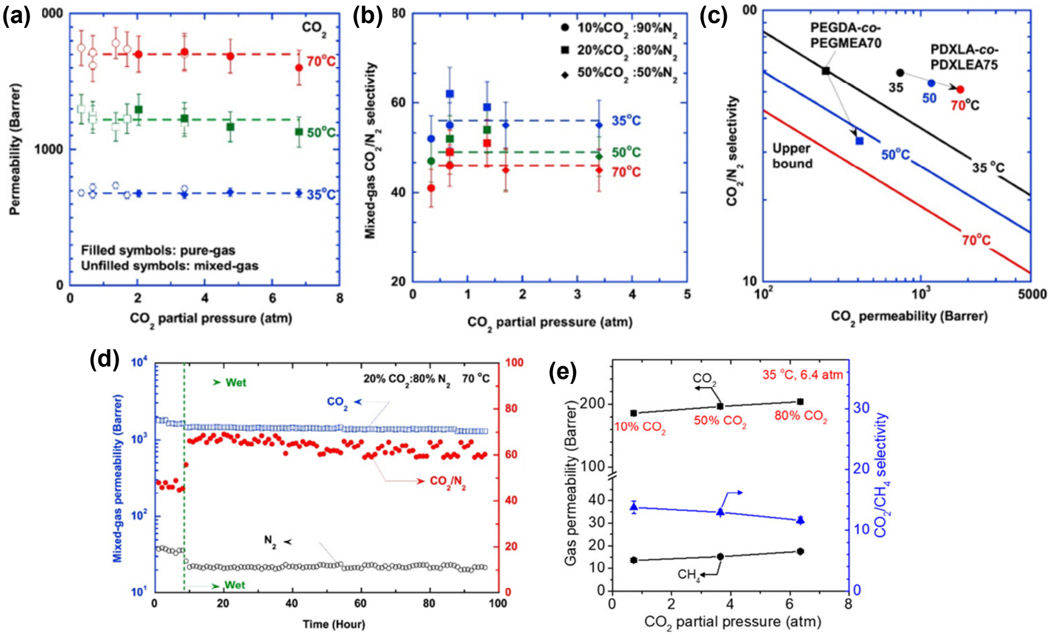


Fig. 2. The CO_2/N_2 separation performance in PDXLA-co-PDXLEA membrane (a-b) Effect of temperature and CO_2 partial pressure on (a) CO_2 permeability, CO_2/N_2 selectivity, and (c) pure gas CO_2/N_2 separation performance in the Robeson's upper bounds at 35°C (black), 50°C (blue), and 70°C (red), and (d) long-term stability in dry and humidified conditions with $CO_2:N_2$ of 20:80 at 70°C for 96 h (Reproduced with permission from H. Lin *et al.*,[30], copyright 2019, Elsevier). (e) Effect of CO_2 partial pressure on the mixed-gas CO_2/CH_4 separation performance of PDXLA8 at 50°C, (Reproduced with permission from H. Lin *et al.*,[47], copyright 2022, American Chemical Society).

it results in increased permeability with the loss of selectivity. Nevertheless, the PDXLA-based membrane displayed superior CO_2/N_2 performance on the upper bound line (Fig. 2c), which may be attained by its high flexibility and solubility selectivity[30,31,47].

5.2. Absence of competitive sorption behavior

The separation performance of the membrane at the mixed gas condition and in the presence of other impurities is crucial as it is the actual scenario for industrial application[30,31,47,48]. Most of the high-performance glassy polymers show worse performance for mixed gas separation compared to ideal gas separation due to the competitive sorption of different gases. In contrast, the PDXLA-based rubbery polymer membranes did show even better performance in the mixed gas separation performance in the presence of other hydrocarbon and humidified conditions (Figs. 2d,e, and Table 1), elucidating its potential in real applications[30,47]. It is attributed to CO_2-selective high ether oxygen in the PDXLA membranes.

5.3. Performance at high pressure

The PDXLA-based polymer membrane displayed much better CO_2 separation performance in a high-pressure environment than pure gas separation performance (Fig. 2)[30,31,47,48]. It is attributed to the competitive effect of plasticization and pressure-induced compaction. In the case of high ether oxygen-containing CO_2 philic flexible polymer, the permeability of polar CO_2 is enhanced by the plasticization effect over polymer densification. In contrast, other gases with large diameters and/or non-polar (e.g., CH_4, N_2) nurture negatively affected by pressure-induced compaction and reduced permeability. Thus, the CO_2/N_2 selectivity increased with increasing pressure. Increasing selectivity while maintaining a nearly constant CO_2 permeability is very beneficial for the CO_2/N_2 gas separation performance[9].

5.4. Performance evaluation over time (Anti-aging)

The gas permeability of the glassy polymer membrane significantly decreases with time because the non-equilibrium free volume is reduced over time and yields compacted polymer with unstable separation performance. The PDXLA-based flexible membranes displayed very stable CO_2/gas separation performance demonstrating its benefit for long-term applications (Fig. 2d)[30,31,47-49].

6. Evaluation of CO_2 Separation Performance of 1,3-dioxolane Membranes

As described in the introduction, the gas separation performance of any polymer-based dense membrane usually can be verified by the well-known trade-off line, called Robeson upper bound line, and high-performance material lies beyond the advanced upper bound line available over time. Prof. Lin's group reported the validity of the CO_2/N_2 and CO_2/CH_4 separation performance of the 1,3-dioxolane-based membranes, as presented in Figs. 3 and 4.

As shown in Fig. 3, the CO_2/N_2 separation performance of pure 1,3-dioxolane containing polymer (PDXLA) membrane is very close, and in some cases, it surpassed the upper bound line 2008, having CO_2 permeability value of 180~220 Barrer and CO_2/N_2 selectivity above 56, using pure and mixed gas experiments (Table 2)[31,47,49]. The high performance of PDXLA membranes is attributed to the presence of an optimum CO_2 selective ether oxygen (O/C ratio-0.66) in this polymer. However, CO_2/CH_4 separation performance

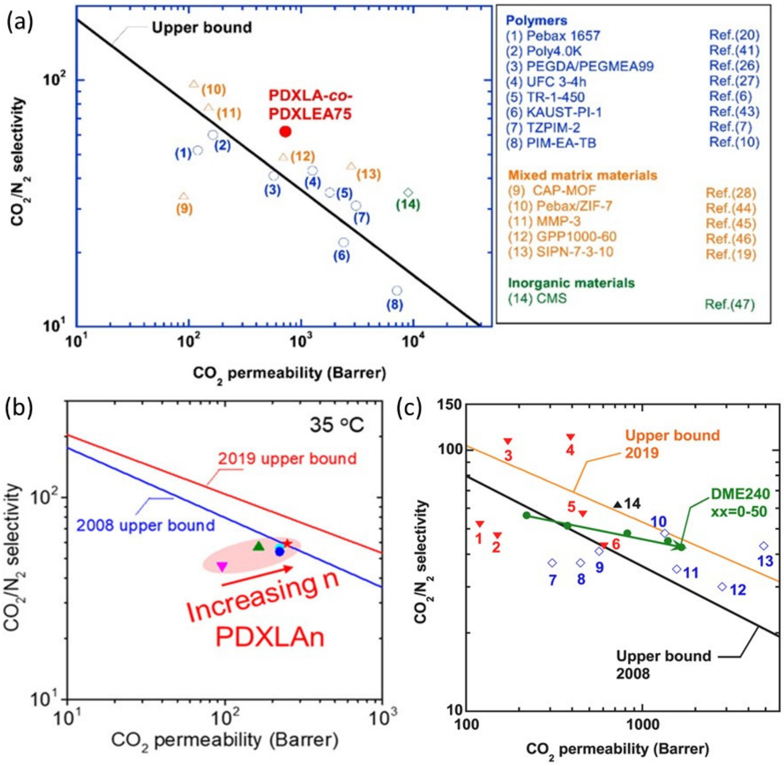


Fig. 3. Robeson Upper bound relation for the comparison of CO_2/N_2 separation performance of the 1,3-dioxolane-based acrylate (PDXL) membranes (PDXLA) with other copolymers or blend composition: (a) copolymer of PDXLA with its ethoxy chain end version (polydioxolane ethyl acrylate, PDXLEA) (Reproduced with permission from H. Lin *et al.*[30], copyright 2019, Elsevier), (b) hyperbranched PDXLAn membranes with a different chain length of (1,3-dioxolane) (Reproduced with permission from H. Lin *et al.*,[47], copyright 2022, American Chemical Society), and (c) PEG/ PEG dimethyl ether (PEGDME) loaded blend PDXLA membranes (Reproduced with permission from H. Lin *et al.*,[48], copyright 2022, Elsevier).

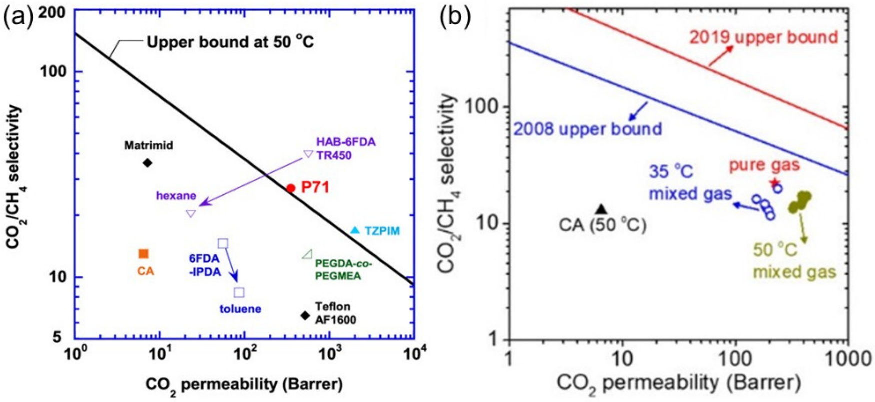


Fig. 4. Robeson Upper bound relation for the comparison of CO_2/CH_4 separation performance of the 1,3-dioxolane-based acrylate (PDXL) membranes (PDXLA) with other copolymers or blend composition: (a) copolymer of PDXLA with 1,3,5-Trioxane[31], and (b) hyperbranched PDXLAn membranes with a different chain length of (1,3-dioxolane) (Reproduced with permission from H. Lin *et al.*,[47], copyright 2022, American Chemical Society).

lies away from the 2008 upper bound line due to the moderate CO_2/CH_4 selectivity (~21) of mixed gas with a similar level of CO_2 permeability (~220 Barrer) (Fig. 4)[31,47].

Various copolymerization or blending approaches have been explored to enhance the separation performance of pure PDXLA membranes. For example, the increase of the ether oxygen content in PDXLA by the incorporation of 1,3,5-dioxane significantly enhanced the CO_2/hydrocarbon separation performance, which surpassed the upper bound line 2008 for CO_2/CH_4 (Fig. 4a) due to the dramatic increase of CO_2 selectivity over other gases[31]. A simple modification at the end of the branch chain of DXLA with ethoxy group greatly enhanced the CO_2/N_2 separation performance, placing them beyond the 2008 upper bound line (Fig. 3a) having a permeability of 1400~1700 Barrer with a flue gas selectivity ranges 47~64 (Table 2)[30]. Finally, the plasticization of PDXLA with PEG/PEGDME as a simple blend membrane demonstrated an outstanding CO_2/N_2 separation performance above the 2008 upper bound line (Fig. 3c) and was very close to 2019[48].

These results demonstrated that the ether oxygen-containing 1,3-dioxolane is very effective in enhancing the CO_2 selectivity over the other gases by increasing solubility selectivity. However, only high ether oxygen content alone in 1,3-dioxolane is insufficient to excel in the overall CO_2 separation performance. It is evident to design polymer materials rationally, combining both solubility and diffusivity-driven parameters. We are happy to share our concept to facilitate the separation performance in the final section.

6. Conclusion and Future Perspective

This review article has summarized up-to-date progress on 1,3-dioxolane-based polymer membranes concerning concering their basic properties and gas separation performance. The polymer membranes obtained from 1,3-dioxolane-based acrylate displayed an excellent CO_2 selective gas separation performance due to optimum ether oxygen (O/C) content with its flexible nature. However, the permeability of these dense membranes is still low (180~220 Barrer) for the cost/energy efficient CO_2 separation application, which rationally demands collaboration/combination with other materials. It is updated that adding helping materials accelerated the separation performance of 1,3-dioxolane-based membranes. However, several staffs have to be improved for real industrial applications, including high flux, mechanical stability, and mechanical stability, and the ability to form thin film for composite membranes.

Based on the experimental results obtained, discussions presented, and conclusions drawn from this

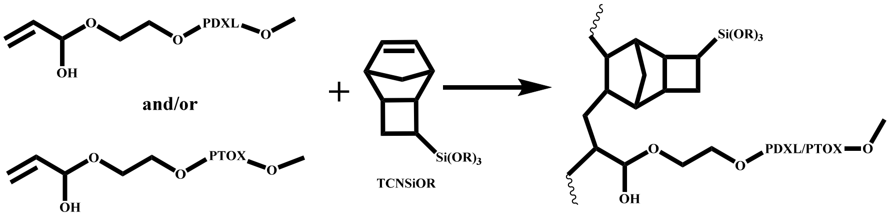


Fig. 5. Copolymerization of DXL with high permeable TCNSi(OR)$_3$.

research study, the following recommendations may provide further insight into future investigations related to developing membranes with potentially high separation performance and innovation in membrane fabrication technology.

6.1. Copolymerization with TCNSi(OR)$_3$

Combination of PDXLA with high permeable and solubility selective "Janus polymer" (glassy polymer, but has rubbery nature as well) such as 3-Tri(n-alkoxy) silyltricyclo[4.2.1.02,5] non-7-ene, (TCNSiOR) would enhance the mechanical durability and gas permeability of the corresponding polymer membranes.

6.2. Combined with PDMS

PDMS is a widely known highly permeable rubbery polymer for various applications, including CO$_2$ separation. PDMS-based macro-monomer can be linked up with PDXLA through random copolymerization. A control phase-separated morphology can be attained from the combination of different types of branched chains, where gas permeability can be facilitated by soft hydrophobic PDMS segment and CO$_2$ selectivity can be achieved by hydrophilic PDXL units.

6.3. Synthesis of solution-processable MOF for hybrid membranes

Porous MOF that can be processed in the solvent while retaining its crystal structure and intrinsic porosity is highly demanding. Either post-synthesis modification of MOF or pre-synthesis linker modification of MOF with this DXL-based monomer is expected to yield a solution processable MOF because of the wide range of solubility of DXL. If so, the polymerization of DXL-modified MOF is expected to yield polymerized MOF-based MMMs with an ideal polymer-MOF-polymer interface. Besides, solution-processable DXL-MOF suspension can be utilized as a thin skin layer of the composite membrane to explore the formation of gas transport channels, which is very challenging and, at the same time, very demanding for membrane-based gas separation. An active channel is expected to boost the hybrid membranes' separation (conductive) performance.

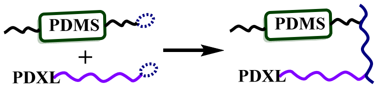


Fig. 6. Combination of DXL with high permeable PDMS.

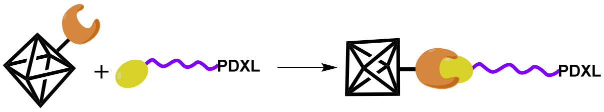


Fig. 7. Combination of DXL with solution-processable MOF.

6.4. Exploring new applications for the PDXL polymers

The 1,3-dioxolane-based membrane displayed good physical properties, including amorphous nature at room temperature and excellent flexibility. These membranes have been utilized only for CO$_2$/gas separation applications. The uses for these polymers should not be limited to gas separation only but could be found in new applications in various fields such as water purification, fuel cell-based polymer electrolyte membranes, battery separators, and organic vapor removal.

Acknowledgments

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