



## Effect of Chain Extender Length on Gas Permeation Properties of Polyurethane Membranes

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### ABSTRACT

The effects of chain extender length on the gas permeability of polyether-based polyurethanes were investigated. Synthesized polyurethanes were based on 1000 and 2000 molecular weight polytetramethylene-glycol (PTMG) with toluene diisocyanate (TDI). Ethylene glycol, 1,4-butane diol (BDO), 1,6-hexane diol (HDO) and 1,10-decane diol (DDO) chain extenders were used to complete the conversion of pre-polymers to the final polyurethanes. Membranes made from polyurethane were used to study the permeability and diffusivity of nitrogen, oxygen, methane, and carbon dioxide. Lag time method was used to determine the diffusivity of gases in polyurethanes. This study indicated that glass transition temperature of the polymers decrease by chain extender's length. The increase in chain extender's length makes the phase separation more probable. DSC and FTIR studies also indicate the extent of the phase separation in polyurethanes. Permeability and diffusivity of gases increase with the increasing length of the chain extenders. Selectivity of CO<sub>2</sub>/N<sub>2</sub> changed by chain extender length, while selectivity of CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> did not show any remarkable changes. This study shows that solubilization is the dominant mechanism in gas permeation process in polyurethane membranes.

### Key Words:

membrane;  
polyurethane;  
chain extender;  
gas separation.

### INTRODUCTION

Polymeric membranes have reached a new and high growth rate in gas separation processes. This growth has achieved a higher task due to low energy consumption and low volume, weight, and investment with the least environmental effects [1]. The improved efficiency of gas separating membranes

has been investigated and research on microstructure of the polymers is currently continued [1-3].

The improved efficiency of the membranes is highly dependent on the factors affecting the functions of these membranes in separation process. In this respect, polyurethanes with rigid urethane/urea

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blocks and soft segments, ethers or esters, have gained a considerable importance and interest. The hard segments of urethane or urea are the result of diisocyanate reaction with diols or diamines while, the diol or diamine is just a chain extender. The soft segments are the ester or ether macromolecules with a high molecular weight. These reactions easily produce a wide variety of microstructure in polyurethane that can allow us to design a membrane with a desired property. Therefore, all important elements considered in the synthesis of polyurethanes including the material selection, mole percent, molecular weight of polyol as well as synthesis method can affect the permeability and selectivity of gases in polyurethane membranes.

The current research works in this area show that the polyol and its length, kind and type of the hard segments greatly influence the gas transport properties of polyurethane membranes [4-19]. In addition, the type of chain extender may influence the crystallinity, phase separation, and density as well, and the glass transition temperature can change the gas separation properties of polyurethanes [6-8]. Teo et al. have shown that amine chain extenders can affect the gas separation properties of polymers by changing the phase separation and glass transition temperature of poly(urethane-urea)s [14-16].

Some research works are focused on addition of soft siloxane chains as soft segments in polyurethane matrices [20-23]. Reported results show that by increasing the siloxane chains in polyurethanes the permeability of carbon dioxide increases up to 900 barrer [22]. The final research carried out by this group has shown that permeability is drastically increased for the soft segment length of polyurethanes with the same hard segment content [24]. In addition, there has been some efforts to enhance separation properties of polyurethanes by blending them with other polymers like polyethylene glycol and poly(methyl methacrylate) in gas separation and pervaporation processes [25-26].

The effects of chain extender lengths on the gas separation properties of polyurethanes have not been reported yet and therefore in this study, four different length chain extenders were used to tailor the gas transport properties by varying the polymer microstructure. The permeability of N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and

CO<sub>2</sub> gases were then studied and the systems capabilities in gas separation processes with the considerable importance, like separations of oxygen and nitrogen from air, carbon dioxide from methane in natural gas treatment application, and carbon dioxide from nitrogen in pollution control in chemical industries have been investigated. In this paper the gas permeation properties of the prepared membranes have been discussed and the structure characteristics of polyurethanes are elucidated in detail.

## EXPERIMENTAL

### Materials

Polytetramethylene glycol, PTMG, ( $M_w=2000$  and  $M_n=1000$ ) were obtained from Arak Petrochemical Complex (Arak, Iran) and dried at 80°C under vacuum for 48 h to remove the residual water before use. Ethylene glycol (EDO), 1,4-butane diol (BDO), 1,6-hexane diol (HDO), and 1,10-decane diol (DDO) chain extenders were purchased from Merck. Ethylene glycol and 1,4-butane diol were dried over 4Å molecular sieves while 1,6-hexane diol and 1,10-decane diol were dried in vacuum oven in 60°C for 5 h. Toluene diisocyanate (TDI) and dibutyltin dilaurate (DBTDL) catalyst were purchased from Merck and used without further purification. Tetrahydrofuran (THF) solvent used for membrane preparation was purchased also from Merck. The CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> used for gas permeation tests were 99.99% pure and they were obtained from Roham Gas Co., Tehran, Iran. Methane with 99.95% purity was also obtained from Air Products Co.

### Polymer Synthesis

Polymerization was performed in a 250 mL three-necked round-bottomed flask equipped with a mixer shaft. Nitrogen gas inlet tube and raw material entrance were placed in 95°C oven for 24 h [20]. Nitrogen gas was dried by passing through concentrated sulphuric acid and silica gel media and entered to the reactor.

All polyurethanes were synthesized by two-step bulk polymerization technique [24]. Polytetramethylene glycol ( $M_n=1000$  and  $M_n=2000$ ) reacted with toluene diisocyanate (TDI) for 2 h at 85-90°C under

nitrogen atmosphere for obtaining macrodiisocyanate prepolymer. The chain extension of polymer occurred by addition of EDO, BDO, HDO, and DDO after prepolymerization step at room temperature. In order to obtain linear polymer, the mole ratio of NCO and OH was kept 1:1. All polymers were synthesized by (1/3/2) mole fraction of (polyol/diisocyanate/chain extender) components.

### Membrane Preparation

Polyurethane membranes were prepared by dry phase inversion method. The synthesized thermoplastic polyurethanes were dissolved in tetrahydrofuran at 50°C under solvent refluxing and cast in Petri dishes at room temperature (the concentration of polyurethane in THF was 10 wt%). The membranes were formed by evaporating the solvent for 24 h at room temperature. For complete removal of the solvent, the prepared membranes were placed in vacuum oven at 60°C for 5 h. The final thicknesses of membranes were 100-150 micrometer.

### Characterization

The obtained functional groups in synthesized polyurethanes were investigated by FTIR spectrometer Bruker model Equinox 55, Germany, in the range 4000-500  $\text{cm}^{-1}$ . The thermal behaviour of polyurethanes investigated by differential scanning calorimetry (DSC) Metler-Toledo DSC822<sup>e</sup>, Switzerland, with 5°C/min heating rate.

### Gas Permeation

The permeability of oxygen, nitrogen, methane, and carbon dioxide were determined using constant pressure/variable volume method at 10 bar pressure and at 25°C [24].

The gas permeability of membranes was determined using the following equation:

$$P = \frac{ql}{(P_1 - P_2)A} \quad (1)$$

where, P is permeability expressed in barrer (1 barrer =  $10^{-10} \text{ cm}^3(\text{STP})\text{cm}/\text{cm}^2 \text{ s.cmHg}$ ), q is flow rate of the permeate gas passing through the membrane ( $\text{cm}^3/\text{s}$ ), l is membrane thickness (cm),  $P_1$  and  $P_2$  are the absolute pressure of feed side and permeate side,

respectively (cmHg), and A is the effective membrane area ( $\text{cm}^2$ ).

The gas permeation tests were carried out at least 3 times and the results with less than 7% error were recorded. The ideal selectivity of membrane was calculated from a single gas permeation experiment from eqn (2):

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

the diffusion coefficient (D) was determined by the time lag method, represented by eqn (3):

$$D = \frac{L^2}{6\theta} \quad (3)$$

where,  $\theta$  is the time lag (s), i.e., the intercept obtained from extrapolating the linear region of the P versus the time plot to the time axis. L is membrane thickness (cm), and D is diffusion coefficient ( $\text{cm}^2/\text{s}$ ). The solubility coefficient (S) was then calculated from the eqn (4):

$$S = P/D \quad (4)$$

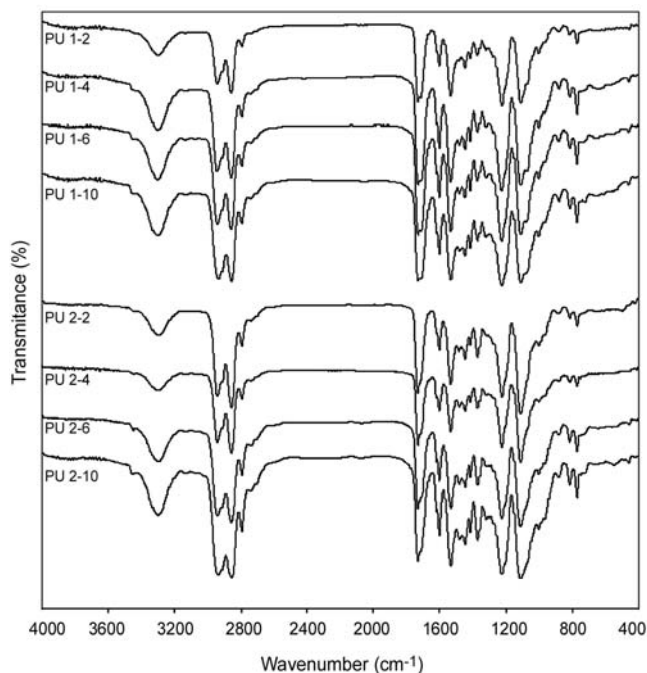
## RESULTS AND DISCUSSION

### FTIR Analysis

Characterization of prepared polyurethanes was studied by FTIR analysis. This analysis was used to check the completion of the polymerization reaction and characterization of the final prepared polyurethanes. The disappearance of NCO peak at  $2270 \text{ cm}^{-1}$  in Figure 1 was used to show that the isocyanate reaction was completed.

The N-H stretching of urethanes appears at  $3300 \text{ cm}^{-1}$  and C=O stretching at  $1600-1730 \text{ cm}^{-1}$  (Figure 1). The  $\text{CH}_2$  signals of polytetramethylene glycol appear at  $2940$  and  $2856 \text{ cm}^{-1}$  and the C-O-C ether at  $1110$  and  $1111 \text{ cm}^{-1}$  for PTMG1000 and PTMG2000 based polyurethanes [24]. The phase separation of hard and soft segments has been studied using the carbonyl stretching in polyurethanes [27-29].

Figure 2 represents the carbonyl stretching peak in

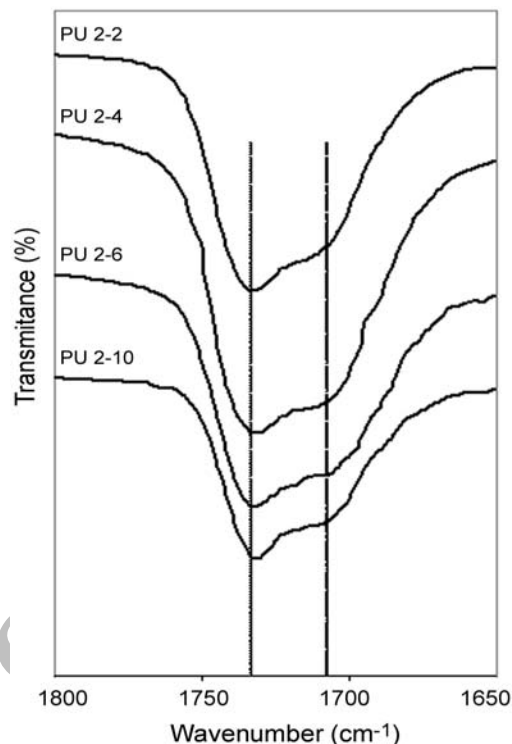


**Figure 1.** FTIR Spectra of synthesized polyurethanes.

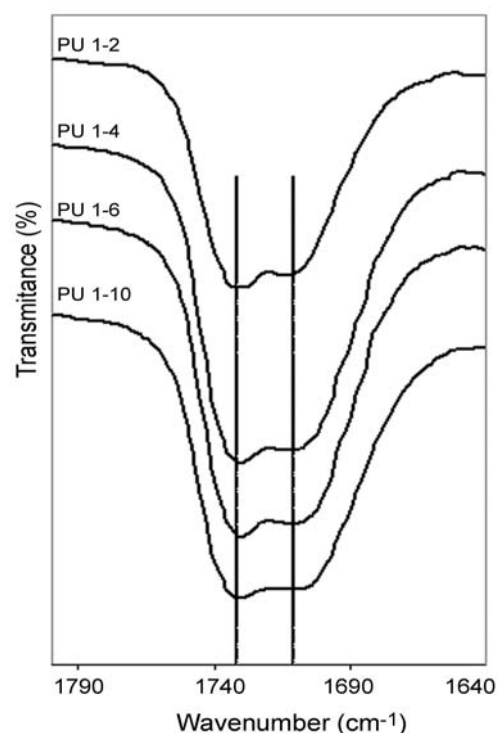
the range of 1650-800  $\text{cm}^{-1}$  for PTMG1000 and PTMG2000 based polyurethanes.

The free carbonyl groups appear at 1732  $\text{cm}^{-1}$  and the peak for carbonyl groups connected to N-H urethane by hydrogen bonding appears in 1710  $\text{cm}^{-1}$  for both two polyurethane groups. The small increase intensity of peaks in 1710  $\text{cm}^{-1}$  and the decrease intensity of peaks in 1732 are related to the increasing chain extender length. The increase in chain extender length may be responsible for the larger phase separation of hard and soft segments. This is expected from the higher hydrogen bonding of the carbonyl groups to the N-H urethane groups.

It is reported that the bonded carbonyl is related to hydrogen-bonded groups in the hard segments while the free carbonyl may correspond to those groups in the hard segment domains, the soft segment domains, or their interfaces [30-32]. The increasing hydrogen bonding between carbonyl groups and N-H urethane groups lead to higher phase separation in polyurethane structure. The increasing bonded carbonyl groups consume a greater amount of N-H urethanes in bonding process. Therefore, there is less bonding available for the hard segments and ether group in the soft segments. Thus, it results in phase separation of hard and soft segments.



(a)



(b)

**Figure 2.** FTIR Spectra in the range 1600-1800  $\text{cm}^{-1}$  (a) PTMG 1000 and (b) PTMG 2000 based polyurethanes.

The amounts and the variation of hydrogen bonding can be represented by hydrogen bonding index, HBI, [28]. HBI value is specified by the ratio of carbonyl bands in eqn (5):

$$\text{HBI} = \frac{A_{\text{C=O,bonded}}}{A_{\text{C=O,free}}} \quad (5)$$

Where,  $A_{\text{C=O,bonded}}$  and  $A_{\text{C=O,free}}$  are the absorbance of bonded and free carbonyls, respectively. The variation of HBI with respect to chain extender length and polyol are investigated in this research. Results indicate that HBI increases by increasing the chain extender length. HBI in PTMG1000 based polymers increases from 0.854 to 0.931 and in PTMG2000 based polymers this increase takes place from 0.847 to 0.877 for ethylene glycol to decane diol, respectively.

### Thermal Analysis

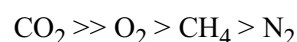
The thermal properties of synthesized polyurethanes were investigated by differential scanning calorimetry method. Our results are reported in Table 1. The comparison between glass transitions of PTMG2000 and PTMG1000 based polymers show that the increasing length of polyol drastically decreases the glass transition temperature. These results are consistent with the higher flexibility related to a longer chain mobility of PTMG2000 based polyurethanes. Therefore, the glass transition temperature in Table 1 decreases with the increasing the chain extender length. This also shows that the decreasing glass transition temperature is

related to the larger mobility of the macromolecule [32]. It is suggested that the larger mobility of polyurethane is based on two mechanisms. The first mechanism is based on the phase separation of hard and soft segments that can lead to greater flexibility of soft segments and larger molecular mobility of polyether chains. The second mechanism that is considered for all polymers is based on the changes of the main chain of the polymer which can lead to higher vibration and mobilities in the macromolecular main chain structure.

As shown, the addition of -C-C- linkage leads to longer chain in polymer, higher molecular vibration, and lower  $T_g$  [32]. The extender chain length in our results shows that the microphase separation of the hard and soft segments may increase because of the higher HBI from FTIR results. We also suggest that the reduction in glass transition temperature of the synthesized polyurethanes in this research is due to phase separation.

### Gas Permeation

The first and more important factor to design a gas separation membrane process is the permeability and selectivity properties of the membrane. In this study, the permeability of  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CH}_4$ , and  $\text{CO}_2$  through prepared membranes were investigated at 25°C and 10 bar pressure. The permeability results for PTMG1000 and PTMG2000 based polymers are shown in Table 2. The permeability of gases changes according to a specific order of:



**Table 1.** Compositions and thermal properties of synthesized polyurethanes.

Polymer code	Components of polymers		Hard segment (wt%)	HBI	$T_{g1}$ (°C)	$T_{g2}$ (°C)
	Polyol	Chain extender				
PU 1-2	PTMG1000	Ethylene glycol	44.3	0.854	-17.19	48.2
PU 1-4	PTMG 1000	1,4- Butane diol	45.8	0.857	-20.83	62.9
PU 1-6	PTMG 1000	1,6- Hexane diol	47.4	0.887	-23.22	48.2
PU 1-10	PTMG 1000	1,10- Decane diol	50.3	0.931	-25.14	49.1
PU 2-2	PTMG 2000	Ethylene glycol	28.4	0.847	-47.14	39.0
PU 2-4	PTMG 2000	1,4- Butane diol	29.7	0.843	-55.00	66.4
PU 2-6	PTMG 2000	1,6- Hexane diol	31.1	0.850	-55.90	48.8
PU 2-10	PTMG 2000	1,10- Decane diol	33.6	0.877	-57.34	60.7

**Table 2.** Permeability coefficients for different gases in various polyurethane membranes at 25°C and 10 bar.

Polymer	Permeability (barrer) ( $10^{-10}$ cm <sup>3</sup> (STP)cm/cm <sup>2</sup> s.cmHg)			
	N <sub>2</sub>	O <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>
PU 1-2	0.70	2.11	1.74	24.20
PU 1-4	0.70	2.40	1.92	26.50
PU 1-6	0.78	2.48	2.15	29.20
PU 1-10	0.83	2.68	2.18	32.13
PU 2-2	2.10	5.80	5.60	70.00
PU 2-4	2.57	7.06	6.35	82.00
PU 2-6	2.83	7.20	6.63	87.40
PU 2-10	3.25	7.30	6.74	90.00

As known in solution-diffusion mechanism, the gas permeability is a function of solubility and diffusivity in polymer [1]. Because of high condensability and low molecular size of CO<sub>2</sub> its permeability is high in comparison with the other gases. In case of oxygen, a higher permeability is observed due to its lower molecular size in comparison to methane and nitrogen. While, in the case of nitrogen and methane the molecular size of methane is higher than nitrogen but the permeability of nitrogen is lower. The higher permeability of methane is due to its higher condensability. Therefore, these results indicate a dominant role of solubility mechanism in permeation of gases in polyurethane membranes.

By comparing the gas permeability of PTMG1000 and PTMG2000 based polyurethanes it becomes evident that the permeability of gases with multiplying factor of 2.7 increases to 3.9 with the longer polyol. This jump in permeability with longer polyols is due to:

1- The hard segment content in PTMG1000 is 1.5 times more than PTMG2000 based polymers. As it is reported by researchers, with increasing hard segment content, the impermeable regions in polymer increase and gas permeability is reduced drastically [17-19].

2- The chain mobility increases in longer polyols and therefore it increases the gas diffusion in polyurethanes [24].

3- The FTIR results indicate that the polyol length phase separates the hard and soft segments of the polyurethane and it increases the chain flexibility and

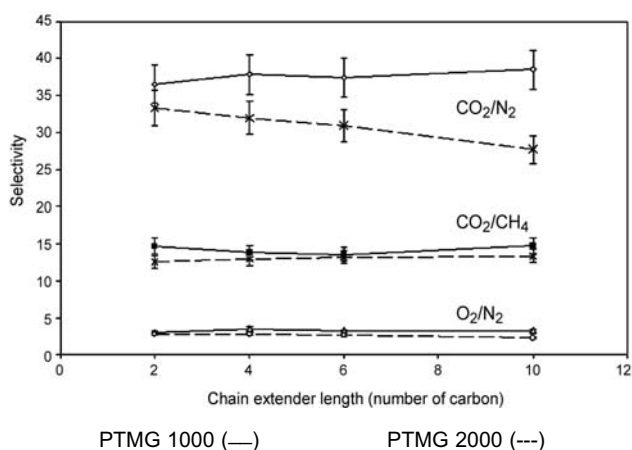
gas solubility in polymer because of the solubility of existing sites in polyurethane.

The comparison between oxygen and methane permeability shows that the ratio of O<sub>2</sub>/CH<sub>4</sub> is increased by decreasing the polyol length. This may be attributed to the nature of the gases and polymer properties. Methane with a larger size is more condensable than oxygen. The increasing length of polyol also makes the polymer more rubbery. In addition, it was shown that by increasing the length of polyol the polymer would be more rubbery, as this makes the gas permeability of methane to be closer to oxygen [1-3].

The results reported in Table 2 show that the chain extender length also has the same effect. The permeabilities of N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> are increased from 0.7, 2.11, 1.74, 24.2 to 0.835, 2.68, 2.18, 32.13 barrer in PTMG1000 based polymers and they are increased from 2.1, 5.8, 5.6, 70 to 3.25, 7.3, 6.74, 90 barrer in PTMG2000 based polymers, respectively.

FTIR analysis shows that by increasing the chain length the phase separation of hard and soft segments increases and leads to less interconnection and interaction of hard and soft segments. This phenomenon leads to more chain mobility [9,19]. The DSC results confirm the same when it is shown that the glass transition temperature is decreased.

Once the chain mobility of the polymer is increased by increasing chain extender length, the space created for diffusion of permeant molecules through membrane is also increased. This makes the pathways for diffusion of gases in free paths to be far



**Figure 3.** Selectivity of CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, and O<sub>2</sub>/N<sub>2</sub> gases vs. chain extender length through polyurethane membranes based on PTMG1000 and PTMG 2000.

greater. The data in Table 1 show that the hard segment increases by chain extender length.

Reported studies have shown that permeability of gases through polyurethane membranes is highly dependent on the chain extender and diisocyanate content in the polymer composition and permeability decreases by increasing in mole fraction of hard segment components [17-19]. Since, the mole fraction of the components in polyurethanes is the same (1/3/2 for polyol/diisocyanate/chain extender) we expect that the increase in the hard segments to be due to the increasing molecular weight of the chain extenders. Therefore, in addition to the existing urethane linkage, the increase in the chain extender length is expected to increase the effective intermolecular distance involved in the hydrogen bonding of the hard segments of the polymer and increase the mobility of the hard segment.

The results of selectivity of CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, and O<sub>2</sub>/N<sub>2</sub> gas pairs in polyurethanes are shown in Figure 3. In this case, solubility mechanism in polymers is dominant and makes the CO<sub>2</sub>/N<sub>2</sub> selectivity to be about twice more than that of CO<sub>2</sub>/CH<sub>4</sub> in polymers. The CO<sub>2</sub>/N<sub>2</sub> selectivity of PTMG1000 based polymers increases from 34.6 to 38.5 for higher chain extender length, while the selectivity of CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> gases is the same and do not show any changes.

The increasing of CO<sub>2</sub>/N<sub>2</sub> selectivity may be due to the increasing of rubbery property of polymer.

While, increasing the hard and soft segment phase separation leads to solubilization as a dominant mechanism in polymer morphology. Because of high condensability difference in CO<sub>2</sub> and N<sub>2</sub> gases by increasing the chain extender length the permeability of carbon dioxide increases more than nitrogen and therefore, the selectivity of this pair of gases increases.

While, CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> gases are condensable and non-condensable pairs, respectively and they display same behaviour, by variation of polymer nature the permeability of both gas pairs change similarly and leave the same selectivity. In PTMG2000 based polymers, by increasing the chain extender length the selectivity of CO<sub>2</sub>/N<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub> decrease from 33.3 to 27.7 and 2.76 to 2.25, respectively. Notice that the CO<sub>2</sub>/CH<sub>4</sub> selectivity does not change.

The reduction in gas selectivity is due to higher molecular motion and decreasing the molecular sieve properties of membrane. A comparison in the selectivities of CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, and O<sub>2</sub>/N<sub>2</sub> in PTMG1000 and PTMG2000 based polymer systems shows that by increasing the polyol length the selectivity of gases decreases. This is due to a larger molecular motion and long segmental mobility of polyol chains in PTMG2000 based polymers that lead to lower molecular sieve properties of polymer.

### Diffusivity and Solubility

In this research the diffusion coefficient of gases through polymers calculated by time lag method using eqn (3). The solubility constant for each gas was calculated from eqn (4). The diffusivity and solubility of gases in synthesized polyurethanes are listed in Table 3.

The diffusivity of gases varies according to the order CO<sub>2</sub>>O<sub>2</sub>>N<sub>2</sub>>CH<sub>4</sub>. The order of diffusivity is the reverse of the kinetic diameter for each gas. By increasing the molecular size, the diffusivity of gas decreases. The reported results indicate the increasing of gas diffusivity by increasing the chain extender length. Wang et al. have shown the free volume sizes and fractional free volume increase by increasing the phase separation in polyurethanes [33]. They established a direct relationship between the gas permeability and the free-volume based on the free-volume parameters and gas diffusivity measured. They show

**Table 3.** Diffusivity coefficients and solubility coefficients for different gases in various polyurethane membranes at 25°C and 10 bar.

Polymer	Diffusivity $\times 10^{-7}$ (cm <sup>2</sup> /s)				Solubility $\times 10^{-3}$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> .cmHg)			
	N <sub>2</sub>	O <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>
PU 1-2	1.03	1.4	1.01	2.68	0.68	1.51	1.73	9.03
PU 1-4	1.04	2.59	1.04	3.80	0.67	0.927	1.85	6.84
PU 1-6	1.05	2.18	0.95	3.47	0.743	1.14	2.26	8.41
PU 1-10	2.11	3.01	1.30	5.48	0.396	0.894	1.68	5.86
PU 2-2	1.01	1.74	0.97	3.29	2.08	3.33	5.79	21.3
PU 2-4	1.25	1.84	1.17	3.75	2.06	3.84	5.43	21.9
PU 2-6	1.65	2.09	1.58	4.25	1.71	3.19	4.20	20.6
PU 2-10	2.28	3.07	2.15	5.07	1.43	2.38	3.13	17.8

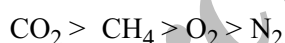
the free volume and fractional free volume increase by decreasing the phase connection and mixing in polymer [33].

As shown by FTIR and DSC analyses the phase separation of hard and soft segments increases by increasing the chain extender length. Therefore, due to FTIR and DSC analyses and the results reported by Wang et al., the increasing diffusivity constant in Table 3 is related to:

1- The higher molecular motion due to phase separation.

2- The increasing size and fractional free volume in polymer.

The gas solubility of polymers reported in Table 3 shows the following order:



This order is similar to condensability of gases and the condensability itself is related to the molecular interactions and solubility of gas molecules in polymers.

PTMG2000 based polyurethane indicated a drastically higher gas solubility which shows that polyol length controls the gas solubility of polyurethane membranes. By increasing the polyol length, the rubbery properties of polymers increased which led to higher condensation of gases in this polymer. These results confirm the domination of solubility mechanism in permeation of gases through the synthesized polyurethanes.

## CONCLUSION

The effects of chain extender length on gas permeation properties of a series of polyether-based polyurethanes were investigated. Ethylene glycol, 1,4-butane diol, 1,6-hexane diol and 1,10-decane diol chain extenders were used to complete the conversion of prepolymers to the final polyurethanes. The permeability and diffusivity of nitrogen, oxygen, methane, and carbon dioxide were studied through synthesized polyurethanes. It indicated that chain extender length increases the phase separation of hard and soft segments in polyurethanes. The permeability and diffusivity of gases increase with the increasing length of the chain extenders. It is obvious that the selectivity of CO<sub>2</sub>/N<sub>2</sub> gases changes by chain extender length, but for CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> gases these changes in selectivities are not remarkable. This study also shows that solubility is the dominant mechanism in the gas permeation process in polyurethane membranes.

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