



## The Effect of Hard Segments on the Gas Separation Properties of Polyurethane Membranes

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Received 25 June 2007; accepted 4 December 2007

### ABSTRACT

Effect of hard segment content was investigated on the gas permeability characteristics of polyether based urethanes. These polymers were synthesized by using 2000 molecular weight polypropylene-glycol (PPG 2000) with toluene diisocyanate (TDI). Conversion of prepolymer to a final PU was carried out by using 1,4-butane diol (BD) as a chain extender. Four different block ratios were chosen in order to prepare polyurethanes with different hard segment contents. The PPG1000 polyol based PU with the same content of hard segment was also synthesized to evaluate the effect of soft segment length on the gas separation properties of the polyurethanes. The prepared polymers were characterized and the permeability of gases was investigated. Permeation measurements of polymers have revealed that the permeabilities of gases decrease with increasing the hard segment content by which the selectivity of gases in polymers increases as well. The polymer containing 42.7 wt% hard segment has shown that its CO<sub>2</sub> permeability coefficients and ideal separation factors relative to N<sub>2</sub> are higher than 38.2 barrer (1 barrer = 1×10<sup>-10</sup> [cm<sup>3</sup> (STP) cm/cm<sup>2</sup>.s.cmHg]) and 33.21, respectively. While, the polymer containing 26 wt% hard segment showed 79.5 barrer and 20.9 values, respectively. The gas permselectivities of polymers containing the same hard segment content with different soft segment lengths have shown that by increasing the soft segment length the permeability towards gases increases, meanwhile their gas selectivity decreases.

### Key Words:

membrane;  
gas separation;  
polyurethane;  
hard segment.

### INTRODUCTION

Membrane-based gas separation method is an energy efficient, low-cost maintenance, non-environmental emission, compact, and modular procedure. Because of these advantages, in the past decade, a great deal of interest has been focused on the development of new high-performance polymer-

ic membrane materials with high permeability and permselectivity for gas separation applications.

The progress in the field of gas separation by membranes has been very fast and a considerable volume of literature is now available [1–15]. Gas separation with polymeric membranes is used in a wide

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variety of applications, such as removal of carbon dioxide and hydrogen sulphide from natural gas, the recovery of hydrogen from ammonia in petrochemical industries, separation of biogas and landfill gas, the production of oxygen and nitrogen enriched stream from air, etc. In search for superior membranes, some investigators have studied gas permeation properties of polyurethanes [4-10].

Polyurethanes (PU) are materials which have been investigated particularly for the possibility of tailoring their transport properties by varying their microstructures. These polymers are composed of alternating urethane or urea hard segments and polyol (polyether/polyester) soft segments. The urethane/urea hard segments consist of organic diisocyanate and low molecular weight diol/diamine chain extender while the soft segments consist of high molecular weight polyether/polyester. Factors such as reagents types, their initial composition, the molar mass of the macrodiol, as well as the synthesis method can affect the rate of permeation of gas molecules through a polyurethane membrane. The studies of gas transport properties of the polyurethane-based membranes have shown that the length of polyol, the type of soft segment, and type and proportion of hard segment influences the permeation properties of the membranes [11-15]. In addition, the type of chain extender also plays important role in permeation properties of the membranes as a result of changing the phase-separated domain morphology, crystallinity, density, and glass transition of the membranes [7-9].

Galland et al. have evaluated the effect of hard segment content on the polyurethane gas permeability by starting with a soft material and increasing its rigidity by variation of the molecular weight of the polyol [6]. Grabczyk et al. [9] and Knight et al. [10] have also evaluated the influence of hard segment on gas permeability of the PUs by variation of the length of polyols. Huang et al. [11] and Ruann et al. [12] have investigated the effect of hard segment content of hydroxyl terminated polybutadiene based polyurethane membranes by evaluating the permselectivity of oxygen and nitrogen gases through synthesized membranes.

In the present study the effect of mole fraction of hard segment components, diisocyanate, and chain extender (hard segment content) on the permselectiv-

ity of polyurethanes have been investigated by using polypropylene glycol ( $M_w=2000$ ), toluene diisocyanate and 1,4-butane diol. For evaluating the gas separation properties of the synthesized polyurethanes, the permeability of oxygen, nitrogen, methane, and carbon dioxide gases was tested through polymers with different hard segment contents. The effect of soft segment length on the gas permeability was also tested by preparation of two different molecular weight polypropylene glycol based polyurethanes with similar hard segment content. The structure-gas separation properties relationship of the prepared membranes is discussed on the basis of thermal behaviour of the polyurethanes.

## EXPERIMENTAL

### Materials

Polypropylene glycols, PPG, ( $M_w=2000$  and 1000) were obtained from Aldrich and dried at 80°C under vacuum for 48 h to remove the residual water before use. 1,4-Butane diol (BD) chain extender was purchased from Merck and dried over 4 Å molecular sieves. Toluene diisocyanate (TDI) was purchased from Merck. The dibutyltin dilaurate (DBTDL) supplied by Merck was used as a catalyst. Tetrahydrofuran (THF) solvent used for membrane preparation was also purchased from Merck. The  $CO_2$ ,  $N_2$  and  $O_2$  (purity 99.99%) gases used for gas permeation tests were purchased from Roham Gas Co., Tehran, Iran and also  $CH_4$  (purity 99.95%) was purchased from Air Products Co., USA.

### Polymer Synthesis

Polymerization was carried out in a 250 mL three-necked round-bottomed flask equipped with a mixer shaft, nitrogen gas inlet tube, and raw material entrance was placed in 95°C oven for 24 h. Nitrogen gas passed through concentrated sulphuric acid and silica gel media for complete drying before entering into the reactor. All polyurethanes were synthesized by a two-step bulk polymerization technique [19]. Polypropylene glycols ( $M_n=1000$  and 2000, Aldrich) reacted with toluene diisocyanate for 2 h at 85-90°C under nitrogen atmosphere for obtaining macrodiisocyanate prepolymer. The chain extending of polymer

occurred by addition of 1,4-butane diol after prepolymerization at room temperature. In order to obtain linear polymer, the mole ratio of NCO and OH was maintained at 1:1.

### Membrane Preparation

Polyurethane membranes were prepared by thermal 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 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 thicknesses of the prepared membranes, measured by a micrometer, were in the range of 150 to 200 micrometers.

### Characterization

The obtained functional groups in synthesized polyurethanes were investigated by FTIR Bio Rad spectrometer in the range 4000-500  $\text{cm}^{-1}$ . The thermal behaviour of polyurethanes was investigated by differential scanning calorimetry (DSC) Mettler-Toledo DSC822e and dynamic mechanical thermal analysis (DMTA) Triton Technology Co. Tritec2000 DMA, via 5°C/min heating rate.

### Gas Permeation

Nitrogen, oxygen, methane, and carbon dioxide permeabilities of the membranes were determined using the constant pressure/variable volume method at room temperature (25°C). The feed side pressure of the gases fixed at 10 bar. The permeate side was maintained at atmospheric pressure. Then, the flux of the permeated gases was measured by a U-shape flow meter. Figure 1 shows the schematic representation of the gas permeation equipment.

By plotting the flux of the permeated gas versus time, the permeability coefficient was calculated via the slope of the linear section of flux-time curve. The gas permeability was determined from the following equation:

$$P = \frac{ql}{(p_1 - p_2)A} \quad (1)$$

where, P is the gas permeability expressed in barrer

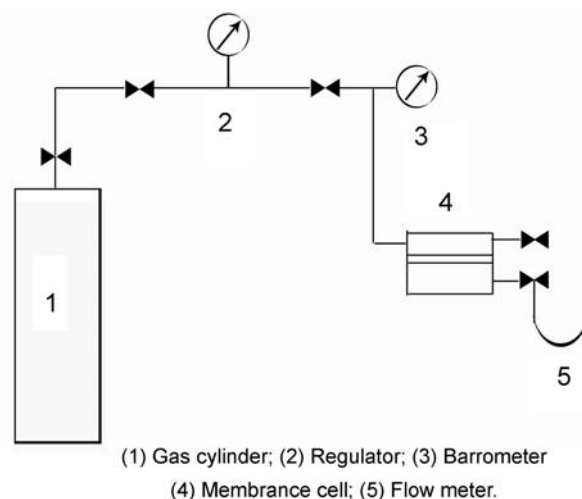


Figure 1. Schematic design of gas permeation apparatus.

units (1 barrer =  $10^{-10} \text{ cm}^3 \text{ (STP) cm/cm}^2 \cdot \text{s} \cdot \text{cmHg}$ ),  $q$  is flow rate of the permeated gas passing through the membrane ( $\text{cm}^3/\text{s}$ ),  $l$  is the membrane thickness (cm),  $p_1$  and  $p_2$  are the pressures at both sides of the membrane (cmHg), respectively and  $A$  is the effective membrane area ( $\text{cm}^2$ ). The ideal gas selectivity of a pair of gases calculated by the following equation:

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

where,  $\alpha_{A,B}$  is the ideal gas selectivity and  $P_A$  and  $P_B$  are the gas permeabilities of A and B gases, respectively.

## RESULTS AND DISCUSSION

### Characteristics of the Polyurethane-based Membranes

The molecular structure of the PU membranes was characterized by FTIR spectroscopy. This analysis was used to check the completion of the polymerization reaction and characterization of the final prepared polyurethanes. In Figure 2, the disappearance of NCO peak at 2270  $\text{cm}^{-1}$  indicates that the isocyanate reaction was completed. N-H Stretching of urethanes appears at 3306  $\text{cm}^{-1}$  and C=O stretching at 1700–1730.7  $\text{cm}^{-1}$ . The  $\text{CH}_2$  signals of propylene glycol appear at 2971 and 2870  $\text{cm}^{-1}$  and the C-O-C of ether at 1106  $\text{cm}^{-1}$  [20].

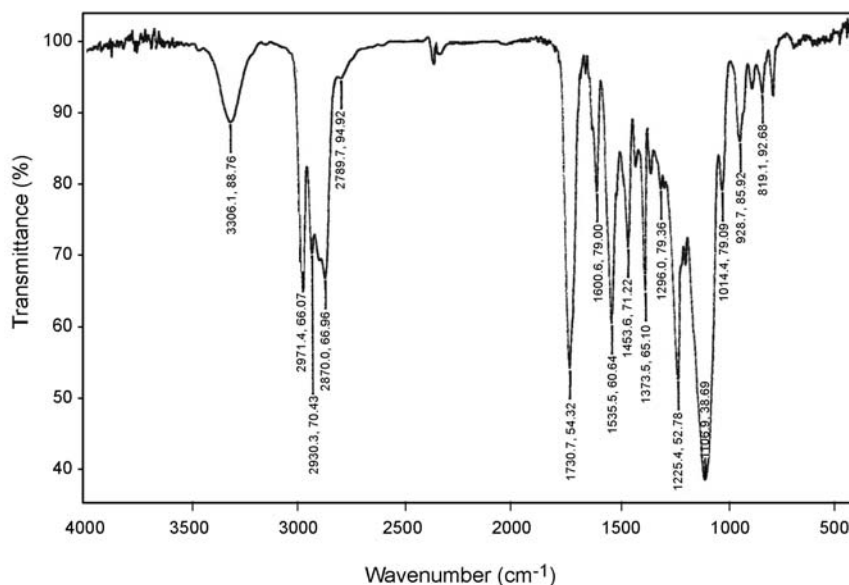


Figure 2. FTIR Spectra of synthesized polyurethane.

DSC and DMTA analyses were used for investigation of the thermal properties of the synthesized polyurethanes. Table 1 shows the thermal properties of synthesized polyurethanes obtained from DSC tests and characterized with their components molar ratios and hard segment contents. The reported data from DSC tests, as shown in Figure 3, indicate two transition points for polymers. The first transition is related to soft segments, this transition occurs in the range of  $-40^{\circ}\text{C}$  to  $-31.06^{\circ}\text{C}$ . The second transition which is related to hard segment occurs at the range of  $+50^{\circ}\text{C}$  to  $+67^{\circ}\text{C}$  for PU1 to PU4, respectively. These results indicate that by increasing the hard segment content of polymer the structure turns more rigid and polar urethane groups in these segments are enhanced which leads to intermolecular interaction between the polymer chains and therefore higher resistance to

flow.

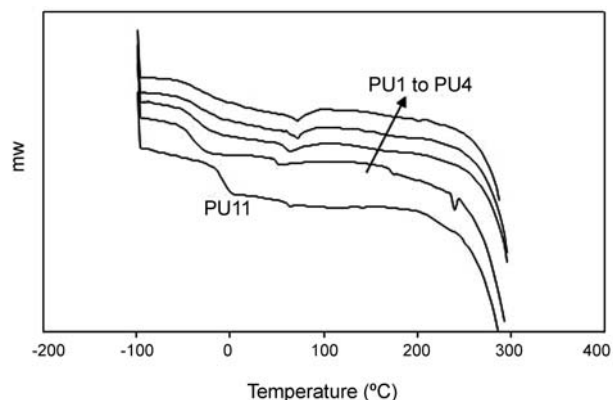
Thermal behaviour of PU11 in Figure 3 indicates that, its first transition temperature is considerably higher than those of the polyurethanes synthesized by PPG2000. Since the length of polyol in PU11 is half the length of that in the other polymers, it is believed that the segmental motions of polyurethane chains have drastically dropped and therefore, as is seen in Figure 3, the glass transition temperature of this polymer has been increased.

For complete investigation of thermal and mechanical properties of the synthesized polyurethanes, DMTA analysis was carried out. The storage modulus ( $G'$ ) and  $\tan\delta$  of the polymers synthesized by using PPG2000 are shown in Figures 4 and 5, respectively. One may consider at least two or three transitions in polyurethane structure.

Table 1. Composition and physical properties of polyurethanes.

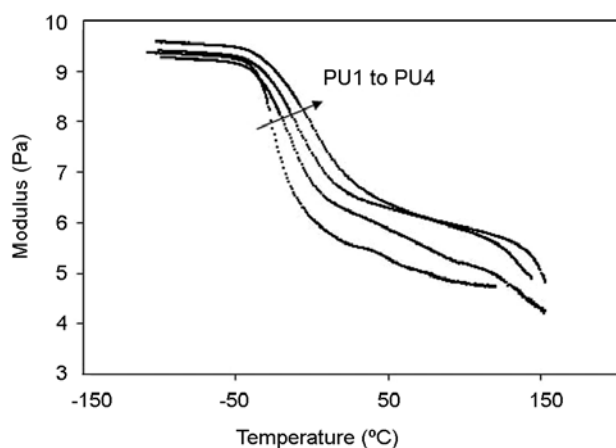
Sample code	Molar ratio (polyol/diisocyanate/diol)	Hard segment (wt%)	T <sub>g</sub> <sub>a</sub> (°C)	T <sub>g</sub> <sub>b</sub> (°C)
PU1	1/3/2	26.0	-40.00	50.00
PU2	1/4/3	32.6	-33.35	57.33
PU3	1/5/4	38.1	-33.00	65.20
PU4	1/6/5	42.7	-31.06	66.26
PU11*	1/3/2	41.3	-6.91	60.58

(\*) PU11 was synthesized by using 1000 g/mol molecular weight polypropylene glycol.

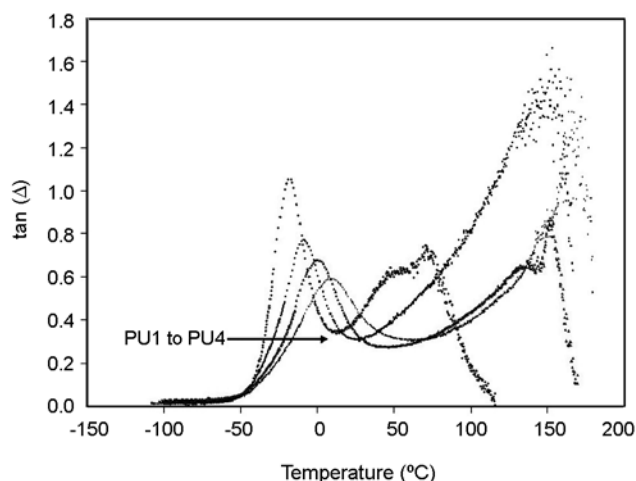


**Figure 3.** DSC Thermograms of synthesized polyurethanes.

As shown in Figure 4 there are two or three transition points for the polyurethanes. These transitions are also listed in Table 2. It is believed that the first transition of each polymer may have been related to the soft segment at  $-39.8$  to  $-32.7^\circ\text{C}$ . Similar results were reported by DSC analysis. Above room temperature there is only one transition in the range of  $50$  to  $67^\circ\text{C}$  in DSC thermograms and also one transition in the range of  $118$  to  $141^\circ\text{C}$  for PU2-PU4 in DMTA results. There is an exception for PU1 which shows two transitions at  $45$  and  $75^\circ\text{C}$  by DMTA analysis. At low temperature (below glass transition temperature), polyurethane acts as a rigid glassy polymer without flexibility and chain mobility. Accordingly, one can confirm the same result from DSC and DMTA on the mechanical properties and the glass transition temperatures of polyurethanes.



**Figure 4.** Change of modulus in polyurethanes of varying hard segment content value.

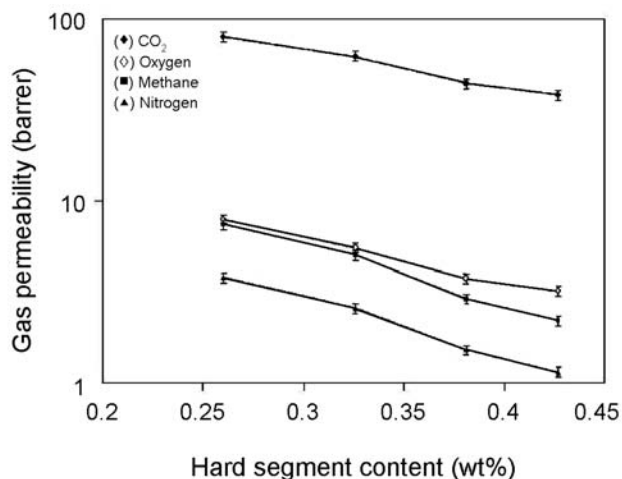


**Figure 5.** Change of  $\tan\delta$  in polyurethanes varying in hard segment content value.

As it is known in literature, the mechanical behaviour of polyurethanes strongly depends on polymer chain mobility. We have concluded that the small changes on the mobility of polymer chains were detected by slight variation in mechanical strength of polymer. Accordingly, at high temperature more transition points are detected by DMTA analysis that cannot be detected by DSC. The comparison between modulus curves of the polyurethanes shows that the decrease in the slope of modulus in the first glass transition temperature was related to the hard segment content or mole fraction of hard segment components of polyurethanes. This is probably due to decreasing of microphase separation of polyurethanes. Because of the increasing hard segment content in polymer, the interaction and chain interconnection between hard to soft segments and the hard to hard segments have been increased in polymer. Therefore, the effects of hard and soft segments on each other have been increased and this phenomenon leads to decreasing

**Table 2.** Transition points obtained by DMTA analysis.

Sample code	T <sub>g<sub>a</sub></sub> (°C)	T <sub>g<sub>b</sub></sub> (°C)	T <sub>g<sub>c</sub></sub> (°C)
PU1	-39.8	45.0	75.2
PU2	-34.8	-	118.8
PU3	-34.4	-	120.9
PU4	-32.7	-	141.0
PU11	-10.1	64.6	-



**Figure 6.** Permeabilities of N<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, and CO<sub>2</sub> gases through PU1 to PU4 membranes.

the microphase separation in polymer.

In Figure 4, the broadening of the transition states of polymers indicates the increasing effects of soft and hard segments regions on each other and therefore, the diminishing microphase separation in polymers. Thus, with less flexibility of the chains the modulus increases. One may also note that in the glassy and rubbery regions, the storage modulus of the polymer increases by higher hard segment content.

### Gas Permeation

Figure 6 shows the permeability of N<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, and CO<sub>2</sub> gases through polyurethane membranes. The order of permeabilities decreases as  $P(\text{CO}_2) \gg P(\text{O}_2) > P(\text{CH}_4) > P(\text{N}_2)$  for all polyurethane membranes. The higher CO<sub>2</sub> permeability is due to the relative high solubility of CO<sub>2</sub> in the membranes when compared with O<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>. In comparison with other gases, CO<sub>2</sub> has a small molecular size and a high condensation temperature. In addition, CO<sub>2</sub> is a polar molecule that can interact with polar chains of polymers [21-23]. Hence, the permeability of CO<sub>2</sub> in comparison with other gases is considerably higher in polyurethane which contains polar groups in its main chains.

As shown in Table 3 the kinetic diameter of methane is greater than nitrogen molecule but the reported permeability in Figure 6 reveals the higher permeability of the methane gas. The comparison of condensability of these two gases indicates that

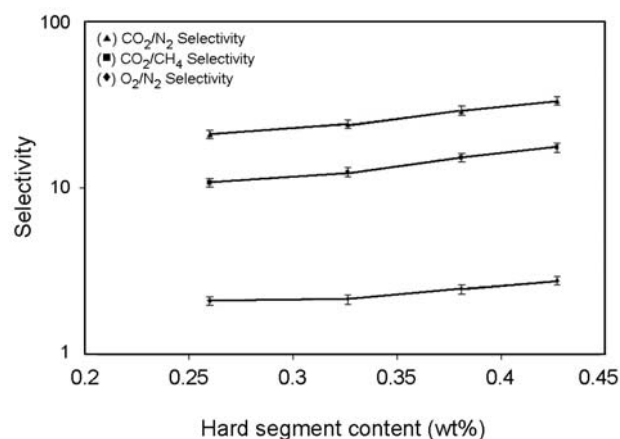
**Table 3.** Condensability and kinetic diameter of studied gases.

Gas	Kinetic diameter (Å)	Condensability (K)
Carbon dioxide	3.30	195
Oxygen	3.46	107
Nitrogen	3.64	71
Methane	3.80	149

methane condenses more with respect to nitrogen. It is known that permeation of gases through polymers has occurred via solution-diffusion mechanism [1]. In solution-diffusion mechanism permeability coefficient is defined as the combination of solubility and diffusivity of the gas through the polymer.

$$P = D \times S \quad (3)$$

where, P, D, and S are permeability coefficient, diffusion coefficient and solubility of gases in the polymer, respectively. The diffusion coefficient of gases depends on molecular size of the gas and rigidity and mobility of polymer chains. The solubility of gases in polymer depends on condensability of the gas and active functional groups present in the polymer backbone. Thus, the higher condensation temperature of methane promotes its solubility in the polymer and leads to a higher permeability of this gas in polyurethanes as compared to nitrogen. Therefore, these results indicate the dominant role of solubility



**Figure 7.** The 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> selectivities through PU1 to PU4 membranes.

mechanism in permeation of gases in polyurethane membranes.

The decreasing gas permeability of polyurethanes and its increasing selectivity with higher contents of hard segment are shown in Figures 6 and 7, respectively. As a first approximation, the effect of decreasing permeability can be explained by the increasing fraction of the hard segments, which act as impermeable barrier to permeating molecules, reducing the area available for transport. It is clear from generally accepted solution-diffusion model of the transport of gases in polymers that glass transition temperature of polymer is an important factor in controlling the diffusion in this process. In general, with the increase of soft segment of the related series of polymers, the glass transition temperature also decreases and many references indicate that both diffusivity and permeability may increase [10-16] for which the same trend has been observed in this work as well.

The chain mobility in polymers decreases with the increasing of hard segment content, therefore, the glass transition temperatures show upward trend resulting from our DSC and DMA studies. It has been well established that thermodynamic incompatibility of segments existing in PU exhibits a microphase-separated morphology, even if this morphology is often hardly defined in terms of interconnected rods or isolated spheres. From the transport standpoint, the soft segmental domains are formed as a result of microphasic separation permeable to molecules, whereas the hard segment domains act as impermeable barriers [17-18]. Although the hard segmental domains are not expected to be accessible to the permeating molecules, they can influence the overall transport process due to their ability to serve as physical cross-links, and changing the dynamics of the soft segments. Once the chain mobility of the polymer is restricted by increasing hard segment, the space created for diffusion of permeant molecules through mem-

brane is also restricted. This makes the pathways for diffusion of gases in free paths to be far more confined and restricted. The presence of the strong interacting groups in polymer also strengthen the existing molecular interactions of the neighbouring polymer chains, which expectedly decreases further the average interchain distances needed for such a confined space and pathway for the gas diffusion in membrane.

Gas selectivity in polymers is considered to occur either via solubility or diffusivity. The solubility selectivity usually occurs by changing the solubility behaviour of the polymer by adding a special functional group to the polymer structure. In this way, the polar, acidic, or other active gases are separated. The other one is diffusivity selectivity, which in this case the selectivity occurs by changing the molecular motion and the size of trapped free volume in polymer structure. The second mechanism enhances the molecular sieve property of polymer and is used for a great numbers of gases with different molecular sizes.

By restricting the chain mobilities and pathways for diffusion of gas molecules through polymer; the separation of large and small molecules are enhanced and membrane becomes more selective. This is the main reason for the molecular sieve property of polymer that while it increases, the selectivity of polymers towards gases also increases as well.

We have compared the permeability and selectivity of polyurethanes PU4 and PU11 in Table 4. As reported in Table 1 these two polyurethanes have the same content of hard segments with different polyol lengths in their structures. The obtained results indicate that gas permeability of polymer decreases while the selectivity increases, these results are due to decreasing length of the polyol in the polyurethane structure. The effect of the hard segments on the dynamics of the PU soft segments has been studied by Grabczyk [24].

From the results obtained by Grabczyk it appears

**Table 4.** Comparison of gas separation properties of PU4 and PU11 membranes.

Sample code	Permeability (barrer)				Selectivity		
	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
PU4	3.19	1.22	2.2	38.2	2.61	31.3	17.36
PU11	1.38	0.44	0.83	15.2	3.13	34.54	18.31

that both structure and length of the hard segment affect mobility of the spin probe dispersed within the soft segment domains of PUs with lower degree of microphase separation. The similar correlations also have been found by Grabczyk between the changes in the hard segment architecture and the diffusivity of cyclohexane or water in polyurethanes [18]. The same result on the flux value has been reported by Grabczyk, as shorter soft segments give a lower flux value. This study has also showed that for longer PU hard segments the flux value decreases and the selectivity increases in a process which is independent of the type of chain extender [18].

The lower permeation value for PUs with shorter soft segments can easily be explained by the mobility of long segments and so increasing the free space for diffusion of polymer molecules. Some authors have explained the lower flux values of PUs with shorter soft segments in higher concentration of the polar urethane groups in the polymer chain, which can form interchain hydrogen bonds with electron donors groups, leading to the reduced mobility of polymer segmental units [18]. The same have also been reported for other block copolymers applied in the separation of various feed mixtures [25-27]. The restrictions in mobility of the soft segments are also regarded responsible for the permeability and selectivity variations resulting from the modifications of the hard segment structure. In our thermal characteristic studies of PUs, our observed results indicate that the glass transition temperature of PU11 is much higher than that of PU4. This discrepancy in glass transition temperature may be explained by the mobility of long segments in PU4 chains as compared to the short mobile polyol segments in PU11.

## CONCLUSION

Polyurethane elastomers were synthesized by using polypropylene-glycol, toluene diisocyanate and 1,4-butane diol with different hard segment contents. The gas separation properties of the synthesized polyurethanes are investigated by using nitrogen, oxygen, methane, and carbon dioxide gases. The effects of hard segments on the flexibility of polyurethane are studied by DSC and DMTA analysis.

The reported data from DSC and DMTA showed more flexibility in hard segment content polymers. The gas separation properties of polymers indicate that by increasing the hard segment and lowering the chain mobility of polymers the permeability of gases decrease and their selectivity increases. Our results also give an indication that in two different polyurethane membranes with the same hard segment content, the gas permeability has increased drastically in polyurethane structures having soft segmental lengths.

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