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Study on the morphology and permeation property of amine group-contained polyurethanes

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The better CO_2 affinity reagents, N-methyldiethanolamine (MDEA) and tetraethylenepentamine(TEPA), were used as chain extenders to prepare MDEA-extended polyurethanes, TEPA- and MDEA/TEPA(1/1 by mole)-extended poly(urethane-urea)s. 4,4′-diphenylmethane diisocyanate (MDI) and poly(ethylene glycol) (PEG) of molecular weights (MW) 400 and 600 were used as hard and soft segments, respectively. The effects of the chain extenders and PEG MW on the mode of urethane moiety association and the polymer thermal transition properties were studied using differential scanning calorimetry, Fourier Transform infrared spectrophotometry (*FT*i.r.) and the deconvolute technique on the *FT*i.r. bands due to stretching vibrations of carbonyl and NH groups. The new chain extenders caused the polymers to have less ordered urethane hard segment domains and a lower T_2. They also caused an increase in the number of hard segments found in soft segment domains and a higher T_{gs}, compared with typical 1,4′-butandiol-extended polyether polyurethanes. The larger MW PEG improved phase separation and exhibited a lower T_{gs}. The polymers were prepared as gas separation membranes for various gases such as He, H_2, O_2, N_2, CH_4 and CO_2. The steady state permeability (P_i), diffusivity (D_i) and solubility (S_i) of the gases permeated through the polymer membranes were determined using Barrer's high vacuum technique and the time lag method. Polymer membranes having PEG soft segments of MW600 showed quite promising performance ($P_i, \alpha_{ij} = P_i/P_j$) for permeation of industrially interesting gas pairs such as CO_2/CH_4, He/CH_4, H_2/N_2, and O_2/N_2. The relation of permeation properties to the molecular properties of the penetrant gases as well as the polymer structure is discussed. The separation mechanism of the gas pairs is also discussed. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: gas permeation; amine-contained polyurethanes; domain structure)

INTRODUCTION

Energy conservation and environmental concerns in recent years have resulted in increased efforts in the industrial world to develop clean and energy efficient separation processes. Membrane-based separation is an energy efficient, compact and modular process. Gas separation with polymeric membranes is used in a wide variety of application areas[1], such as the removal of helium gas from natural gas, the recovery of hydrogen from ammonia, the recovery of carbon dioxide from natural gas, biogas and landfill gas, the concentrating of oxygen from air, etc. In the search for superior membranes, a number of investigators have studied the gas permeation properties of polyurethanes[2–12].

Polyurethanes are usually composed of a polyether or polyester soft segment and a hard segment. The hard segment is formed by extending a terminal diisocyanate with a low molecular weight diol or with a low molecular weight diamine. Because of the incompatibility between the hard and soft segments, polyurethane undergoes microphase separation. The primary driving force for domain formation arises from the intermolecular interaction of hydrogen bonding between hard segments. It has also been shown that some hard segments are dissolved in the soft segment matrix[12–14]. Various techniques such as thermal analysis[13–18], infrared spectroscopy[16,17,19–22], dynamic mechanical analysis[23–25] and scattering techniques[18,26,27] have been employed in the study of the morphology and hydrogen bonding of polyurethanes. They show[12–15] that the gas permeability of polyurethane membranes increases with the decrease of hard segment content and increase of soft segment molecular weight. In addition, the type of chain extenders used also affect the permeation properties of the membranes with the result of changing the phase-separated domain morphology, crystallinity, density and glass transition of the membranes[5,6].

The properties of polyurethanes are easily tailored by introducing controlled changes in polyol chain length as well as by changing the proportions and chemical nature of the constituents which make up the flexible and rigid segments of the polymer chain. Our previous paper[28] chose the CO_2 affinity reagents N-methyldiethanolamine (MDEA) and tetraethylenepentamine (TEPA) as chain extenders to extend 4,4′-diphenylmethane diisocyanate (MDI), obtaining amine-containing polyurethanes and poly(urethane-urea)s. Poly(ethylene glycol) (PEG) of molecular weight 400 or 600 was used as the soft segment component. The permeation and sorption properties of the polymers membranes as well as the transport process mechanism for carbon dioxide were studied. The present paper studies the permeation properties of these same polymer membranes for gases such as He, H_2, O_2, N_2, CH_4, and CO_2. The efficiency of separation and the separation mechanisms for gas pairs of industrial interest are considered, as well as the correlation of permeation properties with the morphology and molecular properties of penetrant gases.

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Table 1 Characteristics of the amine-contained polyurethanes

	Feed composition	EA analysis data			Hard segment content (wt%)	d.s.c.			
Polymer	MDI:MDEA:TEPA:PEG	C (wt%)	H (wt%)	N (wt%)		Endotherm transition temp (°C)			
MPU4	2:1:0:1	61.93	6.90	6.75	61.4(60.8)[a]	27		56	
MTPUU4	2:0.5:0.5:1	67.74	6.98	9.14	62.7(62.8)	21		57	73
TPUU4	2:0:1:1	62.40	7.16	11.37	63.9(63.3)	15			75
MPU6	2:1:0:1	60.42	7.24	5.66	51.5(50.8)	−6		57	
MTPUU6	2:0.5:0.5:1	61.42	7.26	7.71	52.8(52.2)	−13	36	56	72
TPUU6	2:0:1:1	60.47	7.54	9.65	54.1(53.5)	−18	38		77

[a] Calculated values

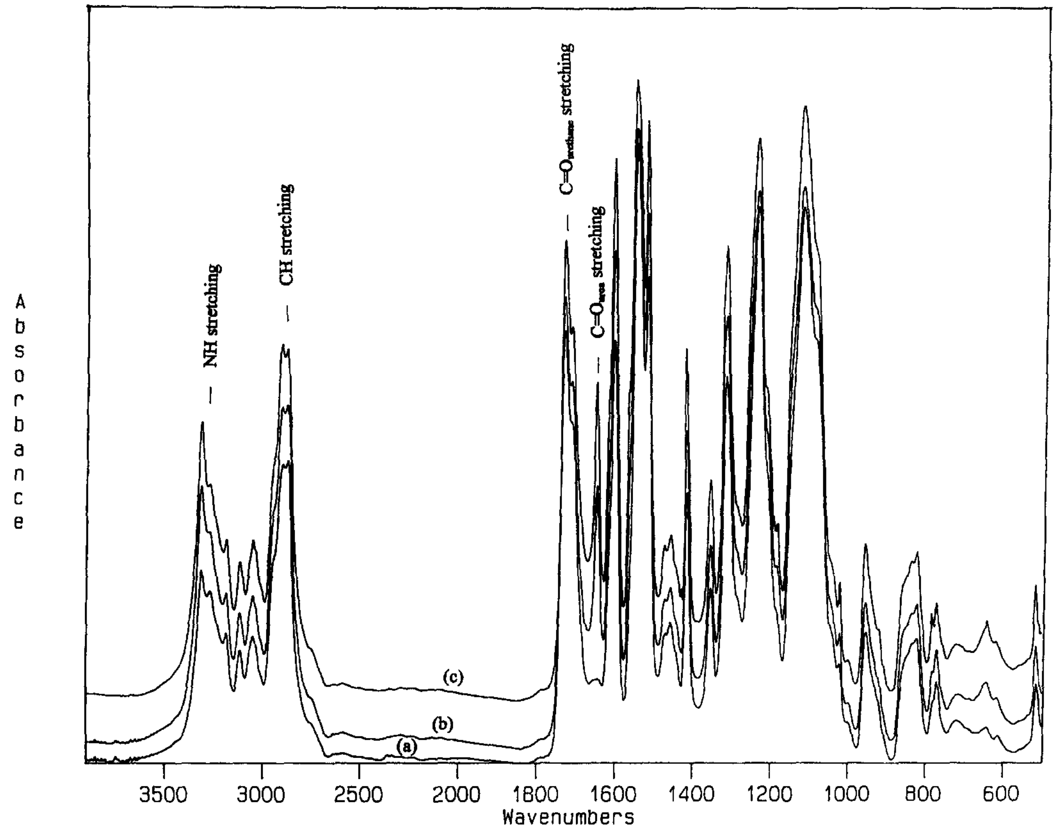


Figure 1 I.r. spectra of the PEG6 polymers at room temperature: (a) MPU6; (b) MTPUU6; (c) TPUU6

EXPERIMENTAL

Polymers

The polyurethanes and poly(urethane-urea)s were prepared by a two step process in N,N-dimethylformamide, as done elsewhere[17,29]. Details of the polymerization procedure have been described previously[28]. The isocyanate-terminated prepolymers, with a MDI and PEG mole ratio of 2:1, were tested using the di-n-butylamine titration method[29]. Chain extension was achieved by reaction with 1.0 mole of MDEA and/or TEPA to obtain the final polymers.

Characterization of polymers

The composition of the polymers studied was determined by a Heraeus CHN-O-RAPID Elemental Analyser (EA). Infrared spectra were obtained with a Fourier Transform i.r. spectrophotometer (Bio-Rad FTS-40A). The samples for infrared analysis were prepared by solution casting of 1% (w/v) polymer in DMF directly onto KBr plates and then placing them in a nitrogen purged oven at 80°C. They were next kept in a vacuum at 50°C for about 3 days to remove the remaining solvent. The films obtained were sufficiently thin for *FT*i.r. spectroscopy. The *FT*i.r. used had a resolution of 2 cm^{-1} and 64 scans were averaged to obtain each spectrum. D.s.c. thermograms were obtained by a DuPont d.s.c. 2910 differential scanning calorimeter linked to a Thermal Analysis 2000 system for data acquisition. The samples were scanned from − 60 to 250°C at a rate of 10°C min^{-1} under nitrogen purging. The samples were prepared as film and those employed were in the mass range of 18 mg.

Permeation test

The polymer membranes were made from DMF solution containing 20 wt% polymer, which was placed in an open-topped container formed by a glass cylinder with a clean polyethylene (PE) film attached to the bottom. Then the system was placed in a nitrogen purged oven at 80°C until the solvent had evaporated to visual inspection (approx. 24 h). Finally, samples were removed from the PE substrate and put in a vacuum at 50°C for about 3 days to remove the remaining solvent. The thickness of the dry membranes varied from 100 to 200 μm.

Gas permeation data were obtained using Barrer's high vacuum method[30]. The purity of gases (He, H_2, N_2, O_2, CH_4, and CO_2) used was 99.5% or higher. The cumulative amount of gas passing through the polymer membrane in a constant volume receiving chamber (V) was measured by the pressure increase on the downstream side (p_d) with a pressure transducer (MKS Baratron 222B with a full scale range of 10 Torr connected to an MKS Type PDR-C-1C readout). The upstream pressure (p_u) was monitored with a pressure transducer (Honeywell). At steady gas flow, the permeability coefficient (P) was determined from the slope (dp/dt) of the linear portion of the p_d *versus* the time plot using the following equation:

$$P = \frac{273 \times V \times L \times \frac{dp}{dt}}{760 \times T \times A \times (p_u - p_d)} \quad (1)$$

where L is the thickness of the membrane, T is the absolute temperature, and A is the area of the membrane. The p_d can be regarded as negligible because $p_d < p_u$.

The diffusion coefficient (D) was determined by the time lag method[31], represented as

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

where θ is the time lag, i.e. the intercept obtained from extrapolating the linear region of the p_d *versus* the time plot to the time axis.

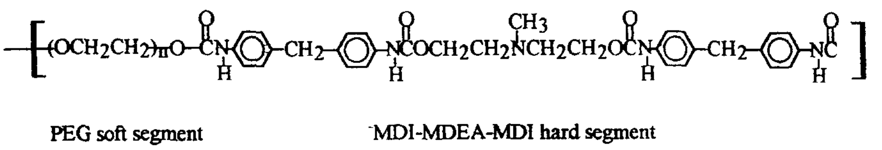
The solubility coefficient (S) was then calculated from the equation

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

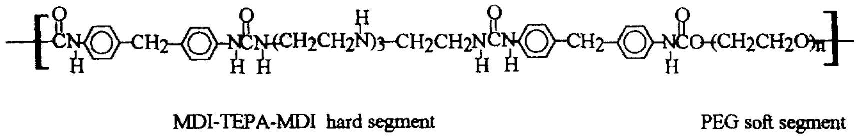
RESULTS AND DISCUSSION

The polyurethanes and poly(urethane-urea)s studied are presented as follows:

MDEA-extented poly(urethane) (MPU)



TEPA-extented poly(urethane-urea) (TPUU)



MDEA/TEPA(1/1)-extented poly(urethane) (MTPUU)

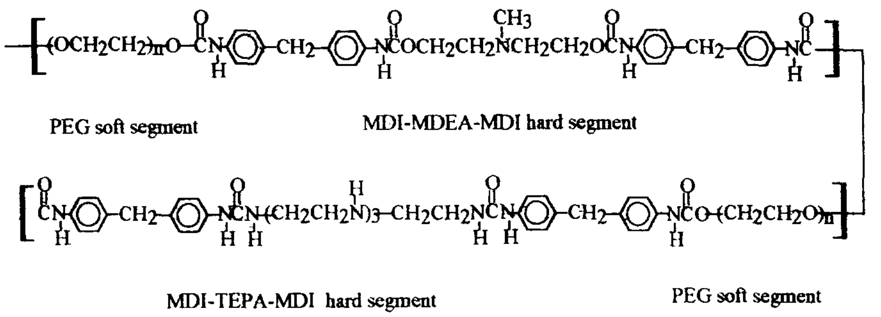


Table 1 shows the polymerization feed composition for obtaining the polymers mentioned previously. *Table 1* also shows the composition by elemental analysis and weight fraction of the hard segment of the polymers. MDEA-extended polyurethanes (MPU4) is our designation of the N-methyldiethanolamine (MDEA)-extended polymers based on 4, 4′-diphenylemthane diisocyanate (MDI) and poly(-ethylene glycol) (PEG) of molecular weight (MW) 400. If the PEG soft segment used was MW600, then the polyurethane obtained is denoted MPU6. TEPA-extended poly(urethane-urea) (TPUU4 or 6) is based on the chain extender tetraethylenepentamine (TEPA), and a base polymer of MDI and PEG of MW400 or 600. MDEA/TEPA(1/1 by mol)-extended poly(urethane-urea) (MTPUU4 or 6) is based on the mixed chain extender MDEA/TEPA (1/1 by mol), and a basic chain of MDI and PEG of MW400 or 600. MDI and chain extenders form the hard segments of the films and comprise around 60% by weight of PEG4-containing polymers, increasing with the extender used from MDEA, MDEA/TEPA, to TEPA.

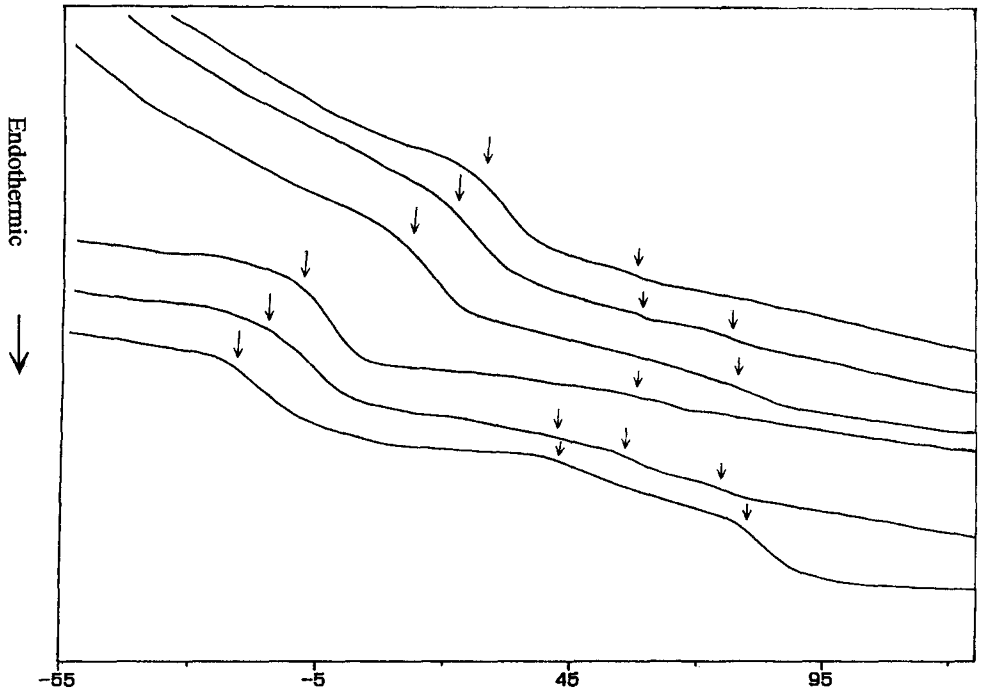


Figure 2 D.s.c. thermograms of the polymers studied

Likewise, the hard segment percentage in PEG6 polymers is greater than 50%, increasing with the extender used from MDEA, MDEA/TEPA, to TEPA.

*FT*i.r. analysis

Figure 1 illustrates the *FT*i.r. spectra of the PEG6 polymers studied at room temperature. It shows[18–21] that the *FT*i.r. data of the carbonyl stretching vibration of polyurethanes provides useful information on the microphase separation resulting from the hydrogen bonding effects of the urethane hard segments. Hence, deconvolution of the carbonyl stretching vibration bands around 1700–1750 cm^{-1} was performed, using Bandfit software supplied by the Bio-Rad company, to obtain the component bands of the region. The best fits were obtained using a Gaussian function. The maximum frequency and area of each band were determined using the Nelder–Mead optimization method. The root mean square deviations were smaller than 0.01. As shown in *Table 2*, the bands arising from stretching vibrations of urethane carbonyls include three or four components, depending on the kinds of polymers. All the PEG4 polymers and MPU6 show three components at 1746, 1728 and 1708 cm^{-1}, while the TPUU6 and MTPUU6 show four components at 1746, 1730, 1722 and 1709 cm^{-1}. The width at half-height of each component shows virtually no change with the different polymers studied. According to the work of Zharkov *et al.*[32], the components at 1746 and 1728–1730 cm^{-1} are assigned to the stretching vibration of free bonded carbonyls. However, for the latter, the urethane group is hydrogen bonded to ether oxygen via an NH group ($C = O$ group remaining free), i.e. (NH–O–) bonding. It indicates that some urethane moieties dissolve in PEG soft segment domains and form hydrogen bonding with ether oxygen. The 1708–1709 cm^{-1} and 1722 cm^{-1} bands are attributed to the stretching vibration of the disordered hydrogen bonded urethane moieties. In the 1708–1709 cm^{-1} bands, the NH linkages of 'head' urethane groups are hydrogen bonded with ether oxygen. In the 1722 cm^{-1} bands, one of the carbonyls is free from hydrogen bonding. Note that none of the polymers studied show an absorption band around 1703 cm^{-1}, which is due to the stretching vibration of the crystalline associated urethane moieties. Furthermore, the poly(urethane-urea)s of TPUU and MTPU show an absorption band at about 1643 cm^{-1}, which is caused by stretching vibrations of bonded urea groups, and they do not exhibit the 1695 cm^{-1} band, which indicates free urea carbonyl[22]. Thus the urea carbonyls of the poly(urethane-urea)s under study are hydrogen bonded. Wang and Cooper[17] suggested that the bonded urea carbonyl in polyether poly(urethane-urea)s occurs in a mixed state with three-dimensional hydrogen bonding and conventional interurea bonds (one urea carbonyl is bonded to one NH group) and is indicated by an *FT*i.r. absorption band around 1645 to 1635 cm^{-1}, the lower the band frequency, the tighter the bonded urea carbonyl. Our observed band at 1643 cm^{-1} indicates that the urea carbonyls association in the poly(urethane-urea)s is not well ordered.

The results of the deconvolution and the summarized fractions of bonded carbonyls and bonded NH groups in the polymers are presented in *Table 2*. Because differing film thickness generates different band intensity and width, the area of each band was normalized based on the area of the band of the CH_2 stretching vibration at 2905 cm^{-1}, since the 2905 band should be the same for any film sample of the same thickness. The fraction of bonded urethane carbonyls was estimated from the ratio of the normalized area of the band under consideration *versus* the total normalized areas of all the carbonyl stretching vibrations bands; this computation is made with the simplifying assumption that the extinction coefficients of the ratio of the hydrogen bonded to free carbonyl groups are 1.0[16]. This shows that the normalized area (A') at 1729 cm^{-1} for all the polymers studied decreases in order of MPU > MTPUU > TPUU, as well as decreasing with increasing PEG MW. This suggests that for a given PEG series group (i.e. PEG4 or PEG6), the MPU soft segment domain dissolved more urethanes than

Table 2 Deconvolution results[a] and mode of hydrogen bonding[b] in the amine-contained polyurethanes

Polymer	Free urethane carbonyl groups						Bonded urethane carbonyl groups						Fraction of bonded $C = O_{urethane}$ group	Fraction of bonded NH group
	ν	$w_{1/2}$	A'	ν	$w_{1/2}$	A'	ν	$w_{1/2}$	A'	ν	$w_{1/2}$	A'	$X_{B,C=O}$	$X_{B,NH}$
MPU4	1746	7.9	0.070	1728	11.2	1.257				1708	10.1	0.730	0.34	0.78
MTPUU4	1746	7.9	0.057	1729	10.6	1.336				1708	10.2	0.668	0.32	0.82
TPUU4	1746	7.9	0.034	1728	10.8	1.274				1709	10.2	0.546	0.29	0.85
MPU6	1746	7.9	0.030	1729	10.5	1.011				1708	10.2	0.693	0.40	0.79
MTPUU6	1746	7.9	0.016	1730	10.6	0.941	1722	7.1	0.062	1709	10.2	0.501	0.37	0.86
TPUU6	1746	7.9	0.011	1730	10.5	0.813	1722	7.2	0.079	1709	10.1	0.374	0.35	0.88

[a] ν: The maximum peak frequency; $w_{1/2}$: the width at half-height; A': the normalized area in which the CH_2 stretching near 2905 cm^{-1} was used as normalizing factor

[b] Taking the ratio of extinction coefficient ϵ_B/ϵ_F equal to 1.0 for urethane carbonyl absorption and 3.46 for NH absorption[16]

did MTPUU, and the soft segment domain of MTPUU contained more dissolved urethanes than did TPUU. Meanwhile, for a given chain extender, the soft segment domains of PEG4 polymers dissolved more urethanes than that of PEG6 polymers. *Table 2* also indicates that the fraction of associated urethane moiety ($X_{B,C=O}$) in the polymers studied is 29%–40%. As indicated in *Table 1*, the total weight fraction of hard segment components (chain extender and MDI) in the PEG6 polymers is 51.5–54.1 wt%, and 61.4–64 wt% in the PEG4 polymers. Therefore, a significant amount of hard segments dissolved in soft segment domains. The PEG6 polymers contain more hard segment domains than the PEG4 polymers. The content of associated urethane hard segment domains apparently increases from MDEA polymers, MDEA/TEPA polymers to TEPA polymers. However, in the latter two polymers, the carbonyls exist in both urea and urethane groups. *Table 2* shows the polymers contain about 78–88% hydrogen bonded NH groups ($X_{B,NH}$), depending on polymer under consideration. Srichatrapimul and Cooper[16] showed that in MDI-based polyether type polyurethanes, about 65% of the urethane carbonyls and about 80% of NH groups are hydrogen bonded at room temperature. Therefore, the polyurethanes and poly(urethane-urea)s obtained in our tests contain a lower content of hard segment domains or a larger fraction of dissolved hard segments in soft segment domains than the usual 1,4-butandiol-extended polyether MDI-based polyurethanes. The pendant CH_3 group of MDEA is quite bulky and the ethylene amine groups($-CH_2CH_2NH-$) of TEPA are relatively asymmetric and of non-regular configuration compared with 1,4-butandiol. The bulky and asymmetric structure of our chain extenders is unfavourable for orderly and tight packing of hard segments and induces the dissolution of more hard segments in the soft segment domains.

Thermal transition properties

Figure 2 illustrates the d.s.c. thermograms of our polymers in the temperature range of −55 to 125°C. The thermal behaviour of these polymers depends upon the kind of chain extender and the PEG molecular weight. A summary of the d.s.c. endothermic transition temperatures for the polymers is presented in *Table 1*. PEG4 polymers show a glass transition temperature (T_{gs}) of the PEG soft segments at 15–27°C, while the PEG6 polymers exhibit a lower T_{gs} of − 1 to − 6°C. The T_{gs} obtained is higher than that of pre-PEG (*ca.* − 40°C)[33]. For a given PEG MW, the T_{gs} decreases in the order of MPU > MTPUU > TPUU. The higher the PEG MW, the lower the T_{gs}. The trend is in agreement with the trend for the changes of the fraction of (NH–O–) bonding (1729 cm^{-1}) with the kind of polymer in the above *FT*i.r. study. Therefore, it seems that more hard segments dissolved in soft segment domains induce the formation of more (NH–O–) bonds, thus causing the PEG chains more stiffness and a higher T_{gs}. It is noteworthy that the polymers exhibit high temperature endotherms around 55–76°C, which fall in the range of the T_2 endotherm reported by Clough and Schneider[13], or the T_1 reported by Cooper *et al.*[14–16]. Therefore, the endotherms may be ascribed to the disruption of short range ordered hard segment domains. For the polymers studied, the endothermic peak arising from disruption of the highly ordered hard segment domains at 150–170°C and the microcrystaline ordering of hard segment domains above 200°C was not found[14,15]. Therefore, the polymers studied consist of a loose ordering of hard segment domains, as confirmed by the *FT*i.r. occurring at the 1709 cm^{-1} absorption peak instead of 1703 cm^{-1}. The TPUUs show a higher T_2 (or T_1) than the MPUs do. This may be due to the presence of more hydrogen bonded urea carbonyls with a mixed state of three-dimensional hydrogen as well as conventional interurea bonds in TPUUs and MTPUUs. The MPUs, however, have only loosely packed urethane carbonyls. Sung *et al.*[18,20] indicated that the urea linkages in the polyether PUUs improved the extent of phase separation compared with butanediol-extended PUs. Thus, polyether PUUs show a lower T_{gs} and a much higher endotherm for hard segment domains than butanediol-extended PUs.

It is noted that MTPUU polymers, which are extended by both MDEA and TEPA with a mole ratio of 1/1, exhibit two high temperature transitions, one around 58°C and the other around 75°C, in addition to the T_{gs}. The former transition temperature is close to that of MPU and the latter is near that of TPUU, revealing that MDEA- and TEPA-extended hard segment domains exist in the polymer matrix and are incompatible with each other. Further, MTPUU6 and TPUU6 show still another endothermic transition at 34 and 38°C, respectively. The transitions in this temperature range seem not to be reported. Looking back to the *FT*i.r. study, one finds that both of the polymers show the 1722 cm^{-1} peak due to stretching vibration of carbonyl groups of urethane dimer[32]. Therefore, the transition might be related to the breaking of the urethane dimer mode of hydrogen bonding.

From the *FT*i.r. and d.s.c. results obtained, we shall attempt to depict the morphology of the polymers studied as follows: the MDEA- and/or TEPA-extended polymers contain soft segment domains which contain a certain amount of dissolved urethane moiety and loosely packed urethane and/or urethane-urea hard segment domains.

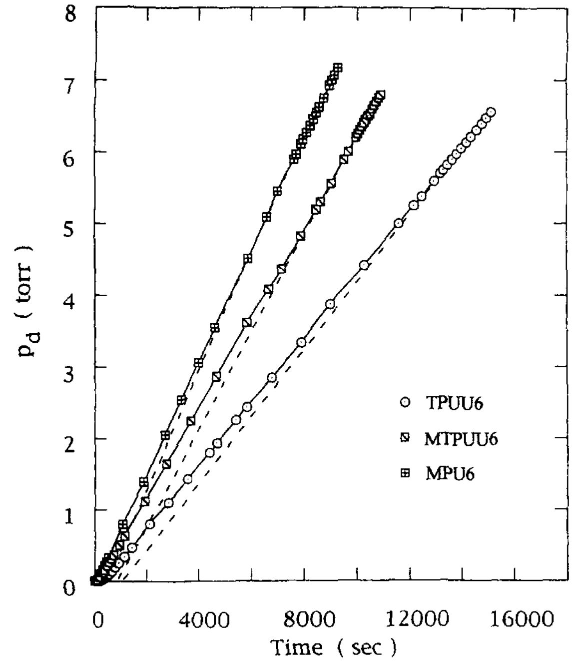


Figure 3 Plot of the downstream pressure of CO_2 (p_d) for PEG6 polymer membranes as function of time (t) obtained at 35°C and 10 atm

MTPUUs consist of three phases: a PEG rich soft segment domain, an MDEA-extended hard segment domain as well as a TEPA-extended hard segment domain. However, the MTPUU6 and TPUU6 exhibit another dimeric associated urethane domain.

Permeation

Permeability is one of the important properties of polymeric materials and is an important parameter in the design of gas separation membranes. The flat thin membranes with thickness of 100 to 200 μm used for this study were cast from DMF solution of 20% solid content on a PE substrate and put in a vacuum at 50°C for 3 days to remove solvent. The solubility parameters of the components of the polymers were estimated by group contributions[34] at 9.4, 12.2, 10.9 and 13.9 (cal cm^3)$^{1/2}$ for PEG, MDI, MDEA and TEPA, respectively. Therefore, the polymer membranes studied are hydrophilic, with solubility parameters greater than 10. The gases studied are the quantum gases He and H_2, as well as O_2, N_2, CH_4, and CO_2. Gas pairs of industrial interest are chosen for study. *Table 3* summarizes the normal boiling point (T_n), the critical temperature (T_c), the Lennard–Jones 6–12 potential molecular diameter (σ) and the kinetic diameter (d) of the gases tested.

Figure 3 illustrates the plot of the downstream pressure of CO_2 (p_d) for PEG6 polymer membranes as function of time (t) obtained at 35°C and an upper pressure of 10 atm. With reference to the measured T_{gs} of the polymers, the experimental temperature is higher than T_{gs} and lower than T_2 (or T_1). Accordingly, the polymer membranes during permeation measurements are rubbery but still contain hard segment domains. In other words, they possess thermal plastic and elastomeric properties simultaneously. Utilizing the slope of the p_d *versus* t plot at steady state and equation (1), one obtains the steady state permeability (P) of the gases through the polymer membranes (*Table 4*). The P obtained is in the range of 0.06–13 Barrers, depending on the kind of penetrant gas, the molecular weight of the PEG soft segment and the kind of chain extender used. For a given PEG4-containing polymer membrane, permeability increases in the following order, regardless of the kind of chain extender used:

$$He > H_2 > CO_2 > O_2 > CH_4 > N_2$$

while for PEG6-containing ones, it changes in the following order, independent of the kind of chain extender used:

$$CO_2 > He > H_2 > O_2 > CH_4 > N_2$$

The permeability of the two series of polymer membranes shows the same trends for the penetrate gases, except for CO_2. The P values obtained do not show an obvious correlation with the Lennard–Jones diameter σ, ϵ, T_c or T_n of the considered gases. However, if one examines the correlation of the P values with the kinetic diameter, d, for the PEG4 polymer membranes, then the P values are found to increase

Table 3 Physical properties of gases tested

Gas	Critial temperature[a] T_c (°k)	Normal boiling point[a] T_n (°k)	Lennard–Jones diameter[b] σ (Å)	Kinetic diameter[c] d (Å)
He	5.2	4.2	2.576	2.6
H_2	33.9	20.4	2.915	2.89
N_2	126.2	77.3	3.617	3.64
O_2	154.6	90.2	3.433	3.46
CH_4	190.6	111.4	3.822	3.80
CO_2	304.2	194.5	3.996	3.3

[a] Smith, J. M., Van Ness, H. C. and Abbort, M. M., *Introduction to Chemical Engineering Thermodynamics*, 5th edn. McGraw-Hill, New York, 1996, pp. 653–636
[b] Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., *Molecular Theory of Gases and Liquid*. Wiley, New York, 1954, p. 1110
[c] Mulder, M., *Basic Principles of Membrane Technology*. Kluwer, Dordrecht, 1991, p. 226

Table 4 Permeability coefficients[a] for different gases in the anine-contained polyurethane membranes at 35°C and 10 atm

Polymer	zP_{CO_2}	P_{O_2}	P_{N_2}	P_{CH_4}	P_{H_2}	P_{He}
MPU4	1.12	0.317	0.0847	0.0969	1.29	1.95
MTPUU4	1.07	0.274	0.0692	0.0828	1.11	1.79
TPUU4	1.01	0.255	0.0558	0.0744	1.05	1.73
MPU6	12.9	1.75	0.374	0.419	60.8	11.3
MTPUU6	12.3	1.51	0.334	0.390	5.55	10.5
TPUU6	11.9	1.40	0.298	0.369	5.13	10.3

[a] Barrers (10^{-9} cm^3 (STP)·cm/cm·s·cmHg)

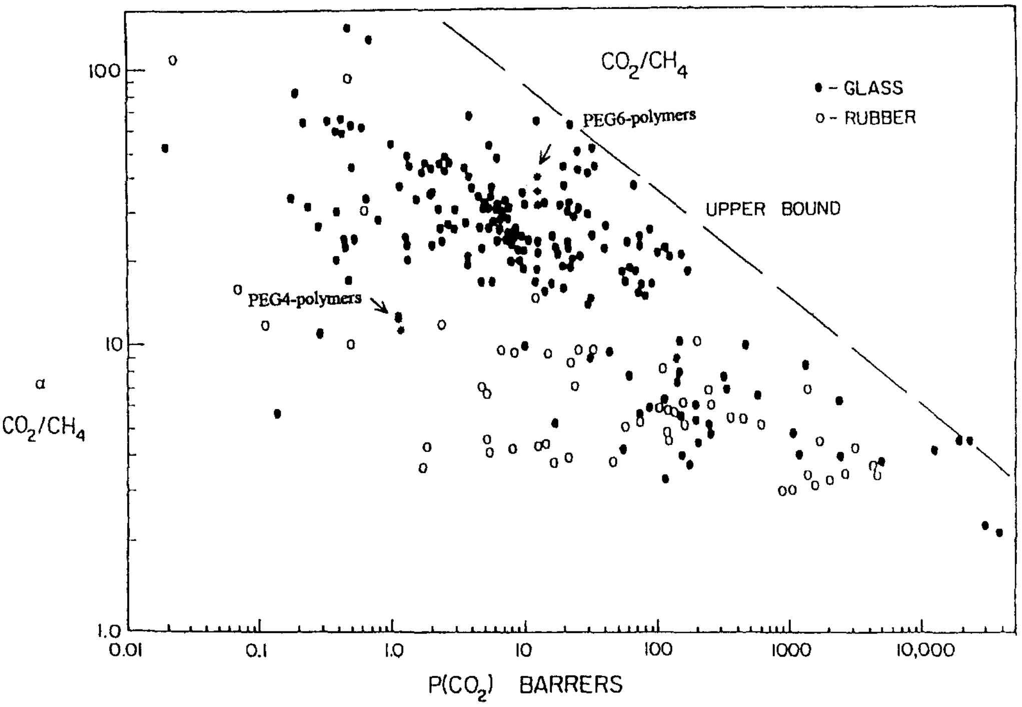


Figure 4 Literature data for separation factor CO_2/CH_4 *versus* CO_2 permeability[36]

Table 5 Permselectivity for different gas pairs in the amine-contained polyurethane membranes at 35°C and 10 atm

Polymer	α_{CO_2/N_2}	α_{CO_2/CH_4}	α_{O_2/N_2}	α_{H_2/CH_4}	α_{H_2/N_2}	α_{He/CH_4}	α_{He/N_2}
MPU4	13	12	3.7	13	15	20	23
MTPUU4	15	13	4.0	13	16	22	26
TPUU4	18	14	4.6	14	19	23	31
MPU6	34	31	4.7	15	16	27	30
MTPUU6	37	32	4.5	14	17	27	31
TPUU6	40	32	4.5	14	17	28	35

with the decrease of the kinetic diameter of gases, except for N_2 and CH_4. However, the *P* values exhibited by the PEG6 polymer membranes do not show the same trend. Apparently the polymeric membranes studied are highly permeable for the condensable gas CO_2 and the quantum gases He and H_2 but relatively non-permeable to the non-condesnsable gas N_2, with the other gases of our study lying between these extremes. An obvious factor affecting the *P* values is the molecular weight of the PEG soft segments. As the molecular weight of PEG increases from 400 to 600, the *P* value of CO_2 increases about 11.5-fold and that of the other non-condensable gases increases about 5–6-fold. However, the influence of the chain extenders on the *P* value is not so obvious as the PEG MW. The MPUs show *P* values no larger than double those of the TPUUs. The larger *P* for the MPUs may be attributed to the lower order associated with MPUs hard segment domains. The *P* values of the MTPUU membranes obtained are about the average of the MPU and TPUU membranes. As mentioned previous, MTPUUs contain MDEA-extended urethane hard segment domains and TEPA-extended urethane-urea hard segment domains. Therefore, we conclude that the main passages for gas permeation are the PEG soft segment domains in the polymer matrix, and the hard segment domains are the minor passages.

Utilizing *Table 4*, one obtains the permselectivity (α_{ij}) of the gas pair by calculating the ratio of P_i/P_j (*Table 5*). The α_{ij} values obtained are from 4 to 40, varying with the kind of penetrant gases. It is noteworthy that the polymer membranes show α_{ij} values of 12–35 for CO_2/CH_4 (natural gas and biogas purification, tertiary oil enhancement), 15–19 for H_2/N_2 (ammonium produce process), 13–40 for CO_2/N_2 (removal of CO_2 from air), 23–34 for He/N_2 (separation of He from air), 20–28 for He/CH_4 (separation of He from natural gas) and 3.7–4.7 for O_2/N_2 (oxygen enrichment). They seem comparable with values reported in the literature[34–36].

Recently, Robeson[36] has done elegant work by surveying of the performance of polymeric membranes for separation of gas pairs from over 300 references. He established the log–log plots of α_{ij} *versus* P_i for gas pairs through various polymeric membranes. He indicated that any gas pair exhibits an upper-bound limit for (α_{ij}, P_i), in spite of the kind of polymer membrane used. The glasslike polymeric membranes generally show a higher (α_{ij}, P_i) than rubberlike ones. In the present work, Robeson's plot is taken as a criterion for the performance of polymeric membranes studied. *Figures 4 and 5* illustrate that (α_{ij}, P_i) of CO_2/CH_4 and He/H_2 pairs permeating through the PEG6 polymer membranes lie quite near the upper bond limit of the related Robeson's plots, suggesting that the performance of the polymeric membranes for the gaseous pairs considered is quite promising and is better than most of the membranes reported in the literature. For the PEG6-contained polymer membranes, the (α_{ij}, P_i) of the gas pairs He/CH_4, He/N_2, O_2/N_2, H_2/CH_4 and H_2/N_2 lying on the related plots in either the bottom region of glassy polymeric membranes or in the upper region of rubberlike membranes, revealing that the

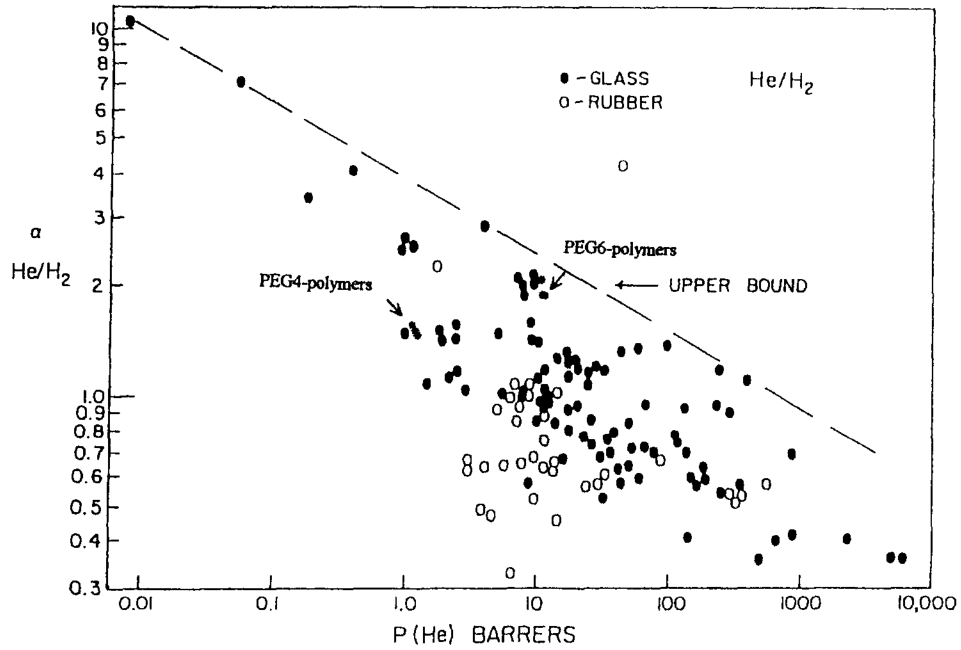


Figure 5 Literature data for separation factor He/H_2 *versus* He permeability[36]

Table 6 Diffusivity coefficients[a] and solubility coefficients[b] for different gases in the amine-contained polyurethane membranes at 35°C and 10 atm

Polymer	D_{CO_2} ($\times 10^{-8}$)	S_{CO_2}	D_{FUNCO_2} ($\times 10^{-7}$)	S_{FUNCO_2} ($\times 10^{-2}$)	D_{FUNCN_2} ($\times 10^{-7}$)	S_{N_2} ($\times 10^{-2}$)	D_{CH_4} ($\times 10^{-8}$)	S_{CH_4} ($\times 10^{-2}$)	D_{H_2} ($\times 10^{-6}$)	S_{H_2} ($\times 10^{-3}$)	D_{He} ($\times 10^{-5}$)	S_{He} ($\times 10^{-3}$)
MPU4	1.61	0.529	2.25	1.07	0.833	0.773	3.98	1.85	2.83	3.46	0.698	2.11
MTPUU4	1.29	0.630	1.68	1.24	0.576	0.914	3.10	2.03	2.34	3.60	0.619	2.20
TPUU4	1.04	0.738	1.29	1.50	0.396	1.07	2.29	2.47	1.97	4.05	0.558	2.35
MPU6	4.04	2.43	7.39	1.80	2.14	1.33	10.4	3.06	11.0	4.21	3.18	2.70
MTPUU6	3.20	2.92	5.80	1.98	1.70	1.49	8.30	3.57	8.99	4.69	2.86	2.79
TPUU6	2.59	3.43	4.65	2.29	1.31	1.73	6.30	4.45	7.33	5.32	2.61	3.01

[a] cm^3/s
[b] cm^3 (STP)/cm^3 of polym.·atm

performance of our polymeric membranes for the considered gas pairs is better than most of the rubbery membranes reported in the literature. However, for the PEG4 polymer membranes, the (α_{ij}, P_i) obtained from the considered gas pairs is not as good as those for the PEG6 polymer membranes. The PEG4 membranes, compared with those in the literature, have a comparable α_{ij} but a lower P_i value.

Diffusivity and solubility

According to equation (3), permeability and selectivity may be governed by either the kinetics of diffusivity coefficient (D) or the thermodynamics of solubility coefficient (S) or both. In the present work, using the time lag method[31], one determines the values of D from the intercept of the steady state slope of the p_d *versus* t curve (*Figure 3*) with the abscissa along with equation (2). The S value is then calculated by equation (3). *Table 6* shows the values of D and S obtained. For the PEG4 polymer membranes, the values of S are in the ranges of 2.11×10^{-3} to 7.38×10^{-1} cm^3(STP)/cm^3 polymer–atm, increasing from He, H_2, N_2, O_2, CH_4 to CO_2 , and the values of D are from 1.04×10^{-8} to 6.98×10^{-6} cm^2/s, decreasing from He, H_2, O_2, N_2, CH_4 to CO_2. PEG6 polymer membranes show S values that range from 2.70×10^{-3} to 3.43 cm^3(STP) cm^3 polymer–atm and D values from 2.59×10^{-8} to 3.18×10^{-5} cm^2/s. The trends for the changes of S and D with the kind of penetrant gases are the same as the PEG4 polymeric membranes. The kind of penetrant gas markedly influences both the D and S. For the PEG6 polymer membranes, the differences of S and D between He and carbon dioxide are about three orders of magnitude, while the differences for the PEG4 polymer membranes are about two orders of magnitude. S and D increase with increasing PEG molecular weight from 400 to 600. For condensable CO_2, the S values of the PEG6 polymer membranes increase 4.6-fold and the D values increase 2.5-fold over the values of PEG4. For the non-condensable gases, the S and D values increase by 1.2~1.8- and 2.6~4.6-fold, respectively. The influences of chain extenders on S and D are not so obvious as the influences of PEG MW. The MPU polymer membranes provide slightly smaller S but larger D than TPUU. And the MTPUU polymer membranes show values of S and D that are about the average of the MPU and TPUU polymer membranes. *Figure 6* shows log D plotted against the σ^2 for gases studied. The constant c used in the plot is simply applied for scale shifting to give a clear view of the data. The data points fall approximately on a straight line in accordance with the square of the Lennord–Jones diameters (σ^2) of gases. The result is consistent with the free volume theory and Meares' model[37]

$$\log D = \log A - \left(\frac{b\pi\lambda}{4\nu}\right)\sigma^2 \tag{4}$$

where A is a constant, b is a geometrical constant, λ is the length of a diffusion step, and ν is the average free volume available per polymer segment at a given temperature.

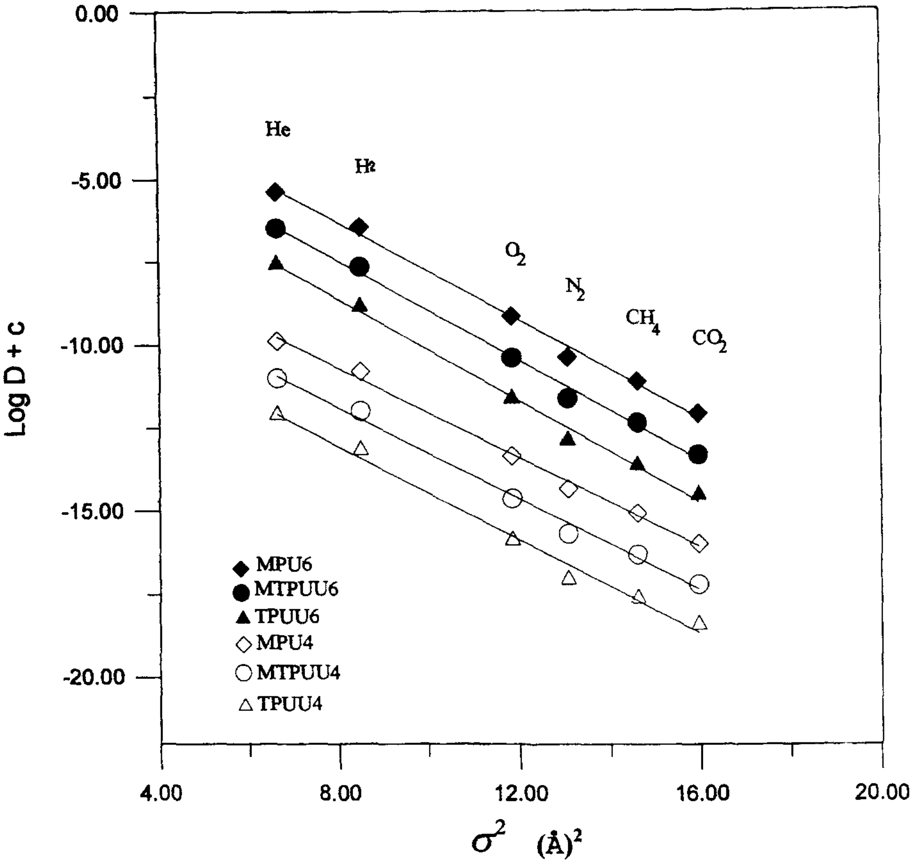


Figure 6 Diffusion coefficient (D) of different gases *versus* the square of the diameter Lennord–Jones (σ^2) of the penetrate gasses: MPU6, $c = 2$; MTPTU6, $c = 1$; TPUU6, $c = 0$; MPU4, $c = 5$; MTPUU6, $c = 4$; TPUU6, $c = 3$

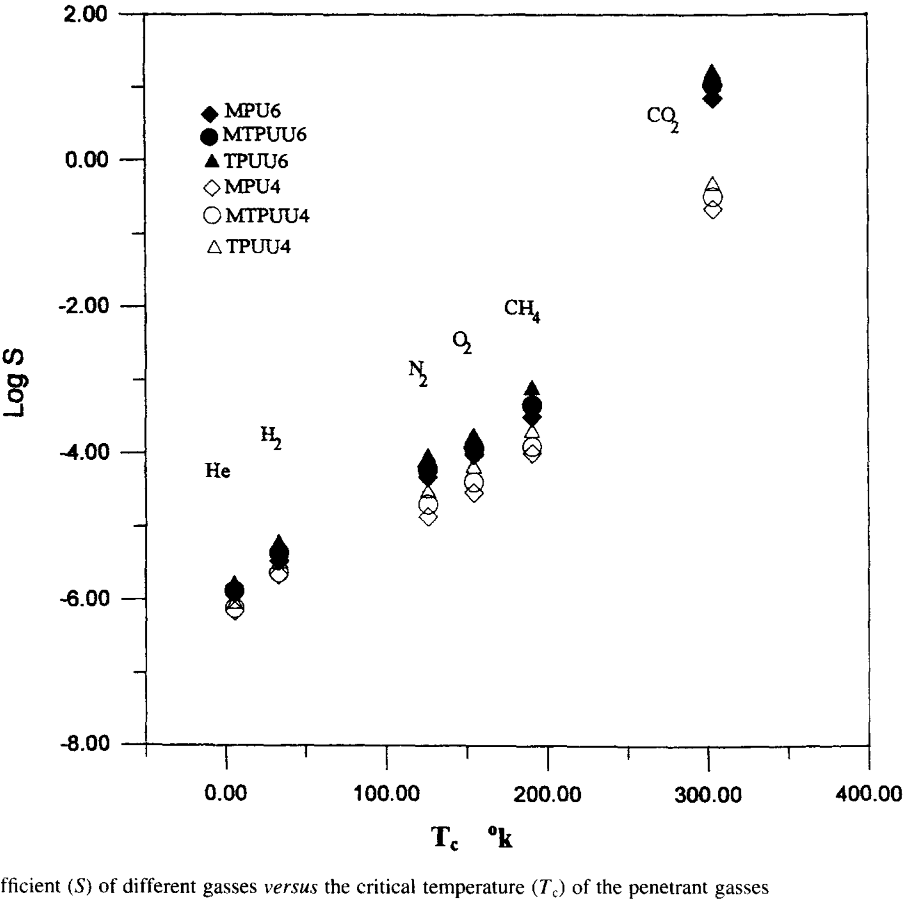


Figure 7 Solubility coefficient (S) of different gasses *versus* the critical temperature (T_c) of the penetrant gasses

Table 7 Diffusivity selectivity and solubility selectivity for different gases in the amine-contained polyurethane membranes at 35°C and 10 atm

Polymer	$\frac{D_{CO_2}}{D_{CH_4}}$	$\frac{S_{CO_2}}{S_{CH_4}}$	$\frac{D_{O_2}}{D_{N_2}}$	$\frac{S_{O_2}}{S_{N_2}}$	$\frac{D_{He}}{D_{N_2}}$	$\frac{S_{He}}{S_{N_2}}$	$\frac{D_{He}}{D_{CH_4}}$	$\frac{S_{He}}{S_{CH_4}}$	$\frac{D_{H_2}}{D_{N_2}}$	$\frac{S_{H_2}}{S_{N_2}}$	$\frac{D_{H_2}}{D_{CH_4}}$	$\frac{S_{H_2}}{S_{CH_4}}$
MPU4	0.40	29	2.7	1.4	84	0.27	175	0.11	34	0.45	71	0.19
MTPUU4	0.42	31	2.9	1.4	107	0.24	200	0.11	41	0.39	75	0.18
TPUU4	0.45	30	3.3	1.4	141	0.22	244	0.10	50	0.38	86	0.16
MPU6	0.39	79	3.5	1.4	149	0.20	306	0.09	51	0.32	106	0.14
MTPUU6	0.39	82	3.4	1.3	168	0.19	345	0.08	53	0.31	108	0.13
TPUU6	0.41	77	3.5	1.3	199	0.17	414	0.07	56	0.31	116	0.12

However, as shown in *Figure 7*, the plots of log *S versus* T_c for the gases tested obeys linear relations less well than the above plots of log *D* vs σ^2.

Table 7 presents the ratios of *Si/Sj* and *Di/Dj* for the pair of considered gases. Obviously, for the CO_2/CH_4 pair, the *Si/Sj* ratio is far larger than the *Di/Dj* ratio, indicating that the separation mechanism of the gas pair is solubility controlled. On the other hand, for He/N_2, He/CH_4, H_2/N_2 and H_2/CH_4, the ratio *Di/Dj* is much larger than the *Si/Sj* ratio. Therefore, the separation mechanism of these four gas pairs is diffusion controlled. For the O_2/N_2 pair, the ratio *Di/Dj* is slightly larger than the *Si/Sj* ratio. Therefore, the separation of O_2/N_2 pair is attained by both diffusivity and solubility, the former being slightly more important than the latter. The ratios of *Si/Sj* and *Di/Dj* of the PEG4 polymer membranes are smaller than those of the PEG4 polymer membranes, and the dominant factor for the separation of the gas pairs is the same as that of PEG6 polymer membranes.

CONCLUSION

MDEA- and/or TEPA-extended polymers, as compared to usual 1,4-butandiol-extended polyether polyurethanes and poly(urethane-urea)s, contain PEG soft segment domains in which is dissolved a significant fraction of urethane moieties, and also have a less ordered packing in the hard segments. The MDEA-containing polymers contain more dissolved urethanes in the soft segment domains and a higher T_{gs} as well as a less order ordered packing in the hard segment domains and a lower T_2 (or T_1) than TEPA-contained polymers. In the MDEA/TEPA(1/1 by mol)-extended polymers, the MDEA- and TEPA-extended hard segment domains are incompatible with each other, and the T_{gs} and the permeability are about the average values of MDEA and TEPA polymers. PEG soft segments of MW600 causes better phase separation than PEG of MW400, resulting in a lower T_{gs}. The soft segment domains are the main passages for gases permeation, with the larger MW PEG soft segments creating the greater permeability. Although the hard segment domains still play a role for permeation of gases, the effects are not so obvious as the PEG MW. The greater the packing density of hard segment domains, the less the permeability. Referring to the log–log plot of α_{ij} *versus* P_i provided by Robeson, one finds that the PEG6 polymer membranes may be one of the best membranes for the separation of the gas pairs CO_2/CH_4, He/H_2, He/N_2, He/CH_4, H_2/N_2, H_2/CH_4 and O_2/N_2. The separation of the CO_2/CH_4 pair is dominated by solubility, while for He/N_2, He/CH_4, H_2/N_2 and H_2/CH_4, the separation is dominated by diffusivity. For the separation of O_2/N_2, both diffusivity and solubility are important.

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