CO$_2$/N$_2$ Separation Ability and Structural Characteristics of Poly(butadiene-*co*-acrylonitrile)-Based Polyurethanes and Hydrogenated Nitrile Rubbers

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ABSTRACT: Two families of rubbery polymers, commercial hydrogenated nitrile rubbers and synthesized poly(acrylonitrile-*co*-butadiene)-based polyurethanes with different amount of nitrile groups were studied as CO$_2$ selective membrane materials. The polymers were characterized by the techniques of FTIR, gel permeation chromatography, WAXD, and differential scanning calorimetry. The permeabilities of pure CO$_2$ and N$_2$ were measured using constant pressure/variable volume method at a feed pressure of 6 atm. With a higher amount of polar nitrile group within a given family of polymers, the permeability coefficient (P) was found to decrease, while the permselectivity (α) of these membranes was found to increase. The trade-off between both transport parameters was less severe for the polyurethanes, which also showed much higher permeabilites. The results obtained were also discussed with respect to the polymer structure, and some relationships were found between P and T_g values. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2690–2696, 2011

Key words: polyurethane; hydrogenated nitrile rubber; carbon dioxide; separation; membrane

INTRODUCTION

Membrane technologies for gas separation have emerged as a viable alternative to traditional acid gas treatment technologies such as absorption using physical or chemical wet scrubbing, pressure swing adsorption, or cryogenic distillation. Compared to others, the membrane process neither involves phase change nor requires the use of other chemicals that need periodic regeneration. Therefore, it can be more energy efficient. It has also other advantages such as small footprint and mechanical simplicity making it relatively easy to operate and control as well as to scale-up. Additionally, the membrane process is regarded as particularly efficient for bulk separation where a very high purity is not required. Thus, it is envisioned that membrane process can be very attractive for the separation of CO$_2$ from the gases of power generation stations, oil refineries, and large cement works. To control CO$_2$ emission from combustion flue gas into the atmosphere is very important, because it is believed that CO$_2$ is a major contributor to global warming. Flue gas usually contains low concentration of CO$_2$. For conventional pulverized coal combustion, the produced flue gas consists of about 15% CO$_2$, 7% water, 3% O$_2$, 74% N$_2$, and less than 1% other gases, including SO$_2$ and NO$_x$. Selectively removing CO$_2$ from flue gas avoids permeation of the major component (N$_2$) across the membrane, thereby reducing the overall membrane area required for separation. On the other hand, the quantity of flue gas to be treated is very large. It is also at a relatively low pressure. Taking into account the gas compression costs, the high membrane productivity, which makes a membrane process economically feasible, is required. It is expected to be achieved by using membrane materials with both a high permeance and selectivity.

Typically, glassy polymers such as polysulfone, cellulose acetate, and polyimide are used in membranes for commercial gas separation.[1] Generally, they show better selectivities, because diffusion coefficients are more dependent on molecular size in this type of polymers than in rubbery ones.[2] However, the interest in membranes prepared from rubbery polymers has been increasing recently. It can be noted that the present CO$_2$/N$_2$ upper bond relationship[3] involves two rubbery polymers, modified PDMS[4] and modified polyphosphazene,[5] as the key data points. It has also been shown that poly(ethylene oxide) rubbers have interesting CO$_2$/N$_2$ separation properties.[6]

The present work deals with gas separation membranes prepared from two different classes of

rubbery polymers, both containing acrylonitrile in their polymer backbone. The first group comprises commercial hydrogenated nitrile rubbers and the second one polyurethanes synthesized using amine functionalized poly(butadiene-co-acrylonitrile). The adopted strategy was to obtain membranes with improved performance due to the increased solubility of CO$_2$ and, as a consequence, increased CO$_2$/N$_2$ permeability selectivity. To study the influence of polar nitrile groups on the polymer gas transport properties, polymers with different acrylonitrile content were selected. Although, it has been suggested that certain polar groups such as ether oxygens, nitriles, carbonyls, acetates, and amides may be useful for improving CO$_2$ solubility and CO$_2$/N$_2$ selectivity, the studies concerning the effect of polar group concentration in the polymer on CO$_2$/N$_2$ separation ability are rather scarce.[7] In contrary, these groups are typically used to improve barrier properties of polymers. Therefore, examining structurally different polymers containing various amounts of nitrile groups should allow to get better knowledge required in the design of membrane materials with optimized separation and permeation properties.

Background

Gas permeation in rubbery polymers has been satisfactorily explained in terms of a solution-diffusion model, and the permeation rate has usually been described by a simple Fick's law.[8] The diffusive flux, J, for isothermal transport of a penetrant gas through a nonporous membrane in steady-state conditions is given by:

$$J_A = D_A \cdot S_A \frac{(p_2 - p_1)}{l} \tag{1}$$

where p_2 and p_1 are the upstream (i.e., high) and downstream (i.e., low) partial pressures of gas A, respectively, and l is the membrane thickness. The product DS is called, by definition, the permeability coefficient. It denotes the rate, at which a penetrant traverses a membrane, and it is commonly expressed in units of Barrers, where 1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cm Hg. The kinetic factor, diffusivity (D), reflects the dynamics of the penetrant–polymer system, whereas the thermodynamic term, solubility (S), depends on the penetrant–polymer interactions. Membranes used in separation processes need to possess both high permeability and high selectivity. When the downstream pressure is negligible, the selectivity for a mixture of gases A and B, $\alpha_{A/B}$, is equal to the ideal selectivity based on the individual permeabilities of both gases, $\alpha^*_{A/B}$ given by:

$$\alpha^*_{A/B} = \frac{P_A}{P_B} \tag{2}$$

When eq. (1) is substituted into eq. (2), the ideal selectivity can be expressed as a product of diffusivity selectivity and solubility selectivity:

$$\alpha^*_{A/B} = \left[\frac{D_A}{D_B}\right]\left[\frac{S_A}{S_B}\right] \tag{3}$$

The diffusivity selectivity reflects the ability of the polymers to discriminate between penetrants on the basis of their sizes and shapes. It is also determined by a polymer chain flexibility, often characterized by polymer glass transition temperature, T_g, and by the fractional free volume in the polymer. The solubility selectivity is governed by the difference in condensability of the gases, often characterized by the gas critical temperature, T_c, and by the differences in their interaction with the polymer matrix.

EXPERIMENTAL

Materials

Hydrogenated butadiene-acrylonitrile rubbers with 34 wt % (H-NBR 1) and 43 wt % (H-NBR 2) acrylonitrile content, and of 0.9% residual double bond (Mooney viscosity at 100°C 63 ± 7) were supplied by Lanxess Deutschland GmbH, Germany.

Polyurethanes with 10 wt % (PU-BAN 1) or 18 wt % (PU-BAN 2) acrylonitrile content were synthesized in DMF solution by the reaction of equimolar amount of 2,4-tolylene diizocyanate (TDI, Aldrich) and aminofunctionalized poly(butadiene-co-acrylonitrile) (BAN 1: eq. wt. = 1200; BAN 2: eq. wt. = 900, Aldrich). The 15 wt % solution of dry macrodiamine in dry DMF was added dropwise to the DMF solution of TDI and stirred for 4 h at 60°C. A slight excess (0.5%) of TDI was used to compensate for side reactions involving isocyanate groups. Afterward, the temperature was raised to 80°C, and the stirring was continued for 48 h. The reaction mixture was then poured into cold MeOH/water mixture to precipitate the polymer. The precipitated polyurethane was isolated by filtration, washed with methanol, and dried in vacuum for 24 h at 100°C. The chemical structures of H-NBR and PU-BAN are presented in Table I.

Nitrogen and carbon dioxide, with a purity of 99.9%, were purchased from Air Products Sp. z o. o. Poland, and they were used as received. Relevant physical properties of penetrants considered in this study are presented in Table II.

Membrane preparation

Membranes were prepared by casting 10 wt % solution of H-NBR and 15 wt % solution of PU-BAN in

| TABLE I |
| Polymers Discussed in This Study |

Polymer	Structure
H-NBR 1,2 Hydrogenated copolymer of butadiene and acrylonitrile	
PU-BAN 1,2 Poly(butadiene-co-acrylonitrile)-based polyurethane	

freshly distilled DMF onto a glass plate and by evaporating the solvent at 60°C in a dry nitrogen atmosphere for 3 days. The thickness of the membranes, calculated as an average of several thickness measurements, was in the range of 100–150 μm.

Measurements

The infrared (IR) spectra of the polymer films were recorded with a Nicolet 6700 FTIR apparatus (Thermo Scientific, USA) by using the ATR technique.

The density of polymer membranes was determined by a buoyancy method by weighing a sample in water and in air. The membrane density was calculated as follows:

$$\rho = \frac{m_A}{m_A - m_L} \rho_0 \qquad (4)$$

where m_A was the membrane weight in air, m_L was the membrane weight in water, and ρ_0 was the density of water.

Differential scanning calorimetry (DSC) data were obtained using TA DSC 2010 apparatus (TA Instruments, Newcastle, DE). The samples were scanned from -100 to 190°C at a heating rate of 20°/min. The glass transition temperature value was taken as the midpoint of the heat capacity step change observed at the second run.

| TABLE II |
| Physical Properties of Gases |

Gas	Kinetic diameter (Å)	Critical temperature (K)
Nitrogen	3.64	126.2
Carbon dioxide	3.30	304.2

Wide-angle X-ray diffraction (WAXD) patterns of the membranes studied were recorded using HZG-4 diffractometer (Carl Zeiss, Jena, Germany) with Cu Kα radiation (wavelength $\lambda = 1.54051$ Å). The X-ray diffraction angle Θ, at which maximum of a broad peak appeared on the WAXD profile, and the following Bragg's expression for unoriented amorphous polymers:

$$d = 1.22 \frac{\lambda}{2 \sin \Theta} \qquad (5)$$

were used for calculation of an average intermolecular distance called as a d-spacing.[9]

Molar masses relative to polystyrene standards were determined by gel permeation chromatography at 80°C in DMF as eluent with a flow rate of 1 mL/min. The Knauer apparatus (Knauer, Bad Hamburg, Germany) equipped with the MIXD-DPL gel columns was used.

Pure gas permeability in the polymers was determined using the constant pressure/variable volume method. The feed side pressure of the gases was set at 6 atm. The permeate side was maintained at atmospheric pressure. Before each measurement, the feed and permeate side of the apparatus were evacuated and subsequently filled with a gas tested. A schematic representation of the gas permeation apparatus is given in Figure 1.

RESULTS AND DISCUSSION

Nitrile rubber is an elastomer commonly used in applications where resistance to oil, solvents, fuel, etc., is required. Hydrogenation of the butadiene
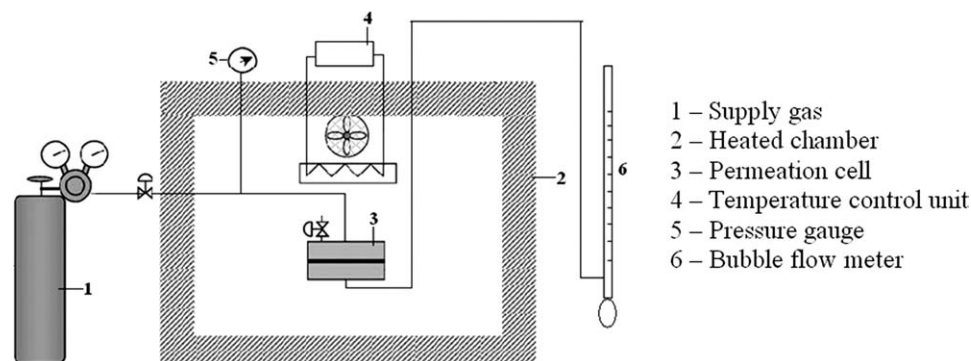

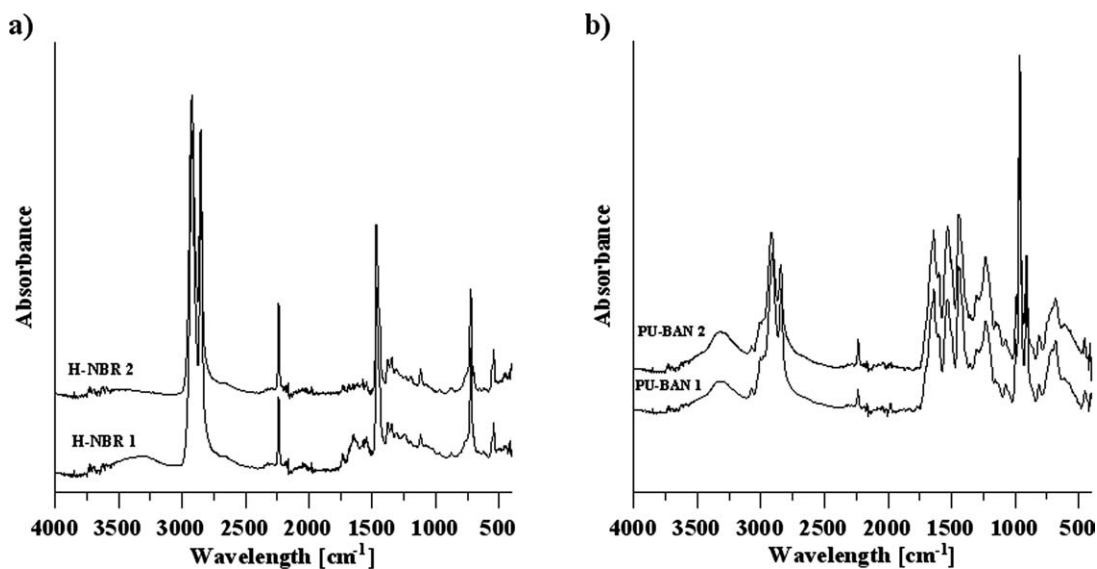**Figure 1** Schematic representation of the permeation apparatus.

Figure 2 FTIR spectra of the nitrile rubbers (a) and polyurethanes (b).

double bonds allows materials with even higher thermal stability and the resistance to different reactive substances to be obtained. The properties of such materials depend strongly upon the extent of polymer saturation and acrylonitrile content. The higher the nitrile group content, the higher will be the resistance to chemicals, but lower will be the elasticity. In this work, H-NBR rubbers with a high acrylonitrile amount (34 and 43% by weight), and with the smallest amount of unsaturation (0.9 wt %) were selected.

The H-NBR chains contain acrylonitrile and hydrogenated butadiene repeat units as well as a few free double bonds placed statistically along the chain. The IR spectra shown in Figure 2(a) demonstrate the presence of those groups, that is, the acrylonitrile band at 2230 cm^{-1} and —CH_2— asymmetric stretching bands at 2930 and 2840 cm^{-1}. On account of their chemical irregularity, these copolymers were

found to be amorphous. The respective WAXD patterns given in Figure 3(a) show a diffuse halo with a fairly well-defined maximum attributed to the amorphous material. The d-spacing values, calculated from the maximum position and listed in Table III, indicate that there is a very similar mean distance between segments of neighboring chains for the both nitrile rubbers studied. The density values determined for those polymers are also very similar. Although the expression (5) giving the interchain distance possesses only rather limited quantitative character,[9] there is correspondence between results obtained from both methods.

In Figure 4(a), the DSC scans of the H-NBR membranes can be seen. The both curves show no endothermic peaks confirming the lack of any ordered region in those polymers. However, we can observed the clear glass transitions in the low temperature region. It is noticeable that the amount of
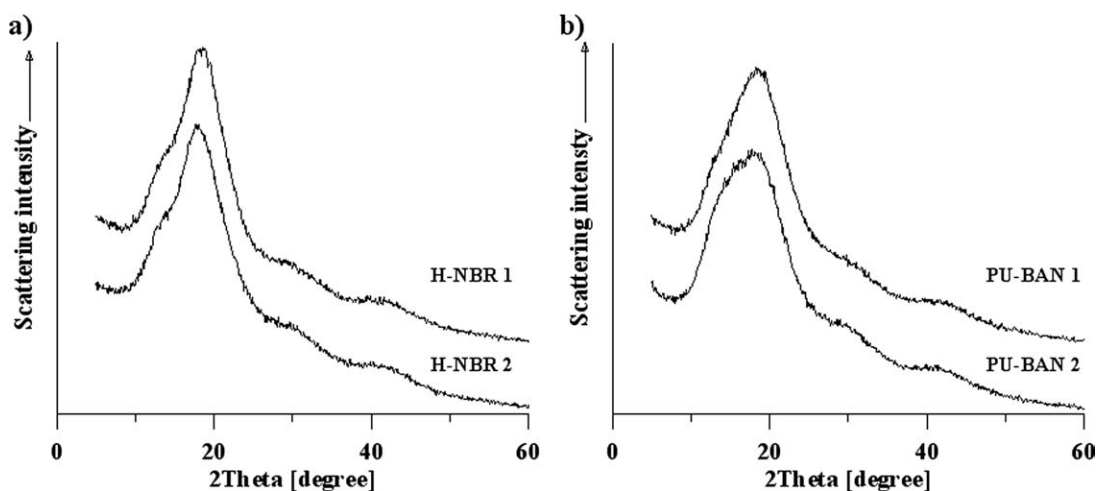

Figure 3 X-ray diffraction patterns of the nitrile rubbers (a) and polyurethanes (b).

Polymer	Nitrile content (wt %)	T_g (°C)	Density (g/cm^3)	d-Spacing (Å)
H-NBR 1	34	−27	0.950	5.84
H-NBR 2	43	−19	0.980	6.08
PU-BAN 1	10	−62	0.996	5.88
PU-BAN 2	18	−49	0.990	6.10

nitrile groups in the polymer chain affects the value of T_g. As demonstrated by the data in Table III, the presence of a greater amount of polar nitrile groups increases T_g. It is due to the increased intermolecular forces, which pull the chains closer together, reducing thereby the free volume. The effect of polarity on the thermal and mechanical properties of H-NBR rubbers has been studied recently, and the similar results have been presented.[10] On the other hand, the fact that the only correspondence found is that between chemical structure of a polymer and its T_g may suggest that the other two parameters, density and d-spacing, may not be suitable for studying the structure-permeability correlations in this type of polymers.

The second group of the membranes studied was polyaddition polymers formed by the reaction of diisocyanate and macrodiamine. As can be seen from Table I, these polymers are composed of a one-component oligomeric block joined to the other component, which produces a small linking group. The similar type of acrylonitrile and butadiene copolymer, however retaining backbone unsaturation, was used to form the polyurethane blocks. The both synthesized polyurethanes had approximately the similar amount of the polar urea linking groups (7–8 wt %) but different acrylonitrile content (10 and 18 wt %) in the polymeric blocks. The relative molar masses, compared to polystyrene standards, were 33,720 and 34,100 for PU-BAN 1 and PU-BAN 2, respectively, and they are comparable to those of conventional polyurethane elastomers. The molar

mass distributions of the synthesized polymers were 1.8 and 1.7 for PU-BAN 1 and PU-BAN 2, respectively, which are close to 2 as expected for conventional condensation polymerization. The chemical structure of the synthesized polyurethanes was verified by IR spectroscopy. The FTIR spectra of PU-BAN 1 and PU-BAN 2 given in Figure 2(b) show that their composition is quite similar. Characteristic bands for polyurethane blocks are those related to the double bond at 995 cm^{-1} (cis-1,4), 965 cm^{-1} (trans-1,4), and 910 cm^{-1} (vinyl) and to the acrylonitrile group at 2230 cm^{-1}. Very strong bands characteristic for the urea linking group are 3310–3440 cm^{-1} (NH stretching), 1615–1650 cm^{-1} (C=O stretching), 1535 cm^{-1} (NH bending and CN stretching), and 1230 cm^{-1} (NH bending and CN stretching). WAXD of these polymers shows amorphous halos [Fig. 3(b)], the position of which has been used to calculate the respective distance between segments of neighboring chains. As demonstrated by the data in Table III, both polyurethanes exhibit similar d-spacing values as well as similar densities. Moreover, these values are also similar to those determined for nitrile rubbers, despite the difference in chemical nature of both kinds of polymers.

The DSC studies, however, revealed those differences. As shown in Figure 4(b), the polyurethane samples exhibit different shift in base line in the region of −70°C to −20°C corresponding to the T_g of the polymeric blocks. Comparing the T_g values given in Table III with those referring to the respective amine terminated oligomeric reagents, which are −65°C and −51°C for BAN 1 and BAN 2, respectively, a small increase in T_g of the polyurethane blocks can be noticed. It can also be found that the higher amount of acrylonitrile groups contributes to the formation of a higher T_g polyurethane, similarly as in the case of the H-NBR rubbers. This is a clear indication of the interactions of polar acrylonitrile groups belonging to different chains, which lead to tighter chain packing and to suppressed chain mobility.
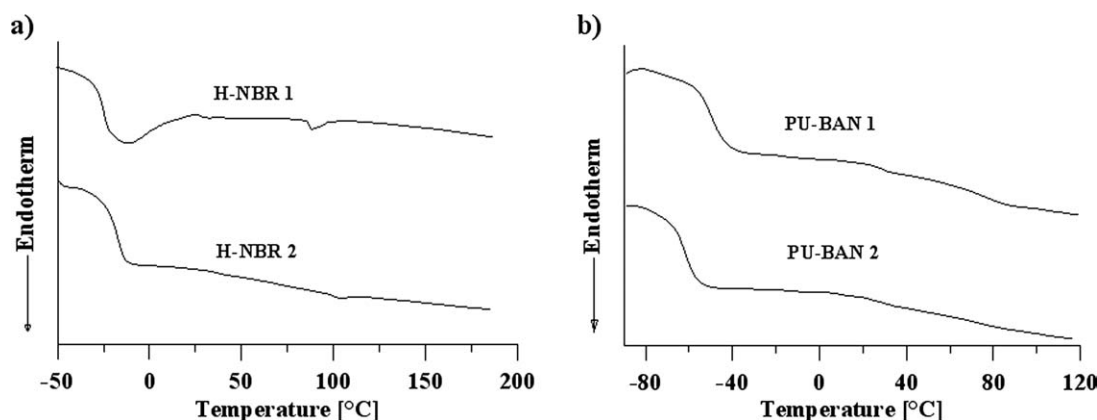
Figure 4 DSC heating curves of the nitrile rubbers (a) and polyurethanes (b).

On the other hand, the presence of polar moieties has been reported to be highly selective for CO_2.[7,11] CO_2 has a quadrupolar moment that can interact favorably with polar groups improving CO_2 solubility.

Table II summarizes the condensability and molecular size of carbon dioxide and nitrogen. Based on relative molecular size difference alone, which is not large between both gases, CO_2 diffusivity should be only slightly higher than that of N_2. Thus, the solubility seems to be the key factor that enables CO_2 to preferentially permeate over the less condensable, as characterized by T_c and therefore less soluble N_2 component.
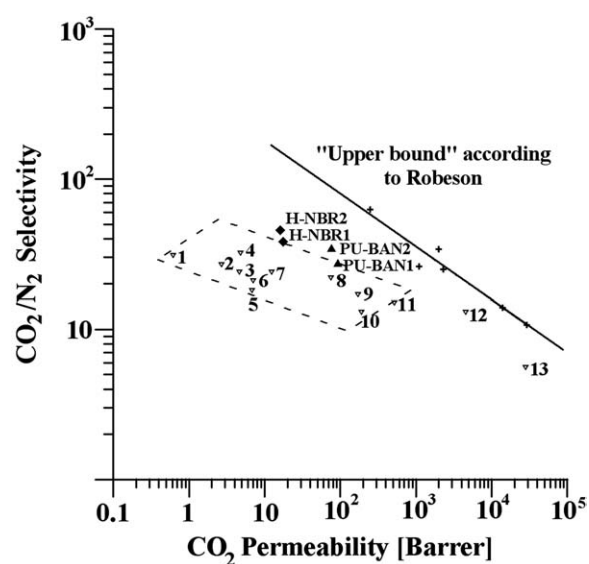
The permeabilities of carbon dioxide and nitrogen through polymer membranes investigated are shown in Table IV.

As can be seen from the results obtained, carbon dioxide appears to be far more permeable than nitrogen. The ideal selectivities calculated from the pure gas permeabilities are relatively high for both nitrile rubbers and polyurethanes. When analyze the experimental P and α values with respect to the upper bound relationship determined by Robeson for CO_2/N_2 gas pair[3] shown in Figure 5, it can be found that although these data comprise the position below the upper bound, they appear on the top edge of the data points cloud. Interestingly, the P values for H-NBR rubbers are much closer to those of glassy polymers such as polystyrene [P (CO_2) = 12.4 Barrer at 35°C] than to those of rubbery ones, for example, poly(cis-isoprene) [P (CO_2) = 191 Barrer at 35°C].[12]

The permeability and selectivity values reported in Table IV were also found to depend on the acrylonitrile group content. The presence of a greater amount of polar nitrile groups lowers the polymers permeability for each family of polymers. The hindered transport of gas molecules through the membrane is consistent with the restricted chain mobility, as illustrated by the higher T_g values of the respective polymers given in Table III. According to the general behavior of polymeric membranes showing the trade-off between permeability and selectivity, the observed decrease in permeability is accompanied by the increase in ideal permselectivity. For the hydrogenated nitrile rubbers, the selectivity appears

Figure 5 Relationship between CO_2 permeability and CO_2/N_2 selectivity of H-NBR (◆) and PU-BAN polymers (▲). Gas separation performance data of some common polymeric membranes reported in literature[12] are included for comparison (data obtained at 35°C): (1) poly(methyl methacrylate), (2) PMDA-4,4′-ODA polyimide, (3) bisphenol-A polysulfone, (4) cellulose acetate, (5) bisphenol-A polycarbonate, (6) poly(ethyl methacrylate), (7) polystyrene, (8) ethyl cellulose, (9) poly(butadiene-styrene), (10) poly(cis-isoprene), (11) poly(dimethylsilmethylene), (12) poly(dimethyl siloxane), (13) poly[1-(trimethylsilyl)-1-propyne]. The upper bound is from,[3] and a dotted line marks the area where the data points show an intensity.

to increase by 19.3% at the expense of permeability, which drops by 9.4%, when the nitrile groups content increases by 9 wt %. For the synthesized polyurethanes, the similar increase in the nitrile groups content (8 wt %) results in the enhancement in selectivity by 25.4%, which is accompanied by 17.2% loss in permeability. Comparison across both families of materials allows some interesting conclusions to be drawn. The PU-BAN 2 and the commercial H-NBR 1 have both the similar permselectivity, but the polyurethane has permeability of CO_2 higher by a factor of 4.3. This polyurethane contains nearly two times less of nitrile groups per mass unit, and despite the presence of additional polar urea groups in the polymer backbone, shows much lower T_g value that is consistent with the observed higher permeation rate. The much greater permeability of the PU-BAN 2 along with its relatively high permselectivity, as well as more apparent influence of polar group concentration on polyurethane transport properties, favors this family of polymers as potential membrane materials for CO_2 separation.

CONCLUSIONS

The results of the present study demonstrate that the incorporation of polar nitrile groups into a

TABLE IV
Gas Transport Properties of Hydrogenated Nitrile Rubbers and Polyurethanes Containing Various Amount of Nitrile Groups; 30°C

Polymer	Permeability coefficient, P [Barrer]		Ideal permselectivity α(CO_2/N_2)
	P (CO_2)	P (N_2)	
H-NBR 1	17.68	0.46	38.4
H-NBR 2	16.02	0.35	45.8
PU-BAN 1	92.31	3.34	27.6
PU-BAN 2	76.41	2.21	34.6

polymer chain has been a satisfactory approach to improve membrane selectivity, however, at the expense of its permeability. In the case of polyurethanes, the applied structural modification allowed materials to be obtained with gas separation properties being closer to the CO_2/N_2 upper bound defined by Robeson. This may create an interesting route for further improvement of the polyurethane-based membrane materials for this kind of application.

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