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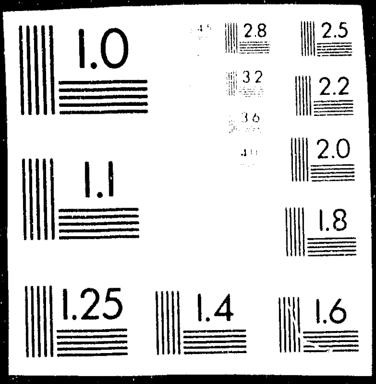

Publications and Presentations Over the Past Year Under DOE Sponsorship

Articles Published: (copies attached)

1. W. J. Koros, M. R. Coleman, and D. R. B. Walker, " Controlled Permeability

DOE/ER/13507-8

SYNTHESIS AND ANALYSIS OF NOVEL POLYMERS WITH HIGH PERMSELECTIVITY AND PERMEABILITY IN GAS SEPARATION APPLICATIONS

Progress Report

DOE/ER/13507--8
DE93 005883

December 1991 - December 1992

Submitted by

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PREPARED FOR THE U.S. DEPARTMENT OF ENERGY UNDER
CONTRACT NUMBER: DE-FG05-86ER13507

Summary of Activities

During the past year of project support, we have made significant progress toward our program goal of developing advanced materials for gas separation membrane applications and rationalizing the patterns emerging with regard to molecular structure and efficacy for these applications. The following specific achievements are noteworthy:

(i)Synthesized and tested polyarylates based on terephthalic or isophthalic acid or a tertiary butyl derivative of the isophthalic acid with different diols to illustrate the effects of: (a) "opening" the matrix by incorporation of bulky packing inhibiting groups such as the tertiary butyl moiety (b) inhibition of backbone motion via meta connected backbone connections and (c)"tightening" of the matrix by incorporation of polar halogens

(ii)Completed high temperature (up to 200-300°C) characterization of sorption and transport properties for novel materials studied previously at 35°C. This study provides preliminary conclusions regarding useful structural aspects in polymers for higher temperature applications.

(iii)Continued studies of the phenyl-substituted polymers aimed at producing super stable high temperature useful polymers for gas separations. Attempts to synthesize tetra phenyl substituted polysulfones, polycarbonates and polyarylates have not succeeded so far.

(iv)Synthesized a polyarylate based on the spirobiindane diol and bibenzoyl acid chloride to incorporate long flat packable bibenzoyl units between packing disruptive spirobiindane units in an attempt to control the segmental level morphology to produce highly selective "bottleneck" regions between highly open regions. This material is being characterized and will be reported on in the future.

(v) *Seven* new papers have appeared in print during the year, and we have five new manuscripts in press under support of DE-FG05-86ER13507. This brings the total to *23* publications in print produced under our six and a half years of DOE support. We are currently preparing three publications which will be submitted by the end of the seventh year of our support.

Details of Program Activities

The following sections provide additional information on the first and second technical items noted above. A listing of publications and manuscripts prepared since the past progress report are given in a separate section at the end of the report.

(i) Terephthalic and Isophthalic Acid Derived Polyarylates

Our earlier studies demonstrated structure-permeability principles for polycarbonates and polysulfones that allowed optimizing materials in these families for gas separation applications. Our most recent work shows that similar principles apply to the polyarylate family as well. Specifically, counterbalancing the packing disruptive effects due to introduction of t-butyl and phenolphthalein units against motion-inhibiting meta vs. para isomers substitutions, coupled with incorporation of polar attractive bromine atoms allows optimizing polyarylate properties very effectively.

Data for permeabilities and permselectivities for O_2/N_2 and CO_2/CH_4 at 35°C at approximately 2 atm feed pressure for O_2 & N2 and 10 atm for CO_2 & CH_4 are reported in Tables 1 and 2 and will be discussed in two parts, one related to each of the groups so structures in these two tables. Additional data are being collected for sorption and diffusion coefficients to further prove the suggestions made here regarding dominate factors responsible for the interesting trends discussed below. Even without these detailed data, however, it is becoming clear that tools for tailoring of permeability and permselectivity tradeoffs are emerging. To illustrate the points, we will consider the O_2/N_2 data. This gas pair is useful, since solubility selectivity effects are generally of much smaller importance than for the CO_2/CH_4 pair, so even without detailed solubility and diffusivity data, mobility selectivity based arguments tend to be adequate.

Figure 1, corresponding to the data in Table 1 shows the typical tradeoff curve for the O_2/N_2 system at 35°C with the area below the line typical of commercially available glassy or rubbery materials. This solid line was determined by an extensive review of the existing literature about ten years ago in preparation of our original proposal to DOE. The dashed line at the top of the figure corresponds to the current boundary above which no structures yet exist in the open literature. This line was taken from a recent review by Robeson, *J. Membr. Sci., 62, 165 (1991).* of the state of the art of the field. Some of the structures that define this upper bound are impossible to form into practical membranes with today's technology, but they still provide a useful limit against which to compare. Fortunately, all of the structures in our study have properties that should make them amenable to membrane formation with current technology.

Table 1: Materials focusing primarily on bisphenol-A based structures.

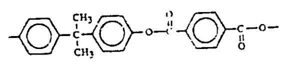
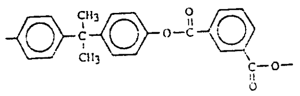
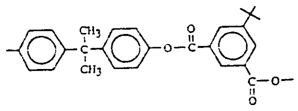
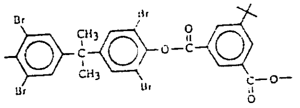
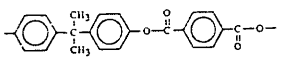
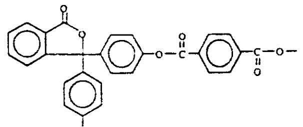
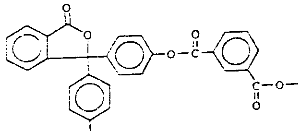
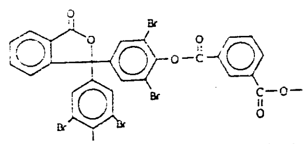
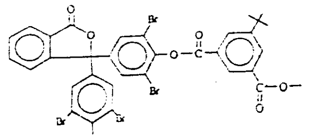
Polymer	P_{O_2} barrers	P_{O_2}/P_{N_2}	P_{CO_2} barrers	P_{CO_2}/P_{CH_4}
 "1": Bisphenol-A/terephthalic acid	2.5	4.0	11.6	17.1
 "2": Bisphenol-A/isophthalic acid	1.5	5.3	5.6	20.9
 "3": Bisphenol-A/tertiary butyl isophthalic acid	5.9	5.0	24	17
 "4": tetrabromo bisphenol-A/ tertiary butyl isophthalic acid	5.7	6.3	21	25

Table 2: Materials focusing primarily on phenolphthalein -based structures.

Polymer	P_{O_2} barrers	P_{O_2}/P_{N_2}	P_{CO_2} barrers	P_{CO_2}/P_{CH_4}
 "1": Bisphenol-A/terephthalic acid	2.5	4.0	11.6	17.1
 "5": Phenolphthalein / terephthalic acid (from Chem. J. M. Sci., 59,293 (1991)	3.2	4.9	17.2	27.0
 "6": Phenolphthalein / isophthalic acid	1.5	5.5	6.7	40
 "7": tetra bromo phenolphthalein / isophthalic acid	2.1	6.9	9.7	44.0
 "8": tetra bromo phenolphthalein / tertiary butyl isophthalic acid	7.7	6.3	34	27

The first set of structures considered consists of the series of polyarylates shown in Table 1 and in Figure 1 are structures "1"-"4" and correspond to: "1" [bisphenol-A/terephthalic acid] , "2" [bisphenol-A/isophthalic acid] , "3" [bisphenol-A/t-butyl isophthalic acid] and "4"[tetrabromo bisphenol-A/t-butyl isophthalic acid] . Consider the dotted line arrows describing a "trajectory" on the tradeoff plot from "1"-->"2" replacement of the para connection (tere) which can undergo relatively free movement at its collinear backbone connections by the noncollinear iso connection. This change causes the selectivity to rise with some loss in productivity due to increased impedance of segmental motion.. Although clearly not near the upper bound property line, such a result is still desirable, since "2" lies favorably off the tradeoff line as opposed to the starting point structure "1". Continuing from "2" to "3" illustrates the effects of introducing the large t-butyl spacer group on the motionally hindered isophthalic acid. A small loss in selectivity occurs, while the permeability rises greatly, actually exceeding that for the starting material "1". Proceeding still further from "3" to "4", illustrates the strong effects of introducing polar attractions within the matrix to hinder segmental motion. Unlike the tere---> iso change, the tetrabromo substitution drives selectivity *up sharply* with almost no loss in permeability. The "4" point lies rather close to the upper bound limit properties. This series shows the advantage of not only inhibiting motion (tere --> iso) but also simultaneously inhibiting packing (iso --> t-butyl iso change) and introduction of polar units (bisphenol A ---> tetrabromo bisphenol A) .

A second, interesting group of structures consists of the series shown in Table 2 and in Figure 2 corresponding to: "1" [bisphenol-A-terephthalic acid] , "5" [phenolphthalein/terephthalic acid], "6" [phenolphthalein/isophthalic acid] , "7" [tetrabromo- phenolphthalein/isophthalic acid], and "8" [tetrabromo phenolphthalein/t-butyl isophthalic acid] .

In this series, as shown by the dotted line arrows in Figure 2, replacement of the bisphenol A, which can undergo relatively free movement at its collinear backbone connections with the noncollinear and highly packing inhibited phenolphthalein "1" -->"5" causes the permeability and selectivity to rise favorably off the standard tradeoff line. Proceeding further from "5" to "6" involves replacement of the para connection (tere) with

Figure 1: Permeability-Selectivity Tradeoff Relationship for the oxygen-nitrogen system with a "trajectory" formed by consideration of the structures "1"-"4" in Table 1. The signficance of the solid and dashed boundaries are discussed in the text.

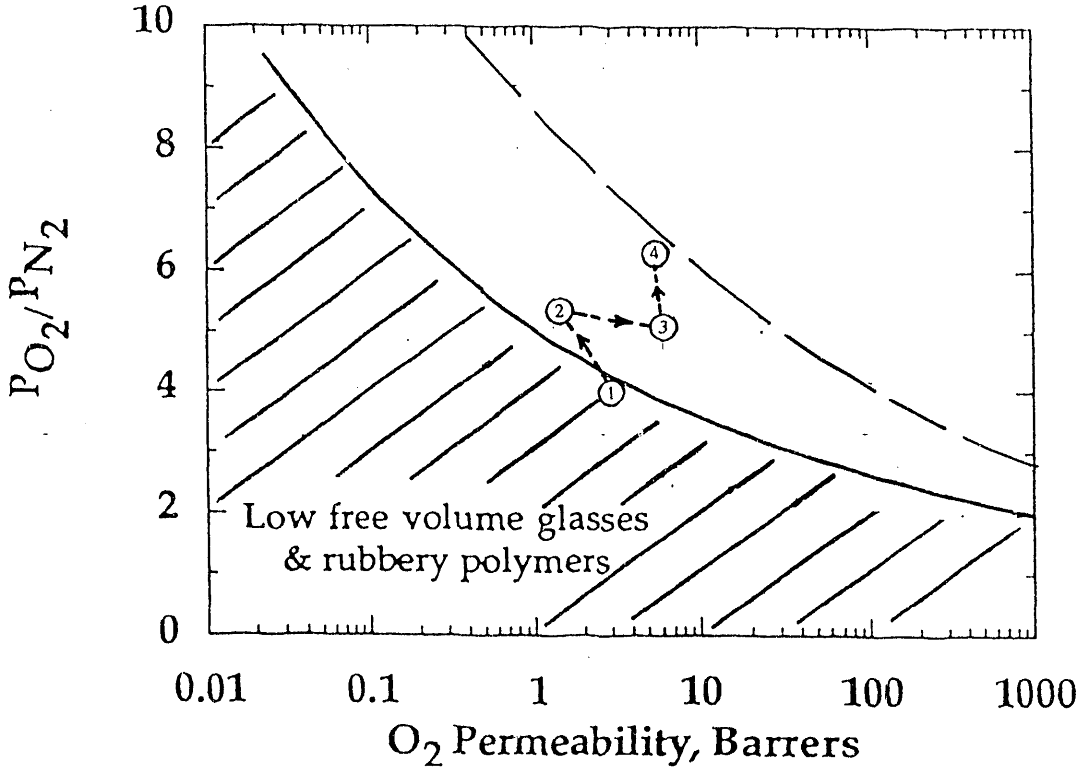
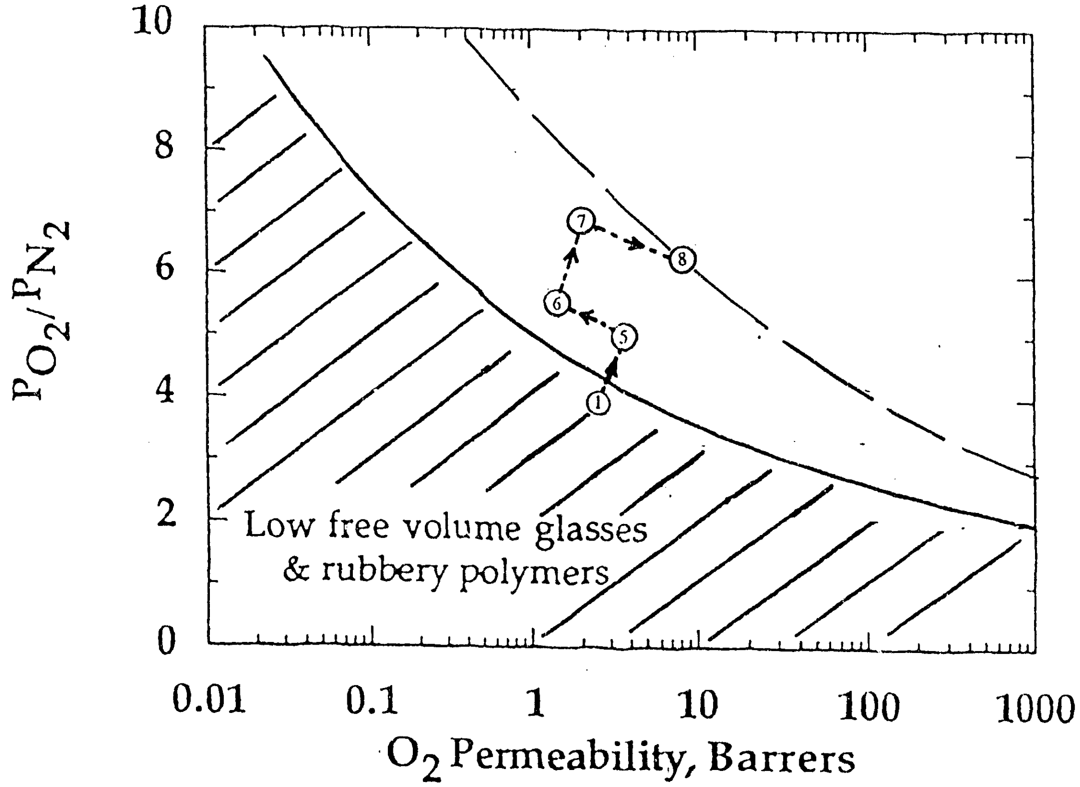


Figure 2: Permeability-Selectivity Tradeoff Relationship for the oxygen-nitrogen system with a "trajectory" formed by consideration of the structures "1"-"8" in Table 2. The signficance of the solid and dashed boundaries are discussed in the text.



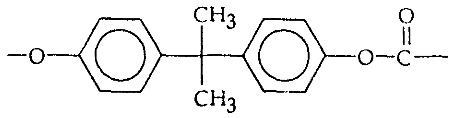
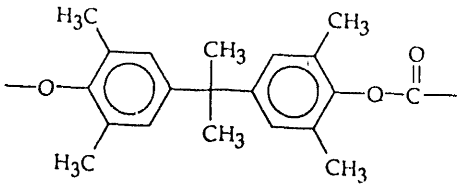
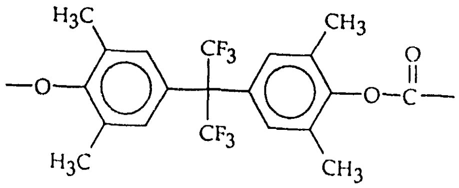
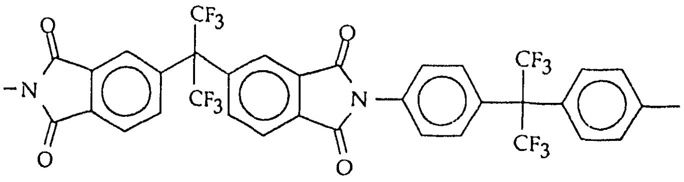
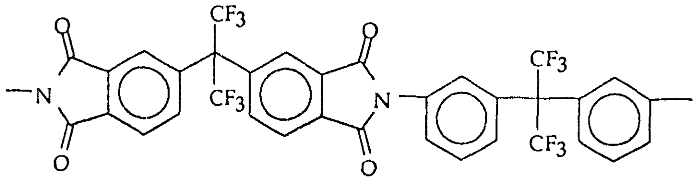
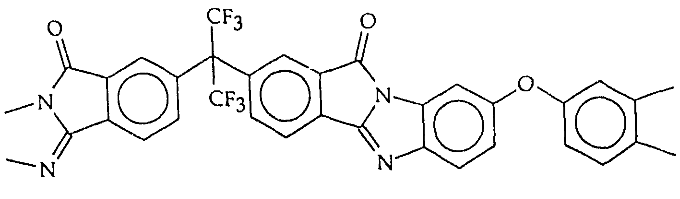
the noncollinear iso connection. This change causes a similar tradeoff with higher selectivity and a loss in productivity like that seen in the first group ("1"-->"2"), supporting the generality of the hypothesized effect. Proceeding still further from "6" --> "7", illustrates the strong effects of introducing polar attractions within the matrix to hinder segmental motion. Unlike the tere---> iso change, the tetrabromo substitution drives selectivity *and* permeability up. Applying the lessons learned in the previous set of structures and proceeding from "7" --> "8" with the introduction of the large t-butyl spacer group on the motionally hindered isophthalic group, a small loss in selectivity occurs, while the permeability rises well above that for the starting material "1". The final "8" point actually lies *on* the upper bound limit properties, while retaining the ability to be processed with current asymmetric membrane technology.

Although other series can also be considered, these two series suffice to show the same intuitively reasonable behavior seen in the polyarylates as we found in the polycarbonate and polysulfone families. Even without a more quantitative tool, these examples illustrate the exciting utility of the emerging data base in understanding the desirability of a particular structural change relative to a starting material, e.g., structure "1" in the two cases considered. This is a significant achievement in its own right and provides industry with a useful instrument to guide the ongoing search for improved materials.

(ii) High Temperature Characterization of Advanced Membrane Materials

The temperature dependence of gas sorption and transport properties for several penetrants in three families of polymers used in membrane separations are being studied in this work. Permeation and sorption equipment was build to allow operation at temperatures up to 300 and 200 °C, respectively. The polymers studied include materials that we have experience with from our previous work: polycarbonates (PC, TMPC, TMHFPC), polyimides (6FDA-6FpDA, 6FDA-6FmDA), and a novel polypyrrolone

Table 3: Structures of Polymers in Temperature Dependent Studies

PC Bisphenol-A Polycarbonate	
TMPC Tetramethyl Polycarbonate	
TMHFPC Tetramethyl Hexafluoro Polycarbonate	
6FDA-6FpDA Polyimide	
6FDA-6FmDA Polyimide	
6FDA- **TADPO** Polypyrrolone	

material (6FDA-TADPO), all of which have been previously studied at 35 °C (Hellums et al. 1989; Coleman and Koros 1990; Walker and Koros 1990). The structures of these polymers are shown in Table 3.

The permeabilities of He, CO_2, O_2, N_2 and CH_4 in all three polycarbonates, the polypyrrolone and the para-connected polyimide have been determined for temperatures up to 300 °C. Thus, these studies have spanned the T_g transition of PC at 150 °C, the sub-T_g transitions of TMPC and TMHFPC at 50 °C and the sub-T_g of 6FDA-6FpDA at 118 °C. Important information about the nature of polymer chain motions may be gained by measuring the effect of temperature on gas permeabilities through these thermal transitions.

The effect of temperature on selectivity for numerous gas pairs has been obtained. Figure 3 shows the temperature dependence of He/CH_4 separation in the materials studied thus far. By comparing PC to the substituted polycarbonates or by comparing 6FDA-6FpDA to the more rigid 6FDA-TADPO, it is apparent that the more intrinsically rigid and packing-inhibited structures are better able to retain selectivity as the temperature is increased. In effect, the loss in diffusivity selectivity can be mitigated by introducing structural changes. Figure 3 also shows a large loss in selectivity of PC as it reaches its glass transition temperature at 150 °C.

On the other hand, Figure 4 shows a He/CO_2 separation, where an increase in *solubility* selectivity with temperature dominates and the overall selectivity actually *increases* with temperature. Again, as PC reaches its T_g, permselectivity drops off dramatically.

Completion of the high temperature sorption system has allowed measurement of gas solubilities for the same penetrants at temperatures up to 200 °C in the polycarbonates and the polypyrrolone material. With this additional information, we are able to divide the *overall* selectivity into *diffusivity* and *solubility* selectivity in order to better understand the effect of temperature on the two factors. Figure 5 shows the temperature dependence of a He/CH_4 separation in TMHFPC. In this case, there is a large loss in diffusivity selectivity due to the large difference in kinetic diameter of the two gases. However, the solubility

Figure 3: Temperature Dependence of Helium/ Methane Selectivities

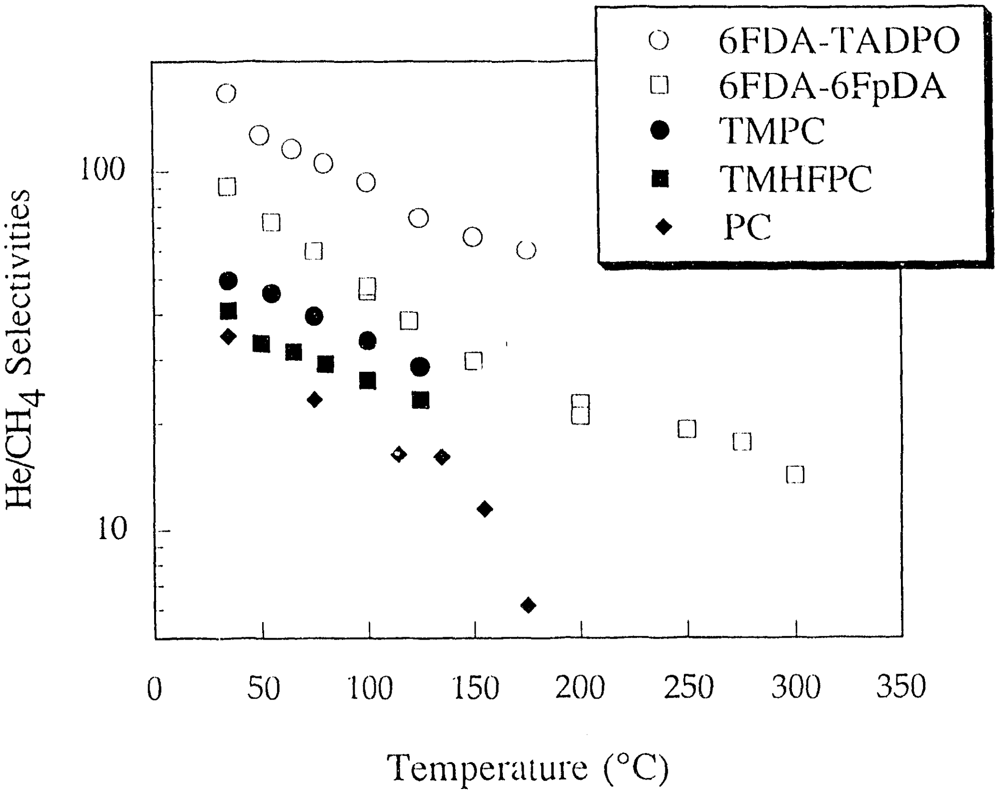


Figure 4: Temperature Dependence of Helium/Carbon Dioxide Selectivities

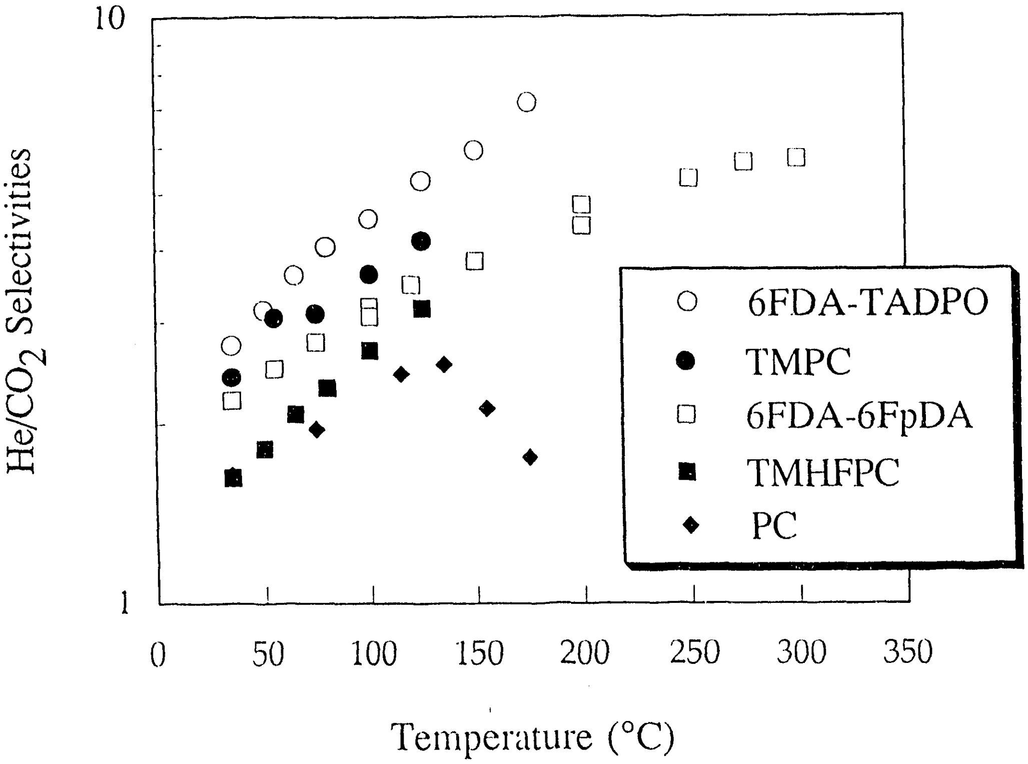
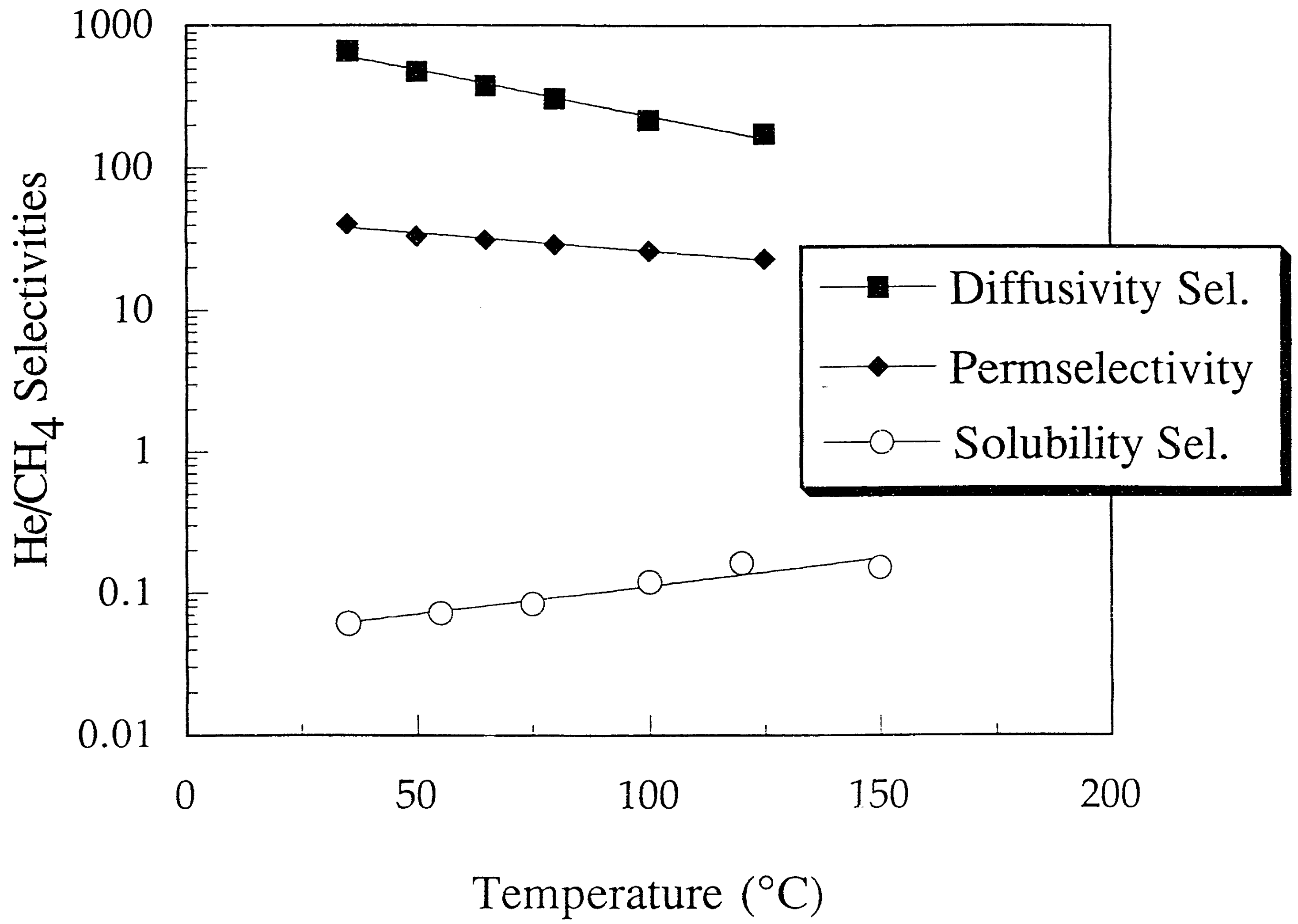


Figure 5: Helium/ Methane Selectivities in TMHFPC Partitioned into Mobility and Solubility Components



selectivity increases with temperature due to the higher condensibility of CH_4, reducing the loss in overall selectivity with temperature.

The activation energies of permeation and diffusion and heats of sorption obtained from these studies are shown in Table 4. These values reveal that the more packing-inhibited materials consistently have lower activation energies for permeation and diffusion due to their larger free volumes or more "open" structures. Also, the larger molecules (N_2 and CH_4) have higher activation energies than small He molecules. The low permeation activation energies for CO_2, however, are explained by examining its heats of sorption. In all cases, CO_2 has the largest negative heat of sorption due to its high "condensibility" or large negative heat of condensation. Table 4 also shows the effect of thermal transitions on the permeation activation energies for PC (T_g transition) and 6FDA-6FpDA (sub-T_g transition). In both cases, the activation energies above the transitions are significantly higher due to the increased region of motion involved with penetrant permeation at these higher temperatures.

Our tentative conclusions at this time include:

- Permeability increases and permselectivity decreases with temperature for <u>most</u> membrane gas separations.
- The effect of temperature on <u>solubility selectivity</u> is governed by the relative condensibilties of the components being separated and their interactions with the polymer matrix.
- The temperature dependence of <u>diffusivity selectivity</u> is governed by the relative sizes of the gases being separated.
- Increased chain motions incited by rising temperature can be probed by measuring gas transport properties over ranges which span thermal transitions of the polymer.
- Thermally stable materials have been studied which exhibit exceptional productivities and reasonable selectivities at high temperatures.

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Table 4. Activation Energies and Enthalpies of Sorption

	E_p (kcal/mol) 5 atm				
	He	CO_2	O_2	N_2	CH_4
PC (below Tg)	4.2	3.0	4.7	6.0	6.2
" (above Tg)	***4.6***	***7.9***	—	***10.3***	***12.8***
TMPC	3.0	1.6	2.8	4.0	4.5
TMHFPC	2.3	0.4	2.1	3.0	3.7
6FDA-6FpDA **(below sub-Tg gamma transition)**	2.0	0.7	2.0	3.2	4.3
6FDA-6FpDA (above sub-Tg gamma transition)	***2.6***	***1.3***	—	***4.1***	***4.8***
6FDA-TADPO	2.2	0.5	2.0	3.2	4.2
	H_s (kcal/mol) 5 atm				
	He	CO_2	O_2	N_2	CH_4
PC	-2.5	-5.3	-2.6	-3.7	-3.8
TMHFPC	-1.3	-4.9	-2.7	-3.1	-3.7
	E_d (kcal/mol) 5 atm				
	He	CO_2	O_2	N_2	CH_4
PC	6.7	8.3	7.3	9.7	10.0
TMHFPC	3.6	5.3	4.8	6.1	7.4

Publications and Presentations Over the Past Year Under DOE Sponsorship

Articles Published: (copies attached)

1. W. J. Koros, M. R. Coleman, and D. R. B. Walker, " Controlled Permeability Polymer Membranes", *Annu. Rev. Mater. Sci., 22*, 47 (1992).
2. M. W. Hellums, W. J. Koros, G. R, Husk and D. R. Paul, "Gas Transport in Halogen-Containing Aromatic Polycarbonates", *J. Appl. Polym. Sci., 43*, 1977 (1991).
3. C. L. Aitken, W. J. Koros, and D. R. Paul, "Gas Transport Properties of Biphenol Polysulfones", *Macromolecules, 25*, 3651 (1992).
4. C. L. Aitken, W. J. Koros, and D. R. Paul, "Effect of Structural Symmetry on Gas Transport Properties of Polysulfones", *Macromolecules, 25*, 3424 (1992).
5. C. L. Aitken, J. S. McHattie and D. R. Paul, "Dynamic Mechanical Behavior of Polysulfones", *Macromolecules, 25*, 2910 (1992).
6. L. M. Costello and W. J. Koros, "Temperature Dependence of Gas Sorption and Transport Properties in Polymers: Measurement and Applications", *I. & E.C Research, 31*, 2708 (1992).
7. M. W. Hellums, W. J. Koros and J. C. Schmidhauser, "Gas Separation Properties of Spirobiindane Polycarbonate", *J. Membr. Sci., 67*, 75 (1992).

Articles Accepted and in Press:

1. C. L. Aitken, D. R. Paul and D. K. Mohanty, "Gas Transport Properties of Poly(arylether bissulfone)s and Poly(arylyether bisketone)s", *J. Polym. Sci. , Polym. Phys. Ed., (in press)*
2. C. L. Aitken and D. R. Paul "Gas Transport Properties of Polysulfones based on Dihydroxynapthalene Isomers", *J. Polym. Sci. , Polym. Phys. Ed., (in press)*
3. M. Agular-Vega and D. R. Paul, "Gas Transport Properties of Polyphenylene Ethers ", *J. Polym. Sci. , Polym. Phys. Ed., (in press)*
4. M. Agular-Vega and D. R. Paul, "Gas Transport Properties of Polycarbonates with Aromatic Substitutions on the Bisphenol Connector Group ", *J. Polym. Sci. , Polym. Phys. Ed., (in press)*
5. L. A. Pessan and W. J. Koros, "Isomer Effects on Transport Properties of Polyesters Based on Bisphenol-A", *J. Polym. Sci. , Polym. Phys. Ed., (in press)*

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