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

Progress Report

December 1990 - November 1991

Submitted by

W. J. Koros and D. R Paul
Department of Chemical Engineering
The University of Texas at Austin
Austin, Texas 78712-1062
(512) 471-5866
(512) 471-5392

November 15, 1991

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

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

COPIES OF THIS DOCUMENT IS UNLIMITED

DEC 17 1991

Summary of Activities

During the past eleven months of project support we have made significant progress toward our program goal to develop advanced materials for gas separation membrane applications. The following specific achievements are noteworthy.

- Synthesized and completed characterization of permeability and selectivity properties of a group of polysulfones and polyether ketones with the potential for higher use temperatures.
- Synthesized and characterized the members of a series of polyesters derived from spirobiindane bisphenol monomer in conjunction with meta and para substituted diacid chlorides. Work was reported in our last annual report on a polycarbonate derived from the spirobiindane monomer.
- Synthesized and characterized the gas transport and thermal properties of diphenyl substituted polyphenylene oxide. The diphenyl substituted material has a potential for higher temperature applications than the standard dimethyl substituted polymer. Also the temperature dependence of the gas transport properties for the oxygen/nitrogen system was characterized over the range from 35 to 65°C for both of these analog materials.
- Five new papers have appeared in print during the year, and we have prepared five new manuscripts and given four presentations at technical meetings under support of DE-FG05-86ER13507. This brings the total to sixteen publications in print produced under our five-and-a-half years of DOE support. We are currently preparing four additional publications which will be submitted by the end of the sixth year of our support.

Details of Program Activities

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

Polysulfones and Polyether Ketones

Extension of our understanding of the detailed structure-property characteristics of the polysulfone family was continued in this fifth year of grant support. The polysulfones are very important since they have proven to have good asymmetric membrane forming capabilities. For instance, the standard bisphenol A based polysulfone formed by condensation with dichlorodiphenyl sulfone is the basis for the highly successful Prism® and Prism alpha® gas separation membrane systems.

Extensions of our prior work were achieved by formation of biphenylene based polysulfones shown as items 2 - 4 in Table 1. The Tg transitions were determined by DSC while the sub Tg transition temperatures were assessed by dynamic mechanical analysis at 110 cycles per second. The d-spacings were determined by x-ray with Bragg's law applied to the maximum in the amorphous scattering response. Carbon dioxide and oxygen permeability as well as carbon dioxide/methane and oxygen/nitrogen selectivity values at 35°C are shown for these materials in Table 2. Item 1, of course, is the bisphenol A monomer used in the formation of standard polysulfone and is included for comparison purposes. Perhaps the most unusual structure considered is the hexamethylbiphenylene ether polysulfone synthesized in our labs. As shown in Table 1, this material exhibits a glass transition of 295°C with an attractive trade-off between permeability and permselectivity for the carbon dioxide/methane and oxygen/nitrogen systems.

Table 1a: Standard Bisphenol A Polysulfone and Biphenylene Polysulfones **Table 1b: Biphenylene Polymers**

Polymer	T _g (°C)	T _γ (°C)	density (g/cc)	d- spacing (Å)	P _{CO₂} (Barrers)	$\frac{P_{CO_2}}{P_{CH_4}}$	P _{O₂} (Barrers)	$\frac{P_{O_2}}{P_{N_2}}$
Standard PSF	185	-85	1.24	5.0	05.6	22	1.4	5.6
BIPSF	231	-83	1.29	4.8	05.6	22	1.3	5.5
TMBIPSF	288	-90, 50	1.19	5.3	31.8	25	5.8	4.8
HMBIPSF	295	-100, 220	1.14	5.3	25.5	27	6.0	5.0

CO₂ and CH₄ at 10 atm, O₂ and N₂ at 1 atm, both systems at 35 °C

A related, smaller scale study done to compare properties of polycarbonates, polysulfones and polyetherketones should also be noted here. The structures of these materials are shown in Table 2, and their physical properties are shown in Table 3a. Summaries of permeabilities and selectivities for the carbon dioxide/methane system and oxygen/nitrogen system are given in Table 3b. A direct comparison of the effect of the ketone versus the sulfone group is possible from these data. The structures referred to as PBK, PBKS, and PBSF have analogous structures that only differ by sulfone or ketone groups in the repeat unit. The higher permeability coefficients for PBSF versus the analogous PBK is interesting. Consistent with typical trade off behavior found related to permeability and selectivity, the selectivity coefficients for the bisketone polymer are higher than those for the bissulfone polymer.

Table 2: Poly(Aryl Ether Bisketones) & Poly(Aryl Ether Bissulfones)

<p>Bisphenol A Polycarbonate PC</p>	<p>Bipshenol A Polybisketone PBK</p>
<p>Biphenol A Polysulfone PSF</p>	<p>Bipshenol A Polybissulfone PBSF</p>
	<p>Bisphenol S Polybisketone PBK-S</p>

Table 3a: Summary of Bis Ketone and Bis Sulfone Polymer Properties

Polymer	T _g (°C)	d-spacing (Å)	Density (g/cc)	FFV $\left(\frac{V-V_0}{V}\right)$	T _γ (°C)
PC	150	5.2	1.20	0.164	-80
PBK	180	4.9	1.12	0.146	-70
PBK-S	219	4.9	1.29	0.143	-50
PSF	185	5.0	1.24	0.156	-85
PBSF	240	5.0	1.27	0.155	-80

Table 3b: Permeabilities & Selectivities for Bisketone & Bissulfone Polymers

Polymer	P _{CO₂} (Barrers)	$\frac{P_{CO_2}}{P_{CH_4}}$	P _{O₂} (Barrers)	$\frac{P_{O_2}}{P_{N_2}}$
Bisphenol A Polycarbonate (PC)	6.8	23	1.61	5.1
Bisphenol A Polybisketone (PBK)	3.3	23	0.75	5.8
Bisphenol S Polybisketone (PBK-S)	3.27	28	0.64	6.0
Bisphenol A Polysulfone (PSF)	5.6	22	1.39	5.6
Bisphenol A Polybissulfone (PBSF)	7.35	17	2.39	5.1

CO₂ & CH₄ data at 10 atm, O₂ & N₂ data at 2 atm

Table 4: Comparison of Bisphenol A (BPA) and spirobiindane (SBI)-based polyesters.

Polymer	P_{O_2} (Barrers)	$\frac{P_{O_2}}{P_{N_2}}$	$\frac{D_{O_2}}{D_{N_2}}$ $\times 10^8$ (cm ² /sec)	$\frac{S_{O_2}}{S_{N_2}}$ cc (STP) cc atm	$\frac{S_{O_2}}{S_{N_2}}$	FFV
BPA/ISO	<u>1.45</u>	<u>5.34</u>	3.83	<u>0.29</u>	1.50	0.1583
SBI/ISO	<u>5.31</u>	<u>5.26</u>	9.83	<u>0.41</u>	1.39	0.1930
BPA/TERE	<u>2.54</u>	<u>4.03</u>	6.66	<u>0.29</u>	1.60	0.1605
SBI/TERE	<u>15.0</u>	<u>4.46</u>	18.73	<u>0.61</u>	1.39	0.1973

1 barrer [=] 10^{-10} [cc(STP) cm]/[(cm² sec cm Hg)]

Aromatic Polyesters Derived from Spirobiindane

In our last annual report we provided data for the permeability and selectivity properties of polycarbonate derived from spirobiindane diol structure. This polymer had been provided to us by request from the General Electric Company because our assessment of its combination of structurally inhibited packing and motion suggested that it would be a good candidate membrane material for oxygen/nitrogen separation. As was reported last year, this turned out to be a correct assessment, and the polycarbonate had attractive properties.

Also reported last year was synthesis and permeability and selectivity characterization of the individual polyesters derived from terephthalic and isophthalic acids condensed with bisphenol A monomer. These materials were chosen as benchmarks for comparison in a series of polyesters planned for synthesis by our group. As a logical extension of the polycarbonate work, the spirobiindane diol was used in the formation of polyesters based on the isophthalic and terephthalic acid chlorides. Over the past year we have completed the characterizations of these polyesters and compared their properties to the aromatic polyesters derived from the more flexible and less packing inhibited bisphenol A monomer. These results are being summarized in a paper currently being prepared for publication, and the essential elements of that paper are abstracted here.

As shown in Table 4, a comparison of the isophthalic and terephthalic acid polyesters derived from bisphenol A and spirobiindane reveal attractive tradeoffs in productivity and selectivity as a result of the replacement of the flexible bisphenol A with the spirobiindane monomer. The higher permeabilities can be attributed to both higher diffusion coefficients and solubilities of oxygen in the spiro-based materials. On the other hand, the overall selectivity of the two materials are rather similar, and this derives from a higher mobility selectivity for the spiro-based materials and a lower solubility selectivity in these more open structures. The

detailed reason for this lower solubility selectivity of oxygen over nitrogen is not well understood but has been observed in other cases where the matrix is "opened" by the addition of structural or packing disrupting units such as the spirobiindane unit.

Phenol Substituted Polymers

The objective of this section of our work is to explore materials useful in oxidizing environments and in higher temperature applications while understanding the fundamental effects on the gas transport properties of polymers caused by attachment of different pendant groups on the backbone. Aromatic groups are of particular interest due to their ability to provide higher temperature stability to membrane materials. The first two materials being compared in this respect are 2,6-dimethyl polyphenylene oxide and a new material, PDPO, polydiphenyldiphenylene oxide. The structures of these two materials are shown below:

Table 5 compares thermal transitions, densities, d-spacings, and free volume fractions for the two materials. The T_β and T_γ temperatures are sub T_g transitions characteristic of the motions of the backbone or pendant groups in the polymer. The glass transition of the diphenyl substituted material is raised to almost 230°C. It was rather surprising that the temperature was not raised more, given the tremendous increase in bulk associated with the substitution.

Table 5: Comparison of Phenylene Oxides Properties.

	$T_g^{(a)}(^{\circ}\text{C})$	$T_{\beta}^{(b)}(^{\circ}\text{C})$	$T_{\gamma}^{(b)}(^{\circ}\text{C})$	$d^{(c)}(\text{\AA})$	$T_d^{(d)}(^{\circ}\text{C})$	$(V-V_0)/V$
PPO	212	-55	-----	6.1	450	0.1988
PDPO	229	80	-140	5.0	564	0.1882

a) at 20°C/min

b) From A. Eisenberg and H. Cayrol, *J. Polym. Sci. Part C*, **35**, 129 (1971)

c) From x-ray diffraction data $\lambda = 1.54 \text{ \AA}$

d) From TGA at 10°C/min

Complete characterization in terms of permeability, solubility, and diffusivity for these two materials are reported in Tables 6a-c for methane/nitrogen and carbon dioxide at 35°C. The selectivities of helium relative to methane, oxygen relative to nitrogen, and carbon dioxide relative to methane for the highly hindered diphenylphenylene oxide are rather low. As is shown in the table of thermal properties, T_{β} which is the next thermal transition peak below the glass transition temperature, appears to have been raised dramatically from - 55°C to + 80°C by the diphenyl substitution. This might, at first glance, suggest a significant inhibition of sub- T_g motion; however, a very low transition peak not apparent in 2,6 dimethylphenylene oxide is apparent at - 140°C in the diphenylphenylene oxide. Such low temperature motions are generally thought to be associated with very small scale movement with possible importance to diffusion in the glass. The motion associated with T_{β} , on the other hand, may be more significant for mechanical properties. If this is correct, more sub T_g motion may actually be present in the diphenylphenylene oxide than exists in the 2,6 dimethylphenylene oxide.

Table 6a: Comparison of Gas Permeability Coefficients of PPO and PDPO

	He	N ₂	CH ₄	O ₂	CO ₂
PPO	8.2	3.5	4.1	14.6	6.5
PDPO	3.3	1.6	2.7	7.7	4.0

Barrer = $10^{-10} [\text{cm}^3 (\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}]$

Table 6b: Apparent Solubility Coefficients, S_a [cc(STP)/(cm³ atm)], @ 20 atm for PPO and PDPO.

	CH ₄	N ₂	CO ₂
PPO	0.7	0.28	2.1
PDPO	0.7	0.21	1.8

Table 6c: Apparent Diffusion Coefficients, D_a , @ 20 atm for PPO and PDPO.

	$D_a \times 10^8$ (cm ² /s)		
	CH ₄	N ₂	CO ₂
PPO	2.9	8.0	18.3
PDPO	2.2	5.4	12.4

Additional work to characterize temperature dependence of the permeability and diffusion coefficients in a wider variety of materials of systematically varied structure is underway in these two materials as well as in our group and should be available by the close of the sixth year of grant support.

In addition to the substituted polyphenylene oxide materials, a large number of phenyl substituted polysulfones and polycarbonates are planned for preparation in the final year of grant support. Structures and their methyl substituted analogs are shown in Tables 7a and 7b. We will begin characterization both in terms of thermal properties and gas sorption and transport properties as soon as the synthesis of these materials is completed. This work should also be underway partially completed by the end of the sixth year of grant support and will continue under a renewal proposal.

Table 7a: Polycarbonates & Polysulfones Based on Bisphenol-A structure with Methyl and Phenyl Substitutions Proposed for Study.

<p style="text-align: center;">PC</p>	<p style="text-align: center;">PSF</p>
<p style="text-align: center;">TMPC</p>	<p style="text-align: center;">TMPSF</p>
<p style="text-align: center;">DPPC</p>	<p style="text-align: center;">DPPSF</p>
<p style="text-align: center;">TPPC</p>	<p style="text-align: center;">TPPSF</p>

Table 7b: Polycarbonates & Polysulfones Based on Bisphenol. Variation of Structure with Methyl and Phenyl Substitutions.

<p style="text-align: center;">BPC</p>	<p style="text-align: center;">BPSF</p>
<p style="text-align: center;">TMBPC</p>	<p style="text-align: center;">TMBPSF</p>
<p style="text-align: center;">TPBPC</p>	<p style="text-align: center;">TPBPSF</p>

**PUBLICATIONS AND PRESENTATIONS OVER THE PAST YEAR GIVEN
UNDER DOE SPONSORSHIP GIVEN SINCE LAST PROGRESS REPORT**

Articles Published

1. McHattie, J. S., W. J. Koros and D. R. Paul, "Effect of Isopropylidene Replacement on Gas Transport Properties of Polycarbonates", *J. Polym. Sci.; Polym. Phys. Ed.*, **29**, 731 (1991).
2. McHattie, J. S., W. J. Koros and D. R. Paul, "Gas Transport Properties of Polysulfones. Part I: Role of Symmetry of Methyl Group Placement on Bisphenol-A Rings", *Polymer*, **32**, 840 (1991).
3. McHattie, J. S., W. J. Koros and D. R. Paul, "Gas Transport of Polysulfones. Part II: Effect of Bisphenol Connector Groups", *Polymer*, **32**, 840 (1991).
4. Koros, W. J. and D. R. B. Walker, "Gas Separation Membrane Materials Selection Criteria: Weakly and Strongly Interacting Feed Component Situations", *Polymer Journal*, **23** (1991).
5. Mohr, J. M., D. R. Paul, G. L. Tullos and P. E. Cassidy, "Gas Transport Properties of a Series of Poly(ether ketone) Polymers", *Polymer*, **32**, 2387 (1991).

Publications Accepted and in Press

6. Koros, W. J., M. W. Hellums and D. R. Paul, "Gas Transport in Halogen-Containing Aromatic Polycarbonates", *J. Appl. Polym. Sci.*
7. Hellums, M. W., W. J. Koros and J. C. Schmidhauser, "Gas Transport in Spirobiindane Polycarbonate", *J. Membr. Sci.*
8. Story, B. J. and W. J. Koros, "Sorption and Transport of CO₂ and CH₄ in Chemically Modified Poly(phenylene oxide)", *J. Membr. Sci.*
9. Koros, W. J., M. R. Coleman, and D. R. Walker, "Controlled Permeability Polymer Membranes", *Annual Review of Materials Science*.
10. Aitken, C. L., J. S. McHattie, and D. R. Paul, "Dynamic Mechanical Behavior of Polysulfones", *Macromolecules*.

Presentations at Technical Meetings

1. Koros, W. J., S. C. Pesek and I. Pinnau, "Material Selection for Gas Separation", Progress in Membrane Science and Technology, Enschede, The Netherlands, 25-28 June 1991.

2. Aitken, C., D. R. Paul and W. J. Koros, "The Gas Transport Properties of New Polysulfone Materials and their Isomers", Progress in Membrane Science and Technology, Enschede, The Netherlands, 25-28 June 1991.
3. Koros, W. J., "Material Selection for Gas Permeable Contact Lenses," Third Annual Meeting on Contact Lenses, St. Louis, Missouri, 15 March 1991.
4. Koros, W. J., "Polymers for Membrane-Based Gas Separation", Gas Separation International, Austin, Texas, 22 April 1991.

END

**DATE
FILMED**

2 / 03 / 92