CRADA FINAL REPORT

CO$_2$ Separation Using Thermally Optimized Membranes: A Comprehensive Project Report (2000 – 2007)

Idaho National Laboratory

and

LANL and Pall Corporation

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ABSTRACT

This is a complete (Fiscal Years 2000–2007) collection of the Idaho National Laboratory's (INL) research and development contributions to the project, "CO_2 Separation Using Thermally Optimized Membranes." The INL scientific contribution to the project has varied due to the fluctuations in funding from year to year. The focus of the project was polybenzimidazole (PBI) membranes and developing PBI compounds (both substitution and blends) that provide good film formation and gas separation membranes. The underlying problem with PBI is its poor solubility in common solvents. Typically, PBI is dissolved in "aggressive" solvents, like N,N-dimethylacetamide (DMAc) and N-methylpyrrolidone (NMP). The INL FY-03 research was directed toward making soluble N-substituted PBI polymers, where INL was very successful. Many different types of modified PBI polymers were synthesized; however, film formation proved to be a big problem with both unsubstituted and N-substituted PBIs. Therefore, INL researchers directed their attention to using plasticizers or additives to make the membranes more stable and workable. During the course of these studies, other high-performance polymers (like polyamides and polyimides) were found to be better materials, which could be used either by themselves or blends with PBI. These alternative high-performance polymers provided the best pathway forward for soluble high-temperature polymers with good stable film formation properties. At present, the VTEC polyimides (product of RBI, Inc.) are the best film formers that exhibit high-temperature resistance. INL's gas testing results show VTEC polyimides have very good gas selectivities for both H_2/CO_2 and CO_2/CH_4. Overall, these high-performance polymers pointed towards new research areas where INL has gained a greater understanding of polymer film formation and gas separation. These studies are making possible a direct approach to stable polymer-based high-temperature gas separation membranes.

This report is separated into several sections due to the complexity of the research and the variation with the development of better high-temperature, gas separation membranes. Several fiscal years are combined because the research and development efforts within those areas crossed fiscal year boundaries.

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SCHEMES

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ACRONYMS

CRADA	cooperative research and development agreement
CU	University of Colorado
DEA	diethylamine
DMAc	N,N-dimethylacetamide
DMF	N,N-dimethylforamide
DMSO	dimethyl sulfoxide
DOTP	dioctyl terephtalate
DSC	differential scanning calorimetry
EE	ethoxyethanol
FTE	full time equivalent
FT-IR	Fourier transform–infrared
FWP	field work proposal
HCl	hydrochloric acid
HDPE	high-density polyethylene
HP	high-performance
INL	Idaho National Laboratory
LANL	Los Alamos National Laboratory
MEE	methoxyethyoxyethanol
MEEP	poly(methoxyethoxyethoxy)phosphazene
NDA	Non-Disclosure Agreement
NMP	N-methylpyrrolidone
NMR	Nuclear Magnetic Resonance
PAL	positron annihilation lifetime
PALS	positron annihilation spectroscopic
PBI	polybenzimidazole

PBI-TMS   poly(bis(trimethylsilylmethyl)polybenimidazole)

PBO   polybenzoxazole (Zylon; Toyobo, Co., Ltd., trade name)

PDMS   polydimethylsiloxane

PEO   poly(ethyleneoxide)

POSS   Polyhedral oligomeric silsesquioxane

PPO   polyphenylene oxide

PS   polystyrene

PTMSP   poly-(1-trimethylsily1)-1-propyne

PVA   polyvinyl alcohol

PVAc   poly(vinylacetate)

RBI   Richard Blaine Industries

TGA   thermogravimetric analyses

THF   tetrahydrofuran

TMA   thermo mechanical analysis

TOTM   trioctyl trimellitate

USPTO   United States Patent and Trademark Office

VTEC   (polyimide, products of RBI, Inc.)

CO$_2$ Separation Using Thermally Optimized Membranes: A Comprehensive Project Report (2000–2007)

REPORT OUTLINE

This report is broken into seven sections, each of which describes in detail the work that has been performed at Idaho National Laboratory (INL) on the project "CO$_2$ Separation Using Thermally Optimized Membranes." Section 1 describes work the develop nanocomposite polybenzimidazole (PBI)-silica membranes. The rationale for attempting these nanocomposites was to gain stability and perhaps enhanced levels of gas selectivity. Section 2 provides a description of research into successful development of soluble N-substituted PBI—a major accomplishment for the project. The reason for making such post polymerization modifications on the PBI was to increase its solubility in normal organic solvents to facilitate membrane formation, control permeability, and gain polymer stability. Section 3 describes a series of polymer modifications that either did or did not work; however, they provided poor membrane material candidates for several reasons, such as poor film formation or low synthetic yields. Section 4 contains information about continued synthetic modifications on PBI that were then expanded to include other high-performance polymers, such as Nylon, polybenzoxazole, Kevlar, polyamides, and polyimides. Section 5 summarizes INL's significant progress on developing an entirely new set of polymers for gas separations applications in general and specifically for the CO$_2$ sequestration efforts. The new polyamide/polyimide materials have proven quite promising for the applications that are targeted by the overall Carbon Sequestration Project. Table 15 is the final product of the challenge that the program manager made to INL. Section 6 provides an overall summary of the report. Section 7 provides an overview of INL's annual tasking and accomplishments coupled with their funding levels. Project progress for each subsection of the project is summarized at the end of each section.

SECTION 1 (FY-00–FY-02)

Nanocomposite Development

Project Development

The project was initiated with preparation of the necessary field work proposal (FWP) in March 2000 with funding arriving in May 2000. INL prepared the necessary laboratory safety review paperwork and had the project approved in June 2000. Several planning conference calls were held during June and early July 2000, followed by the funding arrival ($18,000) in August. The Idaho National Laboratory (INL) Technology Transfer Organization prepared and supplied to Los Alamos National Laboratory (LANL) the needed intellectual property listing for the information that was anticipated to be shared in the project. This information was needed for incorporation into the umbrella of a CRADA (Cooperative Research and Development Agreement) with Pall Corp. The official kickoff meeting for the project took place at LANL July 16–18, 2000; in attendance were personnel from LANL, University of Colorado (CU; Greenberg), and INL (Peterson).

Discussions at the kickoff meeting focused upon the material's synthesis and characterization, and membrane testing methodologies. Additionally, the roles were discussed that each partner would play based upon individual contributor/laboratory capabilities. Tasks were defined, and an initial order of task execution was agreed upon. Finally, a chart describing the order of task execution that brought together LANL, INL, and Colorado from a research and development viewpoint was established. The net result of the kickoff meeting was positive for the project as it provided a framework to the participants for executing the project. The annual report for the first year was scheduled for the first part of July 2001 and was LANL's responsibility.

The FY-00 project execution assignments were:

1. PBI Basic Data Acquisition

    a. CU—Acoustic data

    b. LANL—General data

2. PBI Chemical Modification

    a. LANL—Post-doc 0.25 FTE (full-time equivalent)

    b. INL—Synthetic Chemist 0.1 FTE

3. PBI Characterization

    a. LANL—Thermal, NMR (Nuclear Magnetic Resonance), Film casting

    b. INL—Gas transport of LANL samples

4. Testing of Polymers (resulting from #2 [above])

    a. LANL—Gas permeation testing

    b. CU—Acoustic and permeation testing

5.   Reporting

     a.   LANL—Lead

     b.   CU supporting LANL

     c.   INL supporting LANL

6.   Industrial Partner. (Needs to be identified and brought into the project—LANL's responsibility)

     a.   Shell Oil

     b.   Pall Corporation

     c.   Exxon Oil

     d.   Hewlett Packard.

Results from the kickoff meeting included a plan for regular conference calls (one each month) to update the participants on technical progress in the project. These have proven to be useful for the participants and have allowed the coworkers to become acquainted with each other.

After the kickoff meeting, INL synthesized novel molecular composite materials based upon the PBI and polyvinyl alcohol (PVA). The PVA materials show significant promise as membranes for gas separations at ambient temperatures. The PVA materials were pursued primarily as a means of developing a technique for forming the molecular composites in polymers outside of the polyphosphazene family. With that accomplished, INL turned their attention to the PBI materials and cast INL's first few films during the first 2 weeks of November 2000. These materials were cast into appropriate films and sent to LANL for gas permeation testing.

The project was continued during FY-01 with preparation of the necessary FWP in mid-June 2001 with funding arrival ($30,000) in August 2001. INL prepared the necessary laboratory safety review paperwork and had it approved in mid-September 2001. INL continued to participate in monthly conference calls during the year. Additionally, INL prepared and supplied to LANL the needed intellectual property listing for the information for sharing in the project, and the CRADA was signed in April 2000. During March 2001, the project team had a meeting in Boulder, Colorado. Attending the meeting were Pall Corp. representatives, LANL, University of Colorado (Greenberg), and Idaho National Laboratory (INL).

The FY-01 project execution assignments were:

1.   PBI Basic Data Acquisition

     a.   CU—Acoustic data

     b.   LANL—General data

2.   PBI Chemical Modification

     a.   LANL—Postdoc 0.25 FTE

     b.   INL—Synthetic Chemist 0.1 FTE, 2 months

3. PBI Characterization

    a. LANL—Thermal, NMR, Film casting

    b. INL—Gas transport of LANL samples

4. Testing of Polymers (resulting from #2 [above])

    a. LANL—Gas permeation testing

    b. CU—Acoustic and permeation testing

5. Reporting

    a. LANL—Lead

    b. CU supporting LANL

    c. INL supporting LANL

6. Industrial Partner. (Needs to be identified and brought into the project—LANL's responsibility)

    a. Shell Oil

    b. Pall Corporation

    c. Exxon-Mobil Oil.

Discussions at the annual spring meeting focused upon materials synthesis (LANL is in the lead for new materials) and characterization (INL and Colorado), and membrane testing methodologies. Additionally the data were discussed that had been accumulated to that date, by each of the partners, and their continued roles based upon individual contributor/laboratory capabilities. Tasks were defined/redefined, and the order of task execution was reviewed. Finally, the chart describing the order of task execution that brings together LANL, INL, and Colorado from a research and development viewpoint was reviewed and modified. The net result of the spring meeting was positive for the project as it provided the framework for the participants to continue with project execution in an effective manner.

The team continued to have the monthly conference calls (one each month) to update the participants on technical progress in the project. These have proven to be useful for the participants and have allowed the coworkers to become acquainted with each other.

The FY-02 project execution assignments were:

1. PBI Basic Data Acquisition

    a. CU—Acoustic data and modification

    b. LANL—General data

2. PBI Chemical Modification

    a. LANL—Post-doc 0.25 FTE

b.　　INL—Synthetic Chemist 0.1 FTE, 3 months

3.　　PBI Characterization

　　　　a.　　LANL—Thermal, NMR, Film casting

4.　　Testing of Polymers (resulting from #2 [above])

　　　　a.　　LANL—Gas permeation testing

　　　　b.　　CU—Acoustic and permeation testing

5.　　Reporting

　　　　a.　　LANL—Lead

　　　　b.　　CU supporting LANL

　　　　c.　　INL supporting LANL

6.　　Industrial Partner. (Has been identified and is being brought into the project—LANL's responsibility)

　　　　a.　　Shell Oil

　　　　b.　　Pall Corporation.

Research—Nanocomposite Development

　　　　Since the kickoff meeting in July 2000, INL synthesized novel molecular composite materials based upon the PBI and PVA. The PVA materials show significant promise as membranes are at normal temperatures for gas separations. The PVA materials were pursued primarily as a means of developing a technique for forming the molecular composites in polymers outside of the polyphosphazene family (polyphosphazenes are INL's "pet" polymer. The phosphazene backbone is comprised of alternating phosphorus-nitrogen atoms and each phosphorus atom has two functionalities attached to it.). With that accomplished, attention was turned to the PBI materials and the first few films were cast during the early November 2001. These materials were cast upon appropriate porous metal supports and sent to LANL for gas permeation testing. PBI/silicate molecular composites have proven to be relatively simple to form. The initial bulk materials were formed and characterized, yet molecular composite films of PBI have proven to be somewhat more elusive. Upon formation, the films appear to be well-behaved coatings or films. However, upon solvent loss and silicate condensation reactions, large (as much as 30%) dimensional changes in the film take place. Due to these dimensional changes, upon curing it has proven nearly impossible to obtain good films on the desired substrates for gas testing. The team continued to work with the PBI material and hoped to use interfacial precipitation methods to obtain good stable PBI silicate composites for gas separations studies. Table 1 summarizes the gas permeability studies of PVAc, poly(methoxyethoxyethoxy)phosphazene (MEEP), PBI freestanding films, and their corresponding molecular composites. Rapid solvent removal was pursued from the PBI-silicate composite membranes by super critical carbon dioxide extraction of the films. The formation of an aerogel-polymer-silicate composite was observed. The resulting material was comprised of an opaque, highly-porous, tan-colored material, but seemed to be virtually useless for membrane applications due to their fragile/brittle nature.

Table 1. Summary of polymer molecular composite gas testing data.

MOL-COMP GAS TESTING SUMMARY TABLE							
	Gas Permeability in barrers						
Materials tested	He	H_2	N_2	O_2	CH_4	CO_2	Sample ID
Poly(vinyl acetate), (PVAC) Polymer only	14.8	14.9	1.2	2.3	0.9	13.1	Aldrich (Alan Wertsching)
PVAC/MOL-COMP (55°C) Above T_g		15.4			10.3	8.4	AKW-3601
PVAC/MOL-COMP (30°C) Below T_g		28.3			21.1	18.3	
MEEP Polymer only	12.2	21.0	6.6	12.2	17.2	230.8	
MEEP/3XTEOS (30°C)	13.2	22.0	2.6	8.1	4.7	20.8	3X-TEOS/MEEP
Free Standing Spin-cast PBI film	__	7.24	0.09	0.44	0.09	1.48	

Attempts to make PVA silicate composite membranes were more challenging than initially expected. The prime problem with the films is the brittle and fragile nature of the membranes. These materials seem to have some thermoplastic properties that the team anticipated to use to make good membranes for separations applications. Formation of these composite films was pursued with some novel approaches during FY-02. However, the molecular composites were delayed on the schedule due to the need to form dependable defect-free standing PBI films. These include poly(vinylacetate) (PVAc) and poly(ethyleneoxide) (PEO) systems that were evaluated during FY-02. Others will be formed as it is deemed appropriate. Finally, during FY-02 additional testing was scheduled to be performed of flat sheet free-standing PBI films from LANL for direct evaluation of their gas transport properties. The samples were never supplied by LANL.

Until the end of FY-02, the project focused upon getting good freestanding defect-free PBI films that could be mounted on porous stainless steel supports. Additionally, INL tried to make molecular composites of two additional polymers, and they succeeded at getting the systems to form. They exhibited some interesting physical properties (i.e., the thermoplastic behavior referred to above), but did not show any spectacular enhancement in their gas transport behavior. These materials were of significant interest, and they were studied to understand their formation and morphologic behavior with respect to gas transport, which showed a two-phased system. The team was unable to form membranes dependably with the same physical properties each time the film formed. Considerable effort was made to get good film formation to occur with co-condensation of the silicate portion of the membrane; however, even after successful formation of the films, their properties changed upon standing in air (films that were thermoplastic at completion of the solvent evaporation step, became hard and brittle upon standing, therefore, they were not useful). A serious synthetic effort for modifying the polymers to make them more soluble in common organic solvents is needed so that membrane formation can be pursued in a productive manner.

Figure 1 is an illustration of polymer silicate composite. The silicate portion is represented by the clear cubic matrix. The polymer strands are represented as the ribbons shown penetrating through the silicate matrix. These materials are very similar to interpenetrating polymer networks (IPNs), except one component of these interesting materials is a solid silicate or ceramic precursor.
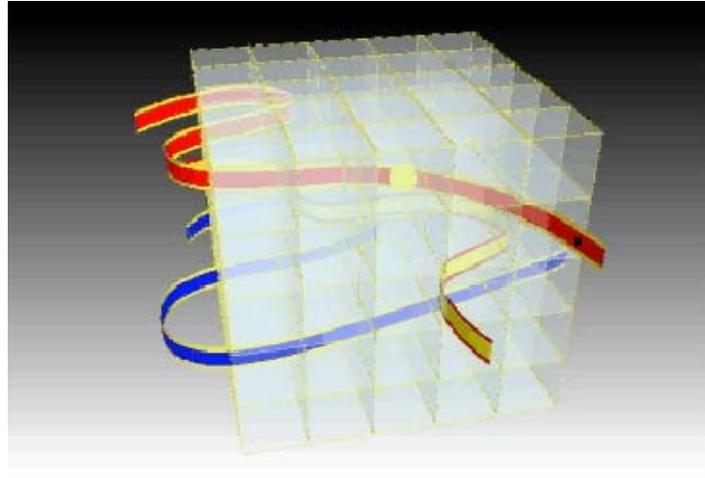
Figure 1. Artist's rendition of a polymer silicate composite.

SECTION 2 (FY-03–PRESENT)

Soluble N-Substituted Polybenzimidazoles

INL's post-polymerization modification process has been successful beyond expectations. The method that was developed by INL is applied throughout nearly all of the synthetic work described in this report. The modified polybenzimidazoles (PBI) may be blended solutions of high-performance polymers. This section and the two following sections present INL's synthetic results. Finally, this project has sponsored several presentations, papers, and patents that have attracted significant national and international attention.

Introduction to the Section

Polybenzimidazole (PBI), also known as Celazole or poly-2,2'(*m*-phenylene)-5,5'-bibenzimidazole (Figure 2), is a polymer that is resistant to strong acids, bases, and high-temperatures (up to 500°C).[1,2] Due to these unique properties, PBI has been used to form membranes,[3] electrically conductive materials,[4] fire resistant materials,[5] ultrafilters,[6] and other types of separatory media.[7] The major drawback for PBI is that it has very poor solubility in common organic solvents. PBI is only soluble after heating in highly-polar, aprotic organic solvents, such as dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMAc), N,N-dimethylforamide (DMF), and N-methylpyrrolidone (NMP). These solvents have high boiling points and low vapor pressures, and sometimes are not preferred for processing. In order for the polymer to be soluble in a wider range of organic solvents, PBI needs to be synthetically modified. This can be accomplished in two ways, either by polymer substitution (grafting) at the reactive benzimidazole N-H sites or by synthetically modifying the monomers prior to polymerization. Several groups[8] have tried modifying PBI with limited success. Synthetically altering the monomers to form the polymer can be difficult, and the resulting polymer molecular morphology can be considerably different from the parent PBI. Therefore, post-polymerization substitution of the polymer is a better choice since the parent polymer can be acquired by commercial means.
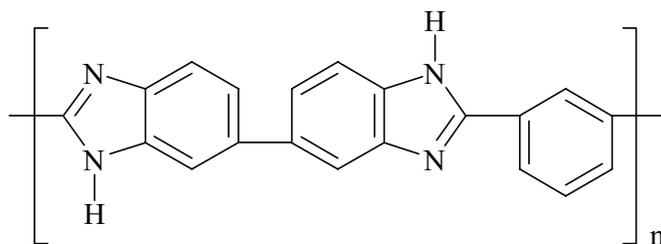
Figure 2. PBI (polybenzimidazole); traditionally drawn structure.

Even though PBI is resistant to harsh conditions, it has reactive imidazole nitrogens that can be used for modification by N-substitution (grafting) of the polymer. Throughout the written literature on PBI, several synthetic methods have been investigated for PBI modification.[9-11] One approach isolates N-aryl substituted PBI, but these polymers were not synthesized by deprotonation (i.e., using NaH), and significant heating was required.[12] In a separate article, PBI resin beads were N-substituted in an aqueous solution, however, the resulting substitution was simply a surface modification of the resin bead and not a fully substituted polymer backbone.[7]

Alternatively, the reactive benzimidazole N-H groups can be used to cross-link PBI or provide substitution points on the polymer chain.[13,2e] PBI was blended using aromatic polyamides or aromatic polyamide-hydrazides to yield heterocyclic linkages.[14] A clear way to use swelled PBI and form a matrix

at room temperature was provided by Onorato, et al.[15] Solubility of the PBI remains a problem in common organic solvents. For typical application(s) using unmodified PBI polymer, the common practice is to form a paste or gel ("dope") in strongly acidic conditions.[7]

Sansone, et al[16-21] provided the first clear synthetic method for N-substituted PBI polymers (Scheme 1).[20] All of Sansone's synthetic methods required a PBI solution using N,N-dimethylacetamide (DMAc) or N-methylpyrrolidone (NMP). However, the polymer solutions were described as having polymer concentrations between 10–25 wt% in PBI, and high-temperatures (and pressure or stabilizers) were needed to fully dissolve the polymer. The literature shows that reaction solutions containing less than 5 wt% in polymer typically were not well substituted. These N-substitution reactions required heat (70–150°C) to decrease the viscosity of the polymer solution enough that the substitution reactions would take place. The modified-PBI with the greatest degree of N-substitution approached 82%; however, increasing concentrations of either base or electrophile (R-CH$_2$X) did not increase the degree of substitution on the PBI backbone. The polymers were purified by precipitation in a non-solvent, such as water or acetone. This precipitation removed any excess solvent, but the percentage of DMAc or NMP that remained in the polymer was not described, and the solubility of the modified PBI in common organic solvents was not discussed.

Reynolds and Geiselman[22,23] improved Sansone's process[16] for producing PBI modified organo-sulfates. They used a 5–10 wt% solution of PBI in DMAc; however, the reaction mixture was a viscous liquid, which required a mechanical stirrer due to ambient temperatures used for the reactions. Polymer precipitation was coupled with dialysis for polymer purification, and the isolated N-substituted PBI polymer was found to be water-soluble. An important aspect of their N-substituted PBI is that it retained the thermal stability of the original polymer.
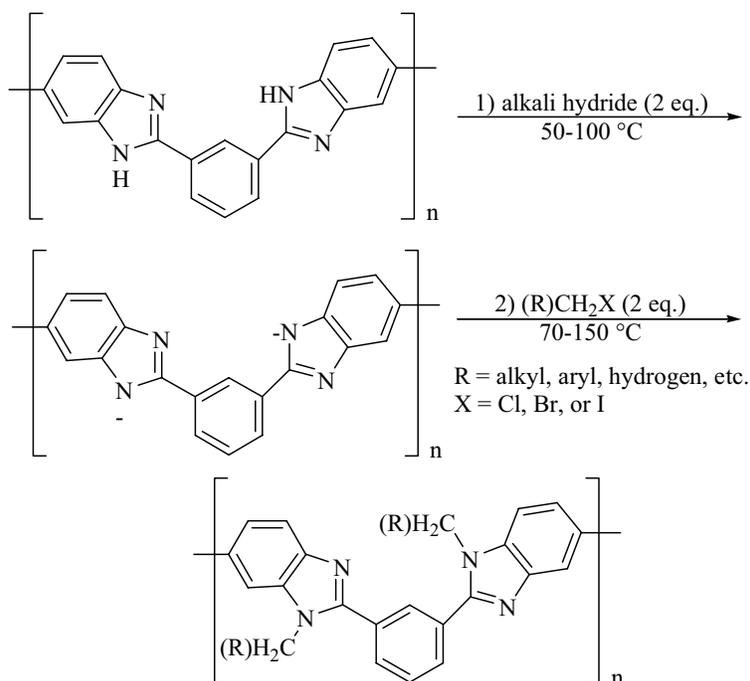
Scheme 1. A general approach to polybenzimidazole synthetic N-substituent modification.

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Results and Discussion

Due to the challenging solubility properties of PBI, the parent PBI (resin) is refluxed with DMAc. However, the parent PBI resin, when dissolved in DMAc, can easily be precipitated into deionized water and air-dried. The precipitated PBI is much easier to re-dissolve back into DMAc or NMP than the original parent PBI resin. This suggests that the original parent PBI resin is more crystalline or densely packed, which causes it to be much more difficult to dissolve into solution. Therefore, it is necessary to break up the packing of the parent PBI.

Traditionally, PBI is drawn as a linear polymer (see Figure 2); however, a symmetrical representation of the polymer (see Figure 3) helps with interpretation of the NMR spectra. From the ^{1}H NMR, the precipitated PBI benzimidazole N-H protons are deshielded (13.47 ppm) (see Figure 4), and this downfield shift is consistent with the benzimidazole N-H being hydrogen bonded, either with another benzimidazole or the solvent. Similar results have been observed previously with PBI using FT-IR (Fourier Transform–Infrared) and Proton NMR (Nuclear Magnetic Resonance) spectroscopy.[25] The symmetry of the aromatic protons of the parent PBI becomes more apparent in the ^{1}H NMR spectrum when the precipitated PBI is deprotonated (see Figure 5). The spectral shifts on deprotonated PBI are changed due to the anionic charge (possibly delocalized) on the backbone.

The nature of the benzimidazole N-H proton on the parent PBI was investigated by titration experiments using concentrated sulfuric and phosphoric (85%) acids. The 1H NMR spectra show that the acidic proton resonance for concentrated sulfuric acid and phosphoric acid (85% in water) are 12.26 ppm and 8.62 ppm, respectively, in DMAc-d_9, well upfield of the observed N-H resonance (13.47 ppm) in the parent PBI precipitate. The addition of 10 µL concentrated sulfuric acid to the PBI DMAc-d_9 solution (~0.05 g/mL) caused the PBI to yield a pale-yellow, insoluble, swelled polymer gel. Addition of more DMAc-d_9 did not dissolve any more of the polymer. However, heating to reflux conditions forced the acidified PBI to dissolve into solution. This suggests that strong acids, such as sulfuric acid, will promote cross-linking between polymer strands through hydrogen bonding and ionic interactions. These observations provide insight into the nature of the parent and provide a rationale for the vigorous techniques that are needed to dissolve the polymer. Nevertheless, when NaH is added to the PBI/DMAc-d_9 solution, PBI remains in solution (Figure 5) and the 1H NMR spectra show PBI's benzimidazole N-H resonance (13.70–13.38 ppm) disappears, but the other polymer resonances remain constant, indicating that the resonance at 13.47 ppm is due to the acidic benzimidazole protons. These limited data provide a hint that the parent polymer has strong interactions with itself either by hydrogen bonding and/or by ionic cross-linking. It is clear that these interactions must be disrupted before the polymer will dissolve.
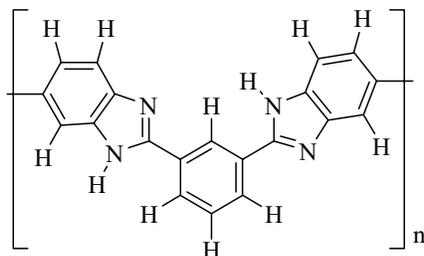
Figure 3. PBI (polybenzimidazole); symmetric structural representation of the parent polymer.
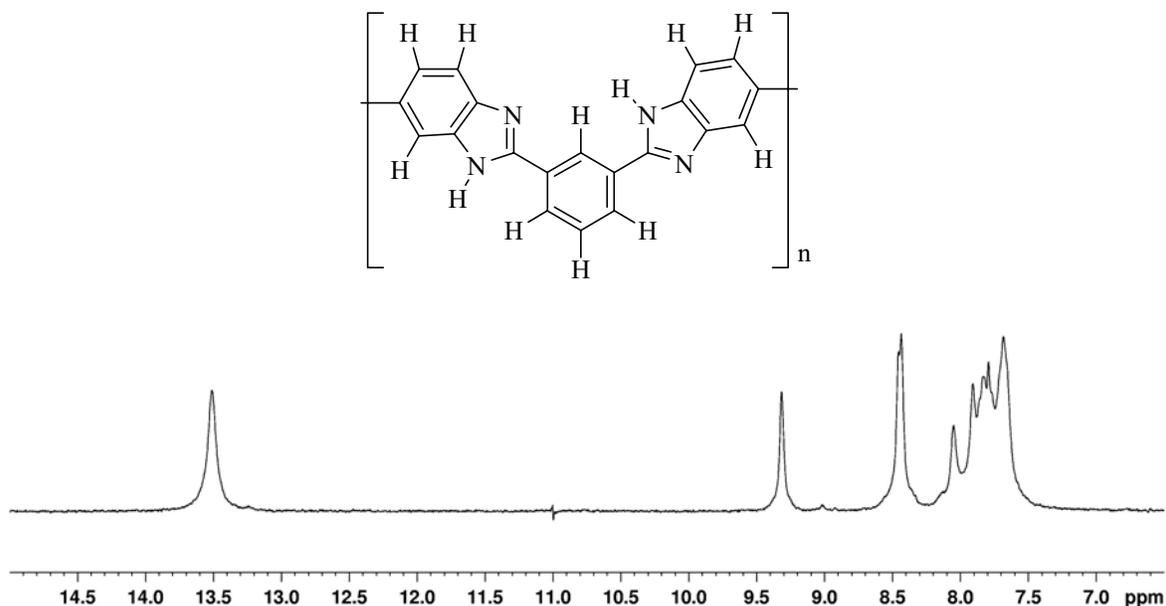
Figure 4. ^{1}H NMR spectrum of precipitated PBI in DMAc- d_9.
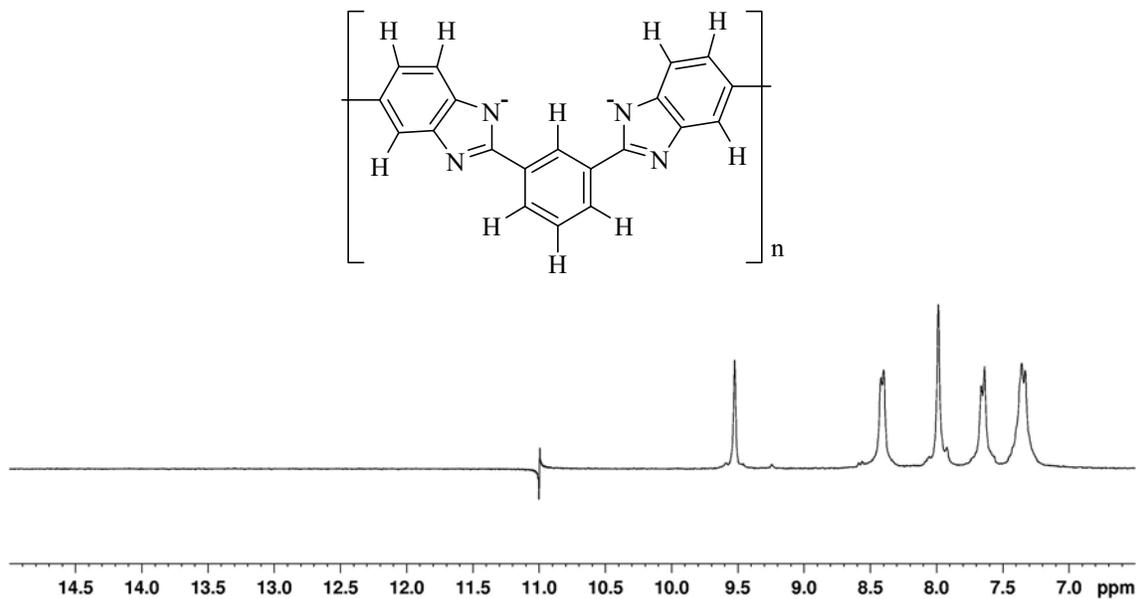
Figure 5. ^{1}H NMR spectrum of precipitated PBI and sodium hydride (80% in oil) in DMAc- d_9, note the missing N-H resonance at 13.47 ppm.

Understanding the inter-polymer molecular interactions of the parent PBI resin makes possible reaction condition modification and provides a synthetic route for PBI derivatization reactions that require less vigorous reaction conditions than those developed by Sansone[20] (Scheme 2). All new reactions proceed with a ~2.5 wt% PBI/DMAc solution. Due to the reduced amount of PBI needed, it is possible to dissolve the parent PBI resin at reflux in DMAc in about 24 hours. After cooling to room temperature, small quantities of dark-brown, granular PBI are observed at the bottom of the flask after standing for

several weeks. This concerned the team because the insoluble PBI in the solutions could affect the reactions; therefore, all of the solutions were filtered using a 0.45 µm filter prior to use of the solutions in reactions. Using the filtered ~2.5 wt% PBI/DMAc solution, the deprotonation reaction was found to proceed at room temperature. At room temperature, a deep red/violet viscous solution can be observed after the sodium hydride is consumed (3–6 hours), which is consistent with Reynolds and Geiselman's[21] reports. A crucial point within this new synthesis is the amount of organosilane used to effect the substitution reactions. It was found that the amount of organosilane added makes a significant difference between soluble and slightly soluble modified polymer products in tetrahydrofuran (THF). The slightly soluble polymer products are the result of an incomplete substitution reaction on the PBI framework. Approximately 20 equivalents of organosilane (based upon polymer concentration) were needed to give the fully substituted, soluble products. In fact, another color change (light reddish-purple) can be observed after the addition of organosilane, and the solution viscosity suddenly decreases dramatically. Over time, the reddish-purple color returns to a yellow-brown solution, similar to the parent PBI/DMAc solution. These reactions take roughly 48 hours to complete at room temperature. The modified PBI polymers can be isolated by simple precipitation in non-solvents, water, and hexanes to give yellow to brownish-yellow powders. The reaction yields among the methyl, vinyl, and allyl-substituted derivatives were approximately 50%; however, the reaction that provided the phenyl derivative resulted in a very low yield. The lower yield was probably due to the phenyl group's steric size and/or its inability to access the deprotonated amine site on the PBI backbone.
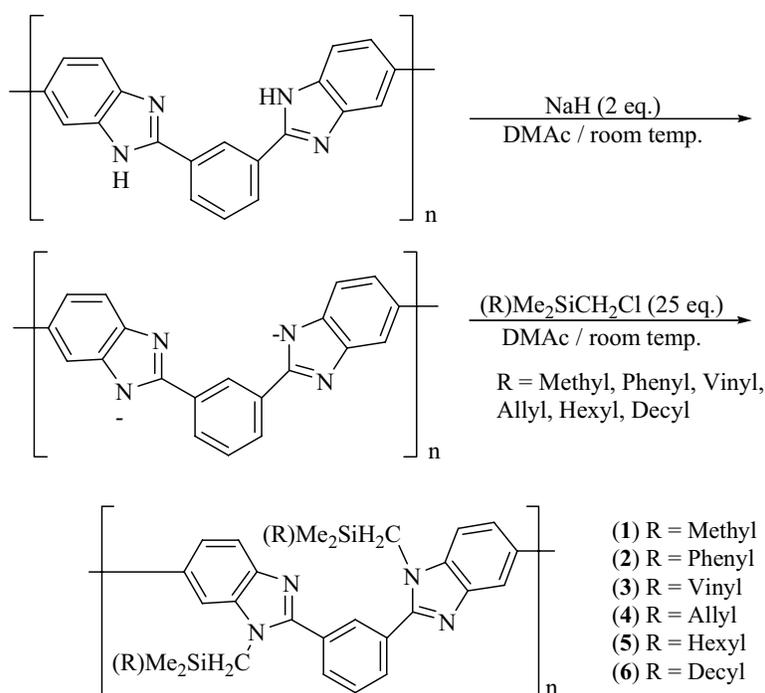
Scheme 2. Synthetic route for N-substituent modification of polybenzimidazole with organosilane groups.

From the literature, there are a very limited number of citations that describe N-substituted PBI materials that are soluble in common solvents. It was found that even minute quantities of polar aprotic solvents, such as DMAc, changed the solubility of the modified PBI materials. However, the purified modified polymers dissolve in THF and chloroform without the aid of a co-solvent, such as DMAc (Table 2). When using dichloromethane, the modified polymers swelled, and (Methyl)Me$_2$SiCH$_2$-PBI (Scheme 2; **1**) was the only one that showed any appreciable solubility at room temperature.

From the NMR analysis, the integration ratios of the ^{1}H NMR spectra show that nearly all of the PBI is substituted with the organosilane. This is further corroborated by the absence of the unsubstituted imidazole (N-H) proton resonance, at 13.47 ppm for the parent PBI, *vide supra*, of polymers **1**–**6**. The difference in spectral resolution (peak sharpness) is especially pronounced in the ^{13}C{^{1}H} NMR spectra from the precipitated PBI (see Figure 6), to the organosilane substituted PBI polymers, **6**, as an example (see Figure 7). These differences are also observed in the ^{13}C{^{1}H} NMR spectra between 2-phenylbenzimidazole and 1-methyl-2-phenybenzimidazole.[26] The resonance of the methylene group between the silicon and the PBI backbone is observed in both ^{1}H NMR (~3.80–4.20 ppm) and ^{13}C{^{1}H} NMR (~35–40 ppm) spectra for all of the compounds, shown in Figures 8 and 9. The methyl groups on silicon for **1**–**6** are near ~0.00 ppm for both ^{1}H NMR and ^{13}C{^{1}H} NMR spectra. Due to the low concentrations, experiments were not performed to assign all of the resonances to the N-substituted PBI polymers. However, the NMR data are consistent with the compounds being the expected modified PBI materials.

The molecular weights that were determined for **1**, **3**–**6** (Scheme 2, Table 3) are lower than the values that Reynolds, et al.[22] reported. However, Reynolds, et al. synthesized organo-sulfate PBI polymers that may have other problems determining the molecular weight due to the highly-ionic behavior of the polymer. They used aqueous 0.3N NaOH for their analysis to overcome the ionic behavior, but there is the possibility of aggregation with the organo-sulfate PBI on itself in the aqueous solution (organic versus aqueous portions). In this report, a "batch mode" molecular weight determination was used with all of the N-substituted PBI polymers in organic solvents. It was found that the parent PBI (precipitate) in DMAc, was in agreement with the previously determined value of 8,000–10,000 g/mol from Kojima, et al.[27] Also, the filtration/precipitation processes, described in this report, may have reduced the quantity of higher molecular weight polymer when comparing the values to Reynolds, et al. Overall, the molecular weights are within the calculated values for substituted PBI with the corresponding added pendant groups.

Table 2. Polybenzimidazole solvent solubility of selected polymer derivatives.

Polymer	Solubility–grams/mL of Solvent				
	THF	CHCl$_3$	CH$_2$Cl$_2$	DMAc	NMP
Parent PBI (Celazole)[a]	Not Soluble	Not Soluble	Not Soluble	Partially Soluble	Partially Soluble
Precipitated PBI	Not Soluble	Not Soluble	Not Soluble	Soluble	Soluble
(Methyl)Me$_2$SiCH$_2$-PBI (**1**)	0.2–0.25	0.2–0.25[b]	0.01–0.05	Soluble	Soluble
(Vinyl)Me$_2$SiCH$_2$-PBI (**3**)	0.2–0.25	0.2–0.25[b]	Swells, Slightly Soluble	Soluble	Soluble
(Allyl)Me$_2$SiCH$_2$-PBI (**4**)	0.2–0.25	0.2–0.25[b]	Swells, Slightly Soluble	Soluble	Soluble
a. Soluble in DMSO; partially soluble in DMF; 0.05–0.06 g/mL in formic acid.[1]					
b. Elevated temperature (~50°C) and constant stirring.					
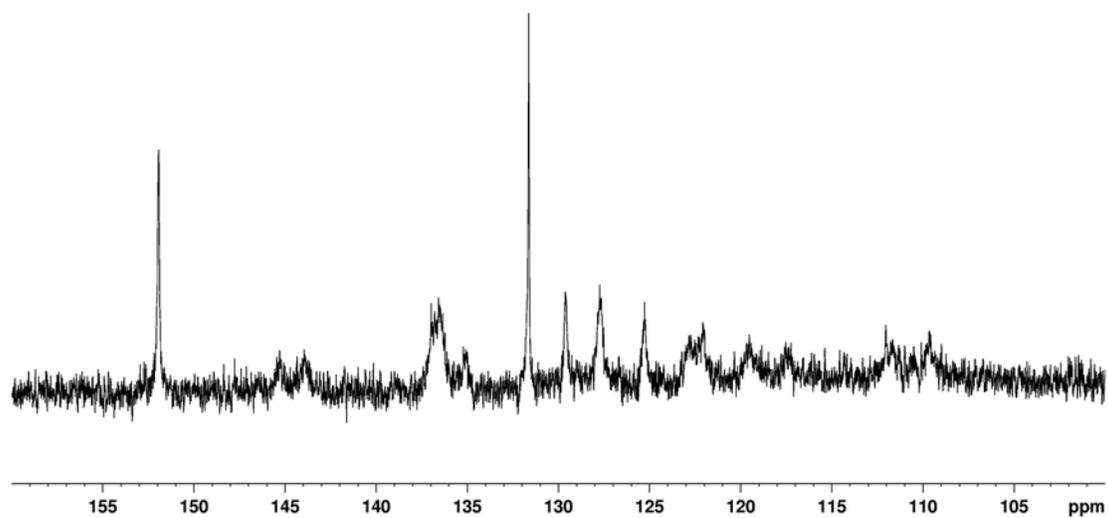
Figure 6. $^{13}C\{^{1}H\}$ NMR spectrum of precipitated PBI in DMAc-d_9 (aromatic region).
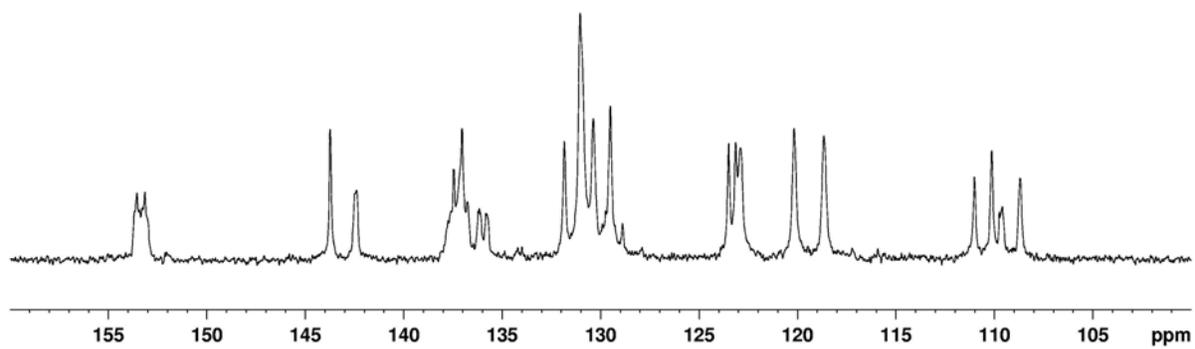
Figure 7. $^{13}C\{^{1}H\}$ NMR spectrum of (Decyl)Me$_2$SiCH$_2$-(PBI) (6) in CDCl$_3$ (aromatic region).
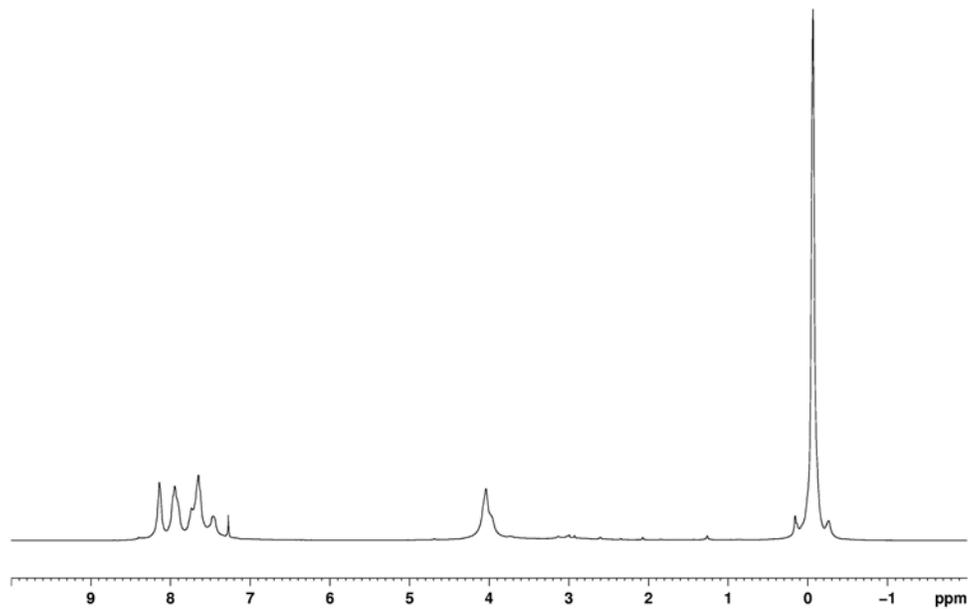
Figure 8. A representative ^{1}H NMR spectrum; (Methyl)Me$_2$SiCH$_2$-(PBI) (1) in CDCl$_3$.
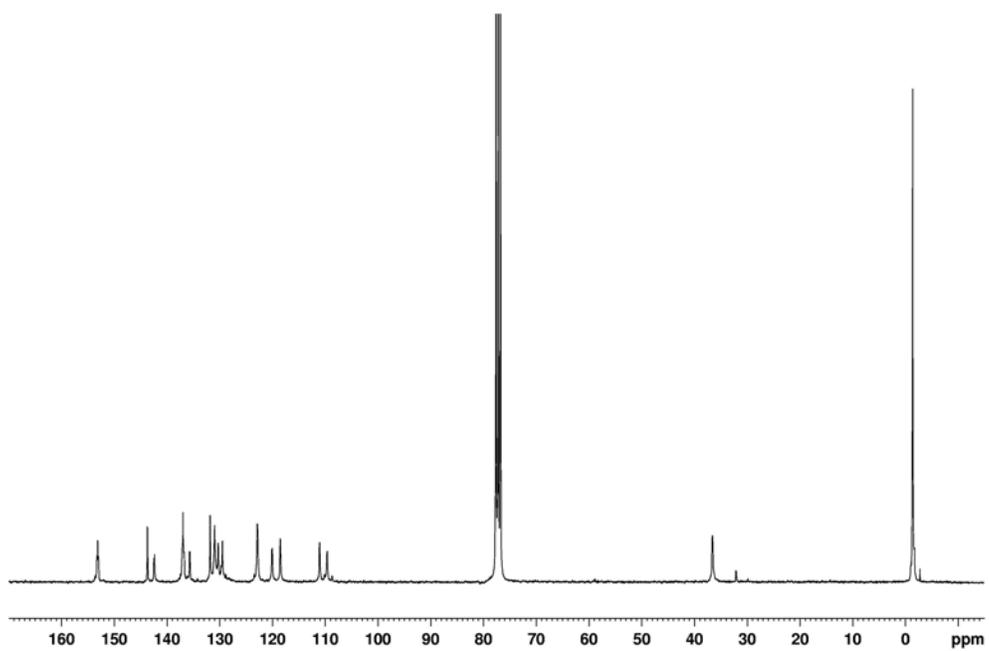
Figure 9. A representative {^{1}H}^{13}C NMR spectrum, (Methyl)Me$_2$SiCH$_2$-(PBI) (1) in CDCl$_3$.

Table 3. Polybenzimidazole macromolecular weight determination and yield.

Polymer	"Batch Mode"–Mw (g/mol)[a]	Yield (percent)
Parent PBI (precipitated)	8,000–10,000[b]	N/A
(Methyl)Me$_2$SiCH$_2$-PBI (**1**)	10,000–15,000	50
(Phenyl)Me$_2$SiCH$_2$-PBI (**2**)	c	15
(Vinyl)Me$_2$SiCH$_2$-PBI (**3**)	10,000–15,000	50
(Allyl)Me$_2$SiCH$_2$-PBI (**4**)	45,000–55,000	50
(Hexyl)Me$_2$SiCH$_2$-PBI (**5**)	45,000–55,000	50
(Decyl)Me$_2$SiCH$_2$-PBI (**6**)	65,000–90,000	50

a. Solvent - THF (Tetrahydrofuran)

b. Solvent - DMAc (N,N-Dimethylacetamide)

c. Not determined.

The thermogravimetric analyses (TGA) for **1**–**6** show initial weight losses for compounds **1**–**4** that are within 60ºC of the parent PBI, but **5** and **6** had lower decomposition temperatures (Table 4). This is possibly due to hexyl and decyl alkyl substituted chain degradation at lower temperatures. From the data, differential scanning calorimetry (DSC) does not provide any information concerning glass transitions (T_g) for any of the compounds, including the parent PBI polymer. However, compounds **3** and **4** show small exotherms that possibly indicate that the vinyl and allyl groups are reacting and cross-linking.

Table 4. Differential scanning calorimetry and thermal gravimetric analysis data for PBI and its derivatives.

Polymer	Thermal Transitions	Initial Weight Loss and Temperature in N$_2$
Parent PBI (Celazole)	$T_g = 450$℃[a]	512℃
Precipitated PBI	b	512℃
(Methyl)Me$_2$SiCH$_2$-PBI (1)	b	448℃
(Phenyl)Me$_2$SiCH$_2$-PBI (2)	b	430℃
(Vinyl)Me$_2$SiCH$_2$-PBI (3)	249℃	464℃
(Allyl)Me$_2$SiCH$_2$-PBI (4)	239℃	451℃
(Hexyl)Me$_2$SiCH$_2$-PBI (5)	b	390℃
(Decyl)Me$_2$SiCH$_2$-PBI (6)	b	382℃

a. From manufacturer.

b. No detectable thermal transitions up to 500ºC.

Conclusions

The synthetic route described in this chapter has expanded previous reactions to include a number of soluble hybrid organic/inorganic PBI-based polymers that exhibit similar thermal properties as the

parent PBI. Six different organosilane polymer derivatives were synthesized, and all of the modified polymers are more soluble in organic solvents than the parent PBI. Interpretation of the NMR spectra indicates that the PBI is almost fully substituted by the organosilane moieties. Some of the modified polymers have similar thermal properties to the parent polymer, and the molecular weights are within the expected values for the substituted parent PBI. Overall, this post-polymerization polymer modification route provides a straightforward synthetic method that can be carried out at room temperature, give reasonable yields, and provide materials that could be more amenable to processing.

References

1.   Vogel, H.; Marvel, C. S. *J. Polym. Sci.* 1961, *50*, 511.

2.   (a) Marvel, C. J.; Vogel H. A. Re. 26065, July 19, 1966. (b) White, D. M. U.S. Patent 3,408,366, October 29, 1968. (c) Chenevey, E. C.; Conciatori, A. B. U.S. Patent 3,549,603, December 22, 1970. (d) Sayigh, A. A. R.; Tucker, B. W.; Ulrich, H. U.S. Patent 3,708,439, January 2, 1973. (e) Sheratte, M. B. U.S. Patent 4,154,919, May 15, 1979. (f) Choe, E. W. U.S. Patent 4,312,976, January 26, 1982. (g) Conciatori, A. B.; Choe, E. W.; Hall, H. K. U.S. Patent 4,483,977, November 20, 1984.

3.   Trouw, N. S. U.S. Patent 4,693,825, September 15, 1987.

4.   (a) Marikar, Y. M. F.; Besso, M. M. U.S. Patent 4,759,986, July 26, 1988. (b) Marikar, Y. M. F.; Besso, M. M. U.S. Patent 5,017,420, May 21, 1991. (c) Sansone; M. J.; Onorato, F. J.; Ogata, N. U.S. Patent 5,599,639, February 4, 1997. (d) Akita, H.; Ichikawa, M.; Nosaki, K.; Oyanagi, H. U.S. Patent 6,124,060, September 26, 2000.

5.   Kasowski, R. V.; Lee, K.-S. U.S. Patent 5,389,326, February 14, 1995.

6.   Sansone; M. J. U.S. Patent 4,693,824, September 15, 1987.

7.   (a) Chanda, M.; Rempel, G. L. *Reactive Polymers* 1989, *11*, 165. (b) Chanda, M.; Rempel, G. L. *Reactive Polymers* 1990, 12, 83. (c) Chanda, M.; Rempel, G. L. *Reactive Polymers* 1990, 13, 103. (d) Chanda, M.; Rempel, G. L. *Reactive Polymers* 1991/1992, 16, 29. (e) Chanda, M.; Rempel, G. L. *Reactive Polymers* 1992, 17, 159.

8.   (a) Jones, D. J.; Rozière, J. *J. Membr. Sci.* 2001, 185, 41. (b) Jones, D. J.; Rozière, J. *Annu. Rev. Mater. Res.* 2003, 33, 503.

9.   Trischler, F. D. U.S. Patent 3,578,644, May 11, 1971.

10.   Bower, E. A.; Rafalko, J. U.S. Patent 4,599,388, July 8, 1986.

11.   Gerber, A. H. U.S. Patent 3,943,125, March 9, 1976.

12.   Hara, S.; Senoo, M.; Uchida, M.; Yoshida, T.; Imai, Y. U.S. Patent 3,518,234, June 30, 1970.

13.   Davis, H. J.; Thomas, N. W. U.S. Patent 4,020,142, April 26, 1977.

14.   Calundann, G. W.; Friedrich, H.; Chenevey, E. C.; Chung, T.-S. U.S. Patent 5,290,884, March 1, 1991.

15.   Oronrato F. J.; Sansone, M. J.; French, S. M.; Marikar, F. U.S. Patent 5,945,233, August 31, 1999.

16.   Sansone, M. J.; Gupta, B.; Stackman, R. W. U.S. Patent 4,814,399, March 21, 1989.

17.   Sansone, M. J.; Gupta, B.; Forbes, C. E.; Kwiatek, M. S. U.S. Patent 4,997,892, March 5, 1991.

18.   Sansone, M. J. U.S. Patent 4,814,400, March 21, 1989.

19.   Sansone, M. J. U.S. Patent 4,868,249, September 19, 1989.

20.   Sansone, M. J. U.S. Patent 4,898,917, February 6, 1990.

21.   Sansone, M. J.; Kwiatek, M. S. U.S. Patent 4,933,397, June 12, 1990.

22.   Gieselman, M. B.; Reynolds, J. R. *Macromolecules,* 1992, 25, 4832.

23.   Gieselman, M. B.; Reynolds, J. R. *Macromolecules,* 1993, 26, 5633.

24.   Lennon, P. J.; Mack, D. P.; Thompson, Q. E. *Organometallics*, 1989, 8, 1121.

25.   (a) Musto, P.; Karasz, F. E.; MacKnight, W. J. *Macromolecules,* 1991, 24, 4762. (b) Kojima, T. *J. Poly. Sci.: Poly. Phys. Ed.* 1980, 18, 1791.

26.   Pouchert, C. J.; Behnke, J. *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra.*-Edition I, Volume 3, American Chemical Society: USA, 1993.

27.   Kojima, T.; Yokota, R.; Kochi, M.; Kambe, H. *J. Poly. Sci.: Poly. Physics Ed.*, 1980, 18, 1673.

SECTION 3 (FY-04)

Other Synthetic Pathways to Soluble N-Substituted Polybenzimidazoles

Introduction to the Section

PBI has been post-polymerization modified with several additional pendant groups. Results for many of the post polymerization modified PBI compounds have been mixed, especially with respect to solubility and film forming properties. The basic idea was to enhance PBI common solvent solubility by adding various pendant groups. All of the pendant groups were added to the polymer primarily with membrane applications, (i.e., gas separations) in mind. Many of these new pendant groups were substituted onto PBI; however, polymer solubility remained poor in many cases. In a few cases, it was not clear if the pendant group substitution onto the PBI had even taken place. Overall, the efforts were split between two categories: inorganic pendant group synthesis (inorganic/organic hybrids) and organic pendant group substitution.

The PBI post-polymerization modification reaction (Scheme 3) was used for all of the following pendant groups, including both inorganic/organic hybrids and organic pendant groups. The general reaction is initiated by deprotonation of the imidazole nitrogen on the polymer backbone. The ligand is added (R-X) where the halogen (X) is displaced by the deprotonated nitrogen. The product is substituted by the pendant group (R). Several of the silane precursors were not available so the syntheses of these silane pendant groups were needed. All of the organic pendant groups were available commercially; therefore, no synthetic pendant group synthesis was needed. Synthetic pendant group preparations were picked with the objective of enhancing gas membrane separation properties coupled with better PBI solubility and film forming properties.
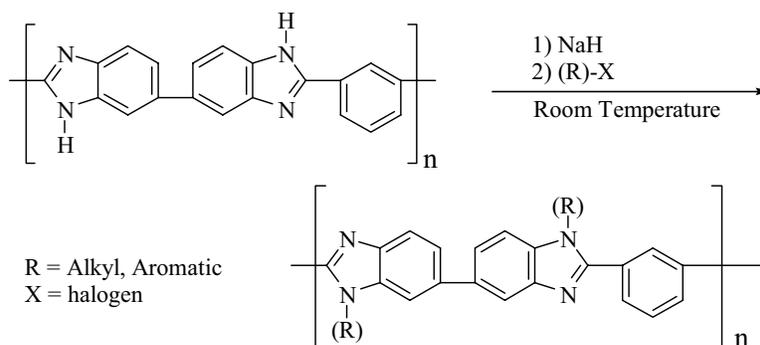
Scheme 3. PBI post-modification reaction.

Other Organosilane N-Substituted Polybenzimidazoles

Several reaction attempts were made using many of the silane-containing compounds with limited success. The chloromethyl silanes that were directly purchased from the manufacturer have been best for the post-polymerization polymer modification of PBI (IDR, Case# B-338 submitted to USPTO [United States Patent and Trademark Office]). From this initial set of silane substituted compounds, a listing of the reactions that were attempted include the bis(chloromethyl)tetramethylsiloxane compounds, which were the most difficult to synthesize (Scheme 4).
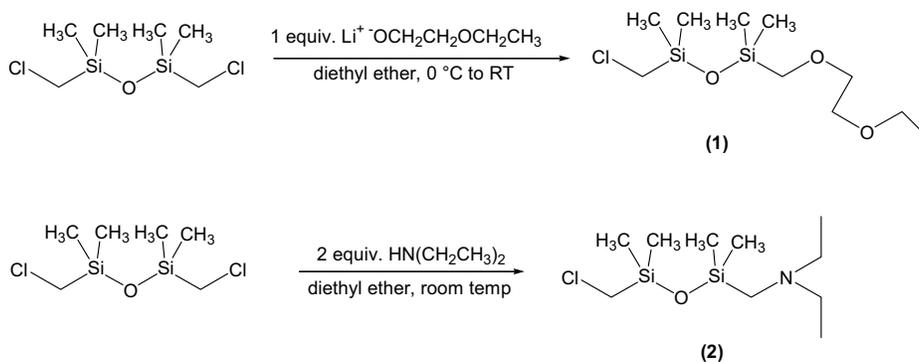
Scheme 4. Bis(chloromethyl)tetramethylsiloxane reactions.

Considering that the silicon-oxygen bond could be cleaved by a strong base, these reactions were carried out at lower temperatures to reduce bond cleavage. Ethoxyethanol (EE) was deprotonated with n-Butyl Lithium prior to the addition of the siloxane. The resulting products were isolated with a column (silica gel); however, the product could not be separated from the starting material, EE. This was determined using TLC plates. In addition, vacuum distillation did not give appreciable amounts of **1**—it possibly decomposed. Another reaction using diethylamine resulted with no product **2** being isolated. It may be assumed that the reactions do occur, but the competing silicon-oxygen cleavage causes other problems. In any event, none of these products were used for the post-polymerization modification of PBI (Scheme 3).

Using the starting material, bis(chloromethyl)dimethylsilane (Scheme 5), all of the precursors [ethoxyethanol (EE), methoxyethyoxy ethanol (MEE) and diethylamine (DEA)] were deprotonated with n-Butyl Lithium prior to the addition of the silane. Side products to these reactions were not a problem since the products could be vacuum-distilled. On the other hand, the isolated yields were not very good. The best yielding product was **3**. This was the only product from the series that was used for the post-polymerization modification of PBI (Scheme 3). There was not enough isolated material for the other two products **4** and **5**. NMR was used to identify the product, but it was difficult to find out if the starting material was completely removed. Using **3**, the PBI post-polymerization modification gave only trace amounts of soluble material. It is unknown if **3** was completely pure before the reaction with PBI, but a crosslinked product resulted. NMR could not be used for the isolated modified PBI material. It can be assumed that the reaction will work, however better isolation methods need to be developed.
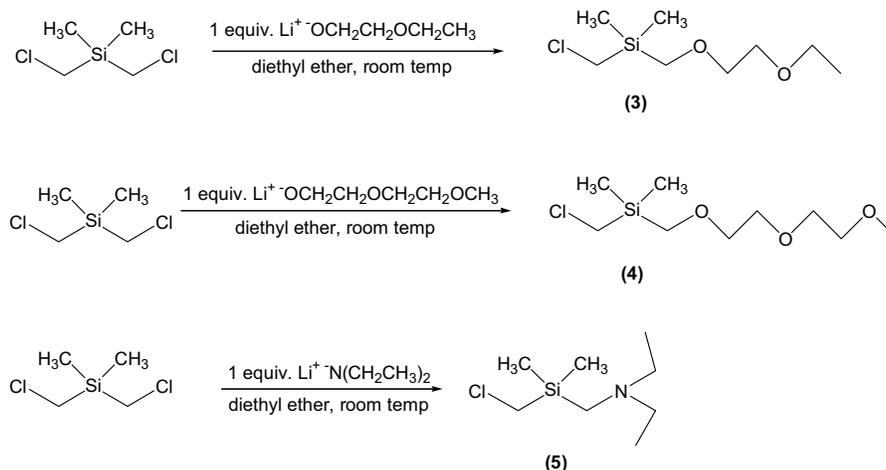
Scheme 5. Bis(chloromethyl)dimethylsilane reactions.

Chlorosilanes were used for the synthesis of new pendant groups for PBI modification. These compounds are somewhat easier to substitute than the previous bis(chloromethyl) silane compounds. It is known that silicon chlorine bonds are reactive; therefore, Grignard reagents (RMgX: R = alkyl, X = Br, Cl) should work (Scheme 6). The reactions were conducted at the same time, yet the overall yields for both of the reactions were not very good, or no reaction took place. It was found that the 3-Chloropropyl dichloromethylsilane will react with Grignard reagents; however, the reaction did not go to completion. The isolation of **6** was only accomplished by vacuum distillation, but ^{1}H NMR never resolved if the mono substituted and the di-substituted products were completely separated from each other. In any case, two reaction products of **6** were combined for the PBI post-modification reaction (Scheme 3). The PBI modification gave very small amounts of soluble PBI product. This could be attributed to impurities of **6** or because the 3-chloropropyl group was not very reactive for the post-polymerization modification reaction. There were no NMR data taken for the modified PBI product due to insufficient yields. The reaction with chloromethylchlorodimethylsilane gave very little or no product (Scheme 6). Various solvents and temperature changes were used to try to increase the yields, but nothing worked.
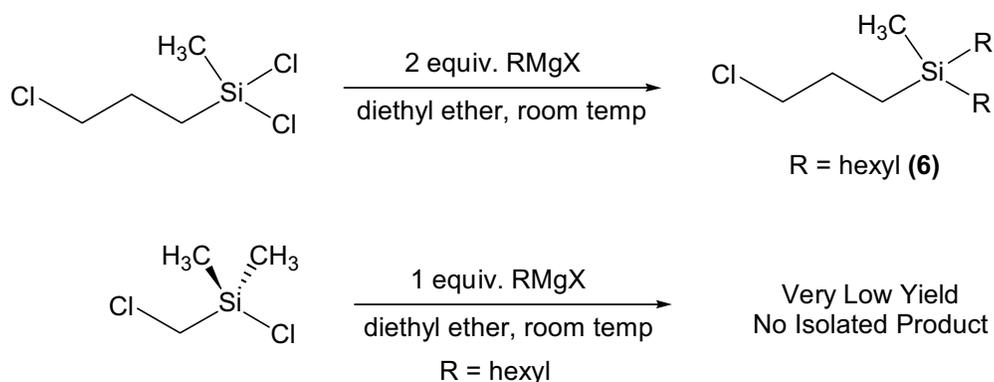
Scheme 6. 3-Chloropropyl and chloromethyl chlorosilane reactions.

Literature searches on the silicon chlorine bonds provided a better understanding about the reaction. Organolithium reagents, such as Methyl Lithium, are preferred for tetrasubstitution of a silane. However, these reagents are more costly and not as easily formed as Grignard reagents (R MgX). The tetrasubstitution reactions with Grignard reagents are very slow; therefore, they cannot give satisfactory yields or purity. It was found that catalytic amounts of thiocyanate ($^-$SCN) along with the Grignard reagents can give high yields under mild conditions (Scheme 7).[1] Grignard reagents will selectively substitute at the silicon-chlorine bond in preference to the carbon-chlorine bond. Using this information, the chloromethylchlorodimethylsilane reaction was repeated. The new reaction conditions gave good yields and the products were isolated through vacuum distillation. Two Grignard reagents were used, hexyl functionalized and decyl functionalized, yielding the corresponding compounds **7** and **8**. Both were used for the post-polymerization modification PBI reaction (Scheme 3). The resulting reaction gave modified PBI products good yields. These products were identified through NMR analysis and show high substitution on the PBI polymer backbone. The thermal behavior of the modified polymers was evaluated using TGA and DSC. The data collected showed that the modified PBI products were of lower thermal stability than the parent PBI. It is possible that the long alkyl chains decompose at very high temperatures, although the solubility of the polymers was greatly enhanced. Gas testing of the polymers showed better gas selectivity and permeability properties compared to the parent PBI.

Further investigation into inorganic/organic hybrid PBI polymers should be continued, especially with the new catalytic reactions. It is very possible that these reactions can give many other products that have enhanced properties and better stability.
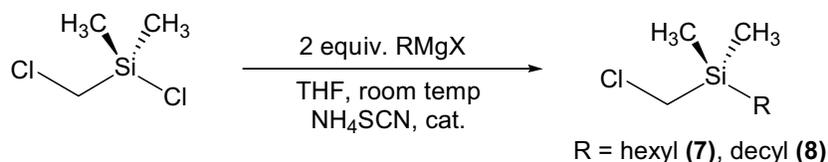
Scheme 7. Catalytic reaction for chloromethyl chlorosilane.

Organic N-Substituted Polybenzimidazoles

To clarify the nomenclature with the series of compounds synthesized, Scheme 8 shows the two reactions used for the organic substitution of PBI (see the post-modification reaction, Scheme 3). Acid chlorides will form amides and chloroformates will form carbamates. Both of these reactions are the same with the displacement of chlorine on the carbonyl group; however, the resulting product's solubility varied greatly depending on the starting ligand. Overall, the resulting PBI amides were not as soluble compared to the PBI carbamates. There is only a subtle change between the two structures, an oxygen atom between the carbonyl group (C=O) and the R group. It could be that there are other interactions with PBI and the ligands, which are needed to facilitate the post-modification reaction. The thermal stability of the carbamates and amides are not that good in comparison to the PBI parent polymer. Carbamates are good amine protection groups for organic synthesis because they decompose upon heating (160–200ºC) or with strong acid. Amides will have a bit better thermal stability (~200ºC), but these will decompose well below the PBI parent polymer decomposition temperature (~500ºC). Still, there could be alternative ligand types that will give better yields along with better thermal stability of the products. The organic post-modification reactions will be split into two categories: carbamates and amides.
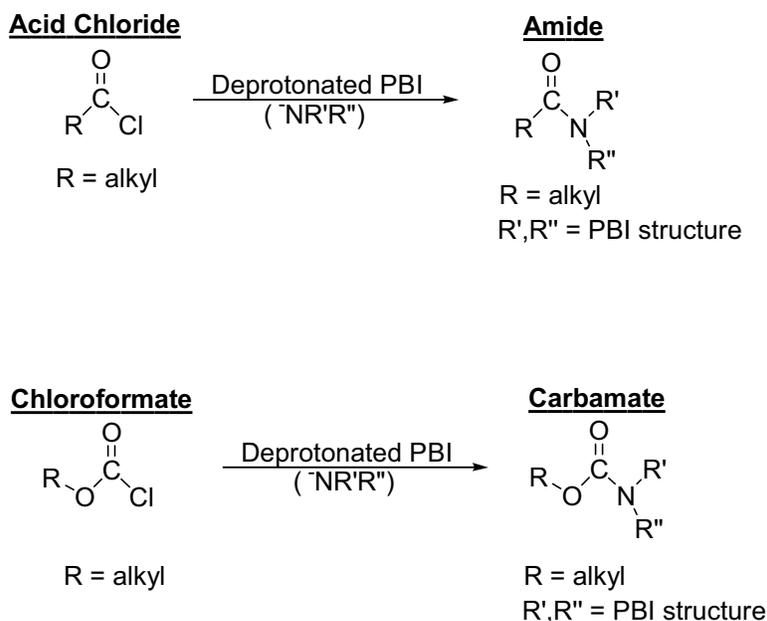
Scheme 8. Acid chloride and chloroformate reactions.

Carbamates. Carbamates were the first series of compounds tested using the same conditions as before with the inorganic/organic hybrid PBI polymers (Scheme 3). Several chloroformate ligands were tested (Figure 10), but the n-octanocarboxyl-tri(ethylene glycol) chloroformate was the only compound that had to be synthesized before it could be used for the post-modification PBI reaction. This reaction (Scheme 9) required a slight molar excess of n-octanol to be deprotonated with sodium hydride. Then, the

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bis(chloroformate) was added to the deprotonated octanol to give the following chloroformate product. Because there is a slight molar excess of deprotonated octanol, small amounts of bis-substituted product (by-product) and the mono-substituted product (preferred product) were formed in the reaction. Since the by-product will not react very well using the PBI substitution reaction (Scheme 3), the mono substituted product will be the main compound that will react with PBI. Therefore, these products were isolated together from the salts that were formed with the reaction, and used "as is" for the PBI substitution reaction. The final products can be purified by simple solvent extraction to give yellow to yellow-orange solids.

Isobutyl chloroformate   Ethyl chloroformate   2-Ethylhexyl chloroformate

9-Fluorenylmethyl chloroformate   Methyl chloroformate   2,2,2-trichloroethyl chloroformate

n-Octanocarboxyl-tri(ethylene glyocol) chlorofomate
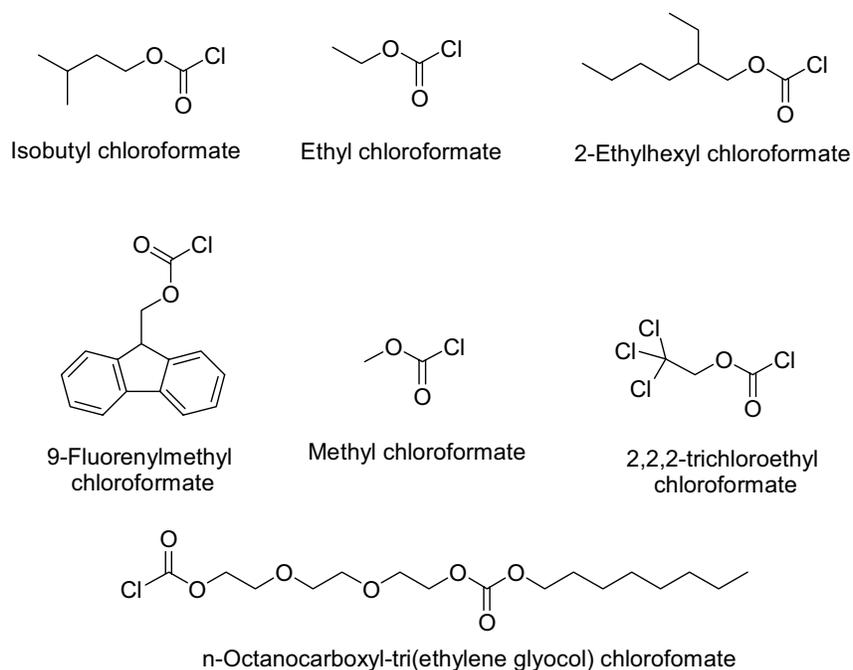
Figure 10. Chloroformate compounds tested.
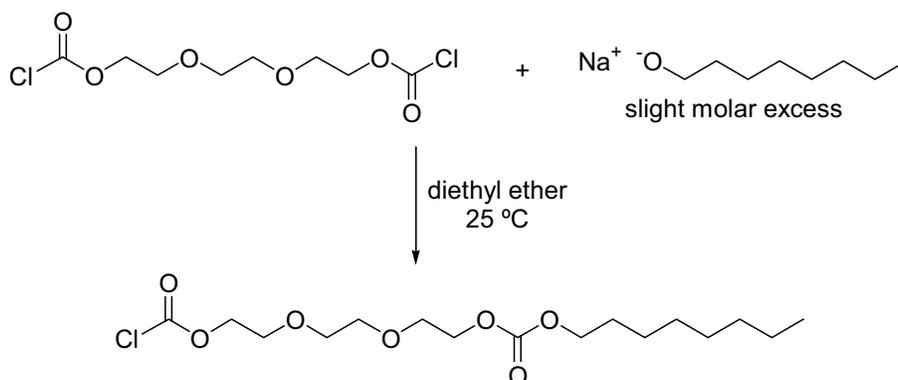
Scheme 9. n-Octanocarboxyl-tri(ethylene glycol) chloroformate reaction.

All of these compounds (Figure 10), except methyl chloroformate, provided yields that could be used for NMR, DSC, and TGA. The overall yields were nearly quantitative with the isobutyl, ethyl, and 2-ethylhexyl functional groups. The other functional groups did not give as good of yields. It is not completely understood why some of these compounds did not work well, however it could be postulated that the bulky groups, such as isobutyl and 2-ethylhexyl, break up the crystalline PBI structure well. The

NMR spectra of the post-modified PBI compounds showed a high-degree of substitution on the PBI polymer. The DSC and TGA of these compounds show a sharp thermal change between 180–200ºC. This thermal change denotes the carbamate decomposition for these modified PBI compounds; therefore, the post-modified PBI polymer reverts to its original parent PBI structure. In addition, the DSC and TGA were placed through a couple of heating and cooling cycles to show if any carbamate functionalities remained after one thermal cycle. It was observed that only one heating cycle is needed to remove all of the carbamate functionalities from the post-modified PBI polymer. This could be useful for other future PBI applications. Gas testing was conducted with the isobutyl and ethyl functionalities. Only the isobutyl functionality provided the best membranes. The ethyl functionality was difficult to form good membranes. Overall, the isobutyl functionality has better gas permeability compared to parent PBI.

Solubilities of many of these post-polymerization modified PBI compounds were highly varied. It was found that the isobutyl and 2-ethylhexyl functionalities were the most soluble, and the aromatic functionality and methyl chloroformate were the worst. The ethyl functionality showed very good solubility characteristics, similar to the isobutyl, when it was first isolated. Nevertheless, over time the ethyl functionality became insoluble. It could be postulated that the ethyl functionality had some traces of DMAc that enhanced its solubility and that solvent evaporated. DMAc is the solvent used for the PBI post-polymerization modification reaction (Scheme 3); however, DMAc was not detected from ^{1}H and ^{13}C NMR spectra. The 2,2,2-trichloroethyl functionality was soluble, but it was soluble mainly in THF and not in chloroform. The tri(ethylene glycol) functionality possibly had unreacted bis(chloroformate) still in solution (Scheme 9), which led to cross-linking the PBI polymer. Further purification and analysis of the tri(ethylene glycol) functionality needs to be conducted to resolve these issues.

Amides. All of these compounds were purchased directly from the manufacturer (Figure 11). Only the oleoyl chloride needed to be purified further by vacuum distillation. Following Scheme 3, the resulting post-modification reaction with these compounds gave varied yields.
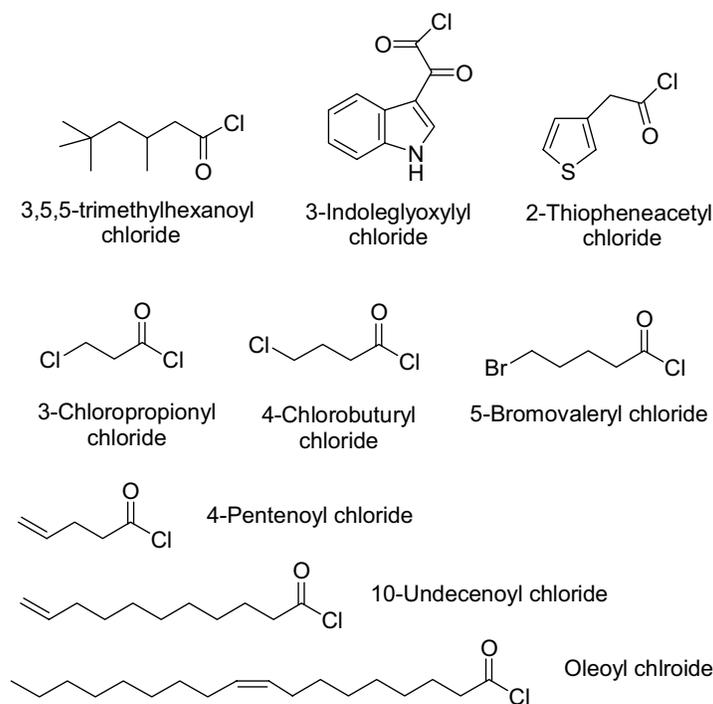
Figure 11. Acid chloride compounds tested.

Many of these compounds are being tested in the laboratory and the results are not complete for several of the post-polymerization modified products. The main reason that further testing is needed is that several post-modified products cannot be purified by the same techniques as found with the previous carbamates. Different techniques are needed and it will take additional time to resolve these issues. What can be stated about the post-polymerization modified PBI compounds are that gross changes to ligand size (bulkiness or size) results to more soluble materials. This is observed with the oleoyl and trimethylhexanoyl functionalities. In fact, the oleoyl functionalized PBI will stay suspended in many organic solvents. This is very important to note because many of the other post-modified PBI polymers are limited to THF.

The indole and thiophene post-polymerization modified functionalities were the most difficult to isolate completely because the starting indole and thiophene would precipitate in the same solvents as the post-modified PBI would. In addition, the isolated post-polymerization modified compounds would dissolve in many organic solvents. These materials were never truly resolved for purifying the final products; however, the preliminary ^{1}H NMR shows the predominance of the indole and thiophene starting materials (carboxylic acid or anhydride by-products). This means that the products isolated are not the post-polymerization modified PBI polymers.

The chloropropionyl, chlorobuturyl, pentenoyl, undecenoyl, and bromovaleryl post-polymerization modified functionalities gave very little to no isolated yield. In the case with chloropropionyl functionality, a highly cross-linked material was formed in the reaction. The rest of these materials are not soluble in chloroform, and different solvent(s) will be needed to complete these studies.

Oleoyl and trimethylhexanoyl post-polymerization modifications were the only products that have given sufficient yields for other studies; however, these compounds are currently being investigated. Both of these post-polymerization modified PBI polymers are soluble in THF. Nevertheless, as stated before, the oleoyl functionalization PBI stays suspended in many organic solvents. The oleoyl PBI product makes a cloudy solution with many of the organic solvents, and it may not be going into solution at all. Because the oleoyl products cannot be identified with ^{1}H NMR, it cannot be fully concluded that the oleoyl functionalities are on the polymer.

Substitution Reactions Using Allyl Functionalized Polybenzimidazole

The last series of post-polymerization modification of PBI used allyl functionalized PBI for further modifications on PBI (Figure 12). In return, these modifications can allow many different and altered structures that enhance desired properties—ideal for gas membranes. Two different reactions types were tried: hydrosilylation reaction and halogenation, followed by amination. Each reaction type required an understanding about the functionalized PBI polymer solubility in solution. Slight changes with different solvent will alter the solubility greatly. This was observed with the all of the reactions. The solubility of the functionalized PBI polymer is critical for any further post-polymerization modification and substitution reactions, especially if there are a high percentage of substitutions needed. Overall, the success for these reactions was to keep everything in solution. Discussions about the substitution reactions will be provided into two parts: hydrosilylation and amination.

Allyl Functionalized PBI
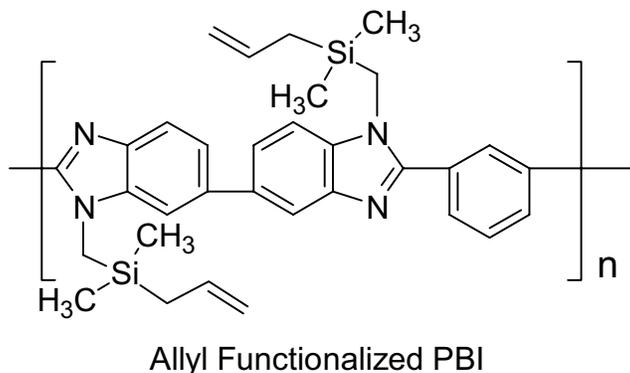
Figure 12. Allyl functionalized PBI.

Hydrosilylation. Hydrosilylation reactions involve a metal catalyst reacting to a hydrogen silicon (Si-H) bond across a terminal alkene resulting in formation of a silicon carbon bond, which no longer has the double bond (Scheme 10). Two different catalysts were used for the hydrosilylation reactions: Karstedt's catalyst [Pt$_2$(CH$_2$=CHSiMe$_2$)$_2$O)$_3$] and Wilkinson's catalyst [(Ph$_3$P)$_3$RhCl]. The Karstedt's catalyst had a 3–3.5% platinum concentration in xylenes, and the Wilkinson's catalyst was a solid. Both of these reactions were attempted following previous literature.[2] This procedure showed that the Karstedt's catalyst can be used in THF at lower temperatures to give the desired products; however, the Wilkinson's catalyst can be refluxed to give desired products. The first synthetic attempts used the Karstedt's catalyst. Later, the Wilkinson's catalyst was used for all of the hydrosilation reactions. An important note is that all of the hydrosilation reactions were restricted to THF solutions, and this could be the problem with all of the hydrosilylation reactions due to the solubility of the allyl functionalized PBI.
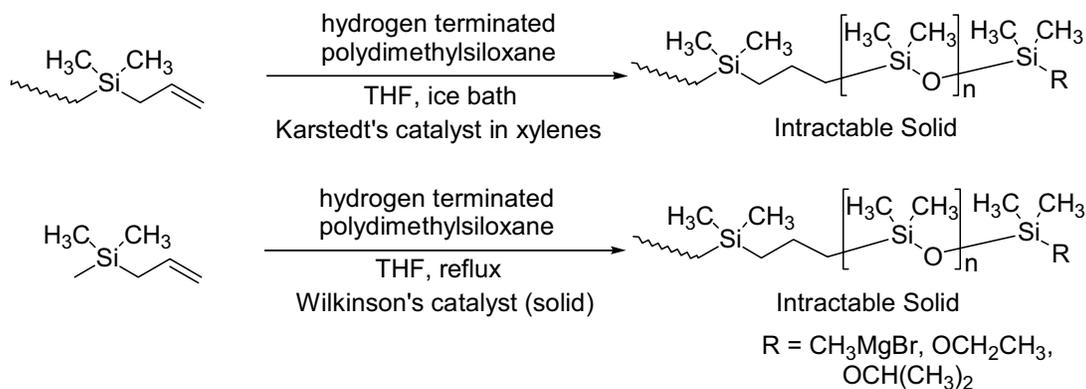
Scheme 10. Hydrosilylation with hydrogen terminated polydimethylsiloxane.

Scheme 10 shows the first modification attempts with oligiomeric polydimethylsiloxane (PDMS) with hydrogen terminations. There was about a 2:1 molar ratio (PDMS/PBI) used, because there are two reactive alkene groups on PBI. However, it is necessary to allow only one addition on the PBI polymer backbone or else cross-linking will occur.[2] After this reaction is finished, the reaction solution is quenched to remove the remaining silicon hydrogen bonds. Some quenching groups were methyl magnesium bromide or alcohols, such as ethanol or isopropanol. This is to prevent any further cross-linking of the products. The synthesis with the Karstedt's catalyst proved very difficult, because the temperature cause the PBI to cloud in THF. In addition, the catalyst in xylenes caused more problems with PBI, which precipitated out of solution. This reaction was attempted only twice; insolubility of the PBI polymer at low temperatures was the main problem. The Wilkinson's catalyst had much better

conditions for PBI and it seemed to work, but the quench would cause the polymer to precipitate out of solution. It was concluded that these reactions are much more difficult to accomplish with PDMS oligiomers and remain soluble in solution. Additional smaller groups are needed.

Scheme 11 shows the next series of compounds attempted with trimethoxysilane. Since there is only one reactive silicon hydrogen bond, the temperature is not an issue and no quenching groups are needed to complete the reaction. The Karstedt's catalyst was used first with these reactions. However, once again, the catalyst in xylenes caused changes in the solvent that made the PBI polymer precipitate out of solution. This reaction did not give the PBI modified compound that was soluble in anything, including dimethylacetamide. It is possible that these compounds can cross-link when exposed to the atmosphere, but it could be that the catalyst is bound to the polymer making it insoluble. The Wilkinson's catalyst did not give any better results. It could be that the reaction conditions were not enough to synthesize the products.
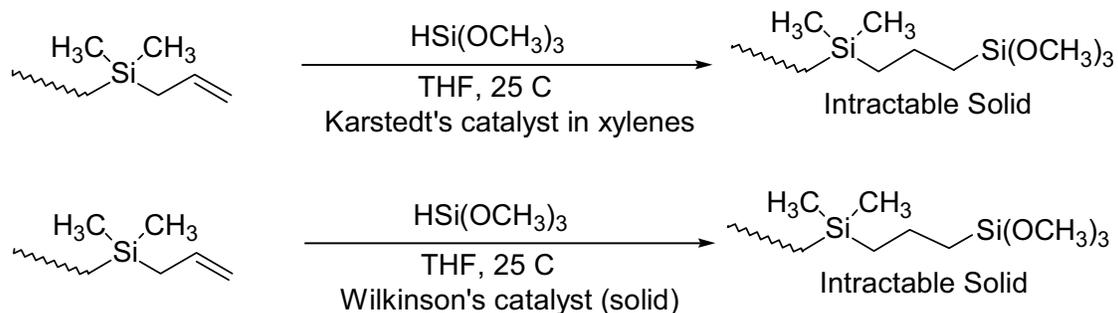
Scheme 11. Hydrosilylation reaction with trimethoxysilane.

Overall, these reactions were not successful; however, in the future, different reaction conditions might be used to give better results with these modifications. There is a possibility that solvent is the primary problem with all of these reactions, therefore a different solvent could be used to ensure that everything remains in solution during the reaction.

Amination. Amination requires two steps to give the desired products using the same allyl functionalized PBI (Scheme 12). These reactions are prepared in a single pot. None of the intermediates were isolated or analyzed. The first step required bromine to react with the alkene. This is a known organic reaction where bromine will give a dibromo-substituted product. The second step is the amination with diethylamine [$HN(CH_2CH_3)_2$]. The amine displaces the bromine to give the diamino functionalize PBI. As stated before, there are two reactive alkene functionalities on PBI, so at least eight equivalences of diethylamine are needed: four equivalences needed for the reaction and four equivalences for hydrogen bromide formation (diethylamine hydrogen bromide salt). Several important factors about the reaction conditions gave a better understanding about the post modification of allyl functionalized PBI. As shown in Schemes 12 and 13, solvent was a factor and other reagents were needed to give soluble polymers.

At first, the reaction was done in THF as the solvent (Scheme 12), but the allyl functionalized PBI polymer was not staying in solution after the addition of diethylamine. Allyl functionalized PBI had problems with the hydrosilylations using THF as the solvent, and the solubility of PBI can change drastically with minimal changes in with the solvent. It was concluded that the solvent had to be changed to something more aggressive, such as DMAc. Bromine was tested with DMAc, and it was observed that bromine did not change color with DMAc using minimal light exposure. In addition, no heat was given off when bromine was added to DMAc. This suggests that bromine will not react very well with DMAc; therefore, DMAc can be used as a solvent. The second reaction (Scheme 12) used DMAc as the solvent. Everything remained in solution after the addition of diethylamine, but the isolation of the products did

not provide anything soluble. It could be suggested that diethylamine is causing cross-linking to occur or the diethylamine hydrogen bromide salt causes other problems with the reaction. It was apparent that another synthetic pathway was needed.
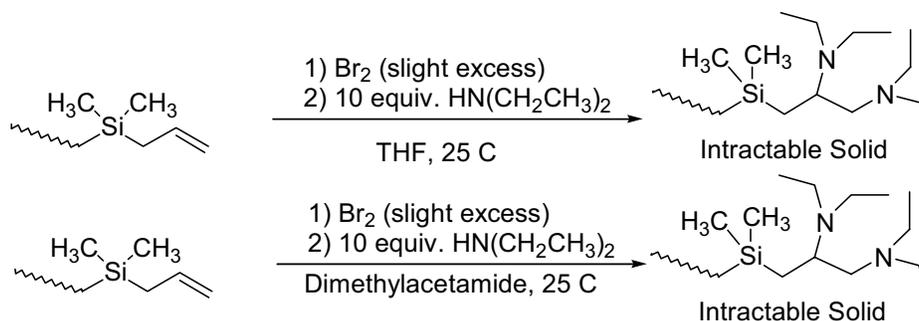
Scheme 12. Amination with diethylamine.

Alkylations of amines are generally conducted with a base, usually a base that will not change the pH of the solution too much. Potassium carbonate (K_2CO_3) is used with many different amination reactions. As seen in Scheme 13, potassium carbonate was used along with only with an equal molar amount of diethylamine needed to complete the amination reaction. This reaction is an ongoing effort in the laboratory, and it was observed that soluble products were formed. However, the products cannot be fully dried because they will not dissolve in any solvent, including DMAc. This suggests that the products could be formed with the reaction, but the workup has to be perfected to give the desired product. This reaction did not produce any soluble final product.
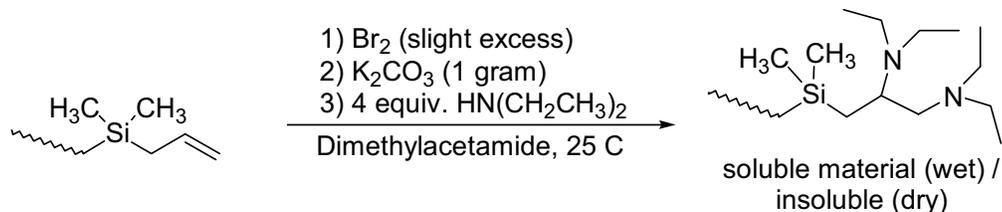
Scheme 13. Amination with diethylamine.

References

1. Lennon, P. J.; Mack, D. P.; Thompson, Q. E. Organometallics, 1989, 8, 1121.

2. Kuhnen, T.; Ruffolo, R.; Stradiotto, M.; Ulbrich, D.; McGlinchey, M. J.; Brook, M. A. *Organometallics*, 1997, 16, 5042.

SECTION 4 (FY-05)

Soluble N-Substituted Polybenzimidazole and Soluble N-Substituted High-Performance Polymer Studies

Introduction

Polybenzimidazole ([PBI], Celazole[®], or poly-2,2'[*m*-phenylene]-5,5'-bibenzimidazole) has been post-polymerization modified with the a variety of pendant groups. Many of the post-polymerization modified PBI compounds have been mixed with other polymers, especially with solubility and film forming properties in mind. The basic idea for the addition of all of the ligand types was to make the modified PBI soluble in common solvents. All the pendant groups were carefully selected with membrane applications (i.e., separation of gases in mind). Overall, the efforts were focused between better PBI film formation and other high-performance polymers (nylon, polybenzoxazole [PBO], kevlar, polyamides, and polyimides).

The PBI post-modification reaction (Scheme 14) was used for the following ligands (including both inorganic/organic hybrids and organic ligands). The general reaction is started by deprotonation of the imidazole nitrogen on the polymer backbone. The ligand is added (R-X) where the halogen is displaced by the deprotonated nitrogen. The product is substituted by the ligand R group. This reaction is kept at room temperature during this process, unlike the previous methods. This reaction has been expanded to using triethylamine for deprotonation, and found to be just as effective as sodium hydride under the same conditions. However, there has not been a complete study with previous ligands to give a clear indication if triethylamine will be a good alternative. The newest addition to the synthetic capabilities is using the microwave. It has shown good results with currently known post-modified PBI reactions, and has dramatically decreased the amount of reaction time from days to approximately 1 hour. This microwave process is the current study for post-modified PBI and high-performance polymers.
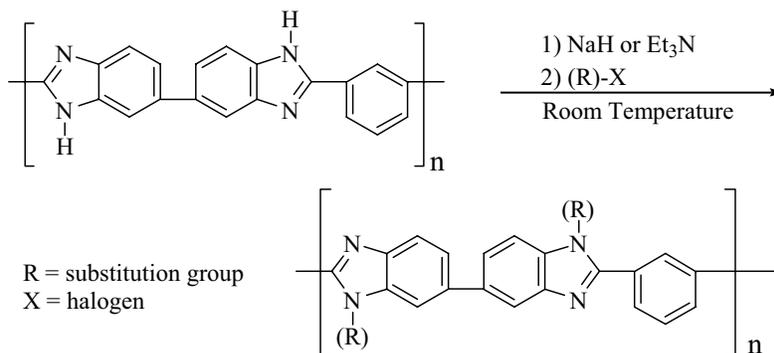
Scheme 14. PBI post-modification reaction.

Overall, the present problem with any of the post-polymerization modified PBI polymers and the parent PBI polymer is stable film formation. Most of the products produce films that appear to be internally stressed and thus are easily fractured. In order to obtain freestanding films, distilled water was used to remove the film from the casting slide, but this proved to be unfavorable because the films generally crack and break apart. These studies were directed towards plasticizers to give better films. From these studies, the team has learned how to dissolve and plasticize both the parent PBI and modified PBI. With this knowledge, the studies were expanded to other high-performance polymers (nylon, PBO, kevlar, polyamides, and polyimides) in which dissolving and casting films is possible with some of these polymers.

Polybenzimidazole and Post-Modified Polybenzimidazole Polymer Film Formation

Films were formed and gas-testing data was obtained with some of the post-polymerization modified PBI polymers. However, most of the modified polymers were very difficult to cast into films using THF as the solvent. Several other solvents were used in previous efforts to attain films with the modified polymer, but they were not consistent film formers. Using Teflon, stainless steel sheets, or glass slides as casting surfaces did not change film behaviors. In addition, films that were removed from these backing mediums by distilled water resulted with shattered pieces. After many different attempts to make films, it became apparent that another process was needed for film (membrane) formation.

The team is certain that the modified polymers were isolated, using the following analytical instruments: NMR, DSC, and TGA. However, molecular weights of the two types of modified polymers, silane substituted and organic substituted (Figure 13), were not conducted last time. Molecular weight analysis ("batch mode") of the modified polymers showed two trends (Table 5): silane substituted polymers gave expected results showing molecular weight increasing from the parent polymer to the size of substituent, and the organo-substituted polymer gave unexpected results with higher-than-normal molecular weights over a magnitude greater compared to the silane substituted. It is postulated that the organic substituted polymer has cross-linked further compared to the parent PBI polymer. From the patent literature, Celanese used various organophosphonic chloride compounds to increase the molecular weight of PBI. The interesting fact is that the increased molecular weights of the organic substituted compounds did not decrease its solubility in THF. In fact, these compounds gave the best overall synthetic yields—90% or greater. There could be cooperation of the acid and PBI to give better solubility even with a higher molecular weight. These analyses gave rise to various other possibilities with plasticizers for film formation.
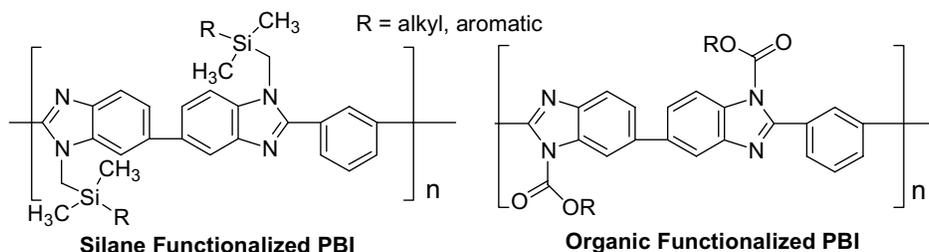
Figure 13. Functionalized PBI.

Table 5. Polymer molecular weights laser light scattering ("batch mode").

Polymer	Molecular Weight (g/mol)	Solvent
Silane Substituted		
Parent PBI	8,000–10,000	DMAc
Methyl PBI	10,000–15,000	THF
Vinyl-PBI	10,000–15,000	THF
Allyl-PBI	45,000–55,000	THF
Hexyl-PBI	45,000–55,000	THF
Decyl-PBI	65,000–90,000	THF
Organic Substituted		
Butyl-PBI	500,000–700,000	THF
EtHex-PBI	900,000–1,200,000	THF

The first series of PBI membranes did not give desirable results. Obtaining freestanding films was even more problematic when the films were exposed to water. The films often fractured or developed fissures due to both the glassy nature of the polymer and its now-understood sensitivity to water. It was evident that additives, such as plasticizers, were needed to obtain consistent quality films. The team used several well-known plasticizers that are commercially available. Trioctyl trimellitate (TOTM) and Dioctyl terephthalate (DOTP) are typical plasticizers that provided mixed results. TOTM and DOTP generally improved the film's properties, but they typically phase separate from the PBI polymer. (It is a behavior that was observed in the films as opaque/white islands or needle crystals.) Overall, the team needed to find better homogeneous casting solutions for the PBI polymers.

The next series of plasticizers were various organophosphate compounds, such as triphenylphosphate. These compounds gave better homogeneous solutions, even when the plasticizer concentration was increased to 20–30 wt% to polymer. Free films could be cast of several of the modified PBI polymers and water could be used to lift the film. Some of these films were used for gas testing, but the majority of these films would fail during the gas testing. This said that some solvent needed to remain in the film to give better stability to the film. The polymer solvent, N,N-dimethylacetamide (DMAc), was normally used to give enough film stability to obtain gas permeation data. These films would eventually fail due to solvent loss/evaporation. It was apparent that a combination of plasticizer and solvent was needed to give good PBI films that are both consistent and stable for long periods in dry gas streams.

Next, the synthetic studies were directed towards organophosphate plasticizer molecules bonded to PBI. Chlorodiphenylphosphate (Figure 14) was used to post-polymerization modify PBI. Several reactions were performed with this molecule, and it was found that the modified products resulted with soluble products that could be dissolved in several solvents, such as methanol, chloroform, acetone, and ethanol. Also, chlorodiphenylphosphate was not completely separated from the modified material. As a result, the phosphorus-chlorine bond slowly hydrolyzed to give the corresponding diphenylphosphonic acid. The phosphonic acid helps in plasticizing/dissolving the PBI, which is found in open literature using phosphoric acid/sulfuric acid for making membranes.[1] This result provided the basis that caused INL to start using various acids for PBI solubilization. Acetic acid, trifluoroacetic acid, phosphoric acid, and sulfuric acid can be used to dissolve PBI into solution. The team was able to isolate the substituted diphenylphosphate PBI polymer from the left over diphenylphosphonic acid; however, the purified substituted PBI polymer did not really give films. It is postulated that the commercial process for formation of PBI films uses variations of phosphoric acid and/or other similar plasticizers due to their very low vapor pressures and thermal stability. Some of the phosphate plasticized films were used for gas testing. The gas permeation results showed that even the phosphate plasticized films were changing with each permeation test. Overall, the gas throughput was observed to be high for the first test cycle, yet the gas permeability decreased as the plasticizer was removed by evaporation during to the consecutive cycles. This means that PBI is only good when the plasticizer/solvent or combination thereof is present. Overall, gas selectivity was not consistent in the course of the studies.
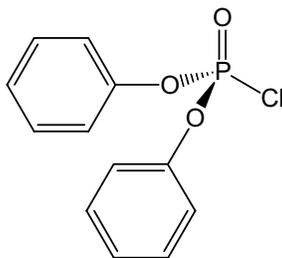
Figure 14. Chlorodiphenylphosphate.

Throughout these studies with chlorodiphenylphosphate, it was found that DMAc and concentrated acid resulted with a real powerful/aggressive solvent. When using some of the insoluble modified PBI materials or parent PBI, these polymers could quickly dissolve using this solvent combination. The team did other investigations with other high-performance polymers that had the similar imide structure (-N=C-NH-), such as amides (-HN-C=O). Several nylons dissolve rapidly in this solution. Other similar PBI materials such as PBO can be dissolved in hot, concentrated sulfuric acid first and DMAc can be added slowly into the PBO/sulfuric acid solution afterwards. It turns out that this solution is very aggressive towards any polymer with heteroatoms (oxygen, nitrogen, sulfur) that can donate its electron lone pairs to hydrogen ions. The DMAc/acid mixture was investigated and published in open literature over 40 years ago.[2] Forty to fifty years ago, this mixture was researched for dissolving DNA/RNA protein strains for structure analysis and various other biological assays. Today, it is seen in ionic liquids, batteries, and hydrogen storage/fuel devices. Presently, this mixture is not thoroughly discussed in open literature for high-performance polymers, but many years ago, DuPont made most of these discoveries for processing Kevlar and other polyamides (nylon types). PBI polymers and similar polymers were not discussed in open literature with this mixture. The team believes this solution and similar solution types are the way to process many different high-performance membranes.

The present research using these aggressive solvents expanded into using lithium salts. DuPont found that a strong acid (hydrochloric acid; HCl) or lithium chloride (LiCl)/lithium bromide (LiBr) produces the same aggressive solvent with DMAc.[3] LiCl/LiBr experiments with nylon, PBI, and Nomex (Figure 15, Kevlar derivative) have been duplicated. It was found that they do dissolve in these solutions upon heating. This proves to be interesting and synthetically advantageous for deprotonation of the nitrogen on polyamides or polyimides. Nomex was also investigated for substituting the amide with alkyl halides. Preliminary results were positive with chloromethyltrimethylsilane.
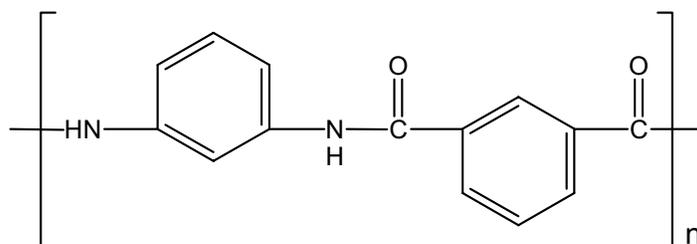
Nomex

Figure 15. Nomex structure.

Polybenzimidazole and High-Performance Polymer Synthesis

The ligands (Figure 16) attempted with the PBI reaction (sodium hydride, room temperature) were not very successful. Many of them resulted with the original ligand being isolated; however, three of the ligands gave the corresponding PBI products. The 11-bromo-1-undecene, ethylene bromide, and chlorodiphenylphosphate all gave soluble products. The polyhedral oligomeric silsesquioxane (POSS) ligands were an attempt to create inorganic-organic hybrid compounds, but no products were isolated with PBI.

11-Bromo-1-undecene

Br

Br

Ethylene bromide

H_3C

Cl

O

Methyl-3-chloro-3-oxopropionate

H_2N

Cl

O

3-Chloropropionyl chloride

H_3C

O

O

Cl

Methyl-4-chloro-4-oxobutyrate

Br

N

O

O

N-(3-Bromopropyl)phthalimide

O

P

Cl

O

O

Chlorodiphenylphosphate

Cl

POSS(cyclohexyl)

Chloropropylcyclohexyl-POSS

O

C

N

POSS(isobutyl)

Isocyanatopropyldimethylisobutyl-POSS
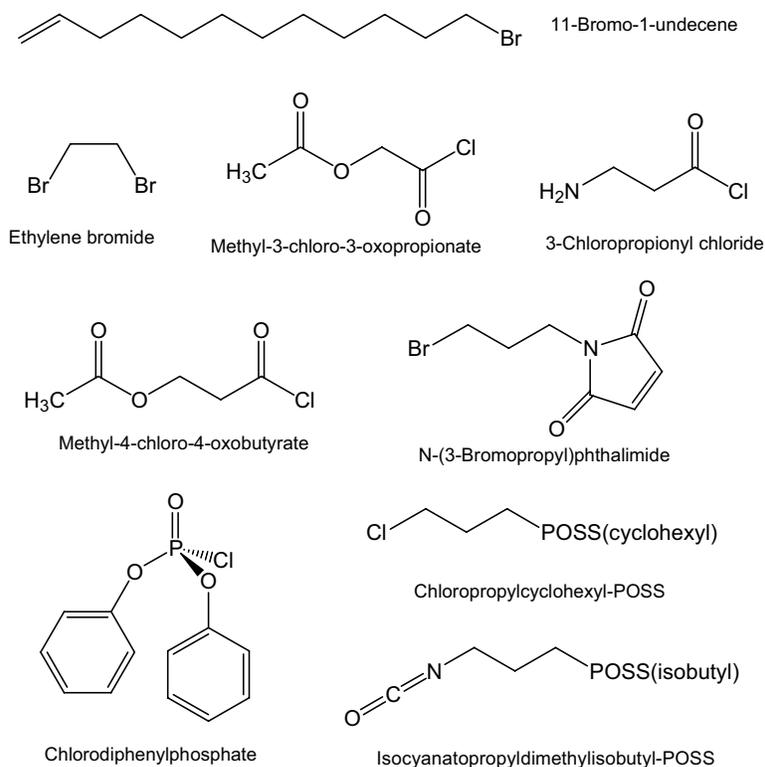
Figure 16. PBI substituents tested.

The synthesis of the postpolymerization-modified PBI polymers evolved from the original route. Typically, (as seen in Scheme 3 above) the nitrogen is deprotonated by a sodium hydride followed by the addition of the ligand, such as alkyl halide, acid chloride, or chloroformate. It has been found that triethylamine can act as the base for the post-polymerization modification reaction. In addition, the reaction can be prepared with the triethylamine and the ligand in situ; therefore, it has decreased the amount of time for the deprotonation step with sodium hydride. This pathway resulted with about the same yields as with sodium hydride under the same reaction conditions, but it has not been fully tested with all the ligand types that have been used in the past. This pathway is still under investigation.

Another addition to the synthetic scheme is the use of microwaves from a common household microwave oven. Recent literature references have shown that organic chemical synthesis with microwaves has varying results.[4] Overall, the major point with using microwaves is the reduction in time needed to complete a reaction. Single step reactions have shown to be completed in approximately 2 minutes, whereas they typically take about 24 hours. This research with microwaves has been extremely positive, and a typical PBI reaction time has been reduced to approximately 1 hour for completion. The long reaction times have been the limiting step to the synthesis of new PBI compounds. Work-up times after microwaving the reaction remain the same, but it now takes only 2 days to isolate new PBI compounds instead of the previous 7 days using more conventional synthetic approaches. The overall yields from the microwave methods are generally the same as the room temperature conditions. It is believed this pathway can be used for many of the new compounds that are anticipated in the future.

The microwave has been used for high-performance polymers, both processing and synthesis. Using the microwave as a heating source, many of these high-performance polymers can be dissolved in DMAc/LiBr solutions. This solution is not protonated by an acid, which is generally done to dissolve these polymers. This allows various bases to be used, such as sodium hydride. The microwave approach

opens up a new set of synthetic pathways for the high-performance polymers. As mentioned earlier, synthetic modification of Nomex is now possible.

Synthetic Direction of Polybenzimidazole and High-Performance Polymers

The synthetic scheme for post-polymerization modified PBI has changed from it original route at room temperature. It has been found that the microwave dramatically decreases the amount of time (from days to about 1 hour) needed to prepare the modified materials. In addition, the overall yields remain unchanged from the previous room temperature reaction. The new microwave process will help with future studies while providing products and answers to questions about those products more quickly than ever before. Since this new microwave process has been discovered, it will take time to understand the scope of other high-performance polymers.

References

1.   (a) Jones, D. J.; Rozière, J. *J. Membr. Sci.* 2001, *185*, 41. (b) Jones, D. J.; Rozière, J. *Annu. Rev. Mater. Res.* 2003, *33*, 503. (c) Oronrato F. J.; Sansone, M. J.; French, S. M.; Marikar, F. U.S. Patent 5,945,233, August 31, 1999.

2.   Klotz, I. M.; Russo, S. F.; Hanlon, S.; Stake, M. A. *J. Am. Chem. Soc.* 86, 4774 (1964).

3.   (a) Kwolek, S.L.; Morgan, P.W.; Schaefgen, J.R.; Gulrich, L.W. *Macromolecules* 10, 1390 (1977). (b) Schaefgen, J.R.; Bair, T.; Balou, J.W., Kwolek, S.L.; Morgan, P.W., Panar, M.; Zimmerman, J. "Ultra-High Modulus Polymers," Eds. Cifferi, A. and Ward, I. M., Applied Science Publishers, London, 173 (1979).

4.   (a) Varma, R. S.; Namboodiri, V. V. *Chem. Commun.*, 7, 643 (2001). (b) Hayes, B.L., *Aldrichimica ACTA,* 37, 66 (2004). (c) Bogdal, D.; Penczek, P.; Pielichowski, J.; Prociak, A., *Adv. Poly. Sci.* 163, 193 (2003). (d) Khadilkar, B. M.; Rebeiro, G. L., *Org. Process Res. Dev.*, 6, 826 (2002). (e) Boivin, J.; Brisson, J., *J. Poly. Sci. A: Poly. Chem.,* 42, 5098 (2004).

SECTION 5 (FY–06)

High-Performance Polymer Evaluation

Introduction

This section summarizes INL's work performed during FY-06 and some of its significant findings that lead to enhanced gas separation and new productivity values for the highly varied family of high-performance (HP) polymers. Careful broad reaching literature reviews, strong experimental evidence, and chemical insight provide a basis for the accomplishments. The research at INL has uncovered many fundamental issues related to synthesis, processing, and testing of the HP polymers, (i.e., polyimides [Kapton®], polyamides [Nylon], and polyazoles [PBI]). During this research, most of the physical property and gas separation data was not comprehended until the team discovered many of the misunderstood fundamental properties of the HP polymers.

INL was challenged in FY-06 to develop a matrix of potential materials for CO_2 separations based upon the literature and the team's previous experience. INL was also tasked with evaluation of the matrix for CO_2 separation membrane materials along with procuring materials for testing (Table A-15 in Appendix A). The matrix was developed and quickly the number of candidate materials was collapsed to about three or four specific polymer types with the polyimides, polyamides, and polyphosphazenes being the primary candidates for testing and evaluation. A proprietary polyimide with the trade name "VTEC" was obtained from RBI, Inc. The VTEC polyimides showed the greatest promise for high-temperature gas separation (H_2/CO_2) coupled with their overall resistance to temperature, atmosphere, and water. The team believes the VTEC polyimides will meet the needed requirements for the Carbon Sequestration program.

Background

Multiple issues have been associated with making good membranes from HP polymers. These challenges range from the simplest—dissolving the polymer into solvents to allow casting of defect-free thin films—while others have included mounting the films onto supports for testing, film brittleness, film self-induced embrittlement, and preventing/enhancing plasticization of the polymer. The result of this research is a set of stable films, spanning several classes of HP polymers, which have consistent performance properties.

INL has tested many different polymers and their corresponding blends with other polymers or additives (i.e., POSS). The list of polymers and the gas (testing) performance data are included in Tables A-3–A-14 in Appendix A. The candidate polymers have been narrowed to the VTEC polyimides, because of their desirable attributes for high-temperature gas separation, and the VTEC materials are a new set of materials that have become available in the market over the past two years. INL is the first to get them for gas separation testing purposes. However, gas permeation testing and evaluation very quickly revealed three areas of specific interest for all of these materials: specific polymer solvents, polymer solution ionic strength and ionic content, and polymer film water content (possibly due to the previous two items). The result of these studies is a significant understanding of in-solution polymer chemistry for not only the specific VTEC materials, but also the HP polymers as a class.

The VTEC materials are a new group of polyamic acids that are functionalized with different chemical groups that make them soluble in solvents. The VTEC solutions can be cast into films by pouring a puddle of the solution onto a glass plate. Over time, the solvent evaporates leaving behind a film on the glass surface. The films are then heat-treated, as described in Scheme 15, which causes a polymeric condensation reaction (similar to a Gabriel Synthesis), eliminating water as a by-product and forming a highly heat-resistant, virtually insoluble film of a polyimide, similar to Kapton®.

Polyamic acid (Pre-polymer) to Kapton®

Kapton®
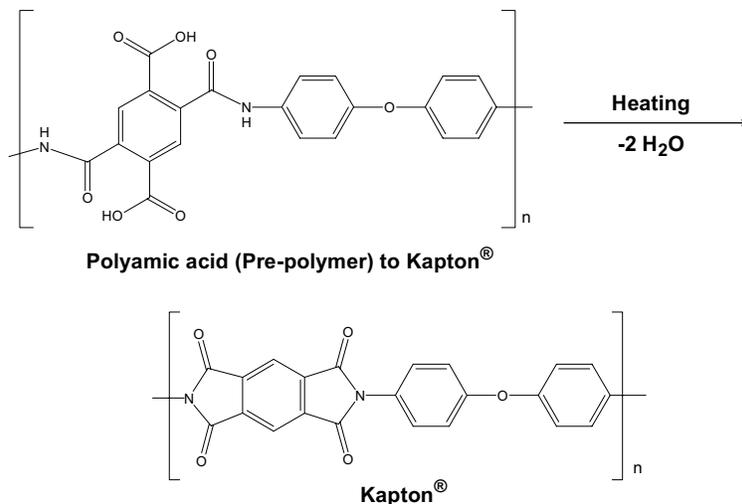
Scheme 15. Polyamic acid (pre-polymer) goes through a condensation reaction to yield the polyimide polymers.

The VTEC polymers are new materials, made in multi-gallon quantities that have not been previously available for membrane applications. The largest problem for polyimides in the past has been their low solubility in solvents, thus making membrane development a serious problem because film casting was not possible. Reports from academic laboratories on these materials describe how Freeman[1] and Koros[2] synthesized their own fluorinated polymers to make them hydrophobic, expensive, and generally not interesting for these types of studies. Both groups found it difficult to get consistent experimental results from the polymers. In addition, they have investigated heating the polymers to high temperatures to provide partial pyrolysis conditions and form carbon molecular sieve membranes by full pyrolysis. While their research on carbon membranes show promise for applications in the area of small-scale gas separations, they remain too fragile to be useful in the near future.

The Case for Solvents (Dissolution)

Dissolving the polymers required a large amount of time. The problem involved finding what solvent is appropriate, what additives are present in the solvent (i.e., salt), and exactly how the solvent interacts with the polymer(s). Much of this work is "lost" science that is being rediscovered in many of the following scientific areas: ionic liquids, fuel cells, dissolution of polymers from either natural sources (cellulose) or synthetic processes (high-performance polymers), and gas transport within polymer films.

INL has discovered this science/technology because, in spite of many years of previous experience, they were not able to cast stable films of either purchased or functionalized PBI. The team searched literature for research on similar polymers to gain insight into how to form stable films. INL found that what solvent is used to dissolve the polymer is the critical issue for many of the HP polymers. In fact, this technical expertise is older than most of today's living scientists.

The origin of "super" solvents began during the 1920s. Various solvent and acid combinations were observed to have tremendous solvating power and commonly became termed "super acids." The super acids were applied to many compounds that were difficult to dissolve. At that time, many of the present analytical methods were still in their infancy or not even envisioned. Therefore, the solvency of many compounds remained a curiosity until the large scientific endeavor of DNA/RNA dissolution emerged in the late 1950s. Following Watson and Crick's discovery of DNA's structure, the biological

community found it important to find ways to dissolve or denature DNA/RNA.[a] As a result, DNA/RNA analyses helped identify the genetic code for the Human Genome Project. Unfortunately, this science seemed to be disconnected from the other science fields, and it remained primarily in the biological community. Note that the same "super" solvents were used nearly 40 years later after their original discovery.[5] Even today, the same solvent/dissolution methods continue to be used for the isolation and identification of strands of RNA/DNA.

Many of the high-performance polymers (polyimides, polyazoles, polycarbonate, polyphenylenesulfide, etc.) were discovered during the 1960s, but were not commercialized until the 1970s. [Polyamides, like nylon, were developed in the late 1920s (Carothers[6]) and not fully commercialized after World War II. Many of these industrial technologies were kept internally for many years.] Due to the Cold War and the Space Race, there was a large expansion in the development of these polymer types. Once again, solvents played a critical role with the synthesis and processing of these polymers. Several reports provided information on certain solvents plus acid or salt (i.e., NMP and H_2SO_4, or DMAc and LiCl) would intimately interact with the HP polymer at the molecular level.[3,5,7] In some cases, the solvents themselves can rearrange to give reactive intermediates for the propagation of the polymers, like the ring-opening of NMP for the polymerization of polyphenylenesulfide.[8] Because the solvent is intimately interacting with the polymer, the door has literally been thrown open to many different types of additives that modify the specific polymer's physical properties (i.e., gas transport, melting/decomposition point, strength).

Schaefgen has supplied the best information about the dissolution of HP polymers, especially nylon and aromatic polyamides. His understanding of the strong interactions of the solvent with acid or lithium salts was closely held within DuPont for years until the late 1970s;[7a,7b] however, he discovered the intense solvent interactions with polyamides in the late 1940s with acids (formic acid and sulfuric acid).[9] The original research was related to polyelectrolyte solutions, but these same discoveries can be traced to today's ionic liquids. His description using lithium salts with DMAc was best expressed in one article where he described the polymer/solvent/salt interactions as "cationic solvating species" for aromatic polyamides (Figure 17).[7b] Schaefgen also states how it is impressive that a non-polar solvent, like toluene, can be added up to 30 wt% without polymer precipitation. In addition, small amounts of water (~1–3 wt%) will stabilize the polymer/salt/solvent solutions, but larger quantities of water will precipitate the polymer. This means that small amounts of water (such as atmospheric water sorption) is not necessarily going to cause immediate problems with these polymer solutions, and these solutions can be stored for long periods without needing to use anhydrous conditions. Overall, Schaefgen's research provides the foundation for the dissolution of several high-performance polymers using acid or salt combination solvents.

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a. Nucleic acid denaturation (definition): The denaturation of nucleic acids is the separation of a double strand into two single strands, which occurs when the hydrogen bonds between the strands are broken.[4]
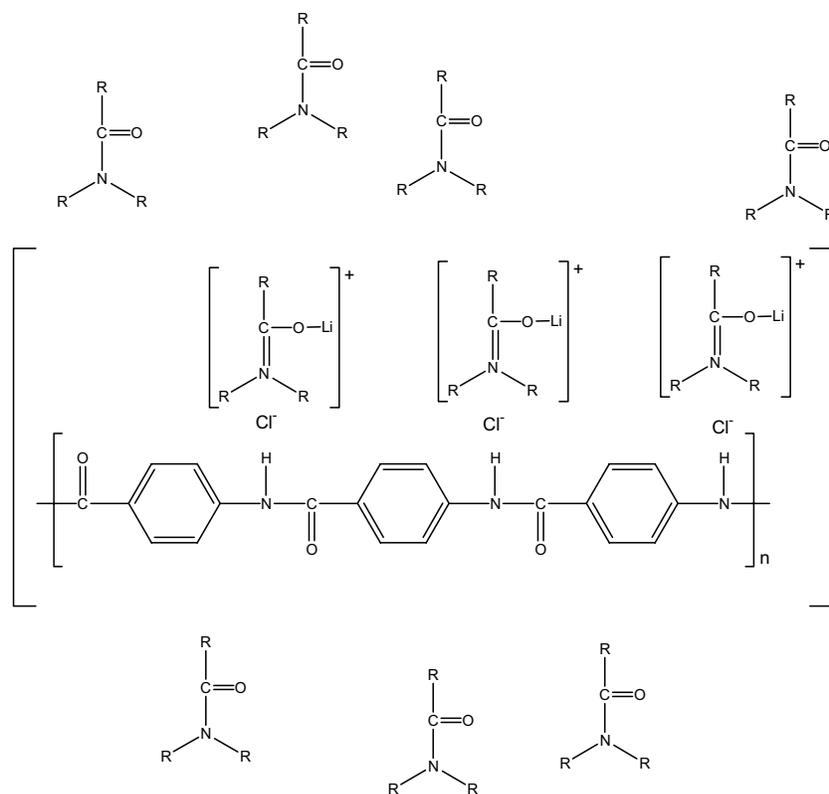
Figure 17. Postulated structure of solvated aromatic polyamide in N,N-dialkylamide LiCl solvent.[3b]

Many of the HP polymers use these solvent mixtures for dissolution (from the manufacturer), but these methods tend to be held as trade secrets. Commonly, the terms stabilizers or additives are used for these salt (i.e., LiCl) or acid (i.e., H_2SO_4) combinations with the solvent. This can be misleading, but it is critical to understand these solvent mixtures can influence membrane formation and possibly alter long-term stability. Most importantly, the stabilizers or additives may remain entrained in the HP polymer and the presence of where moisture/water is within the polymer matrix becomes a serious issue.

The Case for Water in Polymer Membranes

A critical variable when working with the glassy polymers is their moisture content. Moisture content of the polymer solutions plays a major role with the gas selectivity, especially when the gas permeation rates are low. Carbon dioxide can swell/plasticize the polymers, however it has been found that water entrapped within the polymer matrix (either as hydration molecules attached to salts in the polymer, left over solvent, or physisorbed) can also cause the polymer to change dramatically. This is evident with the time lag (gas permeability) values determined in the gas permeation experiments. In some cases, the same membrane gave different gas permeation values simply because the membrane was exposed to a humid environment between tests. These seemingly trivial differences in membrane treatment could label certain membranes a failure rather than a success or vice versa. INL has found that the presence of moisture in the gas stream or in the polymer generally decreases the gas selectivity, while a scrupulously dried membrane will show better performance. An example can be taken from the VTEC gas permeation data. The H_2/CO_2 selectivity does not change significantly due to temperature (30–250°C) (Tables A-13 and A-14 in Appendix A [highlighted in blue]). The team believes that this is due to the moisture content left in the membrane, and that moisture content becomes less of an issue at high-temperatures because the gases behave more like ideal gases. The drying procedure that has been

developed consists of casting the polymer membrane, evaporating the solvent from the polymer film over night, and heating to 100°C to remove any remaining water from the system. Next, increasing the temperature to 150°C to remove any additional solvent/water from the film, further increasing the temperature to 250°C to cause the conversion from polyamide to polyimide to occur, cooling to room temperature, and lifting the films from the glass plates using water. This is followed by a final drying at 150°C and gas transport testing. Upon discovery that moisture from the environment was being absorbed into the membranes, additional effort was made to dry the films prior to testing. These efforts comprised drying at 150°C for longer periods (24–48 hours). In addition, the membranes were sometimes further dried at 250°C for another 24 hours, such as for VTEC PI 08-051 w/10 wt% LiCl. After the drying, the membrane was then quickly transferred to the gas testing apparatus and placed under vacuum for the gas permeation evaluation using dry gas streams.

Therefore, when applied to membrane materials it has become clear the polymer films need to be dried extensively at elevated temperatures prior to permeation testing because without appropriate heat processing, the gas permeation data are most certainly skewed by the presence of residual water (from cross-linking reactions or membrane processing) and/or solvent in the polymer. INL recognizes they are particular with this issue, but meticulous care must be taken when evaluating these polymers as membranes, or the data will be highly misleading. Additionally, it has been found that permeabilities and permeant throughput can be strongly influenced by ionic content within the polymer (many of these polymers cannot be dissolved without some ionic-salt content in the solvent) (see Tables A-4 and A-5 in Appendix A). The team agrees that the new data acquired during FY-06 may be utilized as a tool to determine a means for effectively "dialing in" a specific set of polymer characteristics under a specific set of conditions (temperature, feed stream composition, and feed stream humidity).

A current example, polybenzoxazole (PBO, Zylon [Toyobo Co., Ltd.]) shows a possible water problem. PBO fibers are woven into fabric sheets, like Kevlar, and are used for bulletproof vests/flak jackets by the military and civil defense. Originally, DuPont manufactured PBO up until 1998. At that time, DuPont noticed inconsistencies and problems with the PBO fibers. Later, DuPont sold all manufacturing and patent rights to Toyobo Co., Ltd., of Japan. Recently, a government statement was issued that these vests needed to be replaced due to "possible failures."[10] In fact, Toyobo Co., Ltd. admitted that PBO slowly degraded,[11] even without light present. (Sunlight is a known factor for degrading many HP polymers; consequently, they have to be protected from sunlight.) However, the problem with PBO was traced to moisture content. Over time, the sorbed water would gradually react with PBO, thus slowly degraded the polymer. As a result, the PBO fiber was weakened and it would not perform to its original engineering specifications. This degradation behavior has been verified through FT-IR and mass spectroscopy.[12] Unfortunately, this means that these PBO (Zylon) vests have a limited shelf-life and limited period of use.

Much of INL's rationale for these materials stems from previous literature related to zeolite materials. Water has a long history with zeolites (molecular sieves).[13] An observed trend for zeolites is that exposure to water vapor decreased the zeolites' ability to absorb certain gases. The loss of volume was due to water condensing within the pores of the zeolite. The team believes the trends that moisture showed with zeolites probably has close ties to the glassy polymers as well. Simply put, kinetic gas diameters are the critical parameter. Zeolites are commonly used to capture gases of a specific kinetic diameter (i.e., for oxygen separations in the medical industry by pressure swing sorption). (It is surprising that water (H_2O; gaseous) has a Lennard-Jones kinetic diameter of 2.65-2.85Å.[13-15]) Hydrogen has a Lennard-Jones kinetic diameter of 2.89Å and helium is at 2.6Å (see Table A-1 in Appendix A [highlighted in red]). These data are extremely important for the CO_2 separations due to the gaseous water's ability to penetrate the membrane with ease, like helium and hydrogen. Due to the native functionality of many polymers, water may easily be absorbed by the membrane and form hydrogen bonds with the polymeric matrix, whereas hydrogen and helium generally will not have any effect

because they do not interact with most polymers (see Figure 18). This means that the other larger "kinetic gas diameter" gases will be in competition with water for transport through the void volume of the membrane. It can be postulated that these other gases could be either intimately involved, such as forming new complexes (H_2CO_3), and/or dynamically helpful, which could increase the larger kinetic gas transport due to the solubility interactions and/or polymer "swelling" of the membrane. INL has found that the gas permeation values are different when water is known to be present (see Tables A-4 and A-5 in Appendix A) within the polymer matrix. Also note, the gas selectivity drops for nearly all of the gases, except hydrogen. Overall, water may be more problematic for membrane-based gas separations than previously believed and proper precautions are needed to avoid inaccurate and unstable gas transport data acquisition. The team agrees that many of the gas testing procedures need to be questioned with regard to membrane dryness and the amount of moisture in the gas feed stream.
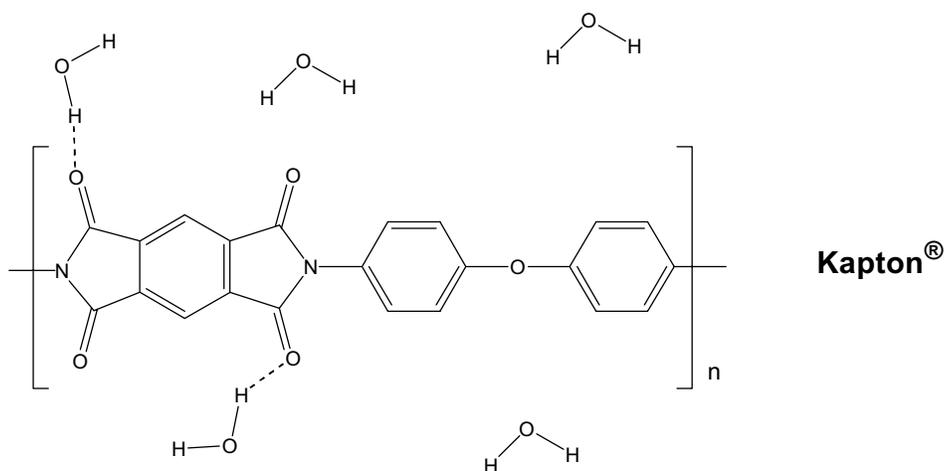
Figure 18. Possible hydrogen bonding modes for polyimides with water and native carbonyl groups (C=O) on the polymer.

The experimental demonstration of the presence of water in the polymeric matrix has been performed by for project using thermal desorption coupled with TGA measurements. Additionally presence of molecular water in the polymer's void volume has been validated through positron annihilation lifetime (PAL) spectroscopy using a polyimide.[11] The results discussed by Dlubek, et al.,[16] showed that water is sorbed mostly in the larger pores with each pore occupied with a single water molecule at relative humidities lower than 30%. At higher humidities, multiple water molecules will occupy the large pores and other sites (like the carbonyl groups) in the polyimide. These data are important to note because water can be trapped in the membrane and change the gas permeabilities, which will give inconsistent transport results.

Results and Accomplishments

During the first quarter of FY-06, a major milestone was met with a Non-Disclosure Agreement (NDA) with PBI Performance Products, Inc. This agreement gives access to the raw PBI polymer source—PBI Performance Products (the only PBI polymer manufacturing source in North America). The PBI polymer can be purchased as a solution or as dry polymer powder. The INL team purchased several PBI solutions of varying polymer concentrations, as well as the dry powder. The team tested each of the PBI solutions when they were received at INL.

During FY-06, the number of polymer classes that can be used for high-temperature gas separations was narrowed and is compiled in Table A-15 in Appendix A. The table summarizes polymer

properties and some known gas separation properties for nine classes of polymers. Thermal and chemical stabilities are the critical components that make a polymer a candidate for membrane materials in the proposed high-temperature CO_2 sequestration applications. Several classes of polymers will not withstand temperatures greater than 250°C, while others may be tolerant of the thermal needs. However, the chemical stabilities of the polymers (i.e., water or organics) are poor. Based upon the data contained in Table A-15 in Appendix A, polyimides (Kapton®, VTEC) and polyazoles (PBI, PBO) were selected as classes of polymers that function at these higher temperatures. Materials like polysulfones by themselves will probably not be useful for the high-temperature gas separations, as anticipated, due to low glass and melt transitions of the polymers.

Tables A-4–A-15 in Appendix A summarize the specific gas permeation testing data that have been acquired to date. The INL team believes the new VTEC materials offer some exciting opportunities that many other polymers lack. The materials are exceptionally thermally stable (up to 500°C), physically strong (sheets of the material may be held like paper and folded over upon themselves), and resilient (the material may be baked in an oven multiple times at 250°C and remain soft and pliable). Additionally the gas transport data from the polymers is quite astonishing and competitive with the other high-performance gas separation polymers. With the observation of the transport properties of the polymers, it became apparent that the polymer processing procedures for preparation of the membranes is critical. Thus, INL developed a heat treatment regimen that gives reliable gas testing data. The regimen consists of casting the polymer membrane, evaporating the solvent from the polymer film over night, heating to 100°C to remove any remaining water from the system, increasing the temperature to 150°C to remove any additional solvent/water from the film, further increasing the temperature to 250°C causing the conversion from polyamide to polyimide to occur, removing the reaction-produced water, cooling to room temperature, lifting the films from the glass plates using water, followed by a final drying at 150°C, and immediate gas permeation testing.

Table A-2 in Appendix A shows the onset of decomposition (under nitrogen) for the VTEC PI 80-051 series of polymers with the decomposition temperatures similar to Kapton®. Even more interestingly, the decomposition temperature does not change dramatically with addition of various additives. The addition of poly(bis[trimethylsilylmethyl]polybenimidazole) (PBI-TMS) substantially decreases the decomposition temperatures close to the original PBI-TMS decomposition temperature. INL has also obtained the TGA data for the VTEC polyamic acid (no heat treatment) and TMA (thermomechanical analysis) data for the "heat treated" VTEC polyimide films. From Table A-3 in Appendix A, the TGA shows that the evolution of water (condensation to the polyimide) occurs at about 240°C. All of the VTEC polymers exhibited high thermal decomposition temperatures (>500°C). The TMA data for the VTEC polymers show very small dimensional changes when heated to 400°C; however, that change occurs at a specific temperature. It is not clear if the observed feature is a glass transition, because the thermal feature is not distinctly observed in the DSC at the temperature that corresponds with the TMA.

To date, long term (>12 hours) high-temperature testing has not been performed with the VTEC materials—the data presented in these tables are the result of approximately 6 months of actual data acquisition. However, the best anecdotal data supplied by the manufacturer shows the material known as PI-1388 has survived 100 hours at 380°C with no deleterious effects. INL's experiments up to 300°C (mixed gas testing [see Table A-6 in Appendix A]) have shown no problems with the materials.

The TGA data, shown in Figure 19, are using VTEC PI 80-051 with and without ~10 wt% elemental bromine added to the polymer. Over the 12-hour period of the experiment, at a temperature of 300°C, (all INL polymers were heat cycled according to the previously described regimen before the TGA evaluation), very little weight loss was shown. The parent VTEC PI 80-051 shows a 1.06% weight loss and the same material with 10-wt% bromine at 300°C over 12 hours demonstrates only 1.5% weight loss.

The weight loss difference between the two films is minor, less than 0.5%; therefore, the loss of the remaining bromine is not an issue. The team believes that the remaining bromine is tightly held by the polymer by either van der Waals interactions or covalent bonding.
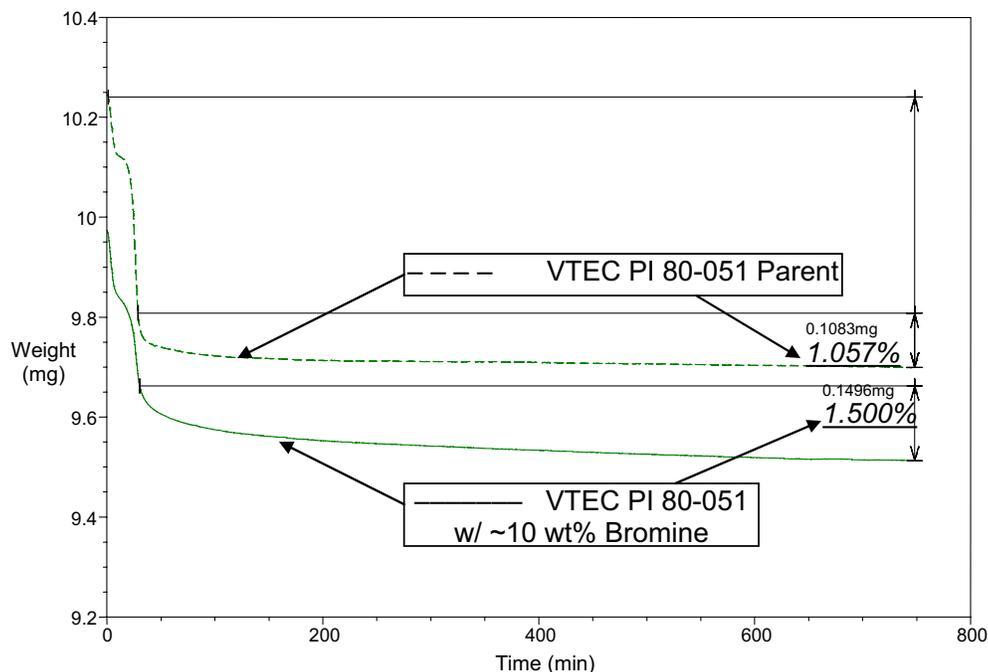
Figure 19. TGA composite of VTEC 80-051 parent and VTEC 80-051 w/~10 wt% bromine at 300ºC for 12 hours.

Due to the screening nature of these experiments, the time has not been taken to collect longer-term data. However, data has been collected for materials that are not heat treated, partially heat treated, and treated according to the regimen described in the report. The resulting data suggest that once the heat treatment regimen has been followed, the permeabilities remain stable over time and temperature ranges of the tests (1 to several hours). In addition, some of the films have been tested multiple times with stable results. There is a membrane contained in Table A-10 in Appendix A that has been tested twice (VTEC PI 80-051/~2 wt% bromine), which shows the membrane permeabilities and selectivities do not change. (Each of the pure gas testing results is comprised of three cycles of the gas [approximately 1 hour each cycle] with the three values averaged to give the reported numbers).

In the tables below, two types of data are shown, Tables A-4, A-5, A-7–A-11, and A-13 in Appendix A are pure gas permeation results, and they explain the fundamental gas transport properties of the polymers under ideal conditions. The data contained in Tables A-6, A-12, and A-14 in Appendix A represent a mixed gas experiment performed at 250°C. Interestingly, the separation data for H_2/CO_2 remains consistent with the low temperature data, as do the pure gas data. The CO_2/CH_4 data also remain consistent with the lower temperature data. This observed behavior is unusual because polymer membranes usually lose selectivity with increasing temperature.

In Table A-7 in Appendix A, the following blends of VTEC and functionalized PBI-TMS polymers show great promise for the CO_2/CH_4 separation at 30°C, where the separation factor α is 31.7 for 1388/PBI-TMS and 26.7 for 80-051/PBI-TMS (pure gas). Films can be simply cast from these solutions. The films were easily lifted from the glass without any water. In addition, these blends seemed to form

the best films. There is a slight increase in gas permeability with these VTEC/PBI-TMS blends compared to the parent VTEC materials, and the astonishing point is that the CO_2/CH_4 separation factor actually increased. However, when the temperature was increased to 250°C (mixed gas) the separation factor dropped significantly (Table A-9 in Appendix A), consistent with normal polymer membrane behavior at elevated temperatures.

From Tables A-8, A-9, and A-11 in Appendix A, there are important trends with various fillers (such as SiO_2) and the blends, because they do not show significant differences from the parent polymer systems. The main problem with many types of filler is they increase the void volume too much reducing selectivity and increasing permeability. In the polymer blend case, the gas permeability data generally followed the polymer of higher concentration. In some cases, the selectivity and permeability are remarkably about the same as the pure polymer system. The problem with polymer blends is that the data can be easily skewed because of the solvent or water content.

The data in Table A-9 in Appendix A directly compare two different HP polymers (polyphenylene oxide [PPO] and VTEC 80-051). The overall productivity (permeability) of these films is slightly increased compared to the parent polymer films. The CO_2 productivity was observed to increase compared to the parent materials, and the CH_4 values remain about the same as the parent polymer. An interesting trend is also observed with other materials, such as PPO represented by data supplied by Phillips Corporation. The polymer was dissolved into two different solvents; the chlorinated solvent (trichloroethylene) and its transport properties were compared with the polymer dissolved in the non-protic solvent (NMP). The gas permeation values for the chlorinated solvent dissolved polymer were nearly two times greater than those used for the NMP dissolved polymer. It is not known if the gas permeation properties of the two PPOs might become more similar upon additional processing (i.e., heat treatments).

Lastly, a study was done with the VTEC polyimides to verify how much water was changing the polymer's void volume (Table A-16 in Appendix A). In these tests, a series of VTEC polyimide membranes were thoroughly heat processed, exposed to standard atmospheric moisture (relative humidity 20–40%), and dried at 150°C for 1 hour. In addition VTEC polyimide membranes (no heat processing), were exposed standard atmospheric moisture (Idaho's relative humidity 20–40%), and compared with the above materials.

Positron Annihilation Spectroscopy Studies Results

The following conclusions can be drawn from the positron annihilation spectroscopic (PALS) measurements (Table A-16 in Appendix A):

1. The differences between the lifetimes and intensities of the spectra for unheated and heated samples are relatively small. Since the microporosity of these samples is low compared to other open volume polymers, their long lifetime and intensity values are also low, thus their values have relatively high uncertainty. The best indicator of any possible change in the structure is the product of the intensity and lifetime. Since the free volume fraction is calculated on the basis of both—lifetime (pore size) and the intensity (pore frequency, rate)—it is the most reliable value to consider while comparing the unheated and heated spectra of polymers.

2. The free volume fraction for VTEC PI 80-051 w/2-wt% Br2, VTEC PI 1388, and VTEC PI 80-051 increased after the polymer was heated.

3. The lowest, although not-negligible, long intensity values were observed for Kapton®-HN. The average lifetime value overlaps in its uncertainty with the water lifetime value quoted from literature.[17]

4. The effect of extended drying of the VTEC PI 80-051 polymer seem to remain constant for at least 2 weeks since the lifetime results for performed are very similar.

5. There is very little difference between the measuring results for the non-heat treated VTEC polyimides, which indicates a high stability, and reliability of the data.

6. The lifetime values vary between 1.5–2.25 ns that correspond to the pore radius of 50–125 Å^3. The longest lifetime values, thus relative micro-pore sizes were seen, besides Kapton®, in VTEC PI 1388 (no heat treatment). The intensity values vary from 2–6 %. The highest intensity values were observed in polymer VTEC PI 80-051 w/~17-wt% PBI-TMS (no heat treatment), and the lowest in the Kapton®-HN film. These results are discussed in Appendix B.

Overall, the PALS analysis indicates that water occupies pore volume in the polyimides when they were not well dried, therefore they showed lower void volumes compared to the dried polyimides.

Summary

This section provided a summary of the research work performed during FY-06, some of its significant findings that lead to enhanced gas separation, and completely new productivity values for the entire highly varied family of HP polymers. The observed solution behaviors, gas permeabilities, and spectral observations summarized in the report support such a statement. The research at INL has uncovered many fundamental issues related to synthesis, processing, and testing of the HP polymers (i.e., polyimides [Kapton®], polyamides [Nylon]), and polyazoles [PBI]). The experiments described in the report have uncovered many of the poorly understood fundamental properties of the HP polymers. Many of the experimental observations provided in this report are "first-time" reported, and will appear in future refereed articles and patents.

The VTEC polyimides offer significant advantages over PBI and its derivatives with:

1. Greater solubility and stability in solvents leading to much more reproducible casting of defect-free thin films

2. The polymers allow the blending of many other types of polymers, fillers (POSS), and additives (bromine)

3. Consistently forming stable, freestanding, defect-free thin films (considering PBI has never really been very good for applications)

4. Greater thermal stability (stable ≥450ºC)

5. Lower coefficients of thermal expansion than most other polymers once cured

6. Better ability to accommodate thermal shocks and physical abrasion

7. Chemical stability

8. Higher productivity for gas separations (permeability)

9.   Good selectivity for gases (selective for gases of interest to the project) at levels that compete with today's commercial membranes.

Conclusion

The above nine points lead to one conclusion—the VTEC polyimides provide a "step-change" for polymer membranes applications over the PBI systems that have been examined over the past several years; therefore, INL has met the requirement that was set for FY-06 to "Find a set of polymers that work better than PBI."

References

1.   (a) R.S., Prabhakar; M.G., De Angelis; G.C., Sarti; B.D., Freeman; Coughlin, M.C., *Macromolecules*, 38, 7043 (2005). (b) Prabhakar, R.S.; Merkel, T.C.; Freeman, B.D.; Imizu, T.; Higuchi, A., *Macromolecules*, 38, 1899(2005). (c) Prabhakar, R. S.; Freeman, B. D.; Roman, I., *Macromolecules*, 37, 7688 (2004). (d) Arnold, M.E.; Nagai, K.; Freeman, B.D.; Spontak, R.J.; Betts, D.E.; DeSimone, J.M.; Pinnau, I., *Macromolecules*, 34, 5611(2001). (e) Merkel, T.C.; Bondar, V.; Nagai, K.; Freeman, B.D.; Yampolskii, Yu.P., *Macromolecules,* 32, 8427 (1999).

2.   (a) Coleman, M. R.; Koros, W. J., *J. Poly. Sci. Part B: Poly. Phys.*, 32, 1915 (1994). (b) Coleman, M.R.; Koros, W.J., *Macromolecules*, 30, 6899 (1997). (c) Coleman, M. R.; Koros, W. J., *Macromolecules*, 32, 3106 (1999). (d) Staudt-Bickel, C.; Koros, W. J., *J. Membr. Sci.,* 170, 205 (2000). (e) Kamaruddin, H. D.; Koros, W. J., *J. Poly Sci. Part B: Poly. Phys.*, 38, 2254 (2000).

3.   Conant, J. B.; Hall, N. F. *J. Am. Chem. Soc.* 49, 3062 (1927).

4.   (a) Michelson, A. M. "The Chemistry of Nucleosides and Nucleotides," Academic Press, London and New York (1963). (b) Arakawa, T.; Timasheff, S.N. *Biochemistry* 23, 5924 (1984). (c) Anfinsen, C.B. *Science* 181, 223 (1973). (e) Scopes, R. K. "Protein Purification," Springer, New York, 60 (1982).

5.   Klotz, I. M.; Russo, S. F.; Hanlon, S.; Stake, M. A. *J. Am. Chem. Soc.* 86, 4774 (1964).

6.   Carothers, W. H. *Chem. Rev. 8*, 353 (1931).

7.   (a) Kwolek, S.L.; Morgan, P.W.; Schaefgen, J.R.; Gulrich, L.W. *Macromolecules* 10, 1390 (1977). (b) Schaefgen, J.R.; Bair, T.; Balou, J.W., Kwolek, S.L.; Morgan, P.W., Panar, M.; Zimmerman, J. "Ultra-High Modulus Polymers," Eds. Cifferi, A. and Ward, I. M., Applied Science Publishers, London, 173 (1979). (c) Fahey, D. R.; Ash C. E. *Macromolecules* 24, 4242 (1991).

8.   (a) Stepniczka, H. E. *Ind. Eng. Chem. Prod. Res. Develop.* 12, 29 (1973). (b) Ross, S. D.; Finkelstein, M.; Petersen, R. C. J. Org. Chem. 31, 133 (1966).

9.   (a) Schaefgen, J. R.; Flory P. J. J. Am. Chem. Soc. 70(8), 2709 (1948). (b) Schaefgen, J. R.; Flory P. J. J. Am. Chem. Soc. 72(2), 689 (1950). (c) Schaefgen, J. R.; Trivisonno, C. F. J. Am. Chem. Soc. 73(10), 4580 (1951). (d) Schaefgen, J. R.; Trivisonno, C. F. J. Am. Chem. Soc. 74(11), 2715 (1952).

10.   (a) Whitaker, J. SSC-Natick Press Release, 03-41 (2003). (b) Tompkins, D. NIJ Journal, 254, 2 (2006). (c) Reisch, M.S. Chem. Eng. News, 83(31), 18 (2005).

11. "PBO fiber Zylon," Toyobo, Co., Ltd. Technical Information Bulletin, 2-2-8 Dojima-Hama, Kita-Ku OSAKA 530-8230, JAPAN (2001).

12. (a) "Third Status Report to the Attorney General on Body Armor Safety Initiative Testing and Activities," National Institute of Justice, NCJ 210418, USA (2005) (b) Gies, A.P.; Hercules, D.M. Macromolecules, 39, 2488 (2006).

13. Breck, D. W. "Zeolite Molecular Sieves: Structure, Chemistry, and Use," John Wiley and Sons: New York, New York, (1974).

14. Ben-Amotz, D.; Herschbach J. Phys. Chem. 94, 1038 (1990).

15. Michaels, A.S.; Bixler, H.J. J. Poly. Sci. 50, 413 (1961).

16. Dlubek, G.; Buchhold, R.; Hubner, Ch.; Naklada, A. Macromolecules 32, 2348 (1999).

17. Li, Y.; Zhang, R.; Jean, Y.C. "Appendix: Free-volume Data in Polymeric Materials," in Principles and Applications of Positron and Positronium Chemistry, Eds. Y.C. Jean, P.E. Mallon, and D.M. Schrader, World Scientific Pub. Singapore, 373 (2003).

SECTION 6

Overall Summary

The "CO$_2$ Separation Using Thermally Optimized Membranes" project was initiated with several partners participating to achieve the objectives of the Carbon Sequestration Program. Los Alamos National Laboratory (LANL) was the lead institution for the project. LANL then contracted gas transport characterization work to University of Colorado because they had a method for simultaneously measuring gas permeation and polymer swelling at both room temperature and elevated temperatures. Idaho National Laboratory (INL) was an active participant in the project and co-authored the proposal that was funded. INL wrote the polymer modification section of the proposal that proposed to provide basic gas room temperature permeation testing to the group while Colorado was providing their specific permeation testing system. The project was initiated with a petrochemical company as a partner, however, due to various changes in the industry, the partner dropped out and a new one was found, and a membrane manufacturer, Pall Corporation, was identified and joined the project as an active participant in the group. LANL was to provide some expertise in polymer modification high-temperature membrane testing using a meniscus membrane test apparatus coupled with mass spectrometry for obtaining very high-temperature testing results (temperatures of 450°C and above). This report summarizes INL's contributions to the project.

Attempts to synthesize polybenzimidazole (PBI) silicate hybrid materials succeeded, but the materials exhibited both large dimensional changes and were too brittle for practical membrane applications. Therefore, the silicate hybrid synthetic efforts were dropped.

The PBI post-polymerization modification synthetic route, which was developed during the third year of the project, expanded upon previous reactions to include a number of soluble hybrid organic/inorganic PBI-based polymers that exhibit similar thermal properties as the parent PBI. Interpretation of the NMR spectra indicated that the PBI is almost fully substituted by the organosilane moieties. Some of the modified polymers have similar thermal properties to the parent polymer, and the molecular weights are within the expected values for the substituted parent PBI. Overall, INL's post-polymerization polymer modification route provides a straightforward synthetic method that can be carried out at room temperature and gives reasonable yields while making materials that could be more amenable to processing.

Additional PBI post-polymerization modification reactions were pursued with different compounds. Results for many of the post-polymerization modified PBI compounds were mixed, especially with respect to their solubility and film-forming properties. The strategy was to enhance the PBI common solvent solubility by adding various pendant groups and maintain or enhance the polymer's gas transport properties. All of the pendant groups were added to the polymer primarily with membrane applications in mind (i.e., gas separations). Many of these new pendant groups were substituted onto PBI; however, polymer solubility remained poor in most cases. In a few samples, it was not clear if the pendant group substitution onto the PBI had even taken place. Overall, the efforts were split between two categories: inorganic pendant group synthesis (inorganic/organic hybrids) and organic pendant group substitution.

The synthetic scheme for post-polymerization modified PBI changed from its original room temperature route. It was found that use of microwaves dramatically decreases the amount of time (from days to approximately 1 hour) needed to prepare the modified materials. In addition, the overall synthetic yields remain unchanged from the previous room temperature reaction. It is believed that the new microwave-based process will help tremendously with future studies while providing products and

answers to questions about those products more quickly than before. Additionally, it believed the new microwave-based process may be successfully applied to synthetic modification and processing of other high-performance polymers.

INL was challenged for FY-06 to find a set of polymers that would be better suited to the needs of the Carbon Sequestration Program than PBI has proven. Table 6 (Section 8.1) is the result of that research and all of the current results point clearly to the polyamide and polyimide families as the major players for high-temperature membranes. This report summarized the research work performed during FY-06 and some of its very significant fundamental findings that lead to enhanced gas separation and completely new productivity values for the entire highly varied family of high-performance (HP) polymers. This is supported by the observed solution behaviors, gas permeabilities, and spectral observations that are summarized in the report. The research at INL has uncovered many fundamental issues related to synthesis, processing, and testing of the HP polymers, (i.e., polyimides [Kapton®], polyamides [Nylon], and polyazoles [PBI]). The experiments described have uncovered many of the poorly understood fundamental properties of the HP polymers.

The VTEC polyimides offer significant advantages over PBI and its derivatives. The following points lead to one conclusion, the VTEC polyimides provide a "step-change" for polymer membranes applications over the PBI systems that have been examined over the past several years; therefore, INL has met its requirement for FY-06, "Find a set of polymers that work better than PBI."

The following points provide a rationale for why INL considers the VTEC polymers to be superior:

1. Greater solubility and stability in solvents leading to much more reproducible casting of defect-free thin films

2. Polymers allowing the blending of many other types of polymers, fillers (POSS), and additives (bromine)

3. Consistently forming stable, freestanding, defect-free thin films (considering PBI has never been very good for applications)

4. Greater thermal stability (stable ≥450ºC)

5. Lower coefficients of thermal expansion than most other polymers once cured

6. Better ability to accommodate thermal shocks and physical abrasion

7. Chemical stability

8. Higher productivity for gas separations (permeability)

9. Good selectivity for gases (selective for gases of interest to the project) at levels that compete with today's commercial membranes

10. Polymer gas transport properties that approach Robeson's famous "Line of Death."

To conclude, the authors ask that the reader recognizes that many of the experimental observations provided in this report are "first-time" reported and will appear in future refereed articles and patents. Above all, this project has sponsored several presentations, papers, and patents that have attracted significant national and international attention (shown below).

1.   Klaehn, J. R.; Orme, C. J. Luther, T. A.; Jones, M. G.; Wertsching, A. K.; Peterson, E. S., "Soluble N-Substituted Organosilane Polybenzimidazoles," *Macromolecules*, accepted 2007.

2.   Klaehn, J. R.; Orme, C. J.; Luther, T. A.; Peterson, E. S.; Urban-Klaehn, J. M., "Polyimide and Their Derivatives for Gas Separation Applications," *PMSE Preprints*, accepted 2007.

3.   Klaehn, J. R.; Orme, C. J.; Luther, T. A.; Peterson, E. S.; Urban-Klaehn, J. M., "Polyimide and Their Derivatives for Gas Separation Applications," *Polymer Materials: Science and Engineering: General Papers/New Concepts in Polymeric Materials*, ACS 234nd National Meeting, 2007. (Presentation).

4.   Orme, C. J.; Klaehn, J. R.; Peterson, E. S.; Stewart, F. F., "Gas Permeability Measurements on Polyimide and Polyimide Blends," ACS-NORM 62nd Northwest Regional Meeting, 2007. (Poster)

5.   Peterson, E. S.; Klaehn, J. R.; Orme, C. J.; Luther, T. A., "Polyimide and Their Derivatives for Gas Separation Applications," Fifth Annual Carbon Sequestration, 2007. (Presentation).

6.   Klaehn, J. R.; Orme, C. J.; Luther, T. A.; Peterson, E. S.; Berchtold, K. A.; Young, J. S.; Greenberg, A. R.; Brahmandam, S.; Acquaviva, J.; Onorato, F.; Hopkins, S., "Polyimide and Polybenzimidazole Derivatives for Gas Separation Applications," *PMSE Preprints*, 2006, 95(2), 333.

7.   Klaehn, J. R.; Orme, C. J.; Luther, T. A.; Peterson, E. S.; Young, J. S.; Berchtold, K. A.; Greenberg, A. R.; Brahmandam, S.; Acquaviva, J.; Onorato, F.; Hopkins, S., "Polyimide and Polybenzimidazole Derivatives for Gas Separation Applications," *Polymer Materials: Science and Engineering: Symposium - Advanced Membranes for Energy and Environmental Applications*, ACS 232nd National Meeting, 2006. (Presentation)

8.   Klaehn, J. R.; Orme, C. J.; Luther, T. A.; Peterson, E. S.; Young, J. S.; Berchtold, K. A.; Greenberg, A. R.; Brahmandam, S.; Acquaviva, J.; Onorato, F.; Hopkins, S., "Polyimide and Polybenzimidazole Derivatives for Gas Separation Applications," *Fifth Annual Carbon Sequestration*, paper #094, 2006. (Presentation).

9.   Greenberg, A. R.; Brahmandam, S.; Berchtold, K. A.; Young, J. S.; Klaehn, J. R.; Orme, C. J.; Luther, T. A.; Peterson, E. S.; Acquaviva, J.; Onorato, F.; Hopkins, S., "Mechanical and Transport Behavior of PBI Dense Films Used for Elevated Temperature Gas Separation," *Fifth Annual Carbon Sequestration*, paper #057, 2006. (Presentation).

10.   Berchtold, K. A.; Young, J. S.; Greenberg, A. R.; Brahmandam, S.; Klaehn, J. R.; Orme, C. J.; Luther, T. A.; Peterson, E. S.; Acquaviva, J.; Onorato, F.; Hopkins, S., "Novel Polymeric-Metallic Composite Membranes for CO2 Separations at Elevated Temperatures," *Fifth Annual Carbon Sequestration*, paper #176, 2006. (Presentation).

11.   Klaehn, J. R.; Orme, C. J. Luther, T. A.; Jones, M. G.; Wertsching, A. K.; Trowbridge, T. L.; Peterson, E. S. INL Tracking #475 (B-481). Title: "Polybenzimidazole Compounds, Polymeric

Medium, and Methods of Post-Polymerization Modifications," U.S. Patent Application No. 20050272880; application - December 8, 2005.

12. Klaehn, J. R.; Orme, C. J. Luther, T. A.; Jones, M. G.; Wertsching, A. K.; Peterson, E. S. INL Tracking #216 (B-338). Title: "Polybenzimidazole Compounds, Polymeric Medium, and Methods of Post-Polymerization Modifications," U.S. Patent Application No. 20050272859; application, December 8, 2005.

13. Klaehn, J. R.; Orme, C. J. Luther, T. A.; Jones, M. G.; Wertsching, A. K.; Trowbridge, T. L.; Peterson, E. S. INL Tracking #475 (B-481). Title: "Polybenzimidazole Compounds, Polymeric Medium, and Methods of Post-Polymerization Modifications," International Patent Application No. 05/19686 (PCT/EPC members), filed June 5, 2005.

14. Klaehn, J. R.; Orme, C. J.; Luther, T. A.; Jones, M. J.; Wertsching, A. K.; Peterson, E. S., "New Soluble Polybenzimidazoles by Post-Polymerization Modification,"*Polymer Preprints*, 2005, 46(1), 708.

15. Klaehn, J. R.; Orme, C. J.; Luther, T. A.; Jones, M. J.; Wertsching, A. K.; Peterson, E. S.; Young, J. S.; Berchtold, K. A.; Greenberg, A. R.; Khare, V.; Acquaviva, J.; Onorato, F.; Hopkins, S., "New Soluble Polybenzimidazoles by Post-Polymerization Modification," *Fourth Annual Carbon Sequestration*, paper #199, 2005. (Presentation).

16. Klaehn, J. R.; Orme, C. J.; Luther, T. A. ; Jones, M. J.; Wertsching, A. K.; Peterson, E. S., "New Soluble Polybenzimidazoles by Post-Polymerization Modification," *Abstracts of Papers of the ACS* 229:455-POLY Part 2, 2005. (Presentation).

17. Klaehn, J. R.; Orme, C. J.; Luther, T. A.; Jones, M. G.; Wertsching, A. K.; Peterson, E. S., "New Solubility Characteristics of Modified Polybenzimidazoles," *14th Annual NAMS Meeting*, Jackson Hole, WY, 2003. (Poster).

SECTION 7

INL Scheduled Funding and Milestones

Table 6. INL's Funding and Milestones Schedule (FY-00–FY-06) for the project, "*CO$_2$ Separation Using Thermally Optimized Membranes.*"

Year (FY)	Funding ($U.S.)	Scope	Result
2000	18,000	Project Startup	
2001	50,000	1. Molecular composite development 2. Baseline performance of PBI	1) Complete 2) Complete
2002	50,000	1. Molecular composite development 2. Baseline performance of PBI 3. Synthetic modification of PBI	1) Complete 2) Complete 3) Complete
2003	75,000	1. Synthetic modification of PBI 2. Characterization of modified PBI 3. Deliver modified PBI films to LANL	1) Complete 2) Complete 3) Postponed
2004	135,000	1. Synthetic modification of PBI 2. Characterization of modified PBI 3. Deliver modified PBI films to LANL	1) Complete 2) Complete 3) Complete
2005	135,000	1. Develop commercial PBI source 2. Synthetic modification of PBI 3. Characterize new group of PBIs	1) Complete 2) Complete 3) Complete
2006	150,000	1. Synthetic modification of PBI 2. Explore new group of polymers for membrane applications 3. Characterize new group of polymers 4. Develop commercial source of new polymers 5. Comprehensive report	1) Complete 2) Complete 3) Complete 4) Complete 5) Complete

SECTION 8 (FY–07)

High-Performance Polymer Testing

Introduction

The INL team broadened their polymer base during FY 2007, focusing on the polyimide known as "VTEC" as the principal candidate polymer for high temperature carbon dioxide separation membranes. The INL team developed potential materials for CO_2 separations based upon the literature and the team's previous experience. In FY 2006, INL was tasked with evaluation of a matrix for CO_2 separation membrane materials along with procuring materials for testing. The best choice was a proprietary polyimide with the trade name "VTEC" obtained from RBI, Inc. The VTEC polyimides showed the greatest promise for high-temperature gas separation (H_2/CO_2) coupled with their overall resistance to temperature, atmosphere, and water. The team believes the VTEC polyimides will meet the needed requirements for the Carbon Sequestration program.

During FY 2007, the INL team has broadened their research to include a single set of objectives for gas performance evaluation. INL was tasked to complete the testing of the VTEC polyimides, and perform gas testing of two VTEC polyimides as "heat treated" membranes for CO_2/CH_4 and CO_2/H_2 separations.

Background

Based upon FY 2006's results, VTEC polyimides were found to be highly durable and gave nearly equal or better gas separation performance than polybenzimidazole (PBI). The VTEC materials are aquired as solutions of polyamic acids, and they are casted easily into films. The films are heat-treated (see Scheme 16) which completes the polymeric condensation reaction, by eliminating water as a by-product. A polyimide film (like Kapton®) is formed that is highly heat-resistant and virtually insoluble in common organic solvents. The INL team concluded that these polymers are very robust and capable of high-temperature gas separations. However, INL has been able to benefit from previous knowledge of casting and gas testing to include more significant findings which can lead to further enhanced gas separation properties.

Polyamic acid (Pre-polymer) to Kapton®

Kapton®
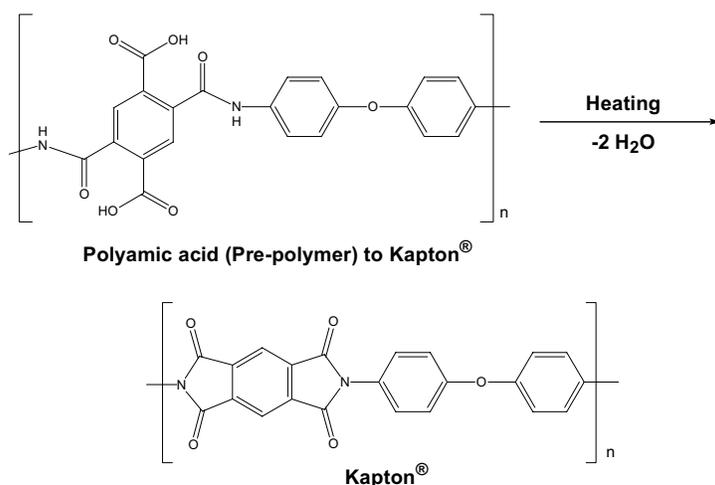
Scheme 16. Polyamic acid (pre-polymer) goes through a condensation polymerization reaction yielding polyimide polymers.

The VTEC polymers are new materials that are made in multi-gallon quantities with applications in the US Navy and other industrial identities. However, these polymers have not been investigated for membrane applications. The largest problem for many of the polyimides is their low solubility in common solvents, thus making membrane development a serious problem because film casting was not possible with common solvents. Additionally, there are few commercial sources for polyimides; therefore, several academic laboratories tend to synthesize their own polyimides. For example, Freeman[1] and Koros[2] chose to synthesize fluorinated (hydrophobic) polyimides. Curiously, they have investigated heating the polymers to high temperatures to provide either partial or full pyrolysis conditions and form carbon molecular sieve membranes. Nonetheless, both Freeman's and Koros' groups found it difficult to get consistent experimental results with these materials. While their research on carbon membranes show promise for small-scale gas separations, these carbonized systems remain too fragile to be useful at large scale.

The Case for Membrane "Conditioning"

Aside from our previously described issues with water and salt, the most notable change that affects gas transport across the membrane is exposure to carbon dioxide. For decades, carbon dioxide has been used as a foaming agent and plasticizing agent with high performance polymers (glassy polymers). Even so, this information is scattered throughout the open literature. The INL team has pieced portions of it together with respect to gas transport. In some cases, the team believes that this technology is retained as internal trade secrets within the polymer and membrane manufacturer companies, because some gas mixtures cause glassy polymers to undergo subtle changes. This section of the report provides the basis for these phenomena and then tries to connect the open literature with an eye for possible future research directions.

In the late 1970s, many glassy polymers (HP polymers) were shown to be effective for gas separations; however, the permeabilities of glassy polymers were poor at best. A number of directions were used to find ways to change the polymer's molecular pore size, but small pore size changes from a 3-5Å to 10-30Å were found to be significantly worse for gas separations (near Knutson diffusion). Later, this led to research involving gas interactions with glassy polymers.[3] This gas interaction (solution-diffusion model) provided a possible key to improving the gas separation and transport. These gas interaction behaviors are most apparent with carbon dioxide, due to its solvent-like nature under pressure. Several published articles have gone into some detail about carbon dioxide (pure gas), and carbon dioxide's effect on many different types of glassy polymers.[4] However, the subtle details within their results generally are not provided or not examined. At present, Koros provides the best information about these effects for gases and glassy polymers. The term "conditioning" or "conditioning agent" was coined by Koros for several glassy polymers. The key to a "conditioning agent" is to swell the membrane (plasticize) without changing the membrane into a rubber-like state. In return, the "conditioned" (plasticized) state allows the membrane to have enhanced gas permeability with negligible change in its gas selectivity. This provided a major advancement for glassy polymers and gas transport. However, this "conditioning" breakthrough for gas transport has remained an enigma for many researchers, and has been the source of inconsistent experimental results. The nuances described in the previous chapter about additives and water could explain why some of their results seemed not to agree. Overall, it is important to understand what glassy polymers are doing at a molecular level.

A noted case of inconsistent "conditioning" results was glassy polymers exposed to acid halides (HX). Kaner (UCLA) discovered certain trends with two different polymers, polyaniline and polypyrrole.[5] These key findings were that the presence of a halogen (fluorine, chlorine, bromine, or iodine) in his polymers changed the overall gas separation properties. Kaner found that with either chlorine or bromine present in the polymer film, the separation factors improved for several gases while the gas permeabilities were enhanced by two fold for hydrogen (see Table 7). The separation factor (α)

for CO_2/CH_4 using a polyaniline film doped with 4 molar hydrochloric acid (HCl) was 151 at 25ºC up from 128 for the untreated base polymer at 25ºC. The separation factor (α) for CO_2/CH_4 using a polyaniline film doped with 4 molar hydrogen bromide (HBr) was 263 at 25ºC up from 128 at 25ºC. This effect was thought to be a molecular sieving effect, which can generally be applied to many of the HP polymers that have a semi-rigid to rigid backbone. This halogen acid "conditioning" effect was documented in several articles and patents.[5-8]

Table 7. Pure Gas Data – Polyaniline with Halogen Acid Treatment.

Polyaniline (Kaner's Data)[1]								
Polymer	Permeability (barrers)						Selectivity α	
	H_2	Ar	N_2	O_2	CH_4	CO_2	$H_2/$ CO_2	$CO_2/$ CH_4
As-Cast Film	**8.79**	0.121	0.067	0.413	0.0156	**2.00**	4.4	**128**
Doped/Undoped 4M HF	**28.0**	0.758	0.378	1.82	0.526	**10.2**	2.7	**19.4**
Doped/Undoped 4M HCl	**17.6**	0.183	0.063	0.546	0.0172	**2.60**	6.8	**151**
Doped/Undoped 4M HBr	**13.7**	0.116	0.032	0.380	0.0089	**2.34**	5.9	**263**
Doped/Undoped 4M HI	**8.17**	0.113	0.047	0.356	0.02	**1.87**	4.4	**93.5**
1. (a) Kaner, R. B.; Anderson, M. R.; Mattes, B. R.; Reiss, H. U.S. Patent 5,096,586, Mar 17, 1992. (b) Kaner, R. B.; Anderson, M. R.; Reiss, H.; Mattes, B. R. U.S. Patent 5,096,586, Oct 25, 1994.								

At one time, the INL team thought that it had discovered something profound with Kaner's results. These results would be astonishing, if they could be preserved for long term. The problem with these findings was that the "conditioning" was temporary, thus the membranes would return to their original state and the corresponding separation properties. When the INL's polyimides were treated with bromine, the results were mixed. For the most part, INL's results showed negligible differences between the untreated and treated polymers (see Section 6; FY06). In the end, this treatment process has not been widely accepted by the polymer community, because the results were difficult to reproduce. Very few researchers have been able to repeat Kaner's treatment method, and even then, the literature reports are restricted to Kaner's original polymers, polyaniline or polypyrrole.[8]

Over a decade before Kaner's works, Koros and Sanders found the most interesting and widely accepted information for glassy membrane "conditioning."[4,9] Their research for intimate gas interactions across glassy polymer membranes provides the basis for INL's most current work for FY 2007. Koros' best explanation for "conditioning" is found in his patent.[9] However, these effects are determined by the gas that is used because some gases interact with the polymer more than others. This is the reason that when using the pure gas testing method, carbon dioxide should be tested last, due to the "conditioning" effect that is described by Koros. Sometimes these effects can be irreversible, but normally the glassy polymers are less prone to the irreversible effects.

The main problem is that these "conditioning" effects are difficult to control, and they are connected to the polymer glass transition (Tg). Many groups from academia and industry have researched to control this effect.[1,2,10] However, the polymer structure has to be preserved to get the desired "conditioning" effects described by Koros. Presently, there seems to be only two pathways that can preserve the polymer structure. One pathway is to freeze the polymer membrane, and the other pathway is

to heat the polymer membrane close to pyrolysis. Since the INL is focused on high-temperature gas separations, the low temperature pathway is not appropriate. Most research that involved heating the membrane to pyrolysis seemed to make the polymer more brittle and fragile. The INL believes that this can be a good pathway to preserve the polymer structure, but robust membranes that function under industrial conditions are desired. Therefore, the INL pursued a middle pathway with the expectation that the VTEC polymers and other polyimide blends would not have the same problems.

Results and Accomplishments

During FY 2007, the INL team was tasked to perform "heat treatments" of polyimides. This was an effort to learn, if gas permeation can be enhanced while maintaining the gas separation properties. In addition, the INL team was tasked to complete their testing of the VTEC polyimides, and to test two VTEC "heat treated" membranes for CO_2/CH_4 and CO_2/H_2 separations. The INL team's preliminary studies showed an enhancement of their permeabilites while retaining good selectivities. The team's previous research focused on a wide array of industrially based products; however, due to our specific focus upon permeability evaluation, some gas transport data were not collected on these materials.

Tables C-4–C-15 (Appendix C) summarize the specific gas permeation data that have been acquired to date. The INL team believes the new VTEC materials offer some exciting opportunities that many other polymers lack. The materials are exceptionally thermally stable (up to 500°C), physically strong (sheets of the material may be held like paper and folded over upon themselves), and resilient (the material may be baked in an oven multiple times at 250°C and remain soft and pliable). Additionally, the polymers exhibit gas transport data that is quite astonishing and competitive with the other high-performance gas separation polymers. As INL's transport property measurements proceded, it became apparent that the polymer processing procedures for preparation of the membranes are critical. Thus, INL developed a heat treatment regimen that gives highly reliable gas permeation data. The treatment regimen consists of casting the polymer membrane by the following: evaporating the solvent from the polymer film over night; heating to 100°C to remove any remaining water from the system; increasing the temperature to 150°C to remove any additional solvent/water from the film; further increasing the temperature to 250°C causing the conversion from polyamic acid to polyimide to occur; removing the reaction-produced water; cooling to room temperature; lifting the films from the casting substrate using water; followed by a final drying at 150°C; and immediate gas permeation testing. These results have led the INL team to speculate that many well-intentioned researchers and graduate students may have "preserved" their membrane matrix under neutral atmospheres (like argon) and serendipitously been conditioning them (either in their favor or not so).

The INL team focused on the polyimides (VTEC) for high-temperature gas separations. Thermal and chemical stabilities are the critical components that make a polymer a candidate for membrane materials in the proposed high-temperature CO_2 sequestration applications. Several classes of polymers will not withstand temperatures greater than 250°C. However, the chemical stabilities of the polymers (i.e., water or organics) are poor. Polyimides (Kapton®, VTEC) and polyazoles (PBI, PBO) were selected as classes of polymers that function at these higher temperatures, in the presence of chemicals.

Tables C-1 and C-2 (Appendix C) show the onset of decomposition (under nitrogen) for the VTEC PI 80-051 series of polymers with the decomposition temperatures similar to Kapton®. Even more interestingly, the decomposition temperature does not change dramatically with addition of various additives. The addition of poly(bis(trimethylsilylmethyl)polybenimidazole), PBI-TMS, substantially decreases the blended polymer decomposition temperatures closer to the original PBI-TMS decomposition temperature. INL has also obtained the TGA data for the VTEC polyamic acid (no heat treatment) and TMA (thermomechanical analysis) data for the "heat treated" VTEC polyimide films. From Table C-3 in Appendix C, the TGA shows that the evolution of water (condensation to the

polyimide) occurs at about 240°C. All of the VTEC polymers exhibited high thermal decomposition temperatures (>500°C). The TMA data for the VTEC polymers showed very small dimensional changes when heated to 400°C. At the time, it was not clear if the observed feature in the TMA is a glass transition, because the thermal feature is not distinctly observed in the DSC at the temperature, which corresponds to the TMA.

For FY 2007, the INL used dynamic mechanical analysis (DMA), shown in Figures 20 and 21, on VTEC PI 80-051 and VTEC PI 1388 to determine their thermal transitions. These polyimides were heat cycled according to the previously described regimen. From Figures 20 and 21, it is clear that the thermal transition found with the Loss Modulus (blue line – circled temperature), which are not distinct using DSC. This thermal transition can be observed only when a direct force is applied on the polymer. Therefore, the team suggests that DMA is the most accurate method for measuring glass transition on these high performance polymers.
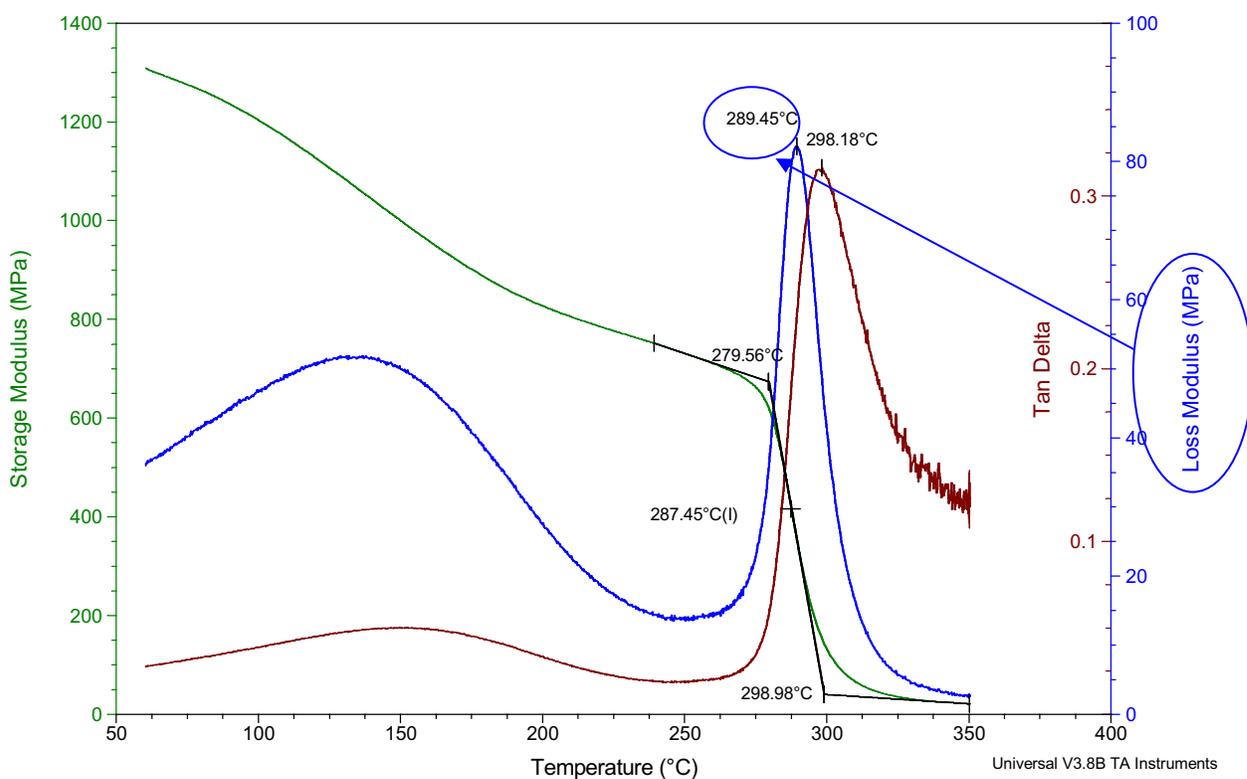
Figure 20. TMA of VTEC 80-051 parent polymer film, heat treated for 300ºC for 1 hour.
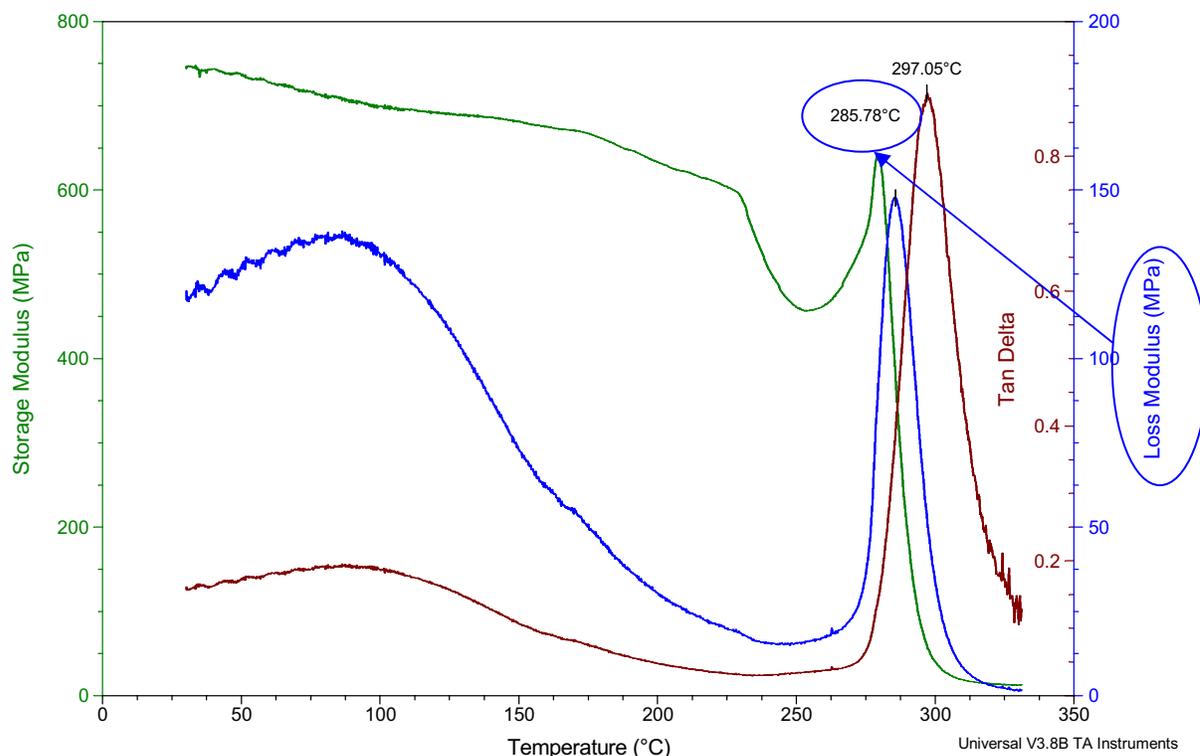
Figure 21. TMA of VTEC 1388 parent polymer film, heat-treated for 300ºC for 1 hour.

For quite some time, the INL team believed that they needed to validate their results, especially for the VTEC polyimides. Since these polymers were shown to have very low permeation, very small changes could affect the overall selectivity. William J. Koros (and his research group) from Georgia Tech assisted INL's gas permeation studies of the parent VTEC polymers and providing pure gas permeability data using Koros' equipment. From Table C-4 in Appendix C, Koros' data showed very similar gas transport numbers to INL's pure gas data. This shows that the INL's gas testing techniques and data acquisition are very good, since the INL's data coincides with another renowned gas testing facility.

During FY07, several polymer blends were created by using VTEC polyimide as the base polymer and blending it with the following polymers: (trimethylsilyl)methyl substituted poly(benzimidazole), PBI-TMS; poly(vinyl alcohol), PVA; and poly(ethylene glycol), PEG. In some cases, the INL was able to blend a large amount of secondary polymer, like 35-wt% of PEG into the parent VTEC without deleterious effects. This is significant because it shows the stability of the parent VTEC polymers even blended with known unstable polymers at high temperature (> 250°C). The INL team was investigating whether the gas permeability of VTEC could be changed. Table C-5 (Appendix C) shows some of these VTEC blends along with Kapton®. Remarkably, 50-wt% PBI-TMS can be included in these blends, and they show the best gas permeation rates when compared to the parent polymers. The VTEC-PEG blend showed a reduction in permeability for all of the gases tested – thus leading to the conclusion that the over all structure of the polymer was "tightened up".

The INL team chose to investigate two of these blends over a broader temperature range. Table C-4 (Appendix C) shows the pure gas testing results for the temperature range of 30°C to 70°C for VTEC PI 1388 with 50-wt% PBI (VTEC/PBI-TMS) and VTEC PI 80-051 with 5-wt% PVA. These results show that the VTEC-PVA blend had no increase in permeability over the base polymer. However, VTEC/PBI-TMS blend showed the best permeability over the temperature range. VTEC/PBI-TMS permeability of H_2

at 30°C increased from 3 barrers to 8 barrers, while CO_2 permeability increased from 0.5 barrers to 2.5 barrers. The VTEC-PVA blends show increases in selectivity for CO_2 over CH_4 as well as O_2 over N_2. Figures 22 and 23 contain activation energy plots for the VTEC blended membranes over the temperature range of 30°C to 70°C. In comparing activation energy plots for VTEC/PBI-TMS and VTEC-PVA, the major difference between the polymer blends is that with VTEC-PVA the activation energy (E_p) CO_2 and H_2 are very similar, suggesting that although contributions to permeability from diffusion and solubility are different they appear to balance each other out. However, VTEC-PBI shows a significant difference between E_p for H_2 and CO_2. This difference could be indicating that CO_2 has much greater solubility interaction than other gases. In Table C-5 (Appendix C), pure gas data collected 30°C is shown for several VTEC polymer blends and Kaption. Using VTEC polyimide as the base polymer in polymer blends, these blended polymers can produce thin film polymer membranes with good thermal resistance and intriguing gas separation performance. In addition, these polymer blends survive temperatures as high as 300°C or higher.
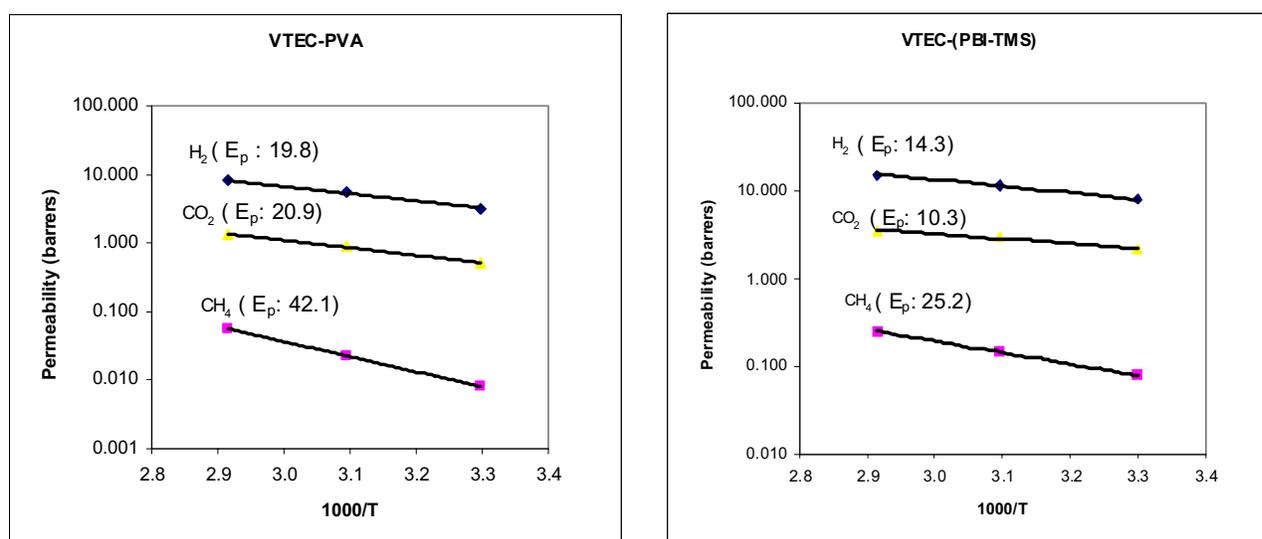
Figures 22 and 23. Activation energy plots for VTEC-PVA and VTEC-(PBI-TMS) blended membranes over the temperature range of 30°C to 70°C.

A small number of polymers are known to survive high temperatures with oxygen present. The VTEC polymers appear to be very stable for hours at 400˚C, even *in air* (~17% O_2 content). When heated to high temperatures, glassy polymers fracture due to the thermal expansion differences between the polymer and support materials. However, VTEC polymers are very robust towards shock and impact, even after heated to dryness. These polymers do not pose any extra complications after made into films and are excellent candidates for heat and environmental treatment studies.

Various heat treatments were conducted by exposing VTEC polymer membranes to carefully controlled temperatures in a furnace. Presently, this thermal treatment process is known to give highly selective membranes for gas separations under inert atmospheres (argon).[10] However, the current literature lacks information regarding controlled heating under oxidizing conditions. In fact, most organic polymers tend to degrade in air above 250˚C, and the VTEC polymers are known to be resistant to these conditions. Using atmospheric oxygen content (~17%), the membranes were heat treated at various temperatures (from 250 to 475˚C) for pure and mixed gas evaluation. These heat treatments were intriguing for the parent polyimides, because the resulting membranes darken, but the films are still robust. In Table C-6 (Appendix C) is pure gas permeation results of various heat treated VTEC membranes and Kapton[®]. Interestingly, the resulting membranes are fairly robust, and they show

increased permeability while maintaining their gas selectivities. INL believes that they can form membranes by this method for future development of their high performance polymers.

Lastly, our analysis focused on the "conditioning effect" that the test gases might provide. It is known that carbon dioxide can swell/plasticize the polymers, however the INL team found that water entrapped within the polymer matrix (either as hydration molecules attached to salts in the polymer, left over solvent, or physisorbed) can also cause the polymer to change dramatically. The INL team has indentified another "conditioning" effect to include other types of gases (like methane), but the membrane seems to be most affected during pure gas analysis. Sanders previously demonstrated this phenomenon before, but the effect seems to be very subtle even with low permeating, glassy polymers.[4a] The conditioning effect was verified through the time lag (gas permeability) values determined in the gas permeation experiments. The time lag for these experiments can extend beyond 3000 seconds, especially for methane. In some cases, the same membrane gave different gas permeation values after extended methane exposure (gas filling equlibrium). The INL team used methane as a "conditioning" gas before conducting some of the experiments. Surprisingly, these seemingly trivial differences in membrane treatment resulted in certain membranes with exceptionally high separation factors and others with average separation factors. The most important feature with this data set is the methane gas permeability numbers (Table C-7; Appendix C). When the membranes were exposed to methane for long periods before gas testing, the membrane gave even better separations than before. The INL team believes that this conditioning effect is very important for showing influence of gaseous atmospheres upon separation factors, especially at ambient temperatures.

Summary and Conclusions

Section 8 of this report has provided a summary of the research work performed during FY-07. Some of its significant findings lead to enhanced gas separation, and completely new productivity values for the entire highly varied family of HP polymers. The observed solution behaviors, gas permeabilities, and spectral observations summarized in the report support such a statement. The research at INL has uncovered many fundamental issues related to synthesis, processing, and testing of the HP polymers (i.e., polyimides [Kapton®], polyamides [Nylon]), and polyazoles [PBI]). The experiments described in the report have uncovered many of the poorly understood fundamental properties of the HP polymers.

The VTEC polyimide and blended polyimide membranes were prepared by solvent evaporation resulting with a thin, dense, defect free film. These polyimide membranes were further processed by heating at 250°C for one hour to finish the condensation polymerization on the polyimide. From the gas permeability testing, the blended VTEC polyimide polymers show a great deal of promise with increased membrane fluxes while maintaining good selectivities, especially for blending VTEC polyimide with a substituted PBI which showed reasonably good increases in permeability for H_2 and CO_2. In addition, the base polymer VTEC membranes showed excellent thermal stability by surviving temperatures as high as 475°C for an hour in air. The resulting heat-treated membranes remained robust, and they showed enhanced permeabilities, while keeping their gas selectivities. Lastly, the exposure of the parent polymer membrane to a methane atmosphere demonstrated small increases of the membranes' selectivity toward methane. The INL team is further developing these last two processes for better gas separation properties for high performance polymers.

To conclude, the authors ask that the reader recognize that many of the experimental observations provided in this report are "first-time" reported and will appear in future refereed articles and patents. Above all, this project has sponsored several presentations, papers, and patents that have attracted significant national and international attention (2007 are shown below along with future presentations).

1. Klaehn, J. R.; Orme, C. J.; Luther, T. A.; Peterson, E. S.; Urban-Klaehn, J. M., "Polyimide and Their Derivatives for Gas Separation Applications," *Advanced Fossil Energy Utilization: Session on Carbon Dioxide Capture and Separation,* AIChE (American Institute of Chemical Engineers) 2008 Spring National Meeting, 2008. (Proceedings)

2. Klaehn, J. R.; Orme, C. J.; Luther, T. A.; Peterson, E. S.; Urban-Klaehn, J. M., "Polyimide and Their Derivatives for Gas Separation Applications," *Advanced Fossil Energy Utilization: Session on Carbon Dioxide Capture and Separation,* AIChE (American Institute of Chemical Engineers) 2008 Spring National Meeting, 2008. (Presentation)

3. Klaehn, J. R.; Orme, C. J. Luther, T. A.; Jones, M. G.; Wertsching, A. K.; Peterson, E. S., "Soluble N-Substituted Organosilane Polybenzimidazoles," *Macromolecules*, 40, 7487 (2007).

4. Klaehn, J. R.; Orme, C. J.; Luther, T. A.; Peterson, E. S.; Urban-Klaehn, J. M., "Polyimide and Their Derivatives for Gas Separation Applications," *Polymer Materials: Science and Engineering: General Papers/New Concepts in Polymeric Materials*, ACS 234th National Meeting, 2007. (Presentation)

5. Klaehn, J. R.; Orme, C. J.; Luther, T. A.; Peterson, E. S.; Urban-Klaehn, J. M., "Polyimide and Their Derivatives for Gas Separation Applications," *PMSE Preprints*, 97, 979 (2007).

6. Klaehn, J. R.; Orme, C. J. Luther, T. A.; Jones, M. G.; Wertsching, A. K.; Trowbridge, T. L.; Peterson, E. S. (INL: B-481). Title: "Polybenzimidazole Compounds, Polymeric Medium, andMethods of Post-Polymerization Modifications," U.S. Patent No. 7,309,758; December 18, 2007.

7. Klaehn, J. R.; Orme, C. J. Luther, T. A.; Jones, M. G.; Wertsching, A. K.; Peterson, E. S. (INL: B-338) Title: "Polybenzimidazole Compounds, Polymeric Medium, and Methods of Post-Polymerization Modifications," U.S. Patent No. 7,259,230 - August 21, 2007.

8. Klaehn, J. R.; Orme, C. J. Luther, T. A.; Jones, M. G.; Wertsching, A. K.; Trowbridge, T. L.; Peterson, E. S. (INL: B-481D1). Title: "Polybenzimidazole Compounds, Polymeric Medium, andMethods of Post-Polymerization Modifications," U.S. Patent Application No. 11/933,604; November 1, 2007.

9. Klaehn, J. R.; Orme, C. J. Luther, T. A.; Jones, M. G.; Wertsching, A. K.; Trowbridge, T. L.; Peterson, E. S. (INL: B-481D2). Title: "Polybenzimidazole Compounds, Polymeric Medium, and Methods of Post-Polymerization Modifications," U.S. Patent Application No. 11/933,652; November 1, 2007.

10. Klaehn, J. R.; Orme, C. J. Luther, T. A.; Jones, M. G.; Wertsching, A. K.; Peterson, E. S. (INL: B-338D1). Title: "Polybenzimidazole Compounds, Polymeric Medium, and Methods of Post-Polymerization Modifications: Polymer Media," U.S. Patent Application No. 11/772,868; July 3, 2007.

11. Klaehn, J. R.; Orme, C. J. Luther, T. A.; Jones, M. G.; Wertsching, A. K.; Peterson, E. S.(INL: B-338D2) Title: "Polybenzimidazole Compounds, Polymeric Medium, and Methods of Post-Polymerization Modifications: Polybenimidazole Compounds," U.S. Patent Application No. 11/772,872; July 3, 2007.

12. Klaehn, J. R.; Orme, C. J.; Peterson, E. S.; Luther, T. A.; Jones, M. G.; Wertsching, A. K.; Urban-Klaehn, J. M. "CO_2 Separation Using Thermally Optimized Membranes: A Comprehensive Project Report (2000-2006)" INL/EXT-07-12376, 2007.

References

1. (a) R.S., Prabhakar; M.G., De Angelis; G.C., Sarti; B.D., Freeman; Coughlin, M.C., *Macromolecules*, 38, 7043 (2005). (b) Prabhakar, R.S.; Merkel, T.C.; Freeman, B.D.; Imizu, T.; Higuchi, A., *Macromolecules*, 38, 1899(2005). (c) Prabhakar, R. S.; Freeman, B. D.; Roman, I., *Macromolecules*, 37, 7688 (2004). (d) Arnold, M.E.; Nagai, K.; Freeman, B.D.; Spontak, R.J.; Betts, D.E.; DeSimone, J.M.; Pinnau, I., *Macromolecules*, 34, 5611(2001). (e) Merkel, T.C.; Bondar, V.; Nagai, K.; Freeman, B.D.; Yampolskii, Yu.P., *Macromolecules,* 32, 8427 (1999).

2. (a) Coleman, M. R.; Koros, W. J., J. Poly. Sci. Part B: Poly. Phys., 32, 1915 (1994). (b) Coleman, M.R.; Koros, W.J., Macromolecules, 30, 6899 (1997). (c) Coleman, M. R.; Koros, W. J., Macromolecules, 32, 3106 (1999). (d) Staudt-Bickel, C.; Koros, W. J., J. Membr. Sci., 170, 205 (2000). (e) Kamaruddin, H. D.; Koros, W. J., J. Poly Sci. Part B: Poly. Phys., 38, 2254 (2000).

3. (a) Sanders, E. S.; Koros, W.J.; Hopfenberg, H.B.; Stannett, V.T. J. Membr. Sci., 13, 161 (1983). (b) Koros, W.J.; Chern, R.T.; Stannett, V.T.; Hopfenberg, H.B. J. Poly. Sci.: Poly. Physics Ed., 19, 1513 (1981). (c) Koros, W. J. J. Poly. Sci.: Poly. Physics Ed., 18, 981 (1980).

4. (a) Sanders, E.S. J. Membr. Sci., 37, 63 (1988). (b) Berens, A.R.; Hopfenberg, H.B. J. Poly. Sci.: Poly. Physics Ed., 17, 1757 (1979). (c) Koros, W. J.; Chan, A.H.; Paul, D.R. J. Membr. Sci., 2, 165 (1977). (d) Chern, R.T.; Koros, W.J.; Sanders, E.S.; Yui, R. J. Membr. Sci., 15, 157 (1983).

5. (a) Kaner, R. B.; Anderson, M. R.; Mattes, B. R.; Reiss, H. U.S. Patent 5,096,586, Mar 17, 1992. (b) Kaner, R. B.; Anderson, M. R.; Reiss, H.; Mattes, B. R. U.S. Patent 5,096,586, Oct 25, 1994.

6. (a) Anderson, M. R.; Mattes, B. R.; Reiss, H.; Kaner, R. B. Synth. Met. 1991, 41-43, 1151. (b) Kuwabata, S.; Martin, C. R. J. Membr. Sci. 1994, 91, 1. (c) Rebattet, L.; Escubes, M.; Genies, E.; Pineri, M. J. Appl. Polym. Sci. 1995, 57, 1595. (d) Chang, M. J.; Liao, Y. H.; Myerson, A. S.; Kwei, T. K. J. Appl. Polym. Sci. 1996, 62, 1427. (e) Lee, M. Y.; Ha, S. Y.; Lee, Y. K.; Suh, D. H.; Hong, S. Y. Ind. Eng. Chem. Res. 1999, 38, 1917.

7. (a) Henis, J. M. S.; Tripodi, M. K. U.S. Patent 4,230,463, Oct 28, 1980. (b) Makino, H.; Kusuki, Y.; Yoshida, H.; Nakamura, A. U.S. Patent 4,378,324, Mar 29, 1983. (c) Makino, H.; Kusuki, Y.; Harada, T.; Shimazaki, H. U.S. Patent 4,378,400, Mar 29, 1983. (d) Hayes, R. A. U.S. Patent 4,838,900, Jun 13, 1989. (e) Simmons, J. W.; Arthur, S. D. U.S. Patent 5,352,273, Oct 4, 1994. (f) Roman, I. C. U.S. Patent 5,868,992, Feb 9, 1999.

8.   (a) Conklin, J. A.; Anderson, M. R.; Reiss, H.; Kaner, R. B. *J. Phys. Chem.* **100**, 8425 (1996). (b) Parthasarathy, R. V.; Menon, V. P.; Martin, C. R. *Chem. Mater.* **9**, 560 (1997). (c) Huang, S.-C.; Ball, I. J.; Kaner, R. B. *Macromolecules* **31**, 5456 (1998). (d) Lee, M. Y.; Ha, S. Y.; Lee, Y. K.; Suh, D. H.; Hong, S. Y. *Ind. Eng. Chem. Res.* **38**, 1917 (1999).

9.   Koros, W.J.; Jordan, S.M.; Fleming, G.K. U.S. Patent 4,755,192, Jul 5, 1988.

10.   S. Stern, V. Shah, and B. Hardy, J. Polym. Sci. Part B: Polym. Phys., 25, 1263 (1987). Hayashi, J-i; Yamamoto, M.; Kusakabe, K.; Morooka, S. Ind. Eng. Chem. Res. 36, 2134 (1997).

Appendix A

Tables and Results

Appendix A

Tables and Results

Table A-1. Lennard-Jones Kinetic Gas Diameter Values—
taken from Breck, D.W. *"Zeolite Molecular Sieves: Structure, Chemistry, and Use,"* (1974).

Gas Molecule	Pauling Length (Å)	Width (Å)	Lennard - Jones	
			r_{min}(Å)	σ(Å)[1]
He	~3	3.0	2.6	
H_2	3.1	2.4	3.24	2.89
Ar		3.84	3.84	3.40
O_2	3.9	2.8	4.02	3.46
N_2	4.1	3.0	4.09	3.64
NO	4.05	3.0	3.58	3.17
N_2O	4.2	3.7		3.3
CO	4.2	3.7	4.25	3.76
CO_2	5.1	3.7		3.3
H_2O	3.9	3.15		2.65
SO_2	5.28	4.0		3.6
CH_4		4.2	4.25	3.8
H_2S	4.36	4.0		3.6
1. Kinetic diameter, σ, calculated from the minimum equilibrium cross-sectional diameter.				

Table A-2. Thermal decomposition of various VTEC polyimides and Kapton®.

Polymer Films	TGA Onset of Decomposition—under Nitrogen
Kapton® (DuPont)	574ºC
VTEC PI 80-051	546ºC
PBI (Celanese)	512ºC
VTEC PI 80-051 w/2 wt% Bromine	556ºC
VTEC PI 80-051 w/10 wt% Bromine	551ºC
VTEC PI 80-051 w/1 wt% ethylene bromide	566ºC
VTEC PI 80-051 w/~20 wt% polysulfone	543ºC
VTEC PI 80-051 w/(~5 wt%) Nomex	545ºC
VTEC PI 80-051 w/~20 wt% PBI-TMS (functionalized PBI)	465ºC
PBI-TMS (Me$_3$SiCH$_2$-PBI) (functionalized PBI)	448ºC

Table A-3. Thermogravimetric analysis (TGA) and thermo mechanical analysis (TMA) of VTEC polyimides.

Polymer Films	TGA Weight Loss under Nitrogen Before heat treatment; Onset to Decomposition	TMA Thermal Transition; heat processed films (dimensional change)
VTEC PI 851	243ºC (-H$_2$O); 512ºC	243ºC (~2.5 μm; to 400ºC)
VTEC PI 80-051	237ºC (-H$_2$O); 524ºC	255ºC (~5.0 μm; to 400ºC)
VTEC PI 1388	241ºC (-H$_2$O); 529ºC	285ºC (~1.0 μm; to 400ºC)
TMA results—Frederick F. Stewart; Idaho National Laboratory		

Table A-4. Pure gas data—VTEC polyimide blends: wet and dry.
(All INL polymers in this table were heat cycled prior to testing)

Polymer	Permeability (barrers) @ 30ºC						Selectivity α		
	H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	H_2/CH_4	CH_4/CO_2
VTEC PI 80-051 w/~10 wt% LiCl (wet)	4.20	0.35	0.11	0.20	1.01	1.38	3.0	4.2	1
VTEC PI 80-051 w/~10 wt% LiCl (dry)	4.30	0.04	0.03	0.18	0.03	0.58	7.4	143.3	19
VTEC PI 80-051 w/~2 wt% ethylene chloride (wet)	3.50	*Not tested*	*Not tested*	*Not tested*	0.21	0.79	4.4	16.67	4
VTEC PI 80-051 w/~2 wt% ethylene chloride (dry)	3.30	*Not tested*	*Not tested*	*Not tested*	0.02	0.45	7.3	165.0	23

Table A-5. Pure gas data—VTEC polyimide blends: wet and dry at 30ºC.
(All INL polymers in this table were heat cycled prior to testing)

Polymer	Permeability (barrers) at 30ºC						Selectivity α		
	H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	H_2/CH_4	CH_4/CO_2
Membranes were exposed to the atmosphere without being thoroughly dried prior to testing									
VTEC PI 80-051 w/~3 wt% $CoCl_2$ (wet)	3.65	0.62	0.59	0.69	0.56	0.93	3.0	6.5	2
VTEC PI 80-051 w/~10 wt% NaBr (wet)	5.90	*Not tested*	*Not tested*	*Not tested*	0.06	1.06	5.6	98.3	18
VTEC PI 80-051 w/~5 wt% KBr (wet)	5.00	*Not tested*	*Not tested*	*Not tested*	0.39	1.19	4.2	12.8	3
VTEC PI 80-051 w/~2 wt% S_8 (sulfur) (wet)	3.60	*Not tested*	*Not tested*	*Not tested*	0.08	0.68	5.3	45	9
Membranes were thoroughly dried before testing									
VTEC PI 80-051 w/~10 wt% $(Bu)_4NBr$ (dry)	3.25	*Not tested*	*Not tested*	*Not tested*	0.02	0.45	7.2	162.5	21
VTEC PI 80-051 w/~2 wt% S_8 (sulfur) and Bromine (dry)	2.96	*Not tested*	*Not tested*	*Not tested*	0.02	0.38	7.8	148	20
VTEC PI 80-051 w/~5 wt% Ammonium diphenyldithiophosphinate (dry)	3.30	0.03	0.02	0.12	0.02	0.45	7.3	165	22

Table A-6. Mixed gas data—VTEC polyimide blends at 250ºC and 300ºC.
(All INL polymers in this table were heat cycled prior to testing)

Polymer	Permeability (barrers) at 30ºC						Selectivity α		
	H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	H_2/CH_4	CH_4/CO_2
Membranes were exposed to the atmosphere without being thoroughly dried prior to testing									
VTEC PI 80-051 w/~3 wt% Ethylene bromide (250ºC)	82.2	12.3	*Not tested*	*Not tested*	11.5	24.5	3.4	7.1	2.1
VTEC PI 80-051 w/~10 wt% Bromine (250ºC)	69.3	5.7	*Not tested*	*Not tested*	4.1	18.8	3.7	16.9	4.6
VTEC PI 80-051 w/~2 wt% Bromine (300ºC)	110.7	15.5	*Not tested*	*Not tested*	12.6	13.9	8.0	8.8	1.1
VTEC PI 80-051 w/~10 wt% LiCl (300ºC)	108.1	12.8	*Not tested*	*Not tested*	13.8	32.3	3.3	7.8	2.3

Table A-7. Pure gas data colleted at 30°C: functionalized bis(trimethylsilylmethylene)-polybenzimidazole (PBI-TMS) and VTEC polyimide blends.
(All INL polymers in this table were heat cycled prior to testing)

Polymer	Thickness (microns)	Permeability (barrers) at 30ºC						Selectivity α		
		H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	H_2/CH_4	CO_2/CH_4
VTEC PI 1388 w/~20 wt% PBI-TMS	14	4.31	0.2092	0.0823	0.28	0.04	1.01	4.3	107.8	25.3
	22	5.5	0.094	0.0558	0.3516	0.034	1.3	4.2	161.8	38.2
	Avg	4.91	0.15	0.07	0.32	0.04	1.16	4.2	134.8	31.7
VTEC PI 80-051 w/~20 wt% PBI-TMS	24	4.3	0.1511	0.0787	0.4028	0.06	1.2	3.6	71.7	20.0
	25	6.6	0.1485	0.0894	0.3789	0.05	1.6	4.1	132.0	32.0
	22	5.5	*Not tested*	*Not tested*	*Not tested*	0.05	1.4	3.9	110.0	28.0
	Avg	5.47	0.15	0.08	0.39	0.05	1.40	3.9	104.6	26.7

Table A-8. Pure gas data—polymers with fillers (SiO_2 or TiO_2).
(All INL polymers in this table were heat cycled prior to testing)

Polymer	Permeability (barrers) at 30ºC						Selectivity α	
	H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	CO_2/CH_4
VTEC PI 1388	3.97	0.055	0.035	0.168	0.05	0.53	7.5	10.6
VTEC blend PI 1388 w/~17 wt% POSS	6.5	*Not tested*	*Not tested*	*Not tested*	0.8	2.1	3.1	2.6
Polymer	He	Ar	N_2	O_2	CH_4	CO_2	He/CO_2	CO_2/CH_4
Ryton (PPS) [1]	1.85	*Not tested*	0.019	*Not tested*	0.022	0.45	4	20.4
Ryton (PPS) w/33wt%TiO2[1]	2.34	*Not tested*	0.032	*Not tested*	0.036	1.07	2	29.7
1. Phillips Corporation; PPS = Polyphenylene sulfide (private communication)								

Table A-9. Pure gas data—polymer blends.
(All INL polymers in this table were heat cycled prior to testing)

Polymer	Permeability (barrers) at 30ºC						Selectivity α	
	H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	CO_2/CH_4
VTEC PI 1388	3.97	0.055	0.035	0.168	0.05	0.53	7.5	10.6
VTEC PI 1388 w/~20 wt% PSF	1.98	*Not tested*	*Not tested*	*Not tested*	0.045	0.34	5.8	7.5
VTEC PI 1388 w/~1 wt% PTMSP	1.56	*Not tested*	*Not tested*	*Not tested*	0.201	0.63	2.5	3.2
Polymer	He	Ar	N_2	O_2	CH_4	CO_2	He/CO_2	CO_2/CH_4
PPSS[1]	1.96	*Not tested*	0.013	*Not tested*	0.036	0.48	4.1	13.3
50/50 PPSS/PPO[1]	3.12	*Not tested*	0.025	*Not tested*	0.031	0.45	6.9	14.5
50/50 PPSS/PSF[1]	2.84	*Not tested*	0.019	*Not tested*	0.015	0.66	4.3	44.0
50/50 PPSS/PES	3.41	*Not tested*	0.025	*Not tested*	0.026	1.1	3.1	42.3
1. Phillips Corporation; PPSS = polyphenylene sulfide sulfone; PPO = polyphenylene oxide; and PSF = polysulfone (private communication)								

Table A-10. Pure gas data—polymers with halogen content.
(All INL polymers in this table were heat cycled prior to testing)

Polymer	Permeability (barrers) at 30ºC						Selectivity α	
	H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	CO_2/CH_4
VTEC PI 80-051	3.56	0.20	0.06	0.19	*0.03*	0.48	7.4	16.0
VTEC PI 80-051 w/~1 wt% ethylene bromide	8.74	*Not tested*	*Not tested*	*Not tested*	*2.7*	2.22	3.9	0.82
VTEC PI 80-051 w/~1 wt% 4-chlorostyrene	5.3	*Not tested*	*Not tested*	*Not tested*	*0.05*	0.9	5.9	18
VTEC PI 80-051 w/~1 wt% PBr_3	3.5	*Not tested*	*Not tested*	*Not tested*	*0.06*	0.66	5.3	11.0
VTEC with Bromine @ 30ºC								
VTEC PI 80-051 w/~2 wt% bromine 1st run[1]	3.7	*Not tested*	*Not tested*	*Not tested*	*0.03*	0.46	8.0	15.3
VTEC PI 80-051 w/~2 wt% bromine 2nd run[1]	3.6	*Not tested*	*Not tested*	*Not tested*	*0.02*	0.45	8.0	22.5
VTEC PI 80-051 w/~10 wt% bromine	4.1	*Not tested*	*Not tested*	*Not tested*	*0.04*	0.62	6.6	15.5
Phillips-Polyphenylene Oxide								
Polymer	He	Ar	N_2	O_2	CH_4	CO_2	He/CO_2	CO_2/CH_4
PPO (trichloroethylene)[2]	66.3	*Not tested*	*3.05*	*Not tested*	*3.75*	68.3	1	18.2
PPO (NMP)[2]	31.2	*Not tested*	*1.42*	*Not tested*	*1.64*	33.5	1	20.4

1. Same membrane tested twice.

2. Phillips Corporation; PPO = polyphenylene oxide (General Electric) (private communication)

Table A-11. Pure gas data comparison of commercial and VTEC-blended polymer films at 30°C.
(All polymers in this table were heat cycled prior to testing)

Polymer	Thickness (microns)	Permeability (barrers)						Selectivity α		
		H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	H_2/CH_4	CO_2/CH_4
Pure Polymers										
Dupont-Kapton®	50	1.6	*Not tested*	*Not tested*	*Not tested*	0.04	0.28	5.7	40.0	7.0
Phillips-PPS[1] (RYTON)	50	1.6	*Not tested*	*Not tested*	*Not tested*	0.02	0.27	5.9	80.0	13.5
Various VTEC Blends										
VTEC PI 1388 w/~20 wt% Polysulfone	28	1.98	*Not tested*	*Not tested*	*Not tested*	0.045	0.34	5.8	44.0	7.6
VTEC PI 1388 w/~1wt% PTMSP	16	1.56	*Not tested*	*Not tested*	*Not tested*	0.201	0.63	2.5	7.8	3.1
VTEC PI 80-051 w/(~1wt%) 4-chlorostyrene	55	5.3	*Not tested*	*Not tested*	*Not tested*	0.05	0.9	5.9	106.0	18.0
VTEC PI 80-051 w/~1wt% ethylene bromide	32	8.74	*Not tested*	*Not tested*	*Not tested*	2.7	2.22	3.9	3.2	0.8
VTEC PI 80-051 w/(~5 wt%) functionalized Nomex-TMS	18	3.24	*Not tested*	*Not tested*	*Not tested*	0.02	0.716	4.5	162.0	35.8
1. PPS = Polyphenylene sulfide										

Table A-12. Mixed gas data for commercial and VTEC polymer films at 250°C.
(All polymers in this table were heat cycled prior to testing)

| Polymer | Thickness (microns) | Permeability (barrers) | | | | | | Selectivity α | | |
		H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	H_2/CH_4	CO_2/CH_4
Pure Polymers										
VTEC PI 80-051	50	83.00	3.10	*Not tested*	*Not tested*	2.30	9.30	8.9	36.1	4.0
PBI (alone)[1]	35 (metal support)	48.70	1.70	*Not tested*	*Not tested*	1.30	4.90	9.9	37.5	3.8
Dupont-Kapton®	50	17.90	2.50	*Not tested*	*Not tested*	1.90	5.01	3.6	9.4	2.6
Phillips–PPS[2] (RYTON) (at 240°C)	50	52.40	3.10	*Not tested*	*Not tested*	2.90	11.50	4.6	18.1	4.0
VTEC/PBI-TMS Blends										
VTEC PI 1388 w/~20 wt% PBI-TMS	15	63.70	7.01	*Not tested*	*Not tested*	4.10	12.40	5.1	15.5	3.0
VTEC PI 80-051 w/~20 wt% PBI-TMS	17	39.00	2.60	*Not tested*	*Not tested*	2.10	8.10	4.8	18.6	3.9
Various VTEC Blends										
VTEC PI 80-051 w/~10 wt% Nomex	34	52.40	3.10	*Not tested*	*Not tested*	2.90	11.50	4.6	18.1	4.0
VTEC PI 80-051 w/~20 wt% polysulfone	20	43.6	2.3	*Not tested*	*Not tested*	2.1	8.3	5.3	20.8	4.0
VTEC PI 80-051 w/~1 wt% polystyrene	35	53.3	2.8	*Not tested*	*Not tested*	2.9	10.9	4.9	18.4	3.8
VTEC PI 1388 w/~1 wt% 4-chlorostyrene		36.6	2.6	*Not tested*	*Not tested*	2.2	6.5	5.6	16.6	3.0

1. PBI (10 wt% in DMAc) used directly from PBI Performance Products, Inc.

2. PPS = Polyphenylene sulfide (Ryton; Phillips Corporation)

Table A-13. Previous pure gas data comparison of commercial and VTEC-blended polymer films at 30°C.
(All polymers in this table were heat cycled prior to testing)

Polymer	Permeability (barrers)						Selectivity α		
	H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	H_2/CH_4	CO_2/CH_4
Kapton®, Poly(pyromellitimide-1,4-diphenyl ether	1.6	*Not tested*	*Not tested*	*Not tested*	0.04	0.28	5.7	40.0	13.5
VTEC PI 1388	3.97	0.06	0.04	0.17	0.05	0.53	7.5	79.4	10.6
VTEC PI 851	3.01	Not tested	Not tested	Not tested	0.53	0.32	9.4	0.6	3.1
VTEC PI 080-051	3.56	0.20	0.06	0.19	0.03	0.48	7.4	118.6	16
VTEC blend PI 1388 w/~20 wt% PBI	3.12	0.05	0.04	0.15	0.03	0.49	6.3	104.0	16.3
VTEC blend PI 80-051 w/~20wt% PBI	3.45	0.05	0.02	0.17	0.02	0.61	5.7	172.5	30.5
Nomex, Poly(1,3-phenylene isophthalamide)	1.4	1.1	2.0	2.9	0.3	0.3	4.7	4.7	1.0
Poly ether sulfone, Bisphenol-A polysulfone	11.3	*Not tested*	1.8	2.6	0.1	3.4	3.3	113	34
Mylar, Poly(ethylene terephthalate)	3.7	*Not tested*	5.1	5	6.7	6.1	0.6	0.55	0.91
Polystyrene (PS)	25.4	*Not tested*	0.5	2.3	0.7	3.2	7.9	36.3	4.6

Table A-14. Previous mixed gas data for commercial and VTEC polymer films at 250°C.
(All polymers in this table were heat cycled prior to testing)

Polymer	Permeability (barrers)						Selectivity α		
	H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	H_2/CH_4	CO_2/CH_4
Kapton®, Poly(pyromellitimide-1,4-diphenyl ether	17.9	2.5	*Not tested*	*Not tested*	1.90	5.01	3.6	9.4	2.6
VTEC PI 851	55.4	2.8	*Not tested*	*Not tested*	1.8	5.6	9.9	30.8	3.1
VTEC PI 080-051	83.0	3.1	*Not tested*	*Not tested*	2.3	9.3	8.9	18.1	4.0
VTEC blend PI 1388 w/~20 wt% PBI	30.5	1.1	*Not tested*	*Not tested*	0.8	4.0	7.6	38.1	5.0

Table A-15. Polymers: physical and gas separation properties–compiled listing of polymers.

Class/Polymer	Pure Polymer Thermal Properties, T_g, T_m, and $T_{decomp.}$ *Must withstand 250ºC*	Pure Gas Permeability (barrers)						
Polyazoles		H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2
PBI (and substituted PBI), Polybenzimidazole (Pure gas permeabilities in barrers from test data)	$T_g \sim 427ºC^1$ $T_g \sim 500ºC$ (after annealing)[1] $T_{decomposition} = >600ºC^1$							
PBI-Butyl at 30°C	$T_{decomposition} = 285ºC$	27.7	1	0.5	1.9	1.8	18.7	**1.5**
PBI-HEX at 30°C	$T_{decomposition} = 392ºC$	20.6	8	8.9	9.9	12.8	18.3	**1.1**
PBI-Allyl at 30°C	$T_{decomposition} = 452ºC$	1.6	0.4	0.2	0.4	0.7	2.5	**0.6**
Parent PBI (DMAc) at 30°C	$T_{decomposition} = 512ºC$	4.6	0.18	0.12	0.29	0.13	0.85	**5.4**
PALL Film A at 30°C	$T_{decomposition} = 512ºC$	3.90	0.07	0.05	0.09	0.04	0.07	**55.7**
PALL Film B at 30°C	$T_{decomposition} = 512ºC$	4.05	1.26	0.75	0.63	0.41	0.86	**4.7**
PALL Film C at 30°C	$T_{decomposition} = 512ºC$	3.2	0.97	0.33	0.21	0.04	0.32	**10.0**
PBI (PBI Performance Products, Inc.) at 250°C	$T_{decomposition} = 512ºC$	48.7	1.7			1.30	4.9	**9.9**
PBO (Zylon), Polybenzoxazole	$T_{decomposition} = >600ºC^1$	No stable film was formed						
Phosphazenes								
Polyphosphazene, semicrystalline poly(2,2,2-trifluoroethoxy)-phosphazene	$T_g = -66ºC^1$ $T_m = 242ºC^1$	129	67.6	38.9	81.3	46.9	420.3	**0.3**
Polyamides								
Nylon 6,12	$T_g = 46ºC^1$ $T_m = 207-247ºC^1$							
Nylon 6,T (co-polymer)	$T_g = 89-135ºC^1$ $T_m = 312ºC^1$							
Nomex, Poly(1,3-phenylene isophthalamide)*(Pure gas data is for Nomex-A, at 30°C)*	$T_g = 280ºC^1$ $T_m = 435ºC$ (DTA transition)[1]	1.4	1.1	2.0	2.9	0.3	0.3	**4.7**

Table A-15. (continued).

Class/Polymer	Pure Polymer Thermal Properties, T_g, T_m, and $T_{decomp.}$ *Must withstand 250ºC*	Pure Gas Permeability (barrers)						
Polyazoles		H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2
Kevlar, Poly(1,4-phenylene isophthalamide)	Tg = 425ºC[1] Tm = 554ºC (beyond decomposition temperature)[1]	No stable film was formed						
Polyimides								
Kapton®, Poly(pyromellitimide-1,4-diphenyl ether	Tg = 360-410ºC[1]	*1.46*		*0.03*	*0.15*		*0.26*	***5.6**
INL Data for Kapton®, Poly(pyromellitimide-1,4-diphenyl ether	Tg = 360-410ºC[1]	1.6				0.04	0.28	**5.7**
Kapton®, Poly(pyromellitimide-1,4-diphenyl ether *(Gas data at 250ºC)*	$T_{decomposition}$ = 574ºC	17.90	2.5			1.90	5.01	**3.6**
Matrimid (Ferraris; UTD) Cast from NMP[2]		13.4		0.10	0.90	0.08	4.1	**3.3**
Matrimid (Ferraris; UTD) Cast from Cl_2HC-$CHCl_2$[2]		17.5			1.47	0.21	7.3	**2.4**
Matrimid blended with MOF-5 (mesoporous titianate) (Ferraris; UTD) Cast from NMP[2]		41		0.34	2.9	0.35	14.2	**2.9**
Various Polyimide Polymers[3] (from Hirayama, et al.) (see Figure A-1 below for structures)								
BPDA-DADM	Tg = 292ºC	4.55 (He)		0.030	0.208	0.021	1.00	**4.5 (He/CO_2)**
BPDA-DADS	Tg = 290ºC	3.70 (He)		0.022		0.016	0.77	**4.8 (He/CO_2)**
BPDA-PASN	Tg = 325ºC	7.03 (He)		0.050	0.348	0.040	1.75	**4.0 (He/CO_2)**
BPDA-HFIP	Tg = 320ºC	34.2 (He)		0.757	3.79	0.460	16.8	**2.0 (He/CO_2)**

Table A-15. (continued).

Class/Polymer	Pure Polymer Thermal Properties, T_g, T_m, and $T_{decomp.}$ *Must withstand 250ºC*	Pure Gas Permeability (barrers)						
Polyazoles		H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2
BPDA-BAPE	Tg = 231ºC	4.05 (He)		0.039	0.256	0.031	1.25	**3.2 (He/CO$_2$)**
BPDA-BAPS	Tg = 284ºC	6.01 (He)		0.054	0.368	0.040	1.85	**3.2 (He/CO$_2$)**
BPDA-BAPP	Tg = 249ºC	7.50 (He)		0.094	0.596	0.085	2.80	**2.7 (He/CO$_2$)**
BPDA-HFBAPP	Tg = 256ºC	18.3 (He)		0.305	1.67	0.216	7.33	**2.5 (He/CO$_2$)**
BPDA-MDT	Tg = 317ºC	8.91 (He)		0.048	0.369	0.028	1.41	**6.3 (He/CO$_2$)**
BPDA-CDM	Tg = 308ºC	6.92 (He)		0.031	0.260	0.016	0.978	**7.1 (He/CO$_2$)**
BPDA-MFA	Tg = 285ºC	4.34 (He)		0.020	0.143	0.013	0.542	**8.0 (He/CO$_2$)**
BPDA-MCA	Tg = 289ºC	3.67 (He)		0.011	0.096	0.006	0.335	**11.0 (He/CO$_2$)**
BPDA-MBA	Tg = 295ºC	3.55 (He)		0.010	0.092	0.005	0.315	**11.3 (He/CO$_2$)**
BPDA-MDX	Tg = 319ºC	31.8 (He)		0.913	4.73	0.818	22.4	**1.4 (He/CO$_2$)**
BPDA-HAB	Not observed	1.09 (He)		0.001	0.010	0.0004	0.031	**34.8 (He/CO$_2$)**
BPDA-TSN	Not observed	12.0 (He)		0.076	0.577	0.037	2.74	**4.4 (He/CO$_2$)**
6FDA-DADE	Tg = 294ºC	33.8 (He)		0.516	2.93	0.273	13.8	**2.4 (He/CO$_2$)**

Table A-15. (continued).

Class/Polymer	Pure Polymer Thermal Properties, T_g, T_m, and $T_{decomp.}$ *Must withstand 250ºC*	Pure Gas Permeability (barrers)						
Polyazoles		H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2
6FDA-DADM	T_g = 296ºC	32.8 (He)		0.563	3.15	0.321	15.1	**2.2 (He/CO₂)**
6FDA-BAPE	T_g = 251ºC	18.3 (He)		0.313	1.73	0.215	7.85	**2.3 (He/CO₂)**
6FDA-MDT	T_g = 288ºC	35.1 (He)		0.406	2.51	0.198	8.75	**4.0 (He/CO₂)**
6FDA-CDM	T_g = 290ºC	30.4 (He)		0.269	1.81	0.121	6.78	**4.5 (He/CO₂)**
6FDA-MDX	T_g = 306ºC	74.4 (He)		2.13	10.3	1.45	43.9	**1.7 (He/CO₂)**
6FDA-HAB	Not observed	29.3 (He)		0.168	1.22	0.056	4.85	**6.0 (He/CO₂)**
6FDA-TSN	Not observed	104 (He)		2.82	14.2	1.49	55.9	**1.9 (He/CO₂)**
PMDA-DADE	Not observed	3.20 (He)		0.026	0.171	0.0183	0.858	**3.7 (He/CO₂)**
PMDA-DADM	Not observed	3.95 (He)		0.033	0.205	0.0223	0.990	**4.0 (He/CO₂)**
PMDA-MDX	Not observed	87.0 (He)		7.08	27.4	8.21	97.6	**0.9 (He/CO₂)**
VTEC Polyimides								
VTEC PI 851 *(Gas data at 30°C; heat treated)*	$T_{decomposition}$ = 512ºC	3.01				0.53	0.32	**9.4**
VTEC PI 851 *(Gas data at 250°C; heat treated)*	$T_{decomposition}$ = 512ºC	55.4	2.8			1.8	5.6	**9.9**
VTEC PI 080-051 *(Gas data at 30°C; heat treated)*	$T_{decomposition}$ = 546ºC	3.56	0.20	0.06	0.19	0.03	0.48	**7.4**

Table A-15. (continued).

Class/Polymer	Pure Polymer Thermal Properties, T_g, T_m, and $T_{decomp.}$ *Must withstand 250ºC*	Pure Gas Permeability (barrers)						
Polyazoles		H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2
VTEC PI 080-051 *(Gas data at 250ºC; heat treated)*	$T_{decomposition}$ = 546ºC	83.0	3.1			2.3	9.3	**8.9**
VTEC PI 1388 *(Gas data at 30ºC; heat treated)*	$T_{decomposition}$ = 529ºC	3.97	0.06	0.04	0.17	0.05	0.53	**7.5**
VTEC PI 1388 *(Gas data at 250ºC; heat treated)*	$T_{decomposition}$ = 529ºC							
VTEC Polyimide Blends at 30ºC								
VTEC blend PI 80-051/~20wt% PBI *(Gas data at 30ºC; heat treated)*	$T_{decomposition}$ = 465ºC	3.45	0.05	0.02	0.17	0.02	0.61	**5.7**
VTEC blend PI 1388/~20 wt% PBI *(Gas data at 30ºC; heat treated)*		3.12	0.05	0.04	0.15	0.03	0.49	**6.4**
VTEC blend PI 80-051/~10 wt% LiCl *(Gas data at 30ºC; heat treated, exposed to the atmosphere moisture)*		4.20	0.35	0.11	0.20	1.01	1.38	**3.0**
VTEC blend PI 80-051/~10 wt% LiCl *(Gas data at 30ºC; heat treated, completely dried)*		4.30	0.04	0.03	0.18	0.03	0.58	**7.4**
VTEC blend PI 80-051/~2 wt% ethylene chloride *(Gas data at 30ºC; heat treated, exposed to the atmosphere moisture)*		3.50				0.21	0.79	**4.4**
VTEC blend PI 80-051/~2 wt% ethylene chloride *(Gas data at 30ºC; heat treated, completely dried)*		3.30				0.02	0.45	**7.3**
VTEC blend PI 80-051/~3 wt% $CoCl_2$ *(Gas data at 30ºC; heat treated, exposed to the atmosphere moisture)*		3.65	0.62	0.59	0.69	0.56	0.93	**3.0**
VTEC blend PI 80-051/~10 wt% NaBr *(Gas data at 30ºC; heat treated, exposed to the atmosphere moisture)*		5.90				0.06	1.06	**5.6**
VTEC blend PI 80-051/~5 wt% KBr *(Gas data at 30ºC; heat treated, exposed to the atmosphere moisture)*		5.00				0.39	1.19	**4.2**

Table A-15. (continued).

Class/Polymer	Pure Polymer Thermal Properties, T_g, T_m, and $T_{decomp.}$ *Must withstand 250ºC*	Pure Gas Permeability (barrers)						
Polyazoles		H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2
VTEC blend PI 80-051/~2 wt% flower sulfur (S_8) *(Gas data at 30°C; heat treated, exposed to the atmosphere moisture)*		3.60				0.08	0.68	**5.3**
VTEC blend PI 80-051/~10 wt% (Bu)$_4$NBr *(Gas data at 30°C; heat treated, completely dried)*		3.25				0.02	0.45	**7.2**
VTEC blend PI 80-051/~2 wt% flower sulfur (S_8) and Bromine *(Gas data at 30°C; heat treated, completely dried)*		2.96				0.02	0.38	**7.8**
VTEC blend PI 80-051/~5 wt% ammonium diphenyldithiophosphinate *(Gas data at 30°C; heat treated, completely dried)*		3.30	0.03	0.02	0.12	0.02	0.45	**7.3**
VTEC blend PI 1388/~20 wt% PBI-TMS *(Gas data at 30°C; heat treated, completely dried)*		4.91	0.15	0.07	0.32	0.04	1.16	**4.2**
VTEC blend PI 80-051/~20 wt% PBI-TMS *(Gas data at 30°C; heat treated, completely dried)*		5.47	0.15	0.08	0.39	0.05	1.40	**3.9**
VTEC blend PI 1388/~17 wt% POSS *(Gas data at 30°C; heat treated)*		6.5				0.8	2.1	**3.1**
VTEC blend PI 1388/~20 wt% polysulfone *(Gas data at 30°C; heat treated)*		1.98				0.05	0.34	**5.8**
VTEC blend PI 1388/~1 wt% PTMSP *(Gas data at 30°C; heat treated)*		1.56				0.20	0.63	**2.5**
VTEC blend PI 80-051/~1 wt% ethylene bromide *(Gas data at 30°C; heat treated)*		8.74				2.7	2.22	**3.9**
VTEC blend PI 80-051/~1 wt% 4-chlorostyrene *(Gas data at 30°C; heat treated)*		5.3				0.05	0.9	**5.9**
VTEC blend PI 80-051/~1 wt% PBr$_3$ *(Gas data at 30°C; heat treated)*		3.5				0.06	0.66	**5.3**

Table A-15. (continued).

Class/Polymer	Pure Polymer Thermal Properties, T_g, T_m, and $T_{decomp.}$ *Must withstand 250°C*	Pure Gas Permeability (barrers)						
Polyazoles		H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2
VTEC blend PI 80-051/~2 wt% bromine 1st run *(Gas data at 30°C; heat treated)*		3.7				0.03	0.46	**8.0**
VTEC blend PI 80-051/~2 wt% bromine 2nd run *(Same membrane as previous, gas data at 30°C; heat treated)*		3.6				0.02	0.45	**8.0**
VTEC blend PI 80-051/~10 wt% bromine *(Gas data at 30°C; heat treated)*		4.1				0.04	0.62	**6.6**
VTEC blend PI 80-051/~5 wt% functionalized Nomex-TMS *(Gas data at 30°C; heat treated)*		3.2				0.02	0.72	**4.5**
VTEC Polyimide Blends at 250–300°C								
VTEC blend PI 80-051/~3 wt% ethylene bromide *(Gas data at 250°C; heat treated)*		82.2	12.3			11.5	24.5	**3.4**
VTEC blend PI 80-051/~10 wt% bromine *(Gas data at 250°C; heat treated)*		69.3	5.7			4.1	18.8	**3.7**
VTEC blend PI 80-051/ ~2 wt% bromine *(Gas data at 300°C; heat treated)*		110.7	15.5			12.6	13.9	**8.0**
VTEC blend PI 80-051/~10 wt% LiCl *(Gas data at 300°C; heat treated)*		108.1	12.8			13.8	32.3	**3.3**
VTEC blend PI 1388/~20 wt% PBI *(Gas data at 250°C; heat treated)*		30.5	1.1			0.8	4.0	**7.6**
VTEC blend PI 1388/~20 wt% PBI-TMS *(Gas data at 250°C; heat treated)*		63.7	7.0			4.1	12.4	**5.1**
VTEC blend PI 80-051/~20 wt% PBI-TMS *(Gas data at 250°C; heat treated)*		39.0	2.6			2.1	8.1	**4.8**
VTEC blend PI 80-051/~10 wt% Nomex *(Gas data at 250°C; heat treated)*		52.4	3.1			2.9	11.5	**4.6**
VTEC blend PI 80-051/~20 wt% polysulfone *(Gas data at 250°C; heat treated)*		43.6	2.3			2.1	8.3	**5.3**
VTEC blend PI 80-051/~1 wt% polystyrene *(Gas data at 250°C; heat treated)*		53.3	2.8			2.9	10.9	**4.9**

Table A-15. (continued).

Class/Polymer	Pure Polymer Thermal Properties, T_g, T_m, and $T_{decomp.}$ *Must withstand 250ºC*	Pure Gas Permeability (barrers)						
Polyazoles		H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2
VTEC blend PI 80-051/~1 wt% 4-chlorostyrene *(Gas data at 250ºC; heat treated)*		36.6	2.6			2.2	6.5	**5.6**
Sulfur-containing Polymers								
Poly(phenylene sulfide) (PPS, Ryton–INL data)	$T_g = 85ºC[1]$ $T_m = 285ºC[1]$	1.6				0.02	0.27	**5.9**
Poly(phenylene sulfide) (PPS, Ryton–Phillips data)	$T_g = 85ºC[1]$ $T_m = 285ºC[1]$	1.85 (He)		0.019		0.022	0.45	**4 (He/CO$_2$)**
Poly(phenylene sulfide) blended with 33 wt% TiO_2 (PPS, Ryton–Phillips data)	$T_g = 85ºC[1]$ $T_m = 285ºC[1]$	2.34 (He)		0.032		0.036	1.07	**2 (He/CO$_2$)**
Poly(phenylene sulfide sulfone) (PPSS–Phillips data)	$T_g = 85ºC[1]$ $T_m = 285ºC[1]$	1.96 (He)		0.013		0.036	0.48	**4.1 (He/CO$_2$)**
50-50 Poly(phenylene sulfide sulfone)/ Poly(phenylene oxide) (PPSS/PPO–Phillips data)	$T_g = 85ºC[1]$ $T_m = 285ºC[1]$	3.12 (He)		0.025		0.031	0.45	**6.9 (He/CO$_2$)**
50-50 Poly(phenylene sulfide sulfone)/ Polysulfone (PPSS/PSF–Phillips data)	$T_g = 85ºC[1]$ $T_m = 285ºC[1]$	2.84 (He)		0.019		0.015	0.66	**4.3 (He/CO$_2$)**
50-50 Poly(phenylene sulfide sulfone)/ Poly(ether sulfone) (PPSS/PSF–Phillips data)	$T_g = 85ºC[1]$ $T_m = 285ºC[1]$	3.41 (He)		0.025		0.026	1.1	**3.1 (He/CO$_2$)**
Poly ether sulfone, Bisphenol-A polysulfone *(INL Gas data at 30ºC)*	$T_g = 186ºC[1]$	11.3		1.8	2.6	0.1	3.4	**3.3**
Ketone/Ester/Ether Polymers								
Polyphenylene oxide (NMP solvent)	$T_g = 363ºC[1]$ $T_m = 535ºC[1]$	31.2 (He)		1.42		1.64	33.5	1 (He/CO$_2$)
Polyphenylene oxide (trichloroethylene solvent)	$T_g = 363ºC[1]$ $T_m = 535ºC[1]$	66.3		3.05		3.75	68.3	1 (He/CO$_2$)
Poly(ether ether ketone) (PEEK)	$T_g = 152ºC[1]$ $T_m = 335-343ºC[1]$							

Table A-15. (continued).

Class/Polymer	Pure Polymer Thermal Properties, T_g, T_m, and $T_{decomp.}$ *Must withstand 250ºC*	Pure Gas Permeability (barrers)						
Polyazoles		H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2
Mylar, Poly(ethylene terephthalate) *(Gas data at 30°C)*	Tg = 69-115ºC[1] Tm = 265ºC[1]	3.7		5.1	5	6.7	6.1	**0.6**
Polycarbonate	Tg = 150ºC[1]							
Cellulose Acetate	Tg = -30 to 200ºC[1] Tm = 307ºC[1]	*3.42		*0.27	*0.75	*0.20	*22.49	***0.15**
Organic Aliphatic Backbone Polymers								
Polystyrene (PS)	Tg = 100ºC[1] Tm = 240ºC[1]	25.4		0.5	2.3	0.7	3.2	**7.9**
High-density Polyethylene (HDPE)	Tg = -123ºC[1] Tm = 118-146ºC[1]							
Polypropylene (isotatic)	Tg = 11ºC[1] Tm = 186ºC[1]							
Silicon-containing Polymers								
Poly(dimethylsiloxane) (PDMS)	Tg = -123ºC[1] Tm₁ = -47 to -41ºC[1] Tm₂ = -37ºC[1]	*593		*287	*644	*875	*2750	***0.2**
Poly(diphenylsiloxane)	Tg = 40ºC[1] Tm = 265ºC[1]							
Poly(1-trimethylsilyl)-1-propyne (PTMSP)	Tg = 230ºC[1]	*14872		*5666	*8588	*14145	*35722	***0.4**

1. James E. Mark, "*Polymer Data Handbook*," Oxford University Press: New York-Oxford (1999).

2. John P. Ferraris (UTD), DOE-document number DE-FG26-04NT42173, March 2005–April 2006.

3. Hirayama,Y.; Yoshinaga,T.; Kusuki,Y.; Ninomiya,K.; Sakakibara,T.; Tamari,T. *J. Mem. Sci.,* 111, 169 (1996).
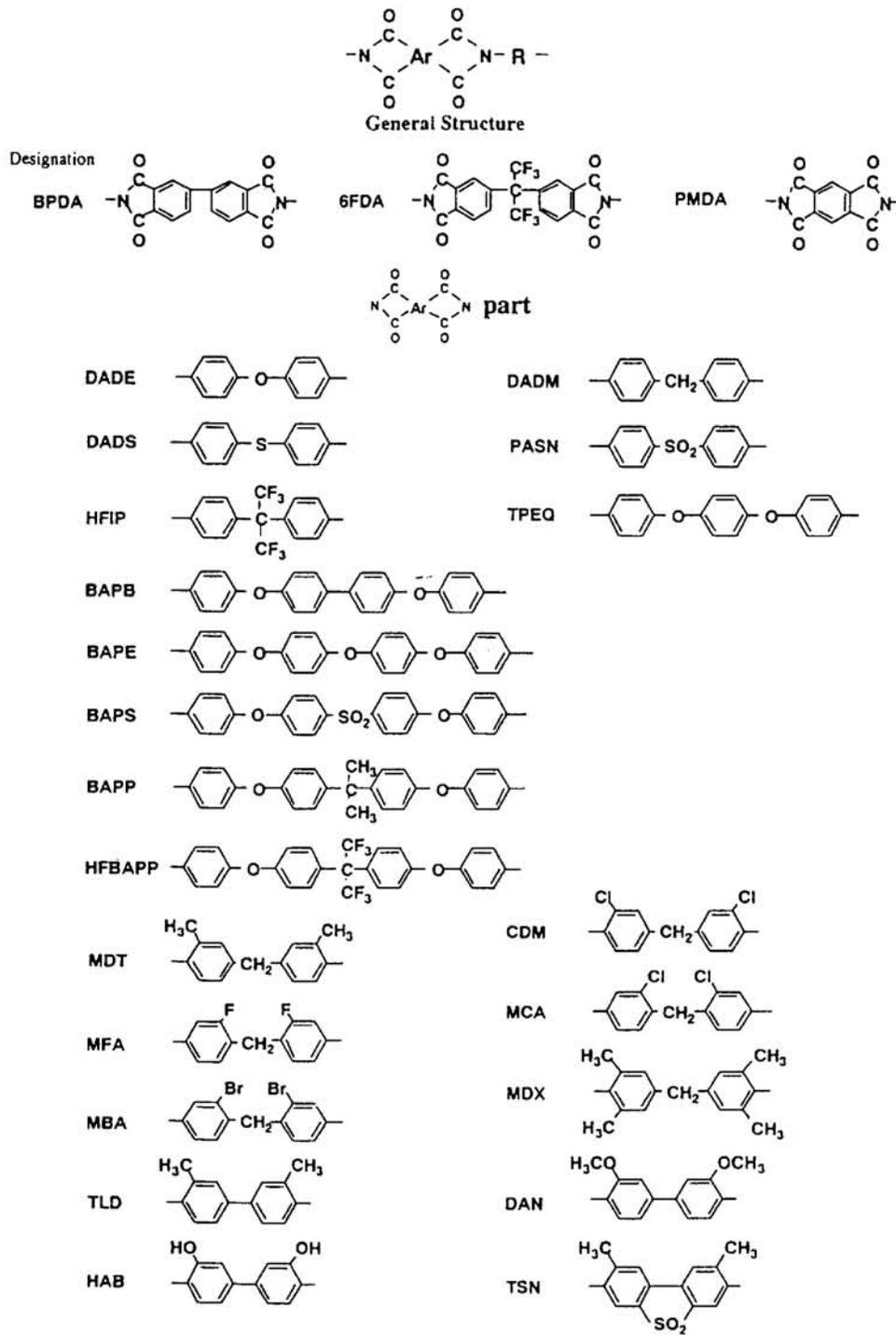
Fig. 1. Chemical structure of polyimide films.

Figure A-1. Illustration of the polyimide structures to the abbreviated names in Table A-15. (From 3. Hirayama, Y.; Yoshinaga, T.; Kusuki, Y.; Ninomiya, K.; Sakakibara, T.; Tamari, T. *J. Mem. Sci.,* 111, 169 [1996].)

Table A-16. Estimation of free volume from positron annihilation measurements.

Sample	τ_L	τ_L error	I_L %	I_L error	Pore Radius [A]	Pore Vol. [A^3]	Free Volume Fraction
VTEC PI 80-051 w/ 2 wt% Br$_2$-*nh*	1.51	0.17	3.92	1.51	2.37(2.16-2.56)	56 (42-70)	0.39 (0.18-0.69)
VTEC PI 80-051 w/ 2 wt% Br$_2$-*h*	2.22	0.37	2.13	0.45	3.07(2.73-3.37)	121 (85-160)	0.46 (0.26-0.74)
VTEC PI 80-051 w/~17 wt % PBI-TMS-*nh*	1.67	0.11	4.56	0.45	2.55(2.43-2.66)	69 (60-79)	0.57 (0.44-0.71)
VTEC PI 80-051 w/~17 wt % PBI-TMS-*h*	1.49	0.12	4.43	0.51	2.35(2.2-2.48)	54 (45-64)	0.43(0.31-0.57)
VTEC PI 1388-*nh*	1.5	0.11	3.75	0.31	2.35(2.23-2.48)	54 (46-64)	0.37 (0.29-0.47)
VTEC PI 1388-*h*	1.74	0.14	3.07	0.34	2.62(2.45-2.76)	75 (62-88)	0.42(0.30-0.54)
VTEC PI 80-051-*nh*	2.15	0.67	2.6	1.6	3.01(2.33-3.55)	114 (53-187)	0.53 (0.10-1.42)
VTEC PI 80-051-*h*	1.8	0.26	4.42	0.86	2.69(2.4-2.93)	82 (58-105)	0.65 (0.37-1.00)
VTEC PI 80-051-*ltah*	1.72	0.17	4.71	0.64	2.60(2.42-2.77)	74 (59-89)	0.62 (0.43-0.86)
Kapton®-HN – *nh*	2.25	0.25	2.19	0.26	3.10(2.88-3.30)	125 (100-150)	0.49 (0.35-0.66)
	1.9	0.1	2.62	0.15	2.78(2.68-2.88)	90 (81-100)	0.42 (0.36-0.50)
VTEC PI 80-051 w/~17 wt % PBI-TMS–film had no heat treatment (mainly polyamic acid)	1.62	0.13	5.46	0.52	2.49(2.32-2.63)	65 (52-76)	0.64 (0.46-0.82)
	1.55	0.04	5.62	0.23	2.42(2.37-2.56)	59 (56-70)	0.60 (0.54-0.74)
VTEC PI 1388–film had no heat treatment (mainly polyamic acid)	1.83	0.04	2.69	0.07	2.72(2.67-2.75)	84 (80-87)	0.41 (0.38 – 0.43)
	1.89	0.21	2.56	1.8	2.77(2.56-2.97)	89 (70-110)	0.41 (0.10 – 0.86)
	1.91	0.1	2.69	0.16	2.79(2.69-2.89)	91 (81-101)	0.44 (0.37 – 0.52)
VTEC PI 80-051–film had no heat treatment (mainly polyamic acid)	1.64	0.16	3.6	0.43	2.51(2.33-2.68)	66 (53-81)	0.43 (0.30-0.58)
	1.47	0.15	3.76	0.65	2.32(2.14-2.49)	52 (41-65)	0.35 (0.23-0.51)

Explanation to the table:

Nh. Normal atmospheric humidity exposure (20-40% relative humidity)

h. Heated in about 150°C for 1 hour

itah. Approximately 2 weeks after heating

Pore Radius [A] was calculated according to Jean formula as

$\lambda^{(n0)}_{po} = \lambda_a * [1-R/R_0+1/2\pi*\sin(2\pi nR/R_0)]^{-1}$ [Ref-11]

with $\lambda_a=1/4\lambda_S* + 3/4\lambda_T \cong 2$/ns, where $\lambda_S = 8$ ns^{-1} is self p-Ps decay rate and $\lambda_T = 7.04*10^{-3}$ ns^{-1} is a self o-Ps decay rate

the lifetime can be found as: $\tau_{po}=1/(\lambda_{po}+ \lambda_T)$

This formula based on the assumption that positronium atom is trapped in the ground state of infinite spherical potential well.

Source correction. Was estimated by use of the Monte Carlo MCNPX simulation which deals with transport of nuclear particles through matter. The simulation took into account thickness, density, and composition of the samples, sources, and backing as well as the geometrical arrangement

Free Volume Fraction calculated according to the formula: $f_v(\%)=0.0018*I_3(\%)*<4/3\pi R^3>$

Appendix B

PALS Results
Jagoda Urban-Klaehn, Ph.D.; Idaho State University

Appendix B

PALS Results

Supplemental-Detailed discussion of PALS Data (for Table A-16: Appendix A):

The following conclusions can be drawn from the positron annihilation spectroscopic (PALS) measurements: (1) the differences between the lifetimes and intensities of the spectra for unheated and heated samples are relatively small. Since the microporosity of these samples is low compared to other open volume polymers, their long lifetime and intensity values are low, thus their values have relatively high uncertainty. In the case of low statistics (less than 1 million counts in the spectrum), the software program may act in the unstable way. Therefore, the best indicator of any possible change in the structure is the product of both (intensity and lifetime). Since the free volume fraction is calculated based on both—lifetime (pore size) and the intensity (pore frequency, rate)—it is the most reliable value to consider while comparing the unheated and heated spectra of polymers. (2) The free volume fraction for VTEC PI 80-051 w/2-wt% Br_2, VTEC PI 1388, and VTEC PI 80-051 increased after the polymer was heated. This may be caused by the fact that more positrons could be trapped inside the volume of the polymers due to the release of the bound water. However, heating VTEC PI 80-051 w/~17-wt% PBI-TMS could cause a different effect, which could affect its free volume structure in the opposite way. This is possibly due to that VTEC PI 80-051 w/~17-wt% PBI-TMS already has a relatively high intensity of the positronium formation (I_L >4%) before heating. (3) The lowest, although not negligible, long intensity values were observed in polymer Kapton[®]-HN. The lifetime and intensity values of the Kapton[®] film are well known and they are about 380 ps. The only explanation of the presence of the low intensity (about 2%) of the long lifetime value is a presence of water. The free water lifetime value is about 1.75 ps. In the case of Kapton[®]-HN, the average lifetime value, overlaps in its uncertainty with the water lifetime value quoted from *Appendix: Free-volume Data in Polymeric Materials*.[a] (4) The effect of extended drying of the VTEC PI 80-051 polymer seem to remain constant for at least 2 weeks, since the lifetime results for performed are very similar. (5) There is very little difference between the measuring results for the non-heat treated VTEC polyimides, which indicates a high stability and reliability of the data. (6) The lifetime values vary between 1.5–2.25 ns that correspond to the pore radius of 50-125 A.[3] The longest lifetime values, thus relative micro-pore sizes were seen, besides Kapton[®], in VTEC PI 1388 (no heat treatment). The intensity values vary from 2–6 %. The highest intensity values were observed in polymer VTEC PI 80-051 w/~17-wt % PBI-TMS (no heat treatment), the lowest in the K_a.

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a. Li, Y.; Zhang, R.; Jean, Y.C. "Appendix: Free-volume Data in Polymeric Materials," in *Principles and Applications of Positron and Positronium Chemistry*, Eds. Y.C. Jean, P.E. Mallon, and D.M. Schrader, World Scientific Pub. Singapore, 373 (2003).

Appendix C

Tables and Results

Appendix C

Tables and Results

Table C-1. Thermal decomposition temperatures of various VTEC polyimides and Kapton[®].

Polymer Films	TGA Onset of Decomposition—under Nitrogen
Kapton[®] (DuPont)	574ºC
VTEC PI 80-051	546ºC
PBI (Celanese)	512ºC
VTEC PI 80-051 w/2 wt% Bromine	556ºC
VTEC PI 80-051 w/10 wt% Bromine	551ºC
VTEC PI 80-051 w/1 wt% ethylene bromide	566ºC
VTEC PI 80-051 w/~20 wt% polysulfone	543ºC
VTEC PI 80-051 w/(~5 wt%) Nomex	545ºC
VTEC PI 80-051 w/~20 wt% PBI-TMS (functionalized PBI)	465ºC
PBI-TMS (Me$_3$SiCH$_2$-PBI) (functionalized PBI)	448ºC

Table C-2. Thermogravimetric analysis (TGA) and thermo mechanical analysis (TMA) of VTEC polyimides.

Polymer Films	TGA Weight Loss under Nitrogen Before heat treatment; Onset to Decomposition	TMA Thermal Transition; heat processed films (dimensional change)
VTEC PI 851	243ºC (-H$_2$O); 512ºC	243ºC (~2.5 μm; to 400ºC)
VTEC PI 80-051	237ºC (-H$_2$O); 524ºC	255ºC (~5.0 μm; to 400ºC)
VTEC PI 1388	241ºC (-H$_2$O); 529ºC	285ºC (~1.0 μm; to 400ºC)
TMA results—Frederick F. Stewart; Idaho National Laboratory		

Table C-3. Koros' pure gas data at ambient tempertures and INL's gas permeability data.
(All INL polymers in this table were heat cycled as described in the report prior to testing)

Polymer	Temp (°C)	Permeability (barrers)						Selectivity α		
		H_2	Ar	N_2	O_2	CH_4	CO_2	CO_2/CH_4	H_2/CO_2	O_2/N_2
VTEC Polymers Tested by Koros' Research Group										
VTEC PI 1388	35	2.68	*Not tested*	0.0168	0.13	0.008	0.448	56.0	6.0	7.7
VTEC PI 80-051	35	4.33	*Not tested*	0.0218	0.168	0.0149	0.772	51.8	5.6	7.7
INL's Gas Permeability Data										
VTEC PI 1388	30	2.603	0.044	0.019	0.109	0.01	0.411	48.2	6.5	5.9
VTEC PI 80-051	30	2.962	-	0.019	0.124	0.007	0.485	69.3	6.1	6.5

Table C-4. Pure gas data collected for temperature range: functionalized bis(trimethylsilylmethylene)polybenzimidazole (PBI-TMS)/ VTEC polyimide blend and polyvinylalcohol (PVA)/ VTEC polyimide blend.
(All INL polymers in this table were heat cycled as described in the report prior to testing)

Polymer	Temp (°C)	Permeability (barrers) at 30ºC						Selectivity α		
		H_2	Ar	N_2	O_2	CH_4	CO_2	CO_2/CH_4	H_2/CO_2	O_2/N_2
VTEC PI 1388 w/ ~50 wt% PBI-TMS	30	8.08	*Not tested*	*Not tested*	*Not tested*	0.078	2.211	28.3	3.7	*n/a*
	50	11.62	*Not tested*	*Not tested*	*Not tested*	0.14	2.949	21.1	3.9	*n/a*
	70	15.519	*Not tested*	*Not tested*	*Not tested*	0.231	3.581	15.5	4.3	*n/a*
VTEC PI 80-051 w/ ~5 wt% PVA	30	3.223	0.035	0.017	0.132	0.008	0.511	63.9	6.3	7.8
	55	5.421	0.079	0.039	0.24	0.023	0.886	38.5	6.1	6.2
	70	8.015	0.14	0.069	0.374	0.056	1.305	23.3	6.1	5.4

Table C-5. Pure gas data at 30ºC —VTEC polyimides blends and Kapton[®].
(All INL polymers in this table were heat cycled as described in the report prior to testing)

Polymer	Permeability (barrers)						Selectivity α		
	H_2	Ar	N_2	O_2	CH_4	CO_2	CO_2/CH_4	H_2/CO_2	O_2/N_2
VTEC PI 80-051 w/ ~50wt% PBI-TMS	12.05	1.077	0.907	1.392	0.849	3.987	4.7	3.0	1.5
VTEC PI 1388 w/ ~50wt% PBI-TMS	6.655	0.156	0.064	0.442	0.026	1.896	72.9	3.5	6.9
VTEC PI 80-051 w/ ~35wt% PEG	1.392	0.017	0.009	0.07	0.006	0.25	41.7	5.6	7.8
VTEC PI 80-051 w/ ~5 wt% PVA	3.223	0.035	0.017	0.132	0.008	0.511	63.9	6.3	7.8
Kapton[®]-HN (DuPont)	1.54	*Not tested*	*Not tested*	*Not tested*	0.0045	0.32	71.1	4.8	*n/a*

Table C-6. Pure gas data at 30 ºC —"Heat treatment" in air of various polyimides and Kapton®.
(All INL polymers in this table were heat cycled as described in the report prior to testing)

Polymer	Permeability (barrers)						Selectivity α		
	H_2	Ar	N_2	O_2	CH_4	CO_2	CO_2/CH_4	H_2/CO_2	O_2/N_2
Kapton®-HN (DuPont) - heat treatment at 500ºC for 1hr.	10.739	*Not tested*	*Not tested*	*Not tested*	4.288	3.417	0.8	3.1	*n/a*
VTEC PI 1388 - heat treatment at 250ºC for 1 hr.	2.603	0.044	0.019	0.109	0.01	0.411	41.1	6.3	5.7
VTEC PI 1388 - heat treatment at 300ºC for 12 hrs.	3.12	*Not tested*	*Not tested*	*Not tested*	0.010	0.50	50.3	6.2	*n/a*
VTEC PI 1388 - heat treatment at 400ºC for 1 hr.	6.49	0.13	0.07	0.39	0.031	1.65	53.2	3.9	6.0
VTEC PI 80-051 - heat treatment at 300ºC for 12 hrs.	2.95	0.04	0.02	0.12	0.007	0.49	69.3	6.1	6.5
VTEC PI 80-051 - heat treatment at 450ºC for 1 hr.	11.03	0.599	0.266	0.918	0.096	4.03	42.0	2.7	3.5
VTEC PI 80-051 - heat treatment at 475ºC for 1 hr.	5.642	0.148	0.09	0.52	0.05	2.44	48.8	2.3	5.8

Table C-7. Pure gas data at 30ºC —VTEC polyimide "conditioned" with methane gas.
(All INL polymers in this table were heat cycled as described in the report prior to testing)

Polymer	Permeability (barrers)						Selectivity α		
	H_2	Ar	N_2	O_2	CH_4	CO_2	CO_2/CH_4	H_2/CO_2	O_2/N_2
VTEC PI 80-051 (No Methane Conditioning)	3.18	*Not tested*	*Not tested*	*Not tested*	**0.026**	0.595	**22.9**	5.3	n/a
VTEC PI 80-051 (w/ Methane Conditioning)	3.112	0.044	0.022	0.146	**0.014**	0.577	**41.2**	5.4	6.6
VTEC PI 80-051 (Large Cell used) (w/ Methane Conditioning)	3.146	0.045	0.02	0.142	**0.008**	0.523	**65.4**	6.0	7.1