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**STRUCTURE-PROPERTY RELATIONSHIPS IN NOVEL
POLY(ARYLENE ETHER KETONE)S**

by

PIERRE R. MOULINIÉ, B. Sc

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of

Doctor of Philosophy

Department of Chemistry

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Ottawa, Ontario
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IN NOVEL POLY(ARYLENE ETHER KETONE)S

submitted by

Pierre R. Moulinié, B. Sc.

in partial fulfillment of the requirements for
the degree of Doctor of Philosophy

Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Abstract

Analogues to the commercial polymer poly(ether ether ketone) (PEEK) were prepared using commercial bisphenols and novel dihalide monomers. The structure-property relationships in three series of polymers were studied by thermal, mechanical and gas permeability characterizations. Series I of the poly(arylene ether ketone)s contained dibenzoylbiphenyl (DBBP) moieties, which also allowed the effects of the biphenyl catenations to be studied. Series II were prepared from a chlorofluorobenzonaphthone monomer containing a bulky naphthalene group. Finally, series III consisted of the same repeat structure as PEEK with an extra tert-butyl group attached to the backbone. This series also contained a co-polymer prepared by polymerization of 4,4'-difluorobenzophenone with a 2:1 ratio of 2-tert-butyl-1,4-hydroquinone and 2,5-di-tert-butyl-1,4-hydroquinone, thereby increasing the tert-butyl content relative to tert-butyl-PEEK. The structures of these polymers gave them rigid backbones and inhibited polymer chain packing. Such features are desirable for preparing gas separation membranes which have high permeabilities and selectivities. All the polymers had T_g 's higher than PEEK's 145 °C, were amorphous and thermally stable. The polymers containing DBBP moieties (series I) showed higher Young's moduli, compared to analogues containing dibenzoylbenzene moieties. Except for polymers with 2,2'-DBBP moieties, the T_g 's of the polymers in series I increased with linearity in the structure of DBBP. A polymer containing the 4,4'-DBBP moiety with extended π -orbital overlap also gave the polymer additional long term thermal stability. Degradation kinetics by variable heating rate

thermogravimetry showed that the activation energies of the polymers in series I were similar to PEEK. The segmental mobilities in series I and II, determined by DMA, demonstrated that sub- T_g transitions were insensitive to changes in the bisphenol structure. The gas permeabilities of all the polymers were higher than that of PEEK. Within each series, the permeabilities and selectivities followed the typical trade off below Robeson's upper bound. Attempts at correlating Fractional Free Volumes were hampered by either density measurements or incorrect molecular volumes using Van Krevelen's method of group contribution. Wide-angle X-ray diffraction patterns revealed a complex packing pattern for 2,2'-DBBP and naphthalene containing polymers, which made permeability correlations with d-spacing difficult.

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NOTE ON UNITS

Although scientific works are recommended to use SI units, this thesis uses units and prefixes which are commonly employed by other researchers in the same field. The following table gives conversions for units used in this thesis.

Measure	Symbol	SI Units	Other Units
Temperature	T	K	$^{\circ}\text{C} + 273.15$
Energy	E	J	4.184 cal
Gas Constant	R	$8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$0.08205 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
Frequency	ν	$\text{Hz (s}^{-1}\text{)}$	$3.333 \times 10^{-10} \text{ cm}^{-1}$
Pressure	P	$\text{Pa (N}\cdot\text{m}^{-2}\text{)}$	10^{-2} kbar $9.8692 \times 10^{-6} \text{ atm}$ $7.5006 \times 10^{-3} \text{ mm Hg}$ $7.5006 \times 10^{-3} \text{ Torr}$ $6.894 \times 10^{-3} \text{ lb}\cdot\text{in}^{-2} \text{ (psi)}$

EXPLANATION OF PREFIXES

The following table explains prefixes often used with unit symbols to denote multiples

Prefix	Symbol	Factor
<i>nano-</i>	n	10^{-9}
<i>micro-</i>	μ	10^{-6}
<i>milli-</i>	m	10^{-3}
<i>centi-</i>	c	10^{-2}
<i>deci-</i>	d	10^{-1}
<i>kilo-</i>	k	10^3
<i>mega-</i>	M	10^6
<i>giga-</i>	G	10^9

ABBREVIATIONS

The following list explains abbreviations often used in this thesis:

Abbreviation	Meaning
PEEK	Poly(ether ether ketone).
DMA	Dynamic mechanical analysis
DSC	Differential Scanning Calorimetry
E'	Young's Modulus.
E_a	Activation energy.
T_d	Decomposition temperature
T_g	Glass-transition temperature
TG	Thermogravimetry
TG-FTIR	Thermogravimetry-Fourier Transform Infrared spectroscopy
TMA/SS	Thermomechanical analysis operated in stress-strain mode.
WAXD	Wide-angle X-ray diffraction

Chapter 1 - Background and Objectives

1.1 Characterizations of Poly(arylene ether ketone)s

Polymers containing phenyl rings in the backbone show superior mechanical properties compared to thermoplastics such as polyethylene and are commercialized as engineering thermoplastics. Polycarbonate, polysulfone and poly(ether ether ketone) are examples of these polymers. Poly(ether ether ketone) - PEEK³ - shown below in Figure 1.1, was first marketed in 1981 by Imperial Chemical Industries (ICI). In addition to its excellent mechanical properties, this semi-crystalline thermoplastic has exceptional solvent resistance and can only be dissolved in sulfuric acid at room temperature.

Figure 1.1 - PEEK, poly(ether ether ketone).

Polymers such as polycarbonates and polysulfones, however, are usually amorphous and soluble in organic solvents such as chloroform. Despite its attractive properties, the applicability of PEEK is limited by its relatively low T_g of 145 °C. Since the introduction of PEEK, several analogues which yield higher T_g 's have been prepared. Staniland¹ and, more recently, Kricheldorf² have reviewed the synthesis of several PEEK analogues via nucleophilic polymerization of dihalide and diol monomers. Many other novel structures for poly(arylene ether ketone)s have also been reported.³⁻¹³

Of the many applications of engineering thermoplastics, polymeric gas separation membranes have recently become significant. Gas separations through polymer membranes are a simple alternative to cryogenic gas separation techniques. Applications of gas-separation membranes include hydrogen recovery, oxygen enrichment of air and the separation of CO_2 and CH_4 from natural gas. A review by Koros and Fleming¹⁴ discusses these and other potential applications, and compares the economics of gas separation membranes to more conventional separation methods.

Several reviews describe the relationships between polymer structures and their gas-transport properties.¹⁴⁻¹⁶ Many of these relationships were established from characterizations of polycarbonates, polysulfones and polyimides. Often, the performance of gas-separation membranes show a trade-off between gas-permeability (flux) and its selectivity (ability to discriminate between different gas molecules), where one usually increases at the expense of the other. Robeson summarized the permeabilities and selectivities of several polymers and first introduced the "upper-bound" which described a ceiling to selectivity and permeability for polymeric membranes. An example of this upper-bound is illustrated in Figure 1.2 for O_2 and N_2 .¹⁷ The apparent slope of this upper bound was also successfully correlated to the size differences between the penetrant gas molecules, supporting experimental findings that gas-transport through glassy polymers is principally governed by diffusion. A more recent report by Robeson confirms that, to date, no glassy or rubbery polymeric membrane has traversed this upper bound.¹⁸

Figure 1.2 Robeson's upper-bound line for oxygen permeability (P_{O_2}) and O_2/N_2 selectivity (α) trade-off.

Diffusion through a polymer is dependent on the polymer chain packing and the segmental mobility of the backbone. Hoehn *et al* first observed that a desirable trade-off relationship was obtained when structural modifications to polymers inhibit both chain packing and segmental mobility.¹⁶ Within a family of polymers, it has been observed that achieving such structural modifications can yield higher permeabilities with comparatively small losses in selectivity. While such structural modifications have not produced membranes with performances beyond the upper-bound shown in Figure 1.2, this relationship forms the basis of preparing "tailor-made" gas-separation polymers.

Polycarbonate and polysulfone are prepared with 4,4'-isopropylidenediphenol (BPA). This bisphenol is also commonly used for preparing poly(arylene ether ketone)s.⁵ Among the most considered structural modifications for increasing permeability with relatively small loss in selectivity for polymers prepared with BPA is the replacement of methyl groups with trifluoromethyl groups. Such modifications are obtained when polymerizations are carried out using 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA), illustrated in Figure 1.3.

Figure 1.3 Structures of BPA and 6F-BPA.

Mohr *et al* studied the effect of this substitution on the gas-transport properties of several poly(arylene ether ketone)s, and correlated the increase in gas permeability with systematic increases in the trifluoromethyl (-CF₃) content.²⁰ The significant increase in gas permeability with minimal loss in selectivity observed when replacing BPA with oF-BPA has also been observed for several other families of polymers.²¹⁻²⁶

Poly(arylene ether ketone)s, polysulfones and polyarylates prepared by polymerization with 9,9-bis(4-hydroxyphenyl)fluorene shown in Figure 1.4 produces amorphous rigid polymers whose T_g's rank among the highest for this class of polymers.²⁷ This bulky connector significantly contributes to the rigidity of the polymer backbone and disrupts chain packing. As such, it has been included in gas transport characterization of several poly(arylates) and polysulfones.²⁶⁻²⁸

Figure 1.4 9,9-bis(4-hydroxyphenyl)fluorene.

A similar effect is observed for polysulfones prepared with 2,2',6,6'-tetramethyl-4,4'-diphenol, shown in Figure 1.5.²⁹

Figure 1.5 2,2',6,6'-tetramethyl-4,4'-diphenol

As with 9,9-bis(4-hydroxyphenyl)fluorene, this bulky and rigid moiety has been reported to give high T_g 's for polysulfones,³⁰ and poly(arylene ether ketone)s.³¹

The incorporation of pendent groups onto the polymer backbone has also produced materials following this favourable trade-off. For example, the addition of *tert*-butyl substituent groups has been shown to increase permeabilities of polyarylates.²⁷ Such structural modifications are easily achieved by incorporating pendent groups onto the diols used for polymerization.

Consideration of these options for improving gas-transport properties are useful since the permeability of PEEK to carbon dioxide has been reported to be much lower than other rigid polymers.³² Although the usefulness of PEEK for gas membranes is limited, synthetic analogues with higher T_g 's and amorphous morphologies may prove to be promising alternatives. Although an extensive body of literature on the preparation of novel poly(arylene ether ketone)s is available, relatively few structure-property relationship studies have been performed. Moreover, discussions on the gas-transport structure-property relationships of synthetic poly(arylene ether ketone)s are mainly restricted to variations of the diol used for polymerization.^{20,33}

The importance of understanding sub- T_g behaviour of polymers has gained significance in polymer gas-transport since several models describing the diffusion of gas molecules through a polymer matrix require the displacement of a polymer segment to accomodate its passage.^{15,34} Thus, since chain packing and segmental mobility influence gas-transport properties, it is necessary to consider each when studying gas-transport properties. The segmental mobilities of polymers can be compared through the temperatures at which sub- T_g relaxations occur. Dielectric measurements and dynamic mechanical analysis (DMA) have proven useful to probe molecular motions in polymers below T_g .

Generally, an increase in a polymer's unoccupied volume (free-volume) without changes to the segmental mobility causes the gas permeability to increase at the expense of selectivity.¹⁵ Thus, information on the segmental mobility of the polymers is required to understand gas-transport properties. Mechanical relaxations have been included in studies of gas-transport of polycarbonates,²³ polysulfones^{29, 35-38} and to a lesser extent poly(arylene ether ketone)s.²⁰ In many cases, the mechanical relaxations have been displaced to higher temperatures when segmental mobilities have been decreased. Furthermore, this often occurred because of increased barriers to phenyl rotation (ie. about its 1,4-axis) brought on by substituents on a phenyl ring. Steric considerations are often the cause of this apparent increase in stiffness, although polar interactions can also be significant for polar substituents.^{20, 30, 39} It is noteworthy, however, that not all substitutions cause an increase in the relaxation temperature. Yee concluded from such

observations in polycarbonates that at least one entire repeat unit participates in the sub- T_g relaxations.³⁹ Furthermore, chain packing considerations may also play a significant role in the apparent differences in sub- T_g relaxations, since interchain hindrances can also affect segmental mobilities.³⁰

Several studies have shown for polycarbonate that rotations of the phenyl rings were a requirement for the sub- T_g relaxations.³⁹ As such, many investigations on sub- T_g relaxations have centered on the barriers to phenyl rotation. Several studies have been conducted on intrachain hindrance to phenyl rotations by using computations based on empirical or semi-empirical algorithms.^{30,40-42} These studies calculated the energies associated with phenyl flips in model compounds and correlated the rotational barriers to their structural features. For polymers, such studies are particularly useful since differences in energy barriers may give insight into polymer segmental mobilities and how they are influenced by intrachain considerations. As such, differences in sub- T_g relaxations may be qualitatively correlated to the energetics associated with the mobilities of local structural features.

1.2 Synthetic Poly(arylene ether ketone)s

From the preceding discussion, it is useful to consider amorphous poly(arylene ether ketone)s which satisfy the requirement for T_g 's higher than PEEK and at the same time meet the "desirable" features for gas-transport. In particular, this section will briefly

review the effects of structural modifications to poly(arylene ethers) to identify favourable features for dihalide monomers.

For high molecular weight polymers, higher T_g 's are typically achieved by the hindrance of large-scale molecular motions of the polymer chains. This can be accomplished by attaching branched or bulky substituents to the backbone, or by attaching polar substituents. Similarly, incorporation of rigid connectors, or groups which have significant rotational barriers are also known to yield higher T_g 's.^{4,5} The effects of several structural changes in the difluoride monomers are illustrated in poly(arylene ether)s reported by Hergenrother *et al.*³ In their work, they illustrated that the T_g of a mono-ketone poly(arylene ether) was increased when an extra "benzoyl" moiety was added to the repeat structure. Addition of a third, however, yielded a T_g similar to that for the mono ketone polymer, as shown in Figure 1.6. Thus, addition of desirable structural features does not necessitate an increase in T_g .

Figure 1.6 Mono, di- and tri-ketone segments in several poly(arylene ether ketone)s prepared from dihalide compounds with bisphenol A.

Previous studies on polysulfones and poly(ether ketone)s have shown that a biphenyl moiety increases the rigidity of the polymer backbone and increases T_g , as shown for PEEK in Figure 1.7.^{1,44,45}

Figure 1.7 Effect of biphenyl connector, compared to phenyl in PEEK.

With respect to gas-transport applications of polymers, this rigid connector has a linear structure, which enhances interchain packing. The necessity for structures which disrupt chain packing while maintaining a rigid character suggest that kinked, non-linear biphenyl structures are more desirable.

Recently, several poly(arylene ether ketone)s which contained a dibenzoylbiphenyl (DBBP) moiety, shown in Figure 1.8, were reported.

Figure 1.8 Dibenzoylbiphenyl moiety

To date, polymers with 4,4'-^{46,47}, 2,2'-^{48,49}, 3,4'-⁵⁰, and 3,3'-^{47,51} substitutions on the biphenyl group have been reported. These poly(arylene ether ketone)s exhibited high T_g 's and excellent mechanical properties. Moreover, many of these polymers are easily cast into thick films, making them suitable for determination of their gas-transport and sub- T_g relaxation properties.

1.3 Objectives

Polymers with novel structures are evolving at a significant rate. However, relatively few detailed structure-property surveys of poly(arylene ether ketone)s have been performed. Moreover, these relationships have been established with changes in the bisphenols used in polymerization. Previous work suggests that consistent trends are observed within polymer families when comparing polymer properties and characteristics with various bisphenol or hydroquinone connectors.³ By analogy, the effects of several structural variations within a polymer can also be studied by modifying the structure of the dihalide monomers.

Most commonly, polymers are usually compared with respect to the glass-transition temperature (T_g), without examining other properties. Clearly, the need for novel polymers which have higher T_g 's than PEEK has been addressed. The applications of these materials, however, are not known since many properties or applications have not been determined. The purpose of this work is to study novel poly(arylene ether

ketone)s and identify structure-property relationships. Furthermore, the purpose of this work is also to study poly(arylene ether ketone)s obtained by more conventional modifications to the diol and compare their properties to polymers obtained from modified dihalide structures.

Three series of poly(arylene ether ketone)s, structurally related to PEEK are examined in this survey. First, the properties of poly(arylene ether ketone)s containing 2,2'- and 3,3'-DBBP will be studied to understand the influence of changes in the biphenyl substitution pattern. Where available, data obtained from polymers with 4,4'- and 3,4'-DBBP groups are also compared. Structural, thermal and mechanical properties are measured and studied and correlated to the changes in the biphenyl catenation. The thermal degradation behaviours of these materials are also investigated, since these characteristics are important when considering applications for new polymers.

In an effort to study polymers which have desirable structural features with respect to gas-transport properties, polymers containing 2,2'- and 3,3'-DBBP groups were prepared using the previously described diols: 9,9-bis(4-hydroxyphenyl)fluorene and 6F-BPA. The rigid and bulky bisphenol 2,2',6,6'-tetramethyl-4,4'-diphenol was also polymerized to form a poly(arylene ether ketone) containing a 2,2'-DBBP moiety. A second series of poly(arylene ether ketone)s prepared from an unsymmetrical dihalide containing a naphthalene moiety will be included in the relaxational and gas-transport measurements to ensure that the desired consistency within the bisphenols are independent of the changes in DBBP units. A third series encompass PEEK analogues

prepared with hydroquinones containing tert-butyl pendent groups and with the 2,2',6,6'-tetramethyl-4,4'-diphenol. The structures of the polymers which will be investigated are shown in Figure 1.9.

Series I

3,3'-DBBP

Ar = BPA, HQ, BP, 6F, FL, SP

2,2'-DBBP

Ar = BPA, HQ, BP, 6F, FL, TM, SP

Series II

NP

Ar = 6F, FL

-Ar-

Series III

Ar = TBPK, COPK, TM

Figure 1.9 Polymers studied in this work.

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Chapter 2 - Background on Polymer Characterization Methods

2.1 Differential Scanning Calorimetry (DSC)

This thermo-analytical technique heats a sample and a reference simultaneously at a constant heating rate and measures the difference in temperature which arises when the sample undergoes a transition such as melting (endothermic) or crystallization (exothermic). Therefore DSC measures the heat flow difference through the sample. A hypothetical DSC curve is illustrated in Figure 2.1. The glass-transition temperature, T_g , for polymers is measured as a change in the sample's heat capacity. The sensitivity of DSC is quantitative in that the intensity of the DSC signal can be analytically correlated.

2.2 Thermogravimetry (TG)

In this technique, a sample is heated as its mass is measured. Thus, the TG signal consists in a weight gain or loss. The thermal stability of polymers are commonly probed by TG scans, and measuring the temperature at which significant weight loss from degradation begins to occur. Two common practices are used for establishing the sample's decomposition temperature, T_d , illustrated in a typical TG curve in Figure 2.2. Either the onset of weight loss (intersection of 2 tangent lines) or temperature corresponding to 5% weight loss (or some other fixed point) are usually reported as T_d . Comparison of these temperatures is often used as a means of qualitatively comparing thermal stabilities of different materials.

Figure 2.1 Hypothetical DSC curve illustrating glass-transition (T_g), crystallization (ΔH_c) and melting (ΔH_m).

Figure 2.2 Typical TG curve, including 1st derivative of weight curve (DTG).

Because the TG experiments are scanned at relatively high heating rates (usually 10 °C/min), the measured T_d may not reflect the overall long term stability of a material. More accurate comparisons for thermal stabilities are obtained by performing kinetic TG experiments, using isothermal or non-isothermal conditions.

Non-isothermal TG kinetics experiments are commonly used to determine kinetic parameters such as the decomposition activation energy, E_a . The theory behind TG kinetics is that T_d is dependent on the heating rate, with higher T_d 's measured when higher heating rates are used. Ozawa¹ and Flynn² derived an equation which described the relationship between the decomposition temperature T_d (at a fixed degree of reaction conversion, α), heating rate (β) and the decomposition activation energy:

$$\log F(\alpha) = \log(E_a \cdot A/R) - \log(\beta) - 2.315 - 0.4567 \cdot E_a/RT_d \quad 2.1$$

where $F(\alpha)$ is the TG weight loss as a function of degree of conversion, α . If the weight loss is not affected by diffusion of degradation products from the sample, $F(\alpha)$ can be taken to represent a TG curve. The degradation reaction activation energy E_a and A obey the Arrhenius equation for a reaction rate constant:

$$k = A \exp(-E_a/RT) \quad 2.2$$

An attractive feature of analysis using equation 2.1, is that it is independent of the order of reaction. The activation energy of a degradation reaction can therefore be obtained from the slope of a plot of $\log \beta$ versus $1/T_d$ and compared for various polymers to compare their thermal stabilities. Equation 2.1 can also be used for predictive purposes (e.g., lifetime prediction).³

2.3 Dynamic Mechanical Analysis

The mechanical properties of a polymer are usually expressed through Young's modulus, E' , which is the proportionality constant relating applied stress to resulting strain when a tensile stress is applied to a sample. Dynamic mechanical analysis (DMA) applies a sinusoidal stress to the sample and measures the resulting time-dependent strain. Using the equation corresponding to a simple oscillator, the time dependent strain in a sample subject to a sinusoidal tensile stress can be written:

$$A = A_0 \sin(\omega t + \delta) \quad 2.3$$

The applied stress has frequency ω and yields a time dependent strain A . The phase angle δ relates how the strain lags behind the applied stress. The modulus, E' , depends on how the material can dissipate the applied energy and therefore depends on the molecular motions occurring within the sample. If the time scale of molecular relaxations are much faster than the time scale of the applied stress, the sample strain behaves in a purely

elastic fashion and δ is very small or zero. If, however, the time scale of the relaxations in the sample and the frequency of the stress are comparable, the time dependent strain will begin to lag behind the applied stress by a certain phase angle δ . The phase angle δ is a maximum when the frequency of the stress and the relaxation match. Thus, it is possible to express the in phase modulus, E' , and the out of phase modulus E'' (also known as loss modulus). The complex modulus, E^* , is known as being composed of both E' and E'' :

$$E^* = E' + iE'' \quad 2.4$$

where $i^2 = -1$. The tangent of phase angle δ can therefore be determined from the ratio E'' and E' :

$$\tan \delta = \frac{E''}{E'} \quad 2.5$$

A decrease in E' related to a molecular motion also results in an increase in E'' and $\tan \delta$. At transitions such as T_g , peaks in $\tan \delta$ and E'' occur. As such, E' or $\tan \delta$ are often used to locate sub- T_g transitions.

The usefulness of DMA studies is several fold: E' can be used to compare the rigidities of different polymers with respect to their structures. Furthermore, DMA is sensitive to sub- T_g relaxations and can be used to study the segmental mobilities polymers. Finally, it is also possible to measure the activation energy associated with a sub- T_g relaxation by measuring E^* at different frequencies.

2.4 TG-FTIR

This hyphenated technique was designed to address a basic limitation of thermogravimetry: identification of products emitted during a TG weight loss. In these experiments, thermogravimetric experiments are performed, and gaseous degradation products are transported via a carrier gas to a FTIR spectrophotometer, in which the products are identified by FTIR spectroscopy. The power of this technique lies in its simplicity and speed. Limitations are that many products are often emitted simultaneously, and spectra therefore correspond to mixtures. FTIR spectra are most often collected at regular time intervals. Spectra corresponding to significant weight losses can be easily located by using the DTG curve, shown in Figure 2.2. The profile of the FTIR detector response during the TG scan, known as a Gram-Schmidt plot (which often has identical appearance to a DTG curve), is also useful for locating FTIR spectra of interest.

2.5 Gas-Transport through polymers

The gas permeability coefficient, P , of a polymer for a given gas can be expressed as the flux of a gas, Q , which is normalized for variables such as the matrix thickness l , its surface area, A and the pressure difference across the matrix Δp :

$$P = \frac{Q \cdot l}{A \cdot \Delta p} \quad 2.6$$

The direction of flux is usually referred to as occurring from upstream to downstream. Because permeabilities account for applied pressure and dimensions of the polymer, it is possible to compare permeabilities of different polymers for various gases. Permeabilities can be measured using a constant volume apparatus, shown in Figure 2.3 in which gas is permeated from the upstream side of a polymer film, to a reservoir of known volume on the downstream side. The volumetric flux can therefore be calculated from the pressure increase of the downstream reservoir. Most commonly, permeability is expressed in units of Barrer:

$$1 \text{ Barrer} = \frac{(\text{cm}^3 / \text{sec}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{cm Hg}} \times 10^{10}$$

Gas permeability is expressed as a product of diffusion and solubility:

$$P = D \cdot S \tag{2.7}$$

Thus, the permeability of a gas through a polymer is composed of both kinetic (diffusion) and thermodynamic (sorption) terms. The gas solubility in a polymer is usually separately measured using volumetric or gravimetric instruments. Diffusion coefficients can be determined from equation 2.7 once permeability and solubility data are available. Methods do exist, however, to determine diffusion coefficients from permeability or solubility measurements alone.

Figure 2.3 Constant volume permeability apparatus.

Figure 2.4 illustrates the typical pressure-time curve measured from permeability experiments using the apparatus in Figure 2.3. The time lag, θ , is the time required for the gas to achieve a "steady-state" concentration gradient across the polymer film. For rubbery polymers (ie. polymers above their T_g), θ is useful for determining diffusion coefficients:

$$\theta = \frac{l^2}{6D} \quad 2.8$$

Therefore for rubbery polymers P and D can be determined in a single permeability experiment.

Figure 2.4 Downstream pressure-time profile during permeability experiments.

For glassy polymers, determination of diffusion coefficients is more complex due to non-linear gas solubility in the polymer. This non-linear behaviour stems from solubility exhibiting behaviour consistent with Langmuir and Henry's law. Diffusion coefficients can be partitioned for each region. Considering the dual-mode sorption model, equation 2.8 becomes:

$$\theta = \frac{l^2}{6D} [1 + f(K, F, b \cdot p)] \quad 2.9$$

where K , F and $b \cdot p$ are parameters which describe the solubilities for regions obeying Langmuir and Henry's law. These parameters can be determined from non-linear regression of solubility isotherms. Consequently, diffusion coefficients for glassy polymers cannot be determined from simple permeability experiments.

The selectivity, α , is used to describe the ability of a polymer to discriminate between a pair of gases, i and j , and is determined from the ratio of their permeabilities:

$$\frac{\alpha_i}{\alpha_j} = \frac{P_i}{P_j} = \frac{D_i}{D_j} \cdot \frac{S_i}{S_j} \quad 2.10$$

Similarly, the diffusivity-selectivities and solubility-selectivities can also be obtained to establish if the selectivity for a given gas pair is governed by diffusion or solubility mechanism. Equation 2.10 does not consider the case where a mixture of 2 gases are permeating through a polymer film, but reflects the 'optimal' performance of a polymer.

For glassy polymers, one of the most influential parameters on gas permeability is the polymer's free-volume. In defining free-volume, the following important distinctions are made: matrix volume (V) and molecular volume (V_o), illustrated below in Figure 2.5. V can be determined from experimental density measurements, for which the specific volume includes the unoccupied volume while V_o corresponds to the volume occupied by the polymer chain molecules only.

Figure 2.5 Molecular volumes, V_o (grey area) and Matrix volumes, V (total area).

Most commonly, V_o have been best determined using a relationship proposed by Bondi,⁴ which uses Van der Waals atomic volumes, V_w :

$$V_o = 1.3 V_w \quad 2.11$$

Van Krevelen⁵ tabulates Van der Waals volumes for several functionalities in polymer repeat units, allowing for group contribution determination of V_o . Therefore, the free

volume (V_F) of a polymer can be obtained from V_o and experimentally determined values for V from density measurements:

$$V_F = V - V_o \quad 2.12$$

Most commonly, V is determined by density gradient column using electrolyte solutions. V_F is sensitive to density fluctuations caused by heavy substituent atoms in the repeat units.⁶ Fractional-Free Volume, FFV, corrects for this:

$$FFV = \frac{V - V_o}{V} \quad 2.13$$

Several works on polysulfones, polyphenylene oxides⁷ and polycarbonates⁸ have successfully correlated FFV to gas-transport in polymers.

2.6 Computational Studies

Computational studies have become useful tools for visualizing molecules and computing molecular geometries and energies. There are several degrees to which molecular computations can be carried out. Semi-empirical calculations using quantum mechanical methods where energies are determined from partial solutions to the Schrodinger equation for a given structure. Although semi-empirical calculations have

often given experimentally verifiable results, approximations based on even more empirical Molecular Mechanics (MM) methods have also proven adequate. Unlike quantum mechanical methods which involve calculations of atomic orbitals, MM methods calculate energies of molecules based on contributions from non-bonding interactions (van der Waals or Lennard-Jones 6-12 relations), dihedral angles, electrostatic interactions, bond stretching and bond torsions. This algorithm has proven particularly useful for polymers, since large numbers of atoms can be involved and computation times are much faster than semi-empirical methods.

The MM method therefore calculates the energies associated with a given arrangement of atoms. This is useful for studying the energetics of motions such as rotations of a phenyl ring within a given structure. This computational method is also useful for locating an optimal geometry for a given molecule.

2.7 References

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Chapter 3 Polymer Syntheses and Characterizations

3.1 Preparation of Dibenzoylbiphenyl (DBBP) Monomers

The dibenzoylbiphenyl (DBBP) polymers shown in Figure 3.1 (series I) were prepared from difluoride monomers containing the DBBP moiety. The reaction scheme for the preparation of these monomers is shown in Scheme 3.1. An appropriately substituted chlorobenzoyl chloride (6-8) was reacted via a Friedel-Crafts acylation reaction with fluorobenzene, yielding the corresponding chlorofluorobenzophenones (9-11). These intermediates were purified and then dimerized via a nickel (0)-catalyzed coupling reaction to produce monomers 12-14, depending on the structure of the initial starting material. The purity of the monomers was verified by comparing previously reported melting points for these compounds.^{1,2}

3.2 Polymer Syntheses

All polymers were synthesized by standard nucleophilic polycondensation reaction using stoichiometric amounts of a difluoride monomer and a bisphenol, shown in scheme 3.2. The structures of the bisphenols used for polymerizations are based on "Ar" groups in Figure 3.1. The polymers are named according to the structures of the dihalide monomers (ie. 22-, 33-, 44-, NP-) and the bisphenols (ie. -BPA, -HQ, -BP, -6F, -FL, -SP or -TMB). PEEK analogues prepared from 4,4'-difluorobenzophenone (series III in

Series I

Ar = BPA, HQ, BP, 6F, FL, TMB

Series II

Figure 3.1 Polymers studied in this work.

Series III

6: 4-Cl
7: 3-Cl
8: 2-Cl

AlCl_3

9 : 4-Cl
10: 3-Cl
11: 2-Cl

$\text{NiBr}_2, \text{Zn}, \text{Ph}_3\text{P}$
DMAc

12 : 4,4'-bis(4-fluorobenzoyl)biphenyl
13 : 3,3'-bis(4-fluorobenzoyl)biphenyl
14 : 2,2'-bis(4-fluorobenzoyl)biphenyl

Scheme 3.1

Synthetic scheme for difluoride monomers used to prepare poly(arylene ether ketone)s containing DBBP units.

Scheme 3.2 Nucleophilic polycondensation scheme for the preparation of poly(arylene ether ketone)s.

Figure 3.1) will be named **TBPK**, **COPK** and **TMBPK** for tert-butyl-PEEK, the tert/di-tert butyl copolymer and tetramethylbiphenyl-PEEK, respectively.

3.2.1 Synthesis of Polymers Containing Dibenzoylbiphenyl (DBBP) groups

Polymers containing 3,3'-DBBP were synthesized with monomer **13** and the bisphenols based on "Ar" groups shown in Figure 3.1. Polymerizations were carried out in chlorobenzene/TMSO₂ in the presence of excess potassium carbonate. The reaction temperature was increased to 180-200 °C within a period of 30 min. The solid content in solution was between 40-50% at the start of the reaction, and decreased as the water formed during the polymerization was quickly removed together with chlorobenzene as an azeotrope. A relatively high concentration of monomers is desired in the reaction mixture to minimize the formation of low molecular weight cyclic compounds. After 3-4 h, the brown, homogeneous reaction mixture darkened and the viscosity increased. At times the increase in viscosity stopped the stirring bar, more TMSO₂ was added to resume normal stirring. Since monomer **SP** contains an electron withdrawing sulfone group and is less nucleophilic than other bisphenols, the reaction temperature was raised as high as 220 °C to maintain the reaction. More time was allowed for the viscosity of this reaction mixture to increase. The polymerization mixture was then cooled to approximately 50°C and diluted with 20 mL of chloroform. The polymer was isolated by transferring the mixture to a 1000 mL beaker containing 500 mL of methanol. The methanol was stirred

during the addition of the polymer solution. After drying the polymer fibres, the polymer was fractionated by dissolving in 80 mL of chloroform, filtering through celite into a vacuum flask and reverse precipitating the polymer by adding methanol. Polymerizations of 336F and 33FL were carried out on larger scales (15 mmol) to provide enough polymer for gas-transport and mechanical characterization. Identical conditions were used with proportionately scaled up quantities of reagents. Polymerizations of these mixtures took longer (approx. 6 h) for the viscosity of the polymerization mixture to reach maximum viscosity.

The reactions for polymers containing 2,2'-DBBP groups were carried out in NMP with toluene as an azeotroping solvent. The temperature was maintained at about 130 °C for 2-3 h, to allow the water-toluene azeotrope to be removed from the reaction system. Polymerizations of 226F, 22FL and 22TMB were carried out on larger scales (15 mmol) for gas-transport and mechanical characterization. For these larger-scale polymerizations, identical reaction conditions were used, with proportionately scaled up quantities of reagents. Distillation of the water-toluene azeotrope, however, occurred over a period of approximately 4 h. The reaction temperature was then increased to 160-180 °C to effect the polycondensation. Once the viscosity increased, the progress of the polymerization reactions were monitored by measuring the apparent molecular weights by GPC of samples from the reaction. Polymer degradation via the cleavage of the ether

linkage in NMP or TMSO_2 can occur if the polymerization temperatures are too high, or the reactions were allowed to proceed for a long period of time.

3.2.2 Poly(arylene ether ketone)s containing naphthalene groups

High molecular weight polymers **NP6F** and **NPFL** (series II in Figure 3.1) used for mechanical relaxation studies and gas-transport characterization were supplied by J. Douglas (Carleton University). The syntheses of monomers and polymers has been reported elsewhere.⁴

3.2.3 Poly(ether ether ketone)s prepared from 4,4'-difluorobenzophenone

Polymer **TMBPK** was prepared with 4,4'-difluorobenzophenone and 2,2',6,6'-tetramethyl-4,4'-diphenol (**TMB**), provided by J. Roovers (National Research Council of Canada). The polymerization of **TMBPK** was carried out using an identical procedure for polymers containing 2,2-DBBP groups. The measured T_g of this polymer was consistent with a previously reported value.⁵ High molecular weight substituted PEEK polymers **TBPK** and **COPK** were supplied by J. Roovers as fibers and were polymerized using previously reported methods by reacting 4,4'-difluorobenzophenone with substituted hydroquinones.⁶ Polymer **TBPK** was prepared with 2-tert-butyl-1,4-hydroquinone; polymer **COPK** was prepared with a 2:1 mixture of 2-tert-butyl-1,4-hydroquinone and 2,5-di-tert-butyl-1,4-hydroquinone.

3.3 Characterizations of polymers

This section examines the characteristics such as molecular weight and morphology. Thermal and mechanical properties such as T_g are compared for the various polymers and discussed with respect to the structures of the poly(arylene ether ketone)s. Particular emphasis is placed on the substitution patterns in the DBBP containing polymers.

3.3.1 Molecular Weights

At low molecular weights, polymers show a strong dependence between molecular weight and their properties. Once the molecular weight has reached a sufficiently high value, their properties become relatively constant, as illustrated below in Figure 3.2 for the dependence of T_g on molecular weight.⁷ Polymers supplied for this work were all previously determined to have high molecular weights. The molecular weight characteristics for the poly(arylene ether ketone)s containing 2,2'-DBBP and 3,3'-DBBP units are shown in Table 3.1 and Table 3.2, respectively. The characteristics of polymer 44BPA are also shown in Table 3.1. All of the molecular weight characteristics were determined to be sufficiently high, as evidenced by measurements with GPC and viscometry. Polymer 33BP containing a 3,3'-DBBP group and a 4,4'-diphenol connector was only partially soluble in chloroform, and its viscosity was determined using TCE.

Figure 3.2 Dependence of T_g on molecular weight. Molecular weight axis shown on logarithmic scale.

The GPC of this polymer was obtained from the soluble fraction in chloroform. The intrinsic viscosity was 1.10 dL/g and apparent weight-average molecular weight M_w was above 10^4 , indicating that the molecular weight of the polymer was suitably high. Polymer 44BPA showed the lowest M_w of all the polymers. Reasons for such a low molecular weight may be related to the purity of the monomer (which was pale yellow, despite repeated recrystallizations). This polymer, however, was able to form a tough film with good mechanical properties, indicating that its molecular weight is acceptable. Since properties such as T_g are relatively constant once a high molecular weight is

Table 3.1

Apparent molecular weights, intrinsic viscosities and T_g 's of poly(arylene ether ketone)s containing 2,2'-DBBP groups and 44BPA.

Polymer	-A-	[η] _{int} (dL/g)	M _w × 10 ⁴	M _N × 10 ⁴	T _g (°C)
<div style="display: flex; justify-content: space-around; align-items: center;"><div style="text-align: center;"> <p>2,2-DBBP</p></div><div style="text-align: center;"> <p>4,4-DBBP</p></div></div>					
22BPA		0.60	10.4	5.70	172
22HQ		0.68	14.8	7.23	175
22BP		1.1	20.1	8.32	193
226F		0.62	12.8	6.43	178
22FL		0.74	15.2	7.53	228
22TMB		1.5	38.0	22.1	233
44BPA		0.52	5.51	2.83	186

Table 3.2

Apparent molecular weights, intrinsic viscosities and T_g 's of poly(arylene ether ketone)s containing 3,3'-DBBP groups.

Polymer	-A-	$[\eta]_{\text{int}}$ (dL/g)	$M_w \times 10^4$	$M_N \times 10^4$	T_g (°C)
33BPA		0.71	11.0	5.44	154
33HQ		0.62	10.4	4.23	155
33BP		1.10	10.1	4.67	164
336F		1.01	21.3	10.5	159
33FL		0.50	9.72	3.89	212
33SP		0.57	8.54	4.39	181

achieved, all properties are relatively insensitive to the slight molecular weight differences observed in viscosities.

3.3.2 Morphologies of Polymers

Apart from T_g 's, the DSC curves for these polymers showed no crystallization exotherms up to 400 °C, suggesting that all polymers were amorphous. Semi-crystalline behaviour is known to be promoted by linearity in the repeat unit, which allows close packing of the polymer chains. Although it was possible to synthesize polymer **44BPA** in high molecular weight, other polymers containing 4,4'-dibenzoylbiphenyl (DBBP) groups precipitated during polymerization in TMSO_2 due to crystallization of oligomers. Some polymers prepared by Mohanty *et al* containing 3,4'- and 4,4'-substituted biphenyl groups polymerized with bisphenol **BP** showed semi-crystalline behaviour.^{8,11} Preparation of these polymers was achieved by preparing high molecular weight precursor polymers.

Polymers **TBPK** and **COPK**, which encompass the addition of pendent groups to the repeat unit of PEEK, showed amorphous character from the DSC curves. Thus, these pendent groups are sufficiently bulky to suppress chain packing for crystallization, as is observed for PEEK. Semi-crystallinity has been observed, however, for methyl-substituted PEEK.⁹ Therefore, the size of the pendent group is also important for preventing chain packing. Moreover, the incorporation of pendent groups does not

necessitate an amorphous morphology. Attempts to prepare di-tert-butyl-PEEK, shown below in Figure 3.3, yielded oligomeric precipitate during polymerization. Polymer COPK was prepared in order to increase the tert-butyl content and preventing semi-crystalline behaviour. Thus, regularity in the repeat structure is also important in promoting chain packing during crystallization.

Figure 3.3 Structure of 2,5-di-tert-butyl-PEEK

3.3.3 Glass-Transition Temperatures (T_g)

The glass-transition temperatures (T_g) determined by the mid-point of the baseline shift in DSC curves are listed in Table 3.1 and 3.2 for poly(arylene ether ketone)s containing 2,2'- and 3,3'-DBBP groups, respectively. All of the DBBP series polymers have T_g 's higher than 145 °C, the T_g of PEEK, indicating that these polymers have more rigid backbones than PEEK.

The T_g 's of polymers containing 2,2'- and 3,3'-DBBP groups show that rigid or bulky bisphenol groups consistently hinder large-scale molecular motions. The observed trends in T_g 's with respect to the bisphenol connectors have also been observed with other

previously reported poly(arylene ether ketone)s.^{8,10} The effect of substituting hydrogen atoms in the isopropylidene moiety in BPA containing polymers for fluorine atoms (bisphenol 6F) shows that T_g is not significantly changed. This is due to the similarity in flexibility of the isopropyl linkage in the polymer, despite additional bulkiness from the larger fluorine atoms. The very high T_g 's observed for polymers 22FL and 33FL, prepared with 9,9-bis(4-hydroxyphenyl)fluorene (FL) are attributed to the bulky cardo structure of this group, which inhibits large-scale polymer chain motions. Other polymers prepared with this cardo group also showed very high T_g 's.¹⁰

The effect of the biphenyl substitution on T_g for DBBP containing polymers is illustrated in Figure 3.4. Data for 3,4'-DBBP and other 4,4'-DBBP containing polymers were previously reported in the literature.^{5,11} The trends in T_g followed 4,4'- > 3,4- = 2,2'- > 3,3'-. Except for the 2,2'-DBBP polymers, it is apparent that there is an increase in T_g with increased linearity in the polymer repeat structure. This apparent increase is most probably due to the decreased degrees of freedom for more linear structures. Substitution at the 2,2'-DBBP moieties, however, sterically hinders mobility of the biphenyl group, inhibiting larger-scale molecular motions. A similar trend for T_g with respect to substitution patterns is apparent for poly(arylene ether ketone)s containing p-, m- and o-dibenzoylbenzene groups, illustrated in Figure 3.5.^{10,12} These polymers show that meta substitution yields the lowest T_g for these polymers. Moreover, the T_g of the p-dibenzoylbenzene polymer (166 °C) is lower, compared to its 4,4'-DBBP analogue

Figure 3.4 Effect of biphenyl substitution pattern on T_g 's for poly(arylene ether ketone)s

Substitution	Repeat unit	T _g (°C)	E' (GPa)	Core Angle (deg)	Ref.
para-		166	2.69	180°	9
meta-		153	2.62	120°	9
ortho-		182	2.10	60°	11

Figure 3.5 Properties of poly(arylene ether ketone)s containing dibenzoylbenzene moieties prepared with bisphenol-A.

(182 °C). Thus, the incorporation of a biphenyl group increases the rigidity of the polymer backbone. DeSimone successfully correlated T_g 's of several polymers to the core-angle of the repeat unit, where lower T_g 's were observed at angles lower than 180 °.¹³ Except for the high T_g observed for the o-substituted polymer, this correlation appears to work for dibenzoylbenzene polymers. Such a correlation for 2,2'- and 3,3'-DBBP groups, however are hampered by the dependence of the core angle on the torsion angle within the biphenyl group and the orientation of the substituents. Spectroscopic measurements have confirmed that significant torsion exists in the biphenyl group of polymers with 2,2'-DBBP groups. The FT-IR and FT-Raman spectra of polymers **22BPA**, **33BPA** and **44BPA** and PEEK are illustrated in Figure 3.6 and 3.7, respectively. These spectra reveal useful information regarding the conformations of these polymers. Figure 3.8 illustrates the 4,4'-DBBP moiety. Because of the potential for extensive π -overlap, near coplanarity is expected in the biphenyl to extend π -overlap across the DBBP group.

Figure 3.8 4,4'-dibenzoylbiphenyl (DBBP) moiety

Conjugated carbonyl stretches can be studied by IR or Raman spectroscopy since conjugation shifts frequencies for C=O stretches to lower wavenumber due to decreased

Figure 3.6 FTIR spectra of PEEK and DBBP-containing polymers 22-, 33- and 44BPA.

Figure 3.7 FT-Raman spectra of PEEK and DBBP-containing polymers 22-, 33- and 44BPA.

double-bond character.¹⁴ For example, Nguyen and Ishida observed that the C=O frequency shifted from 1655 cm^{-1} to 1648 cm^{-1} in PEEK upon crystallization, due to coplanarity of the carbonyl group and adjacent phenyl ring in the PEEK crystal.¹⁵ Polymer **44BPA** contains a linear 4,4'-biphenyl moiety and exhibits the lowest C=O stretching frequency (1657 cm^{-1}), while polymer **22BPA** with the 2,2'-biphenyl group exhibits the highest C=O stretching frequency (1663 cm^{-1}). Similarly, the FT-Raman spectra show that the intensity of the C=C band ($\sim 1600\text{ cm}^{-1}$) for **44BPA** has been enhanced, suggesting that the 4,4'-DBBP polymers benefit from conjugation across the biphenyl group. These effects are not observed for **22BPA** suggesting that steric crowding of the 2,2'-biphenyl groups forces the biphenyl to be non-coplanar, suppressing any conjugation across the biphenyl. Although **33BPA** does not have steric hindrance to the biphenyl group, meta-substitution of the benzene rings prevents conjugation across the biphenyl group.¹⁶ These conclusions are supported by previous studies on the UV-visible absorption of compounds containing DBBP moieties in chloroform.¹⁶

Polymers **NP6F** and **NPFL** had T_g 's of 190 and $260\text{ }^{\circ}\text{C}$, respectively. The high T_g 's of these polymers are attributed to the bulky 1,4-naphthalene group which effectively inhibits large-scale molecular motions which occur at T_g . Furthermore, the T_g 's of these polymers are higher than those of the .BBP analogues prepared using identical bisphenols, indicating that the naphthalene-containing polymers have more rigid backbones than the biphenyl containing polymers.

The T_g 's for substituted PEEK polymers **TBPK** and **COPK** are 176° and 191 °C, respectively. Both polymers have T_g 's above PEEK's T_g of 145 °C, which is consistent with previous observations that T_g is increased by the addition of pendent groups. The effect of increasing the number of tert-butyl groups on the polymer backbone on T_g is demonstrated by polymers **TBPK** ($T_g = 176$ °C) and **COPK** ($T_g = 191$ °C). Polymer **COPK**, a co-polymer prepared from a 1:2 mixture of di-tert-butyl-hydroquinone and tert-butyl hydroquinone, polymerized with difluorobenzophenone shows an increase in T_g (~15 °C), indicating that increasing the number of pendent groups on the polymer backbone also increases T_g . PEEK with a methyl substituent (shown below) has been previously reported to have a T_g of 150 °C.⁶ This polymer, along with **TBPK** and PEEK demonstrate that increasing the size of the pendent group also increases T_g . This effect, however, is limited since long aliphatic chains as substituents are known to exert plasticizing effects on the polymer, thereby lowering T_g .¹⁷

Figure 3.9 Structure of methyl-substituted PEEK.

The effect of inserting a benzophenone moiety in the polymer backbone is illustrated by comparing polymers **22TMB** and **TMBPK** to afford 2,2'- substitution on

the resulting biphenyl moiety, shown in Figure 3.10. The T_g 's for **22TMB** and **TMBPK** are 233 and 240 °C, respectively. Both show significantly higher T_g 's than the other structures described in this work (except **NPFL**), due to the bulky structure of the tetramethylbiphenyl connector. Other previously reported polymers containing the tetramethylbiphenyl connector also showed relatively high values for T_g .¹⁸ Comparison of the T_g for the two polymers, however, shows that insertion of the benzophenone moiety decreases T_g . Polymer **TMBPK** has a more linear structure than **22TMB** and the apparent decrease in T_g may be due to the higher degrees of freedom for motions in polymer **22TMB**.

3.3.4 Thermo-oxidative Stabilities, Kinetics and Isothermal Aging Studies

It is useful to consider the thermal stabilities of these materials and study the influence of the biphenyl substitution patterns for **DBBP** polymers. Knowledge of the thermal stabilities of materials is particularly important when considering the use of polymers in high temperature environments. Techniques useful for assessing thermal stabilities include single TG scans, isothermal TG experiments and activation energies determined from TG experiments at several heating rates. The decomposition temperatures measured at 5% weight loss (T_d) from TG scans at 10 °C/min for 2,2'- and 3,3'-**DBBP**-containing polymers are compared in Tables 3.3 and 3.4, respectively. All

5. **Table 3.3**

Decomposition temperatures, T_d , corresponding to 5% weight loss for poly(arylene ether ketone)s containing 2,2'-DBBP groups and **44BPA**. Determined using TG at 10 °C/min. with either air or N_2 at 200 mL/min purge.

<div> 2,2'-DBBP </div>	<div> 4,4'-DBBP </div>		
Polymer	-A-	$T_d (N_2)$	T_d (air)
22BPA		472	472
22HQ		505	505
22BP		518	514
226F		518	516
22FL		520	520
22TMB		443	441
44BPA		462	445

Table 3.4

Decomposition temperatures, T_d , corresponding to 5% weight loss, for poly(arylene ether ketone)s containing 3,3'-DBBP groups. Determined using TG at 10 °C/min, with either air or N_2 at 200 mL/min purge.

Polymer	-A-	T_d (N_2)	T_d (air)
33BPA		498	479
33HQ		517	513
33BP		526	514
336F		514	491
33FL		562	531
33SP		511	536

Figure 3.10 Poly(arylene ether ketone)s **TMBPK** and **22TMB**, prepared with 2,2',6,6'-tetramethylbiphenyl-4,4'-diphenol.

the T_d temperatures are close to $500\text{ }^{\circ}\text{C}$, suggesting these polymers have excellent thermal stabilities. The lowest T_d value ($443\text{ }^{\circ}\text{C}$) was obtained for polymer **22TMB**. This observation can be rationalized in terms of the weaker sp^3 hybridized bonds in the CH_3 groups. Generally, higher stabilities are obtained for materials with greater bond strengths in the repeat units. For example, polymers **22-**, **33-** and **44BPA** containing sp^3 hybridized carbon atoms in the isopropyl groups had lower T_d 's compared to polymers **22-** and **33HQ**, which didn't have these weaker bonds. Even higher T_d 's were observed for polymers **22BP** and **33BP** which contained 4,4'-biphenyl groups. These higher T_d 's are believed to be due to the π -orbital system across the biphenyl, which would help stabilize this structure.

Polymer **44BPA** had a T_d in nitrogen of 462 °C, the lowest T_d for the polymers prepared with **BPA**. It was expected that the extensive π -overlap in this polymer would have increased the thermal stability of the polymer. The expected thermal stability, however, may be offset by the comparatively low molecular weight for polymer **44BPA** ($M_w = 5.51 \times 10^4$), since thermal stabilities are also influenced by the amount of polymer chain end-groups.

The T_d 's for PEEK analogues **TBPK**, **COPK** and **TMBPK** are listed in Table 3.5. Polymers **TBPK** and **COPK** had T_d (N_2) values of 490 and 492 °C, respectively. These polymers which were supplied to the author had similar molecular weights. Thus, increasing the tert-butyl content in these polymers has not affected the thermal stability of the material. Polymer **TMBPK** had a significantly lower T_d , compared to the other PEEK analogues. This behaviour parallels that described for **22TMB**, whose stability was decreased by the presence of the methyl groups attached the biphenyl moiety.

TG kinetics experiments at different heating rates and isothermal aging tests were performed on polymers **22-**, **33-** and **44BPA** to compare the relative thermal stabilities of the different biphenyl substitution patterns. The variable heating rate method derived by Ozawa and Flynn require that temperatures corresponding to fixed reaction conversions (α , be used when correlating heating rates ($\log \beta$) and decomposition temperatures ($1/T_d$). For the **DBBP** containing polymers, T_d 's were measured at 2 and 5 % weight loss. These weight losses were assumed to represent 2 and 5 % reaction conversions,

Table 3.5 Decomposition temperatures, T_d taken from 5 % weight loss for PEEK analogues prepared with 4,4'-difluorobenzophenone. T_d 's determined by TG at 10 °C/min, and purged with 200 mL/min air or N_2 .

Polymer	T_d (N_2)	T_d (air)
TBPK	490	461
COPK	492	463
TMBPK	457	396

respectively. This assumption was made since the entire polymer was available to the formation of volatile products. Furthermore, a reference point for 100 % conversions could not be accurately established since slow diffusion of volatile products caused the sample weights to continue decreasing, even after TG scans reached 1000 °C and held for about 30 minutes. Figure 3.11 shows plots for $1/T_d$ versus $\log \beta$ for 22-, 33-, and 44BPA at 5% weight loss. Values for E_a were determined from the slopes of the least-squares regression lines and equation 3.1.

$$\text{slope} = \frac{-0.4567 \cdot E_a}{R} \quad 3.1$$

Figure 3.11 Arrhenius plots for decomposition temperatures (T_d) as a function of TG scan rates. T_d 's measured at 5% weight loss.

These plots follow a reasonably good linear relationship, as required for this type of analysis. The values for E_a determined from the slopes of these plots are given in Table 3.6. The values for E_a were reasonably close to the activation energy for PEEK of 230 kJ/mol, previously reported by Day and co-workers.¹⁹ Polymers which contained sp^3 hybridized carbon atoms (polymers prepared with BPA) showed lower values for E_a since their lower bond strengths decrease thermal stabilities.

The E_a 's for BPA polymers with different biphenyl substitutions show that **44BPA** has a slightly higher activation energy compared to **22** and **33BPA**. Despite this apparently higher activation energy, all measured T_d 's for **44BPA** were below those measured for **22BPA** and **33BPA**. Similarly, E_a 's for polymers **33HQ** and **33BP** show that **33HQ** has higher E_a 's, while comparison of their T_d 's (517 °C and 526 °C for **33HQ** and **33BP**, respectively) suggest the opposite. The reasons for the inconsistencies between E_a values and T_d 's are unclear. It is known, however, that variations in samples such as molecular weight, sample mass and particle size can play a role in variations of E_a , thereby limiting relationship between E_a and polymer structure.²⁰

Isothermal aging experiments at 400 °C on **22**, **33** and **44BPA** are shown in Figure 3.12. After 100 minutes of aging, the decomposition of **22BPA** proceeds more quickly and shows a similar weight loss profile as **33BPA**. Both **33BPA** and **22BPA** show greater weight losses compared to **44BPA** after 100 minutes. These experiments suggest that when considering long term thermal stabilities, **44BPA** benefits from

additional stability not available to polymers 22- or 33BPA. These results also suggest that long term thermal stabilities cannot be compared through T_d 's, possibly due to the quick scanning times associated with single scan TG experiments.

Table 3.6 Activation energies (E_a) for DBBP containing polymers determined from TG kinetic experiments.

Polymer	$\alpha = 2\%$	$\alpha = 5\%$
	E_a (kJ·mol ⁻¹)	E_a (kJ·mol ⁻¹)
22BPA	176	166
33BPA	164	168
44BPA	187	193
22HQ	206	222
33HQ	222	222
22BP	213	256
33BP	206	207

Isothermal aging studies were performed on polymers 22BP, 22HQ and 22BPA, to compare the influence of the bisphenols on the thermal stabilities of these polymers. The isotherms at 400 °C, shown in Figure 3.13 demonstrate that degradation of 22BP, containing a biphenyl connector group, proceeds more slowly compared to 22HQ,

Figure 3.12 Effect of biphenyl substitution pattern on TG isotherms at 400 °C for poly(arylene ether ketone)s containing 2,2'-, 3,3'- and 4,4'-DBBP groups.

Figure 3.13 Effect of bisphenol connector groups of DBBP-containing polymers at 400 °C.

containing a 1,4-phenyl connector. Therefore the incorporation of a biphenyl group in the polymer backbone increases thermal stability. These findings are consistent with T_d 's determined in nitrogen for polymers containing **HQ** and **BP** connector groups. Although influences from the molecular weight of **44BPA** prevent correlation between T_d and biphenyl substitution patterns, isothermal TG experiments suggest that the 4,4'-DBBP group does contribute to thermal stability of poly(arylene ether ketone)s. It is therefore believed that high molecular weight **44BPA** would demonstrate additional thermal stability in single-scan TG experiments, due to the the extensive π -system in the 4,4'-DBBP moiety.

3.3.5 Degradation Products

The degradation products of materials can be an important factor when considering potential applications. Thermal degradation products from PEEK have been determined by Thermogravimetry-Mass Spectrometry (TG-MS) by Day and co workers.²¹ In their work, phenol was identified as the most significant degradation product. Other minor products were dibenzylfuran and benzene. From the observed degradation products, they postulated that the mechanism for the degradation of PEEK was random chain scission, in which the gaseous products were cleaved from the polymer chain via a radical mechanism.

TG-FTIR experiments were performed on polymers containing DBBP groups to determine if these polymers behaved similarly to PEEK during thermal degradation, and if degradation products were influenced by the biphenyl substitution pattern. Although FTIR spectra were collected throughout the TG scans, only spectra collected during the TG weight loss revealed degradation products being evolved from the sample. The spectra collected at the same time as the DTG peak were examined closely to identify thermal degradation products. Figure 3.14 shows the TG-FTIR spectra for polymers 22-, 33- and 44BPA and reference spectra which closely matched the observed FT-IR peaks. These products are structurally related to the segments found in the repeat structure, such as phenol, carbon monoxide and bisphenol-A. Biphenyl was expected as a degradation product, but was not found in the TG-FTIR spectra. Its high boiling point (254-255 °C) may have prevented it from reaching the FTIR gas-cell since the transfer line was maintained at 230-240 °C. The observed degradation products suggest that simple chain scission is also occurring in these polymers, in agreement with conclusions drawn from studies with PEEK by Day *et al* for PEEK.²¹

3.3.6 Mechanical Properties

The relative rigidities of the polymers containing DBBP units can be compared from the Young's moduli (E'). The tensile moduli for these polymers were determined using thermo-mechanical analysis (TMA) operated in Stress-Strain mode on thin solvent-

Figure 3.14 TG-FTIR spectra of DBBP-containing polymers 22BPA, 33HQ and 44BPA with matching compounds from spectral libraries.

cast films. The E' values for polymers **22-** and **33BPA-FL** at room temperature are listed in Table 3.7. The values listed show that E' values are similar for all the polymers shown, suggesting that the moduli are not affected by the change in the substitution pattern. Higher E' values are obtained compared to the poly(arylene ether ketone)s containing o-, m and p-dibenzoylbenzene moieties, illustrated in Figure 3.5. The moduli of these polymers were reported to be 2.10¹², 2.62 and 2.69 GPa, respectively¹⁰, compared to moduli of 3.0 GPa or higher for polymers containing DBBP moieties. The generally lower values for the Young's modulus suggest that the incorporation of the biphenyl unit in the polymer backbone has lead to an increase in the rigidity of the polymer. These results also suggest that the overall rigidity of the polymer backbone contributes to the modulus more than the substitution pattern. Polymer **22BP**, derived from 4,4'-diphenol also has a high modulus, suggesting that the additional rigidity from the extra biphenyl group may contribute to the high modulus. The low modulus observed for polymer **33BP**, which also contains the 4,4'-diphenol connector, may be related to residual TCE in the film. TCE has a higher boiling point (147 °C) compared to chloroform (61 °C) and is therefore more difficult to remove.

Table 3.7. Young's Moduli determined using TMA/SS at 25 °C for poly(arylene ether ketone)s containing 2,2'- or 3,3'-DBBP units.

Polymer	E' (GPa)	Polymer	E'(GPa)
22BPA	3.4	33BPA	3.8
22HQ	3.9	33HQ	3.2
22BP	4.6	33BP	3.0
226F	3.5	336F	3.3
22FL	4.2	33FL	4.7

3.4 Conclusions

The glass-transition temperatures (T_g) of the polymers are influenced by the connector groups in the backbone and the linearity of the repeat unit. Bulky and rigid connector groups and linear repeat structures all exhibit higher values for T_g . Steric hindrance to chain mobility for 2,2'-DBBP polymers give these polymers high T_g 's. Spectroscopic studies by FTIR and FT-Raman confirm that the 4,4'-DBBP unit exhibits the expected π -overlap. Moreover, non-coplanarity of the sterically hindered 2,2' DBBP is also observed spectroscopically. Isothermal TG experiments reveal that incorporation of a biphenyl group in the polymer backbone increases its thermal stability. Although the

low molecular weight of **44BPA** gives the polymer low T_d in single scan TG experiments, isothermal experiments suggest that extensive π -overlap in 4,4'-DBBP does contribute to long term thermal stability, since **44BPA** showed smaller weight loss than polymers **22-** and **33BPA**. Activation energies determined for these polymers show reasonable agreement with a previously reported value for PEEK. Identification of degradation products by TG-FTIR suggest that the DBBP- containing polymers undergo random scission reactions during thermal degradation, yielding small molecules related to polymer segments. This behaviour for DBBP-containing polymers is also consistent with previous studies on PEEK. TG-FTIR studies revealed that carbon monoxide and phenol were observed as major degradation products. The insertion of a biphenyl unit appears to increase T_g for linear para- substituted structures, but decrease it for non-linear structures. The insertion of the biphenyl units also appears to increase the moduli of films.

3.5 Experimental

3.5.1 Materials

N-Methyl-2-pyrrolidinone (NMP), tetramethylene sulfone (TMSO₂), 1,1,2,2-tetrachloroethane (TCE), fluorobenzene, triphenylphosphine (Ph₃P), zinc powder, o-,m- and p chlorobenzoyl chlorides were purchased from Aldrich Chemical Co. and used as received. Anhydrous NiBr₂ was obtained by heating its hydrate (Aldrich Co.) under vacuum at 100 °C for 48 h. N,N-Dimethylacetamide (DMAc) (Aldrich Co.) was distilled

over P_2O_5 . All bisphenols: 1,4-hydroquinone, **HQ**; 4,4'-isopropylidenediphenol, **BPA**; 4,4'-diphenol, **BP**; 4,4'-(hexafluoroisopropylidene)diphenol, **6F**; 9,9-bis(4-hydroxyphenyl)fluorene, **FL**; 4,4'-sulfonyldiphenol, **SP**; 3,3',5,5'-tetramethyl-4,4'-diphenol, **TMB** were purified by recrystallization.

3.5.2 Monomer syntheses

Monomers **12** and **14** were obtained from previously carried out syntheses, using a procedure identical as that used for the synthesis of monomer **13**, described below. Monomer **12** was purified by recrystallization from chlorobenzene (mp 266.0-268.0 °C, lit.² mp 269.0-270.0 °C). Monomer **13** was purified by recrystallization from a 1:1 (v/v) chloroform-ethanol mixture (mp 168-170 °C, lit.² mp 163.5-166.5 °C). Monomer **14** was purified by recrystallization from a 1:1 (v/v) acetone-methanol mixture (mp 148.0-150.0 °C, lit.¹ mp 148.5-149.0 °C).

3-Chloro-4'-fluoro-benzophenone (**10**)

A 1 L three-necked, round-bottomed flask was equipped with a mechanical stirrer and m-chlorobenzoyl chloride (86.19 g, 0.496 mol) and fluorobenzene (400 mL). Aluminum chloride (85.33 g, 0.640 mol) was then added to the reaction mixture through a solid addition funnel. The reaction was stirred at 5-10 °C for 1.5 h, then at 50-60 °C for an additional 3 h. The orange-yellow reaction mixture was quenched with water, and the

product was extracted with chloroform. The chloroform extracts were dried over sodium sulfate. The solvent was evaporated in vacuo and the residue was distilled under vacuum to give the desired product as solid: 109.98 g (95.3%); mp 75.0-77.0 °C (lit.²² mp 77.5-78 °C); ¹H NMR (200 MHz, CDCl₃) δ 7.18 (t, 2 H, 8.5 Hz), 7.86 (m, 2H), 7.81 (m, 1 H), 7.70 (d, 1 H, J = 18 Hz), 7.59 (d, 1 H, J = 13 Hz), 7.43 (t, 1 H, J = 7.6 Hz, 8.0 Hz); IR (KBr, cm⁻¹) 1648 (C=O), 1281 (C-F), 752 (C-Cl); MS (EI, m/z, relative intensity) 234 (25.8), 199 (4.2), 139 (19.2), 123 (100.0), 111 (14.6), 95 (32.7).

3,3'-Bis(4-fluorobenzoyl)biphenyl (13)

A 2 L three-necked, round-bottomed flask equipped with a mechanical stirrer was charged with nickel bromide (4.10 g, 18.8 mmol), Ph₃P (38.1 g, 0.145 mol), zinc dust (38.1 g, 0.583 mol). A syringe was used to add DMAc (350 mL). The temperature was increased to 50 °C to generate the red Ni(PPh₃)₄ catalyst. 3-Chloro-4'-fluorobenzophenone (10) (107.59 g, 0.458 mol) was added to the mixture through the solid addition funnel. The green-brown mixture was heated further to 90-100 °C and stirred for 5 hours. The mixture returned to its red colour. The hot reaction mixture was filtered into water to yield the solid crude product. Ph₃P was removed by washing the filtrate with acetone. Zinc was removed from the crude product by dissolving it in chloroform and filtering through a pad of Celite 521 filtering agent. The chloroform was then evaporated and the product was further purified by recrystallization from

chloroform-ethanol (1:1 v/v): 73.42 g (80%); mp 168-170 °C (lit.² mp 163.5-166.5 °C); ¹H NMR (200 MHz, CDCl₃) δ 7.17 (m, 4 H), 7.75 (m, 4 H), 7.82-7.89 (m, 4 H), 7.58 (t, 2 H, J = 9.0 Hz), 8.00 (m, 2 H); IR (KBr, cm⁻¹) 1652 (C=O), 746 (C-F); MS (EI, m/z, relative intensity) 398.0 (31.6), 303.0 (23.4), 275.1 (3.5), 199.0 (2.0), 123.1 (100.0), 91.1 (38.3).

3.5.3 Polymer syntheses

Polymers containing 2,2'-DBBP groups

A typical procedure is as follows: A 100 mL three-necked, round-bottomed flask was equipped with a nitrogen gas inlet and a Dean-Stark trap. The flask was charged with 2,2'-bis(4-fluorobenzoyl)biphenyl (**14**) (2.9873 g, 7.500 mmol), BPA (1.7123 g, 7.500 mmol), potassium carbonate (2.0725 g, 15.000 mmol), toluene (50 mL) and NMP (22 mL). The reaction vessel was then purged with nitrogen (about 100 mL/min) for 20 minutes prior to heating. The reaction was heated to 110-130 °C and stirred slowly. The toluene-water azeotrope was collected in the Dean-Stark trap over a period of 2-3 h. The temperature was then increased to 170-180 °C to complete the distillation of toluene and allow the polymerization reaction to start. As the polymerization progressed, a brown viscous solution resulted. The apparent molecular weight of the polymer in the reaction mixture was determined at various time intervals by GPC. The reaction was cooled as soon as the molecular weight was deemed acceptable, and diluted with chloroform (20

mL). Polymer **22BPA** was isolated by pouring the mixture into a beaker containing methanol (about 750 mL) and further purified by reverse precipitation to remove any cyclics or oligomers, using 20 mL of chloroform per gram of crude polymer.

Polymers containing 3,3'-DBBP groups

Identical procedures for the preparation of 3,3'-DBBP polymers were used. A typical procedure for preparation of **33BPA** is as follows: A 50 mL three-necked, round-bottomed flask was equipped with a nitrogen gas inlet and a Dean-Stark trap. The flask was charged with **13** (1.1949 g, 3.000 mmol), **BPA** (0.6840 g, 3.000 mmol), potassium carbonate (0.539 g, 3.90 mmol), chlorobenzene (1.0 mL) and TMSO_2 (4.0 mL). The reaction vessel was purged with nitrogen for 20 minutes prior to heating. The reaction vessel was placed in an oil bath and heated to 160 °C over a period of 30 minutes. The water-chlorobenzene azeotrope was collected in the trap. The oil bath temperature was then increased to about 180 °C, and the reaction allowed to proceed. A higher reaction temperature (210-220 °C) was used for polymerization of **33SP**. More TMSO_2 (5.0 mL) was added once the stirring bar stopped. The reaction was cooled and diluted with 10 mL of chloroform after the viscosity increased a second time in 3-4 h. The resulting polymer was isolated by precipitation of the reaction mixture in methanol (500 mL).

33BPA: ^1H NMR (400 MHz, CDCl_3) δ 7.997 (s, 2 H), 7.78-7.79 (m, 6 H), 7.74 (d, 2 H, $J = 7.6$ Hz), 7.54 (t, 2 H, $J = 8.9$ Hz), 7.26 (d, 4 H, $J = 8.8$ Hz), 7.04-6.99 (m, 8 H), 1.70 (s, 6 H); ^{13}C NMR (50 MHz, CDCl_3) δ 195.36, 162.04, 153.36, 146.99, 140.55, 138.86, 132.65, 131.70, 130.92, 129.27, 128.98, 128.49, 119.84, 117.22, 42.51, 31.15; IR (film, cm^{-1}) 1657 (C=O) 1591, 1498 (aromatic C=C).

33HQ: ^1H NMR (400 MHz, CDCl_3) δ 8.01 (s, 2 H), 7.86 (d, 4 H, $J = 8.8$ Hz), 7.82 (d, 2 H, $J = 7.6$ Hz), 7.75 (d, 2 H, $J = 8.0$ Hz), 7.56 (t, 2 H, $J = 10.0$ Hz), 7.13 (s, 4 H), 7.05 (d, 4 H, $J = 8.8$ Hz); ^{13}C NMR (50 MHz, CDCl_3) δ 195.15, 161.80, 151.95, 140.43, 138.64, 132.58, 131.82, 130.85, 129.16, 128.88, 128.34, 121.83, 117.00; IR (film, cm^{-1}) 1656 (C=O) 1593, 1493 (aromatic C=C)

33BP: ^1H NMR (400 MHz, CDCl_3/TCE) δ 8.02 (s, 2H), 7.87 (d, 4 H, $J = 8.8$ Hz), 7.82 (d, 2H, $J = 10.8$ Hz), 7.76 (d, 2H, $J = 7.6$ Hz) 7.60-7.54 (m, 6H), 7.16 (d, 4H, $J = 8.8$ Hz), 7.08 (d, 4H, $J = 8.8$ Hz); IR (film, cm^{-1}) 1655 (C=O) 1591, 1489 (aromatic C=C)

336F: ^1H NMR (200 MHz, CDCl_3) δ 8.05 (s, 2 H), 7.91-7.74 (m, 8 H), 7.57 (t, 2 H, $J = 7.6$ Hz), 7.45-7.40 (d, 4 H, $J = 8.6$ Hz), 7.13-7.06 (m, 8 H); IR (film, cm^{-1}) 1659 (C=O) 1593, 1502 (aromatic C=C).

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33FL: ^1H NMR (200 MHz, CDCl_3) δ 8.00 (s, 2 H), 7.85-7.72 (m, 8 H), 7.58-7.23 (m, 14 H), 7.04-6.94 (m, 8 H); ^{13}C NMR (50 MHz, CDCl_3) δ 195.14, 161.60, 154.24, 150.98, 142.03, 140.54, 140.05, 138.66, 132.50, 131.71, 130.72, 129.71, 129.03, 128.86, 128.32, 127.88, 127.71, 126.02, 120.36, 119.80, 117.28, 64.52; IR (film, cm^{-1}) 1658 (C=O) 1591, 1497 (aromatic C=C).

33SP: ^1H NMR (200 MHz, CDCl_3) δ 8.02 (s, 2 H), 7.97-7.75 (m, 12 H), 7.56-7.54 (m, 2 H), 7.18-7.07 (m, 8 H); ^{13}C NMR (50 MHz, CDCl_3) δ 195.47, 160.80, 159.64, 140.89, 138.69, 137.04, 133.94, 132.06, 131.54, 130.48, 129.70, 129.42, 128.80, 119.61, 119.50; IR (film, cm^{-1}) 1657 (C=O) 1582, 1488 (aromatic C=C) 1106 (S=O).

Polymer 44BPA containing a 4,4'-DBBP group

Polymer **44BPA** was synthesized using the same procedure used for polymer **33BPA**, described above. Monomer **12** (1.1949 g, 3.000 mmol) was reacted with **BPA** (0.6849 g, 3.000 mmol) in TMSO_2 / Chlorobenzene in the presence of K_2CO_3 base. Purification of the polymer was done by reverse precipitation in a TCE solution.

44BPA: ^1H NMR (200 MHz, CDCl_3) δ 7.93-7.74 (m, 12 H), 7.33-7.28 (m, 4 H), 7.10-7.02 (m, 8 H), 1.75 (s, 6 H); ^{13}C NMR (50 MHz, CDCl_3) δ 194.83, 161.98, 153.51,

147.03, 143.81, 137.56, 132.611, 131.94, 130.73, 128.54, 127.30, 119.83, 117.31, 42.57, 31.18. IR (film, cm^{-1}) 1654 (C=O), 1498 (aromatic C=C).

3.5.4 Apparent Molecular Weight Determination, M_w and M_n

Relative molecular weights were determined by gel-permeation chromatography (GPC). A Perkin-Elmer GPC with a PL-Gel 10 μm column (1.0 cm diameter x 35.0 cm long) was used with a UV-Vis spectrophotometric detector set to measure absorption at 252 nm. Dilute chloroform polymer solutions (1 μL , ~ 4 mg/mL concentration) were injected into the chromatograph. Solutions were passed through the column at a flow of 1.0 mL/min using a Perkin-Elmer isocratic pump. Apparent number molecular weights (M_n) and weighted average molecular weights (M_w) were obtained using the GPC results by comparing the eluate retention-time profile to those obtained for commercially available polystyrene standards (Polysciences).

3.5.5 Viscosity Measurements

Viscosity measurements were also performed to ensure that high molecular weights were obtained, following synthesis. Specific viscosity η_{sp} measurements were made with chloroform solutions at 0.500, 0.333 and 0.250 g/dL concentrations. The viscosity of these solutions were measured using an Ubbelohde dilution viscometer kept in a water bath at 25.0 °C. Time corresponding to the displacement of a known volume

of solution through a capillary were measured. Specific viscosities (η_{sp}) were calculated with the following equation:

$$\eta_{sp} = \frac{t_c - t_0}{t_0}$$

where t_0 corresponds to the displacement time for the pure solvent (in seconds), and t_c the is the time for displacement of a polymer solution with concentration c . Intrinsic viscosity (η_{int}) values were obtained by plotting η_{sp}/c versus concentration and extrapolating the zero-concentration viscosity (ie y-axis intercept).

$$\eta_{int} = \left(\frac{\eta_{sp}}{c} \right)_{c=0}$$

3.5.6 Thermal Analysis

All polymer samples were characterized using thermal analysis techniques: Thermogravimetry (TG), Differential Scanning Calorimetry (DSC), Thermomechanical Analysis (TMA), each briefly described.

Differential Scanning Calorimetry (DSC)

A Seiko DSC 220C Calorimeter was operated with a heating rate of 10 °C /min and purged with nitrogen flowing at 50 mL/min. Experiments were typically run from room temperature to 350 °C. The instrument temperature and sensitivity were calibrated

with indium (mp 151 °C) and tin (mp 232 °C). Glass-transition temperatures (T_g) were assigned as the mid-point of the baseline shift (heat capacity change) in the DSC curves.

Thermogravimetry (TG)

A Seiko TG/DTA 320 was purged with 200 mL/min of either nitrogen or air. Degradation temperatures (T_d) were determined from experiments carried out at 10 °C/min from temperatures corresponding to 5% weight loss. TG kinetics studies were performed with several heating rates varying from 1.0 ° to 50 °C/min. Temperature calibrations with indium and tin were performed for each heating rate and verified by measuring the fusion temperature of zinc (mp 419.5 °C). For kinetics studies, temperatures corresponding to weight losses of 2% and 5% were measured.

Thermomechanical Analysis (TMA)

The tensile mechanical properties of the polymer films were measured using a Seiko 120C TMA/SS. The Young's modulus (E') of a film strip (length = 7.5 mm, width = 2 mm) was measured at ambient temperature (25 °C) while applying a linear load program. The sample was purged with 100 mL/min with N_2 during the experiment. The stress and strain of the sample were measured during the following load program: offset load = 5 g, initial load = 5 g, final load = 350 g, rate = 40 g/min. E' was obtained from

the slope of the stress-strain plots, and was averaged from two replicate runs for each polymer.

3.5.7 Film casting for TMA and spectroscopic measurement

Except for polymer **33BP**, all polymer films were cast from 300 mg of dried polymer in 3 mL of chloroform. Polymer **33BP** was cast using TCE. The polymers were completely dissolved in a test tube. The solution was then transferred by pipette-filtration into a cylindrical mould on a glass plate (~5 cm diameter). The mould was covered with a glass plate to allow the solvent to evaporate slowly. After the film was dry, the film was removed from the glass plate by adding water to peel off the film. The clear, circular films were then placed in a vacuum oven. The temperature of the vacuum oven was gradually raised to 120 °C, and kept under vacuum for several days.

3.5.8 FT-IR and FT-Raman Spectroscopy

A Nicolet 800 Series spectrophotometer, equipped with a FT-Raman accessory were used to collect FT-IR and FT-Raman spectra. Several sampling methods for FT-IR spectra were used: Photo-acoustic spectroscopy (PAS), and direct absorbance measurements using a thin film. For FT-IR using thin films, at least 100 sample and background spectra were collected at 4 cm⁻¹ resolution. FTIR spectra of PEEK were performed on PEEK pellets (1mm diam x 1 mm thick) prepared by pressing Victrex beads at 200 °C. PAS spectra were obtained with an MTEC photoacoustic spectroscopy

accessory. At least 500 PAS sample and background scans were collected at 8 cm^{-1} resolution with a mirror velocity of 0.32 cm/sec . FT-Raman spectra were collected from the radiation scattered from 1080 nm incident radiation from a Nd:Yag laser, at $0.3\text{--}0.4\text{ W}$ intensity. At least 500 spectra at 4 cm^{-1} resolution for both sample and white-light background were collected and averaged.

3.5.9. TG-FTIR Characterization

TG-FTIR experiments were conducted with thermogravimetry (TG) and FTIR spectroscopy. Volatile products emitted from TG experiments were transferred by a heated transfer line to a gas cell in the Nicolet FTIR spectrophotometer described above. This transfer line was heated in order to minimize loss of volatile products by condensation during transfer. The gas cell was placed inside a heating oven. The transfer line temperature was maintained at $230\text{--}240\text{ }^{\circ}\text{C}$ while the oven temperature was maintained at $260\text{ }^{\circ}\text{C}$ to prevent condensation inside the gas cell. Samples were heated from 25 to $800\text{ }^{\circ}\text{C}$, at $10\text{ }^{\circ}\text{C/min}$. After the TG temperature reached $100\text{ }^{\circ}\text{C}$, the collection of FT-IR spectra was started, collecting 12 spectra per minute. Maxima present in the 1st derivative of TG curves (known as DTG) were used to locate FTIR spectra of interest. Gram-Schmidt reconstructions (GSR) plot describe the total FTIR detector response during the TG-FTIR experiments. Peaks in the GSR were also used to locate spectra of interest. GSR plots are similar to DTG plots, although relative signal

intensities may differ because of different spectral responses for the compounds evolved during TG scans.

3.5.10 Kinetics Studies using TG

TG kinetics were determined from the TG curves of various polymer studied at different heating rates. A Seiko TG-DTA 320 was operated at heating rates of 1.0, 2.0, 5.0, 10, 20 and 50 °C/min. Each experiment were purged with nitrogen at 200 mL/min. Isothermal decompositions were also studied at temperatures of 250 °C, 300 °C and 350 °C. Sample masses were measured at 1.0 min intervals while the samples were held at these temperatures for periods of at least 24 h.

3.6 References

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Chapter 4 Segmental mobilities and Molecular Mechanics

4.1 Biphenyl and Naphthalene Containing Polymers

The $\tan \delta$ curves for the poly(arylene ether ketone)s containing dibenzoylbiphenyl (DBBP) or naphthalene groups are shown in Figure 4.1. A large increase in $\tan \delta$ above 150 °C is apparent for all polymers, except for 33FL ($T_g = 212$ °C) which broke at 170 °C. During the α transition, a peak in $\tan \delta$ is observed, and its maximum often taken as T_γ (E'' peaks have also been used). The temperatures at which large increases in $\tan \delta$ occurred agree reasonably closely with T_g 's measured by DSC. Therefore, these relatively large increases in $\tan \delta$ were interpreted as being due to the α transition.

Shoulders to the α -transitions for polymers containing 2,2'-DBBP and naphthalene groups were assigned to γ transitions. The peaks from these transitions could not be reduced by annealing and were therefore not β transitions. For polymers 336F and 33FL, containing 3,3'-DBBP groups, a broad relaxation from -50 to 100 °C is assigned to the γ relaxation. All the γ -transitions shown in Figure 4.1 are insensitive to changes in the bisphenol connector. Although bisphenols consistently influence the polymer's T_g (ie. FL gives higher T_g than 6F), they have no influence on the segmental mobilities of the polymers. The γ transitions appear at a lower temperature range for 3,3'-DBBP containing polymers, indicating that this moiety increases segmental mobility, compared to the other polymers in Figure 4.1. Thus, the segmental mobilities for polymers

Figure 4.1 $\tan \delta$ curves for poly(arylene ether ketone)s containing biphenyl and naphthalene groups

containing DBBP groups are significantly influenced by the substitution pattern on the biphenyl group, suggesting that the DBBP moiety participates in the motions associated with the γ transition.

Due to the nature of the backbone of PEEK, sub- T_g transitions must involve some localized motion of the benzene rings about their 1,4-axis. Previous studies by David and Etienne suggest that benzene ring rotations about the 1,4-axis play a role in the γ transition of PEEK.¹ Similar studies on polycarbonate by Yee and Smith, however, demonstrated that benzene ring rotations can involve synchronous rotations rather than independent rotations.² Although decreases in segmental mobilities can sometimes be attributed to *intrachain* effects, previous correlations between γ transition temperatures and Fractional Free Volume (FFV) have demonstrated that *interchain* constraints from chain packing are also significant.³

Intrachain considerations for the DBBP moieties were investigated using Molecular Mechanics (MM) computations. The energy required to twist the biphenyl group from 90-0° was calculated for 2,2'-, 3,3'- and 4,4'- substitution patterns. Both phenyl rings were coplanar at 0°. Model compounds, illustrated below in Figure 4.2 were used to model these motions.

Figure 4.2 model compounds used to study biphenyl twisting in DBBP containing polymers.

Two models were used for the 2,2'- and 3,3'-DBBP moieties, since 2 possible conformations existed for these substitution patterns in the polymer backbone. The dihedral angles for these model compounds were rotated such that the biphenyl dihedral angle ring was twisted at 10° intervals. The energies calculated at each angle are illustrated in Figure 4.3. Although different absolute energies were obtained for each compound, rotational barriers can be compared from the difference between maxima and minima in these energy curves. Only slight differences are observed for polymers with 3,3'- and 4,4'-DBBP moieties, with energy barriers of approximately 10 kcal/mol. Significantly higher rotational barriers (22 kcal/mol) were observed for the 2,2'-DBBP

Figure 4.3 Energy curves for 0-90° rotation of biphenyl group for model compounds

model compounds, with higher energies obtained for the "same-side" configuration (38 kcal/mol). These significantly higher energies for sterically hindered 2,2'-DBBP polymers support the increased rigidity of these moieties suggested by $\tan \delta$ curves in Figure 4.1.

Since the γ -transition profiles for 2,2'-DBBP-containing polymers and naphthalene containing polymers were similar, intrachain effects of the naphthalene groups were also studied by MM calculations. Rotations between dihedral angles of -90° and 270° (ie. 360° rotation, offset by 90° from 0°) were carried out for model compounds representative of PEEK and the naphthalene-containing polymers. Figure 4.4 illustrates the model compounds and the energy curves, which were offset such that the curves could be plotted on a common scale. For the PEEK model compound, a barrier height of 16 kcal/mol was observed. Significantly higher energy barriers were observed for the naphthalene model compound, with barrier heights of 30 and 42 kcal/mol. These results suggest that intrachain hindrance to the mobility within the unsymmetrical monomer contributes to its relatively high γ transition temperature.

4.2 Substituted PEEK polymers

Figure 4.5 illustrates the DMA $\tan \delta$ curves for poly(arylene ether ketone)s containing tert-butyl pendent groups. PEEK shows a characteristic broad relaxation from -100 to 0°C , which is consistent with previous studies of "wet PEEK", in which a

Figure 4.4 MM+ Energy curves for -90° to 270° rotation of naphthalene and phenyl groups in model compounds representative of PEEK and naphthalene-containing poly(arylene ether ketone)s

Figure 4.5 $\tan \delta$ curves for PEEK and poly(ether ether ketone)s containing pendent groups.

relaxation due to water at $-100\text{ }^{\circ}\text{C}$ was superimposed with 2 other transitions occurring near $-70\text{ }^{\circ}\text{C}$. Polymer **TBPK**, containing one tert-butyl substituent shows a broad $\tan \delta$ peak between -100 ° to $100\text{ }^{\circ}\text{C}$, due to a γ transition. The γ transition for **COPK**, with a backbone containing both tert- and di-tert-butyl hydroquinone connectors appears as a shoulder from $0\text{ }^{\circ}\text{C}$ to T_g . These results show that the γ relaxation temperature is systematically displaced to higher temperatures with increased tert-butyl content. The glass-transition temperatures also increase with increased in tert-butyl content, indicating that steric hindrance has influenced overall polymer chain mobility, and local segmental mobility.

4.3 Tetramethylbiphenyl Polymers

The $\tan \delta$ curves corresponding to **PEEK** and **TMBPK** and **22TMB** are shown in Figure 4.6. The α relaxations are easily identified by the large increases in $\tan \delta$, occurring at temperatures close to their T_g . Polymer **TMBPK**, which contains the benzophenone and tetramethylbiphenyl connectors shows a transition between -75° and $150\text{ }^{\circ}\text{C}$. The $\tan \delta$ curve for polymer **22TMB** steadily increases from $-75\text{ }^{\circ}\text{C}$ to T_g . A significant difference between these $\tan \delta$ curves and those discussed previously is that it was not possible to anneal the samples at high temperature due to cross-linking of the polymer at elevated temperatures. Since these films were not annealed, the $\tan \delta$ curves may have influences from β relaxations.

Figure 4.6 $\tan \delta$ curves for poly(arylene ether ketone)s containing tetramethylbiphenyl connectors

Nevertheless, the high T_g 's for these polymers ($> 230\text{ }^{\circ}\text{C}$) indicate that mobilities of the polymer chains have been significantly decreased, because of the combination of rigidity and steric hindrance caused by the methyl substituents.

4.4 Sub- T_g Transitions near $-100\text{ }^{\circ}\text{C}$

Each of the $\tan \delta$ curves shown for the poly(arylene ether ketone)s and substituted PEEK's exhibit a transition near $-100\text{ }^{\circ}\text{C}$. The relaxations appear consistent with the relaxations in PEEK at $-90\text{ }^{\circ}\text{C}$, previously attributed to the presence of water.^{4,5,6} Previous studies by Robeson *et al* suggest that water interacts with polar functional groups, such as carbonyl or sulphones. In contrast, polymers without these polar functional groups were insensitive to the presence of water, suggesting that water interacts with polar groups in the polymer chains.⁷ The transitions near $-100\text{ }^{\circ}\text{C}$ for the polymers studied in this work are insensitive to structural changes, suggesting that these peaks may also be due to the presence of water. The DMA experiments were done at ambient humidity conditions, and therefore, the presence of water could not be prevented.

4.5 Conclusions

The sub- T_g transitions studied by DMA illustrate that intrachain steric hindrances are significant in increasing the temperatures of the γ transitions. Although bisphenol connectors influence overall chain mobility (T_g), the connectors from 9,9-bis(4-

hydroxyphenyl)fluorene (FL) and hexafluoroisopropylidene-4,4'-diphenol (6F-BPA) leave the γ relaxations unaffected. The biphenyl substitution pattern in DBBP does influence the γ transition, with steric crowding at the 2,2'- substitution displacing the γ transition to a higher temperature. These findings suggest that segmental mobilities are more significantly influenced by changes in the biphenyl substitution than changes in the bisphenol, and that the DBBP group participates in the motions associated with the γ -transition. Molecular Mechanics computations also suggest that the γ -transition temperatures for DBBP- and naphthalene containing polymers are also influenced by intramolecular rotation barriers within the moieties containing these groups (ie. dihalide monomers used to prepare these polymers). The fact that 22TMB and TMBPK could not be annealed and that their $\tan \delta$ curves may contain β relaxations hamper correlations to the segmental mobilities of these polymers. Low segmental mobilities are anticipated because of their rigid and bulky connector groups. A transition near -100°C for all the polymers suggest that water may also be present in the tested films.

4.6 Experimental

4.6.1 Dynamic Mechanical Analyses

Film strips were cut from the same films used for permeability studies (1.0 mm in width and about 23 mm length). The samples were mounted in the chucks of a Rheometrics Solids Analyzer RSA II, and tested in rectangular tension mode.

Viscoelastic properties were measured from -145 °C to T_g , at 2 °C increments, with a soaking time prior to each measurement. A strain of 0.1-0.2 % in amplitude (depending on the sample) was applied at a frequency of 1 Hz. Except for polymers **22TMB** and **TMBPK**, duplicate films which were annealed below T_g were tested to ensure that β relaxations were not present in the $\tan \delta$ curves.

4.6.2 Computational Studies

Computational calculations were performed using a Molecular Mechanics algorithm to determine the energies involved with motions of various polymer backbone segments. The commercial software package HYPERCHEM version 4.5 was used, using molecular mechanics calculations with a MM+ force field. This force field is an adaptation of a previously described MM2 algorithm described elsewhere.⁶ Limitations of these models include neglects of interchain or packing effects or stabilizations resulting from π -orbital overlap.

Model compounds which approximated the environment of the motion of interest were used in these calculations. Dihedral angles including the plane of the phenyl ring of interest were changed to simulate phenyl ring rotation. The starting geometries for the model compounds consisted in the optimized structure, which was allowed to converge according to a Polak-Ribiere algorithm (a conjugate-gradient method), with a final energy gradient of 0.01 kcal/Å·mol. Following changes to a dihedral angle, the rotated angles

were restrained while the geometry of the rest of the molecule was allowed to converge to a new optimal geometry. The process of changing dihedral angles and re-optimizing the geometry was repeated at each angle increment.

4.7 References

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Chapter 5 - Gas-Permeabilities

5.1 Film Preparation

The removal of solvent is paramount for proper characterization of polymer films. Solvents can exert a plasticizing effect on the polymer, and significantly influence results from characterizations, such as gas permeability^{1,2} or T_g . In many polymer film characterizations, however, few details are given with respect to the preparations of the films, and ensuring that the casting solvent is completely removed. This section briefly discusses characterizations of polysulfone films as they were being dried and subsequently annealed.

Previous work on polymer films revealed that increasing the vacuum oven temperature too quickly can cause the polymer film to foam, due to rapid solvent evaporation. Films were therefore dried by gradually increasing the oven temperature and characterizing samples of the drying film by DSC. Figure 5.1 illustrates the DSC curves obtained for a film prepared from UDEL P3500 polysulfone (PSF), a polymer used as a reference to validate permeability measurements.

UDEL Polysulfone (PSF)

Figure 5.1 DSC curves for polysulfone films during drying program.

The endotherms occurring past T_g were due to the evaporation of chloroform from the sample. The removal of solvent is evidenced by the increase in T_g , and the decrease in endotherms at higher temperatures. Table 5.1 summarizes thermogravimetry (TG) data along with the apparent T_g 's measured by DSC. An important observation from Figure 5.1 is that removal of chloroform in polysulfone is still slow, despite the fact that the sample is under vacuum and its temperature is above the boiling point of chloroform (65 °C).

Simple FTIR depth profiles were obtained by recording Photoacoustic FTIR (PAS) measurements on several of the polysulfone samples at different mirror velocities. PAS spectra for freshly cast, partially dried and annealed PSF films are given in Figure 5.2. Chloroform was identified in the FTIR spectra by its absorption band at 759 cm^{-1} . The removal of chloroform is also evidenced in the PAS spectra by the decrease in intensity of this absorption band.

For PAS depth profiles, the penetration depths can be estimated from

$$L=(D/\pi \cdot f)^{1/2}$$

where L is the penetration depth, D is the thermal diffusivity of the sample and f is the spectrometer laser frequency (which varies with changes in mirror velocity). Thermal diffusivities may be calculated by $D=\kappa/(\rho \cdot C_p)$, where κ is thermal conductivity, ρ is density and C_p is the heat capacity. From data provided by the polymer and

Table 5.1 Thermoanalytical data obtained for polysulfone films.

Drying	Oven	solvent	DTG Peak	
time	Temp	evaporated	Temperature	T _g (observed)
(days)	(°C)	(%)	(°C)	(°C)
0	-	7.8	182.6	81.5
1	25	7.8	181.9	81.5
2	50	7.8	180.1	92.3
3	50	7.8	180.0	100.8
4	75	7.8	182.6	109.9
5	90	6.7	180.3	116.1
7	110	n/a	n/a	140.9
8	120	3.3	208.3	155.2
9	25	n/a	n/a	160.8
11	140	1.4	218.9	178.1
12	160	0	-	188.0
13	190	0	-	188.0

Figure 5.2 PAS-FTIR spectra for polysulfone films at various drying stages.

spectrophotometer manufacturers, the depths of the spectra were estimated at 4.4 μm , 3.5 μm and 3.1 μm for mirror velocities of 0.20 $\text{cm}\cdot\text{sec}^{-1}$, 0.32 $\text{cm}\cdot\text{sec}^{-1}$ and 0.40 $\text{cm}\cdot\text{sec}^{-1}$, respectively.³ Since the specimens were not homogeneous and no internal references were available, it was not possible to accurately determine the sample penetration depths. Regardless of the actual depths of penetration, variation of the mirror velocity allowed for depth profiling of the polysulfone films. To measure the relative CHCl_3 concentrations in these films, several absorption band intensity ratios were measured for each spectrum. All gave identical trends. For presentation purposes, the intensity ratios of absorption bands at 759 cm^{-1} (for CHCl_3) and 1589 cm^{-1} (for PSF) were taken to examine the relative concentrations of CHCl_3 at various depths. Results from these calculations on partially dried samples are shown below in Table 5.2.

Table 5.2 Intensity ratio for 759 cm^{-1} (CHCl_3) and 1589 cm^{-1} (PSF) absorption bands for freshly cast and dried under vacuum at 75 °C.

Mirror velocity (cm/sec)	Freshly cast	Vacuum dried at 75 °C	Vacuum dried at 120 °C
0.20	0.626	0.612	0.294
0.32	0.581	0.547	0.261
0.40	0.566	0.577	0.233

The intensity ratios increase with decreasing mirror velocity, suggesting that chloroform concentrations are higher at greater depths below the film surface. This trend was apparent in all the specimens tested. The polymer film dried up to 120 °C also reveal a lower intensity ratio than for the film dried to 75 °C. It is believed that the apparent concentration gradient for CHCl_3 in PSF films plays a major role in their drying, since solvents can exert a plasticizing effect on the polymers. Usually, plasticizers increase free-volume and diffusion through polymeric materials due to decreased polymer-polymer interactions. At low concentrations however, solvent molecules can act as antiplasticizers since they occupy Langmuir sorption sites, thereby decreasing diffusivity through the polymer.⁴ This creates a “shell” effect, where the solvent is more difficult to remove as drying progresses. Evidence for this effect is also seen in the increasing DTG peak temperatures as drying progresses since higher temperatures are required for the solvent to be removed. Heating the polymer films is therefore an important component in removing the solvent. Furthermore, maintaining the vacuum oven temperature below the apparent T_g is also important to prevent the solvent from leaving the film too quickly, causing foaming. Table 5.1 shows that the target T_g for PSF was achieved following 12 days under vacuum, with the oven temperature at 160 °C. Hence, removal of the solvent does not necessitate heating above T_g .

5.2 Gas Permeabilities

5.2.1 Dibenzoylbenzene and Naphthalene containing Polymers

Figures 5.3-5.7 compare the permeabilities at different pressures for poly(arylene ether ketone)s containing dibenzoylbiphenyl (DBBP) and naphthalene groups for N_2 , O_2 , CH_4 , CO_2 and He, respectively. The permeabilities of polymers containing connector **6F** were consistently higher than polymers containing **FL**. Table 5.3 lists the O_2/N_2 and CO_2/CH_4 selectivities and permeabilities measured at 150 psi. In agreement with the predicted trade-off relationship, the higher permeabilities for polymers containing **6F** are also accompanied by a decrease in O_2/N_2 selectivity. The selectivities for CO_2/CH_4 , however, show consistently the opposite behaviour. The consistencies observed for the bisphenol connectors suggest that specific interactions between the bisphenol moiety and either of the 2 gases may be causing this behaviour opposite to O_2/N_2 selectivities. This difference in trends for CO_2/CH_4 and O_2/N_2 are consistent with previous studies on poly(arylene ether ketone)s⁵ and polycarbonates⁶ containing BPA and 6F-BPA connector groups. Mohr *et al* concluded that for poly(arylene ether ketone)s, this effect was due to a significantly higher CO_2 diffusion coefficient, presumably caused by slightly larger spacings between the polymer chains.⁵

Correlations between permeabilities and the substitution patterns reveal that polymers containing 2,2'-DBBP groups gave higher gas permeabilities than their 3,3'-analogues. Interestingly, the small decrease in O_2/N_2 selectivities related to the substitution changes are comparable to the differences observed with different

Figure 5.3 Nitrogen permeabilities for poly(arylene ether ketone)s containing DBBP and naphthalene moieties.

Figure 5.4 Oxygen permeabilities for poly(arylene ether ketone)s containing DBBP and naphthalene moieties

Figure 5.5 Methane permeabilities for poly(arylene ether ketone)s containing DBBP and naphthalene moieties

Figure 5.6 Carbon dioxide permeabilities for poly(arylene ether ketone)s containing DBBP and naphthalene moieties.

Figure 5.7 Helium permeabilities for poly(arylene ether ketone)s containing DBBP and naphthalene moieties

Table 5.3 O₂ and CO₂ permeabilities with O₂/N₂ and CO₂/CH₄ selectivities from data measured at 150 psi.

polymer	P_{O_2} (Barrer)	α O ₂ /N ₂	P_{CO_2} (Barrer)	α CO ₂ /CH ₄
336F	0.608	7.7	1.95	33.6
33FL	0.530	8.3	1.87	34.0
226F	0.993	6.3	3.12	35.9
22FL	0.720	7.4	2.40	30.8
22TMB	1.86	6.4	3.12	12.1
NP6F	1.85	5.7	6.04	28.8
NPFL	1.41	6.4	4.97	25.9

bisphenols. It was previously shown in Chapter 4 that 2,2'-DBBP groups exhibited less segmental mobilities compared to 3,3'-DBBP polymers. Thus, the slight decrease in selectivity for 2,2'-DBBP polymers suggests that the decrease in segmental mobility for 2,2'-DBBP polymers is also accompanied by hindrances to chain packing. Aitken *et al* previously reported gas-transport of a poly(ether bisketone) containing a 4,4'-DBBP group in the repeat unit (Figure 5.8).⁷ The oxygen permeability for this polymer was reported to be 0.75 Barrer. Polymer 336F had an oxygen permeability of 0.60 Barrer.

Figure 5.8 Poly(ether bisketone)s (PEBK).

Although PEBK contains hydrogens on the isopropylidene moiety, comparisons with polymer 336F can still be made, since the latter exhibits lower permeabilities and replacement of BPA with 6F-BPA usually results in higher permeabilities. Thus, 3,3'-DBBP polymers exhibit lower permeabilities compared to polymers with 2,2'- or 4,4'-DBBP moieties. These findings support previous studies on aromatic polyimides, which showed lower permeabilities for meta- substitutions, compared to corresponding para-substituted isomers.^{8,9,10} Although comparisons between PEBK and the 2,2'-DBBP are not possible, it is interesting to note that oxygen permeabilities for PEBK, 226F and 22FL were 0.75, 0.99 and 0.72 Barrer, respectively. Although 4,4'-DBBP moieties also

seem to yield good gas-transport properties. a significant advantage is that 2,2'-DBBP consistently affords amorphous structures, which are easily cast into films.

Polymer **22TMB**, which contains the 2,2'-DBBP and 2,2',6,6'-tetramethyl-4,4'-diphenol benefits from two rigid and bulky moieties. This polymer exhibits significantly higher gas permeabilities compared to **226F** and **22FL**. Although O_2/N_2 selectivity for the polymer has also decreased by 10 % (relative to **226F**) the O_2 permeability has increased by a factor of nearly 1.9. This effect is attributed to the combination of two bulky and rigid connectors, each contributing to the inhibition of chain packing and segmental mobility.

The naphthalene-containing polymers show significantly higher permeabilities compared to DBBP-containing polymers, except **22TMB**. At the same time, the O_2/N_2 and CO_2/CH_4 selectivities have decreased much more than is observed with the DBBP containing polymers. In chapter 4, DMA studies suggested that these polymers had similar segmental mobilities as compared to 2,2'-DBBP polymers. The significant decrease in selectivities suggests that the packing of these polymers is more disrupted compared to **226F** or **22FL**. In addition to bulkiness of the 2,6-naphthalene group, the chain packing may also be influenced by the unsymmetrical nature of the reacting monomer (the dihalide) and the irregularities it introduces in the polymer backbone.

In an effort to confirm the influences of chain packing, the d-spacings and fractional free-volumes were also measured. The wide-angle X-ray diffraction (WAXD) patterns for the DBBP and naphthalene containing polymers (with **FL** and **6F** connector

groups) are compared in Figure 5.9. Consistency is observed with respect to **FL** and **6F** groups in these polymers. Polymers containing **FL** groups display a narrow peak at low d-spacing (4.4-4.5 Å) and **6F**-containing polymers consistently show narrow distributions at larger spacings (5.6 Å), suggesting the bisphenol groups consistently influence chain packing. The narrow spacing peaks observed for **FL**-containing polymers are consistent with the lower permeabilities observed for these polymers, relative to polymers containing **6F**. The WAXD patterns for polymers **DBBP** groups also reveal an important difference in d-spacing distributions for 2,2'- and 3,3'-**DBBP** moieties. Polymers with 2,2'-**DBBP** and naphthalene groups reveal a complex WAXD pattern, possibly due to superimposed peaks, suggesting these polymers have irregular distributions for their chain packings. Since this complexity is not observed for polymers **336F** and **33FL**, it is believed that these features are caused by the 2,2'-**DBBP** and naphthalene groups.

The influences of these groups can be explained in terms of their structures, and the influence they exert on the polymer structures at the segmental level. The 2,2'-**DBBP** groups can adopt one of two distinct conformations due to restricted mobility of the 2,2'-substituted biphenyl group, giving this moiety axis chirality, illustrated in Figure 5.10.

Figure 5.10 Different conformations for 2,2'-**DBBP** moieties.

Figure 5.9 WAXD patterns for poly(arylene ether ketone)s containing DBBP and naphthalene moieties

These two distinct conformations would pack differently, and therefore influence the polymer chain packings differently. The different packing patterns for the naphthalene containing polymers can be explained in terms of the fact that the unsymmetrical monomer is incorporated in either head-to-head, head-tail or tail-tail fashion during polymerization. Thus, 2 distinct segmental structures are possible in the backbones of these polymers, each having different packing features.

The influences of d-spacings and FFV on oxygen permeabilities are summarized in Table 5.4. Due to the complex patterns for some polymers, the spacings associated with each prominent peak are listed. Although polymers 336F, 33FL, NP6F and NPFL show that higher permeabilities are observed at higher d-spacings, the complexity of the patterns hamper correlations for other polymers. Therefore, these results suggest that better understandings of the d-spacing distributions and their effect on permeabilities.

The effects of FFV on permeabilities are examined in a plot of $1/\text{FFV}$ vs. oxygen permeabilities in Figure 5.11. Previous studies have shown good correlations between diffusion coefficients and $1/\text{FFV}$. No trend is apparent in Figure 5.11. Furthermore, attempts at correlating Helium permeabilities with $1/\text{FFV}$ yielded similar scattering. These inconsistencies between P_{O_2} , P_{He} and FFV cast doubt with respect to the values for FFV. It is believed that the largest influence for erroneous FFV values are from the specific volume measurements (V , $1/\rho$). Previous studies successfully correlating FFV to permeabilities measured V by means of accurate density gradient columns. Density

Table 5.4 d-spacings, FFV and oxygen permeabilities for poly(arylene ether ketone)s containing DBBP and naphthalene moieties.

polymer	Apparent		FFV	P_{O_2} (Barrer)
	X-ray peak (Å)			
336F	5.2		0.153	0.608
33FL	4.5		0.149	0.530
226F	5.6, 4.3		0.171	0.993
22FL	5.9, 4.4		0.147	0.720
NP6F	5.5		0.150	1.85
NPFL	4.7		0.158	1.41
22TMB	5.9, 3.9		0.126	1.86

Figure 5.11 Correlation between FFV and oxygen permeability for DBBP and naphthalene containing polymers

measurements for polymers given in Appendix 3 were obtained from the mass difference observed when the polymer films were weighed while dry, and while immersed in distilled water (Archimidean principle). Despite the small mass differences (and small sample masses also) the relative errors of the density measurements were $\pm 0.1\%$ or less, indicating that any error from this density measurement technique is consistent.

Errors in FFV measurements, however, may have also been introduced from approximations during molecular volume (V_o) calculations. Van der Waals volumes of various functionalities, tabulated by Van Krevelen, did not account for features such as 2,6-naphthalene moieties, cardo groups or for different substitution patterns on bivalent phenyl rings.¹¹ Consequently, the molecular volumes of these polymers were approximated using volumes available other functionalities. Thus, these approximations may have introduced errors in V_o . Interestingly, rigid polyimides prepared by Tanaka *et al* showed considerable scatter between diffusion coefficients and $1/\text{FFV}$. In their study, however, comparison to a large number of polyimides revealed that correlation between oxygen and $1/\text{FFV}$ was still reasonably obeyed and that their polymers fell within the scattering of the population.¹²

5.2.2 Poly(arylene ether ketone)s prepared from difluorobenzophenone

These PEEK analogues include substituted PEEK's and an analogue containing the bulky 2,2',6,6'-tetramethylbiphenyl (TMB) moiety. Figures 5.12-5.16 compare the permeabilities for PEEK and substituted poly(ether ether ketone)s. Each of these

Figure 5.12 Nitrogen permeabilities for PEEK and substituted analogues.

Figure 5.13 Oxygen permeabilities for PEEK and substituted analogues.

Figure 5.14 Methane permeabilities for PEEK and substituted analogues.

Figure 5.15 Carbon dioxide permeabilities for PEEK and substituted analogues.

Figure 5.16 Helium permeabilities for PEEK and its substituted analogues.

polymers exhibit higher permeabilities than PEEK, due to the decreased chain packing for these polymers. Furthermore, P_{O_2} for polymer COPK (2.19 Barrer) is higher than for TBPK (1.39 Barrer), demonstrating that increasing the amount of tert-butyl pendent groups on the polymer backbone further disrupts chain packing and increases permeability. As with previously discussed polymers NP6F and NPFL, chain packing in this copolymer may also be influenced by the irregularities along the polymer backbone.

The O_2/N_2 and CO_2/CH_4 selectivities for the PEEK and analogue polymers prepared from 4,4'-difluorobenzophenone are listed in Table 5.5, below.

Table 5.5 O_2 and CO_2 permeabilities with O_2/N_2 and CO_2/CH_4 selectivities from data measured at 150 psi for PEEK and analogues prepared with 4,4'-difluorobenzophenone.

polymer	P_{O_2} (Barrer)	α O_2/N_2	P_{CO_2} (Barrer)	α CO_2/CH_4
PEEK	0.259	6.5	0.963	31.1
TBPK	1.39	6.4	4.65	21.2
COPK	2.19	6.3	6.91	18.1
TMBPK	4.76	4.9	19.4	18.7

The increase in permeabilities relative to PEEK are accompanied by minor decreases in O_2/N_2 selectivities, decreasing from 6.5 to 6.3, while permeabilities for O_2 increase almost 10-fold. The decrease in selectivity is more pronounced for CO_2/CH_4 , with a decrease in selectivity by a factor of ~ 1.7 . For these gases, however, permeabilities increase almost 7-fold. The relative stabilities of the O_2/N_2 selectivities which accompany the increase in permeabilities suggest that the addition of tert-butyl pendent groups effect a favourable trade-off. This is consistent with previous studies displaying the effects of substituents attached to the polymer backbone.

Polymer **TMBPK** which contains the tetramethylbiphenyl group exhibited significantly higher permeabilities compared to substituted PEEK analogues. As expected, the O_2/N_2 selectivities for **22TMB** have also suffered. Despite the inconclusive evidence regarding segmental mobilities from DMA measurements in Chapter 4, the large difference in T_g with polymer **COPK** suggests that polymer **TMBPK** has lower segmental mobility. Thus, the significantly higher permeabilities for **TMBPK** suggest that its structure inhibits chain packing. Figure 5.17 illustrates the WAXD patterns for the substituted PEEK polymers (ie. polymer **TMBPK** is not shown). Unlike the 2,2'-DBBP polymers discussed earlier in section 5.2.1, these polymers show single-peak WAXD patterns. The measured d-spacings, FFV and oxygen permeabilities are listed in Table 5.6. Interestingly, despite the large difference in O_2 permeabilities for **TBPK** (1.39 Barrer) and **COPK** (2.19 Barrer), the measured d-spacing peaks are identical. Closer inspection of the two patterns shown in Figure 5.17, however, reveals that the

Figure 5.17 WAXD patterns for substituted PEEK polymers.

distributions of the peaks are slightly different, with a slightly wider shoulder at higher spacings for polymer **COPK**. These observations further assert a need to understand the influence of d-spacing distributions, since contributions from large and narrow spacings would each affect gas permeabilities differently.

Except for polymer **22TMB**, increasing permeabilities follow a trend of increasing FFV values. Both polymers containing tetramethylbiphenyl groups show relatively low FFV, despite their higher permeabilities. Polymer **22TMB** and **TMBPK** have FFV values of 0.126 and 0.124, respectively. A plausible explanation for these low FFV values is their high FFV may promote permeation of water molecules into the polymer, decreasing the apparent volume (V) thereby decreasing FFV also. Thus, it is believed that discrepancies between permeabilities and FFV are due to experimental considerations. More direct measurement of FFV using positron annihilation lifetime spectroscopy (PALS) have shown better correlations to gas permeabilities.^{13,14}

Table 5.6 d-Spacing, FFV and O₂ permeabilities of substituted PEEK analogues.

polymer	Apparent		
	X-ray peak (Å)	FFV	P_{O_2} (Barrer)
PEEK	4.7	0.138	0.259
TBPK	5.0	0.147	1.39
COPK	5.0	0.153	2.19
TMBPK	5.5	0.124	4.76

5.2.3 Polymers containing tetramethylbiphenyl groups

Polymer **22TMB** and **TMBPK**, are structurally related through the addition of a benzophenone moiety to **TMBPK**, as illustrated below in Figure 5.18.

Figure 5.18 Polymers **TMBPK** and **22TMB**

The oxygen permeabilities for **TMBPK** and **22TMB** are 4.76 and 1.86 Barrer, respectively. These results indicate that addition of the benzophenone moiety to **TMBPK** has significantly decreased permeability. These results suggest that more compact repeat units are desirable in terms of achieving increased rigidity and disrupted chain packing in these polymers. The WAXD patterns for these two polymers are compared in Figure 5.19. The characteristic complex pattern observed for polymers **226F** and **22FL** (Figure 5.9) is also observed for **22TMB**. Moreover, the peaks for **22TMB** indicate the existence of high and low d-spacings at 5.9 Å, and 3.9 Å, respectively. The permeability through this polymer is believed to be a function of these observed spacings.

5.2.4 Apparent Diffusion Coefficients

Although these polymers are well below T_g and would follow dual-mode sorption, it is still possible to determine apparent diffusion coefficients (D_{app}) based on equation 2.8 (i.e. equation for rubbery polymers), since thicknesses and time lags (θ) are available from permeabilities measured at 25 psi (Appendix 3). From these time lags, apparent diffusivity selectivities (D_i/D_j) were determined, such that the selectivities could be factored into diffusivity and solubility. These results are summarized in Tables 5.7 and 5.8, for poly(arylene ether ketone)s and PEEK analogues prepared from 4,4'-difluorobenzophenone, respectively. For all polymers, DO_2/DN_2 was greater than SO_2/SN_2 , suggesting that α was mostly influenced by diffusivity selectivity, which is

Figure 5.19 WAXD for polymers 22TMB and TMBPK

Table 5.7 Selectivities based on permeability, diffusivity and solubility for poly(arylene ether ketone)s, determined using apparent diffusion coefficients calculated from film thickness and time lag (θ).

Polymer	$\alpha \frac{P_{O_2}}{P_{N_2}}$	$\frac{D_{O_2}}{D_{N_2}}$	$\frac{S_{O_2}}{S_{N_2}}$	$\alpha \frac{P_{CO_2}}{P_{CH_4}}$	$\frac{D_{CO_2}}{D_{CH_4}}$	$\frac{S_{CO_2}}{S_{CH_4}}$
336F	7.30	6.47	1.14	37.7	8.7	4.3
33FL	8.59	6.14	1.39	34.3	6.6	5.2
226F	7.57	5.04	1.50	36.5	9.6	3.8
22FL	8.09	3.30	2.44	35.2	5.5	6.4
22TM	6.44	4.89	1.31	12.9	7.7	1.7
NP6F	5.54	3.49	1.59	33.5	6.7	5.0
NPFL	5.55	5.25	1.06	32.4	6.8	4.8

Table 5.8 Selectivities based on permeability, diffusivity and solubility for PEEK analogues prepared from 4,4'-difluorobenzophenone, determined using apparent diffusion coefficients calculated from film thickness and time lag (θ).

Polymer	$\alpha \frac{P_{O_2}}{P_{N_2}}$	$\frac{D_{O_2}}{D_{N_2}}$	$\frac{S_{O_2}}{S_{N_2}}$	$\alpha \frac{P_{CO_2}}{P_{CH_4}}$	$\frac{D_{CO_2}}{D_{CH_4}}$	$\frac{S_{CO_2}}{S_{CH_4}}$
TBPK	6.54	5.00	1.31	25.5	4.7	5.4
COPK	6.50	4.08	1.59	19.3	10	1.9
TMBPK	4.43	4.15	1.07	20.0	5.67	3.5
PEEK	5.75	7.13	0.807	35.2	9.2	3.8

consistent with transport through glassy polymers. The higher solubility of CO_2 in these polymers is apparent from the higher solubility selectivities observed for $\text{SCO}_2/\text{SCH}_4$.

5.2.5 Comparison of novel poly(arylene ether ketone)s to polysulfone

UDEL Polysulfone is a commercial polymer used for gas-separations. Previously reported gas-permeabilities and selectivities for this polymer are given in Table 5.9, below. These numbers can be compared with previously discussed results in Tables 5.3 and 5.5.

Table 5.9 Permeabilities and selectivities for UDEL polysulfone.

P_{CO_2}	$\alpha_{\text{CO}_2/\text{CH}_4}$	P_{O_2}	$\alpha_{\text{O}_2/\text{N}_2}$
5.6	22	1.4	5.6

All the DBBP polymers, except 22TMB, exhibit lower O_2 permeabilities and higher selectivities compared to polysulfone. Polymers 22TMB, containing the tetramethylbiphenyl group and polymers containing naphthalene groups had higher O_2 permeabilities. Interestingly, however, all the permeabilities which exhibited higher permeabilities, also exhibited higher selectivities. For CO_2 , however, only polymer NP6F had higher permeabilities than polysulfone. The substituted poly(ether ether ketone)s showed almost identical O_2 permeabilities for TBPK and polysulfone, with TBPK having higher selectivity. COPK had even higher O_2 permeability with higher

permeability. The substituted PEEK analogues have similar trends for CO_2/CH_4 also. Thus, substituted poly(ether ether ketone)s, which significantly improve gas permeability of PEEK, offer comparable performances to commercial polysulfone. Competitive performance from poly(arylene ether ketone)s, however, is limited to the naphthalene containing polymers, and 22TMB.

5.2.6 Conclusions

The gas-transport properties for poly(arylene ether ketone)s show consistency within the dihalide and bisphenol moieties. Changes in the biphenyl catenation from 3,3'- to 2,2'- increase permeabilities with comparatively smaller losses in selectivity. Since lower segmental mobilities were observed for 2,2'-DBBP polymers, the small losses in selectivity suggest that this structure also disrupts chain packings. The different distinct conformations of 2,2'-DBBP moieties give these polymers complex d-spacing patterns, which complicate correlations between d-spacings and gas-permeabilities. Other polymers which do not show this complex pattern show increases in permeabilities with d-spacings. The necessity to better understand the influence of d-spacing distribution is also confirmed by polymers TBPK and COPK, which showed similar WAXD peaks, with slight differences in distribution. These polymers showed increases in permeability with the addition of tert-butyl groups onto the polymer backbone, with small loss in selectivity. The tert-butyl groups were also previously shown to decrease segmental mobilities, therefore the increase in permeabilities suggest that chain packing has been

disrupted also. Fractional free volume (FFV) measurements for substituted PEEK polymers showed good correlation to oxygen permeabilities. Significant scattering for naphthalene and DBBP containing polymers suggest that density measurements or group-contribution calculations for measurements of molecular and specific volumes may hamper FFV correlations. Measured FFV values for high permeability polymers 22TMB and TMBPK showed consistently low FFV, despite their high permeabilities. Thus density measurements may be systematically in error. Based on apparent diffusion coefficients calculated from film thicknesses and time lags, the transport through these polymers was found to be governed by diffusion. Comparison of permeabilities for polymers 22TMB and TMBPK, which differ by the addition of a benzophenone moiety, show that 22TMB has lower permeability. The results from these polymers suggest that more compact repeat units are desirable when considering polymers with rigid backbones and inhibited chain packing.

The permeabilities of these polymers demonstrate that the gas permeability of PEEK can be improved through synthetic analogues. Substituted poly(ether ether ketone)s showed performances comparable to commercial polysulfone. Naphthalene containing poly(arylene ether ketone)s also showed gas permeabilities comparable to polysulfone. Figure 5.20 illustrates the O_2/N_2 selectivities and permeabilities, along with a line corresponding to Robeson's upper bound.¹⁵ Although the gas-transport properties of the polymers have not crossed this upper bound, they do lie close enough to conclude

Figure 5.20 Oxygen / nitrogen selectivities and oxygen permeabilities for poly(arylene ether ketone)s and substituted PEEKs with Robeson's upper bound.

that poly(arylene ether ketone)s can be considered polymers in the "tailor-made" approach to membrane design.

5.3 Experimental

5.3.1 Polymer Purification and Fractionation

Polymers characterized for gas-transport characteristics were further purified by fractionation. Chloroform (2 % w/w) solutions were prepared and filtered. The solutions were magnetically stirred as methanol was added dropwise at a rate of 1 drop per second. Completeness of precipitation was checking for turbidity as more methanol was added to the solution. Once the precipitation was complete, the supernatant liquid was decanted. The remaining residue was the desired high molecular weight fraction and was redissolved in chloroform. The polymer was re-precipitated in methanol. Following 1 day of drying in open air, the polymer powder was dried to 120 °C under vacuum. A DSC scan confirmed that all the solvent had been evaporated during drying.

5.3.2 Film Preparation

Dry polymer fibres (2.5 g) were dissolved in chloroform and cast into a mould whose diameter was 14 cm. After at least 3 days of slow evaporation in a glove bag, clear, tack-free films were obtained. The films were placed in a vacuum oven, and dried while slowly increasing the oven temperature to prevent the remaining solvent from "foaming". The oven temperature was raised as a function of the observed T_g ,

maintaining it at least 10 degrees below the observed T_g . The resulting polymer films were clear and approximately 100 μm thick. Previous work on polymer films in our labs revealed that increasing the vacuum oven temperature too quickly can cause the film to foam, due to rapid solvent evaporation. Films were therefore dried by increasing the oven temperature as a function of the experimental DSC and/or TG data. TG data was not possible for all partially dried films, since foaming of the samples during TG scans caused the samples to spill out of their containers and interfere with the TG mechanism.

Samples were also characterized by photo-acoustic infrared spectroscopy (PAS) to obtain FTIR spectra of the partially dried films. The background and sample spectra were averaged from 128 scans at 8 cm^{-1} resolution. Depth profiling of PSF films were performed by recording the spectra with mirror velocities of 0.20, 0.32 and 0.40 cm/sec .

The TG/DTA and FTIR equipment were identical to those described in Chapter 3. A DSC 2910 (TA Instruments) was used to characterize the partially dried films. Scans were performed from 25-350 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C/min}$, with 50 mL/min N_2 purge.

5.3.3 Gas Permeabilities

Permeabilities were studied at 35.0 $^{\circ}\text{C}$ with pure gases (Matheson, UHP) in the following order: nitrogen, oxygen, methane and carbon dioxide and helium. Gas fluxes through these polymers under 25, 75, 150 and 200 pounds per square inch (PSI) pressure were recorded using a constant volume permeability apparatus, designed and constructed at the National Research Council. In addition to a manually controlled system, 2

additional automated systems were used. A schematic of the manually operated apparatus is shown in Figure 2.3. The downstream volume was approximately 175 cm³ and leak/degassing rates of 10 mTorr/hr or less were measured prior to permeability experiments. Fluxes were derived from linear time-pressure increases after at least 3 time lag intervals had passed. Downstream pressures were measured using a 10 Torr transducer (MKS Instruments). A 100 Torr transducer was used for measurements which yielded much higher fluxes. The errors associated with the downstream transducers were +/- 0.1% each. Errors associated with the upstream transducers (Setra) were also +/- 0.1 %. Total errors on permeability experiments depended on the range of the transducers used. Experiments for methane typically lasted 24 hours per pressure, while experiments for carbon dioxide and helium lasted approximately 1 hour. Permeabilities were calculated using gas fluxes - normalized to standard temperature pressure (STP) - the pressure of the upstream gas, and the dimensions of the polymer film.

5.3.4 Density Measurements

Density measurements were performed using a Mettler density measurement accessory for solid samples. This accessory was attached to a Mettler 362E Analytical Balance (+/- 0.00001 g), and measured the masses of a sample in its "dry state" and its mass while suspended in a liquid of known density (distilled water). Densities were

calculated using the archimidian principle:

$$\rho = \rho_{\text{std}} \frac{M_{\text{dry}}}{(M_{\text{dry}} - M_{\text{imm}})}$$

where ρ_{std} is the density of water (at a measured temperature) and M_{dry} and M_{imm} are the masses measured for the dry and immersed samples, respectively.

5.3.5 Wide Angle X-Ray Diffraction

Wide angle X-Ray diffraction patterns were recorded for all polymer samples, to measure the average polymer chain spacing. Scans were performed on films using a Scintag X-ray diffractometer. Samples were scanned, with a 1.5406 Å incident beam wavelength (from a $\text{CuK}\alpha_1$ source). Diffraction from the polymer samples were measured from 0 to 50° at 0.03° steps. Interchain d-spacings were obtained from Bragg's law (ie $n\lambda=2d\sin\theta$).

5.4 References

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Summary

The variation of biphenyl substitution in poly(arylene ether ketone)s containing dibenzoylbiphenyl (DBBP) moieties show that, except for 2,2'-substitution, T_g increases with the linearity of the polymer structure. The high T_g 's for 2,2'-DBBP are due to steric crowding from ortho substitutions on the benzene rings, which hinder the mobility of the polymer chains. Dynamic Mechanical Analyses (DMA) of 2,2'- and 3,3'-DBBP containing polymers also showed reduced segmental mobilities for 2,2'-DBBP-containing polymers.

Although the structures of the bisphenols used to prepare DBBP and naphthalene containing polymers influenced T_g 's and gas permeabilities, no change in γ transitions were observed for polymers containing either 4,4'-(hexafluoroisopropylidene)diphenol (6F) or 9,9-bis(4-hydroxyphenyl)fluorene (FL), suggesting that the structures of the DBBP exert a greater influence on the properties of these polymers.

TG scans on these polymers demonstrated that all polymers had excellent thermal stabilities, with decomposition temperatures, T_d above or near 500 °C. Lower thermal stabilities were rationalized in terms of bond strengths in the repeat units and molecular weight. Activation energies determined from non-isothermal TG experiments showed reasonable agreement with E_a reported for PEEK. Biphenyl connector groups in the polymer backbone were found to increase thermal stability, relative to a benzene connector. In contrast to single scan TG experiments, isothermal TG kinetics

experiments suggest that the 4,4'-DBBP moiety gives polymers higher long term thermal stability, compared to 2,2'- or 3,3'-DBBP polymers, due to the extensive π -orbital overlap in the DBBP unit. The greater π -overlap for 4,4'-DBBP groups was evidenced from FTIR and FT-Raman spectra. Thermal degradation products of DBBP containing polymers were related to small segments in the polymer repeat unit, such as phenol. TG-FTIR studies detected carbon monoxide as a degradation product, which was invisible to previously reported TG-MS studies. Despite the excellent thermal stabilities for these polymers, potentially hazardous materials are emitted during thermal degradation.

Polymers containing 2,2'-DBBP groups gave higher permeabilities, compared to 3,3'-DBBP polymers. The increase in permeabilities for these polymers was accompanied with minimal loss in O_2/N_2 selectivity. Higher losses in selectivity accompanied the even higher permeabilities observed for polymers containing naphthalene groups. The bisphenol connector FL gave consistently lower permeabilities (slightly higher selectivities) compared to connector 6F. Since the 2,2'-DBBP had lower segmental mobilities compared to 3,3'-DBBP polymers, the difference in gas permeabilities was due to differences in the polymer chain packings.

The d-spacings determined by Wide-Angle X-ray diffraction (WAXD) showed that 2,2'-DBBP polymers had complex packing structures, due to the two distinct conformations for the 2,2'-DBBP structure. Complex packing was observed for naphthalene containing polymers. The d-spacings for tert-butyl-PEEK and the di-tert-butyl / tert-butyl co-polymer showed similar WAXD peaks, but with slight differences in

their distributions. The difference in d-spacing distributions are believed to be responsible for the differences in their gas-permeabilities. Hence, better understanding on the influence of packing distributions on gas-permeabilities are needed.

Insertion of a benzophenone moiety in the repeat unit of **TMBPK** yields the structure of polymer **22TMB**, containing a 2,2'-DBBP group. Comparison of these two high T_g and high permeability polymers show lower T_g and gas permeability for polymer **22TMB**, due to higher conformational freedom in polymer **22TMB**. These results also suggest more compact repeat structures are desirable for tailoring gas permeability membranes.

Suggestions for future work

1. Since results from these studies suggest a more compact repeat unit is more advantageous for higher gas-permeabilities. Studies on high permeability poly(trimethylsilylpropyne) (PTMSP) (P_{O_2} of 10,000 Barrer, $\alpha_{O_2/N_2} = 1.4$) have shown that its non-rotating repeat unit and poor packing ability contribute to its high permeability.¹ Tailoring the structures of poly(arylene ether ketone)s such that only sterically hindered ortho-substituted benzene rings are introduced into the repeat unit may achieve such goals, while maintaining a soluble and amorphous nature.
2. As materials can have complex packing structures, there is a need to accurately establish free-volumes and their distributions. Positron annihilation lifetime spectroscopy (PALS) measurements have proven to be a promising technique for this purpose.^{2,3}

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Contributions to Knowledge

1. Although some structure-property studies on poly(arylene ether ketone)s have been performed in the past, this study is among the first extensive structure-property surveys for novel poly(arylene ether ketone)s which include thermal, and mechanical properties as well as a structure-property survey of gas-permeabilities.
2. The results obtained in this work demonstrated that more compact repeat units are more desirable for preparing "tailor-made" polymers, when considering the synthesis of gas-separation membranes.

Appendix A

Table A.1 T_d 's measured at 2 % and 5 % weight loss at different Heating rates for poly(arylene ether ketone)s

1. T_d , 2 % weight loss ($^{\circ}\text{C}$)

POLYMER	Heating Rate ($^{\circ}\text{C}/\text{min}$)					
	1	2	5	10	20	50
22BPA	n/a	422.1	443.0	461.0	480.1	498.0
33BPA	n/a	447.0	470.0	489.3	510.0	537.0
44BPA	391.0	404.3	416.1	432.5	441.4	474.7
22HQ	n/a	451.2	460.1	485.6	504.0	510.3
33HQ	435.0	460.2	464.6	470.0	501.0	510.2
22BP	n/a	461.0	472.0	490.3	509.2	527.0
33BP	n/a	474.3	482.5	510.2	530.0	536.9

2. T_d , 5 % weight loss ($^{\circ}\text{C}$)

POLYMER	Heating Rate ($^{\circ}\text{C}/\text{min}$)					
	1.0	2.0	5.0	10	20	50
22BPA	n/a	428.8	466.8	475.7	494.4	512.6
33BPA	n/a	462.4	482.5	497.8	529.6	548.3
44BPA	417.2	431.1	443.1	461.6	481.5	501.4
22HQ	n/a	473.6	480.3	505.0	520.7	534.7
33HQ	449.3	466.8	479.0	501.2	516.1	525.8
22BP	n/a	484.7	500.3	516.9	527.0	546.1
33BP	n/a	490.1	507.1	526.0	549.4	563.8

Appendix B Density measurements and fractional free volume (FFV) determination.

Polymer	V_w^a ($\text{cm}^3 \cdot \text{mol}^{-1}$)	ρ^b ($\text{g} \cdot \text{cm}^{-3}$)	FFV $\left(\frac{V - V_o}{V} \right)$
336F	339.1	1.334	0.153
33FL	383.1	1.220	0.149
226F	339.1	1.307	0.171
22FL	383.1	1.219	0.147
22TMB	347.9	1.161	0.126
NP6F	266.4	1.121	0.150
NPFL	310.4	1.356	0.157
TBPK	196	1.153	0.147
COPK	210.7 ^c	1.123	0.153
TMBPK	249.6	1.135	0.124
PEEK	151.6	1.261	0.137

^a Computed using Van Krevelen's functional group contribution method.

^b Determined from difference of mass measurements in air and distilled water at 24.0 °C.

^c Estimated using 2:1 ratio of tert-/di-tert-butyl-hydroquinone.

Appendix C

Table C.1 Permeability data for 336F

Nitrogen

p(psi)	P(Barrer)	θ (h)
23.4	0.085	1.17
69.8	0.081	
135.7	0.079	
195.4	0.080	

Oxygen

p(psi)	P(Barrer)	θ (h)
29.6	0.628	0.18
71.1	0.622	
142.0	0.608	
201.0	0.595	

Methane

p(psi)	P(Barrer)	θ (h)
26.8	0.064	7.04
76.6	0.061	
151.0	0.058	
209.0	0.057	

Carbon Dioxide

p(psi)	P(Barrer)	θ (h)
29.3	2.41	0.81
69.0	2.16	
146.0	1.95	
203.0	1.83	

Helium

p(psi)	P(Barrer)	θ (h)
26.1	15.4	0
70.7	15.0	
140.0	14.6	
215.0	14.6	

Thickness: 90.3 μm

Appendix C

Table C.2 Permeability data for 33FL

Nitrogen

p(psi)	P(Barrer)	θ (h)
28.8	0.067	1.23
74.7	0.065	
154.2	0.064	
195.5	0.064	

Oxygen

p(psi)	P(Barrer)	θ (h)
24.3	0.576	0.20
70.8	0.528	
136.4	0.530	
203.9	0.475	

Methane

p(psi)	P(Barrer)	θ (h)
26.0	0.063	7.53
69.8	0.061	
148.0	0.055	
198.8	0.054	

Carbon Dioxide

p(psi)	P(Barrer)	θ (h)
27.6	2.16	1.15
76.4	2.04	
145.5	1.87	
197.9	1.82	

Helium

Thickness: 78.0 μm

p(psi)	P(Barrer)	θ (h)
27.5	12.5	n/a
76.1	12.3	
140.4	12.2	
201.6	12.2	

Appendix C**Table C.3** Permeability data for 226F**Nitrogen**

p(psi)	P(Barrer)	θ (h)
30.2	0.136	1.58
73.2	0.136	
138.3	0.138	
223.2	0.138	

Oxygen

p(psi)	P(Barrer)	θ (h)
25.6	1.03	0.31
70.8	0.995	
136.4	0.993	
203.9	0.984	

Methane

p(psi)	P(Barrer)	θ (h)
26.0	0.098	10.83
69.8	0.091	
148.0	0.087	
198.8	0.087	

Carbon Dioxide

p(psi)	P(Barrer)	θ (h)
27.6	3.58	1.13
76.4	3.38	
145.5	3.12	
197.9	3.04	

Helium

p(psi)	P(Barrer)	θ (h)
27.5	20.8	n/a
76.1	20.5	
140.4	20.4	
201.6	20.4	

Thickness: 130 μm

Appendix C

Table C.4 Permeability data for 22FL**Nitrogen**

p(psi)	P(Barrer)	θ (h)
28.8	0.100	1.14
74.7	0.096	
147.4	0.098	
205.2	0.094	

Oxygen

p(psi)	P(Barrer)	θ (h)
24.9	0.809	0.38
71.0	0.736	
149.7	0.720	
206.4	0.711	

Methane

p(psi)	P(Barrer)	θ (h)
28.8	0.088	6.56
71.0	0.086	
148.3	0.078	
202.8	0.075	

Carbon Dioxide

p(psi)	P(Barrer)	θ (h)
27.6	3.10	1.19
76.4	2.50	
145.5	2.40	
197.9	2.36	

Helium

p(psi)	P(Barrer)	θ (h)
27.5	15.5	0
76.1	15.1	
140.4	15.0	
201.6	15.0	

Thickness: 98.6 μm

Appendix C

Table C.5 Permeability data for 22TMB

Nitrogen			Oxygen		
p(psi)	P(Barrer)	θ (h)	p(psi)	P(Barrer)	θ (h)
22.8	0.295	1.12	27.8	1.899	0.23
52.3	0.304		51.6	1.921	
76.9	0.303		78.8	1.926	
113.2	0.304		102.2	1.923	
131.8	0.299		126.6	1.927	
155.6	0.297		150.0	1.908	
			173.7	1.896	
			198.5	1.887	
Methane			Carbon Dioxide		
p(psi)	P(Barrer)	θ (h)	p(psi)	P(Barrer)	θ (h)
27.6	0.284	5.67	26.5	7.98	0.74
54.1	0.277		51.2	7.82	
74.1	0.276		79.5	7.57	
105.1	0.271		100.7	7.43	
126.1	0.264		150.1	6.96	
153.9	0.264		175.0	6.83	
174.2	0.264		203.4	6.85	
198.4	0.259				
Helium			Thickness: 130 μm		
p(psi)	P(Barrer)	θ (h)			
25.2	22.4	n/a			
75.5	23.5				
149.3	23.3				
201.1	23.3				

Appendix C

Table C.6 Permeability data for NP6F

Nitrogen

p(psi)	P(Barrer)	θ (h)
26.6	0.339	0.39
76.2	0.333	
149.0	0.322	
201.6	0.316	

Oxygen

p(psi)	P(Barrer)	θ (h)
26.6	1.88	0.11
80.6	1.88	
147.3	1.85	
201.6	1.83	

Methane

p(psi)	P(Barrer)	θ (h)
26.9	0.217	2.79
76.0	0.218	
148.6	0.210	
208.2	0.201	

Carbon Dioxide

p(psi)	P(Barrer)	θ (h)
27.3	7.26	0.42
75.9	6.75	
148.0	6.04	
198.3	5.77	

Helium

p(psi)	P(Barrer)	θ (h)
24.9	25.3	n/a
75.8	25.3	
142.8	25.5	
195.1	25.3	

Thickness: 111 μm

Appendix C

Table C.7 Permeability data for NPFL

Nitrogen

p(psi)	P(Barrer)	θ (h)
24.9	0.263	1.02
75.7	0.233	
142.7	0.222	
195.1	0.213	

Oxygen

p(psi)	P(Barrer)	θ (h)
28.9	1.46	0.20
75.0	1.45	
150.5	1.41	
199.5	1.39	

Methane

p(psi)	P(Barrer)	θ (h)
30.3	0.202	5.08
79.4	0.204	
156.5	0.192	
197.6	0.174	

Carbon Dioxide

p(psi)	P(Barrer)	θ (h)
24.9	6.36	0.75
82.6	5.47	
143.4	4.97	
193.0	4.68	

Helium

p(psi)	P(Barrer)	θ (h)
25.8	16.0	n/a
66.9	16.1	
152.8	16.1	
214.5	16.1	

Thickness: 110 μm

Appendix C

Table C.8 Permeability data for PEEK**Nitrogen**

p(psi)	P(Barrer)	θ (h)
27.5	0.045	0.32
75.1	0.04	
139.0	0.039	
213.0	0.039	

Oxygen

p(psi)	P(Barrer)	θ (h)
31.4	0.259	0.09
73.7	0.257	
149.7	0.254	
198.3	0.252	

Methane

p(psi)	P(Barrer)	θ (h)
29.9	0.031	3.08
73.2	0.031	
149.2	0.031	
191.4	0.031	

Carbon Dioxide

p(psi)	P(Barrer)	θ (h)
32.2	1.09	0.31
78.5	1.04	
149.7	0.963	
196.7	0.915	

HeliumThickness: 52 μm

p(psi)	P(Barrer)	θ (h)
31.9	4.51	n/a
72.1	4.84	
142.4	4.88	
200.2	4.85	

Appendix C

Table C.9 Permeability data for TBPk

Nitrogen

p(psi)	P(Barrer)	θ (h)
32.0	0.223	0.97
77.4	0.218	
150.6	0.217	
207.3	0.212	

Oxygen

p(psi)	P(Barrer)	θ (h)
31.2	1.46	0.19
75.5	1.39	
138.5	1.39	
199.2	1.38	

Methane

p(psi)	P(Barrer)	θ (h)
30.4	0.222	3.40
79.9	0.224	
149.5	0.219	
205.3	0.199	

Carbon Dioxide

p(psi)	P(Barrer)	θ (h)
29.3	5.67	0.72
74.7	5.19	
151.3	4.65	
203.0	4.44	

Helium

p(psi)	P(Barrer)	θ (h)
28.1	17.3	n/a
79.6	17.1	
150.6	17.2	
196.0	17.2	

Thickness: 138 μm

Appendix C

Table C.10 Permeability data for COPK

Nitrogen

p(psi)	P(Barrer)	θ (h)
32.1	0.359	0.451
75.8	0.356	
147.3	0.35	
213.7	0.338	

Oxygen

p(psi)	P(Barrer)	θ (h)
28.1	2.333	0.111
75.9	2.243	
152.6	2.189	
198.7	2.148	

Methane

p(psi)	P(Barrer)	θ (h)
25.8	0.439	2.04
75.9	0.406	
152.2	0.381	
212.1	0.365	

Carbon Dioxide

p(psi)	P(Barrer)	θ (h)
28.4	8.465	0.192
83.4	7.502	
149.4	6.909	

Helium

p(psi)	P(Barrer)	θ (h)
26.4	20.46	n/a
71.7	20.49	
144.25	19.71	
199.9	19.64	

Thickness: 110 μm

Appendix C

Table C.11 Permeability data for TMBPK

Nitrogen

p(psi)	P(Barrer)	θ (h)
28.0	1.09	0.25
78.9	0.999	
150.7	0.970	
199.7	0.961	

Oxygen

p(psi)	P(Barrer)	θ (h)
29.8	4.81	0.06
74.4	4.83	
150.1	4.76	
200.5	4.70	

Methane

p(psi)	P(Barrer)	θ (h)
24.9	1.16	1.25
74.6	1.12	
153.0	1.04	
198.6	1.01	

Carbon Dioxide

p(psi)	P(Barrer)	θ (h)
27.2	23.4	0.22
79.6	21.1	
152.0	19.4	
204.2	18.8	

Helium

p(psi)	P(Barrer)	θ (h)
28.2	31.4	n/a
75.7	32.9	
150.0	31.5	

Thickness: 124 μm

END

1 6-0 6-9 7

FIN