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# Gas Transport Properties of Novel Poly(arylene ether ketone)s Containing Dibenzoylbiphenyl and Benzonaphthone Moieties

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**ABSTRACT:** In this work we present the results from studies on novel poly(arylene ether ketone)s, including gas permeability, wide-angle x-ray diffraction (WAXD), and dynamic mechanical analysis (DMA). Poly(arylene ether ketone)s containing 2,2′- and 3,3′-dibenzoylbiphenyl (DBBP) moieties were characterized to study the effect of biphenyl substitution on gas transport properties. Gas permeabilities of naphthalene-containing poly(arylene ether ketone)s were also measured. Higher permeabilities were observed for polymers prepared with 6F-BPA, compared to 9,9-*bis*(4-hydroxyphenyl)fluorene (HPF). The naphthalene-containing polymers exhibited higher permeabilities than the DBBP polymers, except for a polymer having the 2,2′-DBBP and tetramethylbiphenyl moieties. Based on our work, and results reported in the literature, the 3,3′-DBBP polymers showed the lowest permeabilities for DBBP-containing poly(arylene ether ketone)s. The low permeabilities are due to more efficiently packed chains brought on by greater flexibility of the backbone, compared to the other polymers studied. DMA studies confirmed the higher barriers to rotation which are believed to be responsible for 2,2′-DBBP polymers having similar selectivities compared to 3,3′-DBBP polymers.  J Polym Sci B: Polym Phys **36:** 425–431, 1998
**Keywords:** poly(arylene ether ketone); gas permeability

## INTRODUCTION

It has been established that gas permeability, $P$, through polymeric membranes depends on the diffusivity, $D$, and solubility, $S$, of the gas in the polymer. This relationship is quantified by the following equation:

$$P = D \cdot S$$

Several reviews which discuss gas transport through polysulfones, polyimides, and polycarbonates support the idea that stiffening polymer backbones while inhibiting chain packing can lead to higher gas permeabilities, at modest expense to selectivity.[1–3] This effect has been attributed to increased gas-solubility in the polymer, while maintaining diffusion-selectivity by means of chain stiffening. The most common approach to achieving this has been the attachment of pendent groups, which arrest segmental motions while increasing the bulkiness of the repeat unit. More recent studies on polymers such as poly(trimethylsilylpropyne), PTMSP, have revealed that linear rigid rod-like structures are desirable, compared to kinked structures, due to increased degrees of rotational freedom about nonlinear link-

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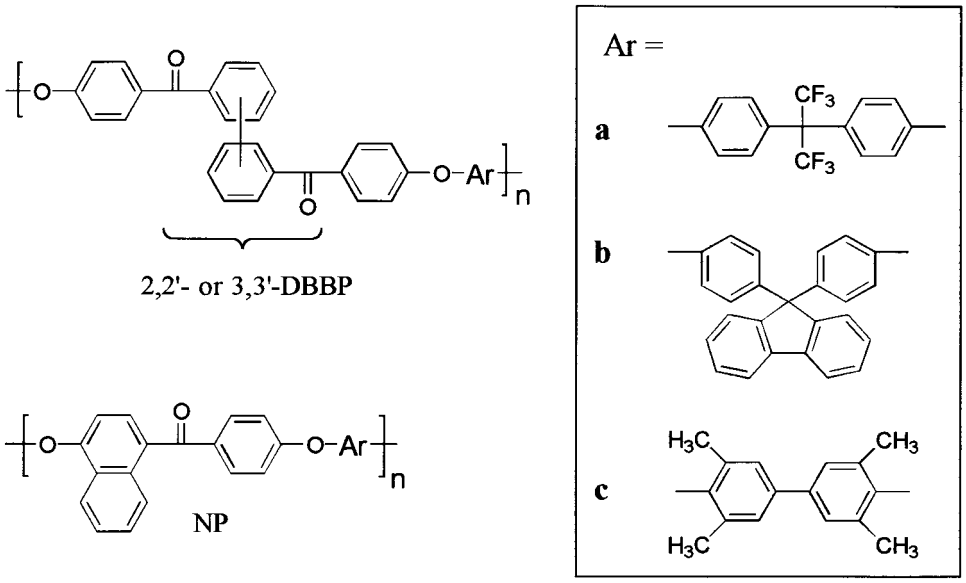


**Figure 1.** Poly(arylene ether ketone)s studied in this work.

ages which help promote chain packing. Based on the extensive body of literature on gas separation membranes, promising polymeric structures are therefore identified by bulkiness of the repeat unit and high glass transition temperatures ($T_g$). While Robeson et al.[4,5] has demonstrated the existence of an upper limit to optimizing the performance of polymeric gas separation membranes, knowledge of the influence of the polymer structure is very useful from the point of view of tailoring properties and performance.

Poly(ether ether ketone), PEEK, is well known for its excellent mechanical properties and thermal stability. PEEK, however, suffers from a relatively low $T_g$ (145°C) and low gas permeability.[6] Compared to polysulfones or polycarbonates, relatively few reports on the gas transport properties of poly(arylene ether ketone)s are available.[7] Recently, we initiated a study on structure–property relationships in poly(arylene ether ketone)s in order to develop polymers suitable for applications such as gas separation membranes.

Figure 1 illustrates poly(arylene ether ketone)s containing either 2,2′- or 3,3′-dibenzoylbiphenyl (DBBP) groups studied in this work. Novel polymers containing naphthalene (NP) groups in the repeat unit were also included in this study. Syntheses of these polymers have been described in elsewhere.[8,9] Table I lists the polymers studied in this work, along with their $T_g$ and $T_\gamma$ values. All polymers were amorphous and have higher $T_g$, compared to PEEK. Polymers with 2,2′-DBBP groups have relatively high $T_g$ values compared to other DBBP-containing polymers due to steric hindrance within the DBBP unit which inhibits overall mobility of the backbone. The choice of polymers with 2,2′- and 3,3′-DBBP units rests with the fact that these polymers are amorphous and are easily cast into dense membranes. More linear structures of DBBP-containing polymers with 4,4′- and 3,4′-substitutions have been reported to exhibit semicrystalline character.[10,11] The presence of the naphthalene ring in the polysulfone backbone has been shown to increase selectivity at the expense of gas permeability.[12] The naphthalene-containing polymers also showed stiff backbones, and were expected to show evidence of hindered chain packing, based on the bulky naphthalene groups in the repeat unit. The choice of the bisphenols (Ar = a–c, Fig. 1) also was based on the fact that they are known to yield

**Table I.** Poly(arylene ether ketone)s Studied in This Work and Their $T_g$ and $T_\gamma$ Values

| Polymer | Repeat Unit[a] | $T_g$, °C | $T_\gamma$, °C[b] |
|---|---|---|---|
| **33a** | 3,3′-DBBP/a | 159 | 25 |
| **33b** | 3,3′-DBBP/b | 212 | 25 |
| **22a** | 2,2′-DBBP/a | 178 | 75 |
| **22b** | 2,2′-DBBP/b | 228 | 75 |
| **22c** | 2,2′-DBBP/c | 233 | 75 |
| **NPa** | NP/a | 190 | 100 |
| **NPb** | NP/b | 260 | 100 |

[a] See structural features shown in Figure 1.
[b] Estimated peak value from Figure 9.

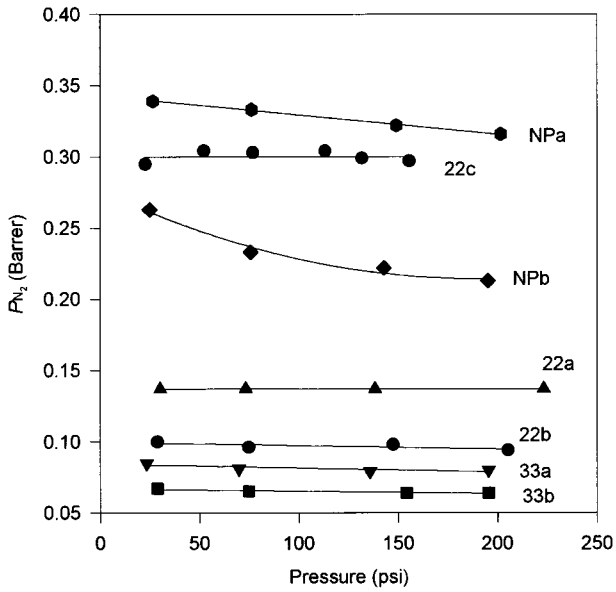


**Figure 2.** Pressure dependence of nitrogen permeability coefficients.

a variety of polymers with desirable gas separation performance.[13–22] Therefore, these polymers were investigated in light of their desirable features for polymeric gas separation membranes.

## EXPERIMENTAL

The procedure followed for polymer purification, film preparation, and film drying was identical to that used in a previously reported study.[23] Reference 23 also describes a constant-volume permeability apparatus and the procedure used for permeability measurements. Permeabilities were measured at 35.0°C in the sequence of $N_2$, $O_2$, $CH_4$, $CO_2$, and He. The $N_2$ permeability was repeated after testing $CO_2$ to ensure the polymers had not been significantly plasticized. The downstream pressure of the permeability apparatus was monitored at 10-s intervals with a PC computer acquiring the voltage output (0–10 VDC) from a 10.0 torr (±0.1%) Baratron transducer (MKS Instruments). Dynamic mechanical analyses (DMA) were measured on film strips (ea. 23 mm length × 1 mm wide) with a Rheometrics Solids Analyzer II. Viscoelastic properties were measured in tension mode from −145°C to the $T_g$ of the sample with a strain of 0.1–0.2% at a frequency of 1 Hz. Wide-angle x-ray diffraction (WAXD) patterns were determined with a Scintag XDS 2000 diffractometer equipped with a CuK$\alpha$ (1.5406 Å) source. Diffraction measurements were performed from 5 to 50 at 0.03° increments.

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 in a liquid of known density (distilled water). Densities were calculated using the Archimidian principle:

$$D = D_{std} \frac{M_{dry}}{M_{dry} - M_{imm}}$$

where $D_{std}$ 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.

## RESULTS AND DISCUSSION

### Permeability

Figures 2 to 6 illustrate the gas permeabilities at different upstream pressures for $N_2$, $O_2$, $CH_4$, $CO_2$, and He, respectively. The trends observed in these figures reflect the influence of the polymer structures on gas permeability. Polymers containing **b** groups, derived from 9,9-*bis*(4-hydroxyphenyl)fluorene (HPF), showed consistently

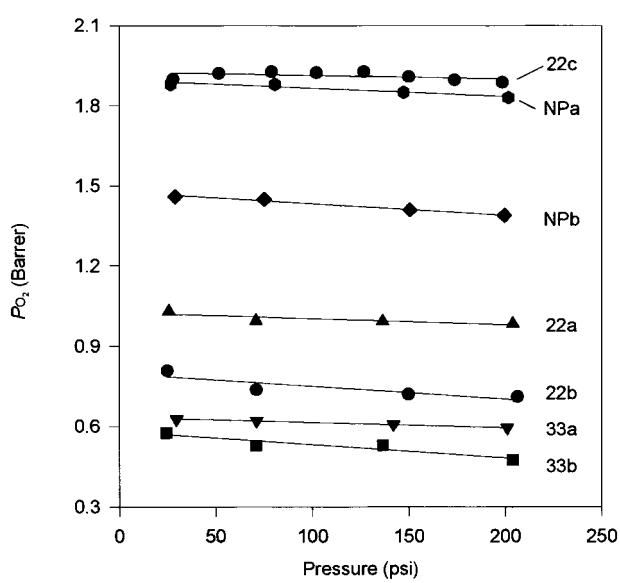


**Figure 3.** Pressure dependence of oxygen permeability coefficients.

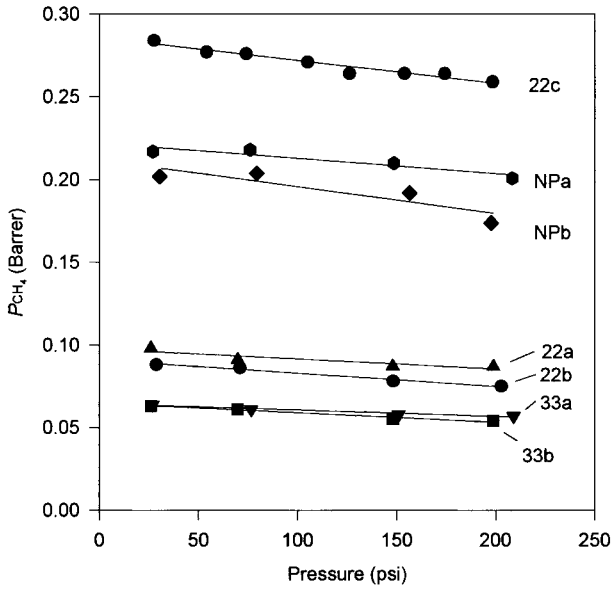


**Figure 4.** Pressure dependence of methane permeability coefficients.

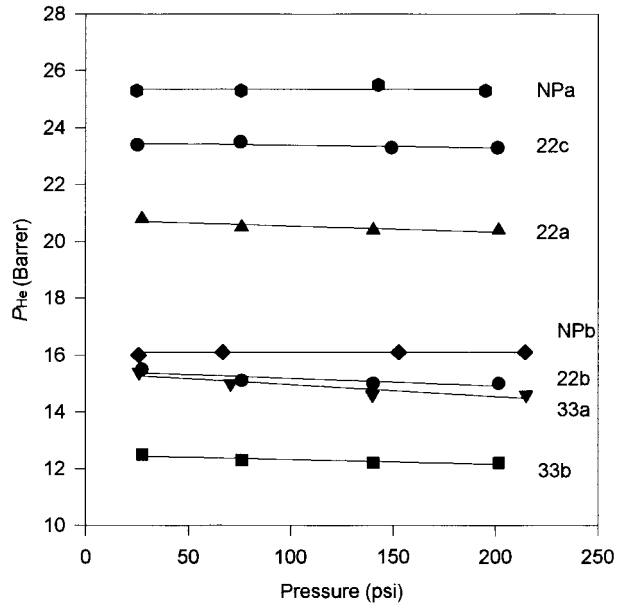


**Figure 6.** Pressure dependence of helium permeability coefficients.

lower permeabilities compared to polymers with a moieties (from 6F-BPA). Lower than expected permeabilities for polyarylates containing **b** groups were observed by Mohr et al.[14] Based on multiple peaks in the WAXD patterns, they attributed the low permeabilities to narrow $d$-spacing domains caused by stacking of the planar fluorene groups. Table II lists the $O_2/N_2$ and $CO_2/CH_4$ permeability and selectivity coefficients measured at 150 psi. The expected trade-off between $O_2$ permeability and $O_2/N_2$ selectivity ($\alpha$) can be observed, where higher permeabilities are accompanied by a slight decrease in $\alpha$. This effect is less obvious for $CO_2$ and $CH_4$, which has been previously observed for polymers containing $CF_3$ groups and most likely due to increased interaction with $CO_2$ molecules.[14,16]

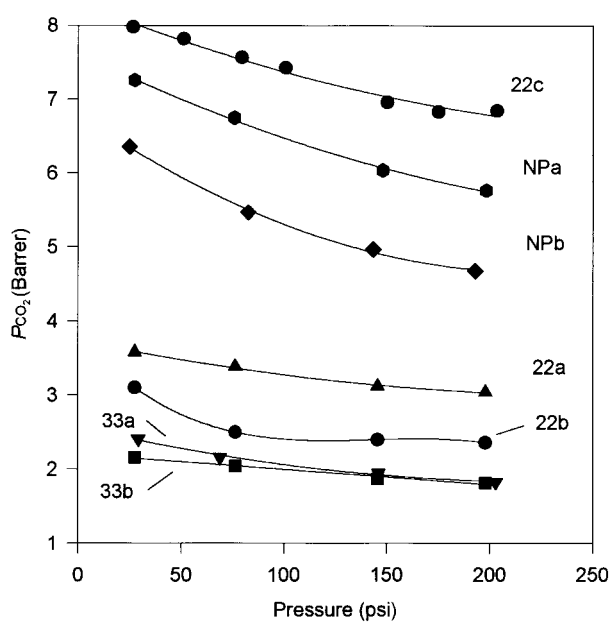


**Figure 5.** Pressure dependence of carbon dioxide permeability coefficients.

Polymer **22c,** which incorporates a tetramethylbiphenyl group, has the highest permeability among the 2,2′-DBBP polymers (**22a–c**). Previous studies have demonstrated that this group effectively disrupts chain packing, while restricting segmental mobility.[23] The relatively small loss in $O_2/N_2$ and $CO_2/CH_4$ selectivity coefficients confirms that this moiety has done the same for the 2,2′-DBBP polymer.

Comparing $O_2$ permeabilities and the biphenyl substitution reveal that polymers with 2,2′-DBBP groups have higher gas permeabilities than their 3,3′-DBBP counterparts. Aitken et al. previously reported gas transport properties for a poly(ether bisketone) (**PBK**, Fig. 7) containing a 4,4′-DBBP group.[24] The $O_2$ permeability for PBK was reported to be 0.75 Barrer (typically at 2 atm). A lower permeability was measured for polymer **33a** (0.60 Barrer, 2–10 atm, Fig. 3). Although the chemical compositions of PBK and **33a** differ slightly ($CF_3$ vs. $CH_3$), the difference in permeabilities between these two polymers is notice-

**Table II.** *d*-Spacing Value, Fractional Free Volume (FFV), Density (D), Permeability (P), and Selectivity Coefficient ($\alpha$) (at 150 psi) for DBBP- and NP-Containing Poly(arylene ether ketone)s

| Polymer | *d*-spacing (Å) | FFV | $D$ ($g \cdot cm^{-3}$) | $P_{O_2}$ (Barr) | $\alpha_{O_2/N_2}$ | $P_{CO_2}$ (Barr) | $\alpha_{CO_2/CH_4}$ |
|---|---|---|---|---|---|---|---|
| **33a** | 5.2 | 0.153 | 1.334 | 0.61 | 7.7 | 1.95 | 33.6 |
| **33b** | 4.5 | 0.149 | 1.220 | 0.53 | 8.3 | 1.87 | 34.0 |
| **22a** | 5.6, 4.3 | 0.171 | 1.307 | 0.99 | 6.8 | 3.12 | 35.9 |
| **22b** | 5.9, 4.4 | 0.147 | 1.219 | 0.72 | 7.4 | 2.40 | 30.8 |
| **22c** | 5.5, 3.9 | 0.126 | 1.161 | 1.86 | 6.4 | 6.96 | 26.4 |
| **NPa** | 5.5 | 0.150 | 1.121 | 1.85 | 5.7 | 6.04 | 28.8 |
| **NPb** | 4.7 | 0.157 | 1.356 | 1.42 | 6.4 | 4.97 | 25.9 |

able, since polymer **33a** contains the hexafluoroisopropylidene group instead of the isopropylidene group. Thus, an analog to **33a** containing isopropylidene (i.e., an isomer of **PBK**) would have gas permeability lower than **33a** and **PBK**, since $CF_3$ groups have been shown to increase permeabilities, relative to $CH_3$ groups. Based on these results, the 3,3′-DBBP polymers should have the lowest permeabilities for polymers with DBBP groups. This is consistent with findings from studies on aromatic polyimides that *meta*-substitutions gave lower $T_g$ values and lower gas permeabilities compared to para-substituted isomers.[13,25,26] The NP polymers show significantly higher permeabilities compared to the DBBP polymers, except in some instances where the permeability of **22c** is higher. At the same time, the $O_2/N_2$ and $CO_2/CH_4$ selectivity coefficients have decreased much more than is observed within the series of DBBP polymers. Therefore, the naphthalene group effectively disrupts chain packing.

### *d*-Spacing and Fractional Free Volume

It is useful to correlate permeabilities with WAXD results since higher *d*-spacing can be interpreted as being due to a more loosely packed matrix.[20] Figure 8 illustrates the WAXD patterns obtained from samples of the films used to measure permeabilities. Polymers containing the 2,2′-DBBP group exhibit complex WAXD patterns, suggestive of irregular packing. Since it is unclear how large and narrow spacings contribute to permeability, it is difficult to make correlations for these polymers. It is felt that this complex packing arises from the asymmetrical structure of the 2,2′-DBBP moiety, since di-*ortho*-substituted biphenyls have axis chirality and are generally resolvable if the substituents are larger than the carboxylic acid group.[27] Calculations by molecular mechanics of various DBBP models revealed significant steric hindrance to biphenyl rotation for 2,2′-substitution.[28] Consequently, the 2,2′-DBBP unit exhibits axis chirality and two stable enantiomeric configurations can be distinguishable at ambient temperatures. Polymers with naphthalene groups (**NPa**, **NPb**) were prepared from unsymmetrical dihalobenzonapthone monomers and also showed evidence of complex packing. These unsymmetrical benzonapthone moieties are present in head-to-head, head-to-tail, and tail-to-tail fashions, which introduce irregularity along the polymer backbone. The more flexible polymers **33a** and **33b** with lower $T_g$ reveal relatively narrow *d*-spacing distribution. In reference to previously reported packing of fluorene moieties,[14] polymer **33b** shows a simple pattern, suggesting that stacking of the fluorene groups cannot be solely responsible for the complex WAXD patterns. Our findings suggest that multiple WAXD peaks appear when the polymers include rigid and unsymmetrical moieties in the backbone.

The influences of *d*-spacings, densities and fractional free volume (FFV) on gas permeabilities are summarized in Table II. Prominent peaks are listed for polymers with complex WAXD pat-

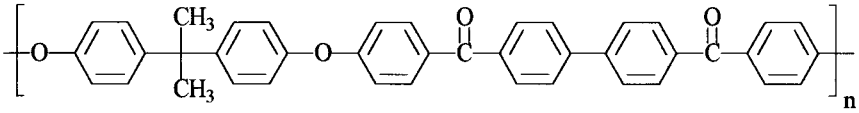


**Figure 7.** Polymer containing the 4,4′-DBBP moiety (**PBK**) studied by Paul et al.[24]

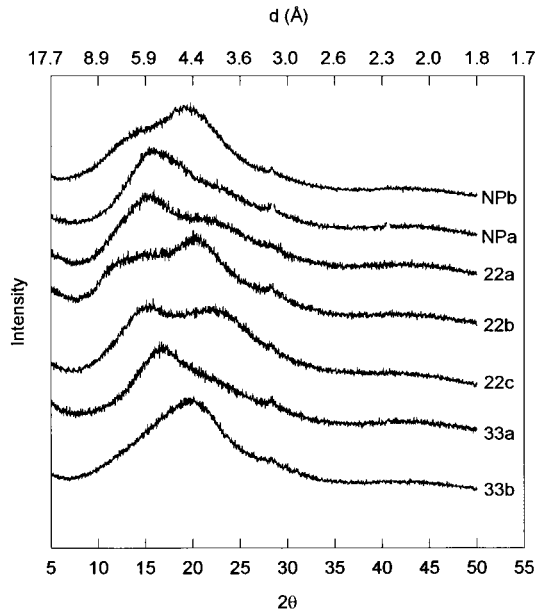


**Figure 8.** Wide-angle x-ray diffraction patterns.

terns. Narrow peaks can be observed for polymers **33a** and **33b**, and higher permeabilities are observed at higher $d$-spacings. Furthermore, the trends observed for permeability also follow the same trends observed for $T_g$. This observation has been explained previously on the basis that greater flexibility of the polymer chain allows for more efficient packing.[29]

The effects of FFV on gas permeabilities are also often examined by plotting 1/FFV vs. permeabilities. However, no apparent linear correlation was found between 1/FFV and $O_2$ permeabilities for these polymers. Attempts at correlating other gas permeabilities with 1/FFV yielded similar scattering. It was felt that discrepancies between gas permeabilities and FFV are due to experimental considerations.

## Sub-$T_g$ Transition

Measurement of sub-$T_g$ transitions by dynamic mechanical analysis (DMA) for polymers are useful in demonstrating that structural modifications have arrested or stiffened segmental motions in a series of polymers. Previous work has shown that increases in $\gamma$-relaxation temperatures has been observed at lower FFV, due to intermolecular restrictions to segmental motions.[30] In cases of intramolecular restrictions, the increased backbone stiffness is a plausible explanation to retained selectivity in situations of increased gas permeability and FFV. Sub-$T_g$ mechanical relaxations are observed most easily through changes in tan $\delta$ (i.e., ratio of loss modulus to elastic modulus). Figure 9 illustrates tan $\delta$ curves obtained from DMA measurements of the polymers studied in this work and Table I lists the estimated $T_\gamma$ peak values. The relatively large increases in tan $\delta$ at temperatures near $T_g$ (which were separately determined by DSC) were interpreted as being due to $\alpha$ transitions. Polymers 33a and 33b, containing 3,3′-DBBP groups, show a broad relaxation from −50 to 100°C due to a $\gamma$ relaxation. To avoid confusion with tan $\delta$ peak nomenclature, the convention followed here is that $\beta$ peaks designate relaxations which are thermal history dependent and could be reduced or eliminated by annealing. Except for **22c**, all the polymers were annealed prior to testing and no $\beta$-peaks were observed. Polymer **22c** could not be annealed due to its high $T_g$, and cross-linking at elevated temperatures. Thus, it is not known if **22c** exhibits a $\beta$ relaxation in its DMA curve. Shoulder peaks observed for **22a–b** (from 50°C to $T_g$) were assigned to $\gamma$ transitions. Relaxations were observed near −100°C for all the polymers studied. Since ambient humidity could not be excluded from the DMA tests, these peaks most probably include a contribution due to the presence of water, as has been previously observed for PEEK.[31,32]

The $\gamma$-transitions shown in Figure 9 are insen-

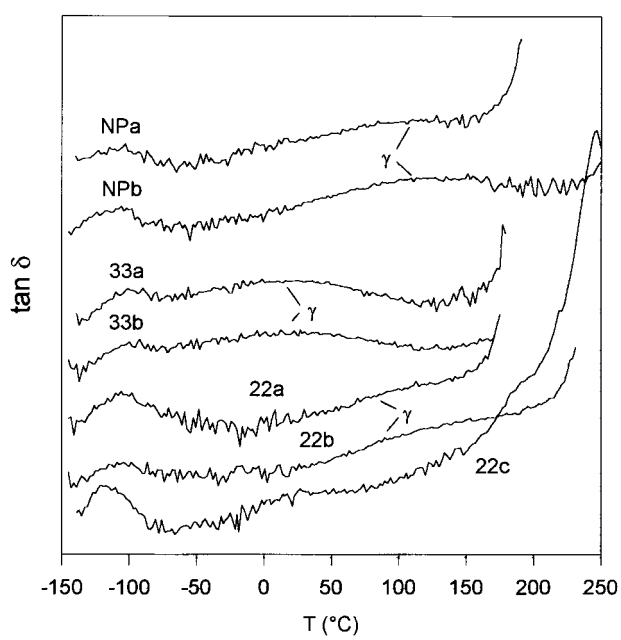


**Figure 9.** Tan $\delta$ curves from dynamic mechanical analyses.

sitive to changes in bisphenol connector a and b. This suggests that segmental mobilities are mostly contributions from the DBBP or naphthalene part of the repeat unit. The apparent higher $\gamma$-relaxation temperatures for 2,2′-DBBP and NP polymers appear to reflect the higher rotational barrier for these groups, compared to 3,3′-DBBP polymers. The decrease in chain mobility for 2,2′-DBBP polymers may explain the similarity between selectivity coefficients for 2,2′- and 3,3′-DBBP polymers, despite the higher gas permeability.

## CONCLUSIONS

The 3,3′-DBBP polymers yield the lowest gas permeabilities among the DBBP polymers, due to close packing of relatively flexible chains. Irregular packing observed for **22a–c** and **NPa–b** may be due to the presence of axis chirality of the 2,2′-DBBP unit and different dyads of unsymmetrical benzonaphthone units. The 2,2′-DBBP polymer containing the bulky tetramethylbiphenyl moiety **(22c)** has the highest gas permeability. In most cases, the naphthalene-containing polymers had higher gas permeabilities than those with DBBP groups.

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