

The Effect of Bisphenol Monomer Structure on the Gas Permeability of Aromatic Polycarbonates

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Synopsis

Permeability measurements for oxygen and, to a lesser extent, carbon dioxide were carried out on a series of 24 structurally different aromatic polycarbonates. Polymers were prepared from bisphenols bearing substituents on the aromatic rings and/or the central aliphatic carbon atom. A strong correlation between monomer structure and polymer permeability was found, with gas transport rates varying by over two orders of magnitude between the most and the least permeable materials. In addition, a semilogarithmic relationship was found between oxygen transmission rates and monomer composition for two series of copolycarbonates. Of several methods explored, an excess free volume model was found best able to relate the experimental permeability values to the polymer molecular structure.

INTRODUCTION

There is great interest in the gas transport properties of polymers due to the increasing use of these materials as gas barriers and separation membranes.¹ Gas permeability properties of most commercially available polymers have been measured and tabulated extensively.² However, there have been few reports of the effect on permeability of varying monomer structures within a specific class of polymer. Recent studies on series of aromatic polyimides³ and silicon polymers⁴ indicate that monomer structure can have a large effect on gas transport behavior. Unfortunately, the limited information on structure-permeability relations for other classes of polymers presently makes it difficult to correlate the reported results, much less to rationally design and synthesize materials with desired transport properties. Therefore, a study was initiated to investigate the gas transport behavior of a number of classes of engineering thermoplastics.

This report summarizes gas permeability measurements made on a series of substituted aromatic polycarbonates. Scattered reports,⁵ dating back 25 years, have indicated some dependence of polycarbonate gas transport properties on monomer structure. More recently, Muruganandam et al. reported⁶ extensively on the gas sorption and diffusion properties of three tetrasubstituted aromatic bisphenol A polycarbonates. In the present work, permeability measurements are described for a large series of systematically varied polycarbonates in order to better define the limits of transport behavior for this class

of polymer and to give further insight into how this behavior correlates with monomer structure.

EXPERIMENTAL

Monomer Synthesis

The bisphenol monomers used in this investigation are listed in Table I. Most of these bisphenols were conveniently prepared by acid-catalyzed condensation of the appropriately substituted phenols and ketones.^{5a} Hexafluorobisphenol **15** and 4,4'-dihydroxydiphenyl ether **21** were purchased from Aldrich and Eastman Chemicals, respectively. Literature methods were followed in the synthesis of bisphenols **13**,⁷ **16**,⁸ and **17**.⁹

Diester bisphenols **18**–**20** were prepared by condensing 4-acetoxybenzoyl chloride⁹ with the appropriate diol, followed by acetate hydrolysis. This reaction sequence is illustrated by the synthesis of monomer **18**: Pyridine (150 mL) was added to a solution of 4-acetoxybenzoyl chloride (79.4 g), 2-hydroxyethylether (21.2 g), and methylene chloride (450 mL) over 0.5 h. After stirring at ambient temperature for 2 h, the solution was washed with 10% HCl solution followed by water. Solvent removal followed by recrystallization from methanol gave the diacetate of bisphenol **18** as small white needles (55.8 g, 66% yield, mp = 75.0–76.0°C). A solution of the diacetate (54.4 g), acetone (600 mL), and 10% HCl solution (200 mL) was refluxed for 5 h. Water and ethyl acetate were added to the cooled solution until two phases separated. The organic fraction was washed with sat. NaHCO₃ solution, water and concentrated *in vacuo* to give bisphenol **18** as a white solid (37.0 g, 71% yield, mp = 136.0–137.0°C).

The previously unreported cyano-functionalized bisphenols **12** and **23** were prepared by converting the corresponding diphenolic esters to the amides followed by dehydration. The synthesis of nitrile **12** serves as an example of this method: Ethyl 4,4-bis(4-hydroxyphenyl)pentanoate (249 g) was stirred with aqueous ammonium hydroxide (29%, 2000 mL) at room temperature for 96 h. The resulting clear brown solution was diluted with water and extracted repeatedly with ethyl acetate. The combined organic fractions were washed with water and concentrated *in vacuo* to give 4,4-bis(4-hydroxyphenyl)pentanamide as a tan powder (156.0 g, 71% yield). A solution of the amide bisphenol (120 g) and acetic anhydride (600 mL) was refluxed for 16 h. The red-orange solution was cooled to room temperature and the volatiles removed under vacuum to leave the nitrile diacetate as a viscous orange oil. This intermediate was refluxed with acetone (500 mL) and 10% HCl for 4 h. The reaction mixture was diluted with ethyl acetate and water to separate an organic layer. Concentration of the organics furnished the crude nitrile which was recrystallized (methanol/water, decolorizing charcoal) to give nitrile bisphenol **12** as white crystals (87.0 g, 77% yield from the amide, mp = 156.0–157.5°C).

Polymer Synthesis

Polycarbonates of most of the bisphenol monomers were prepared by condensation with phosgene under standard^{5a} interfacial conditions. Molecu-

lar weight control of the polymers based upon bisphenols substituted only at the central carbon atom (6–15) was readily achieved by the traditional use of phenol chainstopper at the beginning of the polymerization reaction. However, use of this procedure with the bisphenols substituted at the aromatic 3,3'-positions (2–5 and 22–24) invariably gave polymers with an unacceptably large (5–30%) low-molecular-weight fraction. For these monomers, polymers with a more controlled molecular weight and lower dispersivity were prepared following a slightly modified procedure where the chainstopper (phenyl chloroformate) was added to the reaction mixture over the second-fifth of the phosgene addition. Finally, several bisphenols (17–21) could not be polymerized to high-molecular-weight product by an interfacial procedure, apparently due to their, or their oligomers', limited solubility in the water/methylene chloride solvent system. In these cases, high-molecular-weight polymer could be prepared using pyridine/methylene chloride as the solvent. Poor film integrity (i.e., brittleness) precluded permeability measurements on homopolymers 17 and 19–21. Therefore, copolycarbonates containing 50-50 molar mixtures of the structurally modified bisphenol and bisphenol A 1 were prepared for these samples. Molecular weight data and glass transition temperatures for the polymers used in this study are included in Table I.

Sample Preparation and Permeability Measurements

Solvent casting was the method of choice for preparation of bubble-free films of uniform thickness. Typically a 8–10 wt% methylene chloride solution of a polymer was prepared and passed through a 0.5 μm filter. The filtered solutions were poured onto clean, dried soda-lime glass plates fitted with a glass casting ring. Solvent was allowed to diffuse through a lightly plugged, inverted funnel over 48 h. Drying for 96 h in a vacuum oven (70°C, 15 torr) gave film samples which, with the exception of polymer 18, were clear and ductile.

Oxygen permeability measurements were made using a Modern Controls Inc. Oxtran 100 or 1000 analyzer. Film samples, 5–10 mil thick, were mounted between aluminum foil masks containing 5 cm^2 holes. One side of the film was flushed with a 1 atm stream of oxygen, while the oxygen concentration in the nitrogen stream purging the other side of the film was monitored. Once the oxygen concentration was constant over a 12 h period, it was assumed that a steady-state flux of oxygen through the film was achieved and the permeability value was determined. Control experiments show that reproducibility of the permeability readings had a precision of $\pm 5\%$. Oxygen permeability data for the various polycarbonates are listed in Table II. (For the sake of consistency,¹⁰ all the permeability values in this report are in the units of Barrers, where 1 Barrer = $10^{-10} \text{ cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}$). Carbon dioxide permeability measurements were carried out on a small subset of the polycarbonates using a recently reported¹¹ technique which involves the use of radiolabeled CO_2 . Results from these experiments are also included in Table II.

TABLE I
Properties of Substituted Polycarbonates

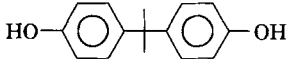
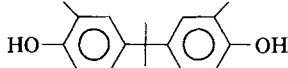
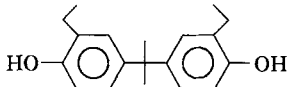
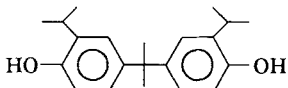
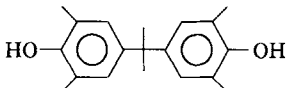
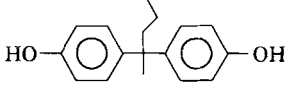
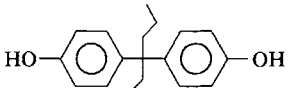
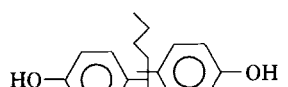
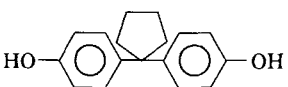
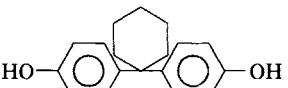
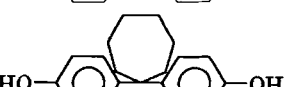
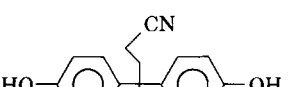
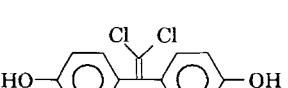
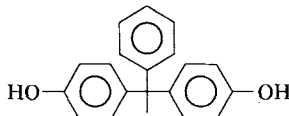
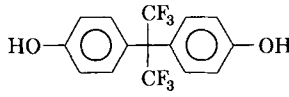
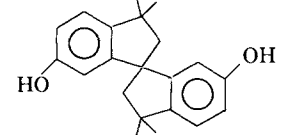
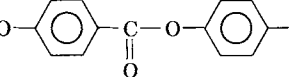
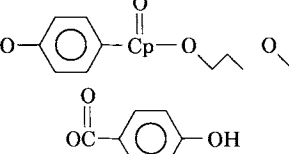
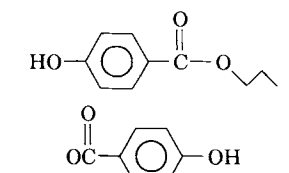
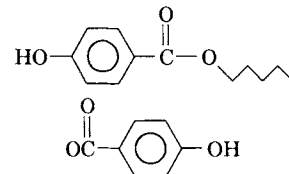
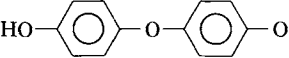
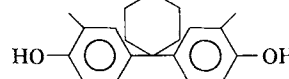
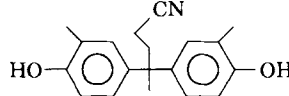
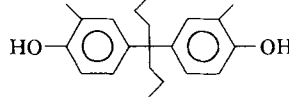
Entry no.	Bisphenol Composition	M_w^a	M_w/M_n^a	$T_g(^{\circ}\text{C})$
1		52,400	2.4	150
2		47,800	2.6	98
3		46,000	2.4	65
4		49,900	2.1	80
5		71,900	4.1	191
6		55,600	4.5	137
7		49,400	2.9	130
8		89,400	3.9	113
9		61,600	3.6	155
10		36,000	5.2	145
11		76,500	2.1	155
12		92,000	5.6	150
13		98,400	5.5	166

TABLE I (Continued)

Entry no.	Bisphenol Composition	M_w^a	M_w/M_n^a	$T_g(^{\circ}\text{C})$
14		53,500	3.8	179
15		33,300	4.8	158
16		97,000	4.8	228
17 ^b		41,000	2.4	140
18		44,900	7.5	51
19 ^b		26,900	3.7	96
20 ^b		37,500	3.5	72
21 ^b		38,600	2.7	127
22		61,000	3.1	140
23		39,000	2.3	117
24		46,000	3.2	101

^a Molecular weight data were determined by gel permeation chromatography and are calibrated against polystyrene standards.

^b Polymer prepared was a 50-50 molar % copolycarbonate with bisphenol A.

TABLE II
Permeabilities of Substituted Polycarbonates

Polymer	PO ₂ (Barrers) ^a	PCO ₂ (Barrers) ^a	α CO ₂ /O ₂
1	1.38	6.00	4.3
2	0.30	1.09	3.6
3	0.72	3.35	4.7
4	1.83	8.64	4.7
5	5.43	26.23	4.9
6	1.48		
7	2.35		
8	3.41		
9	1.35		
10	0.57		
11	0.76		
12	0.33		
13	1.46		
14	2.02		
15	6.29		
16	6.90		
17	0.86		
18	0.04		
19	0.55		
20	0.46		
21	0.88		
22	0.10	0.35	3.5
23	0.21		
24	1.26		

^a Measured at 25°C, 1 atm, 0% relative humidity.

RESULTS AND DISCUSSION

Effect of Sample Preparation on Permeabilities

A recent report³ found gas permeability rates to be unaffected by several variables in solvent casting technique. However, the presence of residual solvent would be worrisome in that it would be expected to modify a polymer film's observed gas transport properties by swelling or plasticizing the polymeric structure. To test if the described drying technique adequately removed all the methylene chloride from the polycarbonate samples, films of several of the polycarbonates (2-4) were dried for varying lengths of time. Portions of the films were pyrolyzed, with the residue being analyzed by ion chromatography to furnish a qualitative measure of volatile chloride present in the film. As shown in Table III, the chloride levels of the films are constant, or nondetectable, after 96 h in the drying oven. (The uniformly high levels found for polycarbonate 2 are thought to be an artifact from incomplete washing of chloride ion from the polymer following its preparation.) Further evidence of complete solvent removal is furnished by ¹H nuclear magnetic resonance (NMR) measurements of the films dried for 96 h, which fail to find a signal corresponding to methylene chloride ($\delta = 5.27$). Finally, oxygen permeabilities of the three samples were, within experimental error, constant after 96 h of

TABLE III
Properties of Oven-Dried Films

Polymer	Time dried ^a (h)	ppm Chloride	PO ₂ (Barrers)
2	24	28.8	0.48
	48	32.2	0.37
	96	24.5	0.32
	120	—	0.31
3	24	8.64	0.74
	48	6.52	0.76
	96	2.34	0.77
	120	—	0.72
4	24	5.68	1.80
	48	1.05	1.96
	96	< 1.0	1.80
	120	—	1.83

^aFilms were dried in a vacuum oven at 70°C, 15 torr.

drying (Table III). These results indicate that the drying technique employed is adequate for the removal of residual solvent.

Annealing at subglass transition temperatures has been shown to affect the gas transport properties of films of glassy polymers, with bisphenol A polycarbonate being the most extensively studied example.¹² It is, therefore, of concern as to whether the inherent transport properties of the substituted polycarbonate samples are being masked by the effects of oven drying. The previously mentioned observations that oxygen permeabilities of samples 2–4 appear to have leveled off after 96 h of oven drying at 70°C suggests that this drying time is adequate for solvent removal, but not long enough to greatly alter the transport properties by way of annealing. Furthermore, differential scanning calorimetry (DSC) measurements failed to find any signs of crystallization or other ordering in the dried samples, with the notable exception of the diester bisphenol based polycarbonate 18. Finally, extruded films of two polycarbonates (1 and 22) were prepared and the oxygen permeabilities of these films were found to be within experimental error of those measured on the solvent cast samples. While the magnitude of the change in gas transport properties caused by a sample's process and thermal history is expected to be dependent somewhat on its T_g ,¹² the above results suggest that the solvent casting and drying technique of sample preparation does not drastically affect the polymers' observed gas permeability values.

Effect of Molecular Structure on Polycarbonate Oxygen Permeability

The results listed in Table II clearly show that monomer structure has a large effect on a polycarbonate's gas transport rates. Structural variation of the bisphenol gives rise to a greater than two order of magnitude range in oxygen permeability among the materials, with polymers based on the spirobiindane monomer (16) and the diester bisphenol (18) exhibiting the highest and lowest permeabilities, respectively. The monomers differ from 2,2-bis(4-

hydroxyphenyl)propane (bisphenol A, **1**) by substitution at the 3,3'-positions of the aromatic rings (entries **2**–**5**), substitution at the "central," aliphatic, carbon atom (entries **6**–**21**), or by substitution at both positions (entries **22**–**24**). Considering these three subsets separately, relationships between monomer structure and the oxygen permeabilities of the polycarbonates can be drawn.

Polycarbonates which contain bisphenol monomers substituted at the aromatic 3,3'-positions (**1**–**5**) exhibit widely varied gas transport rates. Placement of methyl groups at these positions gives a polymer (**2**) with five times lower permeability than the unsubstituted polymer **1**. However, substitution by increasingly bulkier alkyl groups [e.g., ethyl (**3**) or isopropyl (**4**)] goes against this trend by increasing the permeabilities of the polymer to close to, or above, that of **1**. Furthermore, as has been reported,⁶ polymer containing the symmetrically substituted 3,3',5,5'-tetramethylbisphenol (**5**) has a much higher permeability rate than either the unsubstituted (**1**) or dimethyl-substituted (**2**) polycarbonate. The ability of various structure-permeability models to predict these seemingly disjointed results will be discussed later.

A number of types of groups were substituted at, or in place of, the central, aliphatic carbon atom of the bisphenols, giving correspondingly different effects on the resultant polycarbonate's permeability. For example, replacement of the geminal dimethyl groups in bisphenol A-based **1** with longer chain alkyl substituents gave polymers (**6**–**8**) with progressively higher oxygen transport rates. Replacement of the methyl groups by other sterically bulky groups (**14**–**16**) raised the permeabilities in a similar fashion. On the other hand, polymers based upon monomers where the central carbon is contained in a medium-sized aliphatic ring (**9**–**11**) have permeabilities lower than the bisphenol A **1** reference point. This triad of polycarbonates illustrates again the sensitivity of gas permeabilities to small structural changes, with the 6-member ring-containing polymer (**10**) having a lower permeability than either the 5- or 7-member ring-containing polymers. The observation that, of the three, the polycarbonate substituted by the midsized ring has the lowest permeability suggests that the well-known ability of the cyclohexane ring to adopt a sterically compact conformation is helpful in slowing the polymer's gas transmission rate.

Polycarbonates containing bisphenols where the central carbon atom is replaced by sterically small functional groups such as an ester (**17**–**20**) or an ether (**21**) are also found to have low oxygen permeabilities. The homopolycarbonate of diester biphenol **18** has a permeability in the range of that exhibited by structurally analogous alkyl terephthalate polyesters (i.e., PET or PBT). This particular film sample exhibited signs of partial crystallinity after drying (translucent appearance and $T_m = 67^\circ\text{C}$ observed in the DSC) which should lower the observed permeability relative to that of a fully amorphous sample. Nevertheless, the magnitude of the difference in permeabilities between **18** and **1** (a factor of 35) is far greater than would be caused by a change in polymer morphology¹³ and is therefore attributable primarily to molecular structure differences. This issue of structure-permeability relationships between polycarbonates and polyesters will be addressed in greater detail in a forthcoming report.

Parenthetically, two series of copolycarbonates were prepared from bisphenol A and either monomer **2** or **22**. Measurement of oxygen permeabilities on

TABLE IV
Effect of Monomer Content on Copolycarbonate Oxygen Permeability

Monomer composition (mol%)			PO_2 (Barrers)
1	2	22	
100			1.38
75	25		0.98
50	50		0.67
25	75		0.53
	100		0.30
75		25	0.77
50		50	0.36
25		75	0.28
		100	0.10

these materials (Table IV) gives some indication of the effect of monomer composition on gas transport rates through the copolymers. Plots of this data (Fig. 1) reveal a semilogarithmic relationship between the observed permeabilities and monomer composition, such that the copolymer permeability (P_{AB}) is modeled by the equation:

$$\log P_{AB} = X_A \log P_A + X_B \log P_B$$

where X is the molar fraction and subscripts A and B identify the comonomer. This type of relationship has been reported for other random copolymers, such as those prepared from styrene and acrylonitrile.¹⁴ While more data are needed to firmly establish the generality of this relationship, it does allow a rough extrapolation to the expected permeabilities of homopolymers based on monomers 17 and 19–21.

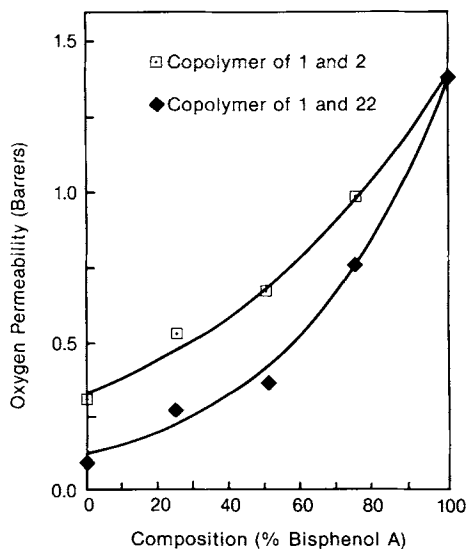


Fig. 1. Oxygen permeability–monomer composition relationship for copolycarbonates. Lines are calculated assuming a semilogarithmic relationship.

Permeability measurements were performed on several polycarbonates (22–24) which, in addition to having different groups at the center carbon atom, also are substituted by methyl groups at the aromatic 3,3'-positions. A comparison between data from these materials and the analogous polycarbonates which are unsubstituted at the aromatic rings shows that, just as in going from polymers 1 to 2, the dimethyl substituents lower the permeability rates in every case. However, the magnitude of this permeability "drop" ranges from nearly sixfold (10 to 22) to a factor of only 1.6 (12 to 23). Thus, while these results suggest some degree of additivity of monomer structural effects toward polymer permeability, it is qualitative at best.

Carbon Dioxide Permeabilities of Substituted Polycarbonates

Carbon dioxide permeabilities measured on a smaller number of the polycarbonates are roughly 3.5 to 4.5 times higher than the corresponding oxygen values, as would be expected (separation factors, α CO₂/O₂, are listed in Table II). These results agree with recent reports which find little change in gas separation factors for structurally related polymers despite large differences in permeabilities.^{4,6,12} More detailed studies of the selective permeability characteristics of these new materials are planned.

Fitting of Transport Data to Structure-Permeability Models

The gas transport data listed in Table II presents an opportunity to test how current structure-permeability models succeed in dealing with series of structurally related polymers. A strictly empirical approach, the Permachor model,¹⁵ was not able to rationalize the observed results. A deficiency of this model is the rather limited list of structural increments tabulated in available reports, a problem compounded by a lack of description as to how the incremental values are determined. This dearth of information precluded the calculation of expected permeability values for many of the structurally varied polycarbonates. In cases where available data do allow for the calculation to be performed, agreement between the predicted and experimental transport rates is limited.

On a molecular level, differences in the permeabilities of polymers are typically rationalized by citing differences in structural factors such as polarity, hydrogen bonding, cohesive energy density, crystallinity, steric hindrance, chain flexibility, and free volume.¹⁶ Polarity, hydrogen bonding, and crystallinity effects may be expected to contribute to the observed gas transport properties of several of the modified polycarbonates, for example, 12 and 17–21. However, the majority of the polymers studied here differ only by varying simple hydrocarbon substituents. Hence their permeabilities are not expected to be affected very differently by these types of factors. Nevertheless, oxygen permeabilities within this subset of hydrocarbon-substituted polycarbonates differ by as much as a factor of 60 (from 16 to 22). Therefore, it remains to rationalize these gas transport differences on the basis of polymer chain flexibility and polymer chain packing.

A closer look at the series of 3,3'-substituted polycarbonates (1–5) may give some insight into the effect of polymer chain flexibility/mobility on polymer permeability. The predominate segmental motion of unsubstituted polycar-

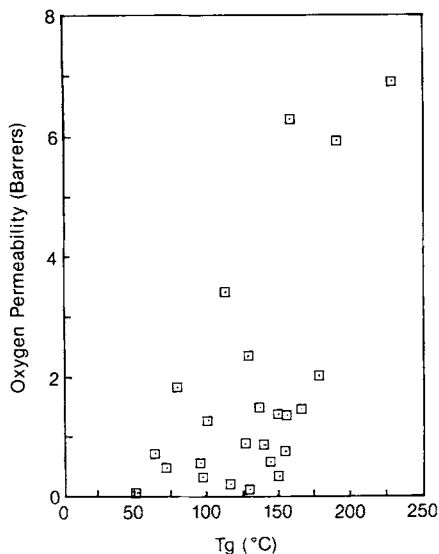


Fig. 2. Relationship of oxygen permeability and glass transition temperature for substituted polycarbonates.

bonate **1** in its glassy state is a partial rotation, or π -flip, of the phenylene group about its 1-4 axis.¹⁷ A large volume element change has been assigned to this motion by dynamic mechanical techniques. On steric grounds, orthosubstitution would be expected to slow this motion and, indeed, this has been found to occur experimentally by dynamic mechanical¹⁷ and NMR techniques.¹⁸ When the experimental data of polymers **1** and **5** and inspection of models of **2-4** are combined, the ordering of segmental motion is expected to be: **1** > **2** > **3** > **4** > **5**. This order is not observed for the permeabilities of the polycarbonates, implying that this particular motion is not a controlling factor for gas transport rates. As further evidence against a correlation between high chain mobility and high gas permeability, it is noted that the polycarbonate based upon monomer **16**, where the spirobiindane structure precludes any rotation of the phenyl rings, has the highest oxygen permeability of the polymers studied. Finally, despite earlier claims,¹⁹ a plot of oxygen permeabilities versus T_g (Figure 2) shows no correlation between these properties. Thus, no obvious general relationship between polymer chain mobility and gas transport rates can be drawn at this point.

A free volume approach is a useful way to relate polymer chain packing to the gas transport process.^{16a} The basic premise of this technique is that a polymer with an open, poorly packed structure will have a large unoccupied free volume through which a gas can diffuse with ease. A model set forth by Lee²⁰ was used to analyze the oxygen permeabilities of most of the polycarbonates. In this manner, the specific free volume (SFV) is defined as $V_m - V_o$, where the molar volume (V_m) of the polymer is determined from its density, and the occupied volume (V_o) is calculated using a group additive method put forth by Bondi.²¹ Table V lists the experimental densities of the polymers which allow for the calculation of the polymer SFVs. A plot of the logarithm of the oxygen permeability coefficients versus the reciprocal of the SFVs, as

TABLE V
Specific Free Volumes of Polycarbonates

Polymer	Density ^a (g/cm ³)	Molar volume (V_o)	Occupied volume (V_m)	Specific free volume ^b
1	1.199	177.0	136.2	0.1380
2	1.167	206.1	158.5	0.1273
3	1.128	232.7	179.0	0.1370
4	1.081	259.2	199.4	0.1592
5	1.086	235.1	180.9	0.1632
6	1.159	203.7	156.7	0.1414
7	1.116	230.3	177.1	0.1544
8	1.098	256.9	197.6	0.1519
10	1.212	208.0	160.0	0.1185
11	1.203	221.3	170.3	0.1137
14	1.208	218.9	168.4	0.1293
16	1.147	247.9	190.7	0.1308
22	1.184	241.5	185.8	0.0955
23	1.192	234.3	180.6	0.1108
24	1.093	259.3	199.4	0.1490

^aDetermined by floating using potassium iodide gradient columns.

^bCalculated by the method of Lee.²⁰

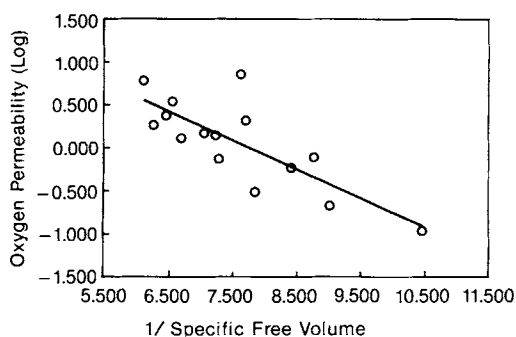


Fig. 3. Correlation of polycarbonate oxygen permeability versus reciprocal of specific free volume (after Lee).

proposed by Lee,²⁰ shows a fair correlation between these values (Fig. 3). At its best, this model correctly predicts the ordering of the permeability of the 3,3'-substituted polycarbonates 1-5. On the other hand, there is substantial scatter in the data, with an extreme example being SBI-based polycarbonate 16 having a much greater permeability than was calculated. Therefore, a free volume approach to modeling polymer permeability, while having merit, also has room for refinement and work continues toward that end.

CONCLUSIONS

Gas transport rates for aromatic polycarbonates were found to be highly dependent on polymer molecular structure. By varying the substituents on the bisphenol monomer, polymers with oxygen permeability either much higher (by a factor of 5), or much lower (by a factor of 35) than the benchmark

bisphenol A polycarbonate could be prepared. In general, replacement of the geminal methyl groups in bisphenol A by sterically larger groups leads to a material with greater permeability, while replacement with smaller groups gave the opposite effect. Substitution by methyl groups at the 3,3'-positions of the aromatic rings was found to be a general way to lower the transport rate of a polycarbonate. On the other hand, substitution at these positions by larger alkyl groups or symmetric, 3,3',5,5'-tetramethyl substitution gives a polymer with higher permeability properties. Using a smaller database, it was found that the ratio of transport rates of CO₂ to O₂ through the polycarbonates remains fairly constant (3.5–4.5), despite large variations in the absolute permeability rates.

Using an existing free volume approach, a qualitative relationship between monomer structure and the experimental polymer permeabilities was found to exist. Attempts to rationalize the results using empirical or chain flexibility-based arguments were not successful. These, and other results are presently being used to refine an excess free volume method in hopes of achieving better estimated gas transport properties based on molecular structure.

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