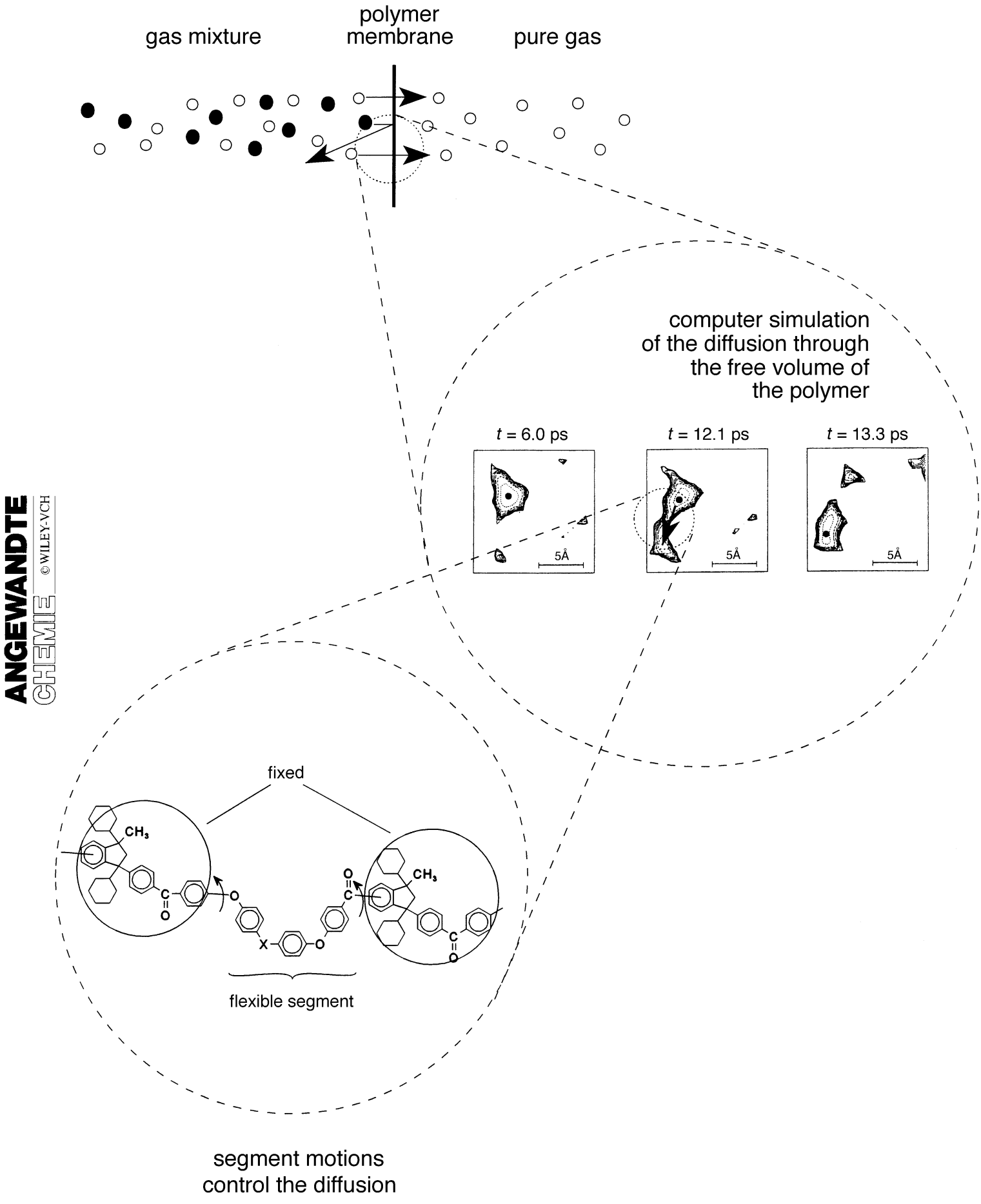

Gas Separation with Polymer Membranes

Gerhard Maier*

The gas permeability of amorphous polymers has been long utilized industrially for the separation of gas mixtures. In spite of a large collection of data regarding permeability coefficients and selectivities of nearly all film-forming polymers, the relationship between the chemical structure of a polymer and its properties as a membrane for gas separation has only been insufficiently explored up to now. Modifications of the chemical structure of a polymer chain often lead to an improvement of the permeability coefficient at the cost of selectivity, or vice versa. The transport of gas molecules in amorphous, vitreous polymers occurs through the free volume, that is, through the gaps between the polymer chains. It is affected by the thermal motion of segments of the main polymer chain. To obtain materials with optimized transport properties, attempts are made to increase the chain stiffness by incorporating rigid and bulky groups into the polymer chain, which in turn, by affecting the packing density, increases the free volume. The goal is to increase simultaneously the selectivity and the permeability coefficients. This approach, however, has failed to succeed up to now, as the structural modifications have been limited—owing to necessary considerations for industrial applications—by the availability of starting materials and the preparative effort during the monomer synthesis. New impulses can come from the synthesis of special polymers, which contain very short, but relatively flexible segments between rigid and bulky structural elements. Such segments should retain limited mobility even in the vitreous state. It is crucial to limit this mobility to the actual flexible segments, as otherwise the selectivity will likely be negatively affected. The transport of the gas molecules should then be primarily controlled by the flexible segments, which should yield hints for further structural optimization, in terms of length and flexibility of these chain segments. Studies on two series of polyimides and one series of poly(ether ketone)s, all containing bulky indane groups as well as flexible phenyl ether segments in the repeat unit, have provided the first indications for such behavior. Relative to observations with known polymers, the polyimides did not exhibit unusual changes in permeability and selectivity when the polymer backbone was altered. The poly(ether ketone)s, however, when compared to polymers studied thus far, did show significant changes in the relationship between free volume and the permeability coefficient as well as in the dependence of the selectivity on the chemical structure of the polymer.

Keywords: gas separation · membranes · polymers

1. Introduction

Gases occupy a central position in the chemical feed stock industry. Six of the ten most important industrial feed stock chemicals are gases: oxygen, nitrogen, ammonia, chlorine, ethylene, and propylene.[1] Their proportions may vary in different industrialized countries, but the general picture remains the same. In 1994 the worldwide market volume for industrial gases was 26 billion US dollars, with an expected annual growth of 4 % in the industrialized countries and up to 14 % in Asia.[2]

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Gases are primarily purified by cryogenic techniques or by adsorption and washing methods. The requirements for purity and, hence, for the purification method, depend heavily on the origin and the application of the gas in question. For nitrogen as inert gas for food packaging, for instance, a purity of 99 % is perfectly adequate. For medical purposes, pure oxygen is usually not required, but air enriched with oxygen to a level of 40 % is sufficient. If purity levels below 99.95 % are adequate, the purification of nitrogen in a membrane setup is usually the most economical procedure.[3]

In principle, all materials that form sufficiently thin films can be used to create membranes. This includes metals, glass, ceramics, and polymers as well as well-ordered monomolecular layers of surfactant molecules in liquid membranes. The thickness of these membranes varies from a few nanometers for Langmuir–Blodgett films (single or multiple layers of molecules which are deposited in a controlled fashion) up to

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hundred micrometers for membranes with strong mechanical properties.

This review is concerned with the field of gas separation with polymers as membrane materials,[3–10] as nearly all commercial membranes for gas separation as well as the overwhelming majority of membranes studied in the laboratory for this purpose consist of polymer films. Polymer membranes operate according to the solution–diffusion mechanism.[3] Other separation mechanisms are found, for example, in metal membranes for the preparation of ultrapure hydrogen,[3, 11] which rely on the catalytic dissociation of hydrogen in palladium–silver alloys, as well as for certain ceramic membranes,[3, 12–15] which utilize a molecular-sieve effect.

2. Industrial Applications of Polymer Membranes for Gas Separation

Even though there are a large number of potential applications for gas separation with polymer membranes,[3–5, 7, 9, 10] only relatively few of them have become applied in practice. The commercial applications began only in 1979 with "prism separators" from Monsanto.[3, 9, 10] These were gas-separation devices with a modular design, which were used for the separation of hydrogen from the product stream of ammonia synthesis[3] and the oxo process.[3] The highlight of applications to date is probably the plant for the separation of air into its constituent gases from Praxair in Loenhout, Belgium, which began operation in 1996 and which can yield up to 19100 $Nm^3 h^{-1}$ (nearly 24 $t h^{-1}$) of pure nitrogen.[2] This plant is about five times larger than those built before, which could yield up to 3500 $Nm^3 h^{-1}$ of nitrogen.[2]

Other applications of membranes for gas separation and purification are quite well developed in some cases, but have so far not been successfully introduced into practical use.[3–5, 7, 9, 10] These include the removal of CO_2, H_2S, and H_2O from natural gas (to increase to fuel efficiency and decrease pipe corrosion), the recycling of hydrogen from the effluent streams of natural gas or crude oil desulfurization and other hydrogenation processes, the preparation of oxygen-enriched air (e.g., for medical purposes), the recycling of helium, the separation of olefins and alkanes (processing of cracking products), and the separation of SO_2 and NO_x from exhaust fumes.

Only integrated asymmetrical and composite membranes are currently used industrially for the separation of gases.[3, 9, 10, 32] These types of membranes are characterized by very thin nonporous layers which are gas-selective and are deposited onto highly porous carrier materials. As the material transport is inversely proportional to the membrane thickness, only such an arrangement yields sufficiently high throughputs. The porous carrier materials provide the necessary mechanical strength, but do not contribute to transport resistance.

3. Quantitative Description of Material Transport through Membranes

In 1866 Graham postulated the model concepts for the mechanism of gas permeation that are still valid today.[16] He observed that the rates at which gases passed through a membrane did not correlate with the well-known gas diffusion constants. From this, he concluded that the transport does not occur through pores (defects in the polymer films), at least not to a significant degree, but indeed through the membrane material itself. According to Graham's model, the passage of a gas through a nonporous polymer film occurs in three stages. Initially, the gas must be dissolved in the membrane material, then the gas particles must diffuse through the polymer, and finally the gas must be released. According to this model, the process is termed a "solution–diffusion mechanism".

In 1955 Fick studied the quantitative description of gas diffusion through nonporous membranes of cellulose nitrate.[17] The relationship between throughput, membrane area, membrane thickness, and driving force which was found by Fick for the stationary state became generally known as "Fick's 1st law" for material transport though boundary layers. According to this relationship, the quantity J_X of gas X which passes through the membrane per unit time and area is proportional to the difference in pressure between the input (p_1) and permeate sides (p_2) and inversely proportional to the

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membrane thickness d [Eq. (1)].[9, 10] In the case of gas permeation, the proportionality constant P_X is called the per-

$$J_X = P_X \frac{p_1 - p_2}{d} \quad (1)$$

$$P_X[\text{Barrer}] = 10^{-10} \frac{V\,[\text{cm}^3(\text{STP})]\,d\,[\text{cm}]}{A\,[\text{cm}^2]\,t\,[\text{s}]\,\Delta p\,[\text{Torr}]} \quad (2)$$

$$P_X = S_X D_X \quad (3)$$

meability coefficient of the given material for the gas X. Hence, it is a substance-specific quantity and characteristic for each membrane material. The permeability coefficient with the unit "Barrer" is defined by Equation (2); V is the permeate volume at standard pressure and temperature (STP), d the membrane thickness, A the membrane area, t the time, and Δp the pressure difference between input and permeate sides. Von Wroblewski showed that the permeability coefficient can be viewed as the product of the solubility coefficient S_X and the diffusion coefficient D_X [Eq. (3)].[18]

The ideal selectivity α of a membrane material for a pair of gases X and Y is defined as the ratio of the permeability coefficients for X and Y [Eq. (4)]. The ideal selectivity is

$$\alpha = \frac{P_X}{P_Y} \quad (4)$$

determined from separate measurements of the two gases X and Y. For real gas mixtures, the different partial pressures on the input and permeate sides must be taken into account. In addition, problems may arise from the different interactions of the gases with the polymer.[7, 9, 10] If, for example, one of the gases softens the polymer, this will not only affect the permeability coefficient of this particular gas, but also that of the other gas. Usually, this leads to a significant loss of selectivity. These types of effects overshadow the sought-after effects of the polymer structure. Therefore, laboratory studies nearly always employ ideal selectivities.

The permeability coefficients of different polymers for the same gas can vary by several orders of magnitude.[3, 7, 19–21] For oxygen, for instance, one finds $P(O_2)$ values from 5×10^{-4} Barrer (with Vectra, a liquid crystalline polyester) to 4×10^3 Barrer (with poly(trimethylsilylpropyne), PTMSP).[20] The selectivity (e.g., $\alpha(O_2/N_2)$) decreases from $\alpha = 15$ (Vectra) to $\alpha = 1.5$ (PTMSP).[20] If the application requires a high selectivity, polymers with $P(O_2)$ values greater than 1 Barrer and $\alpha(O_2/N_2)$ values greater than 5 are of interest. If high productivity is the main goal, it is possible to work with poly(dimethylsiloxane) membranes, which exhibit a selectivity of only $\alpha(O_2/N_2) = 1.5$, but a $P(O_2)$ of 1000 Barrer. Higher purity levels are then obtained using multiple-step plants. This is only economical, however, if the permeability coefficients are very large.

4. Transport Mechanisms and Model Concepts

Knudsen diffusion, the molecular-sieve effect, and the solution–diffusion mechanism are the three general principles that could govern gas separation by membranes.[3, 9] Knudsen diffusion relies on the separation based on the different molecular weights of the gases. The selectivity is proportional to the square root of the inverse ratio of the molecular weights.[3, 9] This means that the best achievable selectivity is too low for many applications: In the case of nitrogen/oxygen separation, $\alpha(N_2/O_2)$ is only 1.07.

To exploit the molecular sieve effect, membranes must be created containing pores with diameters that are in between those of the gas particles to be separated. This is, in principle, possible with glass membranes,[3, 15, 22, 23] for example. Apart from the lack of suitable mechanical properties and the difficulties in creating large membrane surfaces, however, fouling by condensable impurities in the gas stream that clog the pores turns out to be a significant problem.

The membranes that are currently commercially available and the majority of the membranes studied in the laboratory operate according to the solution–diffusion mechanism. Therefore, some related model concepts will now be discussed. In this particular mechanism, the material transport occurs in the three steps already mentioned, namely, absorption, diffusion, and release. The rate-determining parameter is the permeability coefficient, which can be viewed as the product of a solubility coefficient and a diffusion coefficient [Eq. (3)]. The question of which step is actually rate-determining—that is, poses the most resistance to the transport—cannot always be readily answered. Dayes et al. concluded, from measurements in the steady state as well as in the initial non-steady-state stage of material transport through polymer membranes, that in order to describe fully the gas permeation according to the solubility-diffusion mechanism it is necessary to know at least two of the three parameters P, D, and S.[24, 25] This viewpoint formed the basis for most of the studies described in this review.

The theoretical approaches for the description of gas diffusion in polymers and of gas permeation through polymers have been discussed in numerous reviews,[3, 7, 9, 10, 19] and will therefore not be presented here in detail. They are primarily based on the free volume of the polymer, statistical arguments, or energetic considerations. The parameters that are employed in these models to describe the polymer are not directly related to structural elements of the polymer chain. Therefore these models do not yield sufficiently concrete indications of how the chemical structure of a given class of polymers could be optimized.

Models which take the structure of the polymer chains into account, such as that of Pace and Datyner,[26] are more suitable. The first question that arises is the location of the gas atoms or molecules in the polymeric material. It must be realized that the macroscopic space which a polymer occupies is not completely filled by its chains. Gaps between the chains remain which cannot be filled due to conformational constraints (bond angles, steric bulk), especially in the case of amorphous polymers. A fraction of these gaps is large enough to accommodate gas particles.[27] The sum of these gaps is called the "free volume".[28] As the free volume of amorphous polymers is generally much larger than that of crystalline polymers, essentially only amorphous polymers are is used for gas separation.

According to the notions of Pace and Datyner,[26] the transport of gas particles occurs by leaps between these gaps.

These jumps occur when the thermal motions of certain segments of the polymer chain open up a sufficiently large channel to a neighboring gap. The gas particle can then diffuse through this channel. Once the channel closes afterwards, the jump has been successfully concluded. In this scenario, the selectivity of a membrane material depends on the control of these leap channels: Large openings—that is, substantial segment motions—permit the rather unrestricted passage of all present gas particles, whereas more limited motions permit the passage of smaller species much more frequently than of larger particles. A number of computer simulations[29–31] are based on these ideas, and the rapid increase in computing power as well as the constant refinement of programs, potentials, and parameters to describe amorphous polymers as solids promise important future advances in this field. A number of graphic depictions of these processes are shown in Figure 1.

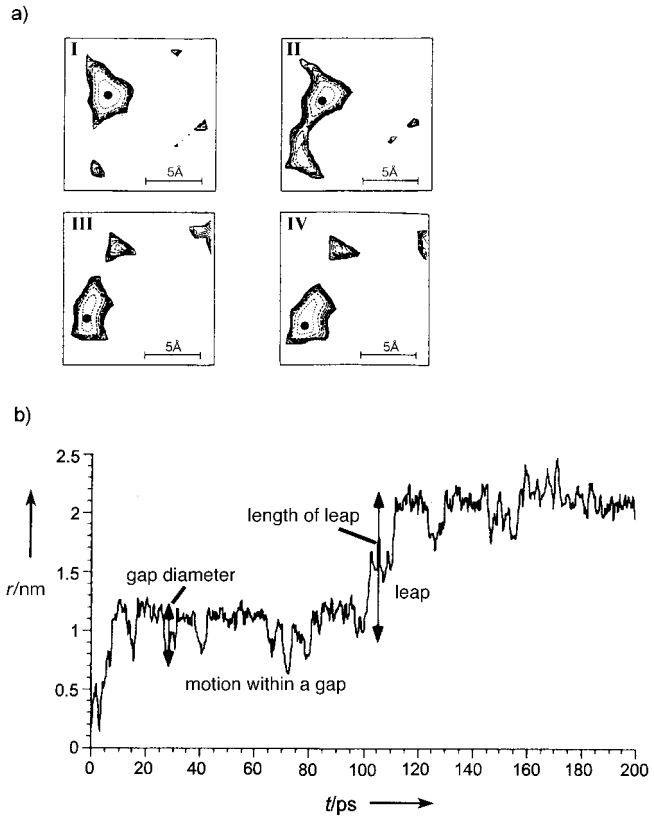


Figure 1. Computer simulation of transport leaps of single gas particles in a polymer. a) Movement of an O_2 molecule in a polymethylene matrix:[29] situation after 6 (I), 12.1 (II), 13.3 (III) and 16.1 ps (IV). b) Relative motion of a CO_2 molecule in a polyimide matrix.[30] r indicates the distance from the starting point of the particle in the computer simulation.

When these models are applied to the problem of determining the structure–property relationships of gas permeation through polymers, the question of which chain segments actually control the leap channels immediately arises. This is the starting point for the systematic variation of substructures within a class of polymers. By comparing permeability coefficients and selectivities for selected pairs of gases, one tries to identify the crucial chain segments. The results are verified by modifying the local chain flexibility at the corresponding critical points by introducing substituents, or by varying the length of the assumed critical segments by inserting or removing small partial structural elements within the repeat unit of the polymer. This leads to an accurate classification of segments of the polymer chain as important or unimportant for gas transport. This, in turn, allows the optimization of the polymer for a given separation task.

5. Conventional Membrane Polymers

The potential application of a polymer as a separation membrane depends upon the possible throughput and the purity of the product. This means that both the permeability coefficient for the gas that is transported more rapidly and the selectivity should be as large as possible. When the selectivity is plotted on a double logarithmic scale versus the permeability coefficient for the more rapidly permeating gas for many different polymers,[20, 21] one finds a relatively unstructured set of data points (Figure 2). It is characteristic that this

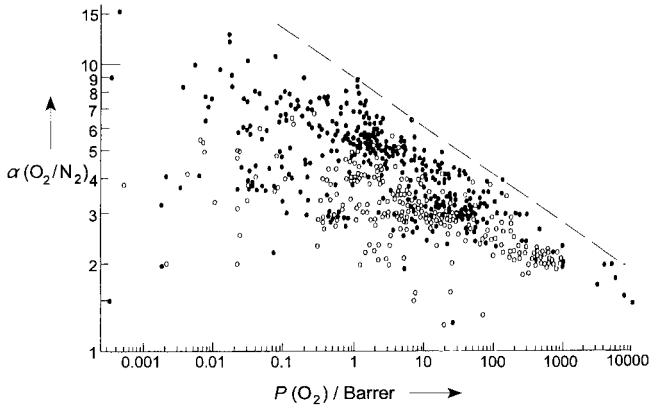


Figure 2. Relationship between the O_2/N_2 selectivity and the O_2 permeability coefficients for conventional polymers according to Robeson.[21] ●: vitreous polymers ($T_g < T_{measurement}$), ○: elastomeric polymers ($T_g > T_{measurement}$). The dashed line indicates the empirical upper bound line.

set of data points shows an apparently linear upper boundary where both P and α are large.[20, 21] It is thus possible to find polymers that exhibit high selectivity and low permeability, and vice versa, in addition to those that combine low selectivities with low permeabilities. There do not, however, appear to be any polymers that show the desired trend to large values for both P and α.

An even more important observation is that simple modifications in the polymer structure often lead only to a trade-off: One of the parameters is improved, while the other is simultaneously affected negatively.[3, 7, 20, 21] Therefore, such measures only shift the compromise between permeability coefficient and selectivity, but do not constitute a real improvement. Table 1 shows the data for three pairs of polymers selected as examples. In each case, only one structural element has been modified. In all three cases it is apparent that the increase in selectivity is accompanied by a lowering of the permeability coefficient.[19, 32]

Table 1. Apparent mutual dependence of selectivity and permeability coefficients.[19, 32]

Polymer	P[Barrer]			α		
	He	O_2	N_2	He/O_2	He/N_2	O_2/N_2
poly(methyl methacrylate)	8.4	0.14	0.02	60	420	7.0
poly(ethyl methacrylate)	23.8	1.9	0.33	12.5	72	5.8
PMDA-ODA[a]	8.0	0.61	0.1	13.1	80	6.1
PMDA-IPDA[b]	37.1	7.1	1.5	5.2	24.7	4.7
cellulose acetate	16.0	0.82	0.15	19.5	107.7	5.5
ethyl cellulose	39.8	12.4	3.4	3.2	11.7	3.6

[a] PMDA-ODA: polyimide from pyromellitic acid dianhydride and 4,4′-diaminodiphenyl ether. [b] PMDA-IPDA: polyimide from pyromellitic acid dianhydride and 2,2-bis(4′-aminophenyl)propane.

This unsatisfactory situation leads to the question of what the detailed relationships between the structure of a polymer and its properties regarding gas separation are. In particular, the connection between permeability and diffusion coefficients on one hand and other physical properties on the other is still unclear. The permeability and diffusion coefficients do not correlate with the density or the glass-transition temperature, as can be seen from published tables or review articles.[7–10, 19] There is, however, a relatively good correlation between the inverse of the fractional free volume in the polymer and the logarithm of the permeability coefficient.[9, 10, 33, 34] The fractional free volume V_f is obtained from the experimentally determined density and the volume that is actually occupied by the structural elements of the polymer chain.[35, 36] The latter is usually calculated by the increment method according to Bondi.[35] Using new data by Park and Paul,[33] which take into account that different fractional free volumes are accessible to gas atoms or molecules of different sizes, one usually finds a relatively good correlation (Figure 3).

This approach should directly allow predictions of the ideal selectivity for any given pair of gases, as the permeability coefficients can be calculated from the free volume. A detailed analysis shows, however, that the calculated value of P for gases such as He, O_2, N_2, and CO_2 can differ from the experimentally found value by a factor of 2 to 5. The prediction of the selectivity is also not yet sufficiently accurate. A series of chemically different polymers which showed experimentally determined selectivities of $\alpha(O_2/N_2) = 7$ yielded calculated values of between 5 and 8.5.[33] However, differences of these dimensions often determine whether an actual installation can be economically operated or not.

Upon detailed examination, it is also clear that the slope of the lines in the plot of $\lg P$ versus $1/V_f$ depends markedly on the polymer class. This observation, however, is often not sufficiently taken into account (Figure 4).

The approach to relate permeability and selectivity to the free volume has two major weaknesses. For one, it is reasonable to assume that not only the total free volume plays a role, but that the distribution of gap diameters is also important.[7] In addition, increment methods, such as the one used to calculate the free volume, can only incompletely reflect the chemical structure of a polymer. To take regioisomers into account, for example, the number of increments must be significantly increased. Bulky substituents in *ortho* positions to flexible groups such as ether or carbonate linkages will contribute much more to chain rigidity than those in the 2,2′ positions of a biphenylene unit, which is

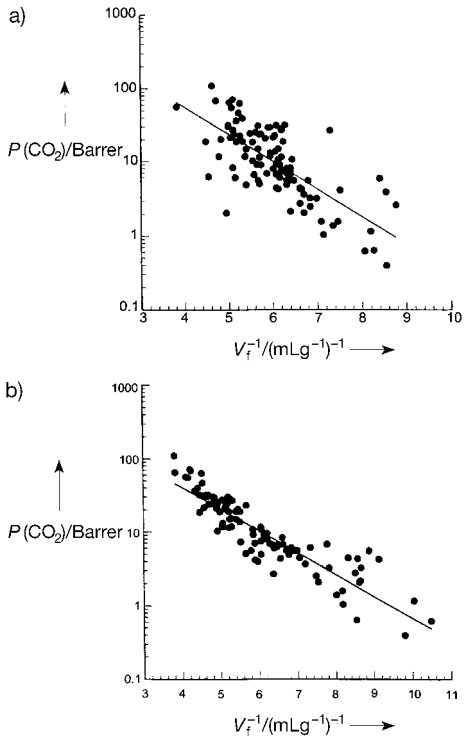


Figure 3. Correlation between the free volume V_f of a polymer and the permeability coefficient P for a specific gas (in this case CO_2). The V_f value was calculated with a) increments by Bondi and van Krevelen,[35] and b) a new set of increments according to Park and Paul.[33]

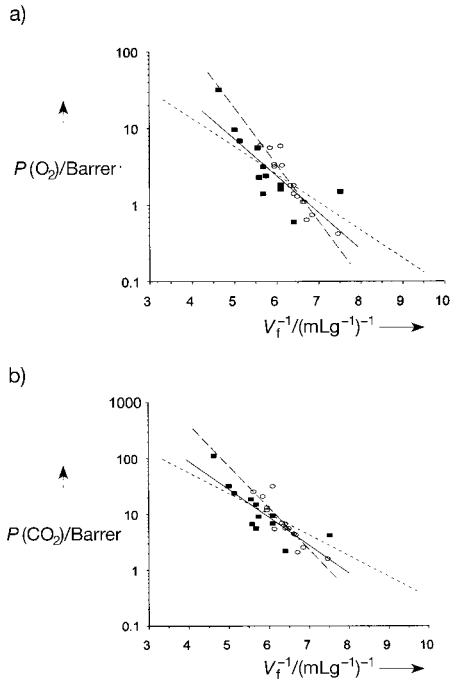


Figure 4. Relationship between permeability coefficient P and the fractional free volume V_f for different polymer classes and the resulting empirical limit. ■, ——: polycarbonates; ○, – – –: poly(ether sulfone)s; - - - -: best fit line from Figure 3b; a) for O_2; b) for CO_2.

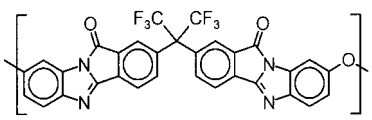
already rigid by itself. This behavior has been observed for a series of polycarbonates and discussed in detail.[3] It was found that the stiffening of the main polymer chain through structural modifications within the bisphenol moiety lead to the typical trade-off (high permeability → low selectivity, and vice versa), while stiffening that involved the carbonate group increased both P and α.

6. Strategy for Structure Optimization

The facts presented so far lead to the conclusion that significant improvements in permeability and selectivity of polymers can no longer be achieved by more or less random, readily performed structural variations of basic structures which are primarily chosen on the basis of availability. The typical and wide-spread trade-off behavior between selectivity and permeability coefficient,[20, 21] the correlation between fractional free volume and permeability coefficient,[9, 10, 33, 34] and the linear relationship between the slope of the empirical boundary line and the difference in diameters of a pair of gases to be separated can be interpreted to imply that the free volume of the conventional polymers studied thus far, or at least the distribution of gap diameters which make up the free volume, cannot be controlled. Instead, a relatively broad distribution develops. The observation of the different line slopes in the plots of $\lg P$ versus $1/V_f$ for different classes of polymers allows the conclusion that the distribution of gap diameters is different for different polymers.

A plausible suggestion for the further development of membrane polymers stems from Koros.[7] He recommended that the central point of this development should be the attempt to control the mean diameter and the distribution of diameters of the gaps between the polymer chains which make up the free volume. Probably more important, however, is the control over the extent and frequency of the segment motions, which, according to the model described earlier, control the leap channels. According to the suggestion from Koros,[7] a narrower distribution of gap diameters could be achieved with a certain type of polymer architecture. Polymer chains that consist of alternating bulky and flat units should be preferentially packed in such a manner that the bulky groups act as spacers and prevent a tight packing of the flat groups. This leaves gaps in the vicinity of the flat chain segments, and their dimensions can be determined directly from the size of the basic chain building blocks. The polypyrrolone 6FDA-TADPO (Scheme 1) has been suggested as an example of such a chain architecture.[3, 7] This polymer is indeed currently one of the best membrane materials for the separation of O_2 and N_2.[21]

The argument that the simple consideration of individual chain segments and their flexibility to explain changes in the permeability coefficients cannot appropriately take into account different solubilities and, hence, cannot provide a sufficient interpretation has some validity. It turns out, however, that in many cases, this is only of secondary importance. Equations (3) and (4) yield expression (5) for the selectivity α; S_X/S_Y is the solubility selectivity, and D_X/D_Y the diffusion selectivity.



Scheme 1. Structural formula of the polypyrrolone 6FDA-TADPO.

$$\alpha = \frac{P_X}{P_Y} = \frac{S_X}{S_Y}\frac{D_X}{D_Y} \quad (5)$$

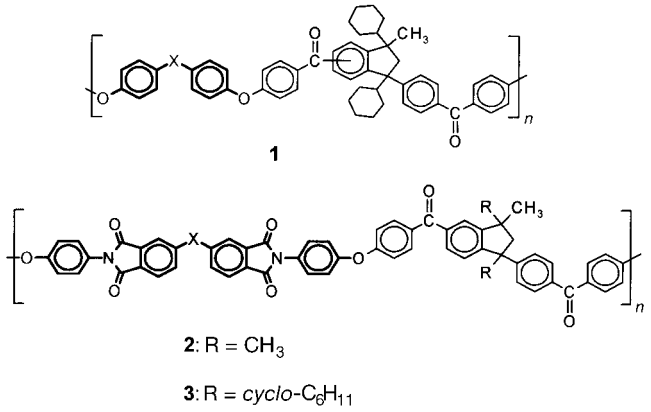
Especially for the frequently studied aromatic polycondensates such as polycarbonates, poly(ether sulfone)s and polyimides, the solubility selectivity for different pairs of gases is practically independent of the polymer structure. For a series of 18 polyimides,[37] the $S(O_2)/S(N_2)$ values were 1.31 ± 0.2, while $S(CO_2)/S(CH_4)$ values were 3.37 ± 0.5. The solubility selectivities of different polycarbonates (PC)[10] and poly(ether sulfone)s (PES)[10] are very similar for those two pairs of gases as well (PES: O_2/N_2: 1.4–1.7; CO_2/CH_4: 2.7–3.7; PC: O_2/N_2: 1.36–1.65; CO_2/CH_4: 2.58–3.62). However, the selectivities α varied from 4.6 to 8.1 (polyimides, O_2/N_2) and 26 to 65 (polyimides, CO_2/CH_4).[37] Similar results are found for polycarbonates and poly(ether sulfone)s.[10] This implies that, at least for these types of polymers, the selectivity is primarily determined by the diffusion selectivity, that is, the different mobility of the gas particles in the polymer matrix. This situation changes when gases are studied that either condense readily or that can undergo strong, specific interactions with functional groups in the polymer matrix, such as water vapor or larger hydrocarbons. If only simple gases such as the nobel gases, hydrogen, oxygen, nitrogen, carbon dioxide, and methane are considered, the effect of the solubility selectivity can be ignored, at least in the case of aromatic polycondensates with high glass-transition temperatures.

7. Polymers with Indane Groups in the Main Chain as Membranes for Gas Separation

7.1. Polymer Structures

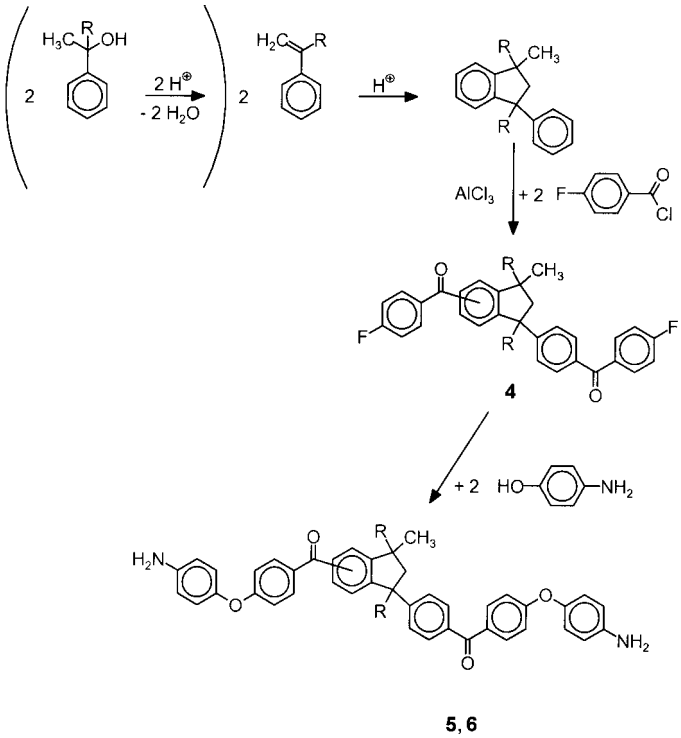
A series of polymers with 1,1,3-trialkyl-3-phenylindane groups in the main chain will now be used to demonstrate how polymers with alternating flexible, sterically undemanding and bulky, rigid segments can be prepared, and how such a chain architecture affects the gas permeabilities and selectivities. The use of an indane derivative as the bulky group has the advantage of easy accessibility. In addition, the bulkiness of this group can be adjusted by varying the alkyl substituents. Oxy-1,4-phenylene chains as linkages between the indane groups represent a good compromise between rigidity (to control the segment motions) and flexibility (to obtain the highest possible number of channels opening up per unit time). The flexibility and bulkiness of these segments can be varied over a wide range. Imide groups were introduced for comparison, as polyimides are empirically known to be good membrane materials for gas separation, and a large amount of

data for this class of polymers is available.[3, 7, 19–21, 37] Scheme 2 shows the polymer structures chosen for this study.



Scheme 2. General structures of poly(ether ketone)s **1** and poly(etherimide)s **2** and **3** with indane groups. For the bridging group X, see Tables 2 and 3.

The synthesis and characterization of these polymers have been described in detail[38–41] and will only be briefly summarized here (Scheme 3). The starting point for the



Scheme 3. Synthesis of the monomers **4**–**6**, the starting materials for the polymers **1**–**3**. **5**: R = methyl, **6**: R = cyclohexyl.

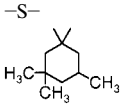
synthesis of methyl derivative **5** is the acid-catalyzed dimerization of α-methylstyrene, yielding 1,1,3-trimethyl-3-phenylindane. Subsequent Friedel–Crafts acylation with 4-fluorobenzyol chloride leads to the methyl derivative of monomer **4**. An approximately equimolar mixture of two isomers is obtained, as 1,1,3-trimethyl-3-phenylindane has more than one position in the phenyl rings that is activated for electrophilic substitution. This, however, has no effect on the properties of the resulting polymers, as was expected based on the asymmetric structure of the indane group. A further reaction with 4-aminophenol in the presence of a base leads to a nucleophilic substitution of the fluorine atoms in the 4-fluorobenzyol groups, yielding the diamino monomer **5**, which is used to prepare the polyimides **2**. The introduction of the cyclohexyl substituents in the indane system is achieved by directly employing the tertiary alcohol from the Grignard reaction between methylmagnesium bromide and cyclohexyl phenyl ketone as starting material for the acid-catalyzed cyclodimerization. In the presence of a strong acid, water is released, and the olefin formed cyclodimerizes to the indane derivative (Scheme 3). The further steps to monomer **6** are the same as for **5**.

7.2. Synthesis and Properties of Polymers with Indane Groups in the Main Chain

The polymer synthesis follows previously described methods.[42, 43] The difluoro monomer **4** (R = cyclohexyl) undergoes condensation with bisphenols in the presence of K_2CO_3 as base and toluene as azeotropic water remover in a dipolar aprotic solvent, resulting in the poly(ether ketone)s **1**. The polyimides **2** and **3** are prepared in two steps from the diamino monomers **5** and **6**, respectively, and aromatic tetracarboxylic acid anhydrides. The diamine and the dianhydride are initially stirred together for several hours in a dipolar aprotic solvent, which leads to the poly(amide acid).[39, 40] The resulting solution is poured into a film. The temperature is then raised in a stepwise manner up to 280 °C in a vacuum, which dries the film and leads to imidization by release of water. Tables 2 and 3 summarize some important data of these polymers.

The segment motions, which have their onset at the glass-transition temperature, are strongly cooperative and involve longer pieces of the main polymer chain (several repeat units). These segment motions can therefore be used as a measure of the global flexibility of the polymer chain, at least within a series of polymers with similar structures.[28] The data

Table 2. Physical properties of the poly(ether ketone)s **1**.[38, 41]

Polymer	X	T_g[a] [°C]	$\bar{M}_n$[b]	ρ[c]	V_f[d] (CO_2)	V_f[d] (O_2)
1a	–O–	232	16600	1.19	0.121	0.124
1b	$-C(CF_3)_2-$	235	17900	1.22	0.170	0.175
1c	–	255	13200	1.20	0.138	0.139
1d	$-C(CH_3)_2-$	234	12700	1.14	0.137	0.140
1e		236	8400	1.18	0.133	0.136
1f	–S–	218	15600	1.19	0.131	0.134
1g		255	14200	1.18	0.126	0.133
1h	–CO–	229	12700	1.19	0.126	0.130
1i	$-SO_2-$	251	17200	1.25	0.147	0.149

[a] DSC, 20 K min^{-1}. [b] In g mol^{-1}, determined by GPC in THF, polystyrene standard. [c] Density in g mL^{-1}, determined by the flotation method. [d] $V_f = (V_S - V_0)/V_S$; V_S: specific volume (from the density), V_0: specific volume at 0 K (from increments by Park and Paul[33]).

Table 3. Physical properties of the polyimides **2** and **3**.[39, 40]

Polymer	−X−	T_g[a] [°C]	$\bar{M}_n$[b]	ρ[c]	V_f[d] (CO_2)	V_f[d] (O_2)
2a	$-C(CF_3)_2-$	241	28000	1.286	0.159	0.161
2b	$-SO_2-$	251	20800	1.275	0.139	0.139
2c	−CO−	232	21300	1.245	0.133	0.132
2d	−O−	233	[e]	1.255	0.123	0.124
2e	–	246	31500	1.240	0.119	0.119
3a	$-C(CF_3)_2-$	269	30700	1.275	0.169	0.169
3b	$-SO_2-$	272	8100	1.235	0.147	0.144
3c	−CO−	261	[e]	1.220	0.139	0.135
3d	−O−	264	[e]	1.215	0.128	0.127
3e	–	274	25800	1.210	0.124	0.122

[a] DSC, 20 K min^{-1}. [b] In g mol^{-1}, determined by GPC in $CHCl_3$, polystyrene standard. [c] Density in g mL^{-1}, determined by the flotation method. [d] $V_f = (V_S - V_0)/V_S$; V_s: specific volume (from the density), V_0: specific volume at 0 K (from increments by Park and Paul[33]). [e] Insoluble in $CHCl_3$.

in Tables 2 and 3 show that the polymers containing indane groups in the main chain exhibit high glass-transition temperatures (T_g), which indicates a relatively rigid main chain. The T_g values of the poly(ether ketone)s **1**,[41] for example, are about 80 K higher than those of analogous polymers without the 1,3-biscyclohexyl-1-methyl-3-phenylindane structural element. A comparison of polyimides **2** and **3** shows that the replacement of the methyl groups by the two cyclohexyl moieties raises the glass-transition temperature by 30 K. Within each series of polymer, the glass-transition temperatures follow the expected trend, dependent on the bridging element X (see Scheme 2).[43, 44] Flexible groups such as ether or sulfide lead to relatively low values of T_g, while rigid or strongly polar groups, such as the biphenyl moiety or the sulfone group, result in the highest glass-transition temperatures.

The molecular masses were determined by gel permeation chromatography (GPC). This is a relative method, which requires calibration with standards having known molecular weights (usually polystyrene). Nevertheless, values within a class of polymers compare relatively well, and it has been our experience, at least for amorphous poly(aryl ether)s, that the average molecular masses determined by GPC measurements in THF or chloroform usually do not differ by more than 10% from the values found with absolute methods, such as membrane or vapor pressure osmometry.[38, 45] Corresponding to the values for $\bar{M}_n$ found in Table 2, the poly(ether ketone)s posses comparable molecular masses, perhaps with the exception of polymer **1e**. As it was possible, however, to cast this polymer into mechanically stable, flexible films as well, it can be assumed that it also falls into the range of molecular masses where the effect of the molecular mass on the physical properties is only of secondary importance.[28] The results for the members of this series of polymers should, hence, be readily comparable with each other.

Similar arguments apply to the polyimides, with the exception that the polyimides **2d**, **3c**, and **3d** in the fully imidized forms are completely insoluble at room temperatures, so that a molecular mass determination was not possible. All polyimides could be obtained as mechanically stable, flexible films.

The polymers **1**–**3** exhibit relatively low densities (see Tables 2 and 3).[3, 10, 37] These value are, however, not unusual when one takes into account the presence of the bulky indane group, which prevents a dense packing of the chains. The V_f values are also in the range expected for poly(arylethers) and polyimides.[3, 10, 37] The data for V_f in Tables 2 and 3 are based on the increment method by Park and Paul,[33] which takes into account that different fractions of V_f are accessible to different gases due to their different molecular diameters. As an example, fractional free volumes are given for CO_2 and O_2 in the Tables. However, these differences are relatively small, only about 2–5%. A comparison of the data for the polymers **2** and **3** is of interest, as it shows that the introduction of the two cyclohexyl substituents on the indane system causes an increase in V_f. This is because of the increased space requirements of this structural element.

7.3. Permeabilities and Selectivities of Polymers 1–3

For the measurement of the permeability coefficients, a cell was employed that was separated into two compartments by the membrane. Both compartments were initially evacuated. To begin the measurement, the input chamber was filled with the gas to be studied. The pressure p_1 in the input chamber was kept constant, while an increase in pressure Δp in the permeate chamber was measured. Once the stationary state was achieved, the increase in pressure was linear with time t. The volume of the measurement cell V, the membrane area A, the membrane thickness d, the temperature T, and the pressure p_1 on the input side are all known and constant, so that the permeability coefficient can be calculated according the Equation (6).

$$P_X = \frac{\Delta p}{\Delta t}\frac{V d}{A p_1}\frac{1}{RT} \quad (6)$$

The permeabilities of hydrogen, carbon dioxide, oxygen, and nitrogen were determined for all polymers **1**–**3**. The measurements were performed at 22 °C and 1.25 bar. The results are summarized in Tables 4 and 5 for poly(ether ketone)s **1**) and in Tables 6 and 7 for polyimides **2** and **3**.

7.3. Discussion of the Permeabilities

7.3.1. Poly(ether ketone)s 1

The measurements of the permeability coefficients for hydrogen, carbon dioxide, oxygen, and nitrogen (Table 4) yield data for six pairs of gases (Table 5). The interpretation of the data is best done with plots of the selectivity versus the permeability coefficient. The identification of general trends is of primary interest, whereas the discussion of specific results will initially be of secondary importance. The goal of our studies is primarily a deeper understanding of generally valid relationships between polymer structure and permeability/selectivity.

Table 4. Permeability coefficients of the poly(ether ketone)s **1** (in Barrer).

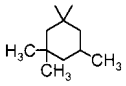
Polymer	X	$P(H_2)$	$P(CO_2)$	$P(O_2)$	$P(N_2)$
1a	−O−	11.6	4.18	1.08	0.21
1b	$-C(CF_3)_2-$	17.3	7.7	1.64	0.32
1c	–	14.9	6.45	1.47	0.42
1d	$-C(CH_3)_2-$	17.7	9.36	1.83	0.33
1e		16.7	7.39	1.57	0.29
1f	−S−	13.5	5.7	1.12	0.2
1g		36	18.9	3.58	0.64
1h	−CO−	12.5	5	1.03	0.16
1i	$-SO_2-$	14.5	7.2	1.32	0.23

Table 5. Selectivities of the poly(ether ketone)s **1**.

Polymer	$\alpha(O_2/N_2)$	$\alpha(H_2/N_2)$	$\alpha(CO_2/N_2)$	$\alpha(H_2/CO_2)$	$\alpha(CO_2/O_2)$	$\alpha(H_2/O_2)$
1a	5.1	55.2	19.9	2.8	3.9	10.7
1b	5.1	54.1	24.1	2.2	4.7	10.5
1c	3.5	35.5	15.4	2.3	4.4	10.1
1d	5.5	53.6	28.4	1.9	5.1	9.7
1e	5.4	57.6	25.5	2.3	4.7	10.6
1f	5.6	67.5	28.5	2.4	5.1	12.1
1g	5.6	56.2	29.5	1.9	5.3	10.1
1h	6.4	78.1	31.3	2.5	4.9	12.1
1i	5.7	63.0	31.3	2.0	5.5	11.0

The plot for O_2/N_2 (Figure 5a) shows that the selectivities of all poly(ether ketone)s **1** (with the exception of **1c**) are very similar. Within this series of polymers, the bridging unit X was the only structural element that was changed, but the differences in polarity, geometry, and steric bulk are considerable. The structural elements varied from small flexible ether or sulfide bridges over rigid biphenyl units or strongly polar sulfone groups to the sterically very demanding trimethylcyclohexylidene group. Nevertheless, the effects of these structural modifications on the selectivity are very small. The group X, however, does show a clear effect on the permeability coefficient. The sterically least demanding groups, such as ether, sulfide, or carbonyl moieties (**1a**, **1f**, **1h**) yield the lowest permeability coefficients, whereas the sterically most demanding species, the trimethylcyclohexylidene group (**1g**), leads to the largest permeability coefficient.

Very similar relationships for the selectivities and the permeability coefficients are found for the gas pairs H_2/N_2 (Figure 5b) and CO_2/N_2 (Figure 5c). Exceptions are polymer **1h**, which deviates for H_2/N_2 towards a larger selectivity, and polymer **1a**, which deviates towards a lower selectivity for CO_2/N_2.

The other pairs of gases (H_2/O_2, CO_2/O_2, and H_2/CO_2) do not exhibit these anomalies regarding the selectivities.

*7.3.1.1. Permeability Coefficients of **1***

At a first glance, the explanation for the relationship between permeability coefficients and the structure of bridging group X appears straightforward: Sterically more demanding groups reduce the packing density of the polymer chains, thereby increasing the free volume and the permeability coefficients. When examined more closely, however, the explanation cannot be that simple. Polymer **1g**, which always exhibits the highest permeability coefficients, definitely does not posses an unusually high free volume (see Table 2). In contrast, the V_f values for this polymer lie in the lower middle of the range found for poly(ether ketone)s. This observation clearly shows that one must not simply consider the total fractional free volume, but only that fraction that is actually accessible to the gas particles during the diffusion process.

Correspondingly, the relationship between permeability coefficients and fractional free volume is very different for the poly(ether ketone)s **1** than for the other polymers studied thus far. Figure 6 shows the plots for O_2 and CO_2 as examples for this behavior; the plots for H_2 and N_2 are very similar. The comparison with Figures 3b and 4 indicates that the best fit lines for poly(ether ketone)s **1** have a much smaller slope than the general best fit line or the best fit lines for the conventional poly(ether sulfone)s and polycarbonates. This implies that the permeability coefficients of the poly(ether ketone)s **1** are much less dependent on the total fractional free volume

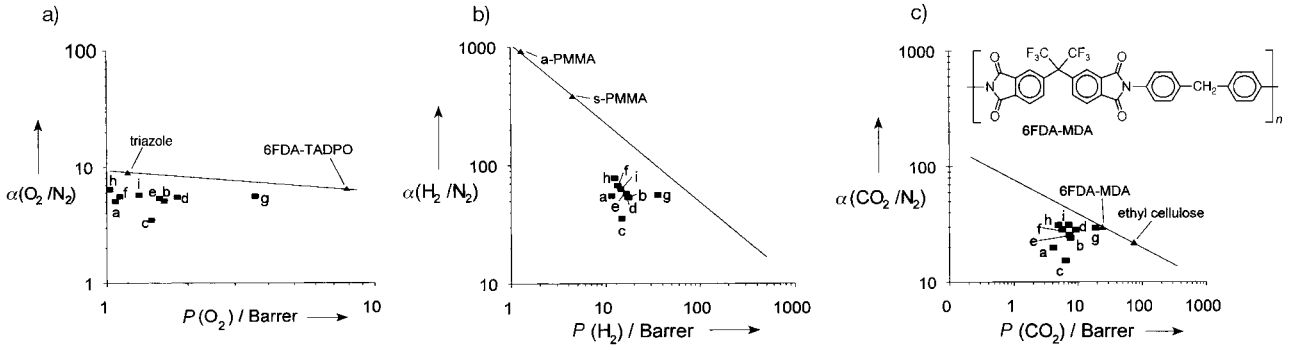


Figure 5. Plots of the selectivity α for the gas pairs a) H_2/N_2, b) CO_2/N_2, and c) O_2/N_2 versus the O_2, H_2, and CO_2 permeability coefficients of poly(ether ketone)s **1**. The graphs show the empirical limits as well as some data points from the literature (▲): triazole (poly(1-phenyl-1,3,4-triazole-2,5-diyl-1,4-phenylen)),[8] 6FDA-TADPO (see Scheme 1),[3] a-PMMA (atactic poly(methyl methacrylate)),[20] s-PMMA (syndiotactic poly(methyl methacrylate)),[20] 6FDA-MDA,[7] and ethyl cellulose.[19]

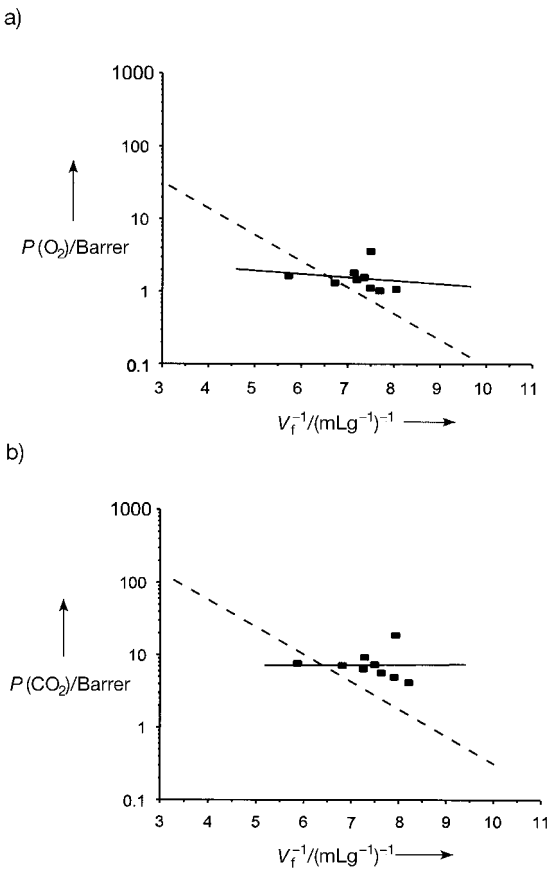


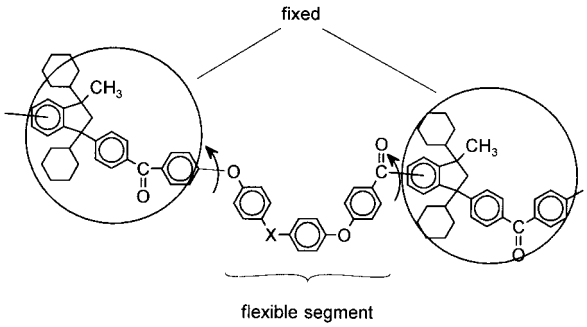
Figure 6. Relationship between permeability coefficient and free volume for poly(ether ketone)s **1** a) for O_2 and b) for CO_2. For clarity, the corresponding general best fit lines are indicated as well (– – –: compare with Figure 4).

than usual. We currently assume that the reason for this behavior can be found in the distribution of the diameters of the voids making up the free volume. The architecture of the poly(ether ketone)s **1** apparently controls these voids to some extent, and the group X resides at a critical position in the polymer chain. It is possible that the void diameters are strongly dependent on the length of the phenoxy segments between the bulky, rigid indane groups. In this case, the bridging unit X exerts significant control over the fractional free volume that is accessible to the gas particles (at least for H_2, CO_2, O_2, and N_2). Therefore, the permeability coefficients vary only very slightly with the total fractional free volume, but quite strongly with the steric demand of the groups X.

According to this scenario, the indane groups themselves do not significantly affect the gas-transport processes, but act as anchors for the flexible segments, which in turn control the gas transport. It is quite likely that not all polymer chains are packed in the manner that is necessary for this idealized situation. For poly(ether ketone)s **1**, it must be assumed, however, that the overwhelming majority of transport leaps and thus the gas transport through the membrane is indeed controlled by the described segments. Otherwise, one would not expect this behavior, which deviates so significantly from the norm.

*7.3.1.2. Selectivities of **1***

The interpretation presented in the previous section also leads directly to a plausible explanation for the different behavior of the selectivity of polymer **1c** (with a biphenyl unit). All polymers **1**, except for **1c**, are bent at the position X. If it is assumed that the segments between the indane groups control the gas transport through their motions, the situation depicted in Scheme 4 can be envisioned. The bend in the



Scheme 4. Chain segments of poly(ether ketone)s **1** which control the gas transport within the polymer (proposal).

polymer chain at the bridging group X could be crucial for the function of the phenoxy segments as controlling elements for gas transport. If X is replaced by a single bond as in polymer **1c**, the possibility of this conformation no longer exists. Instead, a distinctly more stretched arrangement must be assumed. This leads to a significant lengthening of the segment that must move in order to open up a leap channel. This in turn results in a widening of the channels, which reduces the ability to differentiate between gas particles of different sizes.

In the cases of the gas pairs H_2/O_2, CO_2/O_2, and H_2/CO_2, polymer **1c** does not show this deviating behavior. This is understandable when the kinetic diameters of the gas molecules are taken into account. These are 0.289 nm (H_2), 0.33 nm (CO_2), 0.346 nm (O_2), and 0.364 nm (N_2). Hence, nitrogen has the largest molecules of the gases studied. As the polymers **1** show relatively good O_2/N_2 selectivity, the critical segment motions must be capable of differentiating between these two gases. This means that oxygen can diffuse through the channels controlled by the crucial segments, and that diffusion must even be easier for carbon dioxide and hydrogen. This implies in turn that the selectivity between CO_2/O_2, H_2/O_2, and H_2/CO_2 is not necessarily controlled by exactly the same segment motions. In other words, effects which are critical for pairs of gases involving nitrogen do not inevitable influence separations involving gases with molecules smaller than nitrogen to the same degree. This is exactly what is observed for polymer **1c**. In this context, it is interesting that the selectivity of the polymers **1** for H_2 over CO_2 ($\alpha = 1.9-2.8$) is surprisingly low, even though the difference in diameters ($\Delta d = 0.41$ Å) is much larger than for CO_2/O_2, ($\alpha = 3.9-5.5$, $\Delta d = 0.16$ Å), O_2/N_2 ($\alpha = 3.5-6.4$, $\Delta d = 0.18$ Å), and CO_2/N_2 ($\alpha = 15.4-31.3$, $\Delta d = 0.34$ Å). This confirms the conclusion that while the segment discussed thus far, and sketched in Scheme 4, does control the selectivity of the

polymers **1** for smaller gas particles over nitrogen, it does not necessarily control the selectivities for the other gases which all have molecules smaller than nitrogen.

The functionally separated structure of the repeat unit into two segments is the most significant modification which distinguishes the poly(ether ketone)s **1** from conventional polymers, such as the polycarbonates, poly(ether sulfone)s, polyimides, and cellulose derivatives which have been commonly employed as gas-separation membranes. The indane moiety with its substituents serves as a more or less fixed group and acts as a hinge about which a flexible chain segment of defined length can perform its (limited) thermal motions. According to our idealized model, this construction has two important consequences. Firstly, the sequence of bulky indane groups and small, flexible segments leads to a narrower distribution of the gap diameters in the free volume. Secondly, the gas transport through the polymer is primarily controlled by the motions of the segments between the indane groups. The physical structure of the polymer, especially the length and flexibility of the segments between the indane groups, governs which gases can be differentiated and how well, thus determining the possible extent of a separation. Polymers with a conventional structure—such as bisphenol A-polycarbonate, poly(ether sulfone), and polysulfone—do not exhibit a comparable segmentation of the repeat unit. Therefore the hinges and the flexible segments are made up of the same structural elements in these polymers. This is bound to lead to a compromise, as the structural elements cannot be optimized separately for their specific tasks. In addition, all structural modifications, such as the introduction of substituents or the variation of bridging units, affect the hinges as well as the flexible segments. Hence, any simple modification can alter the behavior in an uncontrolled manner. This affects primarily the flexibility and length of the critical segments as well as the distribution of gap diameters in the free volume. It is apparent that for those polymers, it becomes more difficult to derive concrete structure–property relationships on a molecular level and to obtain "blueprints" for better membrane materials.

From the analysis of data obtained for **1**, a general guideline can be derived for the structure of polymers for the further study of the relationship between polymer structure and permeability/selectivity. The polymer chains should incorporate large, bulky structural elements which are linked by flexible segments. The dimensions of the bulky groups and the length of the flexible chain segments in between them should control the distribution of the gap diameters in the free volume. This would bring about the possibility of directly adjusting the fractional free volume that is accessible to gases with different molecular diameters. At the same time, the selectivity should primarily be determined by the length of the flexible segment and its architecture (bond angle, structure) as well as the degree of free rotation around those bonds that form the hinges between the flexible segments and the fixed, bulky groups.

Recently, a research group at Air Products & Chemicals presented an increment method for the calculation of the permeability coefficients of various aromatic polymers for helium, nitrogen, and oxygen.[46] The types of polymers to which this method can be applied include polyesters, poly(aryl ether)s, and polycarbonates. In contrast to the already mentioned approach of Park and Paul,[33] this new method is not based on the free volume of the polymers. Instead, increments were determined for the contributions to the permeability coefficients by various structural elements that are frequently found in polymers. The agreement between the thus calculated permeability coefficients and the actually measured ones is surprisingly good.[46]

There are currently no increments for the 1,1,3-trimethyl- or the 1,3-biscyclohexyl-1-methylindane groups, and so a comparison between the experimental data for the poly(ether ketone)s **1** and calculated values is not possible. There are, however, increments for the 3,3,3′,3′-tetramethylspirobis-1,1′-indane group.[46] By the method by Robeson, Smith, and Langsam, interesting permeability coefficients and, hence, selectivities for the gases O_2/N_2 can be calculated for a number of polymers that are analogous to the poly(ether ketone)s **1**, but contain the tetramethylspirobisindane group instead of the 1,3-biscyclohexyl-1-methylindane moiety. Just like the poly(ether ketone)s **1**, the hypothetical 3,3,3′,3′-tetramethylspirobis-1,1′-indane polymers all show a very similar O_2/N_2 selectivity of around $\alpha = 5$, which is very close to the value of $\alpha = 5.5$ found experimentally for the polymers **1** (see Table 5). The polymers with X = O, S, and CO show relatively low permeability coefficients as well. Unfortunately, there are no increments for the trimethylcyclohexylidene group, so that no similar comparison can be made. The increment method predicts an increase in $P(O_2)$ by a factor of 2 for the relatively bulky structural element 6F relative to the simple ether bridge. Experimentally, the polymers **1** exhibit an increase by a factor of 1.52.

All in all, the predictions of this increment method agree surprisingly well with the experimental data, except for one important point. While calculations for the polymer with the biphenyl unit (X = —) yield a selectivity that is lower than for most other polymers in this group, the difference is not comparable with that found experimentally for the poly(ether ketone)s **1**. This stems from a fundamental difference between the increment approach and our model. The increment method simply sums up the structural elements that are present without considering their relative positions. In our model, however, the position of a structural element plays a crucial role. With the increment method, a polymer that contains several rigid, bulky groups in a row followed by several flexible segments would yield the same permeability coefficients and selectivities as a polymer in which the same structural elements are present in a strictly alternating fashion. According to our model, the polymer with the "segmented" structure should behave very differently from the polymer with the strictly alternating structure, because of the inhomogeneous, sometimes very low, sometimes very large, chain flexibility in the former and the homogeneous local flexibility in the latter polymer. This should then lead to different permeability coefficients and selectivities. Future modifications of the poly(ether ketone)s **1** will show which approach is more useful. In particular, it is planned to introduce methyl groups in the *ortho* position relative to various bridging units between the phenyl rings. This will

show whether this modification has the same effect in all locations within the repeat unit or, as we expect, there are indeed positions where structural modifications have either a very strong effect or none at all.

7.3.2. *Polyimides 2 and 3*

The repeat unit of the polyimides **2** and **3** exhibits, relative to the structure of the poly(ether ketone)s, phthalimide groups that are introduced between the bridging group X and the benzene rings (see Scheme 2). Although the segment between the indane groups is thereby lengthened, its mobility is reduced by the intermolecular dipole–dipole interactions between the strongly polar imide groups. The results of the measurements are summarized in Tables 6 and 7.

Figure 7 shows the plots of selectivity for H_2/N_2, CO_2/N_2, and O_2/N_2 versus permeability coefficient for O_2, H_2, and CO_2, respectively. It is apparent that the behavior of the polyimides **2** and **3** is much less clear cut than what was observed for the poly(ether ketone)s **1**. Some trends are observed, but the relationship between the modifications of the polymer structure and the changes in the permeability data are not only not readily apparent, they are also not unambiguous.

Table 6. Permeability coefficients of the polyimides **2** and **3** (in Barrer).

Polymer	−X−	$P(H_2)$	$P(CO_2)$	$P(O_2)$	$P(N_2)$
2a	$-C(CF_3)_2-$	21.3	5.58	2.05	0.32
2b	$-SO_2-$	12.7	3.6	0.91	0.16
2c	−CO−	8.3	1.96	0.47	0.08
2d	−O−	10.5	3.05	0.68	0.09
2e	–	8.8	2.51	0.57	0.11
3a	$-C(CF_3)_2-$	23.1	9.64	1.92	0.33
3b	$-SO_2-$	10.2	3.2	0.75	0.16
3c	−CO−	9.2	1.68	0.91	0.22
3d	−O−	13.23	3.76	0.9	0.08
3e	–	13.3	5.68	1.11	0.28

Table 7. Selectivities of the polyimides **2** and **3**.

Polymer	$\alpha(O_2/N_2)$	$\alpha(H_2/N_2)$	$\alpha(CO_2/N_2)$	$\alpha(H_2/CO_2)$	$\alpha(CO_2/O_2)$	$\alpha(H_2/O_2)$
2a	6.4	66.6	17.4	3.8	2.7	10.4
2b	5.7	79.4	22.5	3.5	4.0	14.0
2c	5.9	103.7	24.5	4.2	4.2	17.7
2d	7.6	116.7	33.9	3.4	4.5	15.4
2e	5.2	80	22.8	3.5	4.4	15.4
3a	5.8	70	29.2	2.4	5.0	12.0
3b	4.7	63.7	20.6	3.1	4.4	13.6
3c	4.1	41.8	7.6	5.5	1.8	10.1
3d	11.2	165.4	47	3.5	4.2	14.7
3e	4.0	47.5	20.3	2.3	5.1	12.0

The polyimides with $X = C(CF_3)_2$ (**2a**, **3a**) show the highest permeability coefficients in their series (Table 6), while those with X = O (**2d**, **3d**) exhibit the highest selectivities (Table 7). The lowest permeability coefficients for cyclohexyl-substituted polyimides were found for **3b** and **3c**, and, in the case of methyl-substituted polyimides, for **2e** and **2c**. For most pairs of gases studied, the lowest selectivities were observed for **3c** and **2a**. In general, the selectivities of the methyl-substituted polyimides **2** vary less than those of the cyclohexyl-substituted analogues **3**.

As was observed for the poly(ether ketone)s **1**, the order of the permeability coefficients of the polyimides **2** and **3** does not simply follow the fractional free volume (see Table 3). It is possible that also here varying the bridging group X in the main polymer chain affects primarily the fraction of the free volume that is accessible to the gas molecules. This is in itself not surprising, as the architecture of the polyimides is very similar to that of the poly(ether ketone)s.

The effect of exchanging the methyl substituents on the indane system with cyclohexyl groups poses a problem, however. It had been observed earlier that cyclohexyl groups—probably owing to their conformational flexibility—do not lead to significantly improved permeability coefficients.[10] Upon comparison of the polyimides **2** and **3** one finds that the introduction of the cyclohexyl groups can have completely different effects. While with X = O (**d**) there is an improvement in both permeability coefficient and selectivity, with X = − (**e**) there is the typical trade-off, where increased permeability goes hand-in-hand with a lower selectivity. For $X = SO_2$ (**b**) or CO (**c**), one observes a loss of selectivity, which is usually also accompanied by a lower permeability coefficient.

The reasons for this behavior are not clear. The effect of the cyclohexyl substitution appears to be strongly connected to the nature of the bridging group X. Such correlations make the derivation of structure–property relationships much more difficult. It will be necessary to introduce substituents with a lower conformational flexibility than cyclohexyl rings, such as *tert*-butyl groups, to determine whether this observation is limited to the cyclohexyl moiety or represents a more general phenomenon.

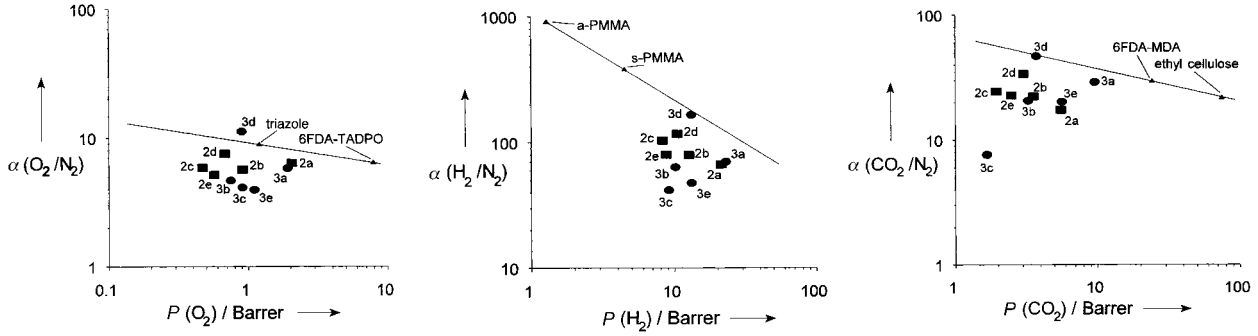


Figure 7. Plots of the selectivity α for the gas pairs a) O_2/N_2, b) H_2/N_2, and c) CO_2/N_2 versus the O_2, H_2, and CO_2 permeability coefficients of the polyimides **2** (■) and **3** (●). The graphs show the empirical limits as well as some data points (▲) from the literature (compare with Figure 5).

One conclusion, however, can be made based on the varying effects of the cyclohexyl groups: If the indane group as a whole participated in the segment motions that control the gas transport, one would expect a rather uniform effect, as the enlargement of the indane moiety due to the introduction of the cyclohexyl substituent should directly affect the mobility of this chain segment. If, however, the indane group itself does not participate in the motions of the critical chain segment, the changes introduced by the bulkiness of the substituent only act indirectly by changing the free volume, which in turn affects the conditions for the rest of the polymer chain. This also explains why the effect of the cyclohexyl substituents is strongly dependent on the nature of the bridging group X. This idea fits very well into the model discussed for the poly(ether ketone)s, namely, immobile indane groups separated by flexible segments.

It must also be considered, however, that very different values for permeability coefficients are reported, in particular for polyimide membranes, even for chemically identical structures. The reason appears to be that often the histories of the membranes are not strictly identical, in particular with respect to contact with solvents and the conditions for imidization. The insolubility of many polyimides requires working with the usually soluble poly(amic acid) precursors, with subsequent imidization in the film. One also finds a strong dependence on the imidization conditions for other macroscopic properties such as the glass-transition temperature, the elasticity module, or the impact strength. Within a given series of polyimides, usually essentially identical imidization conditions are employed, but the comparison between data sets from different laboratories is often difficult. Even though the literature offers the biggest data base for permeability coefficients for polyimides, crucial advances in the search for structure–property relationships are most likely easier and more reliably obtained using other classes of polymers.

To confirm the reliability of our permeability measurements, we had the polymers **2a** and **2d** tested in another laboratory as well.[47] The results differed only very little,[48] so that we consider our results reliable and reproducible in spite of the generally problematic situation for polyimides.

8. Conclusions and Outlook

Future systematic studies on series of polymers in which each member contains only one modified structural element can yield detailed information about the relationship between the structure of a polymer and its suitability as a membrane for gas separation. Whether this information can then also be utilized to create tailor-made membrane materials for any given separation problem depends critically upon the challenge of separating the influence of structural parameters on permeability and selectivity. If this separation is not successful, the further "development" of membrane materials will continue to be limited primarily to the selection of a material that represents an acceptable compromise between price, processing, selectivity, and permeability from a multitude of given polymers that were, in many cases, optimized for other applications (e.g., polysulfones, polycarbonates, cellulose acetate).

Most promising appears to be the proposal by Koros[7] to improve the selectivity without affecting the permeability coefficients negatively by better control of the distribution of the free volume. This approach is limited, however, by the difficulties in gaining experimental access to this distribution. While computer simulations yield plausible results,[27] it is the experimental verification that is crucial. The technique of positron annihilation spectroscopy represents a possible approach to this problem.[49–52] Simply speaking, the polymer sample is irradiated with positrons, and the radiation released by the mutual annihilation of positrons and electrons can yield information about the lifetime of the positrons in the polymer material, which in turn provides information about the free volume. For most polymers, the lifetime distributions of the positrons are made up of three components, the longest of which correlates with the free volume. For polymers with a very large fractional free volume, such as poly(trimethylsilylpropyne), however, a fourth component is observed.[53] At the same time, the contribution of the third component is reduced. This indicates a significant difference in the distribution of the free volume between the classic amorphous polymers and the "high free volume" polymers such as PTMSP. There is much to do in this area, however, until the exact relationships are explored.

The proposal of Koros does provide new ideas for polymer syntheses, which go far beyond the currently employed rule of thumb "bulky groups →large permeability coefficients; rigid polymer chains →high selectivity". Polymers with main chains consisting of alternating bulky, rigid structural elements and flexible segments represent an interesting approach in this context. It is possible to envision an idealized amorphous state in which the gaps between the polymer chains are strongly controlled by the molecular dimensions of the bulky group and the distance between these groups in the main polymer chain. A orderly arrangement of the polymer chains is not necessary in this case. Gas transport, controlled by local segment motions, occurs only through the free volume, actually only through a small fraction of the free volume, as most of it has subatomic dimensions. Therefore, only a small fraction of the chain segments actually influences the gas transport. It is necessary to identify these segments and to control their motions in terms of extent and frequency. The measurement of physical quantities that refer to longer segments or to average values for many polymer chains (T_g, elasticity module, interchain distances, persistence lengths, etc.) cannot yield useful information in this context. Consequently, one finds no correlation between these data and the permeability and selectivity of polymers, in spite of many attempts to find such correlations.

We attempt to use our polymers with indane groups in the main chain to obtain optimized "blueprints" for polymeric membrane materials for a given separation problem. This is done by varying the length of the flexible segments, the rotational barriers around the assumed hinges, the "internal" flexibility of these segments, and their steric bulk. Structural variations in the flexible and the rigid, bulky segments should lead to different effects on the permeability and selectivity of

a series of polymers. In this respect, our approach differs fundamentally from the increment methods that are commonly studied these days. According to these methods, certain structural elements make fixed contributions to the free volume or even directly to the permeability coefficients. These models therefore ignore regioisomerism. The position of a given structural element along the main polymer chain ought to be irrelevant according to these models. Further studies will show which approach corresponds more closely to reality. The indane moiety can very likely be replaced by other structural elements as the bulky, rigid group, and the same is valid for the phenyl ether sequences as the flexible segments. These replacements may even lead to improved results. This area will prove to be a fertile research field for the preparative polymer chemist.

Finally, it should be mentioned that our models only represents an attempt to overcome the often-discussed trade-off problem between general chain rigidity and the free volume. We are aware that our ideas may very well have to be amended after further studies. Compared to the current models, however, our ideas should facilitate the task of selecting structural modifications by kind and position in a more specific manner.

The polymers were prepared and characterized by Dr. Dazhong Yang (currently with Netzsch Gerätebau, Rep. Office Shanghai) and Dr. Martin Wolf (currently with Brückner Maschinenbau GmbH, Siegsdorf, Germany) during their diploma and dissertation studies. They are particularly acknowledged for their efforts regarding the often nontrivial monomer syntheses. The permeability measurements were performed by Dr. Z. Pientka from the Department of Polymer Membranes (Dr. M. Bleha) at the Institute of Macromolecular Chemistry, Prague (Czech Republic). Dr. C. D. Smith and Dr. M. Langsam of Air Products & Chemicals, Allentown, NY (USA) are acknowledged for their help with some of the measurements.

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