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Structure-property Relations between Silicon Containing Polyimides and their Carbon Containing Counterparts

Silke Pelzer and Dieter Hofmann*

GKSS Research Center Geesthacht GmbH, Center for Biomaterial Development, Institute of Polymer Research, Kantstrasse 55, D-14513 Teltow, Germany

Abstract

The present paper examines silicon-containing polyimides and their structural carbon-containing counterparts regarding the relation between their oxygen permeability on the one hand and their microscopic structure on the other hand. There are significant differences in the fractional free volume and the mean squared displacement of silicon-containing polyimides and their carbon counterparts. Compared to the C-polyimides the Si-ones have a greater free volume and show more mobility in the side-groups while the C-ones have a higher mobility in the backbone. These differences are typically connected with higher oxygen permeabilities in the respective Si-containing polymers.

Keywords: Polyimides, Silicon, Fractional Free Volume, Mean Squared Displacement, Oxygen Permeability

Introduction

Polyimides have been important membrane materials for gas separation for many years. Nevertheless there is still a strong need for further improved transport properties of these polymers particularly regarding small molecule permeabilities and the selectivities for certain gas pairs. One problem is that improving the permeability goes normally along with a loss of selectivity. Numerous experiments have been performed to find out which factors might improve the permeability of a polyimide. Higher permeabilities can be e.g. reached increasing the ortho alkylation in the diamine, inserting $-\text{CF}_3$ groups, $\text{SiO}(\text{Me})_2$, $\text{Si}(\text{Me})_3$ or $\text{C}(\text{Me})_3$ groups into the dianhydride, increasing rigidity, decreasing the diamine length or inserting bulky groups. It also turned out that producing a higher free volume leads to a higher permability [1] - [18]. Kim and coworkers [19] - [23] designed and examined various bulky silicon containing structures and their carbon containing counterparts (Figure[1]) with regard to their oxygen permeabilities, Table[1]. The permeabilities between each pair of polyimide (e.g. Si-containing structure and C-containing counterpart) are, except for one case, higher for the Si, than for the respective C-case. Concerning the diffusion (D) and the solubility (S) no experimental data for these types of polyimides are available. To validate the chosen models, experimental wide angle X-ray diffraction (WAXD) measurements reported in the literature [21] are available for two polyimides (A-1 and B-1). The major model properties considered to assess the critical structural differences between

the polymers are the fractional free volume distribution (FFV) and the mean squared displacement (MSD) of the respective polymer atoms. These properties should be closely related to the transport properties of interest.

Computational Details

The amorphous packing model construction and the atomistic simulations of the shown polymers have been investigated using the Accelrys' Materials Studio (MS) Modeling 3.2 program package and the COMPASS force field [24], [25] followed by extensive equilibration procedures. Initial bulk polymer packing cells were created using the amorphous cell module of Materials Studio. The polymer chains were grown at 308 K under cubic periodic boundary conditions. To avoid packing algorithm related catenations and spearings of aromatic units, the initial packing density was very low (0.1 kg/m^3). As no experimental densities were provided through the literature, the Synthia tool of Materials Studio was used to estimate the densities of the different polyimides which were used to help creating the final basic cell for the systems Table[2].

The atomistic chain segment packing cells employed in this work consist of about 4000-5000 atoms. For each of the polyimides 10 independent packing models were obtained to increase the statistical significance of the results. The resulting initial packing models were equilibrated using force field parameter scaling [26] according to the procedure outlined in Table[3]. The individual stages lasted for 1000 fs with a time step of 0.2 fs and were

always preceded by a short energy minimisation of several hundred iteration.

After equilibrating the systems, the MSD results were obtained using the according routines of MS Modelling. For calculating FFV the procedure described by Hofmann et al.[27] has been used. The van der Waals radii of the examined atoms were C: 1.55 [10^{-10} m], H: 1.10 [10^{-10} m], O: 1.73 [10^{-10} m], F: 1.30 [10^{-10} m] and Si: 2.20 [10^{-10} m]. To determine FFV and the fractional accessible volume (FAV) distributions the overlaid three-dimensional probe molecule insertion grid had a grid-size δ of 0.5. An oxygen molecule (O_2 : 1.73 [10^{-10} m]), a positronium (Ps : 1.1 [10^{-10} m]) and a particle with a diameter of 0.4 [10^{-10} m] were used as probe molecules. X-ray scattering calculations have been performed utilising the scattering routine implemented in the forcite module of MS Modelling. The used cutoff was 30 [10^{-10} m] to avoid artefacts, a model size correction of a 1.7 [10^{-10} m] radius was applied and the scattering intensity was plotted against the 2-theta angle. Systematic conformational search procedures applying the Discover module of the MS Modelling software of Accelrys were also performed to determine the energetic potential for the rotation around the central C-C-bond of some of the system.

Results and discussion

Experimental data being available from the literature are the oxygen and nitrogen permeabilities and, for the polyimides A-1 and B-1, wide angle X-ray diffraction (WAXD) measurements. For checking the quality of the models

calculations have been performed for A-1 and B-1 WAXD, as Figure[2] shows.

As it can be seen the calculated and the measured graphs are in good agreement with each other and therefore the chosen equilibration procedure, giving useful results for these polyimides, will be applied to all other polyimides as well. For further validation of the models, experimental information about the density ρ , the solubility coefficient S and the diffusion coefficient D would be helpful, as these values can also be calculated from the models. They are however not available in the literature. Concerning the permeability (P) experience shows that comparing calculated and measured P -values is normally not sufficient. Computationally the permeability will be calculated as the product of S and D and the deviations of the values of S and D compared to the experimental ones, via error propagation will lead to usually quite unsatisfying results of P . The direct model validation is therefore based on the already mentioned WAXD data for A-1 and B-1 indicating reasonably well equilibrated models in these cases. Unfortunately these are the only WAXD data being measured experimentally, but since for the more or less related other polyimides the same basic approach of model construction and equilibration was taken as for A-1 and B-1 it is assumed that also the other models are suited for evaluation. This view is further confirmed by the following approach where in lieu of experimental density data respective prediction from the Synthia module of Materials Studio were taken for comparison with the density values reached in the 1 Bar (NpT) MS-simulation, Table[4].

Synthia is a method developed by Bicerano [29] and is relating the properties of the polymer to a combination of four indices considering the com-

position and topology of the respective polymer repeat. As Table[4] shows the Synthia results are in good agreement with the MD simulated results.

The main focus of this paper is the interpretation of the calculated free volume distribution and mean squared displacements.

As seen from Figure[1] there are two different types of dianhydrides both being very extended in size. The dianhydrides A and B [19], [20] have a very bulky structure while the dianhydrides C and D [22], [23] are rather flat as the geometry optimisations show, Figure[3]. The geometry optimisations also show that in-between the dianhydride couples (A/B and C/D) exchanging the Si(Me)₃-group with the C(Me)₃-group does not significantly change the geometry of the respective dianhydride. Except for the diamine 1 [21] being very bulky as well and structurally comparable to some diamines Langsam et al. examined [1], Kim and coworkers used the common diamines 6FDA (2), MDA (3) and ODA (4). The experimentally measured oxygen permeabilities (P) vary for the polyimides A and B from high values of around 121 (A-1), 110 (B-2) and 105 (A-2) Barrer to smaller ones of 43 (B-3) and 31 (B-4) Barrer, while the polyimides C and D have permeabilities from 56 (C-2) Barrer down to 14 (C-4) and 13 (D-4) Barrer.

It should be noticed, that looking at the permeabilities pairwise, i.e. the silicon containing structures and their carbon containing counterparts, the P values for the silicon containing polyimides are **consistently higher** than for the carbon-containing ones, except for A-2:B-2 where the C-containing structure is higher in permeability than the Si-containing one. **The respective P-differences are however not very large and considering the error of the experimental measurements being around 10 % of the P value, the data pairs**

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A-2:B-2, C-2:D-2 and C-4:D-4 could be considered equal in their permeation values. The considerably higher difference in permeability for the A-1:B-1 pair is a bit unexpected. While all the other pairs differ by not more than 21 Barrer from each other (usually a lot less), the difference of the P values for this pair is 69 Barrer. Since in the following discussion A-1 and B-1 are also the only polymers extremely falling out of the recognisable correlation between atomic structure and macroscopic transport parameters, it is assumed that either A-1 or B-1 might be influenced by some systematic error in the measured permeability.

The calculated size distributions of the free volume regions accessible for an oxygen molecule are given for all investigated polyimides in Figure[4] for group A and B and in Figure[5] for the groups C and D. Looking at the free volume analysis, the graphs follow the same trend, as the permeabilities, the silicon containing polyimides have a larger accessible free volume than their carbon counterparts, see also Table[5]. Looking at these data the FAV behaviour follows

FAV-A-2 > FAV-A-3 > FAV-A-4 > FAV-A-1

FAV-B-2 > FAV-B-1 > FAV-B-3 = FAV-B-4

FAV-C-2 > FAV-C-3 > FAV-C-4

FAV-D-2 > FAV-D-3 > FAV-D-4

while the permeabilities are

PA-1 > PA-2 > PA-3 > PA-4

PB-2 > PB-1 > PB-3 > PB-4

PC-2 > PC-3 > PC-4 >

PD-2 > PD-3 > PD-4

The groups B, C and D show the same order in the sequences of the FAV and the P values. An exception are B-3 and B-4 showing the same value of FAV, but having different permeabilities (43 and 31 Barrer, resp.). Group A shows an inconsistency regarding the polyimide A-1. The FAV and the P value do not match in the way that A-1 shows the smallest FAV value in its group, but has the highest permeability. Since in the following discussion A-1 is also the only polymer extremely falling out of the recognisable correlation between atomic structure and macroscopic transport parameters, it is assumed that B-1 might be influenced by some systematic error in the measured permeability.

All polyimides show a maximum distribution for cavities with a radius of $2-4 \cdot 10^{-10} \text{[m]}$. Additionally some of the polyimides have a second maximum for cavities greater than 5 which might be important for the permeability as stated in the literature [30], [31]. Table 6 shows the percentages of the FAV-elements with radii greater than $5 \cdot 10^{-10} \text{[m]}$. It can be seen that the Si-containing structures have a higher percentage of cavities $> 5 \cdot 10^{-10} \text{[m]}$ than their counterparts containing C. In-between the groups B, C and D the decrease of the percentage of FAV goes along with the decrease in permeability. Group A is again the exception, where A-1 is second highest and A-2

shows the highest value.

Summarising the main result from the FAV analysis, polyimides containing silicon have a higher free volume and cavities of bigger radii than their carbon containing counterparts. Another parameter to discuss is the mean squared displacement (MSD), describing the self diffusion of the polymer chain segments. It is defined as

$$msd(t) = \langle \Delta \mathbf{r}_i(t)^2 \rangle = \langle (\mathbf{r}_i(t) - \mathbf{r}_i(o))^2 \rangle \quad (1)$$

with $\mathbf{r}_i(t) - \mathbf{r}_0(t)$ being the distance travelled by molecule i over the time t . The mean squared displacement is an average over all time intervals and molecules.

Figure[6] and Figure[7] show the MSD for the whole molecule for the groups A and B and C and D, respectively.

The MSD results for the whole molecules reveal that the Si-containing structures show always higher self-diffusion than the respective C-containing ones. Figures[8], [9] and [10] contain respective results for the backbone and sidegroup mobilities.

Compared to the side-groups the backbones are very stiff, but in this connection the C-containing polyimides are more flexible than their Si-counterparts. This is in good agreement with the energetic potential for the dihedral rotation around the central C-C-bond Figure[11] of A and B, as it was obtained from a systematic conformational search procedure applying the Discover module of the MS Modelling software of Accelrys. While for the case of B the rotational barrier reaches not more than 100 kJ/mol, the

barrier for A is extremely high.

For the side-groups the opposite effect is observed, i.e. the Si-containing ones are more flexible. The suggestion lies close, taking the results of the free volume also into account, that the size of the silicon atom is the most important cause of the observed differences in free volume distribution and flexibility of the side-groups. As the silicon is a lot bigger than the carbon, it needs more space and the packing is therefore more loose. As the packing is more loose there is more free volume and the more the sidechains are able to move. On the other hand the backbone for the dianhydride A due to the attached bulky Si(Me₃) side groups is less flexible concerning the rotation around the central C-C-bond. The backbone flexibilities of the related pairs of groups C and D (e.g. C2:D2; C3:D3; C4:D4) are closer to each other especially for C-3:D-3 and C-2:D-2. Due to the very stiff structure of the involved dianhydrides the main mobility contribution belongs to the respective diamines, being the same for each pair, which is why their MSD curves lie close together. The size of the Si does not influence the flexibility as much as in the cases of A and B, because the PMDA structure in the centre of the dianhydride is not flexible at all, so that the two Si-containing sidechains of each repeat unit do not interfere with each other as much as in the case of A and B.

Taking a closer look at Figure[10], the grey and the black line crossing each other at 280 ps on top of the diagram present the polyimides A-1 and B-1. At the beginning the flexibility is quite low of the sidechains of B-1, but during time it is as flexible as A-1. While all the other structures are pretty parallel to each other in the MSD diagram, A-1 and B-1 cross. A MSD run

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over 5 ns, Figure[12], shows that after crossing the two curves run as well parallel to each other. This supports again the earlier mentioned idea that the experimentally obtained P value for A-1 might be too high and should be closer to the one of B-1 as in all the other cases.

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Conclusions

Parallel to the finding that the oxygen permeabilities between Si-containing polyimides and their C-containing counterparts typically are higher for the Si-case, these polymers also differ in their behaviour concerning the free volume and the mean squared displacement the way that the Si-containing structure have a higher free volume and are more flexible in their side-groups. This is due to the fact that the silicon atom is bigger than a carbon atom and because of that needs more space. The more space there is the more the sidechains can move and the more free volume there is. The backbone of the Si-containing polyimides however is less flexible than the carbon ones especially in the case of the groups A and B as the big Si(Me₃) group makes a rotation around the centred C-C bond energetically more demanding.

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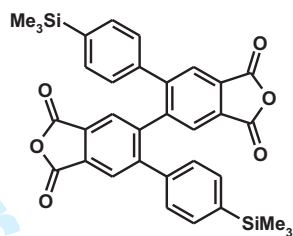
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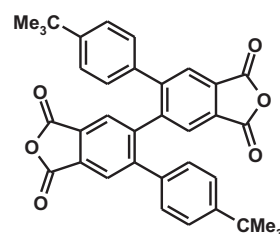
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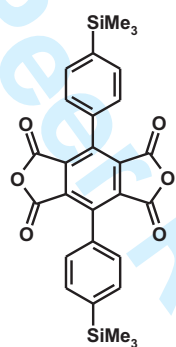
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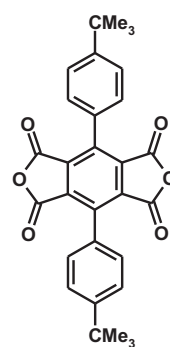
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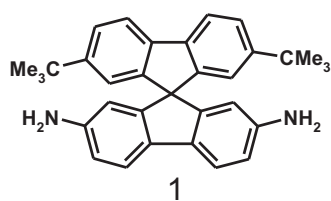


C

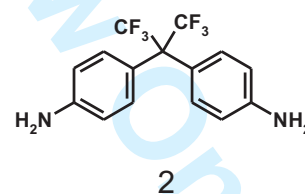


D

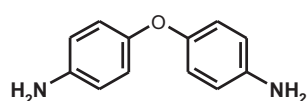
Diamines



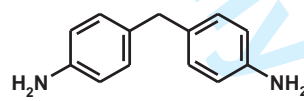
1



2



3



4

Figure 1: Dianhydride and diamine structures of the examined polyimides.

Polyimide	P(O ₂) [(7,5005*10 ⁻¹⁸)m ² /sPa]	Polyimide	P(O ₂) [(7,5005*10 ⁻¹⁸)m ² /sPa]
A-1	121		
A-2	105	C-2	56
A-3	61	C-3	32
A-4	52	C-4	14
B-1	52		
B-2	110	D-2	50
B-3	43	D-3	20
B-4	31	D-4	13

Table 1: Experimental oxygen permeabilities of the chosen polyimides [19]-[23];
exp. setup: membrane thickness = 30-60 [μm], $T = \text{RT}$, $p_{\text{feed}} = 0.94$ [MPa]

polymer	no. of repeat units	no of atoms	density (synthia) [kg/m ³]	av. size of the periodic cell [10^{-10}m]
A1	37	4997	1.143	37.97
A2	45	4547	1.237	37.71
A3	45	4277	1.139	36.68
A4	45	4187	1.154	36.56
B1	37	4997	1.169	37.35
B2	45	4547	1.276	37.90
B3	45	4277	1.175	35.79
B4	45	4187	1.191	35.66
C2	45	4097	1.234	36.65
C3	55	4677	1.126	38.00
C4	55	4567	1.142	37.86
D2	45	4097	1.198	36.51
D3	55	4677	1.164	36.98
D4	55	4567	1.181	36.84

Table 2: Simulation data

stage of equilibration	scaling factor for the torsion term	scaling factor for nonbonded interactions
1	10^{-3}	10^{-3}
2	10^{-2}	10^{-3}
3	1	10^{-3}
4	1	10^{-2}
5	1	1

Table 3: Scaling factors of the five-step equilibration used for packing models

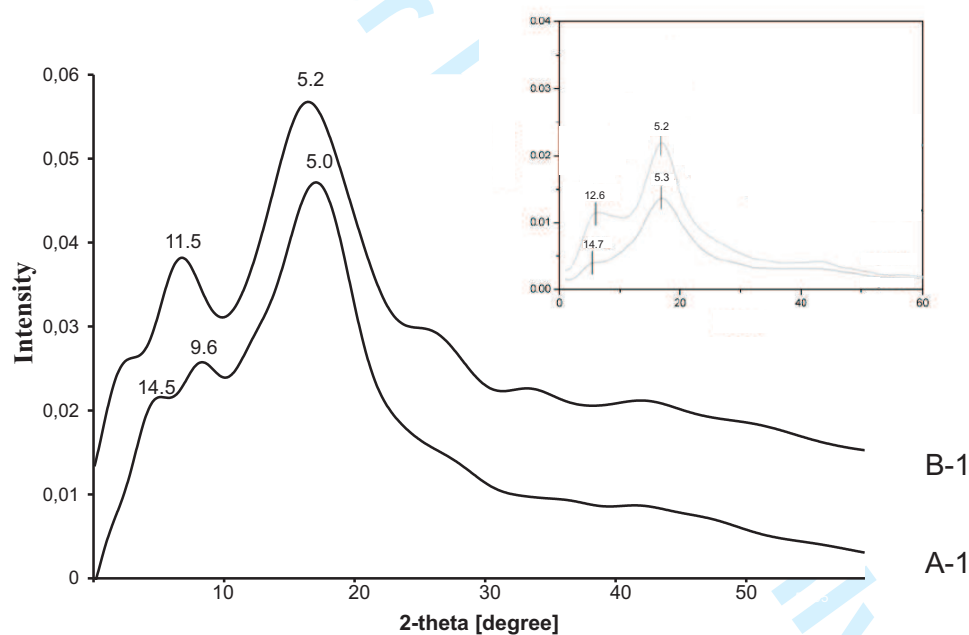


Figure 2: Comparison of the calculated (big graph) and the measured (small graph) [21] wide angle X-ray diffraction of A-1 and B-1. The given numbers in the graph show the calculated d-spacings in 10 nm scale. **The additional peak at 9.6×10 nm is probably due to limited size effects and a slightly higher order in the model than the real system.**

polymer	Synthia	NpT (average over 8-10 packing models)
A1	1.1434	1.1370
A2	1.2374	1.2375
A3	1.1398	1.1395
A4	1.1541	1.1512
B1	1.1691	1.1570
B2	1.2760	1.2746
B3	1.1747	1.1709
B4	1.1905	1.1902
C2	1.2340	1.2345
C3	1.1264	1.1250
C4	1.1420	1.1405
D2	1.2762	1.2985
D3	1.1639	1.1601
D4	1.1813	1.1772

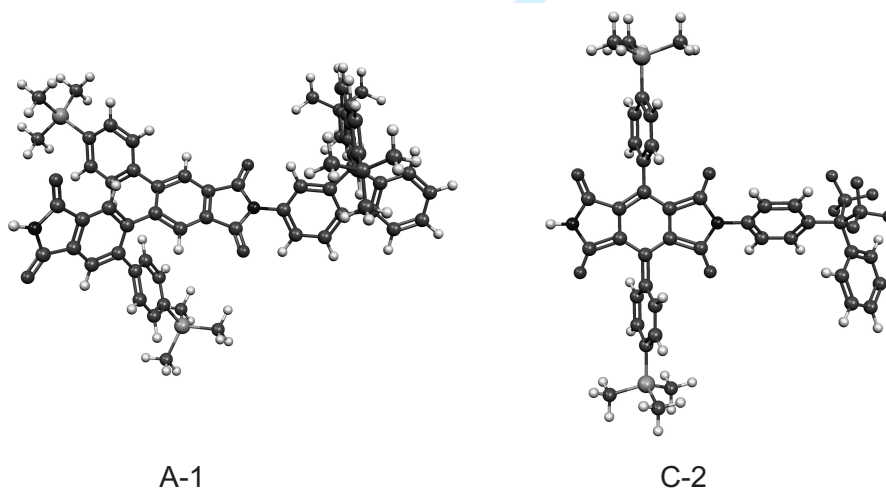
Table 4: Calculated density values given in [kg/m³]

Figure 3: Optimised geometrical structures of A-1 and C-2. While A-1 has a very bulky structure, C-2, especially looking at the dianhydride, is quite flat.

Polyimide	FAV (O ₂)	FAV (Positron)	FAV (0.4)	estimated FFV (0.0)	P(O ₂) [(7,5005*10 ⁻¹⁸)m ² /sPa]
A-1	0.058	0.211	0.310	0.330	121
A-2	0.092	0.275	0.330	0.350	105
A-3	0.080	0.196	0.328	0.405	61
A-4	0.072	0.232	0.324	0.360	52
B-1	0.049	0.261	0.298	0.305	52
B-2	0.064	0.173	0.313	0.390	110
B-3	0.047	0.191	0.306	0.340	43
B-4	0.047	0.202	0.310	0.340	31
C-2	0.114	0.302	0.341	0.345	56
C-3	0.094	0.275	0.338	0.340	32
C-4	0.088	0.264	0.334	0.340	14
D-2	0.071	0.234	0.349	0.380	50
D-3	0.053	0.225	0.319	0.330	20
D-4	0.059	0.226	0.316	0.330	13

Table 5: Calculated accessible free volumes (FAV) for oxygen, a positron and a particle $r=0.4$ [10^{-10} m] and the estimated free volume (FFV).

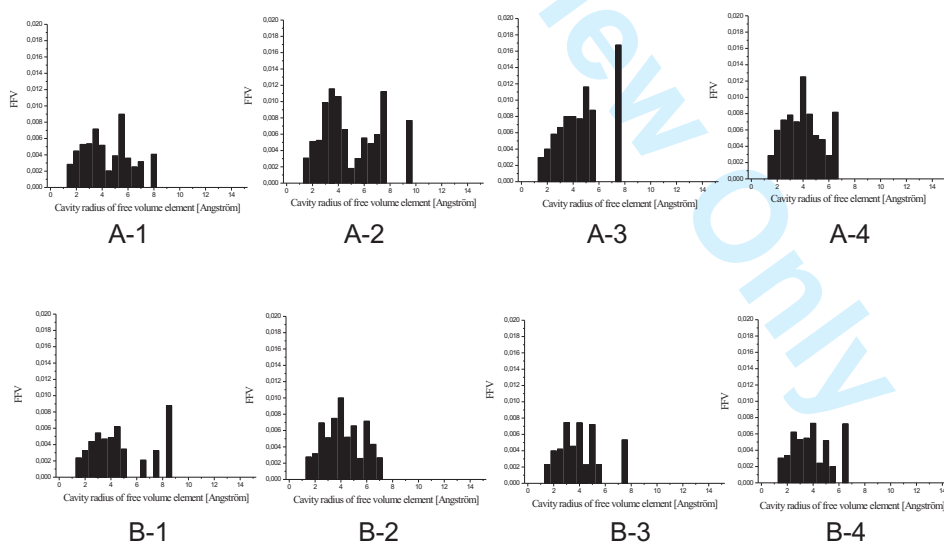


Figure 4: Bar-graph size distribution of free volume elements accessible for O₂ for the groups A and B.

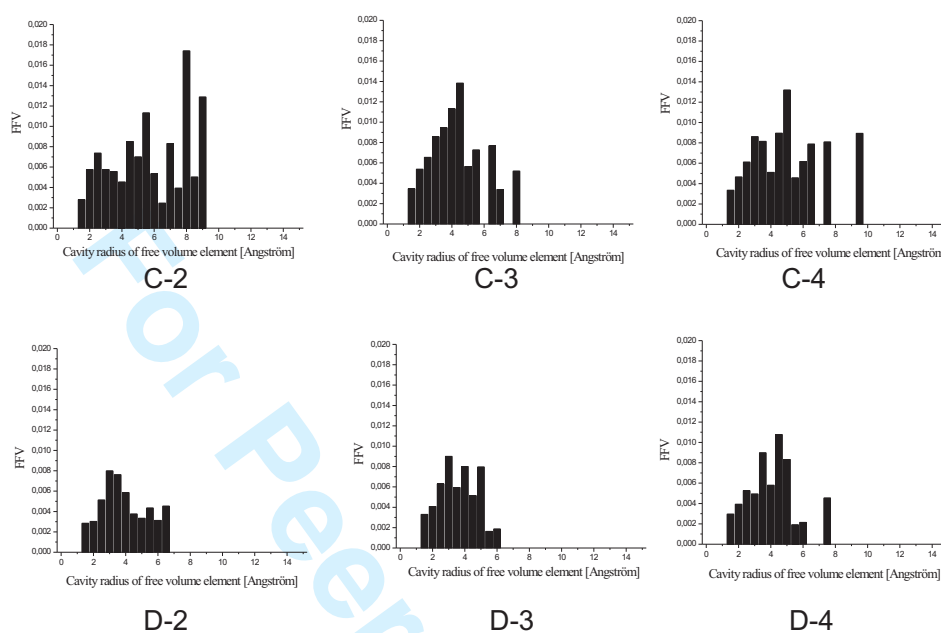


Figure 5: Bar-graph size distribution of free volume elements accessible for O_2 for the groups C and D.

Polyimide	$P[O_2]$ [[$(7,5005 \cdot 10^{-18})m^2/sPa$]	FAV[O_2]	<5 [$10^{-10}m$]	>5 [$10^{-10}m$]	percentage of FAV > 5 [$10^{-10}m$]
A-1	121	0.058	0.036	0.022	0.381
A-2	105	0.092	0.054	0.038	0.415
A-3	61	0.080	0.055	0.025	0.313
A-4	52	0.072	0.056	0.016	0.222
B-1	52	0.049	0.035	0.014	0.286
B-2	110	0.064	0.047	0.017	0.265
B-3	43	0.047	0.039	0.008	0.170
B-4	31	0.047	0.040	0.007	0.148
C-2	56	0.114	0.047	0.067	0.585
C-3	32	0.094	0.058	0.036	0.380
C-4	14	0.088	0.064	0.023	0.268
D-2	50	0.071	0.039	0.012	0.169
D-3	20	0.053	0.050	0.003	0.066
D-4	13	0.059	0.051	0.002	0.033

Table 6: FAV for oxygen. Shown are as well the fraction of cavities smaller than 5 and bigger than 5 and the percentage of the cavities greater than 5 of the all over FAV.

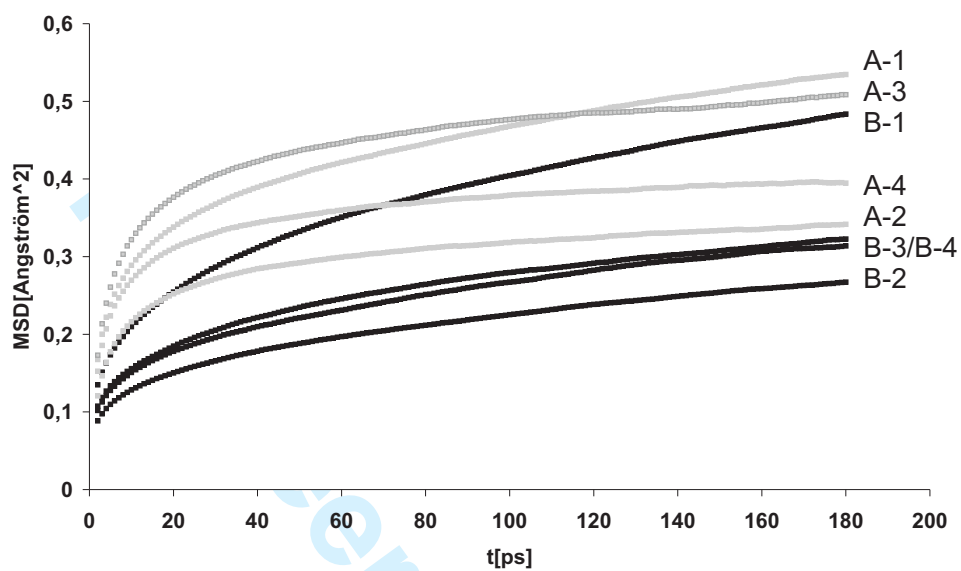


Figure 6: MSD versus the time for the groups A and B.

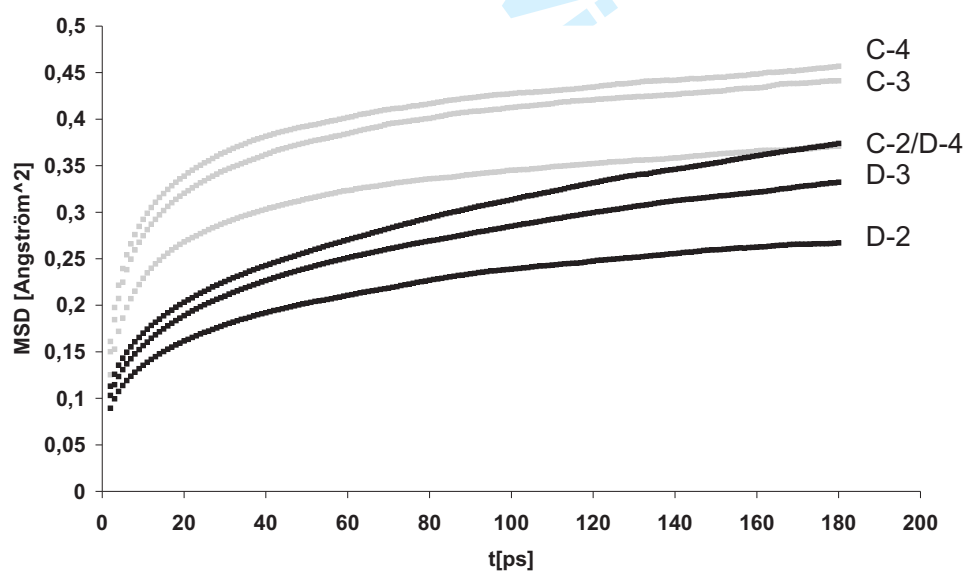


Figure 7: MSD versus the time for the groups C and D.

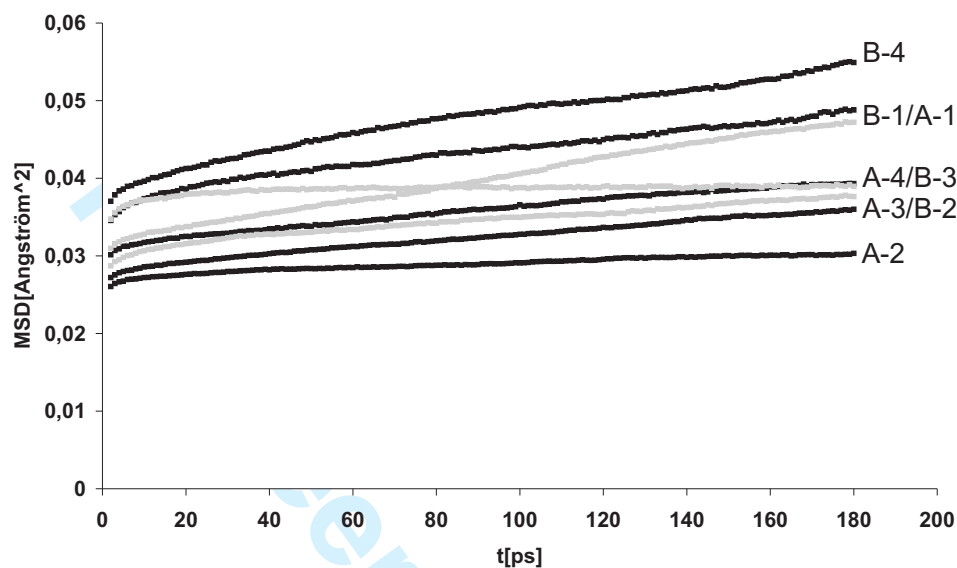


Figure 8: MSD of the backbone versus the time for the groups A and B.

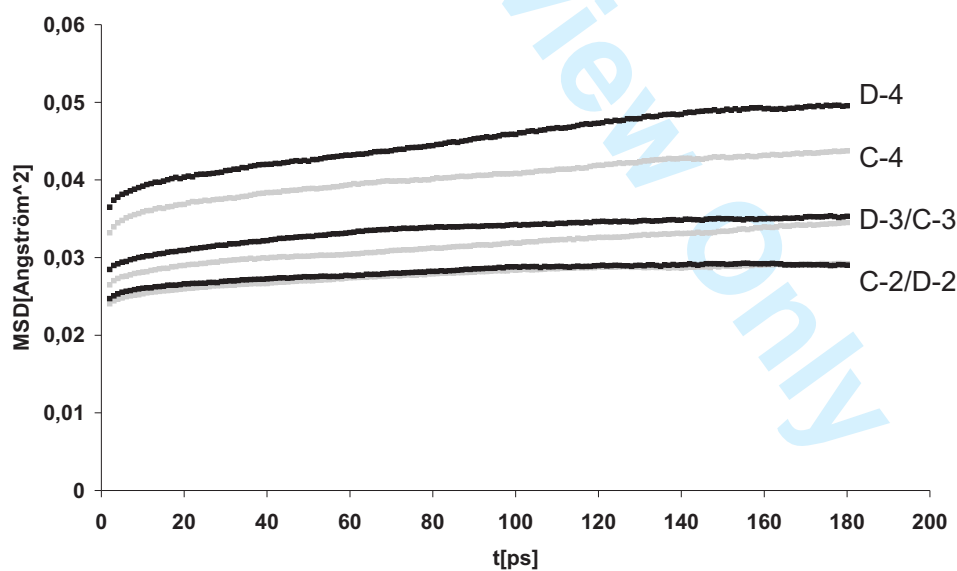


Figure 9: MSD of the backbone versus the time for the groups C and D.

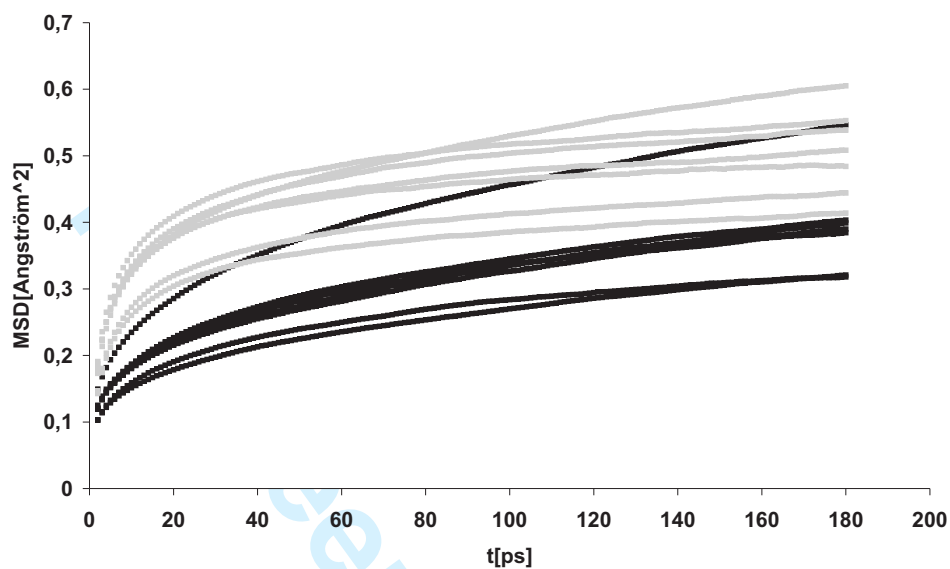


Figure 10: MSD of the sidechain versus the time for all groups. The grey lines represent the Si-containing molecules, the black lines the C-containing ones.

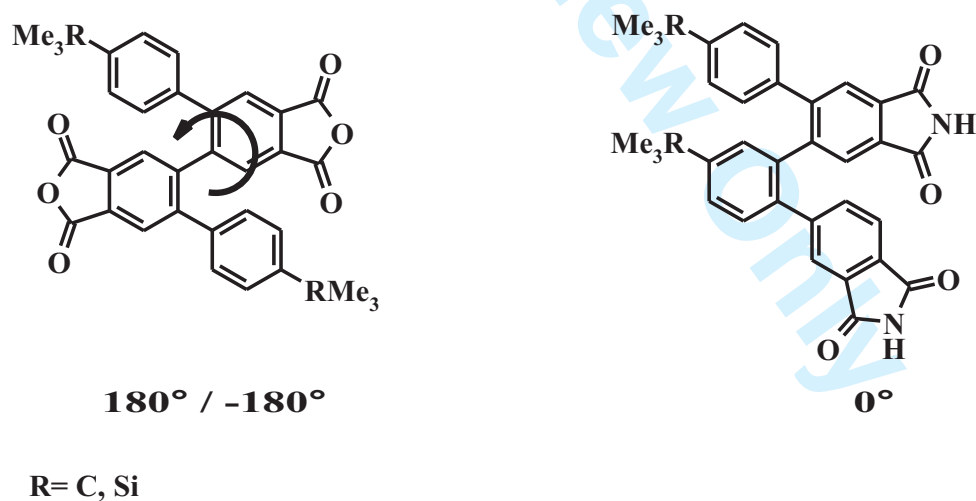


Figure 11: Dianhydride structure showing the conformation at 0° and 180° / -180° , respectively.

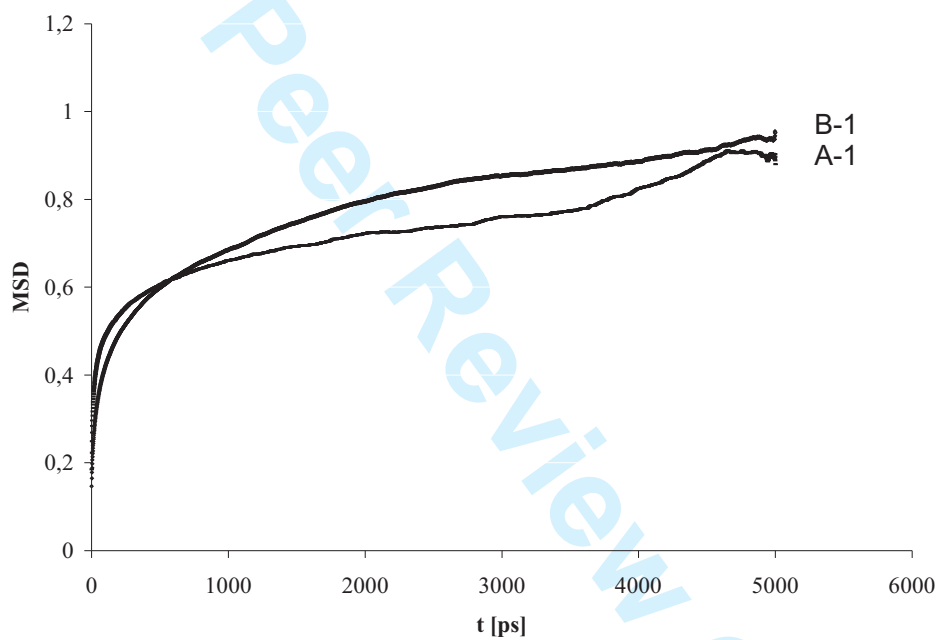


Figure 12: MSD versus the time for A-1 and B-1.