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Molecular dynamics simulation of diffusion of O_2 and CO_2 in amorphous poly(ethylene terephthalate) and related aromatic polyesters

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Abstract

The diffusion of small molecules through polymers is important in many areas of polymer science, such as gas barrier and separation membrane materials, polymeric foams, and in the processing and properties of polymers. Molecular simulation techniques have been applied to study the diffusion of oxygen and dioxide of carbon as small molecule penetrants in models of bulk amorphous poly(ethylene terephthalate) and related aromatic polyesters. A bulk amorphous configuration with periodic boundary conditions is generated into a unit cell whose dimensions are determined for each of the simulated aromatic polyesters in the cell to have the experimental density. The aim for this research is to explore and investigate the diffusion of gases through bulk amorphous poly(ethylene terephthalate) and related aromatic polyesters. The diffusion coefficients for O_2 and CO_2 were determined via NVE molecular dynamics simulations using the Dreiding 2.21 molecular mechanics force field over a range of temperatures (300, 500 and 600 K) using up to 30 ns simulation time. We have focussed on the influence of the temperature, polymer dynamics, number of aromatic rings, *ortho*-, *meta*-, *para*-isomers, density and free volume distribution on the diffusion properties. Correlation of diffusion coefficients with free volume, temperature, number of aromatic rings, *ortho*-, *meta*- and *para*-isomers was found.

Keywords: Molecular dynamics simulation; Diffusion; Free volume

1. Introduction

Polyesters and copolyesters are known to exhibit very low gas diffusion compared with most other polymers such as polyolefin, polycarbonate, polystyrene, etc. Poly(ethylene terephthalate), (PET), has acceptable gas barrier properties for many applications, but requires improvement for packaging of sensitive products. Some related polyesters with different structural features have improved barrier properties. This study is therefore important from the technological point of view, since the possibility of improving the impermeability (barrier properties) of PET and related polyesters is required from many applications. The diffusion of gases through polymers is a topic of broad interest and there has been a growing interest in the understanding of migration of small molecules in polymers from a molecular point of view [1–27]. Diffusion of gases in polymers is an important, and in many cases, controlling factor in a variety of practical applications, such as protective coatings [18–20], membrane separation processes [16,22,29], food packaging [8,11,22,25,28,30,31], and biomedical devices [15,30–34]. The technological relevance of such behavior has become evident in recent years through the rapidly growing demand for polymers with specified gas-transport properties. A visible trend in the area of food packaging is the increasing substitution of thermoplastics for traditional materials such as glass and metal. Plastic packaging materials offer less breakage, lighter weight and a degree of design flexibility that glass and metal cannot provide [11,22,24,31]. However, there are no plastics that are impermeable, at the same time consumers are much more demanding and want food that is perfectly safe, nutritious and tasty. Despite this manifest increase in technological demand, however, there has been, until very recently, a considerable lack of fundamental understanding of a molecular-level mechanism underlying the diffusion of gases through polymeric materials and the

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theoretical understanding of diffusion of gases in polymers is still very limited.

In order to function as food-packaging materials, the polymers should typically be investigated at molecular level to study the atomistic mechanism of the diffusion of gases through the walls of the container. It is a considerable challenge for polymer modelling to predict these properties.

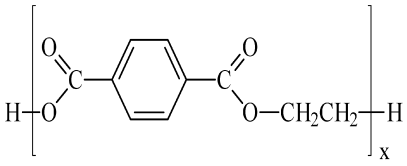
The existing methods have only recently been powerful enough to predict diffusion coefficients, permeability, and selectivity for specific polymer-penetrant systems given only their chemical structure [9–14]. There is a growing demand for better theoretical understanding of the diffusion of gaseous penetrants in polymers to achieve improvements in designing new, better membranes computer and structurally enhanced materials. With the increasing power of available systems a better insight into this phenomenon can only be gained by computer simulation and use of molecular models and simulation techniques for the study of materials at the microscopic and mesoscopic level.

It is, therefore, very desirable to use molecular dynamics (MD) simulation to understand and to predict the transport properties of gases in polymers. Because diffusion is a dynamic problem, the obvious approach in calculation of the diffusion coefficients is through MD simulation.

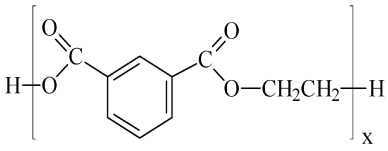
In recent years, a number of such polymers with various structural compositions have been investigated [25–32]. In particular, we are concerned with diffusion of O_2 and CO_2 through bulk amorphous aromatic polyesters, such as PET, (which is one of the most widely used food packaging materials) [12,13,22,31] and related aromatic polyesters. Another reason for this research is to explore the unique properties of the studied polymers in order to gain considerable insight into the behaviour of these polymers. In this study NPT and NVE MD simulations of polymers were performed and aimed to elucidate whether a correlation exists between polymer conformation (structure), polymer dynamics, number of aromatic rings, *ortho-*, *meta-* and *para-* isomers, density, diffusion coefficient and free volume. Until recently, free volume properties have been thought of mainly as theoretical values, however, molecular simulation technique is a novel probe to determine free volume properties.

The aim for this research is to explore and investigate the diffusion of gases through bulk amorphous PET and related aromatic and isomeric polyesters. PET is the most commercially important polyester and a widely used barrier packaging material, and therefore many authors have investigated the correlations between the structural organisation and the properties of this polymer.

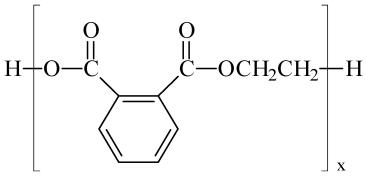
2. Polymers studied



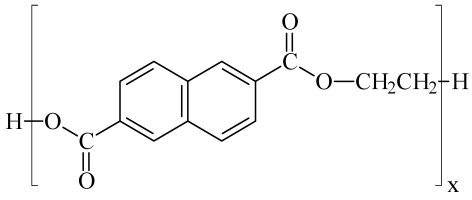
PET Poly(ethylene terephthalate)



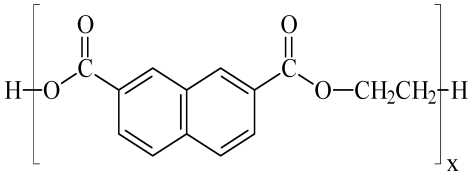
PEI Poly(ethylene isophthalate)



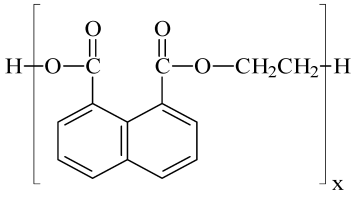
PEP Poly(ethylene phthalate)



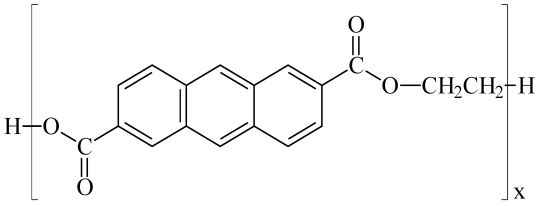
PEN-2,6 Poly(ethylene 2,6-naphthalenedioate)



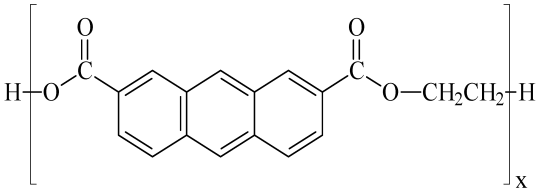
PEN-2,7 Poly(ethylene 2,7-naphthalenedioate)



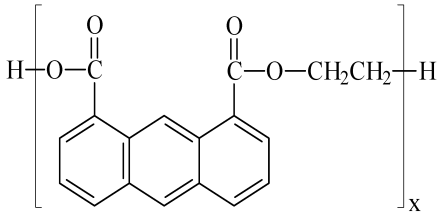
PEN-1,8 Poly(ethylene 1,8-naphthalenedioate)



PEA-2,7 Poly(ethylene 2,7-anthracenedioate)



PEA-2,8 Poly(ethylene 2,8-anthracenedioate)



PEA-1,9 Poly(ethylene 1,9-anthracenedioate)

3. Computational methodology

The simulations were performed for amorphous unit cells of each investigated polyester with 3 polymer chains with degree of polymerization ranging from 20 to 60. Computer modelling of chemical structures of the monomers and polymers, MD simulations, and conformational and MD analyses were carried out using molecular simulation software for material science [35], Cerius^2 version 4.8, designed by Accelrys Inc., San Diego, CA, USA. The Cerius^2 molecular simulation software was run on a Silicon Graphics Origin 2000 workstation. The 3D-Sketcher, Open Force-Field (OFF), charge equilibration, monomer editor, polymer, and amorphous polymer builder, energy minimiser, NVE and NPT MD, polymer properties, and dynamic analysis modules of Cerius^2 software [35] were used in order to perform the computations and to calculate the density, diffusion coefficient, free volume and to predict the correlation between these properties.

The polymer molecule is defined using the monomer Builder (for the monomer) and the Polymerizer (for the polymer) in order to define the structure of the polymer. The OFF module allowed the specification of the force field to be used for these simulations. The Dreiding 2.21 force field described by Mayo et al. [36] and implemented in Cerius^2 OFF module was applied since it was found to be very suitable and reliable for the molecular simulation of aromatic polymers in accordance with previous studies [1, 37–42]. Single chains and amorphous unit cells of the studied polyesters with degree of polymerisation 20 and 60 were used for these simulations. The initial macromolecular conformations of the simulated polymers were optimised and the value of the total potential energy and its components in the investigated polymers were obtained. The energy minimised single chain of the polymers was then used to construct the periodic unit cells of the studied polymers. The total potential energy vs time-step of the single chain of the PEN-2,7 is presented in Fig 1 as an example.

The Dreiding 2.21 force field provides a potential energy interaction function (E_{total}) that accounts for both bonded (E_{b}) and non-bonded (E_{nb}) interactions. The bonded terms typically include harmonic bond stretching (E_{s}), harmonic angle bending (E_{a}), torsional (E_{t}), and inversion (E_{i}) energies. Non-bonded terms typically contain van der Waals (E_{vdW}), electrostatic (Coulombic) (E_{q}) and hydrogen bond (10–12 potential) (E_{hb}) interactions.

In practice it is common to use a suitably large cut-off distance, and so for this study a cut-off distance of 100 Å was used for non-bonded interactions, so for this cut-off distance all the non-bonded interactions of the simulated copolymers are calculated. The Mie 6-12 potential [43–45], that is often referred to in the literature as the Lennard-Jones 6-12 potential function ($u = A/r^{12} - B/r^6$), was used to calculate the non-bonded van der Waals interactions. A and B are parameters which determine the size of the attraction ($-B/r^6$) and repulsion (A/r^{12}) interactions between the atoms which are separated by a distance r equal to the sum of r_{i} and r_{j}, where r_{i} and r_{j} are van der Waals radii of the non-bonded atoms i and j.

The charge distribution in the molecule, due to Coulombic (electrostatic) interactions, of the simulated polymers was obtained with the charge equilibration method described by Rappe and Goddard [44] that is available in the Cerius^2 molecular simulation software for material science. The validity of the molecular simulation calculations depends on the suitability and accuracy of the equations used for the bonded and non-bonded potentials which are of great importance for industrial applications.

The NPT and NVE MD simulations were performed at 300, 500 and 600 K for each constructed and minimised polymer system. For the NVE ensemble, the number of molecules N, volume V and energy E of the system are kept constant, whereas for the NPT ensemble the number of molecules N, pressure P and the temperature T of the system are kept constant. MD calculations simulate the natural motions of all atoms in a polymer system over time

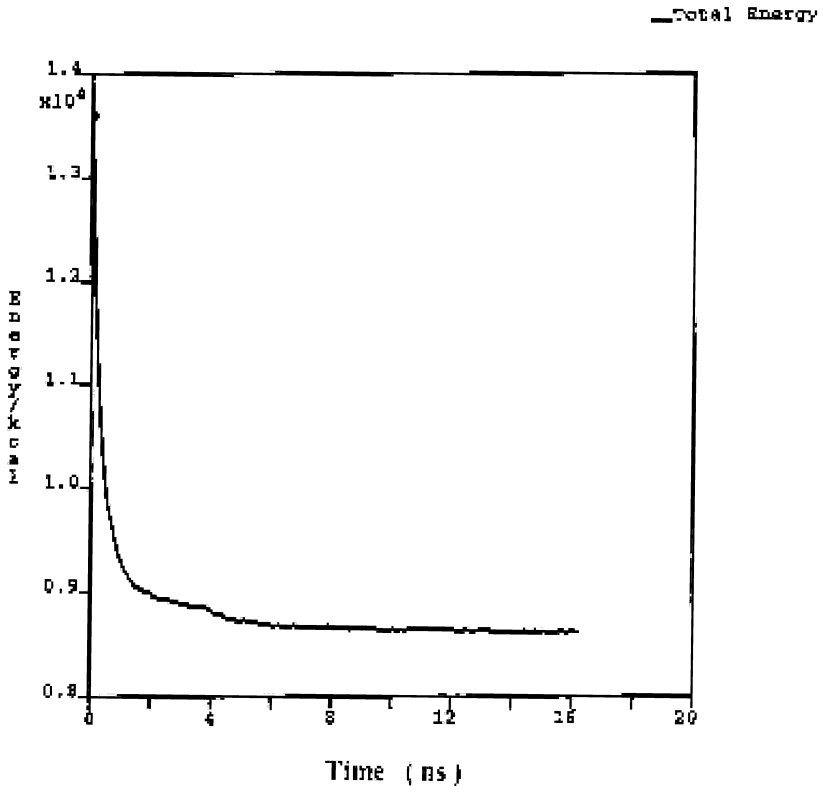


Fig. 1. Total potential energy vs time-step of the single chain of the PEP.

at non-zero temperature and the MD algorithm makes use of Newton's equation of motion ($F = ma$), thus giving a complete dynamic description of the polymeric material. In order to ensure that the simulations are carried out for sufficient time, which is one of the most important criteria in equilibrating the system, the number of steps of NPT MD simulations was 30,000,000 (30 ns), and the output frequency was every 2000 steps. The time step of 0.001 ps is taken to be constant for all the simulations of this study. In this study, the model system exchanges energy with a heat bath in order to maintain a constant temperature. The non-canonical 'T-damping' thermostat described by Berendsen et al. [46] was used for isothermal–isobaric NPT MD simulations. MD studies [1,25–32,35–42] have proven to provide a better insight into the physical phenomena exhibited by polymers. In the case of polymers, this technique can actually be used to predict physical (density, diffusion, and free volume) properties of a polymeric system.

The simulated amorphous unit cells all contained 3 polyester chains for each investigated polyester. The energy of the polymer was minimized using MD and a random conformation is produced for amorphous polymers. The unit cell was displayed and analysed. Each simulated structure was then analysed by the Amorphous_Cell module to obtain density, cohesive energy, pair correlation function (statistical analysis of relative atom positions). The density of the polyester unit cell was equilibrated and compared with actual amorphous densities where available.

Small molecules (O_2 and CO_2) were added to the amorphous cell and they move in the cell during MD. The rate of movement can be used to calculate the diffusion coefficients for the small molecules through the polymer. The distribution of free volume was determined for each simulated amorphous cell. 1 and 5 O_2 molecules and, 1 and 5 CO_2 molecules were inserted in each of the simulated amorphous polyester unit cells described above.

Trajectory file data generated from NPT and NVE MD simulation has been used in all the polymer property calculations and analyses presented in this research. The trajectory files were analysed by polymer properties and dynamics analysis modules. The density of the studied polymers was predicted from the NPT DM trajectory files. The diffusion coefficient of O_2 and CO_2 in polymers was calculated from the NVE MD slope of the mean-square displacement for long times, at these times normal (Fickian) diffusion is observed, and the mean-square displacement is a linear function of time:

$$D = 1/6\lim \mathrm{d}/\mathrm{d}t((\mathbf{r}(t) - \mathbf{r}(0))^2) \quad (1)$$

In Eq. (1), D is the diffusion constant, t is time, $\mathbf{r}(t)$ is the position vector of the gas molecule in space at time t, and the brackets denote an ensemble average, which in these simulations is obtained from averaging over all gas molecules in the polymer system and all time origins $t = 0$. This equation only applies in the limit of large times, times at which the simulated gas molecules have performed

enough jumps for their trajectories to become a random walk in the polymer model.

The computational procedure used in this research includes the following main steps shown in Fig. 2.

4. Results and discussion

This research was performed for single chains and amorphous unit cells for each of the simulated aromatic polyesters. Initially, for each of the investigated polyesters, a single chain was modelled and energy minimized in order to investigate the polymer conformation. An example of the PEI energy minimised conformation is presented in Fig. 3.

Then, an amorphous unit cell with 3 polymeric single chains, previously minimized, for each of the studied polyesters was modelled in order to calculate the density by NPT MD. The density results compared favourably with values for amorphous phase of the actual polyesters, where available. It was assumed that the other densities were also representative of each of the polymers. Density was a guide to the diffusion but the densities were very similar so other factors must be important. Then the predicted density for each of the studied polyesters was used to build a new amorphous unit cell with 1 and 5 molecules of O_2 and CO_2 in order to calculate the diffusion coefficients and free volume at different temperature. Free volume distributions are not available from other measurements. An example of the simulated, investigated, and visually analysed unit cell

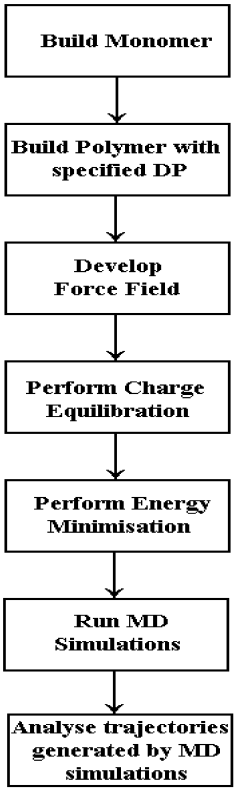


Fig. 2. The main steps in the computational procedure used in this research.

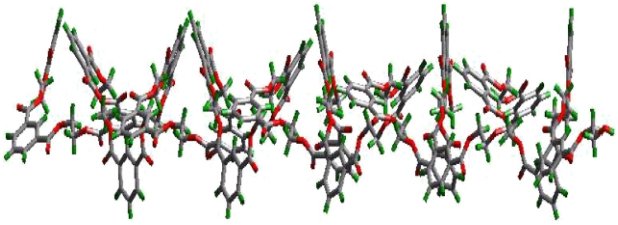


Fig. 3. Minimised structures of aromatic polyester PEI.

for PEN with 1 molecule of carbon dioxide inserted is displayed in Fig. 4. Free volume is calculated as a measured volume of the polymer minus the volume actually occupied by polymer molecules.

An example of the NPT MD calculated density for PEN-2,6 over a wide simulation time range is presented in Fig. 5. As can be observed in Fig. 5 from the equilibration times in NPT MD simulation (after 10 ns) the average simulated density of PEN-2,6 is 1.29 g/cm^3 which is consistent with most of the experimental data reported for amorphous PEN. The experimental data depend on the thermal processing parameters, such as orientation whereas in this study all of the simulated structures are totally amorphous compared with the actual polymer samples. Fig. 5 exhibits typical density vs time behaviour during this part of the NPT-MD simulation for PEN-2,6. The density fluctuations in the simulations for the investigated polymers are less than 0.007 g/cm^3 (see also Fig. 5).

The molecular dimensions, as expressed by the characteristic ratio and end-to-end distance are key parameters in the molecular simulations because they depend differently on the conformational characteristics of the individual bond types in the polymeric chain. These structural parameters were emphasized in testing the model and satisfactory representation was accomplished. In order to confirm the validation of the model of the studied polyesters for PET further MD simulation were performed to calculate the structural parameters, such as end-to-end distance and characteristic ratio which are presented in Figs. 6 and 7, respectively.

The predicted characteristic ratio is about 3.8 and the reported experimental values are between 3.7–4.1 [12–15]. The experimental values are unfortunately somewhat approximate as they are based on viscosity measurements in good solvents and corrections must be made to arrive at unperturbed dimensions.

Diffusion coefficients were obtained for each of the aromatic polyesters from the mean square displacement vs simulation time calculated according to Eq. (1). The diffusion coefficient of gas molecules of the simulated polyesters has been calculated from the slope of the penetrant mean-square displacement for long times. At these times Einstein diffusion is observed, and the mean-square displacement is a linear function of time. An example of the carbon dioxide mean square displacement at temperature of 500 K in amorphous PEN-2,6 is shown in Fig. 8.

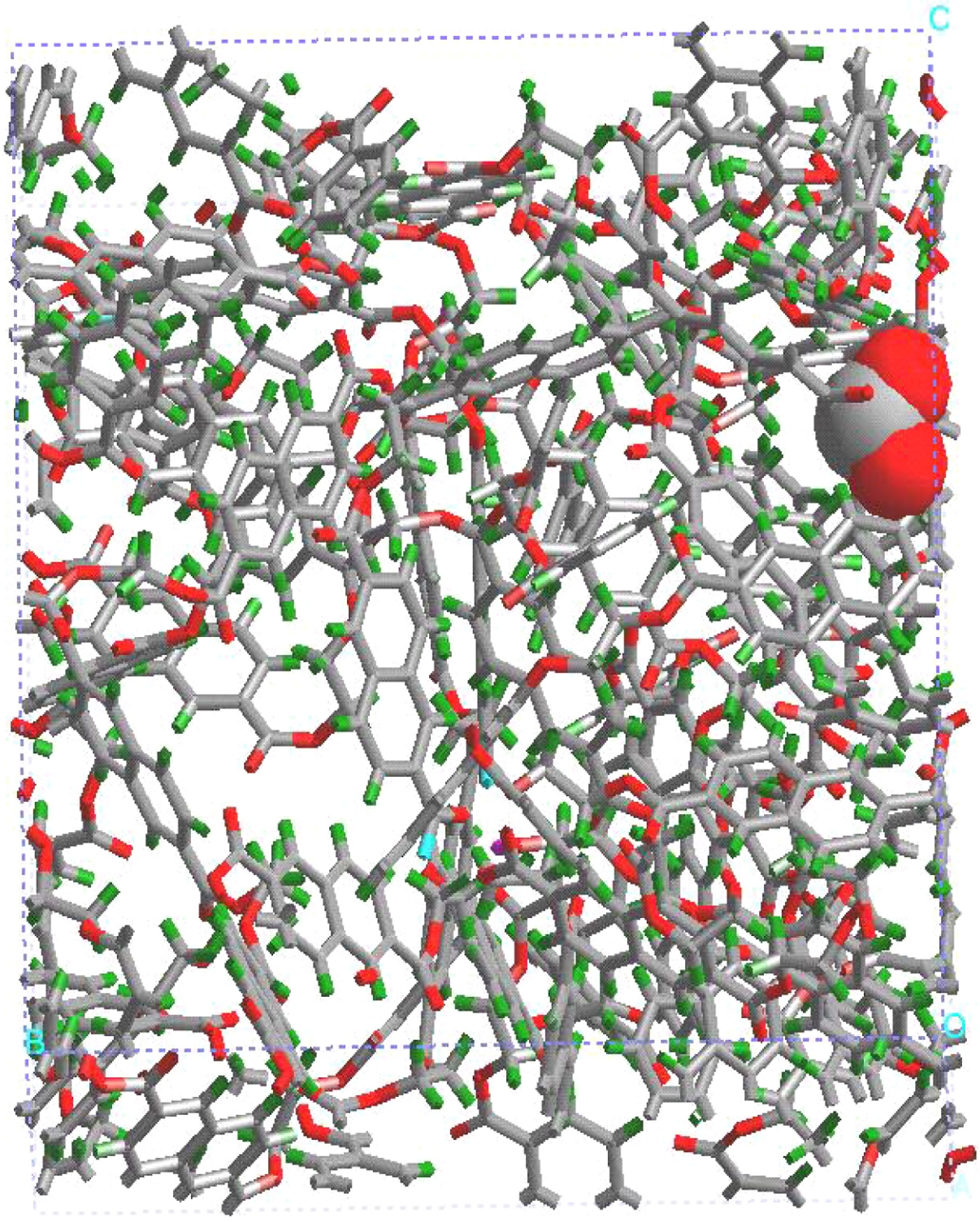


Fig. 4. Amorphous cell structure of PEN-2,6 with 1 molecule of carbon dioxide inserted.

The predicted diffusion coefficients of O_2 and CO_2, densities and free volume for the simulated aromatic polyesters are listed in Table 1.

The coefficients of diffusion for both O_2 and CO_2 for the studied polyesters increase exponentially with increasing free volume. This is clearly evidenced in Fig. 9 for diffusion of O_2 and in Fig. 10 for diffusion of CO_2 through the aromatic polyesters. The mechanism of diffusion involves a series of random 'jumps' ('hopping diffusion') from a free volume between polymer chains to another hole or void (for example see Fig. 4). MD simulations performed during this study have revealed these mechanisms and dynamics, and it

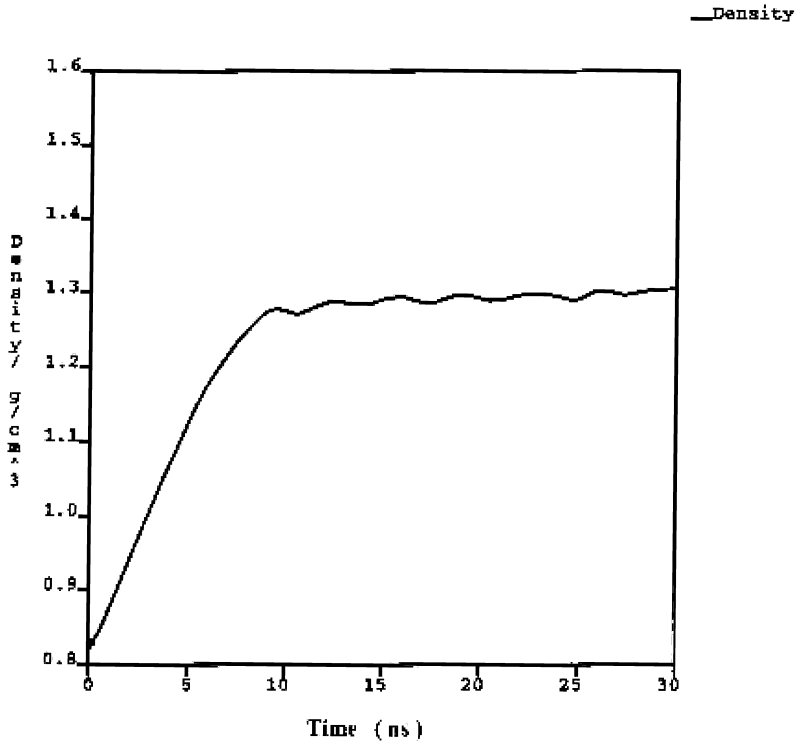


Fig. 5. Predicted density equilibration vs NPT molecular dynamics time for amorphous PEN-2,6.

was shown that molecules of O_2 and CO_2 diffuse through polymer chains in a sequence of activated jumps between neighbouring locations. The gas molecule is only temporarily kept in a cavity of free volume as the thermal fluctuations of polymer atoms constantly create and destroy transient channels of free volume between neighbouring holes/cavities. When the gas molecule is at the right position at the right time having the right velocity it can slip through such a channel into the neighbouring hole. The size and shape of the holes available in a polymer control its rate of gas diffusion as well as its permeation properties. Transport of gas molecules occurs by jumps between individual sections of the free volume (holes) through temporarily open channels. The diffusion coefficient is completely determined by the jump event.

Therefore, for the simulated polyesters it was found that Voronoi free volume plays the most important factor in the process of diffusion, comparing with other factors, such as

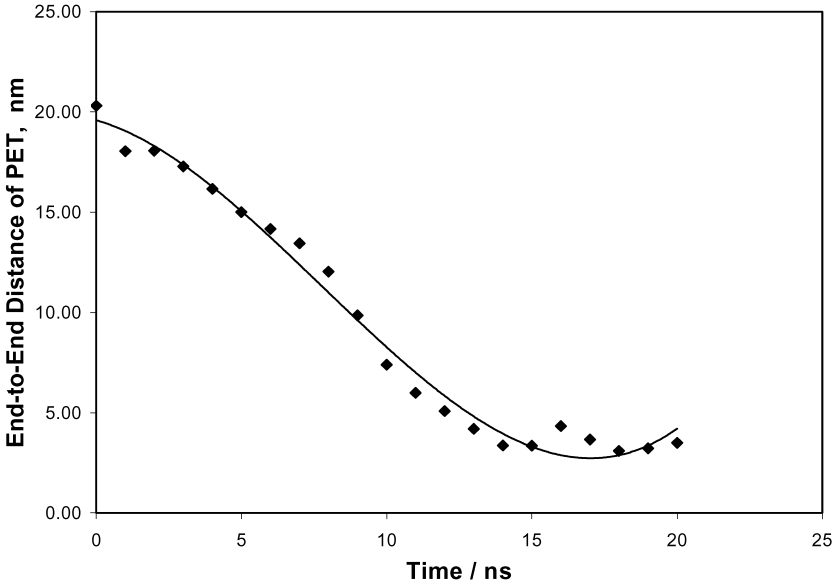


Fig. 6. End-to-end distance of PET obtained by MD simulation.

Table 1
Predicted diffusion coefficients, free volume and density of the simulated aromatic polyesters

Polymer code	Diffusion of O_2 (cm^2/s) $\times 10^4$			Diffusion of CO_2 (cm^2/s) $\times 10^4$			Free Vol. (A^3)	Density (g/cm^3)
	300 K	500 K	600 K	300 K	500 K	600 K	500 K	300 K
PET-*p*	0.1456	0.1913	0.2011	0.1281	0.1632	0.1709	17.8	1.33
PEI-*m*	0.1037	0.1344	0.1402	0.1039	0.1261	0.1281	17.0	1.31
PEP-*o*	0.1291	0.1656	0.1987	0.1011	0.1242	0.1301	17.2	1.32
PEN-2,6	0.0093	0.0262	0.0357	0.0081	0.0219	0.0259	10.3	1.29
PEN-2,7	0.0056	0.0183	0.0204	0.0049	0.0106	0.0174	8.2	1.26
PEN-1,8	0.0081	0.0236	0.0271	0.0053	0.0119	0.0217	8.4	1.25
PEA-2,7		0.0018			0.0031		5.2	1.32
PEA-2,8		0.0009			0.0016		5.0	1.30
PEA-1,9		0.0010			0.0024		5.1	1.31

density. As seen in Figs. 9 and 10, the larger the free volume in a polyester, the greater the gas diffusion. As shown in Table 1, PEA-2,8 has the lowest free volume properties of any of the simulated polyesters, therefore, PEA-2,8 has lower gas diffusion and offers very high barrier properties. Figure 11 displays an example of the distribution of Voronoi free volume in a PEI amorphous sample.

Contrary to our expectation, as it is displayed in Figs. 12 and 13 the predicted coefficients of diffusion for both O_2 and CO_2 for the studied polyesters do not depend on density, therefore, in this study the calculated density was just a guide to the diffusion, but the densities were very similar, so other factors must be important. Similar to the coefficients of diffusion, the predicted free volume for the studied polyesters does not depend on density as well (see Fig. 14). In Fig. 14 it can be observed that for polymers with the same values, or almost the same values, of density we have obtained very different values for free volume. This can be explained by the fact that Voronoi free volume treatment does not include all the space between atoms (related to density), but only considers volumes larger than a certain threshold.

During this research an interesting observation has been noticed, the diffusion coefficient strongly depends on the number of aromatic rings of the monomeric units, the *ortho*-, *meta*-, and *para*-isomers, and of temperature. The amorphous structures of this series of polyesters were modelled and simulated in order to study the influence of polyester structures on barrier properties. The influence of the number of aromatic rings on the coefficient of diffusion is displayed in Figs. 15 and 16. For all of the simulated polyesters the diffusion coefficients for both O_2 and CO_2 molecules decrease from *para* to *ortho* and *meta* isomers.

The *para* is a symmetrical linear geometry. This linear structure in the rigid aromatic system slightly increases the free volume of the amorphous phase and provides a high diffusion. The *meta* is a slightly bent geometry and this gives the lowest diffusion so it must be able to pack better and limit the free volume. The *ortho* is very bent which must make it too difficult to pack closely and so the free volume is larger than the *meta*. The naphthalene 2,7- is shaped like a *meta* while the 1,8- is shaped like an *ortho* so and the results for these are consistent with the results from a benzene. The anthracene 2,8- is shaped like a *meta*, while the 1,9- is shaped like an *ortho* and these behave in the same way as the benzene and naphthalene ring systems. A linear molecule is not as efficient as a bend molecule to have low diffusion, but when the molecule is very bend the

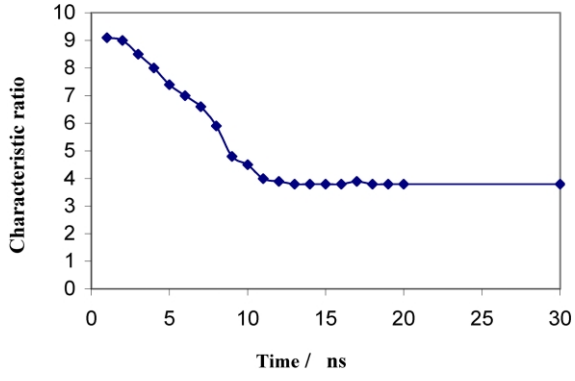


Fig. 7. Characteristic ratio of PET obtained by MD simulation.

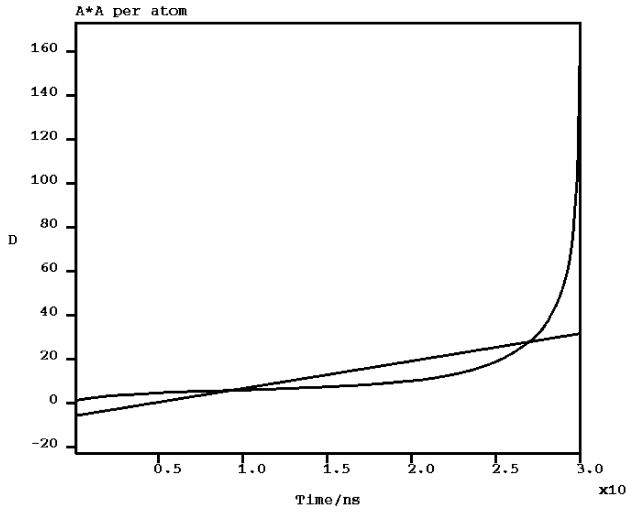


Fig. 8. A snapshot of the mean square displacement and fit line vs simulation time for CO_2 in amorphous PEN-2,6.

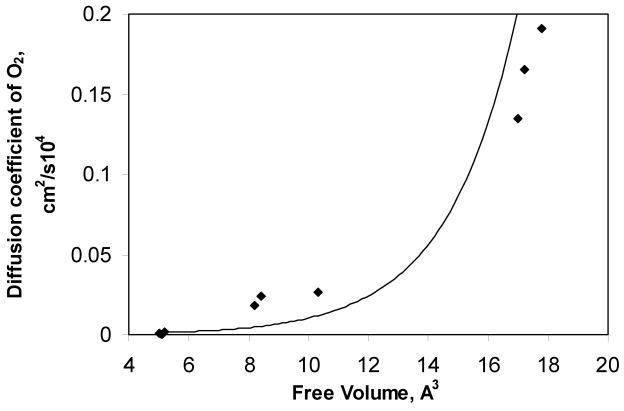


Fig. 9. Diffusion coefficient of O_2 of the studied polyesters vs free volume.

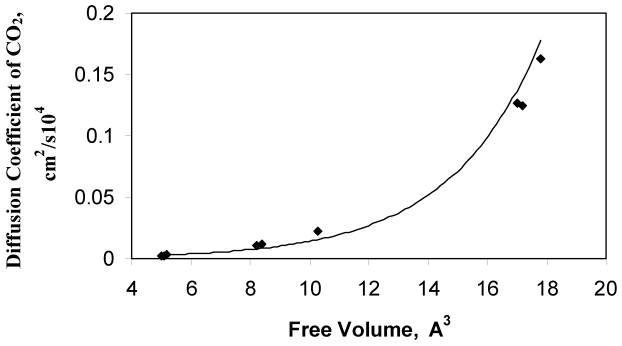


Fig. 10. Diffusion coefficient of CO_2 of the studied polyesters vs free volume.

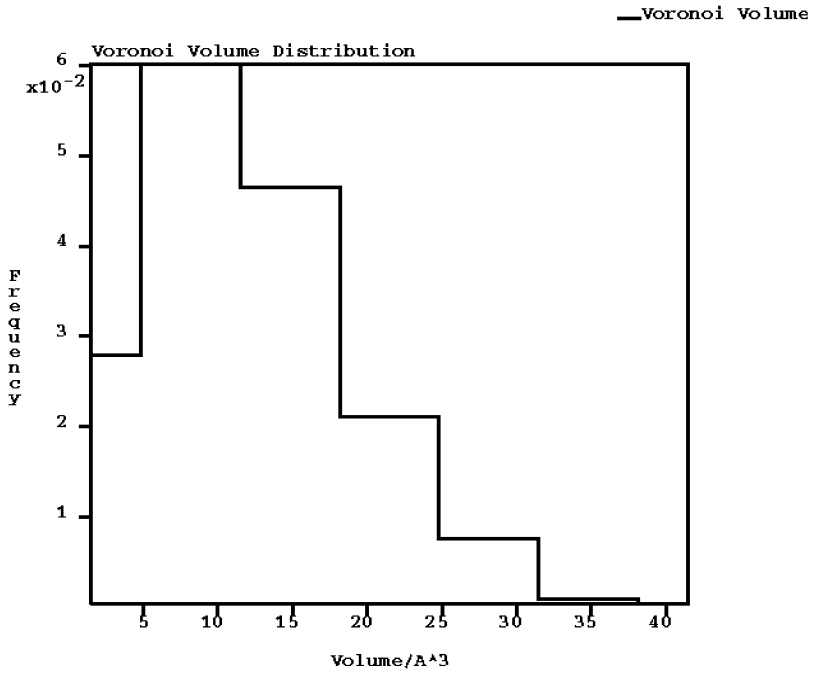


Fig. 11. Distribution of Voronoi free volume in amorphous PEI.

diffusion increase again. This can also be explained by the fact that aromatic rings for *para* isomer can flip freely whereas the aromatic rings for *ortho* and *meta* isomers can hardly flip.

It should also be noted that the diffusion of gases in the studied polyesters increased with the temperature, see Table 1 The O_2 diffuses slightly faster than CO_2 does, which means the diffusion coefficients correlate well with the square of the effective diameter of the diffusing gas, however, the diffusion of O_2 increases linearly with the increase of diffusion of CO_2 for the simulated polyesters (see Table 1). Experimental permeation measurements show CO_2 to be more permeable than O_2 because it has a higher solubility in polyesters.

PEA-2,8 showed the lowest gas barrier properties of the simulated group of polyesters. We can conclude that from the investigated polyesters in this study PEA and PEN polyesters can be considered high barrier polyesters for O_2

Table 2
Reproducability of diffusion, free volume and density for PEA-2,7 simulated samples at 500 K

PEA-2,7 samples	Diffusion of O_2 (cm^2/s) $\times 10^4$	Diffusion of CO_2 (cm^2/s) $\times 10^4$	Free Vol. (A^3)	Density (g/cm^3)
PEA-sample-1	0.00178	0.0031	5.2	1.320
PEA-sample-2	0.00181	0.0030	5.1	1.321
PEA-sample-3	0.00180	0.0031	5.3	1.320
PEA-average	0.0018	0.0031	5.2	1.32

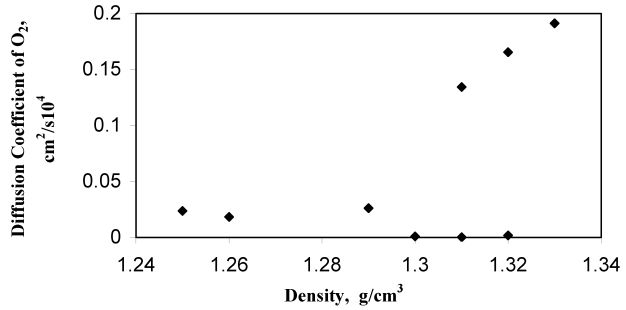


Fig. 12. Diffusion coefficient of O_2 of the studied polyesters vs predicted density.

and CO_2. So, we can say, according to the simulated data, that the PET polyesters are medium barrier polyesters for O_2 and CO_2.

In order to make sure that the simulated data are correct for each of the investigated polyesters, we have run several NPT and NVE MD simulations for each simulated polymeric system and we have calculated the average value of each of the predicted properties presented. The reproducability of diffusion coefficient, free volume and density of PEA-2,7 simulated samples are presented in Table 2.

Work is currently in progress to investigate the diffusion properties of the blends of these polyesters, which will be presented in a forthcoming publication.

5. Conclusions

Atomistic modelling is a useful tool for studying the microscopic structure and understanding the mechanisms of physical processes on atomic and molecular levels. Molecular simulations of polymer structures have reached the level where they are now useful in gaining insights into the molecular origins of behaviour of bulk polymers. In the present work the diffusion of O_2 and CO_2 in models of bulk amorphous aromatic polyesters have been investigated by extensive NPT and NVE MD simulations in order to obtain a better insight into the gas transport mechanism. Extended

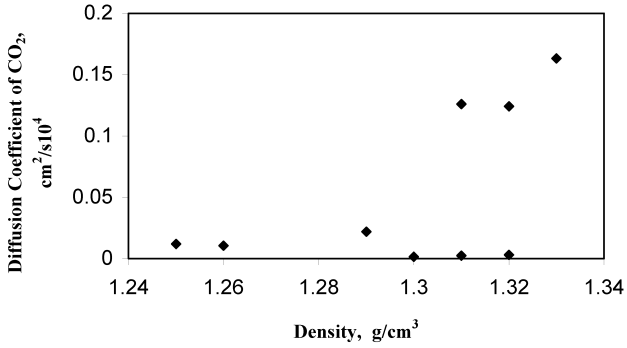


Fig. 13. Diffusion coefficient of CO_2 of the studied polyesters vs predicted density.

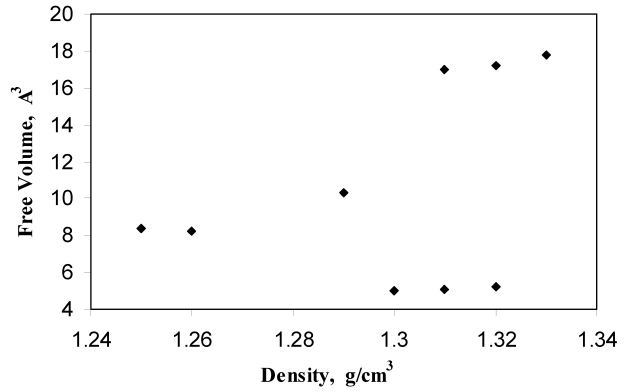


Fig. 14. Predicted densities vs predicted free volume of the simulated polyesters.

equilibration procedures were necessary to obtain reasonable packing models for the simulated aromatic polyesters. A comparison between static structure and the dynamic behaviour of the free volume in the simulated polyesters has revealed qualitative differences, which are decisive for the diffusion of gas molecules in these materials. We have focused on the influence of the polymer structure (geometry, number of aromatic rings of the monomeric units, *ortho*-, *meta*- and *para*-isomers), amorphous phase density, temperature and free volume distribution on the diffusion.

Amorphous unit cell molecular models have been constructed for PET and related aromatic polyesters. MD techniques have been used to obtain the diffusion coefficient for oxygen and carbon dioxide in each of the studied polyesters at different temperatures.

For this group of aromatic polyesters the density does not have a significant influence on the diffusion coefficients. However, there was a tendency of the simulated polyesters for the diffusion coefficients for both O_2 and CO_2 molecules to increase with a decrease in density. It was found that the diffusion coefficients for both O_2 and CO_2 increased exponentially with an increase in free volume. Transport of gas molecules occurs by jumps between individual

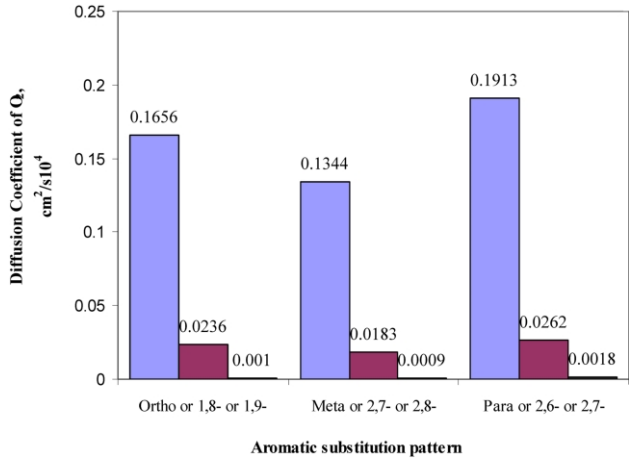


Fig. 15. Diffusion of O_2 vs the numbers of aromatic groups.

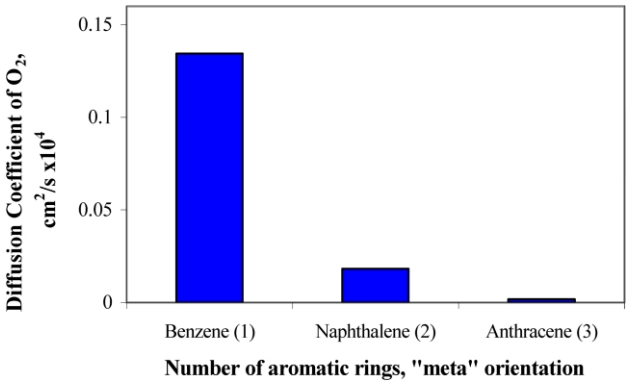


Fig. 16. Diffusion of O_2 vs the numbers of aromatic rings for *meta*-isomers of the simulated polyesters.

sections of the free volume (holes) through temporarily open channels. The diffusion coefficient is completely determined by the jump event. Direct correlations have been observed in simulated polyesters between free volume properties and gas diffusion properties. Such free volume calculation can be helpful in selecting the appropriate polymeric material for technological applications that specify/require high barrier properties. The literature has shown that diffusion coefficients correlate exponentially with accessible free volume fraction.

The number of aromatic rings of the monomeric unit, and the *ortho*-, *meta*- and *para*-isomers of the aromatic moiety have a significant influence on the diffusion coefficients. As a general observation the diffusion coefficients decrease exponentially with an increasing number of aromatic rings. PEAs were found to have the lowest diffusion coefficient of the polyester studied. For all of the simulated polyesters the diffusion coefficients for both O_2 and CO_2 molecules decrease from *para*- to *ortho*- and *meta*- like isomers. A linear molecule is not as efficient as a bend molecule to have low diffusion, but when the molecule is very bend the diffusion increase again. It should also be noted that the diffusion of gases in the aromatic polyesters increased with temperature. The O_2 diffuses somewhat slightly faster than CO_2 does, which means the diffusion coefficients correlate well with the square of the effective diameter of the diffusing gas.

References

[1] Hofmann D, Fritz L, Ulbrich J, Paul D. Molecular simulation of small molecule diffusion and solution in dense amorphous polysiloxanes and polyimides. Comput Theor Polym Sci 2000;10:419–36.
[2] Fried JR, Goyal DK. Molecular simulation of gas transport in poly [1-(trimethylsilyl)-1-propyne. J Polym Sci: Part B: Polym Phys 1998;36:519–36.
[3] Van der Vegt NFA. Temperature dependence of gas transport in polymer melts: molecular dynamics simulations of CO_2 in polyethylene. Macromolecules 2000;33:3153–60.
[4] Ralston ARK, Denton DD. Atomistic modelling of the interaction of CO2 with bisphenol—a polycarbonate. Comput Theor Polym Sci 1996;6:15–27.
[5] Hedengvist MS, Bharadwaj R, Boyd RH. Molecular dynamics simulation of amorphous poly(ethylene terephthalate). Macromolecules 1998;31:1556–64.
[6] Muller-Plathe F. Diffusion of penetrants in amorphous polymers: a molecular dynamics study. J Chem Phys 1991;94(4):3192–9.
[7] Bharadwaj RK, Boyd RH. Small molecule penetrant diffusion in aromatic polyester: a molecular dynamics simulation study. Polymer 1999;40:4229–36.
[8] Takeuchi H. Molecular dynamics simulation of diffusion of simple gas molecules in a short chain polymer. J Chem Phys 1990;92(9):5643–51.
[9] Takeuchi H. A jump motion of small molecules in glassy polymers: a molecular dynamics simulation. J Chem Phys 1990;93(3):2062–7.
[10] Greenfield ML. Molecular modeling of methane diffusion in glassy atactic polypropylene via multidimensional transition state theory. Macromolecules 1998;31:7068–90.
[11] Pant PVK, Boyd RH. Molecular dynamics simulation of diffusion of small penetrants in polymers. Macromolecules 1993;26:679–86.
[12] Takeuchi H, Okazaki K. Dynamics of small molecules in a dense polymer matrix: molecular dynamics studies. Mol Simul 1996;16:59–74.
[13] Pant KPV, Boyd RH. Simulation of diffusion of small-molecule penetrants in polymers. Macromolecules 1992;25:494–5.
[14] Bove L, Aniello CD, Gorrasi G, Guadagno L, Vittoria V. Transport properties of the mesomorphic form of poly(ethylene terephthalate). Polymer 1996;37:5309–11.
[15] Kim Won-Kook, Mattice WL. Molecular modeling of polybenzoxazine: thin film and the diffusion of small penetrant molecules in the bulk. Polym Mater Sci Engng 1977;77:608–9.
[16] Deppes DD, Torkelsons JM. Small molecule probe diffusion in thin polymer films near the glass transition: a novel approach using fluorescence non-radiative energy transfer. Polym Mater Sci Engng 1995;73:388–9.
[17] Craig SH. Recent advances in polymers for barrier applications. TRIP 1997;5:75–9.
[18] Gee RH, Boyd RH. Small penetrant diffusion in polybutadiene: a molecular dynamics simulation study. Polymer 1995;36:1435–40.
[19] Han J, Boyd RH. Molecular packing and small-penetrant diffusion in polystyrene: a molecular dynamics simulation study. Polymer 1996;37:1797–804.
[20] Bicerano J, Ralston ARK, Moll DJ. Modelling of the transport of carbon dioxide through polymers. ANTEC 1994;2105–9.
[21] Eichinger BE, Rigby DR, Muir MH. Computational chemistry applied to materials design-contact lenses. Comput Polym Sci 1995;5:147–63.
[22] Shanks R, Pavel D. Diffusion of O_2 and CO_2 in amorphous poly (ethylene terephthalate) and alkylene isomeric polyesters. Mol Simul 2002;29:939–69.
[23] Fritz L, Hofmann D. Molecular dynamics simulation of the transport of water-ethanol mixtures through polydimethylsiloxane membranes. Polymer 1997;38:1035–45.
[24] McGonigle EA, Liggat JJ, Pethrick RA, Jenkins SD, Daly JH, Hayward D. Permeability of N_2, Ar, He, O_2 and CO_2 through biaxially oriented polyester films—dependence on free volume. Polymer 2001;42:2413–26.
[25] Lee JH, Kim JK, Ha YS. History of permeation studies and permeation theory, 2000, http://www.foodcy2001.or.kr/html/session4/s4_top4_02.htm.
[26] Takeuchi H, Roe R-J, Mark JM. Molecular dynamics simulation of diffusion of small molecules in polymers. II. Effect of free volume distribution. J Chem Phys 1990;93:9042–8.
[27] Pavel D, Shanks R, Hurduc N. Macromol Theory Simul 2003;12:127–41.
[28] Wilfried BW, Model calculation of the temperature dependence of small molecule diffusion in high polymers, 63. Brooklyn, NY: Polytechnic Institute of Brooklyn; 1958. pp. 1080–1084.
[29] Gray-Weale AA, Henchman RH, Gilbert RG, Greenfield ML,

Theodorou DN. Transition-state theory model for the diffusion coefficients of small penetrants in glassy polymers. Macromolecules 1997;30:7296–306.
[30] Lyons EP, Ludovice PJ. Computer simulation of poly(ethylene terephthalate) structure and its ramifications for gas transport, http://www.prism.gatech.edu/-gt6887c/research.html.
[31] Limm W, Begley TH, Hollifield HC. Modeling of additive diffusion in poly(ethylene terephthalate). Polym Preprints 1995;36(1):689–90.
[32] Higuchi H, Yu Z, Rogers CE, Simha R, Mcgervey JD. Gas diffusion properties and free volume. Polym Preprints 1995;36(2):57–8.
[33] Hsinjin EY, Jean YC. Correlation between gas permeation and free-volume hole properties of medical-grade polyesters, http://www.devicelink.com/mpb/archive/98/01/004.html.
[34] Hurduc N, Yarovsky I, Shanks R, Pavel D. Comput Mater Sci 2003; 27:393–402.
[35] Cerius^2 simulation tool user's reference manuals, Molecular simulation software for material science, Accelrys Inc., San Diego, USA, 2002.
[36] Mayo SL, Olafson BD, Goddard III WA. J Phys Chem 1990;94:8897.
[37] Pavel D, Ball J, Bhattacharya SN, Shanks R, Hurduc N. Comput Theor Polym Sci 2001;11:303–18.
[38] Pavel D, Ball J, Bhattacharya SN, Shanks R, Toader V, Bulacovschi V, Hurduc N. Comput Theor Polym Sci 1999;9:1–9.
[39] Pavel D, Ball J, Bhattacharya SN, Shanks R, Hurduc N. Comput Theor Polym Sci 1997;7:7–12.
[40] Pavel D, Ball J, Shanks R, Hurduc N. Patent Application. Melbourne, Australia: RMIT University, submitted for publication.
[41] Pavel D, Shanks R, Hurduc N, Bhattacharya SN. Practical Applications of Molecular Modelling and Simulation of Polymers Junimea, Jassy, 2000.
[42] Pavel D, Ball J, Bhattacharya SN, Shanks R, Hurduc N. J Polym Sci: Part B: Polym Phys 1999;37:2334.
[43] Brostow W. Science of materials. New York: Wiley; 1979. p. 65.
[44] Rappe AK, Goddard III WA. J Phys Chem 1991;95:3358.
[45] Fletcher R, Reeves CM. Comput J 1964;7:149.
[46] Berendsen HJ, Postma JPO, van Gunsteren WI, Di Niola A, Haak JR. J Chem Phys 1984;81:3684.