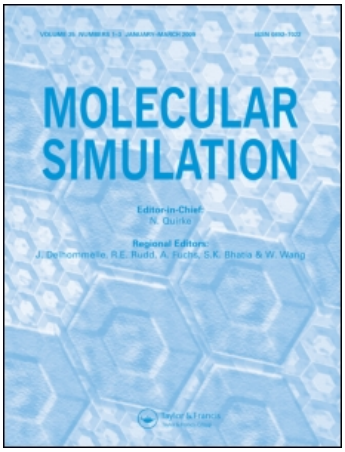

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Simulation of diffusion of O 2 and CO 2 in amorphous poly(ethylene terephthalate) and related alkylene and isomeric polyesters

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SIMULATION OF DIFFUSION OF O_2 AND CO_2 IN AMORPHOUS POLY(ETHYLENE TEREPHTHALATE) AND RELATED ALKYLENE AND ISOMERIC POLYESTERS

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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 carbon dioxide as small molecule penetrants in models of bulk amorphous poly(ethylene terephthalate) (PET) and related alkylene and isomeric polyesters. A bulk amorphous configuration with periodic boundary conditions made into a unit cell whose dimensions were determined for each of the simulated polyesters in the cell having the experimental density. 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 3 ns simulation time. We have focussed on the influence of the temperature, polymer dynamics, number of CH_2 groups, density and free volume distribution on the diffusion properties. Correlation of diffusion coefficients with free volume and number of CH_2 groups was found.

Keywords: Molecular dynamics simulation; Diffusion; Free volume; Polyesters

INTRODUCTION

The aim for this research is to explore and investigate the diffusion of gases through bulk amorphous poly(ethylene terephthalate) (PET) and related alkylene and isomeric polyesters. PET is the most commercially important polyester and a

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widely used barrier packaging material, and therefore many authors have investigated the correlations between the structural organisation and the properties of this polymer. Polyesters and copolyesters are known to exhibit very low gas diffusion compared with most other polymers such as polyolefin, polycarbonate, polystyrene, etc. 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 for 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 [19–21], membrane separation processes [16,22,29], food packaging [1,4,6,8,11,22,25,28,30,31], and biomedical devices [15,30–32]. The technological relevance of such behaviour 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 [11,22,25,31]. 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 theoretical understanding of diffusion of gases in polymers is still very limited.

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

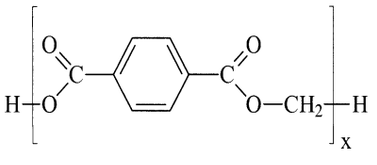
The existing methods have only recently been powerful enough to predict diffusion coefficients, permeability, and selectivity for specific polymer-penetrant systems given only their chemical structure [7–12]. There is a growing demand for better theoretical understanding of the diffusion of gaseous penetrants in polymers to achieve improvements in designing new, better polymeric membranes 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 Monte Carlo (MC) and molecular dynamics (MD) simulation methods to understand and to predict the transport properties of gases in polymers. Because diffusion is a dynamic problem, the obvious approach to the calculation of the diffusion coefficients is through MD simulation.

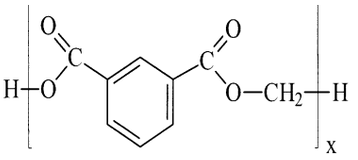
In recent years, a number of such polymers with various structural compositions have been investigated [25–32]. In particular, we are concerned with diffusion of O_2 and CO_2 through bulk amorphous aromatic polyesters, such as PET, (which is one of the most widely used food packaging materials) [12,13,22,31] 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. For most of the polymers under consideration such a study has not been previously conducted. In this study MD simulations of polymers were performed and aimed to elucidate whether a correlation exists between polymer conformation (structure), polymer dynamics, number of CH_2 groups, 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 techniques are a novel probe to determine free volume properties.

Molecular simulation of these aromatic polyesters is unquestionably very challenging because of the complexity of their monomeric units, which emphasises uncertainties in the description of intra- and intermolecular interactions, induces the possibility of complex morphologies with large characteristic length scales. Therefore, MD simulation required limiting the polyester chains to 20 repeat units so that three molecules could be included in an amorphous cell, due to the long computational times required for MD. However, MD simulation is likely to offer explanations that are considerably far more reaching than current experimental techniques.

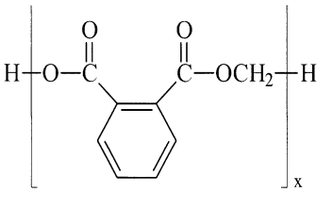
POLYMERS STUDIED



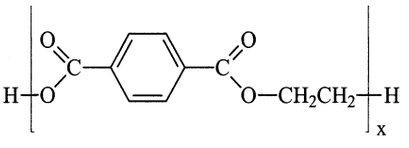
PMT Poly(methylene terephthalate)



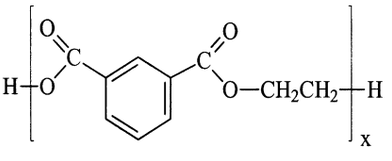
PMI Poly(methylene isophthalate)



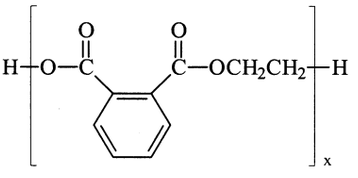
PMP Poly(methylene phthalate)



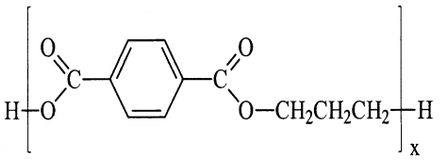
PET Poly(ethylene terephthalate)



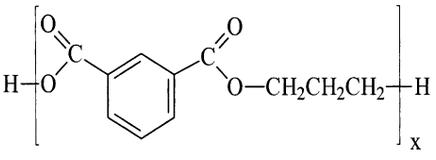
PEI Poly(ethylene isophthalate)



PEP Poly(ethylene phthalate)



PPT Poly(1,3-propylene terephthalate)



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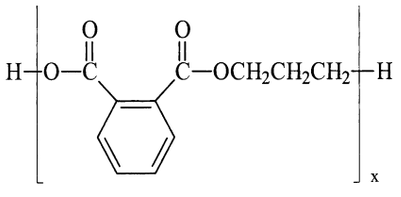
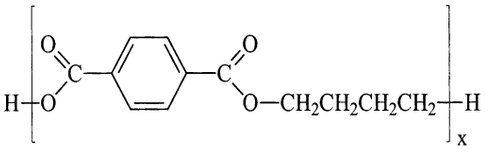
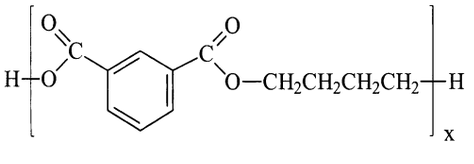


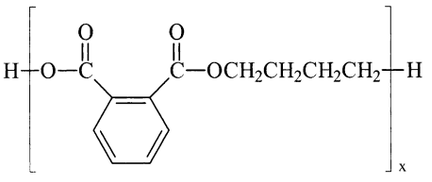
PPP Poly(1,3-propylene phthalate)



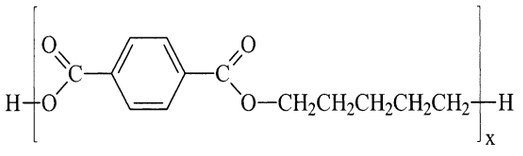
PBT Poly(1,4-butylene terephthalate)



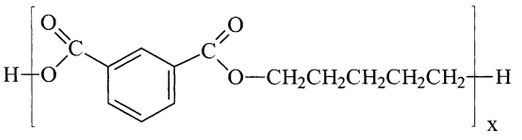
PBI Poly(1,4-butylene isophthalate)



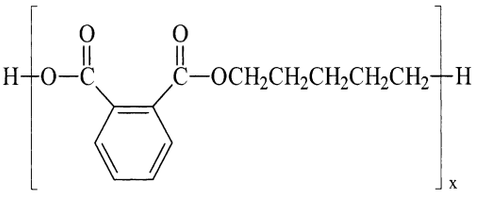
PBP Poly(1,4-butylene phthalate)



PPeT Poly(1,5-pentylene terephthalate)



PPeI Poly(1, 5-pentylene isophthalate)



PPeP Poly(1, 5-pentylene phthalate)

COMPUTATIONAL METHODOLOGY

The simulations were performed for amorphous unit cells of each investigated polyester with three polymer chains wit degree of polymerization 20. Computer modelling of chemical structures of the monomers and polymers, molecular dynamics simulations, and conformational and molecular dynamics analyses were carried out using molecular simulation software for material science [33],

Cerius^2 version 4.0, designed by Molecular Simulations, Inc., San Diego, CA, USA. The Cerius^2 molecular simulation software was run on a Silicon Graphics INDY MIPS R4600PC workstation. The three-dimensional-Sketcher, Open Force-Field (OFF), charge equilibration, monomer editor, polymer, and amorphous polymer builder, energy minimiser, NVE and NPT molecular dynamics, polymer properties, and dynamic analysis modules of Cerius^2 software [33] 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 was defined using the Builder (for the monomer) and the Polymerizer 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.* [34] 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 to previous studies [35–40]. This force field is parametized for a large class of organic molecules involving H, C, O, S, P, F, Cl and Br, allowing it to be applied to bio- and synthetic polymers [33–40]. It was found that the Dreiding 2.21 force field leads to accurate geometries for various polymeric systems and can be used to calculate and minimise the energy of a simulated polymeric system. It is then possible to calculate the forces acting on each atom of a model polymer, which can further be utilised to solve Newton's equations of motion ($F = ma$) for MD simulations.

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 versus time-step of the single chain of the PET is shown 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: $E_{\text{total}} = E_{\text{b}} + E_{\text{nb}}$. The bonded terms typically include harmonic bond stretching (E_{s}), harmonic angle bending (E_{a}), torsional (E_{t}), and inversion (E_{i}) energies: $E_{\text{b}} = E_{\text{s}} + E_{\text{a}} + E_{\text{t}} + E_{\text{i}}$. Non-bonded terms typically contain van der Waals (E_{vdW}), electrostatic (Coulombic) (E_{q}) and hydrogen bond (10–12 potential) (E_{hb}) interactions: $E_{\text{nb}} = E_{\text{vdW}} + E_{\text{q}} + E_{\text{hb}}$.

In practice, it is common to use a suitably large cut-off distance, and so for this study a cut-off distance of 150 Å was used for non-bonded interactions, so for this

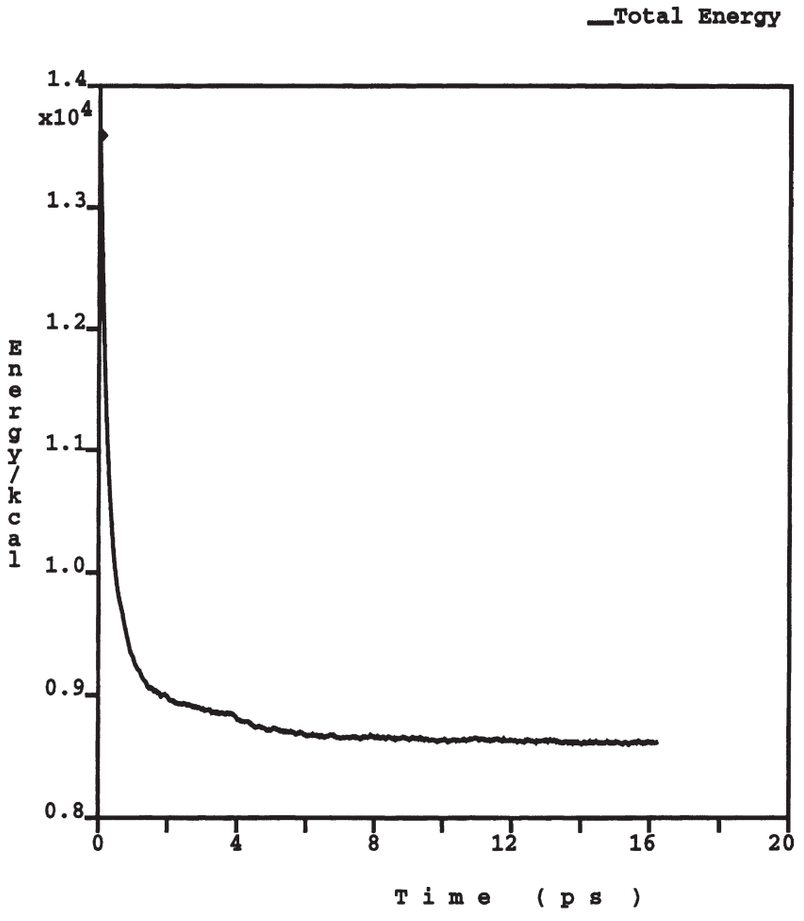


FIGURE 1 Total potential energy versus time-step of the single chain of the PET.

cut-off distance all the non-bonded interactions of the simulated copolymers are calculated. The Mie 6–12 potential [39–41], 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 [42] 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 and scientific understanding.

After the force field is constructed, the total potential energy is likely to be high and not representative of the actual structure. The next logical application of the total potential energy expression is to find an "ideal" structure for the polymer molecule through energy minimisation, where the term "ideal structure" usually is taken to mean the lowest-energy conformation. This involves mathematical methods for shifting the atoms in space to lower the energy and eventually bring the structure to an equilibrium state by adjusting the atomic coordinates and recalculating the energy repeatedly.

The NPT and NVE molecular dynamics simulations were performed at 300, 500 and 600 K for each constructed and energy 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 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 3,000,000 (3 ns), and the output frequency was every 1000 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.* [43] was used for isothermal–isobaric NPT MD simulations. Molecular dynamics studies [25–32,35–40] have proven to provide a better insight into the physical phenomena exhibited by polymers than experiment. 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 three polyester chains for each investigated polyester. The energy of the polymer was minimized using molecular dynamics and a random conformation was 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 or CO_2) were added to the amorphous cell which move in the cell during molecular dynamics. 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. Five O_2 or five CO_2 molecules were introduced in the polyester unit cells described above.

The predictive capability of NPT and NVE MD and polymer properties modules [33] of Cerius^2 has been applied in order to calculate glass transition temperatures of the amorphous structures of the simulated polymers. The glass transition temperature was determined from specific volume versus temperature diagrams by analysing the trajectory file data generated by NPT MD simulation. Trajectory file data generated from MD simulation has been used in the entire polymer property calculations and analyses presented in this research. The trajectory files were analysed by polymer properties and dynamics analysis modules.

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:

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

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.

SYSTEMATIC AND STATISTICAL ERRORS

As with laboratory experiments, computer simulation experiments can have both systematic and statistical errors, which however can be controlled and minimised.

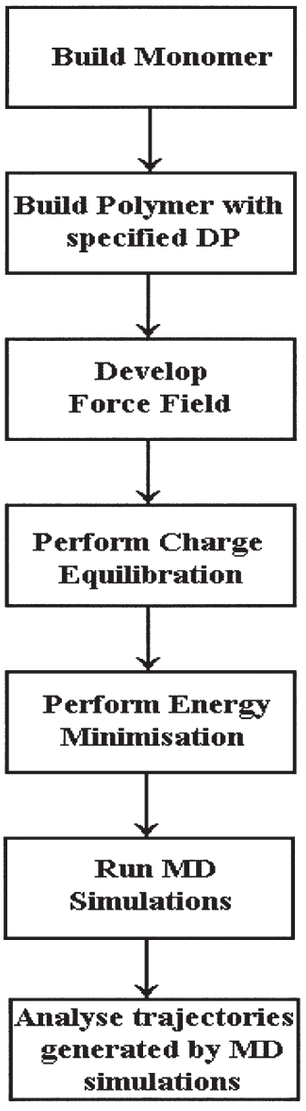


FIGURE 2 Steps in the computational procedure used in this research.

Applying molecular dynamics simulation, the thermophysical, structural and dynamic properties of polymeric materials can be calculated with an accuracy that strongly depends on the reliability of the potential function, in other words, on the errors arising from truncation of the intermolecular forces, and statistical errors, arising from insufficient sampling. In practice, MD simulation studies are presently limited by the speed and storage capabilities of current computers to limited polymer size and computing time scales.

For this study the reliability of the DREIDING 2.1 potential function has been proven and tested by previous molecular simulation studies of polymers [35–40]. It was found that very accurate geometries and potential barriers for various organic polymers have been obtained employing the DREIDING 2.1 force field. Similarly, to the initial samples of laboratory experiments, the results of the molecular simulations will vary strongly depending on the way the system was originally prepared. One of the solutions to address this problem was to start from many, widely different conformations, and to make sure that the results obtained from them did not differ widely. For each simulated aromatic polymer, single chain and periodic unit cell, several cycles of potential-energy minimisations and MD simulations were performed to create very well equilibrated polymer conformations.

The low molecular weights and high degree of rigidity of the backbone of the simulated polymers are highly correlated with the length of time of the simulation used in this study. In contrast to flexible polymer chains, a high degree of rigidity of the polymer chains will determine a shorter time for MD simulation to create equilibrated conformations, and to obtain simulated results of the calculated properties with very low estimated error. However, it is well known that all thermophysical properties of polymers are characterised by a very short relaxation time, measured in picoseconds. It is worth mentioning that there was not any anomalous increase of the temperature during the total run time of all the simulations performed in this research.

In comparison, there are often molecular simulations performed in order to extract a dynamic property, such as diffusivity or viscosity, which depends on the integral of a time correlation function. Since such correlation functions do not have the chance to decay sufficiently in a few nanoseconds, the estimation of such properties requires either bold extrapolations to long times or specially designed coarse-graining techniques.

RESULTS AND DISCUSSION

This research was performed for single chains and amorphous unit cells for each of the simulated polyesters. Initially, for each of the investigated polyester, a

single chain was modelled and energy minimized in order to investigate the polymer conformation and the total potential energy of the polymer chain was predicted. The energy minimised conformation of the PEI polyester chain is shown in Fig. 3. An example of the total potential energy calculated for PET, PEI, PBT and PBI is shown in Fig. 4.

Then, an amorphous unit cell with three 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 five molecules of O_2 or 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 for PET with five molecules of carbon dioxide inserted is shown in Fig. 5.

An example of the NPT MD calculated density for PET over a wide simulation time range is shown in Fig. 6. As can be observed in Fig. 6 from the equilibration times in MD simulation (after 10–11 ps) the average simulated density of PET is 1.33 g/cm^3 which is consistent with experimental data reported for amorphous PET. The experimental data for PET depends on the thermal processing parameters, whereas in this study all of the simulated structures were totally amorphous. Figure 6 shows typical density versus time behaviour during this part of the NPT-MD simulation for PET. The density fluctuations in the simulations for the investigated polymers are less than 0.009 g/cm^3 (see also Fig. 6). The simulated density of PET is higher than that of PBT, which is consistent with experimental results. The dynamics were continued until the density of the polymer in the amorphous cell reached a plateau.

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 a satisfactory structure was accomplished. In order to confirm the validation of the simulated model of the studied polyesters for PET further MD simulations were performed to calculate the structural parameters, such as end-to-end distance and characteristic ratio which are shown in Figs. 7 and 8, respectively.

The predicted characteristic ratio is about 3.8 and the reported experimental values are between 3.7 and 4.1 [12–15]. The experimental values are

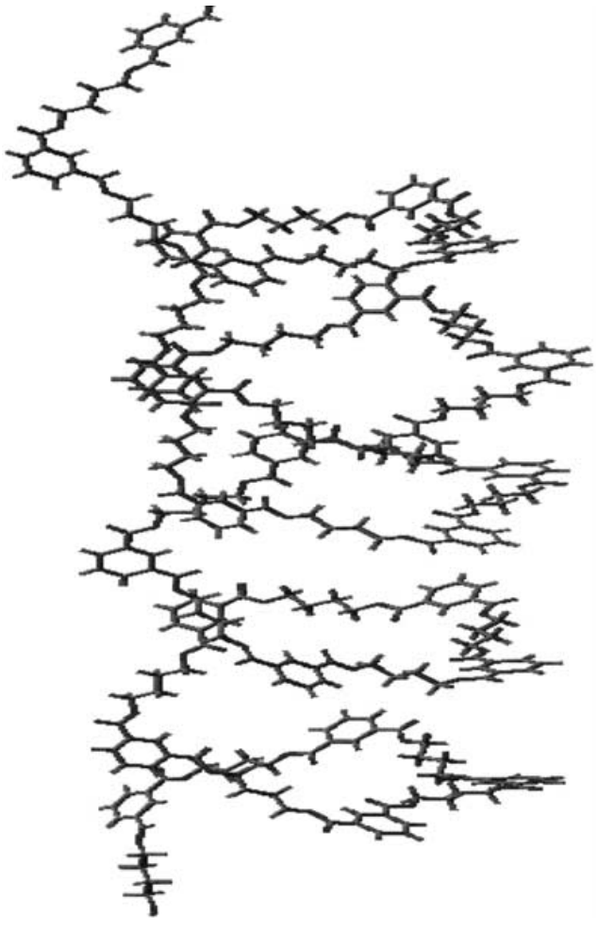


FIGURE 3 Minimised structure of the polyester chain for PBI.

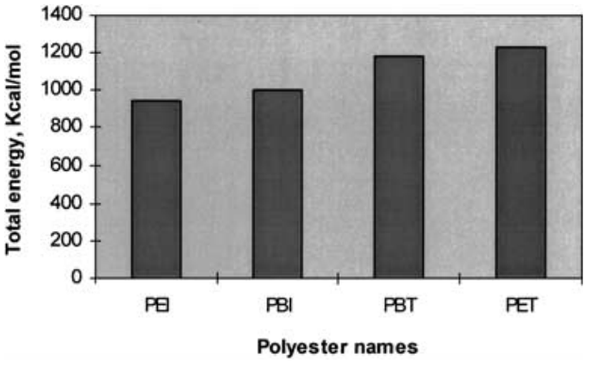


FIGURE 4 Total potential energy of minimized structures of PET, PEI, PBT and PBI polyester chains.

unfortunately somewhat uncertain as they are based on the viscosity measurements in good solvents and corrections must be made to arrive at unperturbed dimensions.

Diffusion coefficients were obtained for each of the polymers from the mean square displacement versus 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 Fickian 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 PET is shown in Fig. 9.

Table I presents the results for all the simulated polyesters. Diffusion coefficients at 300, 500 and 600 K are listed for each of the polyesters. In addition, the free volume calculated at 500 K and the amorphous cell density calculated at 300 K are shown.

The coefficients of diffusion for both O_2 and CO_2 for the studied polyesters increase exponentially with increasing free volume. This is clearly shown in Fig. 10 for diffusion of O_2 and in Fig. 11 for diffusion of CO_2. 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. 5), MD simulations performed during this study have revealed these mechanisms and dynamics, and it 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

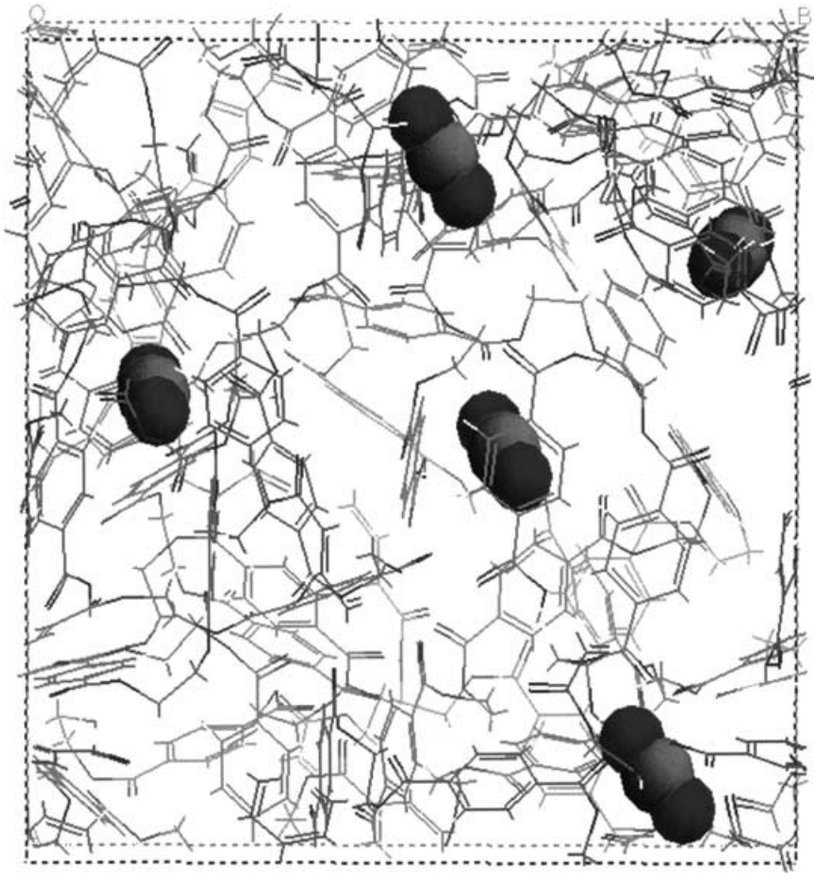


FIGURE 5 Amorphous cell structure of PET with five molecules of carbon dioxide inserted.

channels of free volume between neighbouring holes/cavities. When the gas molecule is at the right position at the right time having a suitable velocity, it can slip through such a channel into a neighbouring hole. The size and shape of the holes available in a polymer control its rate of gas diffusion, which along with solubility determine 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 free volume plays an important part in the process of diffusion, comparing with other factors, such as

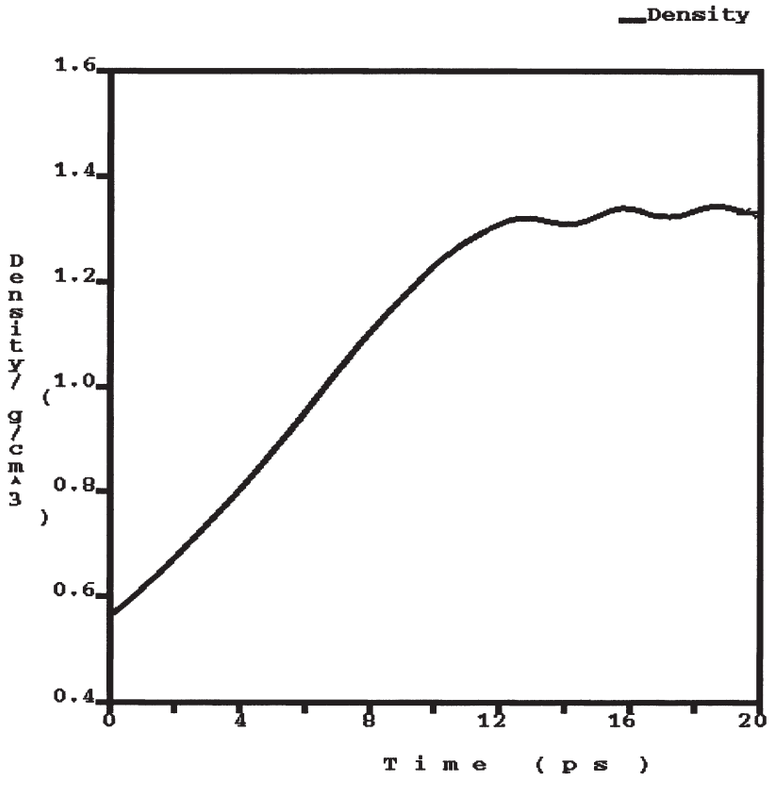


FIGURE 6 Predicted NPT-MD density versus molecular dynamics time for PET.

density. As it is seen in Figs. 10 and 11, the larger the free volume in a polyester, the greater the gas diffusion. As shown in Table I, PMT has the lowest free volume compared with any of the simulated polyesters, therefore, PMT has lowest gas diffusion and offers very high barrier properties. Figure 12 shows the distribution of free volume in a PET amorphous sample.

Contrary to our expectation, as it is shown in Figs. 13 and 14, 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 structural 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. 15). In Fig. 15, it can be observed that for polymers with the same values, or almost the same values, of density we have obtained different values for free volume. However,

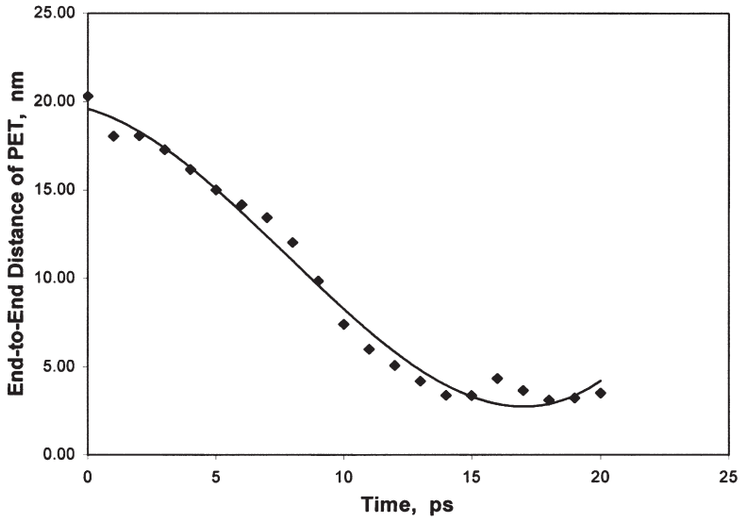


FIGURE 7 End-to-end distance of PET obtained by MD simulation.

there is a preponderant tendency of free volume to decrease with the increase of density.

During this research, an interesting observation has been noticed, the diffusion coefficient strongly depends on the number of CH_2 groups, and an odd–even effect for the number of CH_2 is displayed. The diffusion also depends on shape so that *ortho*-, *meta*-, and *para*-isomers have different values. The amorphous

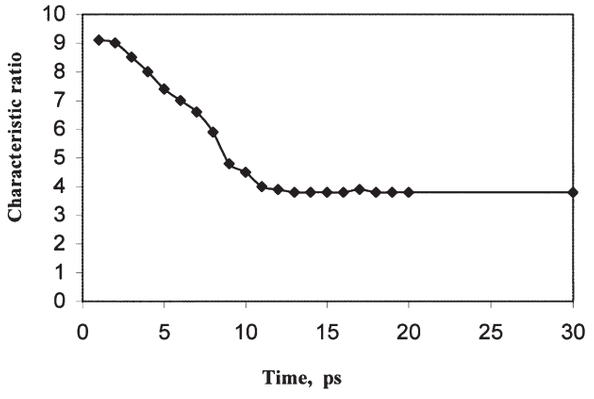


FIGURE 8 Characteristic ratio of PET obtained by MD simulation.

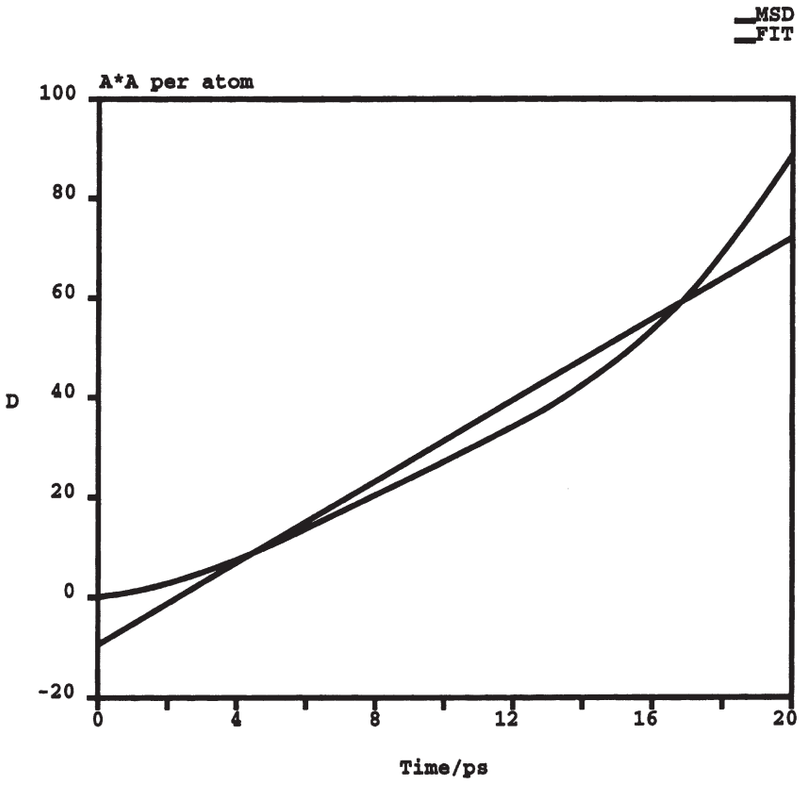


FIGURE 9 Plot of mean square displacement and fit line vs simulation time for CO_2 in amorphous PET.

structures of this series of polyesters were modelled and simulated in order to study the influence of polyester structures on barrier properties. The odd–even effect of the number of CH_2 groups on the coefficient of diffusion is shown in Figs. 16 and 17. The density of the simulated polyesters does not depend on the odd–even number, it decreases smoothly with an increasing number of CH_2 groups in the alkylene part of the monomeric unit. It should also be noted that the diffusion of gases in the studied polyesters increased with the temperature, see Fig. 18 for diffusion of O_2 vs. temperature and Fig. 19 for diffusion of CO_2 vs. temperature, and also see Table I. The O_2 diffuses somewhat 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 coefficient of O_2 increases linearly with the increase of the diffusion coefficient of CO_2 for the simulated polyesters, see Fig. 20.

TABLE I Predicted diffusion coefficients, free volume and density of the simulated polyesters

Polymer code	Diffusion of O_2, $cm^2/s10^4$			Diffusion of CO_2, $cm^2/s10^4$			Free vol., A^3	Density g/cm^3
	300 K	500 K	600 K	300 K	500 K	600 K	500 K	300 K
PMT-*p*		0.0079			0.0058		6.3	1.39
PMP-*m*		0.0031			0.0047		5.9	1.41
PMP-*o*		0.0091			0.0074		6.7	1.39
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
PPT-*p*	0.0381	0.0403	0.0491	0.0314	0.0311	0.0563	12.3	1.28
PPI-*m*	0.0871	0.1002	0.1023	0.0683	0.0900	0.0971	14.8	1.27
PPP-*o*	0.0923	0.0981	0.1302	0.0732	0.0901	0.0991	15.1	1.27
PBT-*p*	0.1831	0.1987	0.2400	0.1657	0.1702	0.2031	18.9	1.241
PBI-*m*	0.2007	0.2256	0.2487	0.1739	0.1835	0.2004	19.6	1.235
PBP-*o*	0.1901	0.2134	0.2471	0.1691	0.1758	0.1943	19.4	1.242
PPeT-*p*		0.1603			0.1503		18.3	1.21
PPeI-*m*		0.1853			0.1631		18.5	1.20
PpeP-*o*		0.1573			0.1450		17.1	1.22

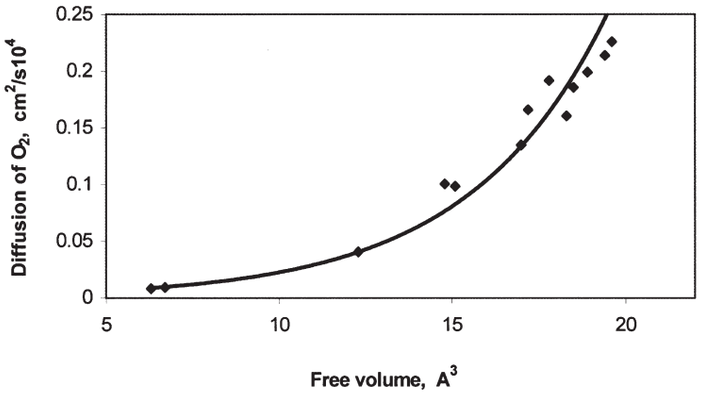


FIGURE 10 Diffusion coefficient of O_2 of the studied polyesters vs free volume.

PMT showed the lowest gas barrier properties of the simulated group of polyesters. We can conclude that from the investigated polyesters in this study only PMT, PMP, PPT and PMI can be considered high barrier polyesters for O_2 and CO_2. So, we can say, according to the simulated data, that the rest of the simulated polyesters are medium barrier polyesters for O_2 and CO_2. Three-dimensional representation of diffusion coefficients of O_2 and CO_2 through the simulated aromatic polyesters versus dicarboxylic acids and glycols are shown in Figs. 21 and 22.

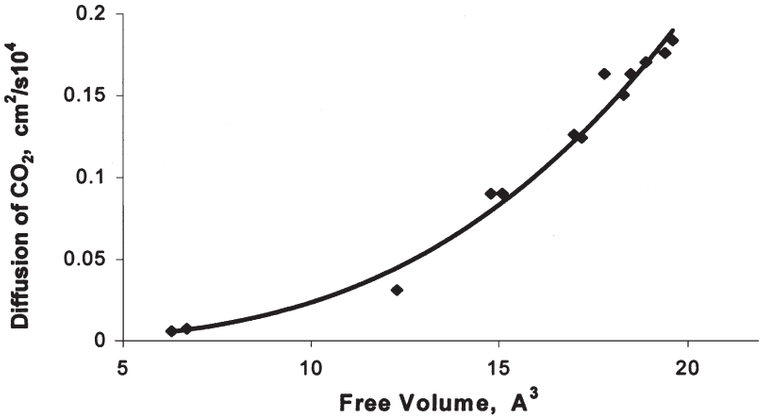


FIGURE 11 Diffusion coefficient of CO_2 of the studied polyesters vs free volume.

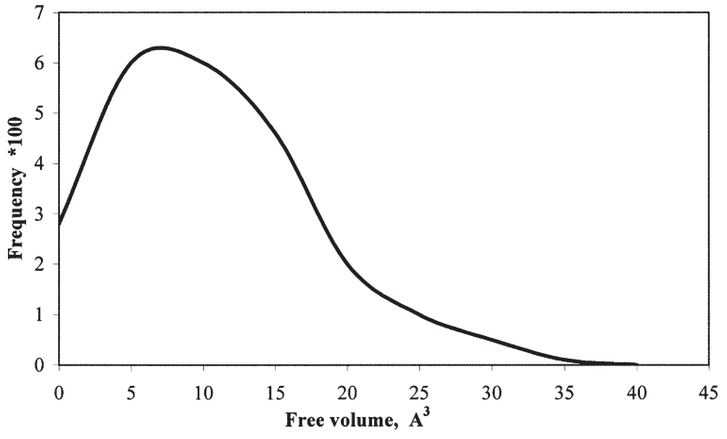


FIGURE 12 Distribution of free volume in PET.

In order to make sure that the simulated data are correct for each of the investigated polyesters we ran several MD simulations and have calculated the average value of each of the predicted properties presented in this research. Table II provides an analysis of the reproducibility of the simulated results for PET. Each of the PET simulations shown are the result of a completely independent amorphous cell computation. The results show that the diffusion coefficient, free volume and density were reproduced accurately by the simulation procedure.

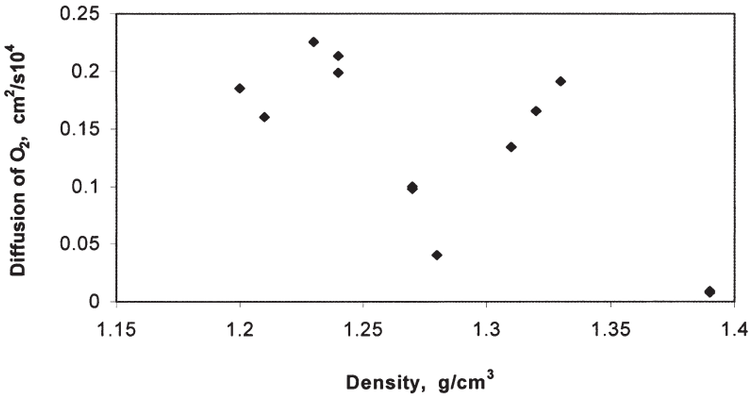


FIGURE 13 Diffusion coefficient of O_2 of the studied polyesters vs predicted density.

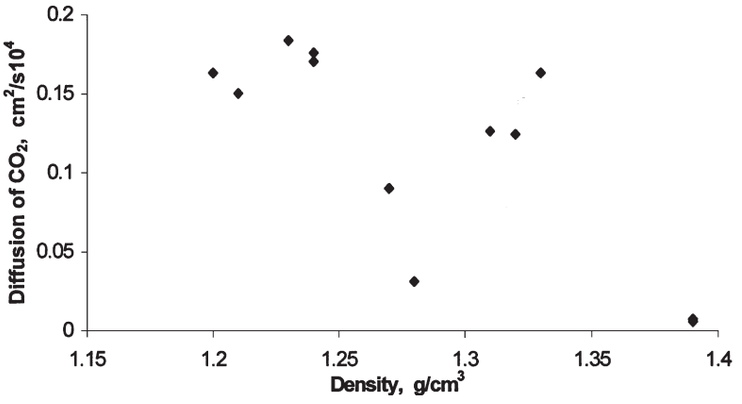


FIGURE 14 Diffusion coefficient of CO_2 of the studied polyesters vs predicted density.

TABLE II Reproducability of diffusion, free volume and density for PET simulated samples

PET samples	Diffusion of O_2 $cm^2/s10^4$	Free vol. A^3	Density g/cm^3
PET-sample-1	0.1913	17.9	1.33
PET-sample-2	0.2001	17.8	1.33
PET-sample-3	0.1971	17.7	1.33
PET-average	0.1961	17.8	1.33

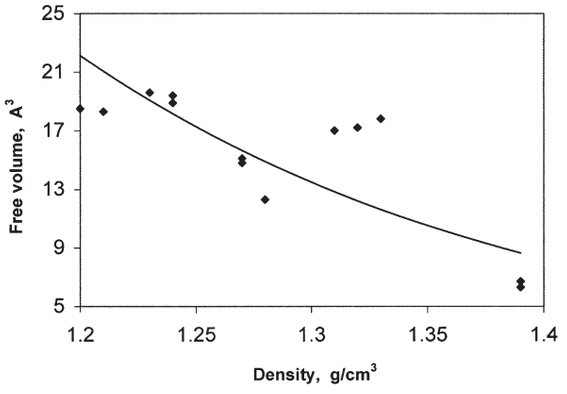


FIGURE 15 Predicted densities vs predicted free volume of the simulated polyesters.

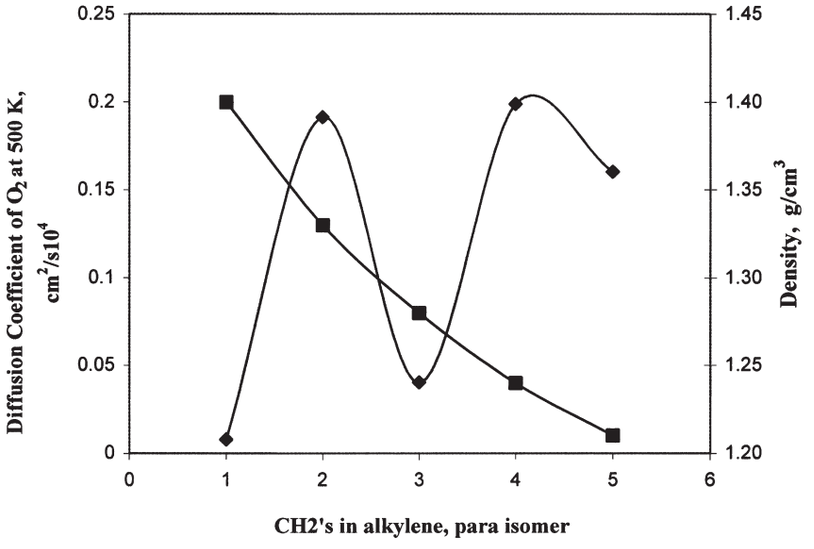


FIGURE 16 Diffusion of O_2 vs density (■) and the numbers of CH_2 groups (◆) for *para*-isomers of the simulated polyesters.

Work is currently in progress to investigate the diffusion properties as a function of the number of aromatic rings within the monomeric unit and other related polyesters, which is going to be presented in a forthcoming publication.

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 structure have reached the level where they are now useful in gaining insights into the molecular origins of the behaviour of bulk polymers. In the present work, the diffusion of O_2 and CO_2 in models of bulk amorphous polyesters have been investigated by extensive NVE MD simulation investigations in order to obtain a better insight about the gas transport mechanism. Extended equilibration procedures were necessary to obtain reasonable packing models for the simulated polyesters. A comparison between static structure and the dynamic behaviour of the free volume in the simulated polyesters have 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, methylene sequence length, odd–even number

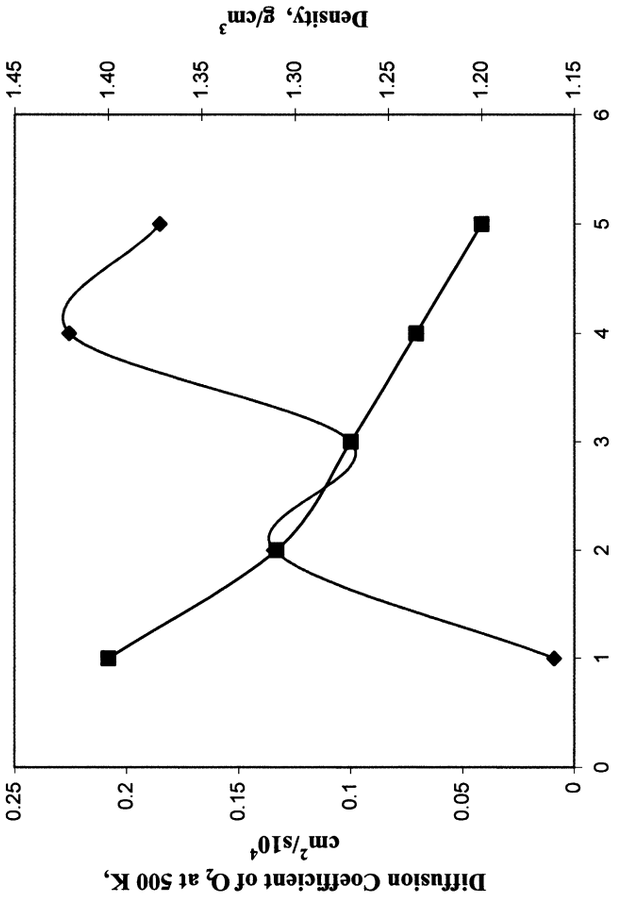


FIGURE 17 Diffusion of O_2 vs. density (■) and the numbers of CH_2 groups (◆) for *meta*-isomers of the simulated polyesters.

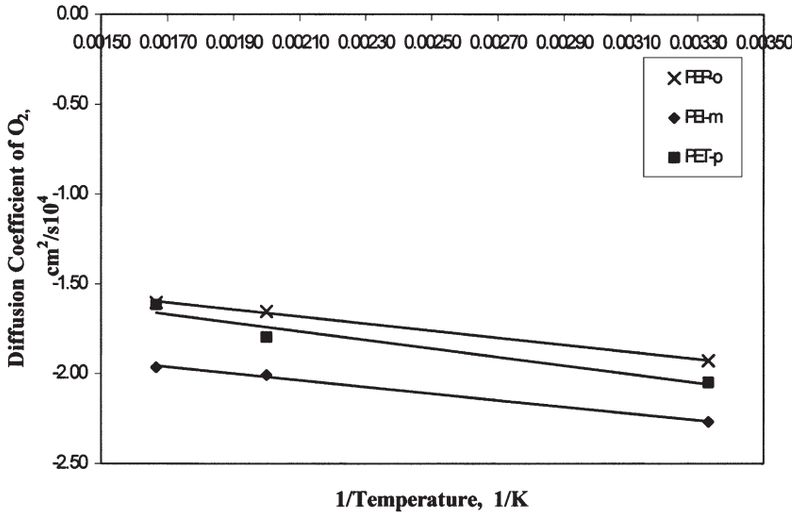


FIGURE 18 Diffusion coefficient of O_2 of PET (*para*), PEI (*meta*) and PEP (*ortho*) vs temperature.

of the CH_2 groups, *ortho*-, *meta*- and *para*-isomers), density, temperature and free volume distribution on the diffusion.

Amorphous unit cell molecular models have been constructed for PET and related polyesters. Molecular dynamics 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 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 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 number of CH_2 groups in the alkylene part of the monomeric unit, the odd–even number of CH_2 groups, and the *ortho*-, *meta*- and *para*-isomers of the aromatic moiety have a significant influence on the diffusion coefficients. As a

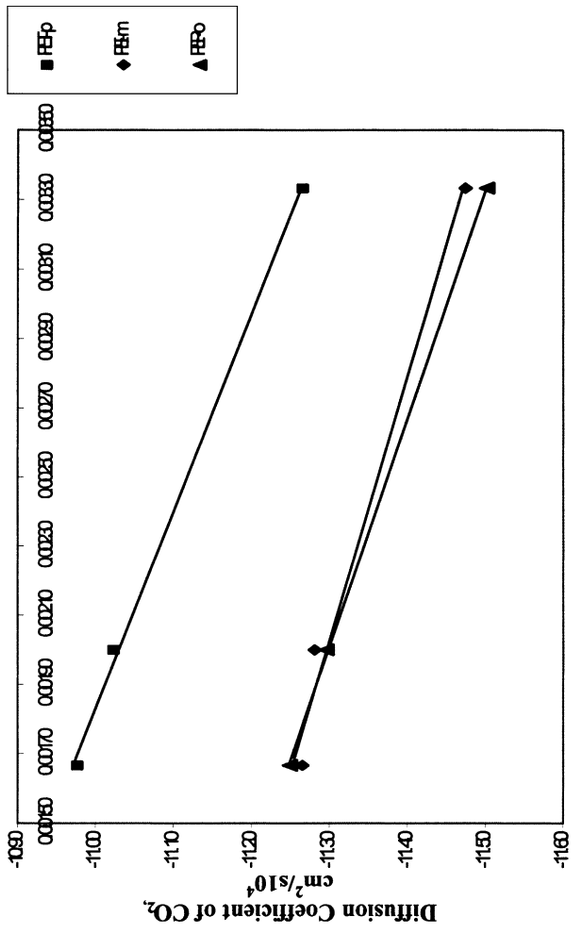


FIGURE 19 Diffusion coefficient of CO_2 of PET (*para*), PEI (*meta*) and PEP (*ortho*) vs temperature.

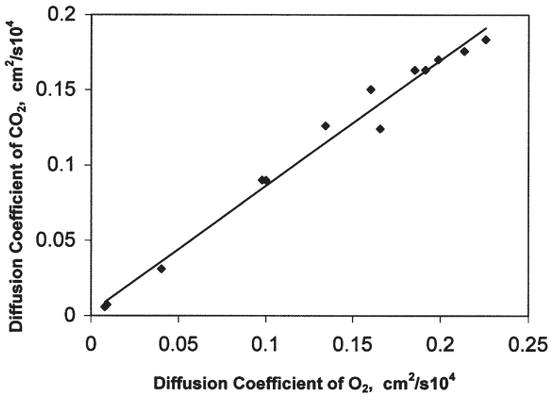


FIGURE 20 Diffusion of O_2 vs. diffusion of CO_2 of the simulated polyesters.

general observation the diffusion coefficients increase with an increasing number of CH_2 groups. For polyesters with an even number of CH_2 groups there was a higher diffusion coefficient than in the case of polyesters with a odd number of the CH_2 groups. For most of the simulated polyesters the diffusion coefficients for both O_2 and CO_2 molecules decrease from *para* to *ortho* and *meta* isomers. It

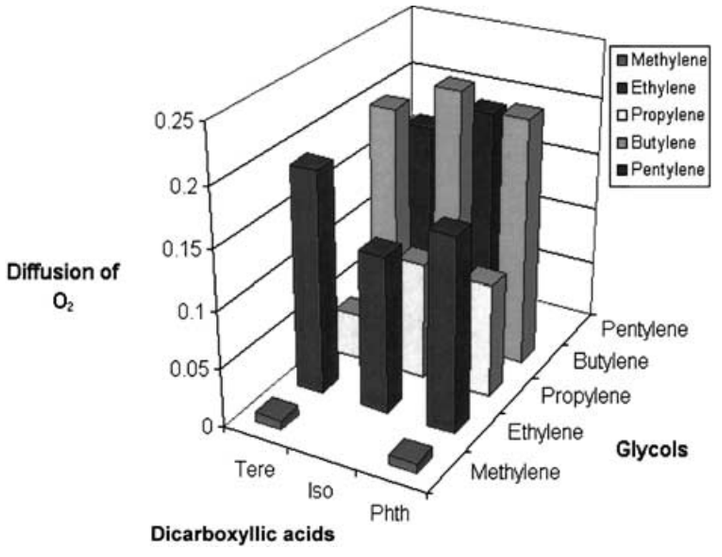


FIGURE 21 Three-dimensional representation of diffusion coefficient of O_2 vs. dicarboxylic acids and glycols.

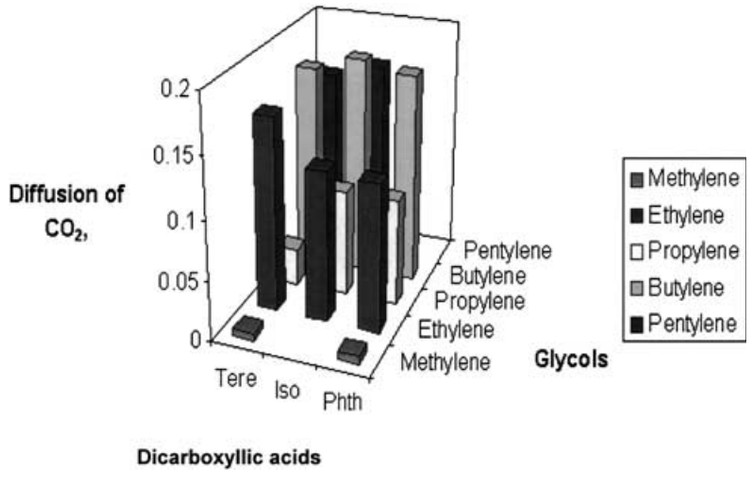


FIGURE 22 Three-dimensional representation of diffusion coefficient of CO_2 vs. dicarboxylic acids and glycols.

should also be noted that the diffusion of gases in the polyesters increased with temperature.

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