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Interplay of the polymer stiffness and the permeability behavior of silane and siloxane polymers ☆

Tarek M. Madkour*, Sahar K. Mohamed, Abdalla M. Barakat

Department of Chemistry, Helwan University, Ain-Helwan, Cairo 11795, Egypt

Abstract

The effect of the modification of the molecular structure on the stiffness of the polymeric backbones in relation to the diffusion coefficients of typical rubbery and glassy silane and siloxane polymers at different temperatures was investigated. The inflexibility in the polymeric chains as deduced by higher values for the persistence length was shown to correspond consistently to lower values for the self-diffusion coefficients. Increasing the temperature resulted in decreasing the persistence length of the silane polymers and increasing it in the case of the siloxane polymers. This was found to be due to the fact that the bond angle about the oxygen atoms is approximately 144° and rotations about the oxygen atoms for the *trans* isomeric states will bring the side groups on the neighboring Si-atoms in close proximity to each other thus increasing the torsional energies of the *trans* isomeric states considerably. The obtained simulation results showed an excellent agreement to those determined experimentally. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Torsional energies; Polymers; Persistence length

1. Introduction

All polymers are permeable to gases and vapors to some extent, which makes permeability through polymeric membranes a physical property of great importance in a variety of industrial and biomedical applications. Examples of these applications are separation of gas mixtures, food packaging, protective coatings (paints and varnishes), biomedical devices substrates for microelectronics and many others. Polymers are commonly used in these applications in the form of nonporous membranes (films, sheets, hollow fibers, or capillaries) [1]. A large number of new polymers have been synthesized in recent years for various applications that depend on gas permeability, but in particular for potential use as membrane materials for gas separation processes.

Synthetic membranes are thin, solid-phase barriers that allow preferential passage of certain substances under the influence of a driving force, which is governed by both the chemical and the physical nature of the membrane material. Polymers provide a range of properties important for separations, and modifying them can improve membrane selectivity. A material with a high glass-transition temperature (T_g), high melting point, and high crystallinity is preferred. Baker et al. [2], indicated that glassy polymers (i.e. polymers below their T_g) might have stiffer polymer backbones and therefore let smaller molecules such as hydrogen and helium pass more quickly; larger molecules such as hydrocarbons permeate the membrane more slowly. Rubbery polymers (i.e. polymers above their T_g), in contrast, allow the hydrocarbons to permeate more readily than the smaller gas molecules [3,4].

Gas diffusion through nonporous membranes occurs because of a concentration gradient that, for gases, is directly proportional to pressure [5]. Hence, membrane gas separation is often described as a pressure-driven diffusion process. Separation is achieved because of differences in the relative transport rates of the feed components. A membrane will separate gases only if one or more components pass through the membrane more rapidly than others. The separation, in this case, is based on the solution-diffusion mechanism as shown by Zolandz and Fleming [6]. This mechanism involves molecular-scale interactions of the permeating gas with the membrane polymer. The model assumes that each component is sorbed by the membrane at one interface, transported by diffusion across the membrane through the voids between the polymeric chains known as free volume and desorbed at the other interface.

Kesting and Fritzche [7] have realized that the diffusion

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* Corresponding author.

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coefficient decreases and the solubility increases with an increase in the molecular size of the gas. Consequently, gases with higher permeabilities enrich on the permeate side of the membrane, and gases with lower permeabilities enrich on the feed side of the membrane. Gas molecules permeate through a rubbery polymer quickly because the binding force between molecular segments of the polymer is not strong. Therefore, segments can move relatively easily to open a channel through which large molecules may go through. Furthermore, solubility often dominates permeability characteristics for transport in rubbery polymers. Thus, volatile organic compounds, which have a strong affinity (high solubility) for polymeric materials, permeate through a rubbery polymeric membrane faster than the much smaller oxygen and nitrogen molecules. Membranes prepared from rubbery polymers such as poly(dimethylsiloxane) and composite poly(ether imide)-silicone rubber membranes are effective in removing high volatile organic compounds from air as was explained by Baker et al. and Belfort and co-workers [2,8]. Because the chain segment motions in glassy polymers are more restricted than those in rubbery polymers, glassy polymers can discriminate between extremely small differences in the dimensions of common gases. Transport in glassy polymers is not governed by solubility but by the size of the molecule and the diffusion coefficient. Thus, because hydrogen molecules are the smallest (high diffusion coefficient), membranes prepared from glassy polymers are used effectively for hydrogen separation. Similarly, in CO_2–CH_4 separation, CO_2 permeates through glassy membranes much faster than methane, partly because CO_2 molecules are slightly smaller than CH_4 molecules. Currently, almost every polymeric gas-separation membrane is either entirely glassy or primarily glassy with a minor crystalline component because these materials are more size- and shape-selective than rubbery polymers [7]. Rubbery membranes, however, are 1000 times more permeable than glassy membranes. Typical examples of glassy polymeric membranes in commercial use are cellulose acetate, polysulfone, and poly(ether sulfone). Aromatic polysulfone is among the most successful gas-separation membrane. However, rigid polymers such as poly(ether imide) and polyimide, which have higher T_g and greater resistance to organic solvents, are sometimes required.

It is the purpose of this article to investigate the effect of the modification of the molecular structure on the stiffness of the polymeric backbones in relation to the diffusion coefficients of typical rubbery and glassy silane and siloxane polymers at different temperatures.

2. Computational methodology

RIS Metropolis Monte Carlo calculations were performed in order to evaluate the persistence lengths of poly(dimethylsiloxane), poly(diphenylsiloxane) and poly(n-hexylmethylsilane) polymers in relation to the diffusion coefficients of carbon dioxide molecules through the different polymers [8,9]. The persistence length is a measure of the polymer chain stiffness. It is the average distance traversed by the chain backbone along its initial direction before the chain loses 'memory' of this direction. RIS Metropolis Monte Carlo technique is a torsion-space simulation method for calculating the conformational properties of polymers using an atomistic force field. This approach thereby avoids the need for the statistical weights that are required by the traditional RIS approach [10,11]. Unlike traditional rotational isomeric states methods, Metropolis Monte Carlo method allows torsion angles to vary continuously and therefore does not impose the assumption of discrete rotational states. The method is thus based on relative energies of the new and the old conformation. The bond-based cut-off method was used for the simulations of the single polymeric chains in the θ-condition. In this method, the number of bonds $n_{\min}$ and $n_{\max}$ affect the way van der Waals and Coulomb energies are evaluated in the RMMC simulation. The nonbond energies were not computed for atoms that are closer than $n_{\min}$ or further apart than $n_{\max}$. The usual value for $n_{\min}$ was 3 whereas that of $n_{\max}$ was taken as 6 in order to include the interactions of the side chains of the neighboring repeat units in the energy evaluation.

RIS Metropolis Monte Carlo methods simulations were done for polymers with increasing number of repeat units at the three different temperatures of 248, 298 and 348°C. The molecules were preminimized using the COMPASS force field before the simulation [12]. The number of the equilibration steps was 10,000 for each rotatable bond. This stage was necessary to bring the polymer chain from its initial conformation to a conformation typical for the chain in solution or melt at the desired temperature. The number of simulation steps was 20,000 steps for each rotatable bond. The block-averaged values of the mean squared end-to-end distance and energy were plotted as functions of the simulation step number in order to determine if the system was fully equilibrated. There was no evidence of any long-term drift in mean squared end-to-end distance and energy over the course of simulation, which indicated that the chains had reached a steady state. According to Honeycutt [12], the 'flexible' constraint assumption, with no extra terms in the Boltzmann factor, could be applied for the RIS Metropolis Monte Carlo algorithm. In this case, the force constants for the constrained coordinates are regarded as so large that the coordinates do not move significantly from their equilibrium values, but the conjugate momenta are activated.

3. Results and discussion

3.1. The persistence length

As was mentioned before, the persistence length is a

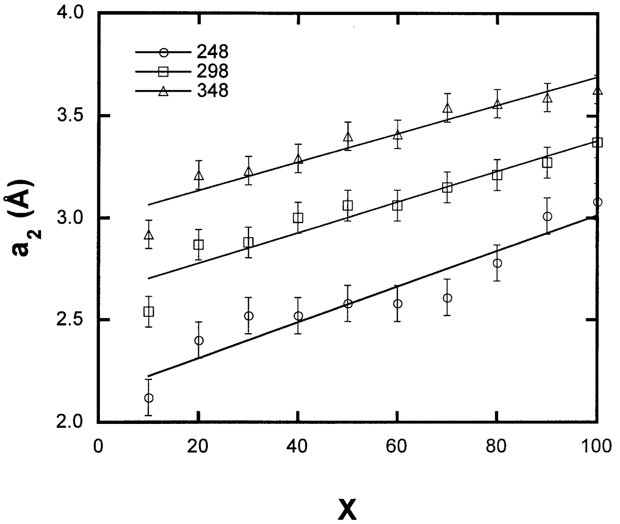

Fig. 1. The dependence of the persistence length on the degree of polymerization of PDMS at the three different temperatures.

measure of the polymer chain stiffness. It is defined as the average distance traversed by the chain backbone along its initial direction before the chain loses memory of this direction. Mathematically, the persistence length, a_1, can be defined as the mean projection of the end-to-end vector on the first bond of the chain. An alternative definition, a_2, is the mean projection of all subsequent bond vectors on a bond in the chain backbone, averaged over all bonds between the two chain ends. The second of these definitions was calculated, using Metropolis Monte Carlo methods, since it provided a better statistical average and is plotted in Figs. 1–3 as a function of the degree of polymerization of the various polymers, X [13]. The figures represent the evaluated persistence length for the three different polymers under study, PDMS, PDPhS and the polysilane polymer, respectively. It is obvious from the figures that the persistence length is increasing in the order of PDMS < PDPhS < silane, probably due to the effect of the steric hindrance of the bulky side groups, which will hinder possible rotations about the single bonds of the main backbone of the polymeric chains. It is also obvious from the figures that while the temperature had a proportional effect on increasing the persistence length at higher temperatures, it had a detrimental effect for the polysilane. This could be explained by the fact that there are three different isomeric states known for these polymers, *trans* (*t*), *gauche*+ (*g*+) and *gauche*− (*g*−). In case of the silane polymer, the main backbone of the chains consists of all silicon atoms, which renders the all *trans* conformation to have the lowest conformational energy. At higher temperatures, the polymeric chains will naturally access higher energy conformations that involve *gauche* isomeric states. This will cause both the end-to-end distance and the persistence length of the polymeric chains to decrease. In case of the siloxane polymers, the presence of the oxygen atoms in the main backbone of the chains will cause the polymeric chains in the *trans* state to turn onto itself thus corresponding to lower values for the end-to-end distances. The *gauche* isomeric states will, however, correspond to higher values for the end-to-end distances, thus forcing the chains to increase their persistence lengths at higher temperatures as a result of the increase in the end-to-end distances. This is because the bond angle about the oxygen atoms is approximately 144° and rotations about the oxygen atoms for the *trans* isomeric states will bring the side groups of the neighbouring Si-atoms in close proximity to each other. Moreover, the presence of the larger phenyl side groups in case of PDPhS will naturally decrease the ability of the chains to lose the memory of its initial direction, i.e. have higher persistence length than in case of PDMS. It could be shown from the figures that the silane polymers had the highest persistence length at all different temperatures as a result of the presence

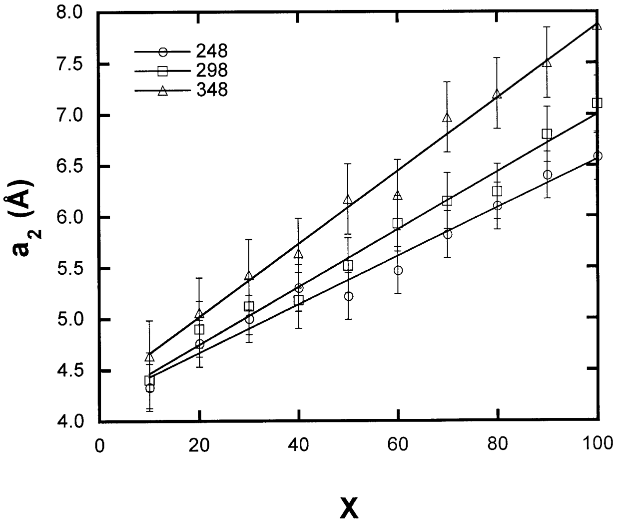

Fig. 2. The dependence of the persistence length on the degree of polymerization of PDPhS at the three different temperatures.

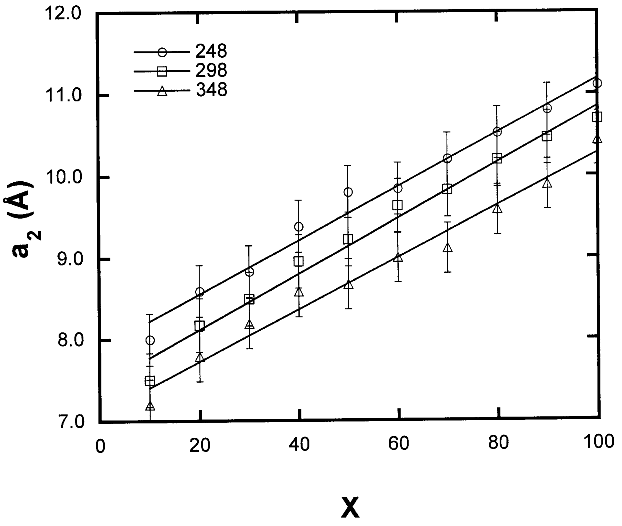

Fig. 3. The dependence of the persistence length on the degree of polymerization of the silane polymer at the three different temperatures.

of the side groups on every atom in the main backbone of the chains as compared to the siloxane polymers which have the side groups connected to every other atom in the main backbone separated naturally by the alternating oxygen atoms. In all cases, the molecular weight of the polymer had a proportional effect on the persistence length due to the corresponding increase in the end-to-end distances of the polymers.

3.2. The molar stiffness function

The intrinsic viscosity is known to depend on the average molecular weight of the polymer by a power law behavior [14]. For a dilute polymer solution under θ-condition, it is given by:

$$[\eta]_\theta = K_\theta M_\mathrm{v}^{0.5} \tag{1}$$

where M_v is the viscosity-average molecular weight. The K_θ parameter in Eq. (1) is related by definition to the molar stiffness function, K_stiff, and the molecular weight per repeat unit, M. Eq. (1) could thus be rewritten as:

$$[\eta]_\theta = (K_\mathrm{stiff}/M)^2 M_\mathrm{v}^{0.5} \tag{2a}$$

as

$$K_\mathrm{stiff} = M K_\theta^{0.5} \tag{2b}$$

If $[\eta]_\theta$ has the units of cc/gram, then K_stiff has the units of grams$^{0.25}$cm$^{1.5}$/mole$^{0.75}$. The molar stiffness function is a measure of the flexibility of the polymeric chains since it will affect its flow properties. K_stiff, K_θ and $[\eta]_\theta$ could all be calculated using the Metropolis Monte Carlo methods by evaluating the end-to-end distances of the polymeric chains according to the following formula:

$$[\eta]_\theta = \Phi \langle r_\theta^2 \rangle^{3/2} / M_\mathrm{v} \tag{3}$$

where Φ, the hydrodynamic constant, is 2.1×10^{21} dl cm^{-3} and $\langle r_\theta^2 \rangle$ is the mean squared end-to-end distance of the polymeric chains in the θ-condition simulated using Metropolis Monte Carlo methods. Figs. 4–6 represent the molar stiffness function, K_stiff, calculated from Eqs. (1)–(3) as a function of the degree of polymerization of the different polymers at the various studied temperatures. Similar observations to those made in case of the persistence length could be deduced in this case as well. While the temperature had a proportional effect on the K_stiff of the siloxane polymers, it had a detrimental effect on the K_stiff of the silane polymer. This could be explained as well on the basis of the presence of the alternating oxygen atoms in the main backbone of the siloxane polymers, which will give rise to lower values for the end-to-end distances of the polymeric chains and consequently lower values for the K_stiff of the polymer as could be inferred from Eqs. (1)–(3).

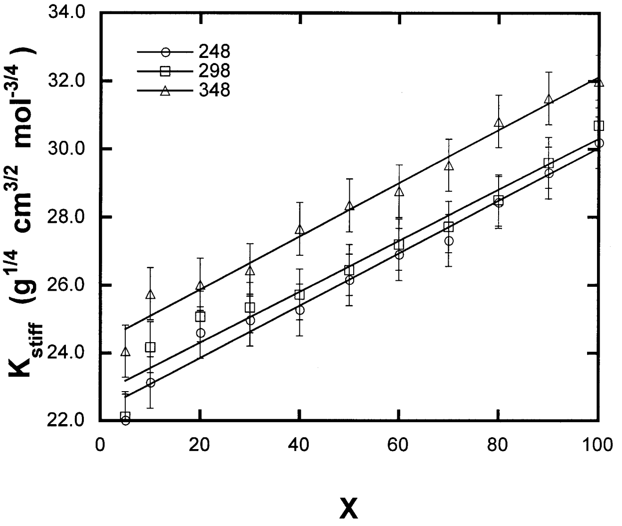

Fig. 5. The dependence of K_stiff on the degree of polymerization of PDPhS at the three different temperatures.

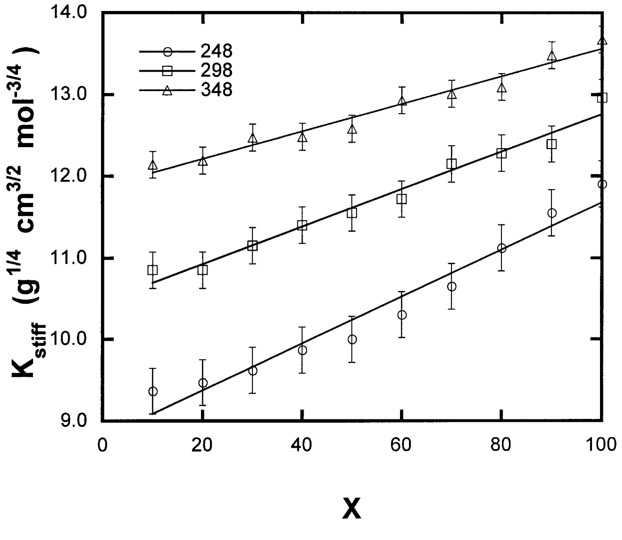

Fig. 4. The dependence of K_stiff on the degree of polymerization of PDMS at the three different temperatures.

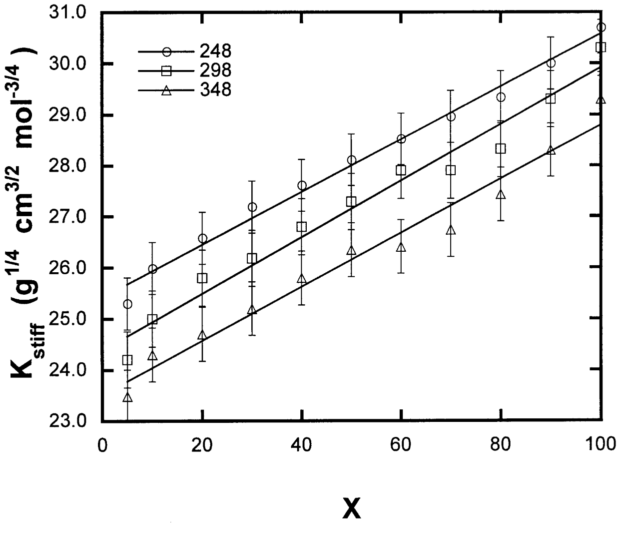

Fig. 6. The dependence of K_stiff on the degree of polymerization of the silane polymer at the three different temperatures.

An interesting observation from these figures is that the values of the K_{stiff} of PDMS are extremely low as compared to those of PDPhS and the silane polymer. This is possibly due to the difference between the two polymers in terms of their rheological behavior. In all cases, the values of K_{stiff} did increase by increasing the degree of polymerization, X, as a result of increasing the end-to-end distances of the polymeric chains.

3.3. The dihedral angle distribution

Fig. 7 represents the dihedral angle distribution of the three isomeric states, *trans*, *gauche*+ and *gauche*− for the three different polymers at the three different studied temperatures. A few observations could be deduced from the figure in relation to the difference in the conformational behavior of the three polymers at the different temperatures. For instance, it could be observed that the distribution of the dihedral angles is highly influenced by the presence of the bulky side groups attached to the main backbone of the polymers. This could be particularly observed for the silane polymer as compared to the siloxane ones, which is probably due to the presence of the bulky groups on every backbone atoms, whereas in case of the latter, the side groups are present only on every other backbone atom. This factor will certainly affect the probability of the torsional angles in such a way that the distribution of the *trans* torsional angle at 0° would be much higher than that of the *gauche* ones for the silane polymer. Close inspection of the dihedral angle distribution in case of PDMS as compared to that of PDPhS will indicate the effect of the presence of the bulky side groups on the dihedral angle distribution as highlighted by the sharp definition in case of the former. The effect of varying the temperature on the dihedral angle distribution is mostly shown for PDPhS. This is probably because, at higher temperatures, equal probabilities of all dihedral

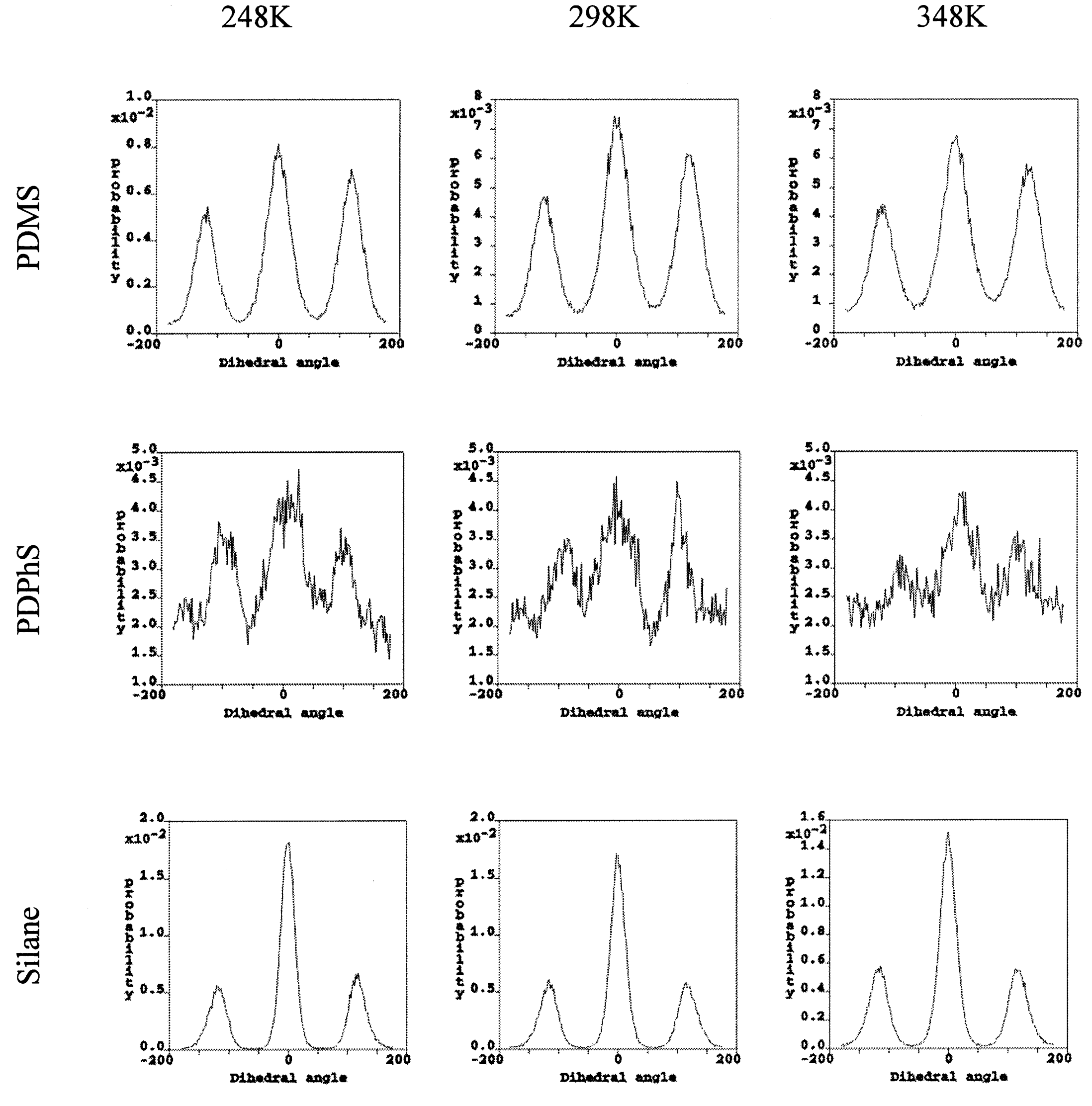

Fig. 7. The dihedral angle distribution of the three different polymers at the various studied temperatures of 248, 298 and 348°C.

Table 1
The self-diffusion coefficients (cm^2/s) of the PDMS polymer and the diffusing gas molecules at the different simulated temperatures

Temperature (°C)	Polymer molecules	CO_2 gas molecules
248	5.63×10^{-6}	1.99×10^{-5}
298	7.84×10^{-6}	3.89×10^{-5}
348	13.31×10^{-6}	3.92×10^{-5}

angles could be observed and more rotation around the alternating silicon and oxygen atoms is thus expected corresponding to temperatures close to the glass transition temperature of PDPhS. In case of PDMS, the various temperatures are all above the glass transition of the polymer.

3.4. Relationship with the diffusion coefficients

The effect of the molecular structure depicted by the polymer stiffness on the diffusion behavior of the various polymers could be deduced by considering the diffusion coefficients of the various polymers evaluated in a separate study [13]. Tables 1–3 present the values of the diffusion coefficients of the three different polymers calculated at the different temperatures using the molecular dynamics techniques and applying the Einstein relationship. A simple comparison among all presented data indicates that, PDMS has a much lower persistence length and molar stiffness values as compared to those of PDPhS and the silane polymer corresponding to a much higher diffusion coefficients for both the polymer and the diffusing gas molecules. Both of the PDPhS and the silane polymers have similar values for the stiffness properties as well as the diffusion coefficients, which indicate the possible relationship between the polymer stiffness and the diffusion behavior of the polymers. The wide difference between PDMS on one hand and the PDPhS and the silane polymers on the other hand is probably due to the fact that the former is a rubbery material whereas the other two are glassy ones.

Table 2
The self-diffusion coefficients (cm^2/s) of the PDPhS polymer and the diffusing gas molecules at the different simulated temperatures

Temperature (°C)	Polymer molecules	CO_2 gas molecules
248	1.12×10^{-7}	5.92×10^{-7}
298	1.64×10^{-7}	7.03×10^{-7}
348	4.10×10^{-7}	4.73×10^{-6}

Table 3
The self-diffusion coefficients (cm^2/s) of the silane polymer and the diffusing gas molecules at the different simulated temperatures

Temperature (°C)	Polymer molecules	CO_2 gas molecules
248	2.65×10^{-7}	3.04×10^{-7}
298	7.31×10^{-7}	1.20×10^{-6}
348	8.80×10^{-7}	4.38×10^{-6}

4. Conclusions

Rubbery membranes are 1000 times more permeable than glassy membranes. However, since the chain segment motions in glassy polymers are more restricted than those in rubbery polymers, glassy polymers can discriminate between extremely small differences in the dimensions of common gases (0.2–0.5 Å). Metropolis Monte Carlo calculations were performed in order to evaluate the persistence lengths of various silane and siloxane polymers in relation to the diffusion coefficients of carbon dioxide gas molecules through the different polymers. The persistence length is a measure of the polymer chain stiffness. It is the average distance traversed by the chain backbone along its initial direction before the chain loses memory of this direction. The persistence length was shown to increase in the order of PDMS $<$ PDPhS $<$ silane, probably due to the effect of the steric hindrance of the bulky side groups, which will hinder possible rotations about the single bonds of the main backbone of the polymeric chains. The temperature had a proportional effect on increasing the persistence length for the siloxane polymers and a detrimental effect in case of the silane polymers. In case of the siloxane polymers, the presence of the oxygen atoms in the main backbone of the chains will cause the polymeric chains in the *trans* state to turn onto itself thus corresponding to lower values for the end-to-end distances. This is because the bond angle about the oxygen atoms is approximately 144° and rotations about the oxygen atoms for the *trans* isomeric states will bring the side groups of the neighboring Si-atoms in close proximity to each other. Similar observations were also shown for the molar stiffness function as a consequence of the difference between rubbery and glassy polymers in terms of their rheological characteristics. Close inspection of the dihedral angle distribution in case of PDMS as compared to that of PDPhS will indicate the effect of the presence of the bulky side groups on the dihedral angle distribution as highlighted by the sharp definition in case of the former. A simple comparison among all presented data indicates that, PDMS has a much lower persistence length and molar stiffness values as compared to those of PDPhS and the silane polymers corresponding to a much higher diffusion coefficients for both the polymer and the diffusing gas molecules. Both of the PDPhS and the silane polymers have similar values for the stiffness properties as well as the diffusion coefficients, which indicate the direct relationship between the polymer stiffness and the diffusion behavior of the polymers.

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