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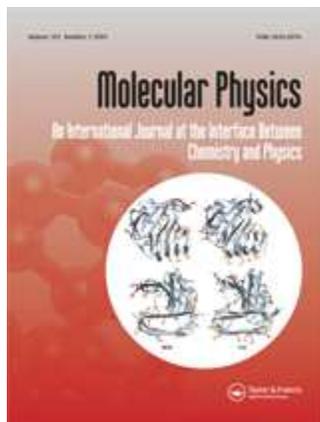
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Diffusion of Small Penetrant Molecules in Polybutadienes

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The diffusion coefficient D in the dilute limit for three different penetrants—oxygen, water, and methanol—in three different conformations of polybutadiene (all cis-1,4, all trans-1,4, and a random copolymer containing 50% trans-1,4, 40% cis-1,4, and 10% vinyl-1,2 repeat units) has been computed using molecular dynamics simulations for temperatures in the range $T = 300$ – 400 K. Simulations runs of 25 and 50 ns made for each of the 45 combinations of penetrant, conformation, and temperature studied. Over this temperature range the density of the all-cis-1,4 conformation is higher than that of the all-trans-1,4 and random copolymer conformations, which are approximately equal. For all three conformations, D for oxygen and water are comparable and larger than that of methanol. However for a given penetrant, strong differences were observed in the rate of increase of D for the three conformations. We find that the activation barriers for the three penetrants are generally between 20 and 30 kJ/mol, in agreement with experimental results. The magnitude of the activation energy is directly proportional to the size, rather than the mass, of the penetrant molecule.

1 Introduction

Polybutadiene (PBD) is widely used industrially, in applications ranging from the production of seals and tires to coatings for electronic assemblies. An advantage of polybutadiene for these applications is that it has excellent barrier properties compared to many other elastomers. However, in spite of the industrial importance of polybutadienes, it is not yet known how the permeability of small penetrant molecules depends on the chemical structure of the monomer or the aging conditions of the polymer. Aging of polymers is a critical phenomenon in determining their stability, as it can lead to both in increased crosslinking and oxidative damage induced via thermal or radiation exposure. Molecular dynamics (MD) simulations are especially suitable for addressing the molecular basis for permeability since it can follow the time trajectories of all the atoms in the systems, thereby providing detailed information of the motion of the penetrant molecules and how they interact with their environment.

For polybutadiene, there have been a number of studies reporting penetrant diffusion in PBD using both experiment and simulation. Pauly [1] reported the diffusion coefficient D of a number of small penetrants, including oxygen, methane, and carbon dioxide, in amorphous cis-1,4-PBD, while Cowling and Park [2] examined a similar range of gases in amorphous and crystalline 1,4-PBD. Cai et al. [3] have used capillary-column inverse gas chromatography to study the diffusion of large solvent molecules in PBD. Matteucci et al. [4] have studied diffusion of carbon dioxide, methane, and nitrogen in 1,2-PBD containing magnesium oxide. Gee and Boyd [5] used MD simulations to study the diffusion of methane in cis-1,4-PBD using a “united-atom” model in which CH_n monomers are treated as a single site. More recently, Meunier [6] and Gestoso and Meunier [7] studied the diffusion of Ar, O_2 , N_2 , CO_2 , and CH_4 in amorphous cis-1,4-PBD for a range of temperatures from 250 K to 400 K using the explicit-atom COMPASS force field model for all of their simulations. Tsolou and co-workers [8] have also used a united-atom model to measure the self-diffusion coefficient of cis-1,4-PBD.

Another issue of interest in the diffusion of small penetrants in polymers is the nature of the actual trajectories followed by the molecules. In general, caging occurs when the penetrant molecule are trapped in a small region within the melt for extended periods of time, followed by relatively rapid movement to a new region of the melt. Previously, Takeuchi [9] observed a “caging” and “jumping” process for oxygen

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1 molecules embedded in a polyethylene melt. The physical mechanism for this process was later elucidated
2 by Müller-Plathe [10]: molecules alternate between being trapped in “cages” and periods of relatively
3 unimpeded motion in which the penetrants move across relatively large distances. Gusev et al. [11] and
4 Greenfield and Theodorou [12] have studied the phenomena using transition state theory in addition
5 to molecular dynamics simulation. A more extensive literature review of such processes is provided in
6 Hofmann et al. [13].

7
8 In the present work, we have used molecular dynamics simulations to model the diffusion of oxygen,
9 water, and methanol in three model polybutadiene systems containing different amounts cis-1,4, trans-
10 1,4 and vinyl-1,2 isomers. The diffusion coefficients for these three penetrant molecules for a range of
11 temperatures between 300 K and 400 K were determined and compared to experiment. By examining
12 oxygen, water, and methanol, we explore the effects of nonpolar, polar, and organic penetrants on diffusion
13 behavior. Varying the composition of the PBD allows us to cover a broader range of experimentally-
14 observed polymer morphologies, including a random copolymer whose composition is comparable to that
15 used commercially. We also analyze the trajectories of individual molecules to examine how the penetrants
16 diffuse through polybutadiene. This work is part of our effort to improve our understanding of basic
17 physical properties as a function of chemical variations and network formation in elastomers [14–18].

18 In Section II, we briefly present the model and methodology used in the simulations. In Section III we
19 present our results on the density of the different polymer conformation and their relationship to penetrant
20 diffusion. We also discuss our findings for the diffusion constants of oxygen, water, and methanol, as well
21 as discuss the trajectories of the different penetrant molecules and their implications on the diffusion
22 mechanism. We summarize our conclusions in Section IV.
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26
27

28 2 Models and Methodology

29
30 Three chemical structures of polybutadiene were studied: all-cis-1,4 PBD, all-trans-1,4 PBD, and an en-
31 semble of random copolymer chains of PBD with a microstructure consisting of 50 % trans-1,4, 40 % cis-1,4,
32 and 10 % 1,2-vinyl monomers. This distribution for the microstructure is taken from experimental mea-
33 surements observed in industrially produced polybutadiene [19]. The fully atomistic OPLS-AA force field
34 of Jorgensen et al. [20] was used for all simulations. The van der Waals interactions were truncated at 12 Å.
35 The long-range Coulomb interactions were calculated with the fully periodic particle-particle particle-mesh
36 method [21] with an accuracy greater than one part in 10^4 .

37 To produce each of the three polybutadiene samples, 25 polybutadiene molecules, each containing 100
38 monomers, were constructed in a cubic box of length 130 Å using Accelrys Materials Studio. These confi-
39 gurations were then used to construct data files suitable to be read by LAMMPS [22], which was used for
40 all of the molecular dynamics simulations reported here [12]. The simulation cell was then slowly deformed
41 at $T = 300$ K over a period of 10 ns, until the resulting density was slightly larger than the experimen-
42 tal density. The simulation was then allowed to equilibrate for 10 ns in an NPT ensemble simulation at
43 $T = 300$ K and $p = 1$ atm. The system was then heated to $T = 1000$ K over a period of 1 ns, where it was
44 maintained in an NVT ensemble for 5 ns, before slowly cooling over a period of 5 ns back down to 300 K.
45 We saved configurations of the system during the cooling cycle at the various desired temperatures. For
46 each temperature we ran an additional 5 ns in the NPT ensemble to equilibrate the systems further before
47 introducing the penetrant molecules.
48
49

50 For molecular oxygen, the force field is taken from Powles and Gubbins [23]. For water we used the
51 SPC/E force field [24] while for methanol we used the OPLS force field [20]. The SPC/E water model,
52 as originally parameterized by Berendsen et al. [24], has fixed bond lengths and bond angles; the oxygen
53 and methanol potentials have flexible bonds, and in the case of methanol, angles and torsions as well.
54 The penetrant molecules were inserted into the polymer matrix by searching for voids large enough to
55 accommodate the molecules. The criterion for large enough voids involves finding the minimum distance
56 between the center of mass of the compound and the nearest atom in any of the polybutadiene molecules
57 or previously inserted penetrant molecules. If this minimum distance r_{\min} satisfied $r_{\min}^2 > 4 \text{ \AA}^2$ for oxygen,
58 $r_{\min}^2 > 5 \text{ \AA}^2$ for water, and $r_{\min}^2 > 8 \text{ \AA}^2$ for methanol, the insertion was accepted.
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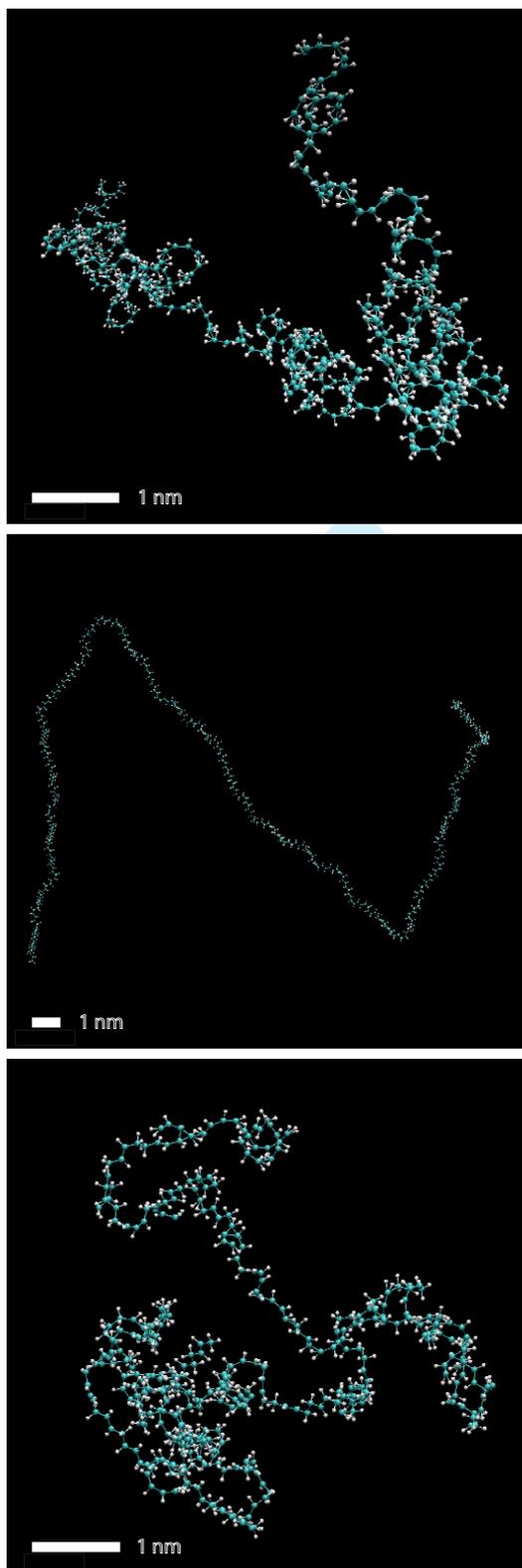
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Figure 1. Conformations of PBD chain of 100 repeat units from the all-cis-1,4 (top), all-trans-1,4 (middle) and random copolymer (bottom) conformations of PBD; molecules have radii of gyration close to that of the sample average for their respective conformations. Length scale shown for each figure.

1 While we are interested in the dilute limit, for computational efficiency we simulated systems containing
 2 five penetrant molecules for oxygen and methanol. For these two molecules, the penetrants did not phase
 3 separate and remained as single molecules during the course of the simulations. When we inserted five
 4 water molecules into the PBD samples, however, three or four of the molecules quickly phase separated
 5 into small clusters. Consequently, for water we ran five separate simulations, each containing a single
 6 water molecule inserted at different locations, for each temperature and PBD conformation. After the
 7 molecules were inserted we re-equilibrated each system at constant pressure for 1 ns. The simulations
 8 for the diffusivity measurements were then performed in the NVT ensemble with a weak coupling to a
 9 Langevin thermostat with damping constant $\Gamma = 0.001 \text{ fs}^{-1}$. In previous work, it has been shown that the
 10 effects of including a Langevin thermostat on the overall dynamics is small, particularly for the very weak
 11 coupling constant Γ used here [25].

12 The positions of each penetrant molecule were stored every 250 fs during runs of 25-50 ns for each system.
 13 Every tenth stored configuration was used as a starting point to determine the mean squared displacement,
 14 for a minimum of 10 000 starting points for each penetrant molecule. The diffusion coefficient D was then
 15 computed from the Einstein relation,
 16

$$17 \quad D = \lim_{\Delta t \rightarrow \infty} \frac{\langle \mathbf{r}(t + \Delta t) - \mathbf{r}(t) \rangle^2}{6\Delta t}, \quad (1)$$

18 where the ensemble average is taken over both the trajectory of all the water oxygen atoms and all available
 19 initial starting configurations. The position $\mathbf{r}(t)$ is defined as the center of mass of the molecule. Separate
 20 values of D was obtained for each molecule and the resulting values were averaged to give the reported
 21 diffusion coefficients. An example of the mean square displacement versus time for O_2 in cis-1,4 PBD at
 22 300 K for each of the five molecules studied is shown in Figure 2.

23 It should be noted that while some of the molecules in Figure 2 exhibit at long times
 24 displacements which grow at rates slightly greater than $r^2 \sim t$, the exponents associated with
 25 this diffusion process are usually less than 1.03. These values are well within the range of
 26 other simulation studies in this field; Narros *et al.* have observed exponents as large
 27 as 1.10 for the relationship between mean-squared displacement and time [26]; Paul *et al.*
 28 have seen exponents as large as 1.22 [27]. Furthermore, for some of the molecules shown in
 29 Figure 2, the growth rate of the mean-square displacement is slightly slower than $r^2 \sim t$; it
 30 is partially for this reason that we average over multiple molecules to determine the overall
 31 diffusion constants. Additionally, it is possible that the discrepancy could be due to the lack
 32 of sufficient data samples for averaging, as non-linear behavior is clearly expected when small
 33 numbers of trajectories are averaged together [10]. In all cases, only the linear portion of
 34 the data to determine the estimates for D : for instance, for O_2 at 300 K, this corresponds to
 35 approximately the first 3 ns of data, as shown in Figure 2).

36 For individual molecules, the uncertainty in the slope of the regression line, and hence the diffusion
 37 constant, is less than 1 percent. However, because of the difference in conditions in the melt for different
 38 molecules, there is as much as a factor of two variance between the diffusion constants measured for different
 39 molecules within a sample. This is well within the experimental range of diffusion constant measurements,
 40 which can vary by an order of magnitude or more [18].

41 In addition to computing the diffusion coefficients as a function of temperature, it is possible to use the
 42 variation in temperature to estimate the “activation energy” barrier for the diffusion process. It has been
 43 shown for a number of cases [6,9] that above the glass transition temperature, the diffusion constant varies
 44 according to an Arrhenius-like rate law,
 45

$$46 \quad D = D_0 \exp\left(-\frac{E_a}{RT}\right), \quad (2)$$

47 where D_0 is the prefactor for the diffusion constant and E_a is the activation energy of the process.

48 If we assume that diffusion of gases in polybutadiene at and above room temperature follows Eq. 2, then
 49 the activation energy can be computed using a least-squares regression fit of the diffusion data versus the
 50

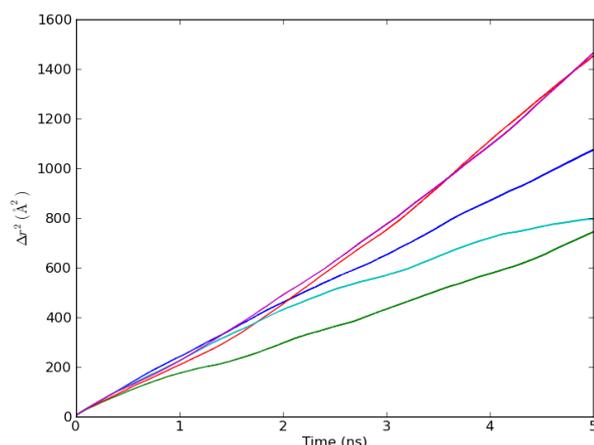


Figure 2. Mean square displacement as a function of time for the five oxygen molecules dispersed in a cis-1,4-PBD melt at 300 K.

inverse temperature. For the calculations reported here, the uncertainty in E_a is approximately 10 per cent, or between 2.0 and 3.0 kJ mol⁻¹.

3 Results and Discussion

3.1 Density of Polybutadiene

The density of the cis-1,4, trans-1,4, and random copolymer conformations of PBD as a function of temperature are shown in Figure 3. The cis-1,4 conformation consistently has the highest density for all temperatures while the random copolymer and trans-1,4 conformations have approximately the same density. As a result of this difference, we would expect that the latter configurations have slightly greater void volumes than the cis-1,4 conformation, and consequently should also have higher diffusivities on account of the larger void space available for the penetrant molecules. However, as shown below, this is not the case for all of the penetrants.

To compare these results to experimentally observed results, we also show experimental data reported by Yi and Zoller for a random copolymer blend that they fit to the Tait equation of state [28]. We note that there exists qualitative agreement between our results using the OPLS-AA force field and experiment. Table 1 gives the coefficients of linear expansion $\alpha_L = (1/L)(\partial L/\partial T)$, where L is the length of the simulation box, for each of the three PBD morphologies. As seen in Table 1, the present model yields results which are approximately 20 percent larger than the experimental results of Paul and Di Benedetto [29]. Our estimates of α_L are, however, close to the value of $\alpha_L = 7.7 \times 10^{-4} \text{ K}^{-1}$ reported by Gee and Boyd from their simulation [5]. Comparing our results for density with those obtained by Meunier [6], we find that our results are somewhat lower, probably due to the difference in the force fields, as the OPLS force field has a slightly larger values for the Lennard-Jones σ parameters than other alkane force fields [30,31].

Table 1. Coefficients of thermal expansion α and activation barriers E_a for penetrants in polybutadiene

PBD conformation	α_L (K ⁻¹)	Activation energy (kJ/mol)		
		O ₂	CH ₃ OH	H ₂ O
cis-1,4	8.4×10^{-4}	16.1	25.5	24.5
trans-1,4	8.0×10^{-4}	19.3	23.6	20.7
random	8.2×10^{-4}	20.1	28.1	21.5
experimental ^a	6.7×10^{-4}	20–30 kJ/mol		

^aExperimental results for α_L taken from Paul and Di Benedetto [29]; estimates of E_a taken from Pauly [1].

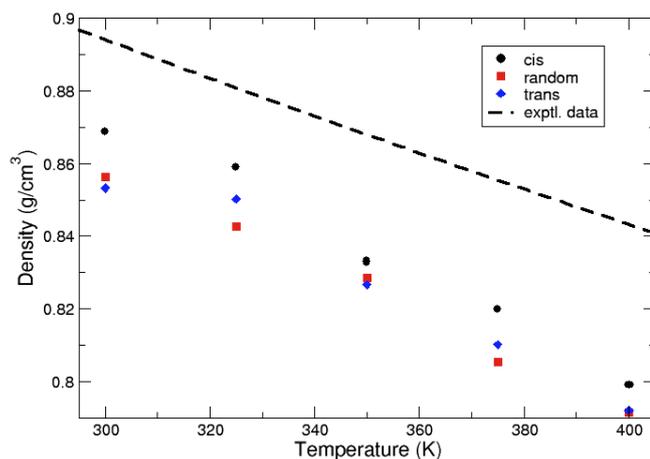


Figure 3. Density of the cis-1,4, trans-1,4 and random copolymer of PBD as a function of temperature. Also shown is the fit to the Tait equation of state calculated from the experimental data of Yi and Zoller [28] for a random copolymer blend.

3.2 Diffusion of Penetrant Molecules

3.2.1 Oxygen. The diffusion coefficient for oxygen as a function of temperature is shown for the three different structures in Figure 4. As expected, D increases monotonically as a function of temperature, from a value of approximately $D = 5 \times 10^{-5} \text{ cm}^2/\text{s}$ at 300 K to $D = 3 \times 10^{-4} \text{ cm}^2/\text{s}$ at 400 K. However, the ratio of the diffusion coefficients for the three microstructures depends on the temperature. At low temperatures, the cis-1,4 conformation has the largest diffusion coefficient, while at higher temperatures, D is largest for the random copolymer. This would suggest that obstacles created from the inclusion of the branching vinyl groups in the random copolymer that could serve to hinder the motion of the O_2 molecules at low temperatures become less significant at higher temperatures.

Because oxygen molecules are both small and nonpolar, we expect that O_2 should have very little interaction with the polymer and therefore have the largest diffusion coefficient of any of the three molecules tested. This is the case for temperatures below 350 K. However, at 375 K and 400 K, the diffusivity of water in some of the PBD conformations is greater than that of O_2 , suggesting that at high temperatures, the dependence on molecular weight may become more dominant than intermolecular interactions in determining the magnitude of D . Comparing previously reported results in cis-1,4 to ours at 300 K, we find that our results are substantially larger than either the previous experimental results of Pauly [1], which found $D = 1.5 \times 10^{-6} \text{ cm}^2/\text{s}$, or the simulation results of Meunier [6], who reported a value of $D = 9.5 \times 10^{-6} \text{ cm}^2/\text{s}$. At 400 K, Meunier reported a value of $D = 8 \times 10^{-5} \text{ cm}^2/\text{s}$, which is also significantly lower than our result. These results are consistent with the lower density for the polybutadiene melts observed in our simulations.

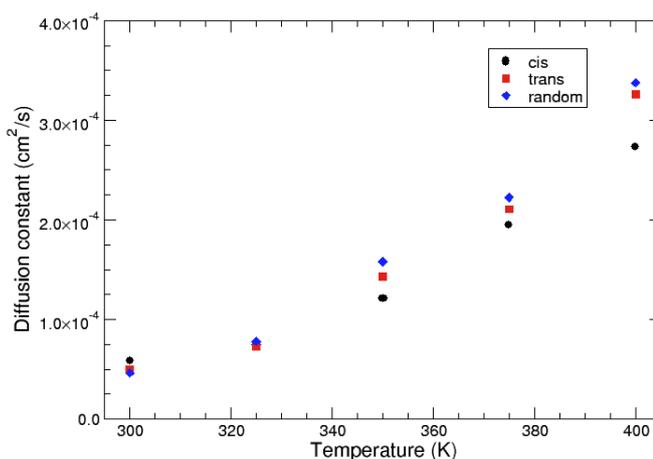


Figure 4. Diffusion coefficient D of oxygen as a function of temperature for cis-1,4, trans-1,4, and random copolymer of PBD.

3.2.2 Methanol. The diffusion coefficients D for methanol as a function of temperature for the different conformations is shown in Figure 5. We find that the cis-1,4 configuration, which nominally has the highest density, has the highest diffusion coefficient for methanol, while the trans-1,4 and random copolymer have diffusivities which are approximately 50% smaller. For the random copolymer, the presence of the vinyl groups appears to lead to constrictions in the paths available to the penetrant molecules. This may lead to more frequent deflections in the trajectory of the methanol molecules, which are much larger than either of the other molecules considered here, thereby leading to a lower diffusion coefficient.

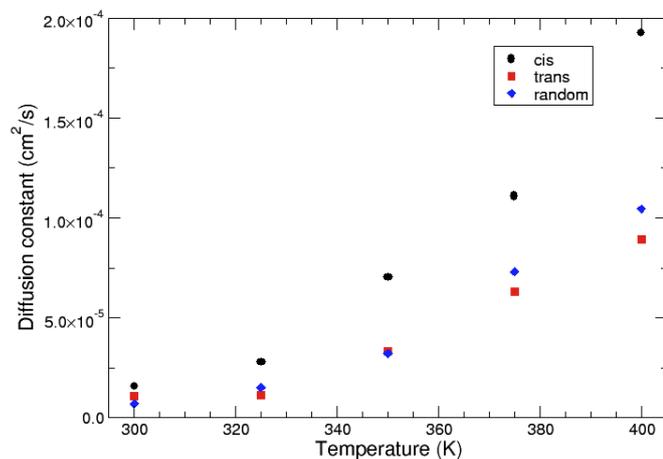


Figure 5. Diffusion coefficient D for methanol as a function of temperature for cis-1,4, trans-1,4, and random copolymer of PBD.

3.2.3 Water. The diffusion coefficients D for water as a function of temperature and conformation are shown in Figure 6. The overall trends for water are closer to those observed for the polar methanol molecule than for the uncharged oxygen molecule. At lower temperatures, D grows slowly, followed by faster growth at higher temperatures. Similarly, the increase in D for the cis-1,4 structure is significantly faster than in the trans-1,4 and random copolymer structures. Again, this may be a result of the increased size of the charged molecules relative to oxygen. The decrease in density associated with the higher temperatures to increase the “lane widths” sufficiently for oxygen to be able to pass through, but still not wide enough for enhanced diffusion of water or methanol. In addition, the conformational structure of the trans-1,4 and random copolymer mean that more charges are “exposed” and can therefore interact more easily with the polar penetrants.

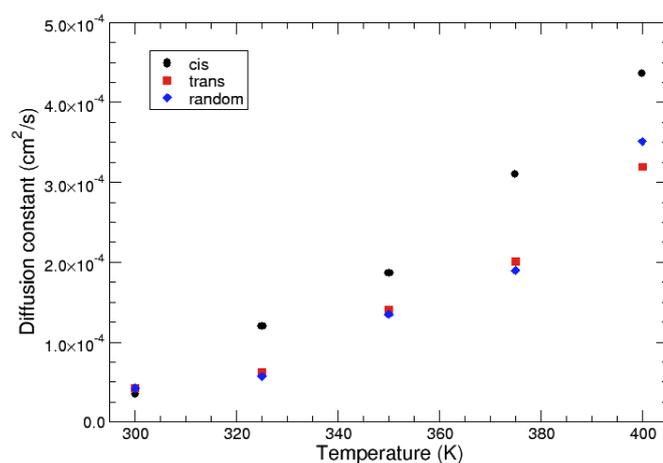


Figure 6. Diffusion coefficient D of water as a function of temperature for cis-1,4, trans-1,4, and random copolymer of PBD.

3.3 Activation energy

Using the data shown in Figure 4 through Figure 6, we have calculated the energy barriers for diffusion in the different conformations for the three permeants; the results are shown in Table 1, and the Arrhenius plot for the three penetrants diffusing through the all-cis-1,4 conformation is shown in Figure 7. There are few consistent patterns that can be determined for the activation barriers as a function of either penetrant or conformation, except that the barrier for oxygen is always smaller than the comparable barriers for methanol and water. In addition, the greater variance between penetrants for a given conformation, relative to the variance between conformations for a given penetrant, suggests that the intermolecular interactions between the penetrant and the specific conformations plays a more significant role than the size or mass of the penetrant in determining activation energy barriers.

Comparing these results to other investigations, we find that our results are comparable to those obtained experimentally, which find activation barriers in the range of 20-30 kJ/mol [1]; our simulations give energies that are in the same range. In contrast, the earlier work of Meunier [6] gives activation energies that are less than 10 kJ/mol for penetrant diffusion, including oxygen, in cis-1,4-PBD.

Moreover, Meunier suggests that at lower temperatures, for some penetrants there is a decrease in the activation energy barrier, which can be detected if the Arrhenius plot is strongly non-linear as $1/T$ increases. For the penetrants studied here, we see very little indication of this behavior. For oxygen, it appears that the activation barrier in fact decreases with temperature; while methanol, which is slightly larger than methane, for which Meunier showed a decrease in activation energy, shows no such trend.

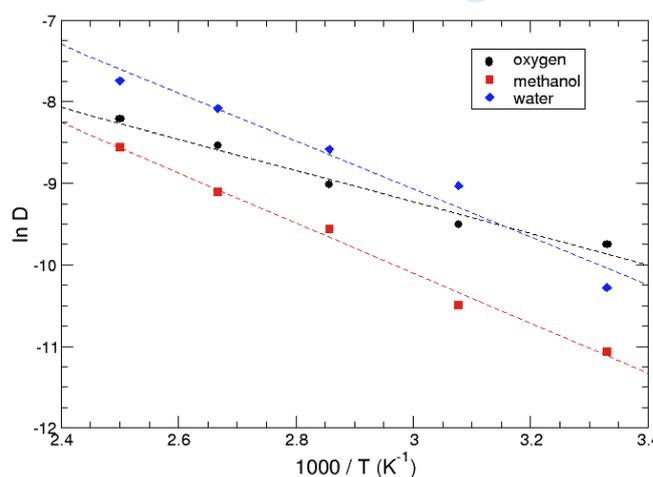


Figure 7. Arrhenius plot showing $\ln D$ as a function of inverse temperature for oxygen, methanol, and water diffusing through cis-1,4-PBD.

3.4 Trajectories of penetrant molecules

Trajectories for the five O_2 molecules in cis-1,4 PBD at 300 K are shown in Figure 8, while trajectories for the 5 methanol molecules in cis-1,4 PBD at 300 K and 400 K are shown in Figure 9. Clear differences can be observed between the two penetrants at 300 K. For the smaller penetrant O_2 , the trajectories are much more diffuse, both exploring a greater volume and for several molecules, traversing a more tortuous path than the methanol molecules. Although PBD at 300 K is substantially above its glass transition temperature, reported to be 170 K for cis-1,4 PBD [32], such behavior is consistent with weak penetrant caging.

By contrast, the methanol trajectories at 300 K are much more compact than for O_2 , and the regions of space explored by the molecules are more connected. This suggests that the “caging” of methanol may be more effective than for the other penetrants, which can escape through smaller “holes” than the much larger methanol molecule. At 400 K, the methanol trajectories look more like those of O_2 at 300 K. However, because of the larger distances travelled at the higher temperature, caging does not appear to

play a role in the diffusion process. The lower density of the melt allows for larger channels through which all of the penetrants, including the methanol, can pass.

Further demonstration of the lack of caging is shown by considering the net displacement of a molecule relative to its starting location. An example, for a methanol molecule at 300 K, is shown in Figure 10. During the time span shown in the figure, we can see instances of tunneling behavior only around 7 ns. In this particular case, the tunneling appears to be associated with the molecule entering and leaving a relatively confined volume within the melt. However, even during this limited “caging” period, the fluctuations in the positions are much greater than those observed by Müller-Plathe and by Takeuchi for oxygen in polyethylene [9, 10].

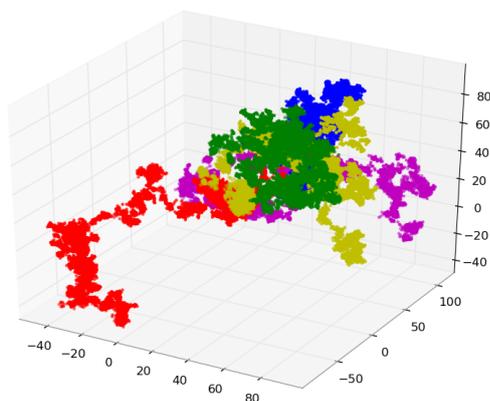


Figure 8. Trajectories of the five O_2 molecules in a cis-1,4 PBD during a 25 ns run at 300 K. Each color represents the trajectory of the five O_2 molecules. The PBD chains are not shown.

3.5 General observations

Based on the results reported in the previous subsections, we can draw some general conclusions regarding the diffusion of small penetrants in polybutadienes. Because the density of our polybutadiene samples was slightly below the reported experimental densities at the respective temperatures, there are greater void volumes available to penetrants, regardless of their size. Consequently, our estimates for represent upper bounds for the actual diffusion constants. However, because our results for the activation barriers are consistent with experimental results, the trend lines that we observe, as well as the relative differences between the behaviors of the various solvents and conformation combinations, should still be valid.

4 Conclusions

We have used molecular dynamics simulations to estimate the diffusion coefficients D of three small penetrants in different conformational of polybutadiene. As expected for all penetrants and conformations considered, the D increases with temperature. We find that the diffusion for water and methanol is largest for in cis-1,4 PBD at all temperatures, while it is largest for O_2 in cis-1,4 PBD at low temperatures and in the random copolymer at higher temperatures. This may be a result of the relationship between the size of the penetrants and the available “lanes” in the polymer. These effects are partially, but not entirely, accounted for by differences in the density of the different polymer conformations.

Analysis of the trajectories of the penetrant molecules show very limited evidence of the “caging” and “jumping” phenomena reported by Takeuchi [9] and Müller-Plathe [10]. Oxygen molecules show signs of traveling through more tortuous paths that do not appear to be available to the larger water and methanol molecules. This effect is strongest in the higher-density cis-1,4 PBD conformation than in the trans-1,4 and random copolymer structures. This caging phenomena may in part explain the larger diffusivities observed

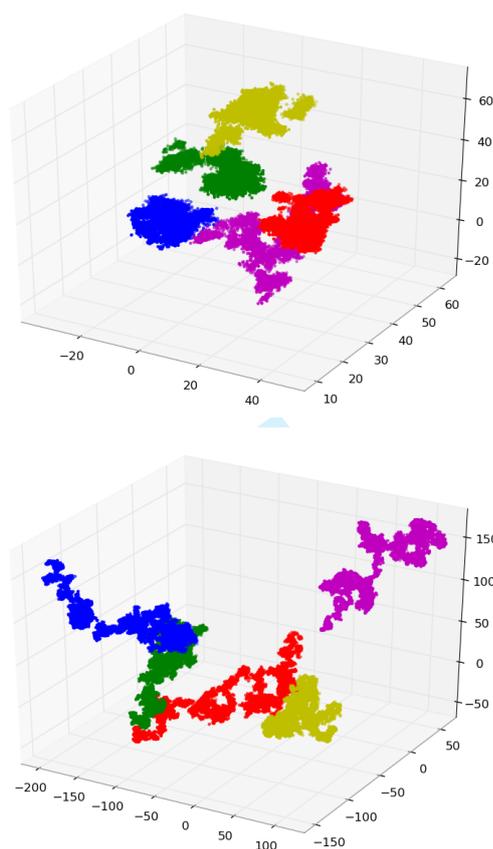


Figure 9. Trajectories of methanol molecules in a cis-1,4 PBD at 300 K (top) and 400 K (bottom) during a 25 ns run. Each color represents the trajectory of one of the 5 methanol molecule. The PBD chains are not shown.

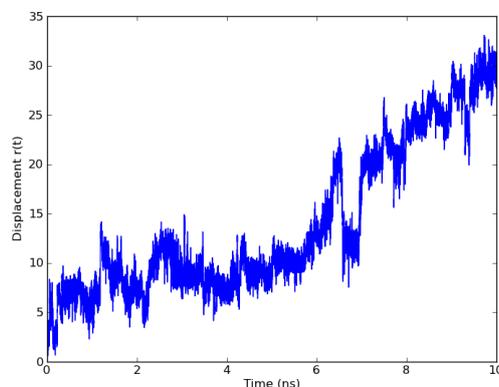


Figure 10. Displacement $r(t)$ of a methanol molecule relative to its starting location for a methanol molecule as a function of time.

in oxygen, especially compared to the simulation results of Meunier [6], whose simulations may not have been sufficiently long to permit observation of this phenomenon.

5 Acknowledgments

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