Sorption and diffusion of methane and carbon dioxide in amorphous poly(alkyl acrylates): a molecular simulation study

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Abstract

Molecular simulations were carried out to understand the structural features, and the sorption and diffusion behavior of methane and carbon dioxide in amorphous poly(alkyl acrylates) in the temperature range of 300–600 K. The hybrid Monte Carlo/molecular dynamics approach was employed to address the effects of polymer swelling and framework flexibility on the gas sorption. Simulations show that the glass transition temperature decreases with side-chain length of poly(alkyl acrylate), consistent with experiments. This is due to the fact that the shielding of the polar ester groups increases with side-chain length. The simulated sorption isotherms for methane and carbon dioxide were in agreement with the experimental data. The polymer swelling becomes more pronounced, especially in the case of sorption of carbon dioxide. A significant swelling occurs possibly due to the greater interaction between carbon dioxide and the polar ester groups in the polymers. The uptake of methane and carbon dioxide by poly(alkyl acrylates) generally increases with side-chain length. Our simulations confirm the experimental findings that the diffusion coefficients of methane and carbon dioxide in poly(alkyl acrylates) increase with side-chain length. Interestingly, the activation energies of gas diffusion decrease with side-chain length. The diffusion coefficients of penetrants have an exponential relationship with the void fraction, which is in agreement with the free volume theory.

1 Introduction

Poly(alkyl acrylates) have a wide variety of industrial applications such as in adhesives, coatings, paints, and textiles.¹ The side-chain length of poly(alkyl acrylates) play an important role in determining the local nanostructure and crystallinity,²⁻⁵ the chain dynamics,⁶ the glass transition temperature,^{7,8} the degradation rate,^{9,10} and gas sorption and transport^{11,12} in the polymer material. For example, independent of the backbone, crystallinity is usually present for side-chains containing more than about 10 carbon atoms.²⁻⁴ The side-chains can also aggregate in the melt and form self-assembled nanodomains.^{5,6} The side-chain motion was relatively slower due to the presence of the local nanodomains.⁶ It was found that the glass transition temperature of poly(alkyl acrylates) typically decreases with increasing side-chain length.^{7,8} Also, the degradation rate of poly(alkyl acrylates) decreased with increasing side-chain length.^{9,10}

The copolymers of poly(alkyl acrylates) are used in several industrial applications.¹³⁻¹⁹ For example, ethylene-alkyl acrylate copolymers are used in the semiconducting layers of electric cables.^{13,18} The cross-linked polyethylene is usually used in cable insulation due to its improved properties such as thermal stability compared to the untreated sample. A common way to achieve the cross-linking of polyethylene chains is by making use of the peroxide initiated free-radical reactions. However, unwanted byproducts such as CH_4 are also formed during this reaction. The removal of CH_4 is important because of safety concerns related to its flammability. Gas diffusion in semiconducting layers can affect the removal of byproducts such as methane formed during the peroxide-induced cross-linking of polyethylene.

The release of carbon dioxide from burning of fossil fuels and other industrial processes is currently measured at about 36 billion tons per year, and is projected to increase in the future.²⁰ Greenhouse gases such as carbon dioxide and methane absorb infrared radiation and contribute to the global warming.^{21,22} Although methane has a much higher global warming potential, carbon dioxide is known to be the major con-

tributor toward global warming effects. In this context of environmental protection, efficient capture of carbon dioxide received great attention.^{23–33} Common examples of sorbents include zeolites,^{23,24} zeolitic imidazolate frameworks,²⁵ metal-organic frameworks,^{24,26} clays,^{27–30} and polymers.^{23,31–33} The use of polymers may offer a number of advantages over other materials including chemical diversity, cost-effective manufacturing, and thermal and chemical stability.

There have been extensive studies of gas sorption and transport in polymer systems.^{11,12,23,31–53} A few general observations can be made concerning these studies. These studies have shown that the polymer fractional free volume (FFV) increases with temperature. Furthermore, the solubilities of small penetrants such as helium and nitrogen increase with increasing temperature or FFV. This might be due to the fact that the hindered rotation and degree of confinement of the penetrants decrease with increasing FFV (entropic factor). In contrast, the solubilities of penetrants such as CO₂ and CH₄ typically decrease with increasing temperature or FFV. This might be due to the fact that the penetrant-polymer interaction decreases with increasing FFV (energetic factor). In general, the gas diffusion coefficient D has an exponential relationship with FFV, which is in agreement with the classical free volume theory.^{41–43} The free volume theory is based on the concept that the redistribution of the free volume is responsible for the diffusive displacement, and the relation is $D = A \exp(-B/\text{FFV})$, where A and B are constants. Typically, the value of A is dependent on the gas-polymer interaction, and the value of B is dependent on the polymer-polymer interaction.

Mogri and Paul have systematically studied gas sorption and transport in poly(alkyl acrylates).^{11,12} These studies showed that gas permeability in amorphous poly(alkyl acrylates) increases with increasing side-chain length. Moreover, the relatively large change in permeability in going from poly(methyl acrylate) to poly(ethyl acrylate) reflects the trend observed mainly for the diffusion coefficient. A similar effect of side-chain length on gas permeability was observed for polymers such as poly(alkyl methacrylates).⁵¹ However, the effect of side-chain length on gas permeability depends strongly on the type of polymer and penetrant.^{11,12,46–52} For example, gas permeability

in polymers such as poly(silylpropynes)⁴⁸ and polynorbornenes⁵⁰ was found to decrease with increasing side-chain length. Therefore, a detailed molecular-level understanding of gas sorption and transport in poly(alkyl acrylates) is necessary to gain insight into the effect of side-chain length on gas permeability. We note that previous simulation studies dealing with poly(alkyl acrylates) have concentrated on structure and chain dynamics,^{54,55} and did not consider the effect of side-chain length on gas permeability.⁵³

In this work, we employed molecular simulations to understand the sorption and diffusion behavior of methane and carbon dioxide in amorphous poly(alkyl acrylates) at temperatures from 300 to 600 K and at pressures up to 15 atm. Four cases were considered in this study, namely, poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), poly(butyl acrylate) (PBA), and poly(decyl acrylate) (PDA). Our earlier studies have shown that, Monte Carlo (MC) and molecular dynamics (MD) simulations are excellent methods for determining the static and dynamic properties of a system.^{27–29,33,56–60} Here the sorption isotherms were estimated using the grand canonical Monte Carlo (GCMC) simulation method. Note that, as in our earlier work,³³ a hybrid MC/MD simulation approach was used to incorporate the effects of polymer swelling and framework flexibility on the gas sorption. The simulated sorption isotherms for methane and CO₂ were in good agreement with the corresponding experimental data.¹² In comparison to the case of methane, we find that poly(alkyl acrylates) swell significantly in the presence of CO₂. Furthermore, MD simulations allowed us to assess the dynamic properties of the system. Our simulations confirm the experimental^{11,12} observations that the diffusion coefficients of methane and CO₂ in amorphous poly(alkyl acrylates) increase with increasing side-chain length. Furthermore, our simulations establish a quantitative relation between the gas diffusion coefficient and the polymer fractional free volume.

2 Simulation details

We carried out molecular simulations to understand the structural features, and the sorption and diffusion behavior of methane and carbon dioxide in amorphous poly(alkyl acrylates) in the temperature range of 300–600 K. The simulation model and method were similar to those used in our previous study.³³ GCMC simulation is a statistical method suited to quantify the gas sorption in porous materials and MD simulations allow one to probe the dynamic behavior of the system. We performed GCMC simulations using RASPA⁶¹ package and MD simulations were carried out using LAMMPS⁶² package. The model system of atactic poly(alkyl acrylate) was composed of 30 flexible main-chains, each having 80 carbon atoms on the backbone (Fig. 1). Furthermore, the flexible side-chains of poly(alkyl acrylates) contained methyl, ethyl, n-butyl, and n-decyl groups as the alkyl substituents. A united atom representation was used for CH₄, CH₃, CH₂, and CH groups (Figure S1, Supporting Information). The transferable potentials for phase equilibria united-atom (TraPPE-UA)⁶³ force field was used to model the polymer and the methane molecules. Note that each bond in the polymer was considered to be flexible.^{64,65} The EPM2⁶⁶ force field (rigid version) was used to model the carbon dioxide molecules. The potential forms of such as the torsional interaction used in our simulations along with the corresponding parameters are presented in Tables S1 and S2. More details can be found in our previous work.³³ In addition, Fig. 2 shows the torsional energy profiles^{63,67,68} of all the dihedrals considered here for the poly(alkyl acrylate) system.

The initial configurations for the poly(alkyl acrylates) are obtained using the Packmol software.⁶⁹ By using MD simulations, the initial configurations in the molten state were rapidly cooled to the required condition (1 ns MD) and then relaxed for 15 ns in the *NPT* ensemble (see below). The periodic box size was 5.3–6.5 nm at 300–600 K and 1 atm. A hybrid MC/MD simulation method was used to evaluate the gas sorption isotherms. First, GCMC computations were carried out in the grand canonical statistical ensemble by imposing chemical potential μ , volume V , and temperature T .

Widom insertion is used to obtain the sorbate chemical potentials. Note that a rigid framework was employed in all GCMC simulations. These simulations were run for at least 10^7 Monte Carlo steps. Then, MD simulations were carried out in the *NPT* ensemble, where the system is allowed to swell for 1 ns. The velocity Verlet algorithm was adopted to integrate the equations of motion. A time step of 1 fs was used for all MD calculations. The desired temperature and pressure were maintained using the Nosé-Hoover thermostat and barostat, respectively. The relaxation times of Nosé-Hoover thermostat and barostat were 0.1 ps and 1 ps, respectively. A 15.0 Å nonbond cutoff distance was used, and the Ewald summation and the particle-particle particle-mesh methods were used for calculating the long-range Coulombic interactions in the GCMC and MD studies, respectively. A precision of 10^{-5} was used for the calculations of the electrostatic interactions. The above procedure is repeated 15–22 times, and last few cycles are examined to calculate the sorption isotherms (see below). In our simulations, good statistics were obtained by averaging over six independent trajectories.

The radial distribution function (RDF)⁷⁰ for species β around α was estimated as: $g_{\alpha-\beta}(r) = (1/(4\pi\rho_\beta r^2))(dN_{\alpha-\beta}/dr)$, where ρ_β is the number density of β particles and $dN_{\alpha-\beta}$ is the average number of β particles between the distance of r and $r + dr$ from a central α particle. The solubility constant S is estimated from the limiting slope of the sorption isotherm: $S = \lim_{P \rightarrow 0}(c/P)$, where c is the concentration and P is the pressure. To estimate the dynamical properties such as the self-diffusion coefficient D_s , the last configurations from the hybrid MC/MD simulations were further used in the *NVT* ensemble MD simulations (15 ns). The self-diffusion coefficient is calculated by the Einstein relation: $D_s = \lim_{t \rightarrow \infty}(1/6t)\langle|\vec{r}(t) - \vec{r}(0)|^2\rangle$, where $\vec{r}(t)$ is the particle position at time t and $\langle|\vec{r}(t) - \vec{r}(0)|^2\rangle$ is the mean square displacement (MSD) of the particle.

3 Results and discussion

3.1 Structure of poly(alkyl acrylates)

In order to understand the gas sorption and diffusion behavior in poly(alkyl acrylates), it is very important to analyse the structural properties of the polymer. Fig. 3 displays the simulation results (open symbols) and the corresponding experimental data⁸ (closed symbols) for the specific volume of poly(alkyl acrylates) versus temperature. We find a good agreement between the simulation results and the experimental data. Also, our results are in good agreement with the previous simulation data.⁵⁵ At a given temperature, the specific volume of the poly(alkyl acrylate) system increases with side-chain length. The specific volumes are in the ranges of about 0.85-1.0 cm³/g and 1.0-1.4 cm³/g at 175 and 600 K, respectively. The specific volume of the poly(alkyl acrylate) system increases linearly with temperature, but with a change in slope at the glass transition temperature. The experimental glass transition temperatures are about 270, 260, and 228 K for PMA, PEA, and PBA, respectively.^{7,8} The simulated glass transition temperatures are about 340, 319, 296, and 269 K for PMA, PEA, PBA, and PDA, respectively. The simulated glass transition temperatures are higher than the experimental ones in all cases. This may be due to various factors such as force-field limitations and/or differences in molecular weights,⁷¹ tacticities,⁷² and cooling rates^{71,73} of simulated and experimental samples. Furthermore, Figure S2 shows the time evolution of the specific volumes of poly(alkyl acrylates) resulting from the MD simulations (*NPT*) after annealing. We see that the relaxation steps used here can greatly speed up the equilibration process. Also, our results show that the glass transition temperature decreases with increasing side-chain length of poly(alkyl acrylate). This is probably due to the fact that the shielding of the polar ester (-COO-) groups increases with side-chain length. Fig. 4 shows the RDFs between oxygen atoms (double bonded) and carbon sites in the poly(alkyl acrylate) system. For simplicity, interactions between atoms in the same bond, angle, or dihedral are not shown. It is clear from this plot that the shielding of the oxygen increases with side-chain length.

For example, both in the glassy and rubbery states of the polymer, the peaks in the range of about 4-5 Å increase in magnitude as the side-chain length increases.

The empty space of the polymer matrix accessible to a probe molecule was estimated using the Poreblazer package.⁷⁴ We used helium ($\sigma_{\text{LJ}} = 2.58$ Å and $\epsilon_{\text{LJ}}/k_{\text{B}} = 10.22$ K) as the probe for the calculation of the free space in the polymer matrix.^{33,74,75} The void fraction was estimated as the ratio of the internal free space to the total volume of the polymer material. Fig. 5 shows the void fraction of the poly(alkyl acrylate) system versus temperature. The void fraction increases linearly with temperature, but with a change in slope at the glass transition temperature. Furthermore, Figure S3 shows the maximum pore diameter and the pore limiting diameter of the poly(alkyl acrylate) system versus temperature. The maximum pore diameter is associated with the largest cavity available in the polymer matrix. Note also that the molecules that are smaller than the pore limiting diameter can freely diffuse in the material without overlapping one or more framework atoms. We see that similar to the cases of specific volume and void fraction, both the maximum pore diameter and the pore limiting diameter increase with temperature.

In all cases, the void fractions are $\lesssim 0.05$ below the glass transition temperatures. At 600 K, the void fractions are in the range of about 0.2-0.3. Our results show that the void fraction increases with increasing side-chain length of poly(alkyl acrylate) above the glass-transition temperatures. Thus the void fractions increase with increasing shielding of the polar ester groups in the polymer. Note, for example, that the lack of any polar group as in polyethylene³³ resulted in a void fraction of about 0.3 at 600 K. However, an opposite trend is obtained in the glassy state of the poly(alkyl acrylates). Furthermore, a similar behavior was observed for the maximum pore diameter and the pore limiting diameter of the poly(alkyl acrylate) system. In all cases, the maximum pore diameters and the pore limiting diameters are about 4 Å and 1 Å, respectively, below the glass transition temperatures. At 600 K, the maximum pore diameters and the pore limiting diameters are in the ranges of about 6-8 Å and 2-2.5 Å, respectively. Note that the penetrant sizes are about 3.73 Å for CH₄ and 3.03 Å for carbon dioxide

(5.33 Å in long axis). Therefore, it is clear that these penetrants cannot freely diffuse in the material without overlapping one or more framework atoms. As an aside, it can be seen (Figures S4-S5) that the main-chain dynamics is slower than the side-chain dynamics. Note, however, that the side-chain motion was relatively slower in the polymer due to the presence of the local nanodomains.⁶ We did not observe local nanodomains in our samples at least within the simulation time of tens of nanoseconds. Typically the homogeneous crystal nucleation may require several hundreds of nanoseconds.⁷⁶ We see that the initial ballistic regime (slope of 2) is generally followed by the subdiffusive Rouse regime (slope of 0.5). However, a plateau region is identified between the short time ballistic motion and the subdiffusive Rouse behavior in the vicinity of the glass transition, which may be attributed to the cage effect.⁷⁷ In all cases (300–600 K range), MSD increases with side-chain length, which may be attributed to the effect of free volume upon chain mobility. In short, above the glass transition, both free volume size (see, e.g. Fig. 5) and polymer chain mobility increase with side-chain length.

3.2 Sorption of CH₄ and CO₂ in poly(alkyl acrylates)

Sorption isotherms of CH₄ and carbon dioxide in amorphous poly(alkyl acrylates) were obtained using MC/MD simulations. Figure S6 shows the effects of polymer swelling and framework flexibility on the sorption isotherms. It can be seen that the equilibrium is achieved in less than about 20 MC/MD cycles. Our results show that the polymer swelling becomes more pronounced, especially in the case of sorption of CO₂ at high pressures (Figures S7-S8). For example, the samples are swollen up to about 1% and 10% for methane and carbon dioxide, respectively, under studied conditions. A significant swelling occurs probably due to the greater interaction between carbon dioxide and the polar ester groups in the polymers. Note, for example, that the lack of any polar group as in polyethylene^{33,78–81} resulted in negligible swelling under similar conditions. However, polyethylene exhibits significant swelling at high pressures.^{78–81} In general, the swelling of poly(alkyl acrylates) increases with increasing pressure and side-chain length and decreases with temperature. Also, the uptake of gas

by poly(alkyl acrylates) follows the same trend as swelling (see below). The measurement of swelling in a carbon dioxide-poly(methyl methacrylate) system showed similar results.^{82,83} Theoretical models^{84–86} such as the statistical association fluid theory have been used recently for describing these experimental results.

Fig. 6 shows the sorption isotherms of CH₄ and carbon dioxide in both PEA and PDA obtained from simulations (open symbols) and experiments¹² (solid symbols) at 308 K. The simulation results are in good qualitative agreement with the experimental data. The simulation results were generally larger than the corresponding experimental values by a factor of about 2. The simulation results were also fitted using the dual-mode sorption model^{33,87,88} (lines). This model is based on two different sorption processes, ordinary dissolution (Henry’s law) and a hole-filling mechanism described by the Langmuir sorption. Furthermore, Figures S9-S10 shows the sorption isotherms of CH₄ and carbon dioxide for all studied cases. Our results show that the sorption amount is higher for carbon dioxide compared with CH₄. For example, it can be seen from Fig. 6 that the CO₂ uptake is about an order of magnitude higher than that of methane at 15 atm. This is expected due to the strong interaction of CO₂ with the polar ester groups in the polymer system. In general, the lack of any polar group as in polyethylene^{33,44,45,89–94} leads to similar uptake values for methane, but a lower uptake of CO₂. However, below its melting temperature, the polyethylene system may exhibit a markedly lower uptake of the gas molecules due to the presence of the semicrystalline phase. We have seen above that the structural properties such as the void fraction of the poly(alkyl acrylate) system increase with temperature. However, the sorption amount of methane and CO₂ decreases with temperature, indicating the exothermic nature of the sorption process. We have also seen that, for example, the void fraction increases with side-chain length in the temperature range 300-600 K. In general, a similar behavior is obtained for the sorption of methane and CO₂ as a function of side-chain length.

Fig. 7 shows the simulated solubility constants (open symbols) as a function of temperature. As in the case of sorption isotherms, our simulated solubility results are

in reasonable agreement with the experimental data¹² (closed symbols) at 308 K. By applying the van't Hoff equation ($S \sim \exp(-\Delta H_S/RT)$, where ΔH_S is the heat of solution) in the temperature range of 300-600 K, the simulated values of $-\Delta H_S$ for CH_4 and carbon dioxide were in the ranges of about 3.6–7.6 and 14.9–19.5 kJ/mol, respectively. Our results show that the values of $-\Delta H_S$ decrease with increasing side-chain length, consistent with experiments.¹² Note that the experimental heats of solution for CH_4 in PEA and PDA were about -10.0 and -8.0 kJ/mol, respectively.¹² In the case of CO_2 , the experimental heats of solution in PEA and PDA were about -14.2 and -12.1 kJ/mol, respectively.¹² We find that the solubility of methane and carbon dioxide in poly(alkyl acrylates) decreases with temperature. To gain further insight, in Figure S11 we plot the solubility constants as a function of void fraction. Our results show that the solubility of methane and carbon dioxide decreases with void fraction. This may be due to the fact that the gas-polymer interaction decreases with increasing void fraction (energetic effect). Similar solubility behavior has been reported in the case of, for example, polyethylene system.^{33,44,45,93,94} The solubility behavior may be explained based on a combination of entropic and energetic effects. For example, the solubility of small molecules such as helium in polyethylene increases with increasing temperature (or void fraction). This may be due to the fact that the hindered rotation of the probe molecule and the degree of confinement decrease with void fraction (entropic effect).

3.3 Diffusion of CH_4 and CO_2 in poly(alkyl acrylates)

The self-diffusion coefficients of CH_4 and CO_2 in amorphous poly(alkyl acrylates) were obtained using MD simulations carried out in the NVT (canonical) ensemble. Fig. 8 shows the self-diffusion coefficients of CH_4 and carbon dioxide in poly(alkyl acrylates) obtained from simulations (open symbols) and experiments^{11,12} (solid symbols) at 308 K. The simulation results are in good qualitative agreement with the experimental data. We see that an increase in the simulated main-chain length leads to a better agreement with the experimental data. However, the simulation results of PMA were

generally larger than the corresponding experimental values by a factor of about 5. We also find that the diffusion coefficients are not much affected by the tacticity of the polymers (data not shown). The results show that the gas diffusion in poly(alkyl acrylates) increases with increasing side-chain length. In general, the lack of any polar group as in polyethylene^{33,45,89,90,92–95} resulted in a higher mobility of the penetrant species. However, below its melting temperature, the polyethylene system may exhibit a markedly lower mobility of the penetrant species due to the presence of the semicrystalline phase.

Furthermore, Fig. 9 shows the self-diffusion coefficients of CH₄ and CO₂ in poly(alkyl acrylates) in the temperature range from 300 to 600 K and at 1 atm. By applying the Arrhenius equation ($D_s \sim \exp(-E_D/RT)$, where E_D is the activation energy of diffusion) in the temperature range of 300–600 K, the simulated activation energies for CH₄ and carbon dioxide in poly(alkyl acrylates) were in the ranges of about 19.4–33.2 and 15.8–25.5 kJ/mol, respectively. Our results show that the activation energies of gas diffusion decrease with increasing side-chain length, consistent with experiments.¹² Note that the experimental activation energies of diffusion for CH₄ in PEA and PDA were about 44.0 and 36.4 kJ/mol, respectively.¹² In the case of CO₂, the experimental activation energies in PEA and PDA were about 35.1 and 29.7 kJ/mol, respectively.¹² We find that the diffusion of CH₄ and carbon dioxide in poly(alkyl acrylates) increases with temperature. This is probably due to the fact that the waiting time for a penetrant molecule in a cavity before the jump decreases with temperature.^{33,34,38,40} The jump length and jump time may be determined by the chain oscillations (see, e.g., Figures S4-S5) and the cavities nearby.

To gain further insight, in Figure S12 we plot the diffusion coefficients as a function of void fraction. We see that the diffusion coefficients of CH₄ and CO₂ have an exponential relationship with the void fraction, which is in agreement with the classical free volume theory.^{41–43} The free volume theory is based on the concept that the redistribution of the free volume occasionally opens up local voids large enough into which a diffusing molecule can move. From this simple notion, it is easy to show that

the diffusion coefficient can be expressed as $D = A \exp(-B/\text{FFV})$, where A and B are constants. Using the helium void fraction as a measure of the FFV, the simulated values of A for CH_4 and carbon dioxide were in the ranges of about 4.2–8.2 and 3.1–4.3 $\times 10^{-8} \text{ m}^2/\text{s}$, respectively. The simulated values of B for CH_4 and carbon dioxide were in the ranges of about 0.27–0.36 and 0.22–0.29, respectively. In general, the values of A are dependent on the gas-polymer interaction, and the values of B are dependent on the polymer-polymer interaction.^{42,43} Also, the gas diffusion coefficients increase with both maximum pore diameter and pore limiting diameter of the poly(alkyl acrylate) system.

4 Conclusions

In this paper, we have studied the structural features, and the sorption and diffusion behavior of CH_4 and carbon dioxide in amorphous poly(alkyl acrylates) in the temperature range of 300–600 K. Here four cases were examined, namely, PMA, PEA, PBA, and PDA. The sorption isotherms were obtained using GCMC simulations, and the hybrid MC/MD approach was used to address the effects of polymer swelling and framework flexibility on the gas sorption. Also, MD simulations allowed us to assess the dynamic properties of the system. Our results show that the glass transition temperature decreases with side-chain length of poly(alkyl acrylate), consistent with experiments.^{7,8} This is due to the fact that the shielding of the polar ester groups increases with side-chain length. We see that the void fraction increases with side-chain length of poly(alkyl acrylate) in the temperature range of 300–600 K.

The simulated sorption isotherms of methane and CO_2 were in reasonable agreement with the experimental data.¹² The polymer swelling becomes more pronounced, particularly in the case of sorption of CO_2 . For example, the samples are swollen up to about 1 and 10% for methane and carbon dioxide, respectively, under studied conditions ($\leq 15 \text{ atm}$). The poly(alkyl acrylate) system shows a significant swelling probably due to the greater interaction between carbon dioxide and the polar ester

groups in the polymers. Similar to the cases of, e.g., the void fraction and the swelling, the uptake of methane and CO₂ by poly(alkyl acrylates) typically increases with increasing side-chain length. The lack of any polar group as in polyethylene generally leads to similar uptake values for methane, but a lower uptake of CO₂.^{33,44,45,89–94}

Our results confirm the experimental^{11,12} observations that the diffusion coefficients of methane and CO₂ in poly(alkyl acrylates) increase with increasing side-chain length. An important result is that the activation energies of gas diffusion decrease with increasing side-chain length. The diffusion coefficients of methane and CO₂ have an exponential relationship with the void fraction, which is consistent with the free volume theory. The lack of any polar group as in polyethylene generally resulted in a higher mobility of the penetrant species.^{33,45,89,90,92–95} This study can help understand the structural features, and gas sorption and diffusion in poly(alkyl acrylates) for their potential applications such as in adhesives, coatings, paints, textiles, cables, and carbon dioxide capture. Future studies are needed to explore the molecular-level details of the effects of high pressure and main-chain stiffness (e.g., poly(alkyl methacrylates)) on such polymer systems.

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Supporting Information

Additional details of simulation analysis are provided in the Supporting Information.

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Figure 1: Equilibrium snapshot of poly(butyl acrylate) at 300 K and 1 atm. Color code: C-site: Cyan; O: Red.

Figure 2: Torsional energy profiles of the dihedrals^{63,67,68} for the poly(alkyl acrylate) system.

Figure 3: Specific volume of poly(alkyl acrylates) as a function of temperature at 1 atm. Error bars are smaller than the size of the symbols. The lines are a guide to the eye.

Figure 4: RDFs between oxygen atoms (double bonded) and carbon sites in the poly(alkyl acrylate) system at (a) 175 and (b) 600 K.

Figure 5: Void fraction of the poly(alkyl acrylate) system as a function of temperature at 1 atm. Error bars are smaller than the size of the symbols. The lines are a guide to the eye.

Figure 6: Sorption isotherms as computed from simulations (open symbols) and the corresponding experimental data¹² (solid symbols) for methane (circles) and carbon dioxide (squares) in (a) PEA and (b) PDA at 308 K. The lines are fitting curves to the simulation data.

Figure 7: Temperature dependence of the solubility constants of (a) methane and (b) carbon dioxide in poly(alkyl acrylates). The lines are a guide to the eye.

Figure 8: Side-chain length (number of CH_x and CH_x^{et} groups in the side-chain) dependence of the self-diffusion coefficients of methane and carbon dioxide in the poly(alkyl acrylate) system as computed from simulations (open symbols) and the corresponding experimental data^{11,12} (solid symbols) at 308 K and 1 atm.

Figure 9: Temperature dependence of the self-diffusion coefficients of (a) methane and (b) carbon dioxide in poly(alkyl acrylates) at 1 atm. The lines are a guide to the eye.

TOC Graphic

Sorption and diffusion of methane and carbon dioxide in amorphous poly(alkyl acrylates): a molecular simulation study

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KEYWORDS. Polymer, sorption, molecular dynamics, Monte Carlo simulations.