# Supporting Information for "Sorption and Diffusion of Methane and Carbon Dioxide in Amorphous Poly(alkyl acrylates): A Molecular Simulation Study"

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January 23, 2020

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**Table S1:** Lennard-Jones(LJ) parameters of the poly(alkyl acrylates)[a].

| Potential form | Type | Parameters | |
|---|---|---|---|
| LJ: | | $\epsilon_{ii}$ (kcal/mol) | $\sigma_{ii}$ ($\AA$) |
| $E_{\mathrm{LJ}} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$ | $C^{cbn}$ | 0.0795 | 3.82 |
| | CH | 0.0199 | 4.68 |
| | $CH_2$ | 0.0910 | 3.95 |
| | $CH_2^{et}$ | 0.0910 | 3.95 |
| | $CH_3$ | 0.1950 | 3.75 |
| | $CH_3^{et}$ | 0.1950 | 3.75 |
| | $O^{cbn}$ | 0.1570 | 3.05 |
| | $O^{et}$ | 0.1090 | 2.80 |

[a]Martin and Siepmann, 1999; Kamath, et al., 2006; Maerzke, et al., 2009.

**Table S2:** Bonded potential forms and parameters of the poly(alkyl acrylates)[a].

| Potential form | Type | Parameters | | | |
|---|---|---|---|---|---|
| Harmonic bond: | | $k_b$ (kcal/mol/$\AA^2$) | $l_0$ ($\AA$) | | |
| $E_{\text{Stretch}} = k_b(l - l_0)^2$ | $C^{cbn}$-$O^{cbn}$ | 700.000 | 1.200 | | |
| | $C^{cbn}$-$O^{et}$ | 449.570 | 1.344 | | |
| | $C^{cbn}$-CH | 449.570 | 1.520 | | |
| | $CH_x$-$CH_y$, $CH_x$-$CH_2^{et}$ | 449.570 | 1.540 | | |
| | $CH_x^{et}$-$O^{et}$ | 449.570 | 1.410 | | |
| Harmonic bend angle: | | $k_\theta$ (kcal/mol/rad$^2$) | $\theta_0$ (deg) | | |
| $E_{\text{Bend}} = k_\theta(\theta - \theta_0)^2$ | CH-$C^{cbn}$-$O^{et}$ | 35.074 | 111 | | |
| | $CH_x$-CH-$CH_y$, $CH_x$-CH-$C^{cbn}$ | 62.100 | 112 | | |
| | $CH_x$-$CH_2$-$CH_y$, $CH_x$-$CH_2$-$CH_2^{et}$ | 62.100 | 114 | | |
| | $CH_x$-$CH_2^{et}$-$O^{et}$ | 35.074 | 111 | | |
| | $CH_x^{et}$-$O^{et}$-$C^{cbn}$ | 62.100 | 115 | | |
| | $O^{cbn}$-$C^{cbn}$-CH | 40.042 | 126 | | |
| | $O^{cbn}$-$C^{cbn}$-$O^{et}$ | 40.042 | 123 | | |
| Dihedral angle: | | $A_1$ (kcal/mol) | $A_2$ | $A_3$ | $A_4$ |
| $E_{\text{Dihedral}} = \sum_{n=1,4} A_n cos^{n-1}(\phi)$ | $C^{cbn}$-$O^{et}$-$CH_2^{et}$-$CH_x$ | 1.900 | -1.886 | 0.651 | 4.437 |
| ($\phi = 180°$ at trans) | CH-$C^{cbn}$-$O^{et}$-$CH_x^{et}$ | 13.019 | 3.112 | -8.338 | 1.568 |
| | $CH_x$-CH-$C^{cbn}$-$O^{cbn}$ | 2.228 | 0.284 | -0.230 | -2.331 |
| | $CH_x$-CH-$C^{cbn}$-$O^{et}$ | 2.228 | -0.284 | -0.230 | 2.331 |
| | $CH_x$-$CH_2$-CH-$CH_y$, $CH_x$-$CH_2$-CH-$C^{cbn}$ | 0.785 | -1.779 | 0.445 | 3.508 |
| | $CH_x$-$CH_2$-$CH_2$-$CH_y$, $CH_x$-$CH_2$-$CH_2$-$CH_2^{et}$ | 1.967 | -4.052 | 0.271 | 6.290 |
| | $O^{et}$-$CH_2^{et}$-$CH_2$-$CH_x$ | 1.669 | -4.239 | 0.212 | 6.120 |
| | $O^{cbn}$-$C^{cbn}$-$O^{et}$-$CH_x^{et}$ | 12.890 | -3.445 | -8.183 | -1.219 |

[a]Martin and Siepmann, 1999; Kamath, et al., 2006; Maerzke, et al., 2009.

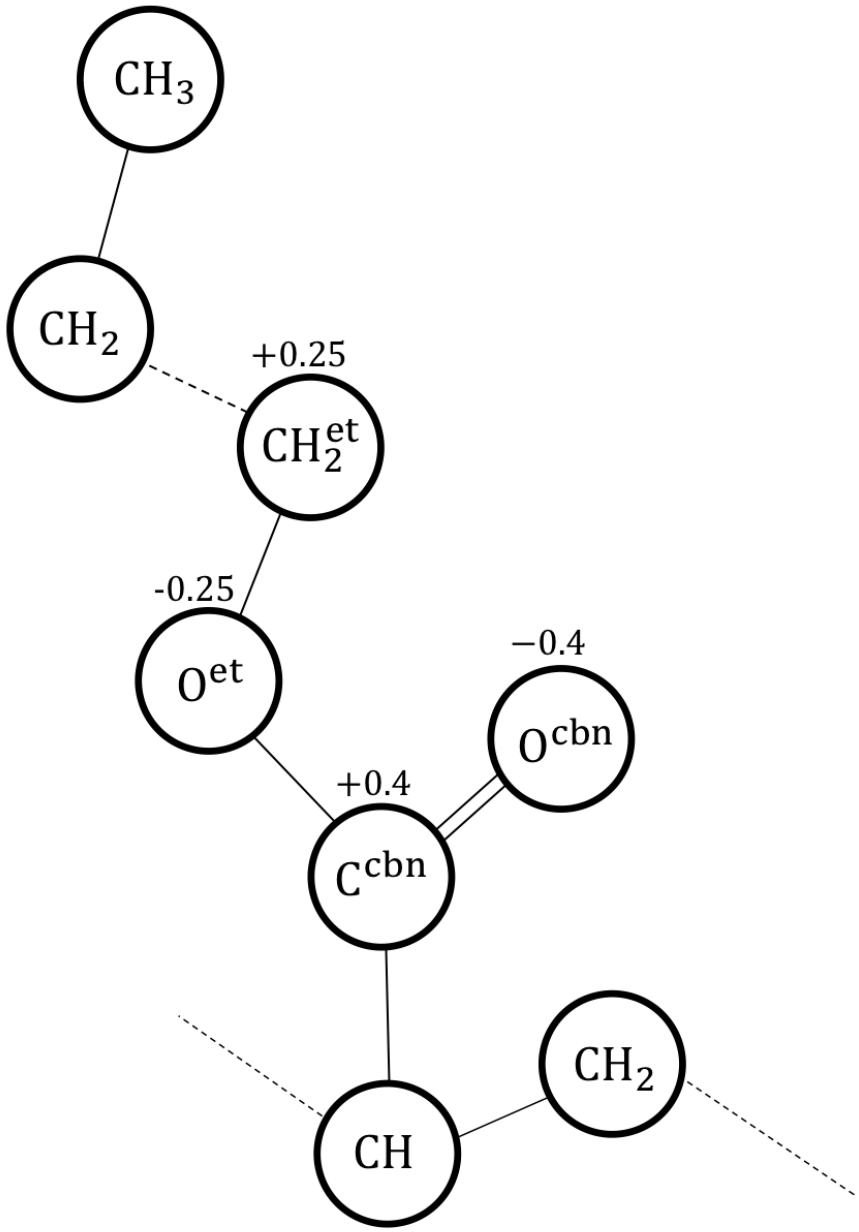


**Figure S1:** United-atom representation of the poly(alkyl acrylate) repeat unit where the various united atoms and charges are shown. Note that $CH_3^{et}$ (same charge as $CH_2^{et}$) is bonded with $O^{et}$ for PMA.

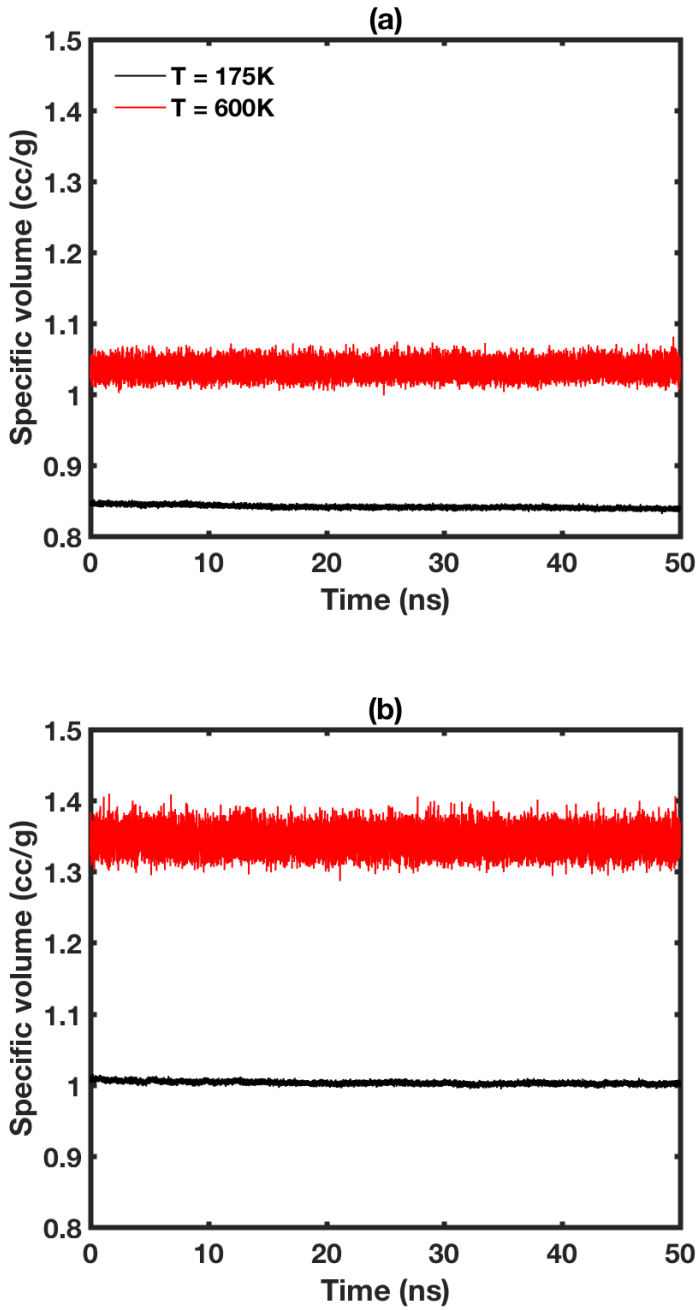


**Figure S2:** Time evolution of the specific volume of (a) PMA and (b) PDA at 1 atm. The system was rapidly (1 ns MD) brought to the required condition from a molten state at time 0.

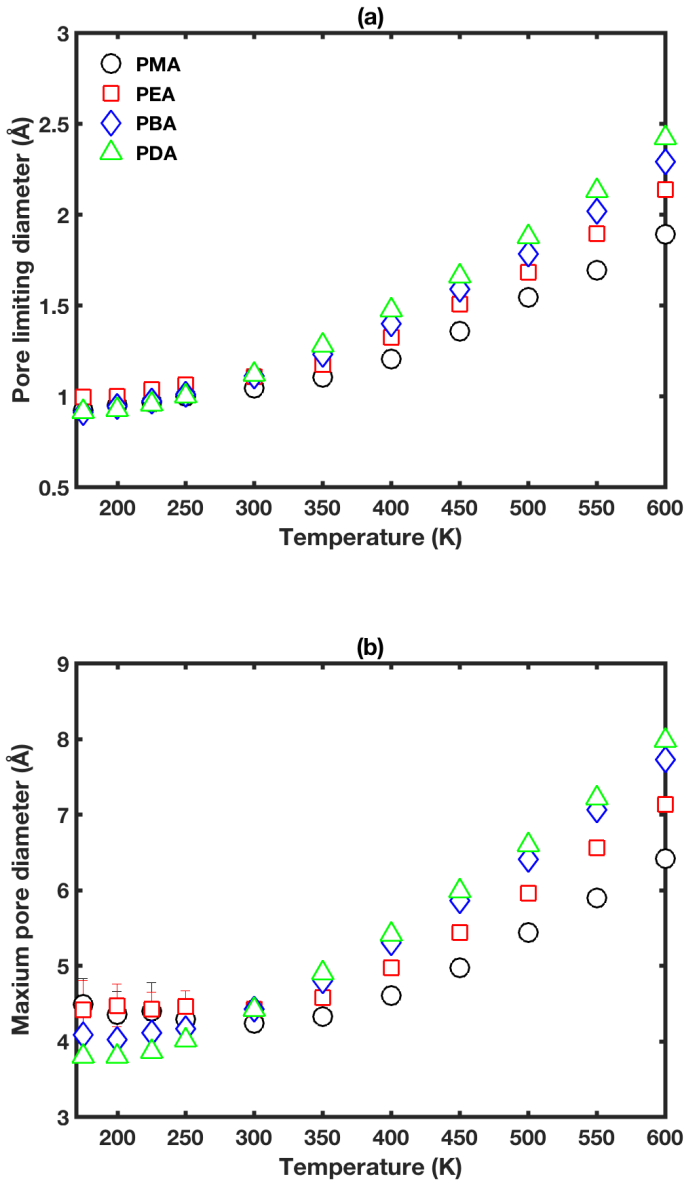


**Figure S3:** (a) Pore limiting diameter and (b) maximum pore diameter in the poly(alkyl acrylate) system as a function of temperature at 1 atm.

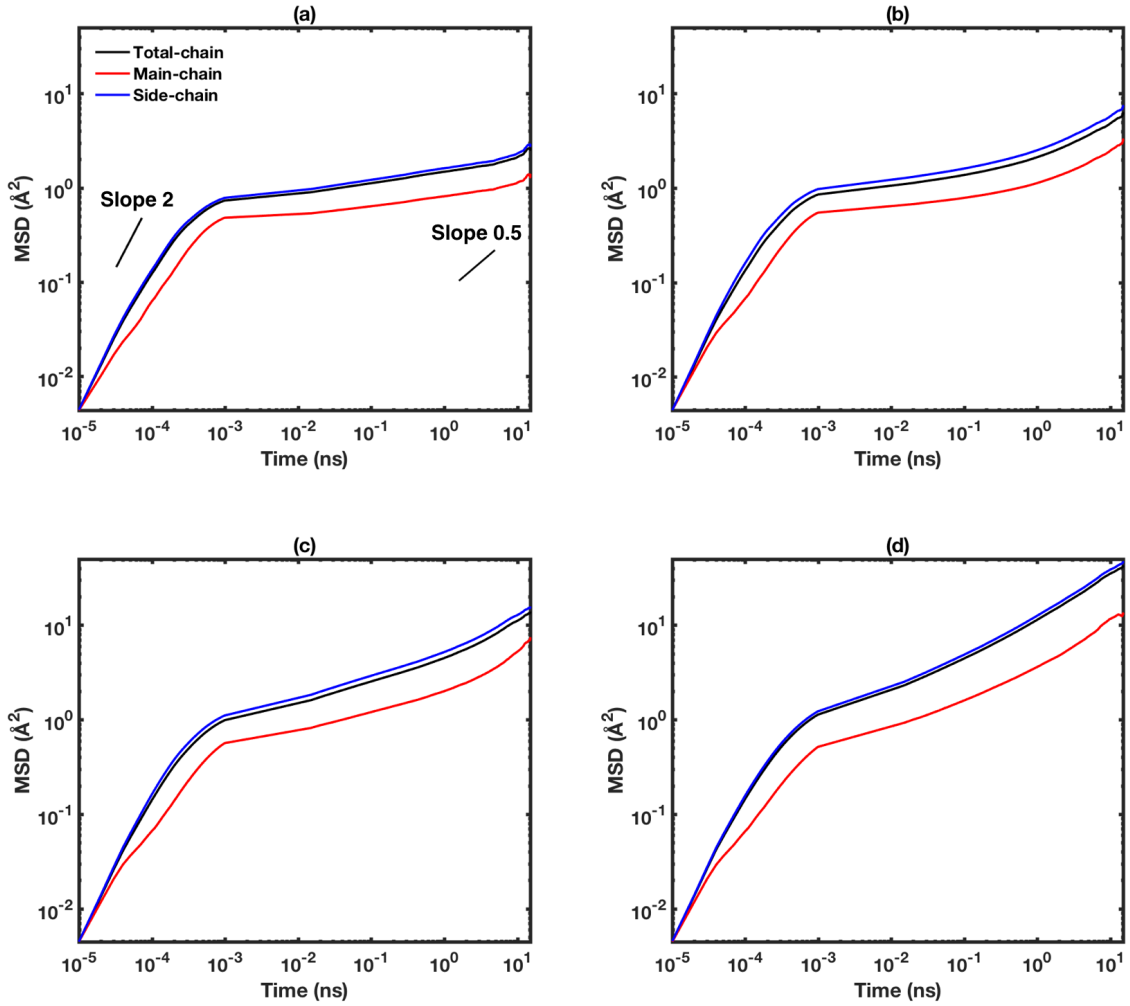


**Figure S4:** Log−log plot of the MSDs of main-chain and side-chain monomers as a function of time in the poly(alkyl acrylate) system at 300 K and 1 atm: (a) PMA, (b) PEA, (c) PBA, (d) PDA.

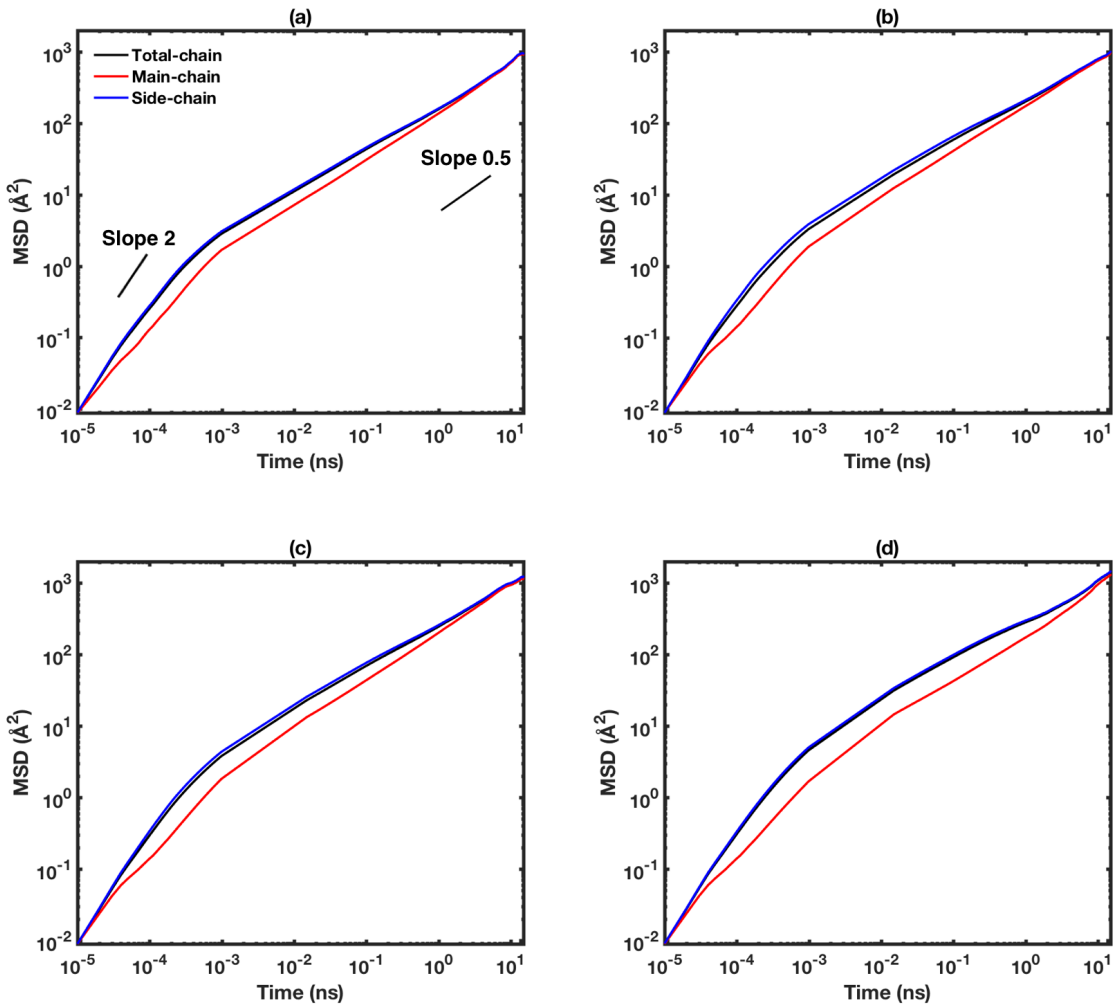


**Figure S5:** Same as in Fig. S4, but at 600 K.

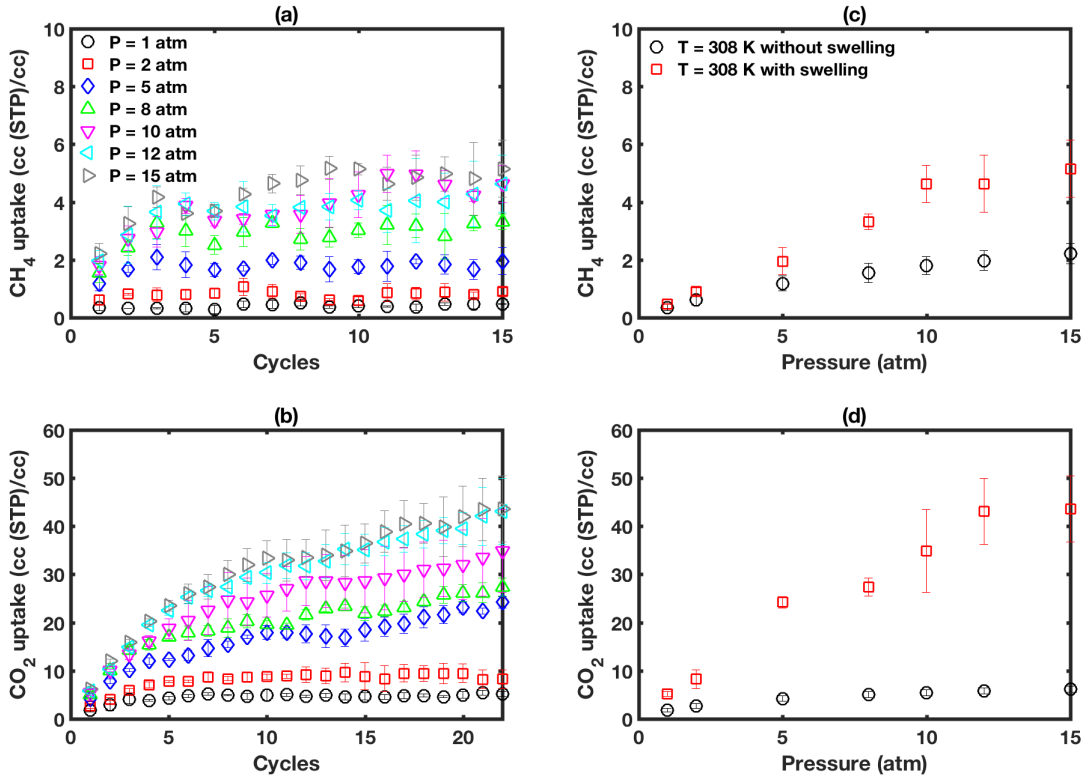


**Figure S6:** Variation of the sorption amount for (a) methane and (b) $CO_2$ in PMA as a function of the number of hybrid MC/MD cycles at 308 K. Also shown is the effect of swelling on sorption isotherms of (c) methane and (d) $CO_2$ in PMA at 308 K.

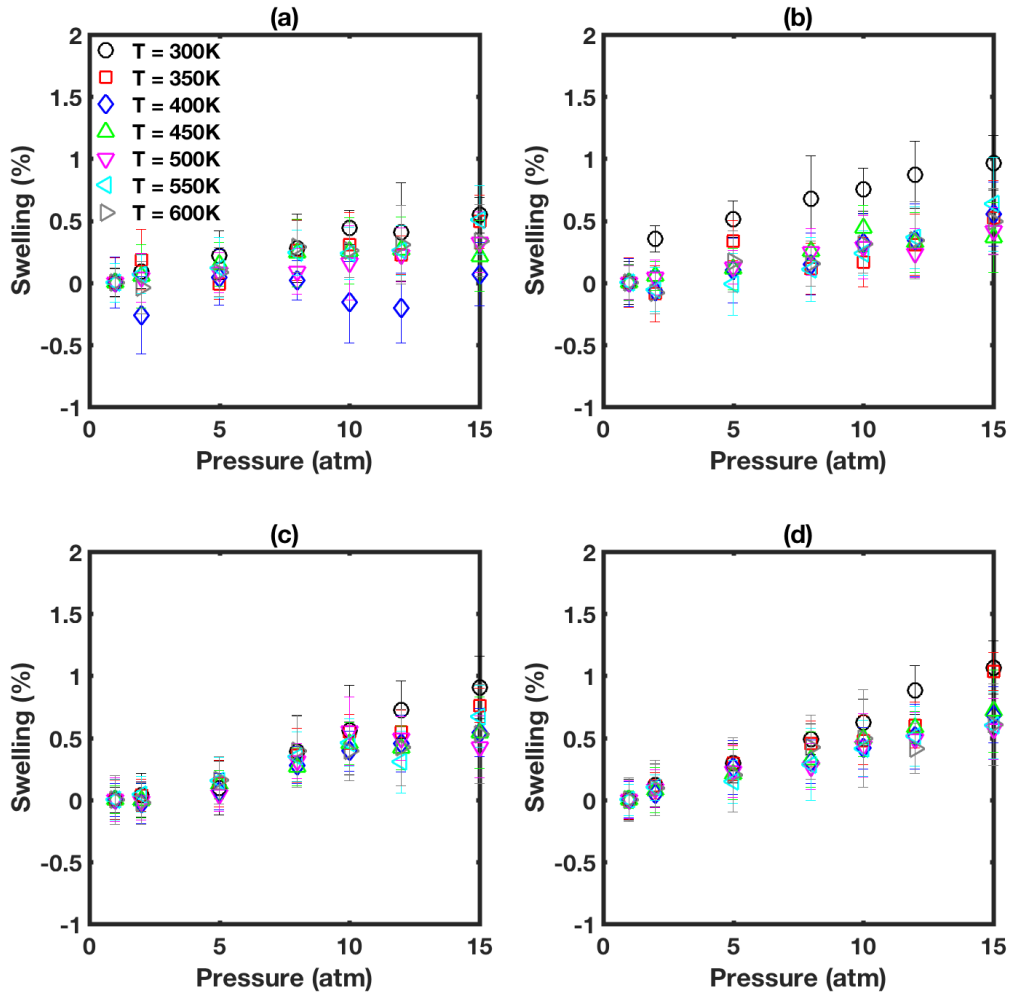


**Figure S7:** Temperature dependence of the swelling ($\Delta V/V$) of the poly(alkyl acrylates) in the presence of methane: (a) PMA, (b) PEA, (c) PBA, (d) PDA.

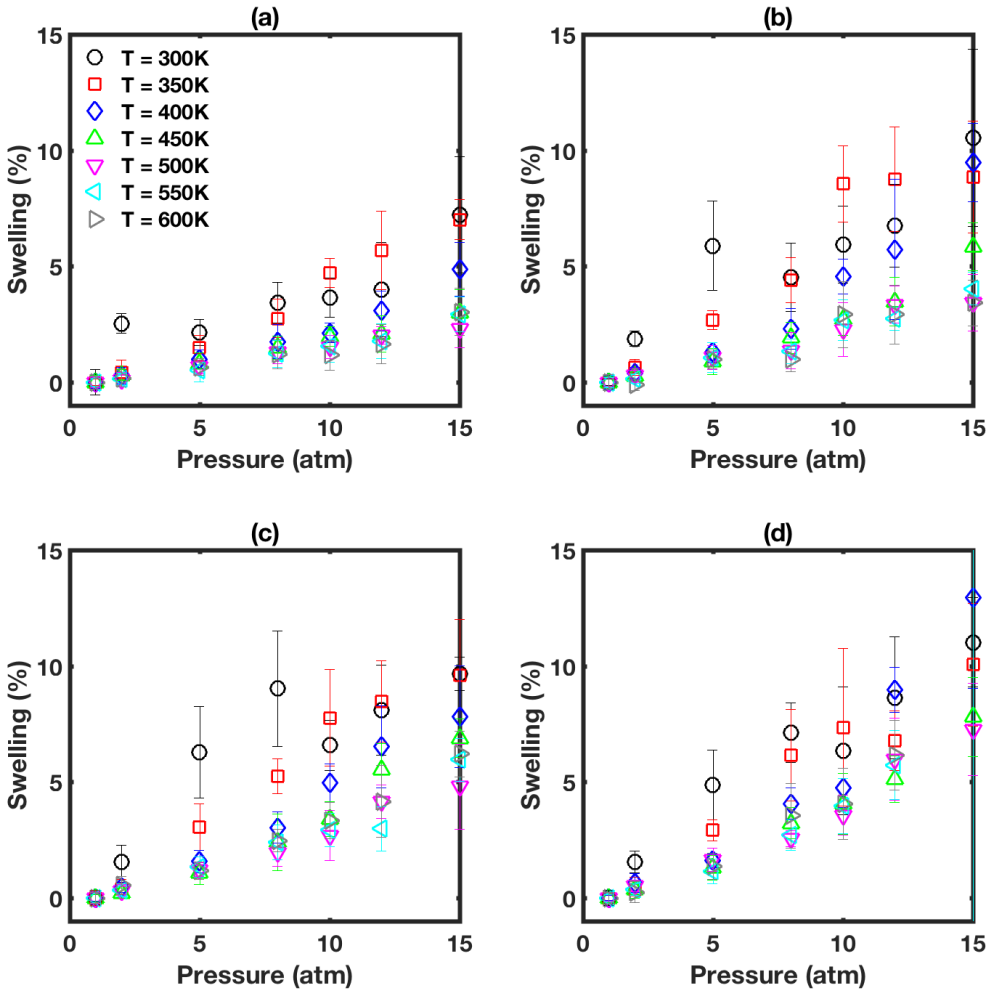


**Figure S8:** Same as in Fig. S7, but for the $CO_2$ case.

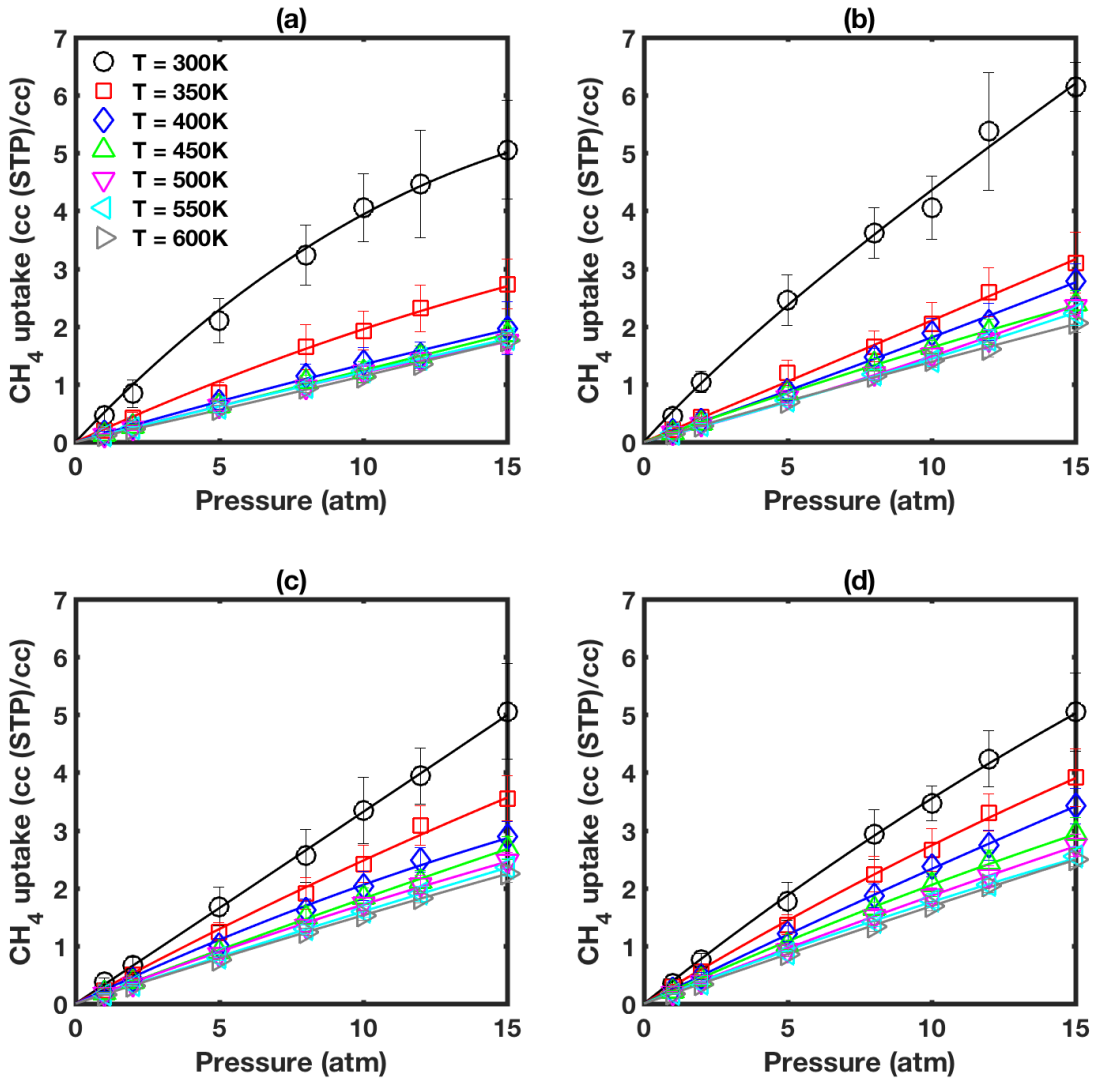


**Figure S9:** Sorption isotherms as computed from simulations (symbols) of methane in the poly(alkyl acrylate) system: (a) PMA, (b) PEA, (c) PBA, (d) PDA. The lines are fitting curves to the simulation data.

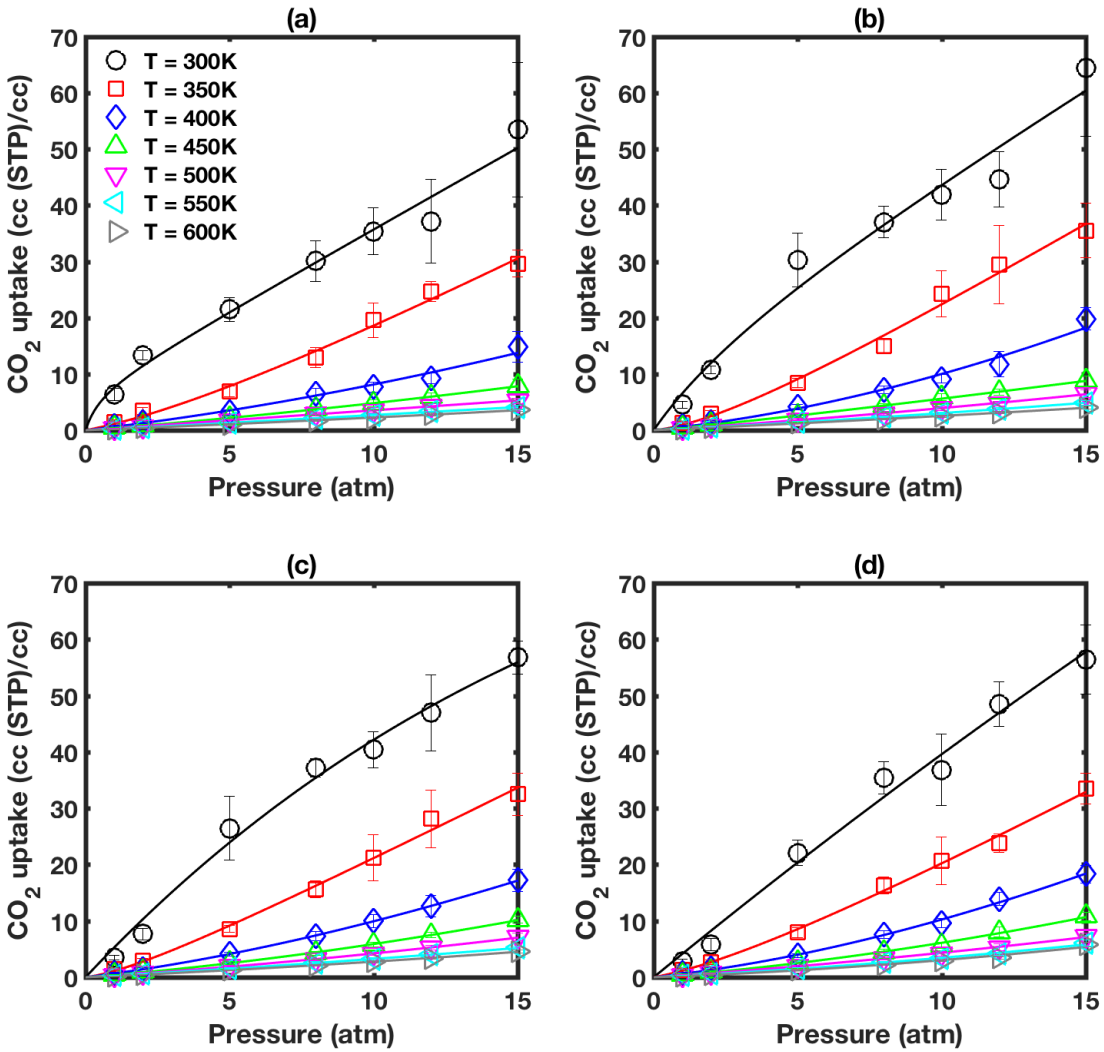


**Figure S10:** Same as in Fig. S9, but for the $CO_2$ case.

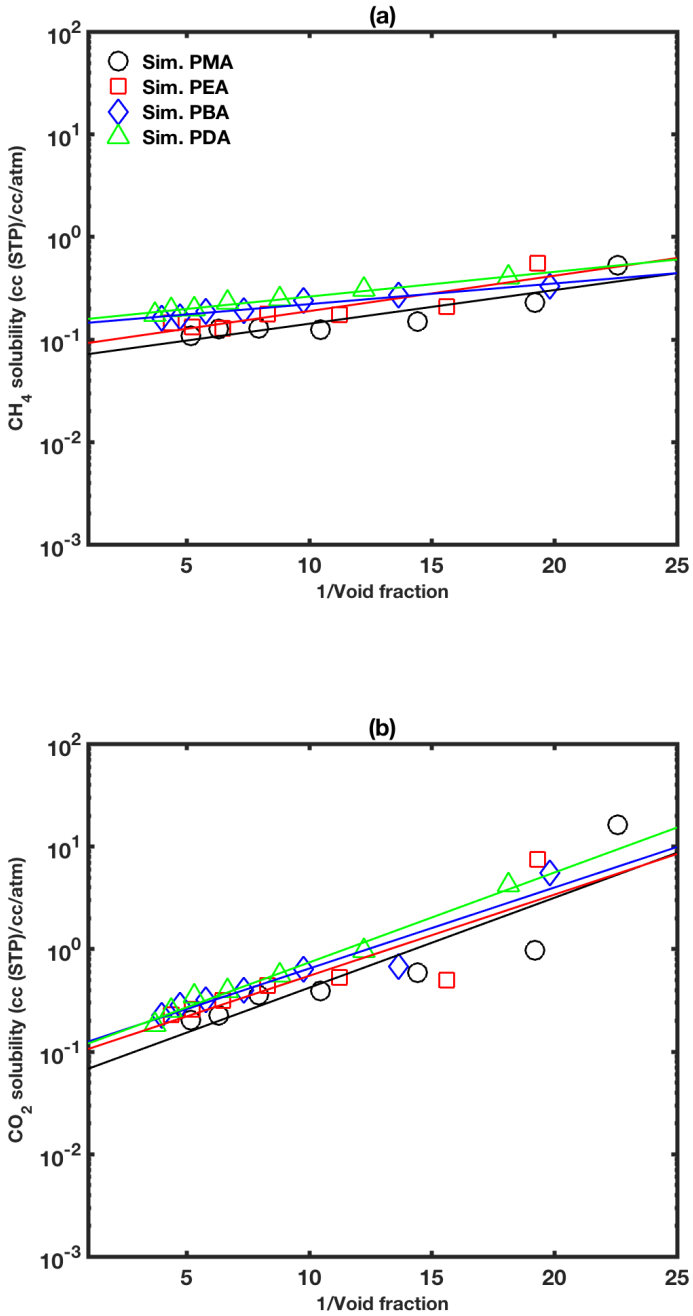


**Figure S11:** Void fraction dependence of the solubility constants of (a) methane and (b) carbon dioxide in poly(alkyl acrylates). The lines are a guide to the eye.

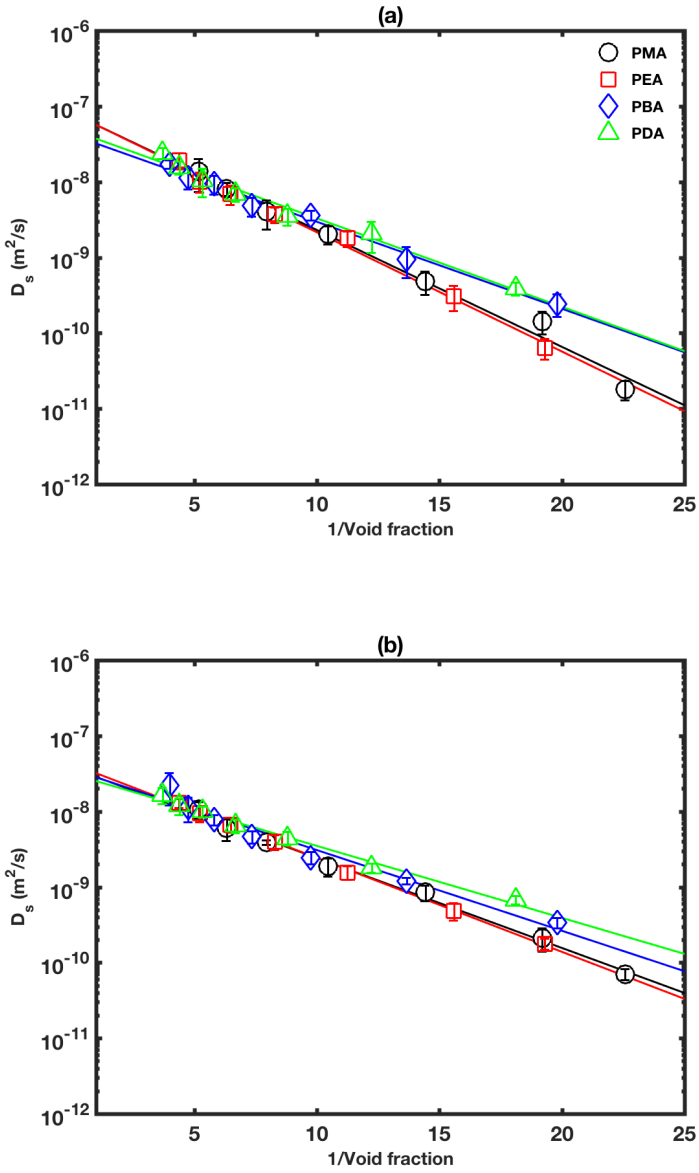


**Figure S12:** Void fraction dependence of the self-diffusion coefficients of (a) methane and (b) carbon dioxide in poly(alkyl acrylates) at 1 atm. The lines are a guide to the eye.