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Polyethylene Glycol (PEG) in a Polyethylene (PE) Framework: A Simple Model for Simulation Studies of a Soluble Polymer in an Open Framework

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ABSTRACT

Canonical molecular dynamics simulations are performed to investigate behavior of single-chain and multiple-chain polyethylene glycol (PEG) contained within a cubic framework spanned by polyethylene (PE) chains. This simple model is first of its kind to study the chemical physics of polymer threaded organic frameworks which are materials with potential applications in catalysis and separation processes. For a single chain 9-mer, 14-mer, and 18-mer in a small framework, the PEG will interact strongly with the framework and assume a more linear geometry chain with an increased radius of gyration R_g, compared to a large framework. Interaction between PEG and

the framework decreases with increasing mesh size in both vacuum and water. In the limit of an framework with infinitely large cavity (infinitely long linkers), PEG behavior approaches simulations results without a framework. Solvation of PEG is simulated by adding explicit TIP3P water molecules to a 6-chain PEG 14-mer aggregate confined in a framework. The 14-mer chains readily solvated and leach out of a large 2.6 nm mesh framework. There are less water-PEG interactions in a small 1.0 nm mesh framework, as indicated by a smaller number of hydrogen bonds. The PEG aggregate, however, still partially dissolves but is retained within the 1.0 nm framework. The preliminary results illustrate effectiveness of the simple model to study polymer threaded framework materials and to optimize polymer or framework parameters for high performance.

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INTRODUCTION

With over 20,000 reported structures, metal organic frameworks (MOF) are a new class of materials attractive for their very high porosity reaching ~3.0 mL/g and surface area exceeding 3000 m^2/g.[1] Application studies for storage, separation, and catalytic processes involving small molecules, e.g. H_2 and CO_2[2, 3, 4] are widely reported. In a new direction, there has been growing interest in polymers caged in metal organic frameworks (MOF) as a hybrid material with unique functional and structural properties.[5, 6, 7] Polymers in MOF was first reported by Kitagawa and co-workers[6, 8] using MOF as a sacrificial template to synthesize polymers with a unique ordered structure.[9, 10, 11] Polymerization is in situ after impregnating the MOF with monomers and the synthesized polymer chain is spread across cavities of the framework. Later developments see interest in retaining the MOF structure to obtain a hybrid composite with distinct functional properties.[12, 13, 14, 15, 16] The isolation of polymer chains and their close interaction with the framework lead to unique physical behavior that are advantageous in specific applications. For example, polyelectrolyte threaded in MOF have shown to give aqueous ion exchange performance superior to their bulk counterparts.[17, 18] An interesting aspect of this application is the solvation of the polymer threaded inside the MOF and its interaction with water or other solvent molecules. A readily soluble polymer may lead to its leaching and separation from the MOF host and would be undesirable as a heterogeneous recoverable extractant material. Covalent organic frameworks (COF) are another class of materials similar to MOF but with vertices of the framework covalently bonded to the linkers.[19] They are metal free-frameworks typically composed of atoms from C, N, O, B, and H. A few polymer threaded COF materials have also been reported.[20, 21] Flexibility of an ionic polymer within the COF has shown to be critical in providing catalytic activity of the composite material.[21] In general, a MOF or COF

with small cavities and openings can trap the polymer but may over-restrict mobility, hinder solvent-polymer interaction, and lower the activity of the polymer. These basic considerations demand optimization of polymer and framework properties including their dimensions and require a much improved understanding of polymer-solvent interaction in the presence of a framework. It will be necessary to study the behavior of this system via computer simulations at the molecular level in lieu of experiments offering similar details.

Previously, molecular simulations have been reported for polymers confined in nanotubes[22, 23, 24, 25] and between slits.[26, 27, 28] Interesting behavior, e.g. enhanced mobility, due to confinement are reported.[29] One can perhaps distinguish confinement in a MOF from other nanostructures since the openness of a 3D framework allows more degrees of freedom for the polymer guest molecule. For example, the polymer can be present in many cavities and channels in the three dimensional space, though its lateral dimension and segmental motion has partially reduced freedom. The term partial confinement has been used by Jin and Wu[30] as opposed to hard impenetrable confinement of nanotubes and slit pores. Li et al.[31] have also conducted molecular simulations to study behavior of a polymer-filler composite where the polymer is "partially confined" between immobile spherical beads at the grid points of a cubic lattice.

Many possibilities exist for pairing polymers and MOF to create new hybrid composites with various close range interactions between functional groups of the guest and the host. The behavior of a polymer inside a framework is very different to that of a bulk polymer due to *i)* isolation of chains, *ii)* restriction of polymer configurations by the framework, and *iii)* specific short range interaction with functional groups of the framework. MOF, which are composed of metal oxide/hydroxyl vertices and organic linkers, have very distinct chemical properties, they

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can also be considered as an inert host providing high porosity, high surface area, and a very uniform and ordered porous structure.

Uemura et al.[32] have reported molecular dynamics simulations of an oligomeric chain penetrating into a $[Zn_2(bdc)_2(ted)]_n$ MOF (bdc=1,4-benzenedicarboxylate, ted = triethylenediamine) with qualitative comparison to AFM experiments. For the study reported here, it will useful to focus primarily on the confinement effect on the polymer by the MOF host by treating the framework as an inert host without chemical or electrostatic interactions. We perform simulations with a model that accounts for the most basic interactions of van der Waals (vdW), exclusion, between the polymer and the framework, and remove the more specific "chemical" interactions arising from special co-ordination or distribution of charges. To avoid the directional interactions of metal centers, we choose a metal-free framework with neutral phosphorous atom as corner atoms where the linkers meet. Phosphorous is chosen since it would be six-coordinated for a particular valency with charge adjustment. The phosphorous atom loses all its chemical character and is simply a Lennard Jones sphere with size and energy parameters of a phosphorus atom. This choose of metal-free framework model is closer to the class of covalent organic frameworks (COF) which are metal-free framework materials.[20, 21] The linkers of MOF and COF may contain phenyl rings, carboxylic acids, and other groups. Phenyl groups can rotate and lead to variations in confinement while carboxylic acid can interact with water via hydrogen bonding. To avoid these effects in the first study of polymers in framework, we choose polyethylene linkers with simply Lennard Jones interactions. Furthermore, a cubic framework is constructed for convenient visualization and analysis of the confinement and solvent effects. Following this approach, a cubic metal-free framework composed of polyethylene linkers connected by Lennard Jones (phosphorous) atoms has been created. The polyethylene linkers are

methylene chains represented by Lennard Jones atoms with parameters from those of carbon and hydrogen. This construction drastically differs from constituents of a MOF or COF, but can serve as a simple model to understand the behavior of a polymer chain confined in the open porous framework.

Perhaps, the most interesting feature of polymers threaded frameworks is its behavior in a solvent with duality of homogeneous and heterogeneous character. Polymers are dissolved by the solvent within the framework but the composite material can be phase separated from the solvent. It will be more feasible to simulate solvation of polymers in the simple framework model using explicit solvent molecules.

In order to address solvation effects, polyethylene glycol (PEG) equivalent to polyethylene oxide (PEO), is used as the polymer model. PEG is soluble in water except when molecular weight is very high in the order of thousands. It consists of both hydrophobic and hydrophilic components. Therefore it will lead to interesting behavior inside or outside the cubic PE framework and respond differently in solvent or solvent-free environment.

Here we report molecular dynamics simulations studies of a polyethylene glycol polymer in a cubic polyethylene framework. Radius of gyration, shape, and other structural parameters are computed. Polyethylene glycol polymers of three different lengths and framework of three different sizes are simulated. In the limit of a very large framework with very large cavities and windows, the behavior of the polymer will approach the behavior of a free polymer or a polymer in solution. Explicit water molecules are introduced to investigate solvation effects in different dimensions of polymer and framework. In addition to simulation of a single chain polymer in a framework, multiple chains simulations are performed to investigate the interaction of solvent

with an assembly of chains inside a framework. The following sections provide a detailed description of the model, computational method, results, discussion, and conclusions.

MODEL AND SIMULATION DETAILS

Polymer

As a starting configuration of a simulation, a single polyethylene glycol (PEG) chain was inserted randomly into the three-dimensional space of the framework. Different lengths of PEG composed of n monomers are used with n = 9, 14, and 18 having corresponding fully stretched lengths of 4.21, 6.39, 8.12 nm, as shown in Illustration 1. The parameters of PEG were taken from the CHARMM35 force field revised by Lee and coworkers[33] with methyl terminating groups at the end of a chain instead of $-CH_2OH$ terminating groups. All bonded and non-bonded intramolecular interactions for PEG are included.
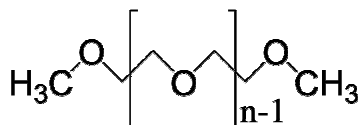

Illustration 1. Molecular structure of PEG.

Framework

The cubic framework model is constructed by linear chains of methylene $-(CH_2)_n-$ repeat units connected at 6-coordinated Lennard-Jones vertices, as shown in Figure 1. Lennard-Jones parameters of carbon and hydrogen are used for the polyethylene linkers whereas those of phosphorus are used for the vertices, as tabulated in Table 1. Lennard-Jones parameters from CHARMM35 ether force field were adopted for the framework. The interaction between frameworks and guest molecules were described by Lennard-Jones interactions as follows,

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{1}$$

Three frameworks with different window sizes, 1.0, 1.5 and 2.6 nm, are used and denoted as FR1, FR2, and FR3, respectively. The frameworks are all large enough for water to diffuse freely but have different impacts on polymer behavior depending on their characteristic lengths. Since the focus is on the polymer and the framework is viewed as an inert host, all components of the framework are fixed (frozen) at ideal initial positions throughout all simulation runs. MOF simulations with framework frozen at crystallographic positions have been used successfully in the literature.[34, 35, 36]

Water Solvent

The molecular dynamics (MD) simulations were carried out in explicit TIP3P water model[37] and in vacuum. The number of water molecules used ranges from 2218 to 5411 depending on size of simulation boxes set up for FR1, FR2 and FR3, as tabulated in Table S1 together with other simulation parameters. The interaction between polymer and water were described by Lennard-Jones and Coulombic interaction. MD simulations for single PEG chain in water and in vacuum without frameworks were conducted as controls of polymer behavior in absence of a framework. All MD simulations were performed using GROMACS software package.[38] The integration time step was set to 2 fs. The temperature for polymers and water was maintained at 300 K using the V-rescale thermostat with a coupling time constant of 100 fs. The long-range interactions were computed using the particle mesh Ewald method.[39, 40] The Lennard-Jones interactions were calculated using a cutoff of 1.2 nm.
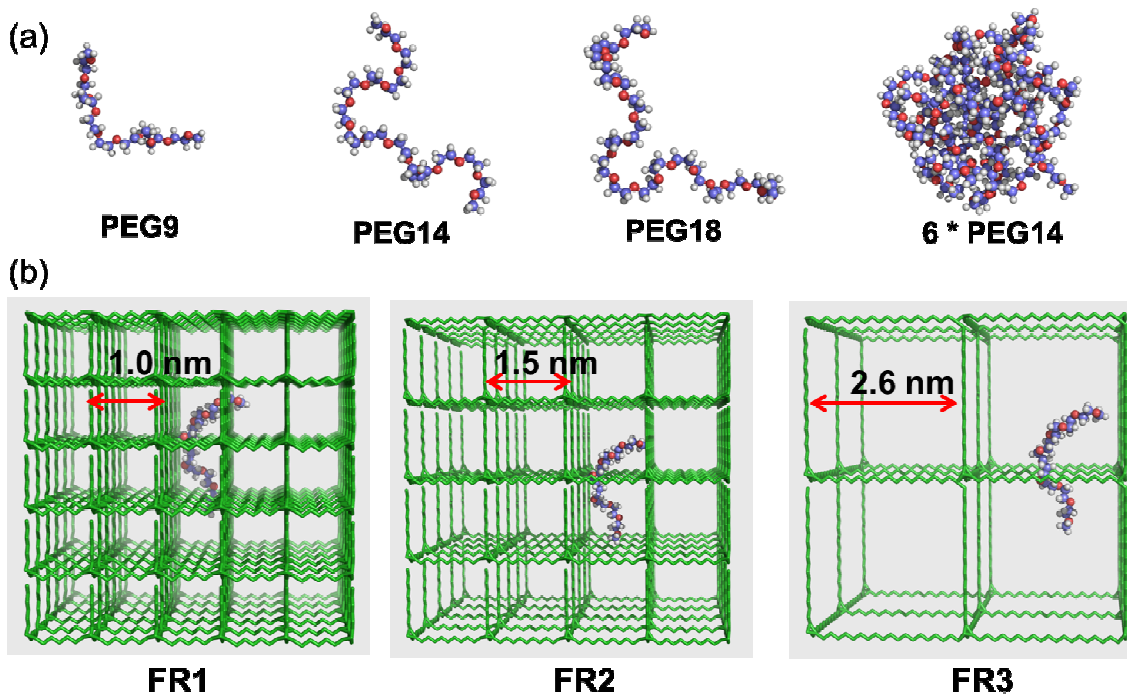
Figure 1. (a) Polyethylene glycol chains simulated. (From left to right: single chain of 9-mer, 14-mer, 18-mer, and six chains of 14-mer PEGs. Oxygen, carbon, and hydrogen atoms are in red, blue, and white, respectively). (b) Model frameworks constructed from linear $-(CH_2)_n-$ repeating units. Hydrogen atoms of the framework are hidden for easier visualization. The frameworks are denoted as FR1, FR2 and FR3 with mesh spacing of 1.0, 1.5, and 2.6 nm, respectively.

Table 1. Lennard-Jones parameters of model atoms according to CHARMM35.

	ε (kJ/mol)	σ (nm)
C	0.234	0.358
H	0.146	0.239
O	0.418	0.294
P	2.448	0.383

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RESULTS AND DISCUSSION

PEG configurations

Representative structures of PEG in vacuum and bulk water are shown in the 1st column of Figure S1. The conformation of a single chain in a good solvent is a self-avoiding walk of thermal blobs[41] while the conformation in vacuum is a collapsed globular shape. The more elongated configuration of the polymer chain in water can be quantitatively represented by the radius of gyration R_g calculated to be 0.61 nm in water compared to 0.45 nm in vacuum. The shape anisotropy κ^2 used to quantitatively describe the shape of the PEG is defined as

$$\kappa^2 = \frac{3}{2}\frac{\lambda_x^4 + \lambda_y^4 + \lambda_z^4}{(\lambda_x^2 + \lambda_y^2 + \lambda_z^2)^2} - \frac{1}{2}, \tag{2}$$

where λ_x^2, λ_y^2 and λ_z^2 are the eigenvalues of the radius of gyration tensor, which has been explicitly addressed by Šolc.[42, 43] The value of κ^2 is bounded between 0 when it is spherical and 1.0 when it is linear.

Figures 2(a) and 2(b) shows how configurational averages R_g and κ^2 vary for PEG of three different lengths (PEG-9, PEG-14, PEG-18) in frameworks of three different sizes (FR1, FR2, FR3) in water and in vacuum. Also located in Figures 2(a) and 2(b) for reference are the values of R_g and κ^2 for PEG in vacuum and water without the presence of a framework.

When the mesh size of framework is much larger than the size of the polymer chain, behavior similar to a polymer free of confinement is expected, and can be verified by comparing the values of R_g and κ^2 between that of FR3 (2.6 nm window) and without framework. This is observed for the solvated polymer (all cases of PEG-9, PEG-14, PEG-18). However, some influences of FR3 still exist in vacuum with R_g^2 and κ^2 values slightly different from those in absence of a framework. Solvated polymer can be fully detached from a large framework

whereas in vacuum the polymer is still attracted to part of the framework by van der Waals forces which are more concentrated at vertices of the cubic grid where the polyethylene linkers meet. As expected for confinement effects, the framework has a large effect for the small framework (FR1) with the largest values of R_g and κ^2, indicating the distortion from its natural framework-free configurations. The impact of the framework is also larger on a long polymer. For PEG-18, there are larger differences in R_g and κ^2 between FR1 and without framework, as compared to the shorter PEG chains. Relevant impacts of the framework can be judged by a scaling of mesh size with characteristic lengths of the PEG, such as R_g in absence of framework or fully stretched polymer length which are compiled and listed in Table S2 and Table S3 for the nine pairings of PEG lengths and framework sizes.
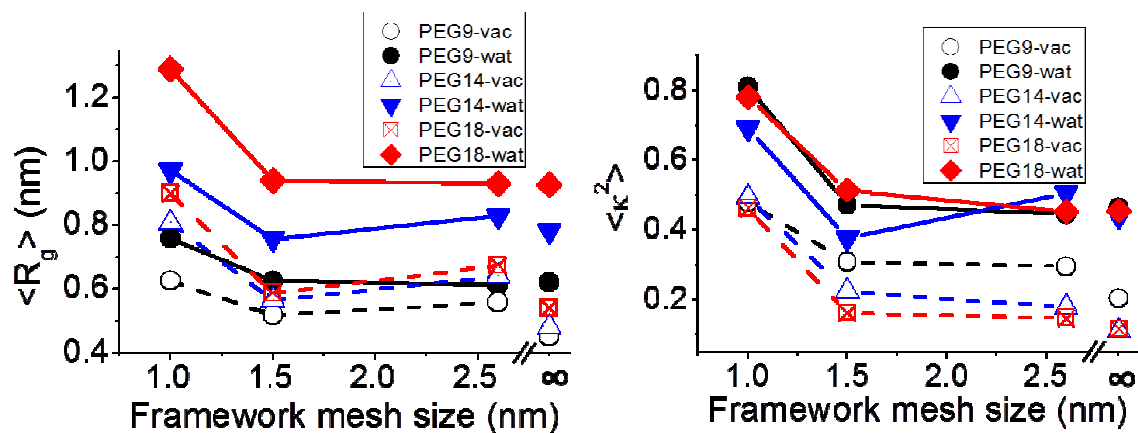

Figure 2. Radius of gyration (R_g) and relative shape anisotropy κ^2 against frameworks with different openings. The unconnected points are values of in absence of a framework, denoted as cases of FR∞ in bulk water and vacuum)

Interaction of PEG with Framework

The impact of the framework can be further analyzed in terms of the proximity of the polymer to the framework by counting the number of close contacts between atoms of PEG and the

framework. We count a contact when the atoms are less than 3.4 Å (vdW diameter of carbon atom) apart. Figure 3(a) shows the average number of PEG-Framework contacts for the nine pairs of PEG and frameworks in vacuum and in water. In general, the number of contacts increases with increasing confinement (decreasing framework size). This is clearly observed when solvent molecules are present and polymer detached from the framework. However, in vacuum, the trend is less clear with a reverse trend for PEG-14 and a non-monotonic trend (minimum number of contacts in FR2) for the cases of PEG-9 and PEG-18. The impact of solvation is also opposite for small and large frameworks with increasing contact in FR1 and decreasing contact in FR3. These intricate trends can be rationalized by the subtle variations of polymer configurations and interaction with different parts of a framework. As seen in Figure S1 for framework-free environment, the natural bending and coiling of PEG will depend on the length of the monomer unit and the bond angles along the chains. The trends of PEG-framework interactions versus framework size are more or less monotonic and uniform when number of contacts are normalized to the dynamic quantity, the end-to-end distance length of the polymer, as shown in Figure 3(b). It is noted that there is a higher concentration of atoms at the vertices of the cubic framework where linkers from three axes intersect. A polymer chain coiling around the vertex points of the framework will contact more atoms compared to lying along a polyethylene linker, as illustrated by the two typical configurations in Figure 3(c). The effect of solvation is also more clearly in Figure 3(b) with more linear uncoiled PEG configurations and in the largest framework possible detachment.
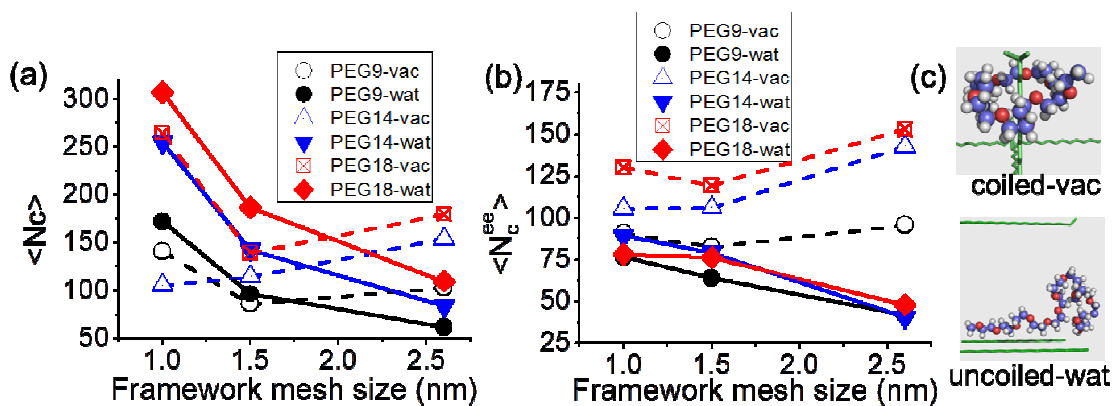
Figure 3. (a) Number of contacts between PEG and frameworks within 3.4 Å in frameworks with different frameworks. (b) The number of contacts normalized to a dynamic quantity which is the average end-to-end distance of the polymer chain. (c) Typical coiled and uncoiled configurations of a PEG chain.

Interaction energy between PEG and framework

The interaction between PEG-9 and frameworks can also be described by $\rho(E)$, the distribution of vdW energy between a PEG-9 chain and the framework in units of kJ/mol, as shown in Figure 4. Both in vacuum and in water, the vdW energy correlates linearly with the number of contacts as shown in Figure 5 in which the number of contacts is plotted against average vdW energy. For FR1 and FR2, interaction between polymer and frameworks will be weaken by solvation but at the same time the polymer has stretched and the number of PEG atoms in close proximity to framework will increase. The number of contacts of PEG-9 with framework increases from vacuum to water environment as shown in Figure 3 but without an accompanying change in vdW energy as shown in Figure 4(a), 4(b). In Figure 5, the data points for FR1 and FR2 in water environment are directly above those in vacuum. It can be rationalized that the higher number of contacts in water are slightly off the framework, i.e. the PEG-9 is less adsorbed on the framework. Behavior in FR3 in water seems to be uniquely different from FR1 and FR2. As shown in Figure 4(c) and Figure 5 there is a decrease in contacts with the addition of water

together with a decrease in the magnitude of vdW energy (less negative -91.7 kJ/mol to -51.5 kJ/mol). As discussed earlier in Figure 3, the coiled up configuration in vacuum for FR3 has a number of contacts similar to that of FR2 and the configuration will readily uncoil and partially detach leading to a significant decrease in number of contacts.
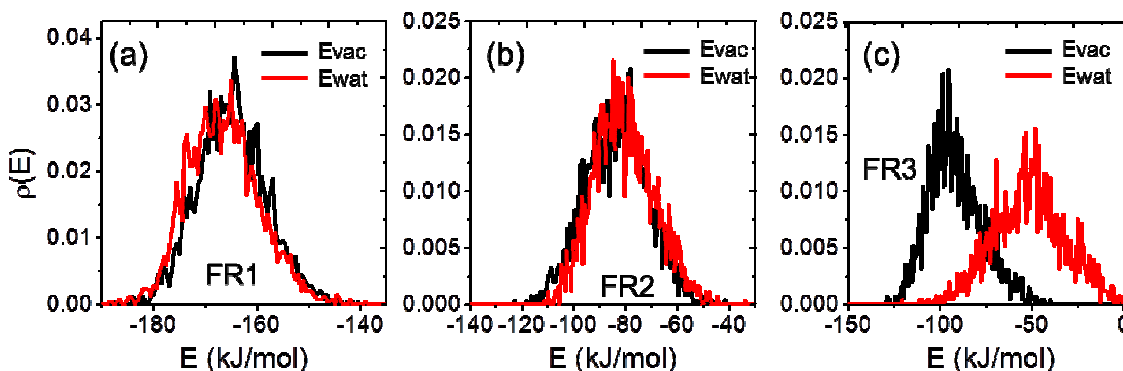

Figure 4. Distribution of van der Waals energy between PEG-9 and frameworks. The interaction energy between (a) PEG-9 and FR1; (b) PEG-9 and FR2; (c) PEG-9 and FR3.
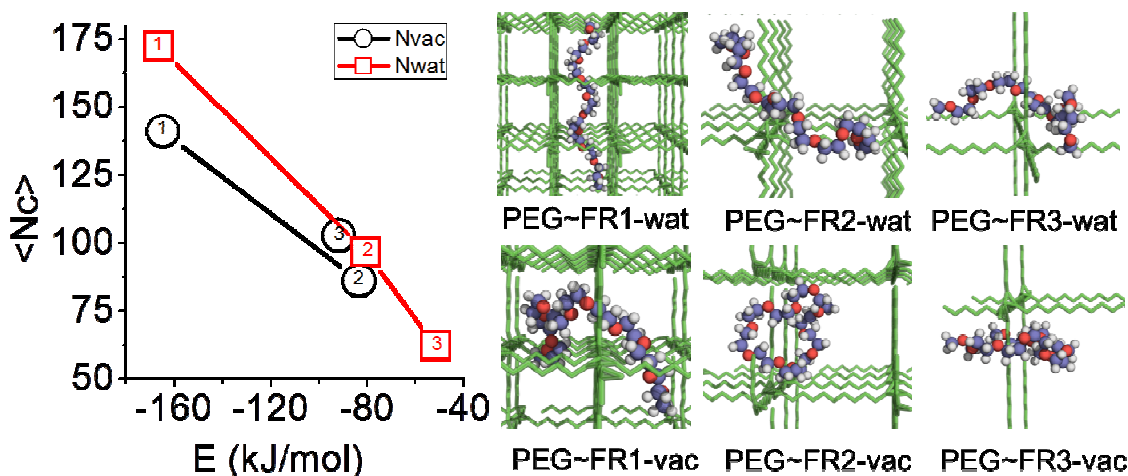
Figure 5. Relationship of average number of contacts and vdW energy for the PEG-9 chain. Symbols in plot are numbered according to indices of frameworks FR1, FR2, and FR3.

The impact of framework's attractive energy can be studied with different values of ε_{fp}, the LJ energy parameter, in separate simulation runs. For each framework FR1, FR2, FR3, simulation

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runs of ε_{fp} ranging from 0 to 6.5 ε were performed and the various radii of gyration, in $\langle R_g^2 \rangle$ for

PEG-9 are computed and shown in Figure S2. When ε_{fp} is zero, the presence of the framework is

not felt and is expected to be 0.45 nm, the R_g value of PEG-9 in absence of a framework (Table

S2). This is true for PEG-9 in FR2 and FR3 with $\langle R_g^2 \rangle$ = 0.20 nm^2 at ε_{fp} = 0.1 ε. For FR1,

however, the value of $\langle R_g^2 \rangle$ at ε_{fp} = 0.1 ε is 0.4 nm^2 correspond to R_g = 0.62 nm. The opening of

FR1 is 0.64 nm (1.0 nm - $\sigma_{\phi fp}$) where the subtracted term is cross-section diameter of the linker.

Thus the opening is smaller than $2 \times R_g$ of the framework free diameter of gyration so that

exclusion effect will prevent the PEG-9 folding. There is a similar study in the literature of how

the radius of gyration of a vdW polymer chain is influenced by beads located at vertices of a

cubic grid.[31] Qualitative features of a maximum or saturated R_g at large ε_{fp} can be observed.

Compared to the results of Li et al., there are more fluctuations in the R_g versus ε_{fp} curves in

Figure S2. This is due to the embedded bond angle energies and lower elasticity of the PEG

molecule compared to the very flexible pure Lennard-Jones chain in Li et al.[31]

Solvation of Multiple Chains

An attractive feature of a polymer-MOF composite in applications is the duality of solubility

and separability. A soluble polymer is contained inside a framework so that it can be easily

separated from a solution in which the polymer has performed a function of ion-exchange or

extraction. Severe confinement in the framework, however, may over-restrict the mobility of the

polymer, reduce solvent-polymer interaction, and hence impair its solubility and functionality.

On the other hand, polymers may leach out due to insufficient containment in a large framework.

Optimization of framework size to match the polymer's dimensions and solubility can be

explored with molecular simulations. We have performed three sets of simulations for six PEG-14 chains contained within three different individual frameworks: FR1, FR2, and FR3.
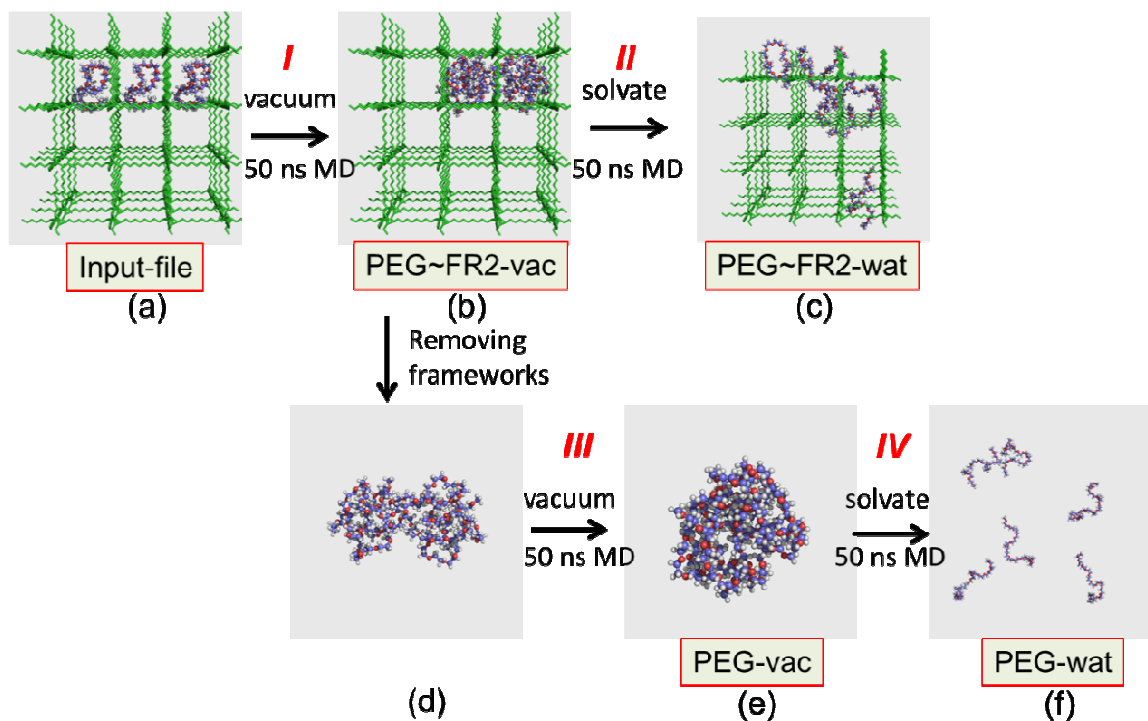
Figure 6. Sequential simulation runs to study solvation of six PEG-14 chains with and without a confining framework.

The sequence of simulation steps performed for each framework are shown schematically in Figure 6. Initially six PEG-14 chains are placed in the cavities of the PE framework (configuration a) and allowed to equilibrate for 50 ns MD steps in vacuum (configuration b). Water molecules are then introduced before another 50 ns MD steps were made, reaching configuration c. A separate parallel run of 50 ns is performed starting with configuration b in vacuum but the framework removed (configuration d) leading to a pseudo-equilibrium configuration in vacuum (configuration e). Water molecules are added to this 6-chain PEG aggregate for another 50 ns MD steps, reaching a solvated state of the PEG chains (configuration

f). The simulation details for the three sets of simulations, including number of water molecules

are given in Table S1.

Solvation of PEG chains with and without the framework can be compared by steps II and IV

and resulting configurations c and f of Figure 6. Figure 7 compares the solvation process without

framework and from the three frameworks by plotting the number of hydrogen bonds between

water and the 6 PEG-14 chains against time. As we expect, the steady-state number of hydrogen

bonds increases from a small to a large framework, approaching that of bulk PEG-14 for FR3.

Complete dissolution behavior and full water-polymer interaction in the FR3 framework means,

however, that the PEG-14 chains will leach out, since the polymer concentration within the FR3

cavity will be higher than that of bulk water and a functional composite cannot be maintained.

On the other hand, though the number of hydrogen bonds in FR1 is only half of that in bulk

water, it may be sufficient for extraction, ion-exchange and other function in the solvent. Water

penetration into FR1 is immediate and there is no obvious lead time required to reach the steady

state of hydrogen bonding. Comparison of time required to reach steady-state water-polymer

interaction in the three frameworks are tabulated in Table S4. Depending on the specific function

in solvent, optimizing of framework size can be made to attain maximum water-polymer

interaction without risking leaching of polymer chains. The computed time intervals to reach

steady-state PEG-water interaction for the three frameworks are listed in Table S4.
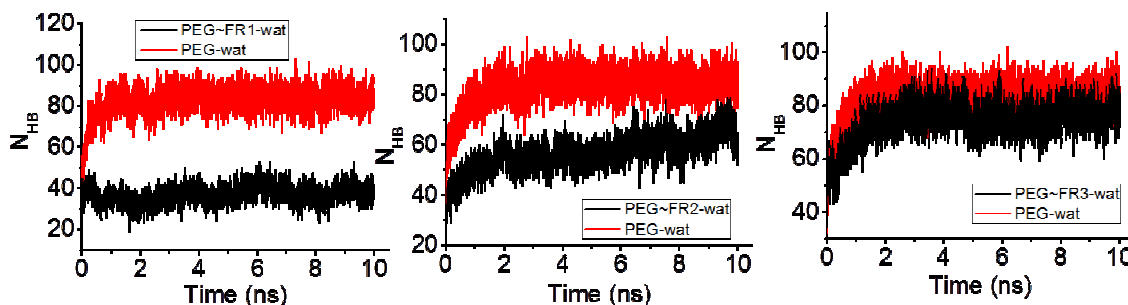
Figure 7. Number of hydrogen bonds between atoms of the PEG-14 and water molecules. Panels are in increasing size of frameworks, from left to right FR1, FR2, and FR3.

The distribution of PEG-14 chains can be compared by plotting the accumulated number of atoms radially outward from the COM (center of mass) of the PEG chains, as shown in Figure 8. Again, it can be seen that there is little difference for PEG-14 chains with and without FR3 either as a homogeneously dissolved polymer solution in water (Figure 8(d)). This is also observed for a compact aggregate in vacuum with or without FR3 (Figure 8(a)). The role of the framework is evident for FR1 and FR2 for segregating the chains in vacuum (Figure 8(a)) and retaining them within a small domain in water (Figure 8(b) (c)), contrasting the corresponding distributions without FR1 or FR2. Corresponding radial distributions, g(r) of atoms from the center of mass of all six chains, normalized to total number of atoms, in vacuum and water are shown in Figure S3.
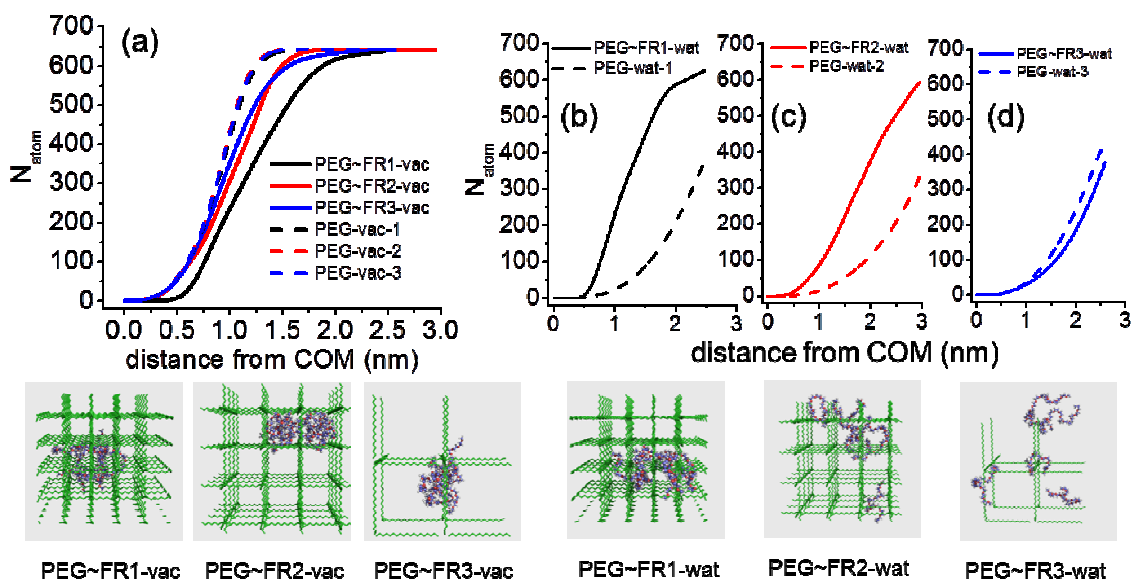
Figure 8. Effects of framework on PEG-14 chains distribution in vacuum and in water. (a) Accumulated number of atoms away from center of mass (COM) in vacuum with and without framework FR1, FR2, or FR3; (b) in water with and without FR1; (c) in water with and without FR2; and (d) in water with and without FR3.
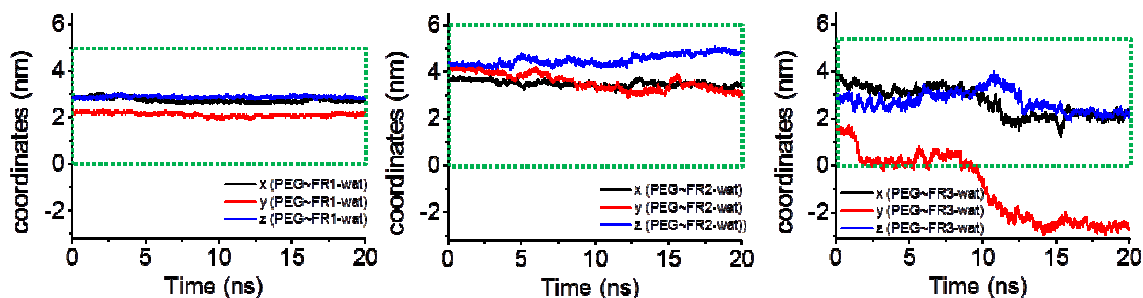

Figure 9. Coordinates of a selected PEG-14 chain in the given frameworks versus number of time steps in simulation. The periodic boundary of the cell shown in green is applied during simulation but turned off to display the true coordinates of the PEG-14 chain.

The retention of PEG-14 chains in small frameworks (FR1 and FR2) and the loss of them in large framework (FR3) during solvation can be seen in Figure 9 which shows the x, y, z coordinates of a PEG-14 chain in a 20 ns period. Coordinate changes in vacuum for the three frameworks are shown in Figure S4.

The preliminary results show very interesting behavior of PEG chains partially confined with an open framework. Although the cubic PE framework model is artificial and the freezing assumption of a large framework with long linkers is unrealistic, it provides the basic features of an open framework to influence intra-chain and inter-chain interactions of PEG. On the other hand the PEG chains are realistically represented together with explicit TIP3P water molecules. The partial dissolution of PEG chains within a framework is of particular interest. The polymer can be retained within the framework but without losing flexibility and mobility. Extension of these simulation studies to other geometries and functional groups can help experimentalist to identify matching polymer and framework for desirable function, such as extraction and catalysis in water.

CONCLUSIONS

Molecular simulations of PEG in a cubic PE framework effectively reveal interesting features of how polymers behave in an open framework. Configurations of a PEG chain can be stretched by a confining framework leading to a larger radius of gyration. PEG-framework interaction increases with smaller framework as quantified by the increase in number of close contacts and decrease in vdW energy between PEG and framework. The framework has the same impacts on PEG in the presence of water with increasing radius of gyration, increasing number of contacts and magnitude of vdW interaction in a smaller framework. The role of the framework is more significant when comparing dissolution of PEG chains. A small framework allows solvation and retention of PEG chains whereas in a large framework PEG chains readily dissolve and leach away. The combination of a realistic polymer and explicit water molecules in a semi-realistic

framework is a useful tool to explore the physical phenomena and molecular behavior in the

hybrid material of polymer threaded framework.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Typical MD simulation settings, conformational properties, representative structures, effect of

framework energy parameter ε_{fp} on polymer R_g^2 of PEG-9 in vacuum, radial distribution

function, and coordinates of PEG in vacuum. (PDF)

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Notes

The authors declare no competing financial interest.

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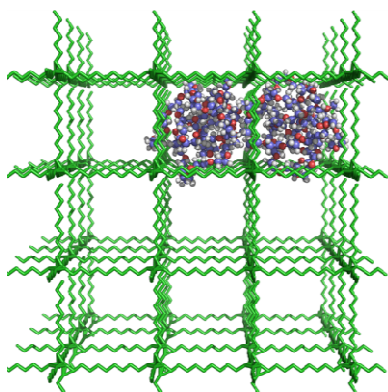(41) Dobrynin, a.; Rubinstein, M. Theory of Polyelectrolytes in Solutions and at Surfaces. *Prog. Polym. Sci.* **2005,** *30*, 1049-1118.

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For Table of Contents

Six PEG-14 chains in vacuum   Six PEG-14 chains in water

5063 water
molecules

dissolution