Research paper

A computational study of a phenolic based polymer with a spring-like structure

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A B S T R A C T

We report the stretching potentials for a helical phenolic-based polymer with high symmetry and a spring-like structure that can be stretched by a factor of 4 along the spring direction and still return to its original structure. We hope that synthetic polymer chemists assess if this polymer or a similar one can be synthesized and tested.

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1. Introduction

Carbon phenolic is an important polymer in thermal protection systems (TPS), for example it is used to protect reentering space craft. In a series of recent manuscripts [1–3] we investigated the thermal and mechanical properties of carbon phenolic. We observed that the thermal and mechanical properties depended on the degree of cross-linking, as expected. Our simulations found a maximum of approximately 85% of the possible sites were cross-linked, which is the same value deduced from experiment. Increasing the cross linking is a possible way to improve the mechanical and thermal properties. However, for the current polymer, where the C_6H_3OH units are bridged by CH_2 groups, it is highly unlikely that the percentage of cross linking can be increased. Since synthesizing a starting material with different bridging groups between the C_6 rings is straight forward experimentally [4,5], we investigated alternative bridging groups that would introduce more flexibility, in hope that this would lead to an increase in the cross-linking.

One of the systems that we considered [3] replaced the CH_2 bridges with C_2H_4 groups. While this change did not significantly change the strength of the bridge bonds, the longer bridge groups introduced extra degrees of rotational freedom. In subsequent simulations of a single carbon phenolic chain, we discovered that it could wind into a helical or spring-like structure. By cross-linking the springs, it is possible to create a low density 3D structure. With low density being one of the desired properties for TPS on space craft. In this manuscript we report on computational study of one possible structure of these connected springs that has a very interesting stretching potential.

2. Methods

Density functional theory (DFT) calculations were performed at 0 K using the Gaussian 09 program system [6]. The BPW91 [7,8] functional and the 6-31G* basis set [10] were used. Periodic boundary conditions (PBC) were applied in three directions. This level of theory was used because it gives a good description of organic systems; for example the C–H and C–C bond energies in C_2H_6 (96 and 88 kcal/mol, respectively) are in good agreement with the best values (101 and 90 kcal/mol) deduced from the heats of formation given in the NIST chemistry webbook [9]. The geometry was fully optimized, that is, both position of the atoms and the lattice vectors were optimized. Starting from this equilibrium geometry, one lattice vector was expanded or contracted in steps of 0.25 Å and the atomic positions and the other two lattice vectors were optimized at each step. This corresponds to an infinitely slow strain rate.

3. Results and discussion

The fully optimized phenolic based polymer is shown in Figs. 1–3. Fig. 1 shows the unit cell, which contains four phenolic segments.

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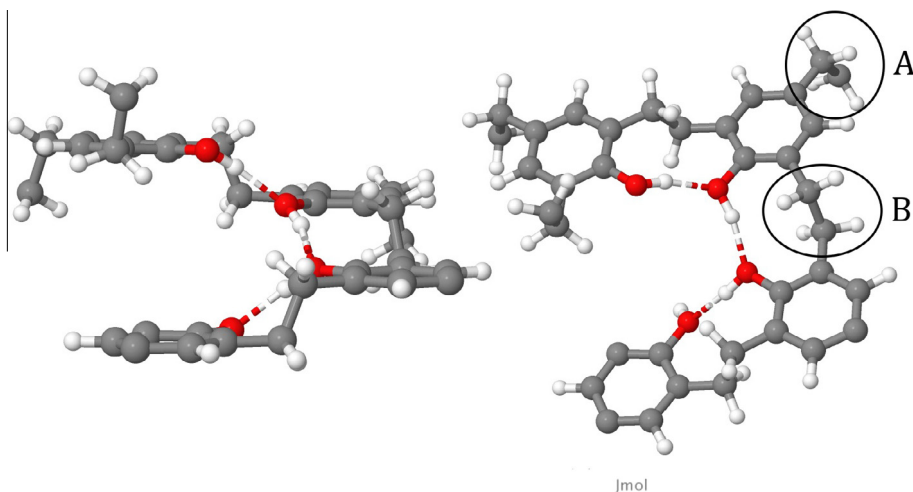*E-mail address:* Charles.W.Bauschlicher@nasa.gov

Fig. 1. Two views of the unit cell consisting of 4 phenolic segments connected by C_2H_4 bridges. The hydrogen bonds are shown as dashed lines. The oval labeled A shows a C_2H_4 bridge between springs while B shows a C_2H_4 bridge in the same spring structure.
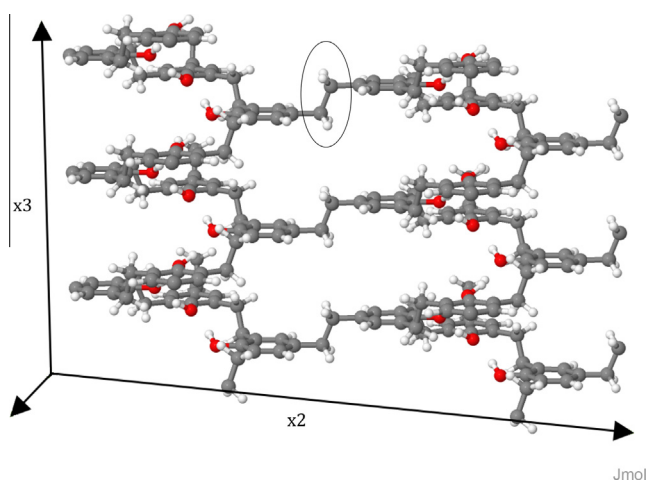

Fig. 2. A $(3 \times 2 \times 1)$ cell showing two springs of three turns each. One of the C_2H_4 bridges between the two springs is enclosed in the oval. The lattice vectors are also shown.
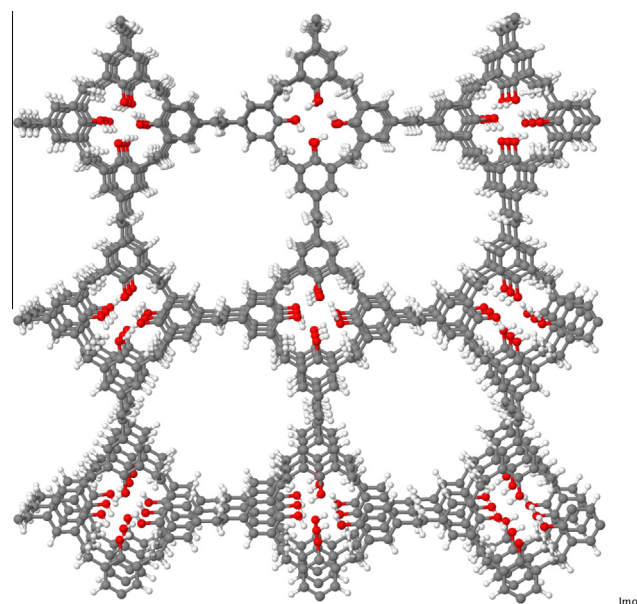

Fig. 3. A view down the springs.

The hydrogen bonds between the phenolic segments are visible. A C_2H_4 bridge between chains is shown in the oval labeled A in the figure, while a C_2H_4 bridge along the backbone of the spring is shown in B. Fig. 2 shows a $(3 \times 2 \times 1)$ cell with two spring units visible; also shown are the C_2H_4 bridges between the two springs. Springs along the third lattice vector are also connected by C_2H_4 bridges, but are omitted for clarity. The C_2H_4 bridges between the adjacent springs means that the springs are shifted along the spring direction with respect to each other, leading to a monoclinic cell where the angles between the lattice vectors are not 90°. A view down the springs is shown in Fig. 3. The very open structure between the springs is clearly visible in this orientation. The optimized lattice vector along the spring direction is 6.30 Å, while the other two vectors are 15.38 Å. This yields a system with a density of 0.600 g/cm³, which is about half the density of cross-linked carbon phenolic with the standard CH_2 bridges.

The stretching potentials are shown in Fig. 4. The potential associated with the stretch along the springs axis rises slowly until approximately 16 Å then flattens out. This initial rise is associated with stretching and then breaking the hydrogen bonds between the OH groups on the spring. In the flat region, the springs are elongating by rotation about the C_2H_4 bridges. At approximately 26 Å,

the elongation shifts to bond stretching and the energy rises steeply, as expected. Compression along the spring direction quickly results in atoms in one rotation of the spring interaction with the banging into atoms in the next twist of the spring and not surprisingly the energy rises quickly.

The stretching along the spring appears to be reversible even for displacements of a factor of 4 or more for finite temperatures, which should allow the contracting spring to pass over the small barrier at about 18 Å. Such a dramatic stretch is perhaps not completely unexpected for a spring-like structure.

The stretching along the lattice vector that is approximately perpendicular to the spring is very different. Stretching along this direction quickly leads to a rapid quick rise in energy as the C(ring)–C_2H_4 angles bend and C–C bonds stretch. On the other hand, the compression is much easier as the spring can begin to slip and tilt and it is not until it is very distorted that atoms begin to collide and the energy begins to rise quickly. The beginning of this compression is shown in Fig. 5, where the tilt of the springs is visible.