



## COMPUTER SIMULATION OF TRIAZOLE-MODIFIED URETHANE SEGMENTS

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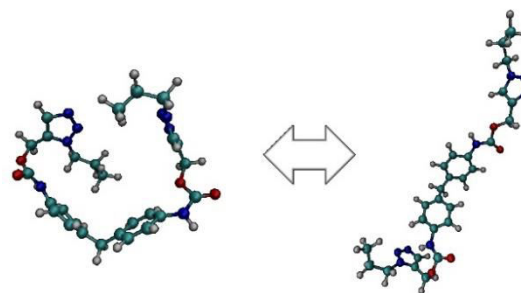
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### Abstract

The focus is on the development of siloxane-urethane block copolymer matrices for additive manufacturing applications, including soft robotics. Molecular dynamics simulations compare classical urethane segments with the triazole-modified ones, revealing temperature-dependent behaviors in their conformational structures. The results suggest the potential for tailoring the mechanical properties of polyurethanes through molecular modification, which is crucial for optimizing additive manufacturing processes. Further research could advance material design for customizable objects with desired mechanical response.

**Key words:** urethane, triazole, molecular dynamics simulations.



### Introduction

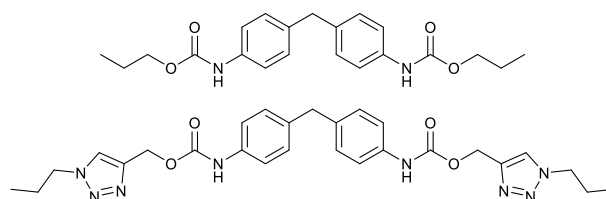
For a number of applications of the objects obtained using additive technologies (3D printing), the materials in use must possess a specific set of properties determined by both the manufacturing method and desired mechanical properties of the product. In particular, for the creation of magnetopolymeric compositions and printing of soft robots controlled by a magnetic field, block copolymers based on siloxane and polyurethane segments have been synthesized [1]. It was shown that changing the composition of the copolymer is an effective way of controlling the mechanical properties of the resulting material, and the possibility of using it in 3D printing was demonstrated.

To investigate the characteristics of the microstructure and the details of intermolecular interactions in systems with rigid urethane segments, a computer simulation of the rigid part was conducted using the molecular dynamics method. Specifically, a comparative analysis was performed on the simulation results of a classic urethane segment (Fig. 1, top) and one similar to it, but modified with a triazole unit (Fig. 1, bottom). A series of simulations of single molecules were carried out in a wide range of temperatures, with the conformational behavior of the molecules being compared based on the dependences and distributions of the radius of gyration.

### Model

The following two types of molecules were simulated: urethane and triazole-modified urethane (Fig. 1).

The molecular models were all-atomic. The simulation was carried out in the GROMACS 2020.1 software package [2, 3].



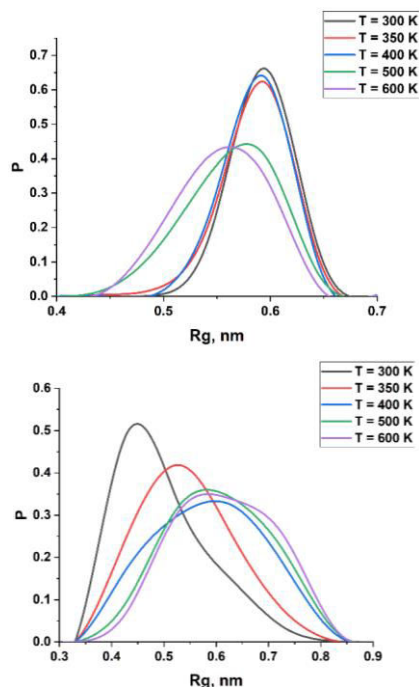
**Figure 1.** Chemical structures of the studied urethane (top) and triazole-modified urethane (bottom) segments.

Starting conformations and molecular parameterization files were created using Automated Topology Builder (<https://atb.uq.edu.au>) [4–6]. The corresponding molecule identifiers are 1670214 and 1279084. GROMOS96 54a7 force field [7], with additional parameters calculated by ATB, was used. In accordance with the recommendations of the documentation accompanying the force field, a single cutoff of 1.4 nm was used for the Lennard-Jones interactions. A single Coulomb cutoff of 1.4 nm was used with a reaction field. The starting conformations of single molecules obtained in ATB were further minimized by the classical steep algorithm, after which simulation was carried out in a cell of a sufficiently large size (about 3 nm). The simulation was carried out in the NVT ensemble, using a v-rescale thermostat [8] with a time constant of 2 ps and in a wide temperature range (300, 350, 400, 500, and 600 K) without generating starting velocities. Trajectories of more than 100 ns were obtained for each simulated system.

### Results and discussion

As the first step in the investigation of the proposed copolymers, the temperature behavior of the radius of gyration

$(R_g^2 = \frac{1}{MN} \sum_i^N m_i (\vec{r}_i - \vec{r}_0)^2$ , where  $M$  is the total mass of the molecule,  $N$  is the number of atoms,  $m_i$  is the mass of  $i$  atom,  $\vec{r}_i$  is the radius vector of the  $i$  atom, and  $\vec{r}_0$  is the radius vector of the mass center of the molecule) of the rigid segments was analyzed. For both types of the urethane segments at all temperatures, the distribution shown in Fig. 2 was constructed.



**Figure 2.** Distributions of the gyration radius ( $R_g$ ) of the studied urethane (top) and triazole-modified urethane (bottom) segments.

All the resulting distributions (Fig. 2) are quite symmetrical. However, the behavior of the urethane segment modified with a triazole unit at 300 K stands out somewhat, exhibiting a noticeable shoulder at large values of the radius of gyration. It is noteworthy that the distribution shifts to the region of low values with increasing temperature for urethane segments. This implies that the enhanced mobility of the molecule enables it to adopt more compact conformations. For the urethane segments modified with triazole, the situation is reversed, with a shift occurring to the region of higher values. Due to the greater length of the molecule and the initially greater mobility in the triazole segment, the molecule already assumes a compact conformation at low temperatures, and becomes more unfolded with increasing temperature.

## Conclusions

A comparative analysis of the conformational behavior of single urethane and triazole-modified molecules using molecular dynamics simulations was performed. The atomistic models of the studied molecules were created. The simulation was performed at different temperatures ranging from 300 to 600 K.

It was shown that the presence of triazole rings qualitatively changes the molecule size and its evolution with temperature. Namely, at room temperature, the terminal modification of urethane with triazole rings leads to the compaction of the molecule, *i.e.*, the maximum of the gyration radius distribution shifts to smaller values compared to that of unmodified urethane. Furthermore, while the classical urethane adopts more compact conformations with increasing temperature, the size of the triazole-modified molecule grows with temperature. These results highlight the effect of the molecular modification on the behavior of the molecule and serve as a basis for further studies of such molecules in the bulk.

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