

BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI  
Publicat de  
Universitatea Tehnică „Gheorghe Asachi” din Iași  
Volumul 63 (67), Numărul 2, 2017  
Secția  
CHIMIE și INGINERIE CHIMICĂ

## CONFORMATIONAL ANALYSIS OF POLYSILOXANES SUBSTITUTED WITH AZOBENZENE

BY

SIMONA CIOBOTĂRESCU<sup>1,2</sup>, ELENA-LUIZA EPURE<sup>1,\*</sup>  
and NICOLAE HURDUC<sup>1</sup>

<sup>1</sup>“Gheorghe Asachi” Technical University of Iași,  
Department of Natural and Synthetic Polymers  
<sup>2</sup>University of Angers, France  
Physics Department

Received: May 28, 2017

Accepted for publication: July 5, 2017

**Abstract.** This work presents a molecular modeling study with regard to the conformational behaviour of azo-polysiloxane in function of the content in cis azobenzene (CA). Molecular dynamics was used to carry a NVT simulation of azobenzene substituted polysiloxane in bulk. Conformational analysis was performed to determine how the CA concentration affects the polymeric chain's three-dimensional structure. The radius of gyration was found not to change with the variation of CA content, while the potential energy increased with the increasing of CA percentage. The low change in free volume from one structure to another supports the constant radius of gyration. The correlated results suggest that the CA brings conformational tension on the structure. The macromolecular chain is unable to position itself in a less structural conflictive arrangement and determines a growth in potential energy. More studies are needed for further investigation and to link these findings with simulations in layer and solution.

**Keywords:** molecular modelling; azo; isomerisation; configuration.

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\*Corresponding author; *e-mail*: lepure@tuiasi.ro

## 1. Introduction

Azobenzene containing polymers draw attention of different research groups since early 80s. While some researchers tried to find the source of chains spatial re-organization (Ciardelli *et al.*, 1984) other focused on the application possibilities enabled by the birefringence property (Todorov *et al.*, 1984). Later, azo-polymeric films were found to be suitable for sinusoidal topography inscription through light irradiation (Rochon *et al.*, 1995; Natansohn and Rochon, 1995).

The key point in this system is the azobenzene, whose photochemistry enables the trans – cis isomerization, a reversible process. The two isomers differ in geometrical shape, specific volume and dipole moment. When linked to a polymer chain or mixed in a polymer matrix, azobenzenes photoisomerization can trigger motions in the entire polymeric catenae, thus changing the overall arrangement (Natansohn and Rochon, 2002). This phenomenon provides the necessary context for a mass transport process, a particularity exploited to obtain controlled nano-features on the azo-polymeric film surfaces with a light beam (Barrett *et al.*, 1998). Due to the nano-inscription attribute along with the polysiloxane's flexibility and biological inertness (Yilgor and McGrath, 1988), the application possibilities cover a wide range of fields, from cell cultures (Resmerita *et al.*, 2009; Hurduc *et al.*, 2013; Rocha *et al.*, 2014) and protein folding trigger (Sporlein *et al.*, 2002) to optoelectronics (Luo *et al.*, 2004; Katsonis *et al.*, 2007; Hvilsted *et al.*, 1998).

Understanding of the mass transport phenomenon starts with the isomerization process that provides the driving force. The differences in length scale between the two configurations are very small (angstroms) and the characteristic photoisomerization times are low (picoseconds). Nevertheless, these properties induce a spatially ample material re-organization (microscale), making the surface structuration a complex process (Yager and Barrett, 2001). In this context, computational chemistry can be of real help to comprehend the series of changes that lead to macroscopical effects.

Molecular modeling has been, thus, used by different researchers to address matters like the isomerization mechanism (Schultz *et al.*, 2003; Wang and Wang, 2007; Ootani *et al.*, 2009; Cembran *et al.*, 2004; Cattaneo and Persico, 1999), trans isomer's stability (Kurita *et al.*, 2002), isomerization driven deformation in azo-polymeric materials (Ilnytskyi *et al.*, 2006), the influence of temperature and (Yager and Barrett, 2004) and isomerization rate in mass transport (Accary and Teboul, 2013), the mass transport mechanism (Teboul *et al.*, 2011; Teboul *et al.*, 2009; Teboul and Accary, 2012;

Toshchevnikov *et al.*, 2009; Toshchevnikov *et al.*, 2012; Ciobotărescu and Teboul, 2016).

Considering the enormous size of polymers, comparing with small molecules, their spatial arrangement has uncountable possibilities. Therefore, the description of chain conformation is in terms of statistical averages of some characteristic properties (radius of gyration, potential energy, free volume).

## 2. Calculations

Molecular dynamics of azobenzene substituted polysiloxane in bulk was performed with Materials Studio software v.4.0 from Biovia (Hurduc, 2007).

A polysiloxane chain with 10 structural units was built (two  $\alpha$  – units and eight  $\beta$  – units to follow experimental data, where 25% of the units are always in  $\alpha$  form). Using Anneal dynamics with 5 heating cycles from Forcite module, 5 conformations (from each Annealing cycle) of lowest energy were obtained. These conformations were then submitted for a Geometry Optimization calculation with Forcite module, and a minimum energy conformation was attained. After these procedures, nine of the ten structural units were modified with an azobenzene molecule, by substituting the chlorobenzyl group, to correspond to a 90% azobenzene substituted polysiloxane. Trans and cis configurations were used to acquire different percentages of CA: 0, 22, 44 and 78%. The new structures were again supposed to a Geometry Optimization calculation. The cubic simulation box was built with Amorphous Cell module – Construction for the unmodified polysiloxane, and for the azo-polysiloxane as well. The cell was formed from 5 molecules, using the following parameters: temperature  $T = 298$  K, density  $\rho = 1.2$  g/cm<sup>3</sup>, and pcff force field. Eight different cells were constructed for the polysiloxane with CA and one cell for the polysiloxane with 0% CA. The method computes between one and ten possible arrangements (frames) for each cell. The cells went through a Basic Refine Protocol, a NVT molecular dynamics for 10 picoseconds. The structures were submitted also to Temperature Cycle Protocol, but these results will be useful for later calculations, not covered by this paper. Hence, the structural analysis was performed on these systems after the molecular dynamics. After eliminating the faulty structures (too high energy because of conformational unrealistic features), 101 structures were left for the analysis. Fig. 1 displays a simulation cell for exemplification, in a manner that allows the viewing of the periodic boundary conditions.

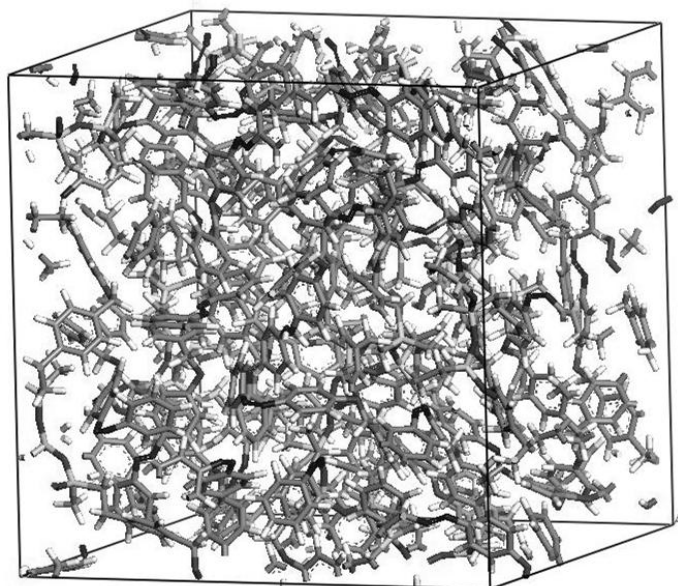


Fig. 1 – Simulation box of 47% CA structure exhibiting periodic boundary conditions.

During the cell construction and the following steps, the cis and trans configurations were not constrained to remain fixed, so they were subjected to re-arrangements by reason of energy requirements. As a consequence, a few isomers passed from cis to trans or backward, resulting in configurations with small geometrical deviations from the standard cis and trans. As a consequence, the previously designed sets of percentages could not be respected. For example, the 0% CA intended structure, ended up with 7% cis isomer. Likewise, no structure could keep more than 69% CA, even though they were initially designed with 78% cis. Thus, the following structures with 7, 22, 47, and 69% CA were chosen as representative and reflect the real CA percentages. This phenomenon of isomerization during the calculations will be a focus point for the authors' future research.

### 3. Results and Discussions

The radius of gyration  $r_g$  for all the atoms in the azo-polymeric chain, as well as for the N atoms in the azo groups on the chain, was calculated as described in Eq. (1).

$$r_g^2 = \frac{\sum_{i=1}^N m_i s_i^2}{\sum_{i=1}^N m_i} \quad (1)$$

where:  $N$  is the number of atoms,  $m_i$  is the mass of atom  $i$  and  $s_i$  is the distance between atom  $i$  and the molecule's center of mass. The radius of gyration  $r_g$  defines the root mean square distance between the atoms and their common centre of mass.

Table 1 outlines the  $r_g$  analysis for all the chain atoms and for the N atoms in the azo group. An examination of  $r_g$  in function of CA content shows that it varies less than one angstrom. These small differences are within the normal fluctuations in the structure, thus the  $r_g$  does not depend on the CA percentage. For comparison, the unmodified polysiloxane structure is listed, pointing an average difference of 2.6 Å between polysiloxane and azo-polysiloxane. This change in  $r_g$  occurs after the functionalization with the bulky molecules of azobenzene. Noting that the substitution degree on the chain is 90%, the  $r_g$  extension is a normal expected effect.

**Table 1**

*The Average Radius of Gyration  $\langle r_g \rangle$  and its Standard Deviation for the Atoms in the Polymeric Chains and in the Azo Groups*

Structure	$\langle r_g \rangle$ , [Å]		Standard Deviation, [Å]	
	All chain	Azo group	All chain	Azo group
Polysiloxane	7.671	–	0.21	–
7% cis	10.34	11.82	0.28	0.64
22% cis	10.40	12.49	0.52	0.81
47% cis	10.25	12.73	0.15	0.27
69% cis	10.28	12.68	0.39	0.71

The literature regarding three-dimensional modification of polymeric chains states that it is strongly dependent on the chemical structure of the polymer. Azobenzene containing polystyrene chains experience a compaction after trans – cis isomerization, while other chains, like the ones with methyl groups along the chain, can remain unchanged due to the methyl groups ability to absorb the strain through synergetic effects (Winnik, 2012).

The structures' potential energies were analysed to evaluate the change in conformational stability with the CA content.

**Table 2**

*The Potential Energy  $E_p$  Variation with the cis Content*

Structure	$E_p$ , [kcal/mol]	$E_p$ referenced to E7, [kcal/mol]
7% cis	E7 = -2344.42	–
22% cis	E22 = -2284.61	E22 – E7 = 59.81
47% cis	E47 = -2232.42	E47 – E7 = 112.00
69% cis	E69 = -2162.78	E69 – E7 = 181.63

Table 2 lists the potential energy  $E_p$  values for the different CA contents. The structure least rich in CA is characterized by the minimum value of energy,  $E_7 = -2344.42$  kcal/mol. Energy  $E_7$  is used as a reference and deducted from the following higher values to better quantify the energy variation. The subtraction results show that there is a clear energy augmentation with the increasing of CA concentration. The greatest subtraction – between the highest energy (corresponding to the structure most abundant in CA) and the lowest energy  $E_{69} - E_7 = 181.63$  kcal/mol – implies a significant energy growth.

The increasing potential energy can be interpreted in the context of constant radius of gyration as a consequence of the structure's insufficient conformational adaptation to the isomerization. As a consequence of the gained CA while remaining in the same conformation, the chain's potential energy raised.

In this respect, the energy elevation with the CA content, could explain the low maximum percentage of CA that could possibly be obtained in the present simulation, 69%. The increase of potential energy over a certain value as a consequence of an advanced CA content, forced some of the CA from the starting structure to unfold to trans configuration, thus lowering the overall CA concentration.

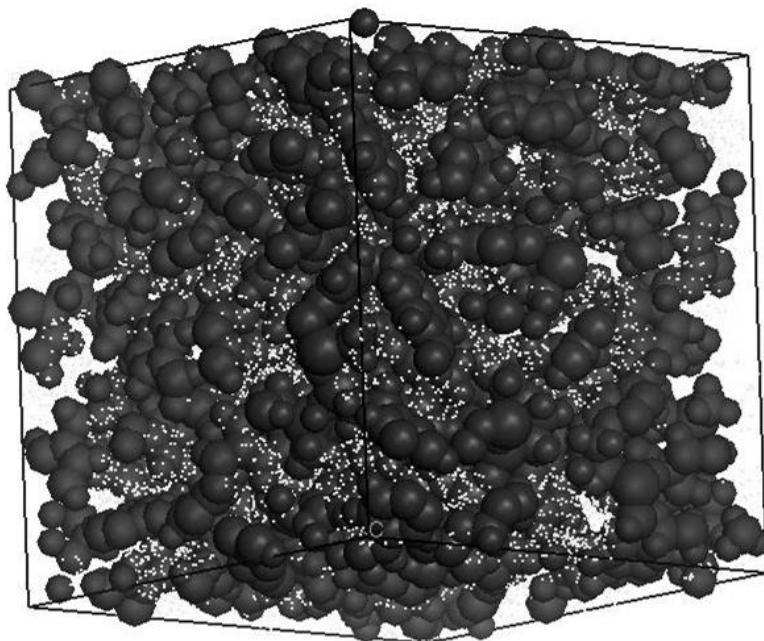


Fig. 2 – Simulation cell for 7% CA structure disclosing the free volume (the spaces punctated with white dots).

The calculation of the free volume in the simulation cell reveals that the simulation cells still hold around 11% unoccupied space, *e.g.* the cell

corresponding to the 7% CA structure has 10.97% free volume, while the box for the 69% CA structure possesses 11.19% free volume. This very low difference in free volume between the two cells indicates that despite the increasing of CA content in polysiloxane, the spatial conformation compaction is limited to a small change. This suggests that the 7% CA structure is already confined in the three-dimensional space, so that adding more CAs to the structure will not drive the chain to a pass through a severe volume modification.

#### 4. Conclusions

The conformational analysis of azobenzene substituted polysiloxanes in bulk reveals the relationship between CA content and structural characteristics as radius of gyration and free volume, as well as the structures' energies. The increase in potential energy with the CA percentage can be interpreted in correlation with the constant radius of gyration, as a low constriction capacity of the chains, resulting in energy augmentation.

For a more extended view of the azo-polysiloxane three-dimensional behaviour in function of CA concentration, further studies are needed. These results will serve as a comparison with future planned work, namely the conformational analysis of the azo-polysiloxane in solution and in layer. The layers hold less steric pressure on the structure than the bulk, thus the effects on the conformation are expected to be greater. In solution, the dipole moment difference of approx. 3 D between cis and trans isomers constitutes a source of variation in the polymer – solvent interactions and can serve as additional driving force to induce conformational modifications to the chains.

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## ANALIZA CONFORMAȚIONALĂ A POLISILOXANILOR SUBSTITUIȚI CU AZOBENZEN

(Rezumat)

Conformația polisiloxanilor și distribuția spațială a moleculelor de azobenzen de pe lanțul polimeric constituie factori de influență pentru fenomenul de transport de masă prin care are loc în procesul de nano-structurare a filmelor azo-polimerice. Lucrarea de față prezintă un studiu simulare și modelare moleculară privind relația dintre aranjarea tri-dimensională polisiloxanilor substituiți cu azobenzen și concentrația configurațiilor cis. S-au investigat catene cu grad de polimerizare 10 și substituție cu azobenzen de 90%, având diferite procente de izomer cis, prin analiza energiei potențiale și a unor proprietăți structurale (funcția de distribuție radială și volumul liber).