

PAPER

Transferability of Polymer Chain Properties between Coarse-Grained and Atomistic Models of Natural Rubber Molecule Validated by Molecular Dynamics Simulations

To cite this article: Jiramate Kitjanon *et al* 2017 *J. Phys.: Conf. Ser.* **901** 012096

View the [article online](#) for updates and enhancements.

Transferability of Polymer Chain Properties between Coarse-Grained and Atomistic Models of Natural Rubber Molecule Validated by Molecular Dynamics Simulations

Jiramate Kitjanon^{1,2,3}, Wasinee Khuntawee^{1,2,3}, Thana Sutthibutpong^{2,3,4},
Phansiri boonnoy^{1,2,3}, Saree Phongphanphanee^{2,3,5}, Jirasak Wong-ekkabut^{1,2,3*}

¹Department of Physics, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand

²Computational Biomodelling Laboratory for Agricultural Science and Technology (CBLAST), Faculty of Science, Kasetsart University, Bangkok 10900, Thailand

³Thailand Center of Excellence in Physics (ThEP Center), Commission on Higher Education, Bangkok 10400, Thailand

⁴Department of Physics, Faculty of Science, King Mongkut's University of Technology Thonburi (KMUTT), Bangkok 10140, Thailand.

⁵Department of Material Science, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand

*E-mail:jirasak.w@ku.ac.th

Abstract. In this study, we have successfully parameterized the coarse-grained (CG) model of *cis*-1,4-polyisoprene (main component of natural rubber) based on the MARTINI force field. An isoprene monomer is mapped into one bead of CG model. The structure, bulk and thermodynamics properties of *cis*-1,4-polyisoprene with new CG model are well comparable to the atomistic simulation model and experiment. Our CG model of *cis*-1,4-polyisoprene will be helpful to study in the advanced rubber nanocomposite materials.

1. Introduction

Rubber is one of the most important natural resources and has a very high impact on Thailand's economy. It is composed mainly of high molecular weight polymer *cis*-1,4-polyisoprene (*cis*-PI). Computer simulations can play role in the advanced rubber technologies as the virtual experiments, carried out in silico, to observe and fine-tune the chemical details of both rubber and rubber composites. These numerical experiments can greatly reduce time and cost from trial and error processes in the laboratories. However, there are still rooms for improvement as the traditional detail-riched atomistic model of polymers are still consuming a large amount of computer time to produce the well-equilibrated conformation of polymer networks. Therefore, some efforts were put to provide the more simplified representations of polymer molecules, namely the MARTINI force field [1]. The MARTINI models were built for amino acids, water, phospholipid cell membranes, fullerenes and some other polymers [2-5], but there is no parameter for rubber molecules yet. In this study, CG model of *cis*-PI chains were parameterized based on MARTINI scheme [1]. Solvation free energy and chain properties of *cis*-PI were calculated in water, cyclohexane and in own melt-state. A series of molecular dynamics (MD) simulations of CG model were performed in comparison with the united-atom(UA) model to verify the transferability between two length scales.

2. Methodology

2.1. MD simulations

2.1.1. United-atom (UA) Model. Simulations of the *cis*-PI were performed in melts and solvents (water and cyclohexane molecules) with the united-atom force field. The united-atom model was used as a reference because of its ability to reproduce the experimental results, such as density, glass transition temperature of the polymer network and self-diffusion of the polymer chains [6]. For the solvated systems, a *cis*-PI chain with the length of 100-mer was solvated by 22331 single point charge (SPC) [7] water and 5000 cyclohexane. For the system of *cis*-PI in melts, 500 chains with the length of 100-mer were used. After an energy minimization using the conjugate gradient algorithm [8], the MD simulations of *cis*-PI in solvents and melts were performed under the constant of number of particles, pressure, temperature (NPT) with GROMACS package version 5.1.1 [9]. The temperature was kept constant at 300 K by Parrinello-Donadio-Bussi velocity rescale thermostat algorithm [10], while the pressure was set at 1 bar by Parrinello-Rahman algorithm [11, 12]. The simulations were run for 200 and 500 ns for the systems of *cis*-PI in solvents and in melts, respectively. The trajectories after 150 ns and 200 ns were used for the analysis for the systems in solvents and in melts, respectively.

2.1.2. Coarse-grained (CG) Model. The CG simulations were performed with the newly parameterized coarse-grained force field in order to reproduce the thermodynamic and conformational features, observed in the simulations under united-atom model. The CG model was described in the next session. With the similar setup protocols to the united-atom simulations, MARTINI model of 5000 CG water beads and 5000 CG cyclohexane molecules [1] were added in the simulation box of a CG *cis*-PI. For CG *cis*-PI in melts, 500 chains of *cis*-PI with the length of 100-mer were built. All MD simulations were performed in the NPT ensemble with 300 K and 1 bar constant. The MD parameters can be seen in [5, 13]. The simulations of *cis*-PI in solvents and melts were run for 1.5 and 6 μ s, respectively. The trajectories after 200 ns were used for all analysis.

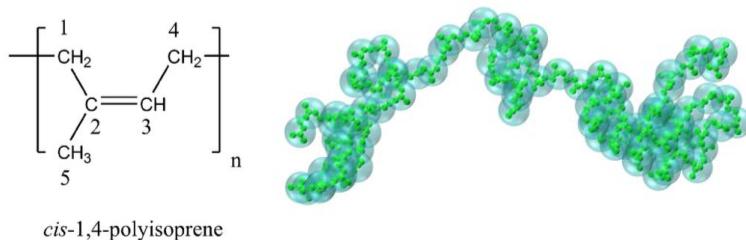


Figure 1. (Left) two-dimensional chemical structure of *cis*-1,4-polyisoprene; (Right) superimposition of the coarse-grained *cis*-1,4-polyisoprene chain (big blue sphere) to the united-atom model (green bond and stick), an isoprene monomer is mapped to a coarse-grained bead.

2.2. Free energy calculations

The free solvation energies of an isoprene monomer in water and cyclohexane were calculated by using thermodynamics integration (TI) approach [14]. The free energy of united-atom (UA) and coarse-grained (CG) simulations were compared. Each system was composed of an isoprene monomer solvated by 4000 water, 512 cyclohexane or 500 *cis*-PI chains. To reduce the bad interactions in the systems, the steepest descent minimization was applied. Afterward, the system was equilibrated with NPT ensemble. Finally, the production runs with specific λ for the UA and CG systems were performed under the constant of number of particles, volume, temperature (NVT) ensemble for 2 ns and 300 ns, respectively. The λ value is varied from 0 to 1 with 0.1 interval. The free energy differences were estimated by the Bennett Acceptance Ratio as implemented in gmx bar in GROMACS package [9, 15].

3. Results and discussions

3.1. Coarse-Grained Representation Mapping and Parameterization

To obtain a simplified model, the united-atom model was mapped into a coarse-grained representation, in which a monomer consisted of only one superatom bead (see Figure 1). The C3 type in MARTINI force field were chosen for the non-bonded parameters [1]. Bond lengths and angles were measured between centers of mass of

two and three isoprene monomers, respectively. Bond stretching and angle bending between groups of atoms defined in the coarse-grained representation were extracted from the united-atom MD trajectories of the *cis*-PI in melts, as shown in the probability distribution histogram in Figure 2 (red lines). For bonded parameters, the force constants of stretching and bending harmonic potentials were fitted from an equivalent UA simulation. The normalized bond and angle distributions can be converted to the potential of mean force (PMF) using $V = -kT \ln \Omega$ where k is Boltzmann constant, T is Temperature in Kelvin unit and Ω is the normalized distribution. The bond and angle force constants were extracted by fitting the PMF plots with the functions of $V_{bond} = \sum_{bond} \frac{1}{2} k_b (r_i - b_0)^2$ and $V_{angle} = \sum_{angle} \frac{1}{2} k_\theta (\cos(\theta_i) - \cos(\theta_0))^2$, respectively. As the results, the equilibrium bond length (b_0) was 0.46 nm and the force constant (k_b) was 5000 kJ·mol⁻¹nm⁻² for the bond stretching parameter. The 110 degree equilibrium angle (θ_0) and 37 kJ·mol⁻¹ force constant (k_θ) were used for bond bending parameters. The coarse-grained MD was then performed and compared to the bond length and angle distribution of the united-atom MD simulation (see Figure 2 (blue lines)).

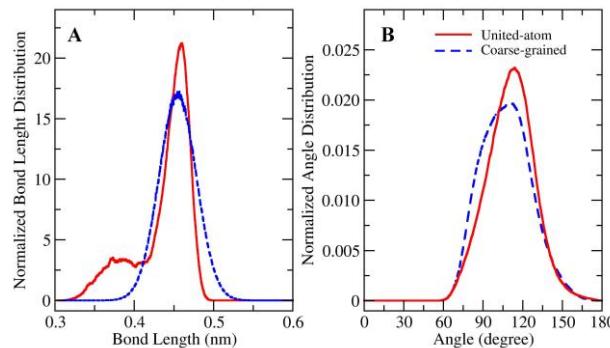


Figure 2. Normalized probability distribution of A) bond length and B) angle parameters, compared between the *cis*-1,4-polyisoprene chains parameterized by united-atom (red) and coarse-grained force fields (blue)

To ensure the reliability of the force field parameters, we calculated the solvation free energies of the isoprene monomer in different environments using both UA and CG models (Table 1). The hydration free energy of *cis*-PI with the CG model is in agreement with the UA model and the previous studies [16]. Water was shown to be the bad solvent for *cis*-1,4-polyisoprene according to the positive solvation free energy in both force fields. In contrary, the solubilities of *cis*-PI in cyclohexane and in melts are negative. As the results the most favorable solvent for *cis*-1,4-polyisoprene is in cyclohexane, followed by in melts and water, respectively.

Table 1. Solvation free energies of an united atom and a coarse-grained *cis*-1,4-polyisoprene in water, cyclohexane and melts, Solvation free energy in water was also compared to an experiment and a previous MD simulation data.

Models	Water (kJ/mol)	Cyclohexane (kJ/mol)	Melt (kJ/mol)
United-atom	5.78 ± 0.23	-15.67 ± 0.15	-12.65 ± 1.06
Coarse-grained	4.72 ± 0.04	-17.90 ± 0.01	-8.73 ± 0.02
References	$2.9^a, 3.0 \pm 0.3^b$	N/A	N/A

^aExperiment[17], ^bMD simulation[16]

3.2. Validations of the CG PI

Table 2. The autocorrelations relaxation time of the end-to-end distance (R_0) and the radius of gyration (R_g) for 100-mer *cis*-1,4-polyisoprene in water, cyclohexane and melts for the united-atom and coarse-grained models.

Models	Water		Cyclohexane		Melt	
	R_0 (ns)	R_g (ns)	R_0 (ns)	R_g (ns)	R_0 (ns)	R_g (ns)
United-atom	14.00	3.40	7.10	5.60	192.32	193.40
Coarse-grained	3.37	0.84	79.43	60.58	105.75	183.33

Equilibrations of UA- and CG-*cis*-1,4-polyisoprene in melts were monitored through their chain properties such as the end-to-end distance (R_0) and the radius of gyration (R_g). Autocorrelations relaxation time of R_0 and R_g

were calculated and shown in Table 2. Then, time-averaged R_0 , R_g and bulk density after equilibrium were determined and shown in the Table 3. The average R_0 and R_g of the coarse-grained *cis*-PI chains were in a similar order of magnitude with the UA model. Moreover, the bulk densities of both models were comparable to the experiment [18] and the previous MD simulations [19]. In water, R_0 and R_g were observed to be smaller than those in cyclohexane. This result corresponded to the tendency to collapse of rubber chains when surrounded by polar molecules, referred as the ‘bad’ solvation. In contrast, the large R_0 and R_g values for *cis*-1,4-polyisoprene were observed in cyclohexane, implying the swelling of the rubber chains when surrounded by non-polar molecules. Similar trend was observed in both the united-atom and coarse-grained simulations, suggesting a good transferability of the models. Moreover, the averaged densities of the *cis*-PI in melts were 861.02 ± 0.59 kg/m³ and 1091.70 ± 0.00 kg/m³ for the UA and the CG model, respectively. These values are also in agreement with the experiment (910 kg/m³) [18] and the previous MD simulation (885.1 ± 0.2 kg/m³) [19].

Table 3. End-to-end distance and radius of gyration of 100-mer *cis*-1,4-polyisoprene in water, cyclohexane and melts for the united-atom and coarse-grained models.

Models	Water		Cyclohexane		Melt	
	R_0 (nm)	R_g (nm)	R_0 (nm)	R_g (nm)	R_0 (nm)	R_g (nm)
United-atom	1.87 ± 0.44	1.13 ± 0.01	6.83 ± 3.14	2.87 ± 0.68	4.60 ± 0.06	2.04 ± 0.02
Coarse-grained	1.63 ± 0.01	1.09 ± 0.00	8.98 ± 1.04	3.81 ± 0.24	6.65 ± 0.01	2.70 ± 0.01

4. Conclusions

The thermodynamic and polymer chain properties of *cis*-1,4-polyisoprenes from our coarse-grained model were in good agreement with those from united-atom MD simulations. The bulk density was also in a reasonable agreement with the experiment. The *cis*-1,4-polyisoprene chains tended to be stretched in non-polar solvent (cyclohexane), while tended to be shrunk in polar solvents (water). This was verified by the solvation free energy calculation, in which the solvation free energy of *cis*-1,4-polyisoprene in cyclohexane was significantly larger than in water. In conclusion, the coarse-grain model has been proven to be a promising tool for simulating the advanced rubber materials because of its potentials to reproduce the chain and bulk properties and to speed-up the atomistic simulation.

5. Acknowledgments

This work was financially supported by Kasetsart University Research and Development Institute (KURDI) at Kasetsart University. J.K. gratefully acknowledges financial support from the Graduate School at Kasetsart University.

6. References

- [1] Marrink S J, Risselada H J, Yefimov S, Tieleman D P and de Vries A H 2007 *The Journal of Physical Chemistry B* **111** 7812-24
- [2] Monticelli L, Kandasamy S K, Periole X, Larson R G, Tieleman D P and Marrink S J 2008 *Journal of Chemical Theory and Computation* **4** 819-34
- [3] Marrink S J, de Vries A H and Mark A E 2004 *The Journal of Physical Chemistry B* **108** 750-60
- [4] Wong-Ekkabut J, Baoukina S, Triampo W, Tang IM, Tieleman D P and Monticelli L 2008 *Nat Nano* **3** 363-68
- [5] Rossi G, Monticelli L, Puisto S R, Vattulainen I and Ala-Nissila T 2011 *Soft Matter* **7** 698-708
- [6] Harmandaris V A, Doxastakis M, Mavrntzas V G and Theodorou D N 2002 *The Journal of Chemical Physics* **116** 436-46
- [7] Berendsen H J C, Postma J P M, van Gunsteren W F and Hermans J 1981 *Intermolecular Forces* vol 4, ed. B. Pullman, Springer Netherlands vol chapter 21 pp 331-342.
- [8] Payne M C, Teter M P, Allan D C, Arias T A and Joannopoulos J D 1992 *Reviews of Modern Physics* **64** 1045-97
- [9] Abraham M J, Murtola T, Schulz R, Páll S, Smith J C, Hess B and Lindahl E 2015 *SoftwareX* **1–2** 19-25
- [10] Bussi G, Donadio D and Parrinello M 2007 *The Journal of Chemical Physics* **126** 014101
- [11] Nosé S and Klein M L 1983 *Molecular Physics* **50** 1055-76
- [12] Parrinello M and Rahman A 1981 *Journal of Applied Physics* **52** 7182-90
- [13] Nisoh N, Karttunen M, Monticelli L and Wong-Ekkabut J 2015 *RSC Advances* **2015** **5** 11676-85
- [14] Kollman P 1993 *Chemical Reviews* **93** 2395-17

- [15] Bennett C H 1976 *Journal of Computational Physics* **22** 245-68
- [16] Siwko M E 2008 *Disturb or stabilise? Effects of different molecules on biological membranes* PhD Thesis Rijksuniversiteit Groningen
- [17] Floris F M, Tomasi J and Ahuir J L P 1991 *Journal of Computational Chemistry* **12** 784-91
- [18] Fetters L J, Lohse D J and Graessley W W 1999 *Journal of Polymer Science Part B: Polymer Physics* **37** 1023-33
- [19] Sharma P, Roy S and Karimi-Varzaneh H A 2016 *The Journal of Physical Chemistry B* **120** 1367-79