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Temperature-Dependent Conformations of Model Viscosity Index Improvers

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Introduction

Lubricants are comprised of base oils and additives where additives are chemicals that are deliberately added to the oil to enhance properties and inhibit degradation of the base oils. Viscosity index (VI) improvers are an important class of additives that reduce the decline of fluid viscosity with temperature [1], enabling optimum lubricant performance over a wider range of operating temperatures. These additives are typically high molecular weight polymers, such as, but not limited to, polyisobutylenes, olefin copolymer, and polyalkylmethacrylates, that are added in concentrations of 2-5% (w/w). Appropriate polymers, when dissolved in base oil, expand from a coiled to an uncoiled state with increasing temperature [2]. The ability of VI additives to increase their molar volume and improve the temperature-viscosity dependence of lubricants suggests there is a strong relationship between molecular structure and additive functionality [3]. In this work, we aim to quantify the changes in polymer size with temperature for four polyisobutylene (PIB) based molecular structures at the nano-scale using molecular simulation tools. As expected, the results show that the polymers adopt more conformations at higher temperatures, and there is a clear indication that the expandability of a polymer is strongly influenced by molecular structure.

Methods

Molecular Dynamics (MD) simulation, a computational tool that provides an explicit representation of molecular structure, is the primary method used in this investigation. Two types of molecules, polyisobutylene (PIB) as the polymer additive and 9-N-octylheptadecane (TOM) as the base oil matrix, are used in this work (Figure 1(a)). As illustrated in Figure 1(b) and 1(c), four molecular structures of PIB - linear, comb, hyperbranched, and star-branched - with comparable molecular weights, are created and placed in a periodic simulation box (5.0 nm x 5.0 nm x 5.0 nm) containing TOM molecules. The All Atom Optimized Potentials for Liquid Simulations (OPLS-AA) force field with a global cutoff of 1.2 nm is used to describe bond, angle, torsion, and non-bonded interactions between all atoms. MD simulations are run on the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software at low (40°C) and high temperatures (100°C). These are the reference temperatures typically used to measure the viscosity index of a lubricant. Changes in the polymer size are characterized by the radius of gyration of the molecule.

Results

The radius of gyration of each molecule at each temperature is collected over 100 ns of simulation time. This data is used to plot distribution histograms to visualize the frequency of specific conformations. A Gaussian function is then fitted to the histogram to quantify the distribution. It is

noted that, while the Gaussian fit may not be the best fit for all the structures, it provides a reasonable quantitative means of comparison.

Figure 2 shows the distribution of the radius of gyration for the linear PIB structure. The size of the linear structure increases with temperature, implying that the polymer is uncoiling with temperature. This observation is supported by an increase in the mean and maximum value of the radius of gyration. For the linear PIB structure at 40° C, the mean and maximum radii are 21.6 Å

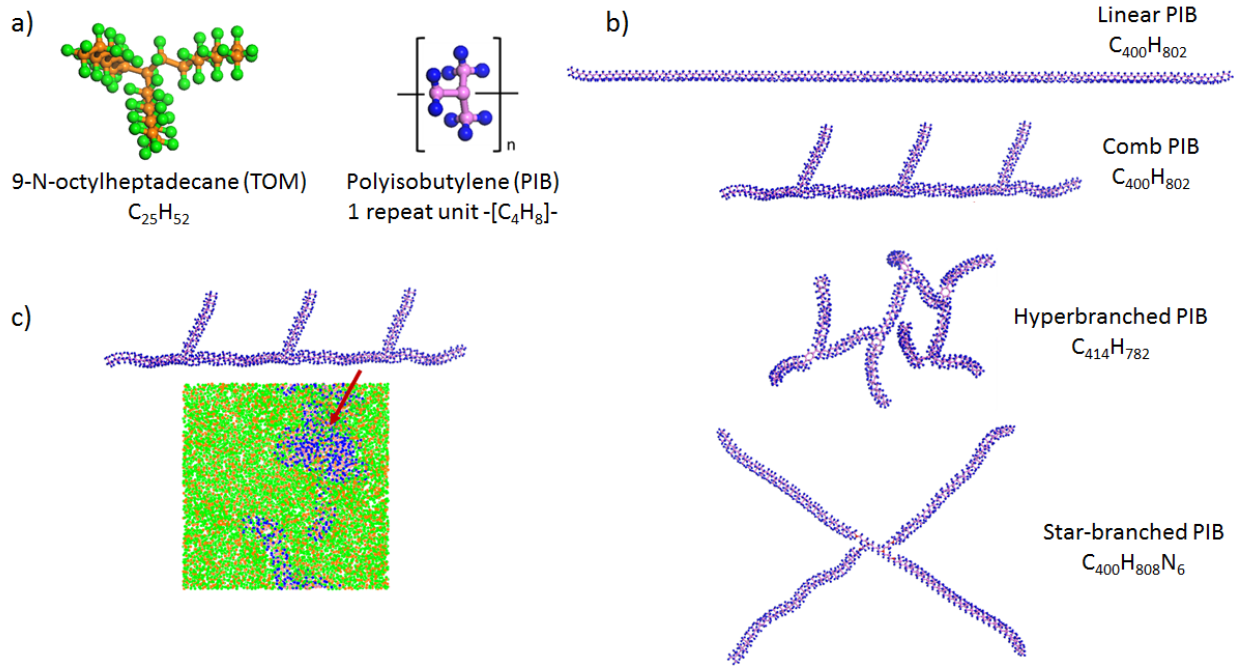

Figure 1: a) Fully atomistic structure of TOM and PIB. b) Linear, comb, hyperbranched, and star-branched PIB structures. c) Representative periodic simulation containing a comb PIB molecule and TOM molecules. Colored spheres represent individual atoms: Orange-carbon, green-hydrogen, pink-carbon, blue-hydrogen, and red-nitrogen.

and 27 Å, respectively; at 100°C those values increase to 26.2 Å and 38 Å. Similar expansions are observed for the comb structure, but not the hyperbranched and star-branched structures.

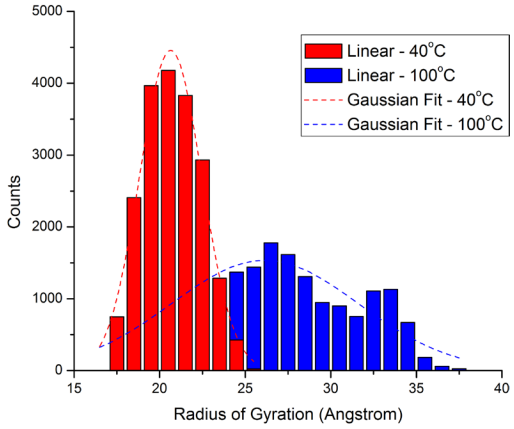

Figure 2: Distributions of the radius of gyration of the linear PIB structure at 40°C and 100°C.

The Gaussian fit in Figure 2 enables evaluation of the number of conformations available to the molecule. This feature is captured by the standard deviation of the fit, where a larger distribution indicates that the molecule is able to assume more conformations. Based on Figure 3, larger standard deviations are observed at higher temperatures for all structures examined in this study, which indicates that all structures are able to adopt more conformations at 100°C than at 40°C.

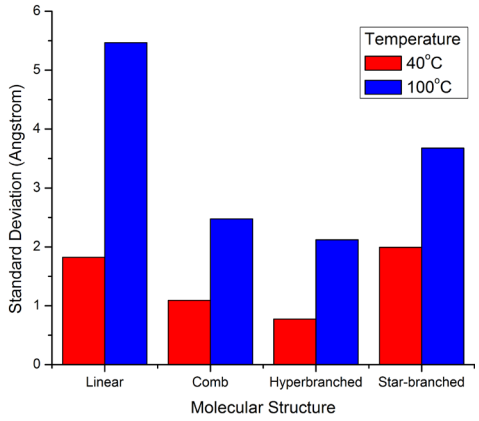

Figure 3: Standard deviation of the Gaussian fit at 40°C and 100°C for all structures

Conclusion

This work presents a method to quantify changes in polymer size with temperature for different PIB molecular structures using MD simulations. The width of the distribution of the radius of gyration indicates that the polymers are able to achieve more conformations at higher temperatures. The results also show that there is a strong relationship between molecular architecture and expansion of the polymer with temperature.

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