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ARTICLES

Order−Disorder Phase Transformation of Triacylglycerols: Effect of the Structure of the Aliphatic Chains

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Plant oils have been used as environmentally benign lubricants since they present high viscosity index and flash points and low evaporation loss. Triacylglycerols (TAG) are the major components of naturally occurring oils and fats and are able to produce high strength lubricant films. One of the main concerns that hinders the usage of triacylglycerols as lubricants, however, is the thermal stability of these molecules. In this paper, we report on the effect of chain structure on density, viscosity, and thermal stability of triacylglycerols using molecular dynamics simulations. The selected triacylglycerols are trilauroylglycerol (LLL-TAG), tristearoylglycerol (SSS-TAG), *trans*-trioleoylglycerol (*trans*-OOO-TAG), and *trans*-trilinolenoylglycerol (*trans*-LeLeLe-TAG). The first two TAGs are saturated molecules with a different number of carbons in the chain, and the second two TAGs are monounsaturated and polyunsaturated molecules, respectively. The computed results demonstrate that the length of the aliphatic chain influences the physical properties of triacylglycerols. TAGs with short chain (LLL-TAG) show higher density than TAGs with longer chains. Viscosity is determined by the degree of recoil of the aliphatic chains and by the number and location of unsaturated bonds. Thermal stability, as represented by the ability of triacylglycerols to stay in a disordered phase during the cooling process, is related to the order−disorder phase transition temperature. Since the phase transition temperature can be correlated to the thermal stability during the cooling process, LeLeLe-TAG shows the highest thermal stability among the systems considered. These results can aid in the design of molecules with specific lubrication properties.

Introduction

As petroleum reserves dwindle, researchers have begun focusing more intently upon searching for alternative solutions. In addition to fuel, engine lubricants are also a very important area to explore as focus shifts to plant-derived renewable sources.

The concept of plant-derived engine lubricants concerns not only resource but environmental issues as well. In North America alone, several billion dollars have been spent in the past two decades to clean up accidental oil spills. Moreover, it is claimed that 32% of lubricant oils sold in the US ended up in the landfills or were improperly dumped. These petroleum-derived lubricants contaminate soil, surface water, groundwater, and drinking water. As these petroleum products are not biodegradable, they cause long-term contamination of our environment. Most plant-oil-based lubricants are rapidly and completely biodegradable and thus could help preserve our environment in addition to the benefits of being a renewable resource.

Plant oil exhibits excellent lubrication properties such as high viscosity index, good lubricity, high flash points, and low evaporation loss. Triacylglycerols, also known as triglycerides or TAGs, are the major components of naturally occurring oils and fats, e.g., corn, sunflower, and soybean. They are abundant and biodegradable.[1−3] Reports have shown that coconut oil is already widely used as a two-stroke engine lubricant in autorikshaws and scooters in Kerala, a southern state of India.[3] Users have claimed that there are many advantages over traditional lubricants including improved mileage, better acceleration, smoother engine operation, and less smoke.

The design of triglycerides with specific lubrication properties would benefit from theoretical models capable of predicting viscosities and thermodynamic properties from knowledge of molecular structures and composition.

Triglycerides are formed from the condensation reaction of glycerol and fatty acids.[4,5] The fatty acids can vary in structure and functionality. The three long aliphatic chains (alkanes and alkenes) can be identical or can vary in length, structure, and functionality. The chains are attached to the hydroxy groups via ester linkages as shown in Figure 1a. The molecule can be separated into two groups: a polar part containing the glycerol backbone and aliphatic fatty chains, which produce high strength lubricant films that interact with metallic surfaces reducing surface wear and friction. In addition, the strong interactions between TAG molecules confer to the films stable viscosity and resilience to the temperature changes. There are, however, some drawbacks that hinder the usage of triacylglycerols as lubricants compared to mineral-based lubricants. The primary issues concern the oxidative and thermal stabilities.[2,6−8] The oxidative stability can be attributed to the presence of unsaturated double bonds in the aliphatic chains, which are active sites for oxidation

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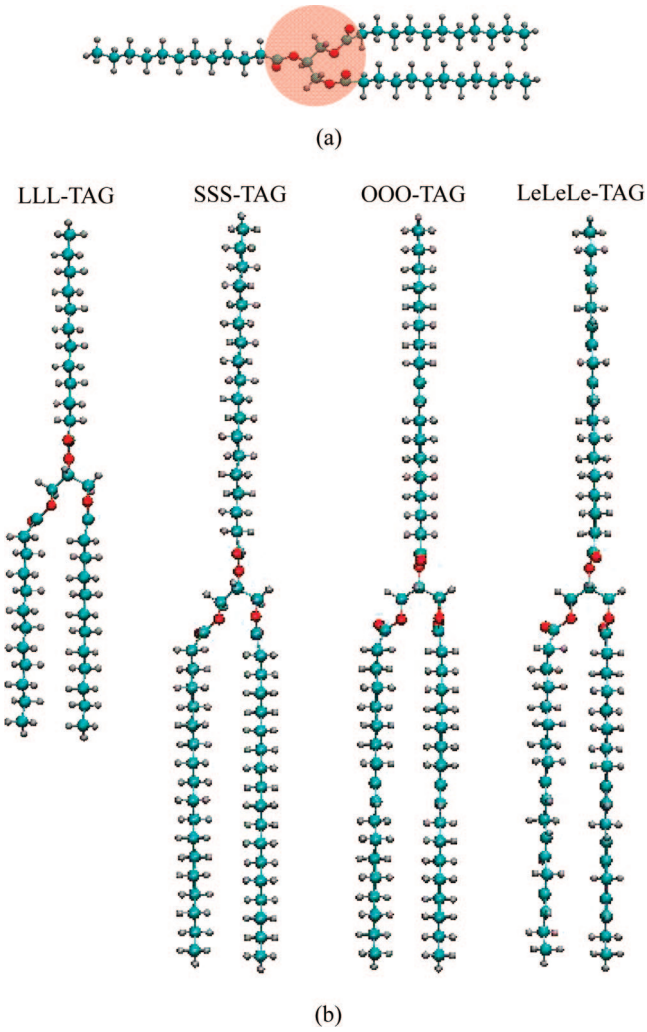


Figure 1. (a) Molecular model of triacylglycerols. The molecules are composed of a polar part, circled in red, containing the glycerol backbone and aliphatic chains. (b) Molecular structures of LLL-TAG, SSS-TAG, *trans*-OOO-TAG, and *trans*-LeLeLe-TAG.

reactions. The oxidation of triacylglycerols increases the wear during the boundary lubrication.[8,9] Another concern is the susceptibility of triglyceride esters to hydrolysis that degrades the triglycerides fatty acids, decreasing the lubrication properties.

The thermal stability is related to the strong intermolecular interactions of TAGs, which cause poor low-temperature properties, such as wax formation and limit their potential applications as industrial lubricants.[3,7] The strength of the intermolecular interactions is determined by the polar group, the number of saturated/unsaturated sites, and the length of the aliphatic chain.[10]

Computer simulations can isolate these effects revealing the mechanisms responsible for the thermal stability of the TAG molecules. In this study we, therefore, report a detailed analysis of the thermal stability of TAG molecules with different lengths of the aliphatic chains and numbers of unsaturated double bonds to evaluate their properties as lubricants. To this end, we identified four TAG molecules. LLL-TAG representing the trilaurin triacylglycerol molecule, which is formed from the condensation reaction of glycerol and three lauric acid (L): SSS-TAG (stearic acid), *trans*-OOO-TAG (oleic acid), and *trans*-LeLeLe-TAG (linolenic acid). Typically, TAGs are often identified by a three-letter acronym representing the respective fatty acids and their order in the molecule. Figure 1b reports the schematics of these structures. In naturally occurring oils, the fatty acids tend to have an even number of carbons, usually between 16 and 20. LLL-TAG and SSS-TAG are both saturated molecules but present different lengths of the aliphatic chains, being 12-carbon and 18-carbon, respectively. *trans*-OOO-TAG and *trans*- LeLeLe-TAG are unsaturated molecules with the same 18-carbon chain length but differ in the number of unsaturated double bonds: one in *trans*-OOO-TAG (monounsaturated) and three bonds in *trans*-LeLeLe-TAG (polyunsaturated).

Molecular dynamics (MD) simulations are employed to gain insights into the effect of molecular structure on the physical properties of the selected TAGs in the temperature range 0−200 °C. The order−disorder phase transition is also studied as well as detailed mechanisms that are responsible for the phase transformation. The results provide useful guidance for the design of vegetable oil mixture for use as engine lubricants.

Computational Details

As reported in the previous section, TAGs are composed of aliphatic chains and a polar head. In this work, we adopted the NERD force field[11−13] to describe the aliphatic part of the molecules. This united atom model (methyl or methylene groups are represented by a single interaction site) has proven to accurately predict the thermophysical properties of a variety of straight chain and branched alkanes as well as alkenes. For the polar group, following the work of Sum et al.,[14] we adopted the NERD force field parametrized using results from quantum-chemical calculations. This approach relies to a significant extent on information generated by means of quantum-chemical calculations. To test the accuracy of the combined force fields, we computed the densities of the condensed phases of LLL-TAG and *trans*-OOO-TAG at 80 °C and 1 bar using MD simulations. The results show very good agreement when compared with available data in the literature.

Lennard-Jones and electrostatic interactions were truncated and shifted at a cutoff radius equal to 12 Å so that the force profiles decrease smoothly to zero at that point. This "cut-shift" approach is employed in all calculations due to the time efficiency and simplicity of the method. In order to verify that the electrostatic forces are treated properly, two other methods, the particle-mesh Ewald (PME)[15,16] and reaction field correction,[17] were also tested. The three approaches produced similar results. A detailed discussion is reported in the Results section.

The systems evolved with a leapfrog algorithm using 1 fs time step. MD simulations were performed using the Groningen Machine for Chemical Simulations (GROMACS) software.[18,19]

Both the NVT and NPT ensembles were employed with periodic boundary conditions. Constant temperature and constant pressure simulations were maintained with the Berendsen's thermostat and barostat, respectively. The thermostat was applied on every atom in the system throughout the simulations. The time constant for the thermostat and barostat coupling was set at 0.1 ps. The systems were initially equilibrated at 0 °C at constant volume for 6 ns to release any strain. The NPT simulations were performed in the range of temperatures 0−200 °C at 1 bar for an additional 6 ns. The equilibrium of the system was confirmed by the convergence of the potential energy curve. The density and radial distribution functions of the systems were obtained by averaging data from the last 3 ns.

The viscosity calculations were performed using the final equilibrium structures of each system. The pressure fluctuation[20,21] and periodic perturbation[20] methods were used to determine the viscosity. The pressure fluctuation method, which uses the

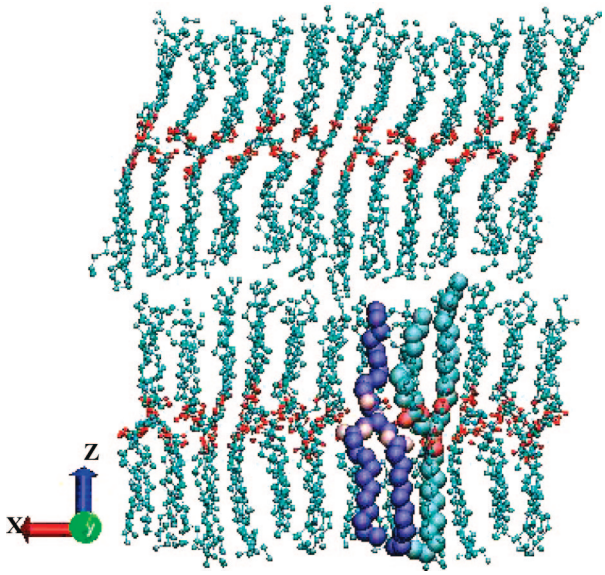


Figure 2. TAG bilayers. The molecule in blue shows the alignment of the three legs in the bilayers.

Einstein relation to calculate the viscosity, converges very slowly because of the significant fluctuations of the pressure in the simulation box. Thus, a very long simulation time is required to accurately measure viscosity. NVT simulations were performed for 20 ns to accumulate the pressure tensor data for the viscosity calculations using the Einstein relation.

Rather than measuring the intrinsic fluctuations of the system at the equilibrium state, we calculated the viscosity using an estimate of the velocity profile generated by an external force.[20] The magnitude of the external force can be selected such that the effects are much easier to measure than the internal fluctuations. The applied external force generates a velocity field in the system according to the Navier−Stokes (N−S) equations. The viscosity is computed by solving the N−S equations with a known external force profile. Since the N−S equations are not valid for microscopic length scales, the simulation model should be at least 1 order of magnitude larger than the size of the molecule. Thus, in this work, the TAG models utilized in the simulations were duplicated $5 \times 10 \times 10$ times in x, y, and z directions, respectively, producing 1000 molecules in the systems. Various amplitudes of the acceleration were tested to acquire accurate viscosity values.

Results and Discussion

The models for the selected TAGs were built based on the assumption that the molecules are fully extended and oriented along the z axis in the condensed phase (cf. Figure 2). The unit cell was then duplicated in the x (two times), y (five times), and z (two times) directions. The dimensions of the unit cell for the selected TAGs were obtained from the molecular density with rational assumption on the conformation and orientation of the chains.[4,5,22−24]

The simulation box for each TAG system consisted of 40 molecules arranged in double-layer array as shown in Figure 2. This size of the system has been reported as suitable for these calculations.[14]

Experiments reported in the literature have shown the formation of bilayer structures for triglycerides in the gel and solid states.[25] Our simulations reveal a strong tendency of the polar groups to aggregate and form structures resembling bilayers. Figure 2 shows a snapshot of one of our simulations.

TABLE 1: Density Values for the Four Selected Triacylglycerols at 80 and 100 °C Obtained Using the Cut-Shift, PME, and Reaction Field Methods for Electrostatic Forces; Last Two Columns Report Data Available in the Literature[a]

TAG	T (°C)	cut	PME	reaction	literature[14]	experiment
LLL-TAG	80	828.67	854.10	829.66	918	880[5,23,24,29 b]
SSS-TAG	80	808.79	808.16	805.58	895	862[5,23,24,29, b]
trans-OOO-TAG	100	793.96	791.75	792.42	925	899 [b]
trans-LeLeLe-TAG	100	801.95	802.77	797.47	931	−

[a] Experimental data for compounds at 80 °C obtained using the empirical formula in ref 14. [b] Experimental data for compounds with double bonds do not specify the measured temperature and the configuration.

For each TAG, two of the aliphatic chains are oriented in the same direction, while the third leg points toward the opposite side with respect to the polar region. In Figure 2, this conformation is highlighted for clarity. This system was used to study the physical properties of TAG molecules at various temperatures.

Table 1 shows the computed densities of the four selected triacylglycerols at 80 and 100 °C using the cut-shift, PME, and reaction field methods to describe the electrostatic forces during MD simulations. The three methods show very similar results. In the same table we also report for comparison data present in the literature.[4,5,22−24] The MD simulations underestimate the densities of the systems by 6% for LLL-TAG and SSS-TAG and 10% for *trans*-OOO-TAG and *trans*-LeLeLe-TAG. Although the predicted densities are slightly lower than the values reported in the literature, they are qualitatively consistent with the experimental results. This indicates that the combined force fields are suitable for simulating the systems of triacylglycerols.

Figure 3 shows snapshots of the LLL-TAG bilayers at different temperatures. Initially, the system presents a very ordered structure ($T = 0$ °C), but as the temperature increases, the molecules are able to move with more degrees of freedom. Between 60 and 80 °C the structures of the layers change dramatically, and the TAG molecules show a transition from an ordered to a disordered phase. The extent of the ordering can be evaluated by pair distribution functions as shown in Figure 4. At 0 °C there are two peaks at $r = 0.5$ nm and $r = 0.9$ nm. However, at 80 °C the intensity of the first peak decreases and the second peak almost disappears, suggesting that the TAG molecules are arranged in a disordered way. This phenomenon becomes more evident at high temperatures (160 °C).

Though the triacylglycerols are in a disordered phase at high temperatures, the polar groups show a pronounced tendency toward aggregation, which has also been reported in other simulations.[14]

The densities of triacylglycerols at different temperatures are plotted in Figure 5. Figure 5a shows the effect of the chain length on density by comparing LLL-TAG and SSS-TAG. The TAG layer composed of shorter alkane chains (LLL-TAG) has higher density than the system made of TAGs with longer chains. This phenomenon can be inferred to the size of the molecules since small molecules readily pack to higher density than large molecules do.

Because of the thermal expansion of the system, the density of TAGs decreases as the temperature increases. Between 40 and 80 °C, the density of the systems changes significantly, showing a phase transformation as highlighted in the snapshots in Figure 3. LLL-TAG exhibits higher phase transition tem-

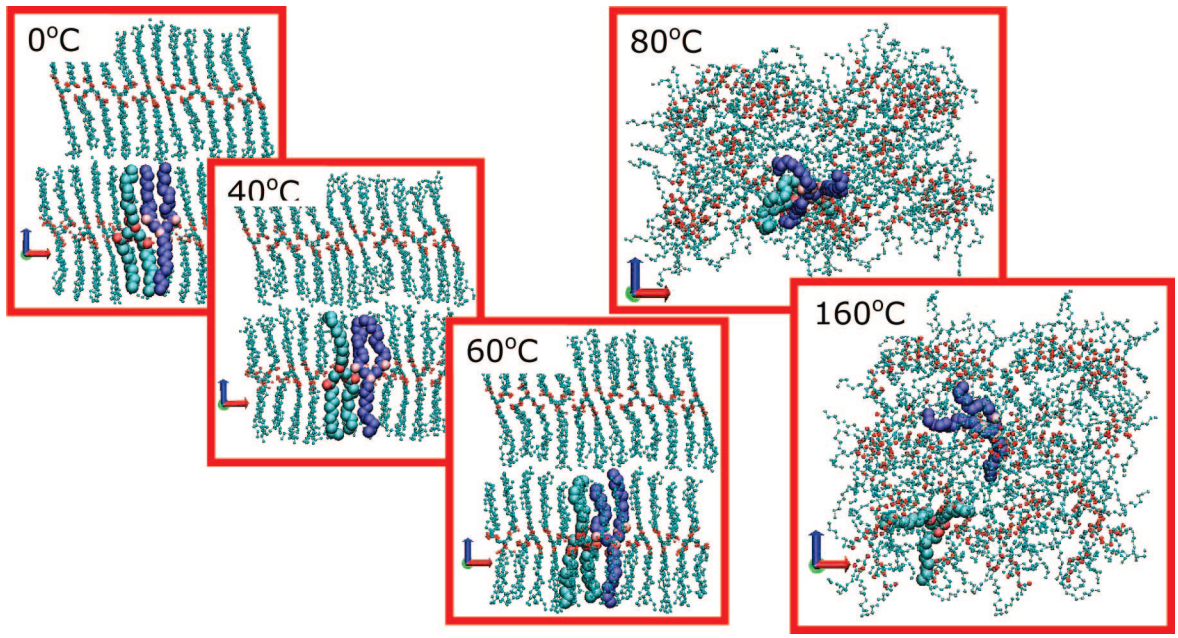


Figure 3. Snapshots of the LLL-TAG bilayer at different temperatures.

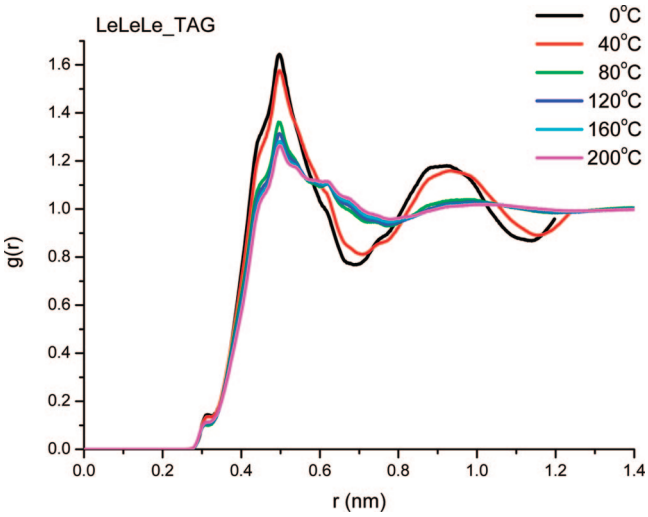


Figure 4. Pair distribution functions of LLL-TAG at various temperatures.

perature than SSS-TAG does. Such behavior is the result of a high-density packed structure (LLL-TAG) that requires more energy when changing phase than the SSS-TAG does. The slopes of the curves are almost the same in these two cases, showing that the densities of both TAGs decrease by 17% between 0 and 100 °C. The result is attributed to the similarity of the two molecules with the only difference present in the length of the alkane chain.

Above the phase transition point, the chains recoil changing the average size of the TAG bilayers. The extent of the recoiling can be expressed quantitatively by calculating the average length of the alkane chains, defined as the distance between the carbon in the carbonyl group of the polar head and the last carbon in the alkane chain. The results are shown in Figure 6. The relative distance is obtained from the ratio between the averaged alkane chain length at a particular temperature and the value at 0 °C. At 100 °C the alkane chains of LLL-TAG and SSS-TAG molecules become 82% and 71% of the original lengths (at 0 °C), respectively. Though the alkane chains of SSS-TAG recoil more than the chains of LLL-TAG, the average length of the

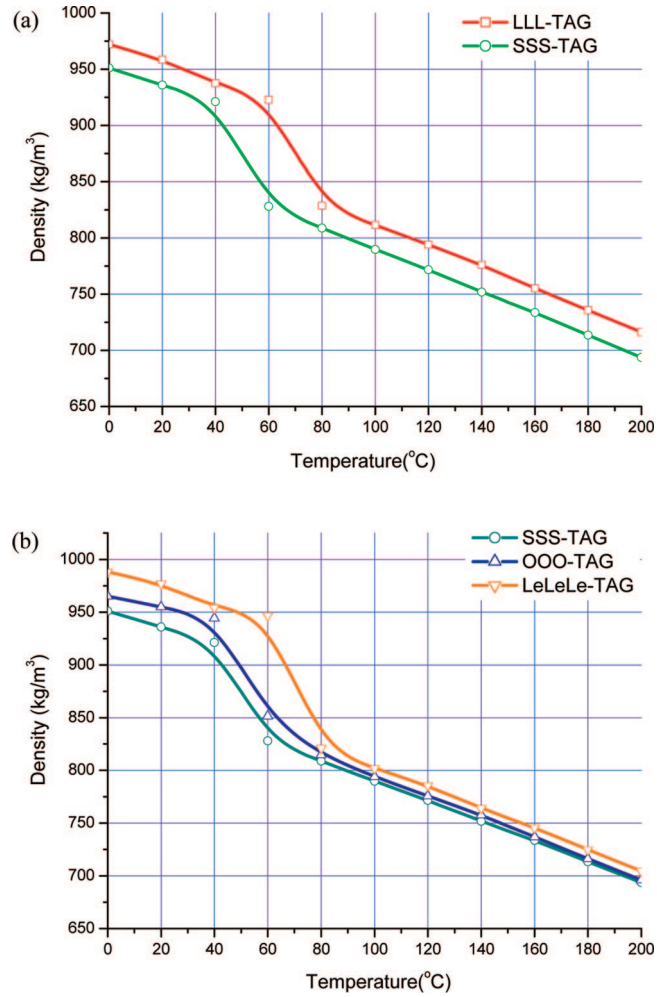


Figure 5. (a) Density values of LLL-TAG and SSS-TAG systems as a function of temperature. (b) Density values of SSS-TAG, *trans*-OOO-TAG, and *trans*-LeLeLe-TAG systems at various temperatures.

SSS-TAG chains is still longer than that of LLL-TAG. Therefore, the LLL-TAG molecules are smaller and thus denser than the SSS-TAG molecules.

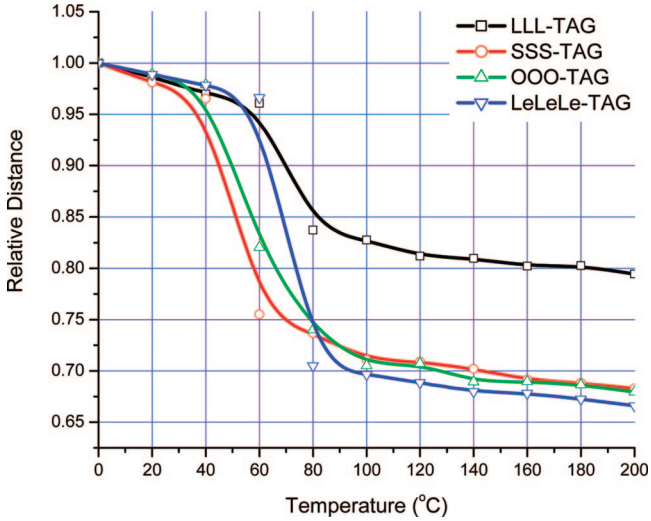


Figure 6. Average distances between the carbonyl carbon in the polar group and the last carbon of the chain of triacylglycerols.

The influence of the number of unsaturated double bonds on the densities of TAGs are reported in Figure 5b for molecules having zero (SSS-TAG), one (*trans*-OOO-TAG), and three (*trans*-LeLeLe-TAG) unsaturated double bonds per aliphatic chain. The double bonds are located at the middle of the aliphatic chains in the *trans*-OOO-TAG molecule and at the end of the tails for *trans*-LeLeLe-TAG. The computed density of *trans*-LeLeLe-TAG is higher than *trans*-OOO-TAG, while SSS-TAG presents the lowest density. These results seem to contradict the common knowledge that molecules tend to kink where there is a double bond keeping the chains from packing closely. In the *trans*-conformations, however, this effect is small compared with the *cis*-configuration, and consequently it does not change much the linear shape of the aliphatic chains. In addition, the unsaturated sites of the *trans*-aliphatic chains occupy smaller space than fully saturated chains, leading to systems with chains that can fit together tightly. Since *trans*-LeLeLe-TAG has the highest number of double bonds, it can produce systems with high density.

Between 40 and 80 °C the densities of the TAGs changes, and the transition temperature shows a behavior that is dependent on the number of unsaturated double bonds. We can infer that more unsaturated double bonds contribute to a higher transition temperature. Aliphatic chains with double bonds are more rigid than chains with only single bonds, and therefore they require high temperatures to recoil and hence to show an order−disorder phase transformation. Therefore, the system density as well as the phase transition temperature is higher for *trans*-LeLeLe-TAG than SSS- and OOO-TAG.

These three TAGs have the same number of carbon atoms in the aliphatic chains. The recoil of the aliphatic chain at high temperatures can also influence the density of the system. The extent of the recoiling for these three TAGs is reported in Figure 6. Since these molecules have the same number of carbon atoms in the aliphatic chains, the initial average lengths of aliphatic chains are very similar. As temperature increases, the chains start recoiling. Between 40 and 80 °C, corresponding to the phase transition regime, the lengths of the chains decrease by 30% in the three cases.

The results show that the rigidity of unsaturated bonds influences the transition temperatures, requiring more energy than a system without double bonds (SSS-TAG) does. Above

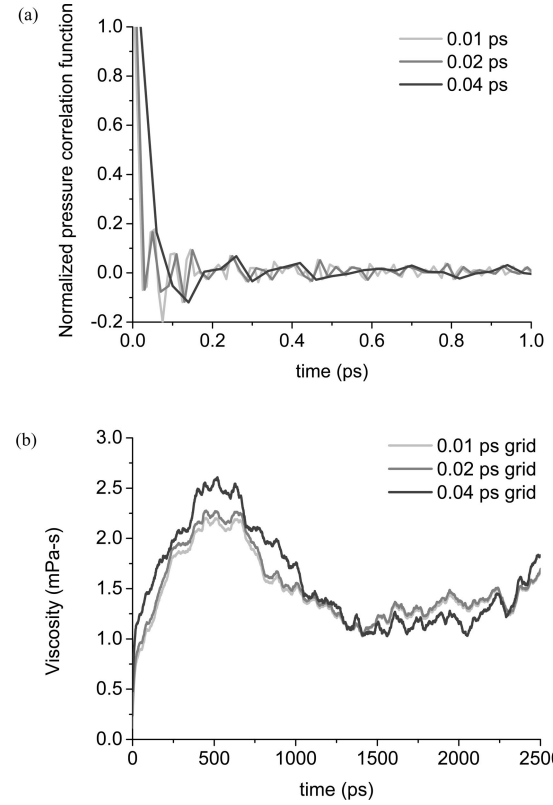


Figure 7. (a) Pressure cross-correlation functions calculated at different time intervals. (b) Viscosity values (integral of cross-correlation function) of triglycerides.

80 °C, SSS-TAG reaches its disorder phase while OOO-TAG and LeLeLe-TAG complete the phase transformation above 90 °C.

At 100 °C the lengths of the chains become 71%, 70%, and 69% of the original length for SSS-TAG, *trans*-OOO-TAG, and *trans*-LeLeLe-TAG, respectively. The results indicate that the presence and location of the unsaturated bond influence the degree of recoil. For example, in the *trans*-LeLeLe-TAG, the unsaturated sites are gathered at the tail of the chains. Therefore, the chain is more flexible at the head and stiffer at the tail. Once the molecule starts to recoil, the junction between the tail and the head of the molecule can bend more in the *trans*-LeLeLe TAG than in the OOO-TAG, which presents the unsaturated sites at the middle of the chain. The results are consistent with the densities predicted in Figure 5b, indicating that the degree of recoil controls the density at high temperature and the intermolecular interactions determine the density at low temperature, for molecules of similar size.

Viscosity is an important physical property since it influences the rates of conformational changes in the condensed phases. The pressure fluctuation method, based on the Einstein relation, evaluates the integral of pressure correlation function over time. Figure 7a shows the normalized pressure correlation function at the first 1 ps of the simulation at different time intervals. A time interval of 0.02 ps gives enough resolution for the pressure correlation calculations. The viscosity can be derived from the integral of pressure correlation function over time as shown in Figure 7b. The results, however, indicate that the viscosity value is not converged even when the simulation time reaches 20 ns. This creates difficulties for the prediction of viscosity of triacylglycerols, as pressure fluctuates rapidly and widely during the simulation. Increasing the system size smoothes the fluctuation; however, running a larger system simulation over a longer period of time is challenging.

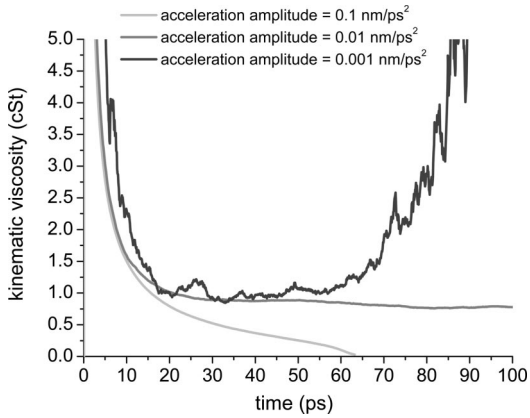


Figure 8. Kinematic viscosities calculated using the periodic perturbation method with different acceleration amplitudes.

TABLE 2: Viscosity Values for the Four Systems of Triacylglycerols at 100 °C Calculated Using the Periodic Perturbation Method

kinematic viscosity (cSt)	LLL-TAG	SSS-TAG	*trans*-OOO-TAG	*trans*-LeLeLe-TAG
100 °C	0.774 99	0.975 54	0.965 53	1.3875
experiment[4,5,22−24]	5.6	10.5	8.1	−

The other method employed in this study to calculate viscosity is the periodic perturbation method. Figure 8 shows that a proper choice of the acceleration amplitude is necessary to obtain converged values of the viscosity. If the amplitude of the acceleration is too large (0.01 nm/ps^2), then the system is not in steady state and the values of the viscosity decrease. Values of the acceleration amplitude that are too small (0.001 nm/ps^2) result in large fluctuations of the viscosity values. We chose the value of 0.01 nm/ps^2 for the acceleration amplitude that shows a converged value for the kinematic viscosity.

Table 2 reports the viscosity of triacylglycerols calculated using the periodic perturbation method. Though the computed values are smaller than the experimental results, the trend is correct and consistent. Similar predictions by the same method were also reported by other research groups.[20,26] The differences in the viscosity between experiments and calculations can be improved by adjusting the atomic charge and cutoff treatment in the calculation as mentioned by Hess et al.[20] As shown in Table 2, the viscosity of SSS-TAG is higher than LLL-TAG, while the density results for these systems show the opposite trend. The difference can be inferred to the fact that viscosity is a dynamic property, and it is related to the conformational changes during the flowing of the liquid while density is a static property, associated with the molecular packing. Therefore, the higher the degree of entanglement between the molecules, the higher the viscosity. The degree of entanglement can be expressed
by the degree of recoil as shown in Figure 6. Thus, SSS-TAG exhibits higher viscosity than LLL-TAG. The same correlation applies to *trans*-LeLeLe-TAG, *trans*-OOO-TAG, and SSS-TAG. These three systems have similar densities at 100 °C. The degree of entanglement, however, is different in each case due to the number and location of unsaturated bonds. From Figure 6, *trans*-LeLeLe-TAG has the highest degree of recoil; thus, its viscosity is higher than SSS-TAG and *trans*-OOO-TAG.

The results presented in this work show that in order to study the thermal stability of TAGs at low temperatures, it is important to consider the phase transformations during the cooling process. The stability of TAGs in the disordered phase can be qualitatively estimated from the transition temperature from ordered to disordered phase since the latter is determined by the density and the rates of conformational changes. High ordered to disordered phase transition temperatures indicate that high energy is needed for the transformation and that the opposite transition to ordered phase requires long time and low temperatures. The phenomenon has been also observed in experiments with differential scanning calorimeters heating and cooling thermopeaks.[27,28] Therefore, *trans*-LeLeLe-TAG has the highest thermal stability among the four selected TAGs.

Conclusions

The physical properties of triacylglycerols are influenced by the length of aliphatic chains and the number and location of unsaturated bonds. For saturated triacylglycerols such as, LLL-TAG and SSS-TAG, the density is determined by the length of the chains. LLL-TAG with a 12-carbon chain has higher density than SSS-TAG (18-carbon chain) due to the high packing factor. The ordered to disordered phase transition temperatures can also be correlated with the length of the alkane chains.

The length of the aliphatic chains, however, has an inverse effect on viscosity. This physical property is associated with the rate of conformational change of the systems. SSS-TAG, which has a longer alkane chain than LLL-TAG, presents a high degree of recoil and hence a great entanglement between molecules. Therefore, the viscosity of SSS-TAG is higher than that of LLL-TAG.

The effect of unsaturated bonds is studied by comparing SSS-TAG, *trans*-OOO-TAG, and *trans*-LeLeLe-TAG which have zero, one, and three unsaturated bonds, respectively. The density is proportionally related to the number of unsaturated bonds in the ordered phase. The viscosity is influence by the number and location of the unsaturated bonds since both factors affect the molecular recoiling. *trans*-LeLeLe-TAG exhibits the highest viscosity in this study.

The ability of TAG to stay in the disordered phase during the cooling process can be related to the ordered−disordered phase transition temperatures, since the phase transformations are determined by the density and the rates of conformational changes. Triacylglycerols exhibiting a high phase transition temperature will also display high thermal stability during the cooling process.

In summary, the presence of unsaturated bonds along the aliphatic chains confers thermal stability to the system. The *trans*-LeLeLe-TAG bilayer has the highest thermal stability among the four systems studied.

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