



공학박사 학위논문

All-atom Molecular Dynamics Simulation Study on Structure and Behavior of Molecular Modified Polymeric Compounds

전원자 분자동역학 전산 모사를 통한 분자 개질 고분자 화합물의 구조와 거동 연구

2023 년 2 월

서울대학교 대학원

화학생물공학부

이 민 환

All-atom Molecular Dynamics Simulation Study on Structure and Behavior of Molecular Modified Polymeric Compounds

지도 교수 이 원 보

이 논문을 공학박사 학위논문으로 제출함 2023 년 2월

> 서울대학교 대학원 화학생물공학부 이 민 환

이민환의 공학박사 학위논문을 인준함 2023 년 2 월 위 원 장 <u>이규태 (인)</u>

부위원장		이원보	(인)
위	원	오준학	(인)

위 원 남재욱 (인)

위 원 _____ 김용주 (인)

Abstract

All-atom Molecular Dynamics Simulation Study on Structure and Behavior of Molecular Modified Polymeric Compounds

Minhwan Lee

School of Chemical & Biological Engineering Graduate School of Seoul National University

In this dissertation, all-atom molecular dynamic (AAMD) simulation studies on polymeric compounds are presented. Conventionally, polymer models for computer simulations have been neglecting the atomistic details and focusing on reproducing long chain-like configurations, but nanoscale structures become important as newly developed polymeric compounds contain molecular modifications for various purposes. Among such polymeric compounds, ones with functionalized short oligomers and with various chemical structure functional groups are investigated as they can not be reproduced without an atomistic model. Two cases are demonstrated as examples of the compounds with the former type of modification; the molecular rotor with a farnesyl group and the alkylated graphene oxide (AGO). Meanwhile, the mesogen epoxy resins with various functional groups are provided as a study to show the latter kind of modification. Therefore, totally three systems are dealt with in this dissertation to show how AAMD can be applied to understand the polymeric system.

At first, the farnesyl-(2-carboxy-2-cyanovinyl)-julolidine (FCVJ) is one kind of fluorescent molecular rotor that is enabled to measure the glass transition point (T_g) of a polymer matrix due to the functionalized farnesyl group. The MD simulation reproduces the fluorescent experiment to measure $T_{\rm g}$ and explains the principle of the molecular rotor by coupling a hightemperature thermostat to the FCVJ. The $T_{\rm g}$ measured from which the point that uneven kinetic energy distribution arises is well agreed with the experiment. The bulkiness and the heterogenetic structure derived by the farnesyl group are attributed to the ability to measure the T_g of the FCVJ. Next, the AGO is the derivative of graphene oxide (GO) whose properties can be modulated by functionalized alkyl groups. As the molecular structure of the AGO is not defined yet, systematic computational modeling is suggested combining the grand canonical Monte Carlo (GCMC) and the AAMD to construct reasonable configurations of the AGO. As a result, the structural and mechanical properties of the layered AGO are calculated as a function of the chain length of the alkyl chain which gives a guide for the material design with AGOs. Lastly, mesogen epoxy resins have been investigated as a highly thermal conductive thermoset plastic. The mesogenic groups in a polymer network tend to be aligned in one direction so form a microphase that provides

a route for the fast phonon transfer. The detailed observation by the AAMD elucidates how the different kinds of mesogenic groups affect their aligning tendency of them and the thermal conductivity (TC) of the resin.

An extensive AAMD study on these representative polymeric systems is provided, which demonstrates how the molecular level modification can affect the properties and behavior of the polymeric system which results to emphasize the importance of atomistic detail in studying polymer science and engineering.

Keyword : All-atom Molecular Dynamics Simulation, Polymeric Compound, Molecular Modification, Microscopic Structure, Macroscopic Property, Dynamic Behavior

Student Number: 2017-29678

Table of Contents

Abstract	i
List of Figures	vi
List of Tables	ix
Chapter 1. Introduction	1
Chapter 2. Theoretical Background	5
2. 1. All-atom Molecular Dynamics	5
2. 2. FCVJ Molecular Rotor	9
2. 3. AGO	12
2. 4. Mesogen Epoxy Resin	15
chapter of Dynamics and Structure of Singemen Function	alized
Compunds	alized 17
Compunds	alized 17 17
 Compunds	alized 17 17 18
 3. 1. Glass Transition Temperature Measurement by FCVJ Molecular Rotor 3. 1. 1. Computational Methods	alized 17 17 18 20
 Compunds	alized 17 17 18 20 22
 Compunds	alized 17 17 18 20 22 24
 Compunds	alized 17 17 18 20 22 24 34
 Compunds	alized 17 17 18 20 22 24 34 35
 Compunds	alized 17 17 18 20 22 24 34 35 36
 Compunds	alized 17 17 18 20 22 24 34 35 36 41
 Compunds	alized 17 17 18 20 22 24 34 35 36 41 46
 Compunds	alized 17 17 18 20 22 24 34 35 36 41 46 51
 Compunds. 3. 1. Glass Transition Temperature Measurement by FCVJ Molecular Rotor 3. 1. 1. Computational Methods	alized 17 17 18 20 22 24 34 35 36 41 46 51 56

Chapter 4. Effects of Chemical Structure of Functional Groups on Bulk Material
4. 1. Thermal Conductivity of Mesogenic Epoxy Resin
4. 1. 1. Crosslinked Polymer Construction
4. 1. 2. MD Simulation Details
4. 1. 3. Monomer Effect
4. 1. 4. Flexible Chain Spacer Effect75
4. 1. 5. Hardener Effect
4. 1. 5. Summary
Chapter 5. Concluding Remarks
5. 1. Conclusion
5. 2. Future Directions
Bibliography
감사의 글

List of Figures

Figure 1 Chemical structures of julolidine-based fluorescent molecular rotors, (Left) DCVJ and (Right) FCVJ. Upon electronic excitation, these rotor molecules can relax non-radiatively by internal rotation around the double bond (marked with an asterisk) which separates the julolidine headgroup from the tail moiety. 1
Figure 2 (a) A molecular structure t of an FCVJ embedded in a PS_{20} matrix. The double bond (separating the julolidine headgroup from the farnesyl tail) is the axis of rotation (marked with an arrow). (b) The radii of gyration of the head and tail groups ($R_{g,head}$ and $R_{g,tail}$, respectively) and the end-to-end distance of the tail group ($R_{e,tail}$) calculated as functions of temperature by MD simulation
Figure 3 The center-of-mass mean square displacements (MSDs) of center of mass of the PS ₂₀ monomers and of the head and tail moieties of FCVJ calculated by all-atom MD simulation. Data represent averages over 20 independent MD simulation runs at each temperature
Figure 4 The total kinetic energies (i.e., the sums of the kinetic energies over all atoms) of the FCVJ molecule and also of the head and tail groups of the FCVJ molecule embedded in the PS ₂₀ matrix as function of temperature. The $T_{g,KE}$ was determined by fitting the FCVJ head and tail kinetic energy profiles to a Heaviside step function based on two different linear equations for high- and low-temperature regions
Figure 5 The ratio of kinetic energies per atom of the head and tail groups of FCVJ. The ratio is constant and nearly equal to unity at $T > T_{g,KE}$ but deviates from unity at $T < T_{g,KE}$
Figure 6 Schematic illustration of local frictional environments of FCVJ's head and tail groups. The farnesyl tail plasticizes the PS matrix because of its conformational flexibility; in the immediate vicinity of the tail, the polymer may remain liquid-like (viscous) at $T < T_{g,KE}$
Figure 7 The local volumes of the FCVJ's (a) head and (b) tail groups as a function of temperature. The head and tail volumes were estimated using the convex hull method; the boundary of the FCVJ molecule was defined using midpoints between an individual atom of the FCVJ molecule and the ten nearest atoms from the matrix PS chains surrounding that particular atom of the FCVJ molecule
Figure 8 The specific volume of PS ₂₀ calculated as a function of temperature by MD simulation. 3 1
Figure 9 The kinetic energies per atom of (a) 9-methyljulolidine and (b) farnesyl cyanoacetic ester embedded in PS ₂₀ . MD simulations were performed using the same procedure as used to obtain data shown in Figure 4 of the main text

Figure 10 An overall schematic representation of procedure to construct layered AGOs. The structure of AGO was obtained using the hierarchical

multiscale simulation method; the representative configurations of each step are illustrated for pristine graphene, GO, AGO, and layered AGO. The computational modeling methods and results are provided below the corresponding configuration. 4 0 Figure 11 The bond autocorrelation function depending on the separating bond number. The black square is the calculated results. The red dashed line is fitting result to calculated persistence length. (a) The end-to-end distance Figure 12 (a-c) MC cycle evolution of the adsorption number of n-butylamine (black curve) and n-octadecylamine (blue curve) on each functional group: Side epoxy group (a), basal epoxy group (b), and side carboxyl group (c). (d) Total adsorption number of alkylamine on GO as a function of the chain Figure 13 The representative GCMC snapshot after the adsorption number Figure 15 Structure analysis of the AGO layers using MD simulations. The positional distribution (a) and probability distribution in reciprocal space (b). The interlayer distance (c) and density (d) depend on the alkyl chain Figure 16 The snapshot of AGO molecules to present the chain conformations whose chain length is 4 (a) and 18 (b). 54Figure 17 The Gaussian curvature parameter depending on the chain length. 5 5 Figure 18 The strain-stress curves obtained from MD simulations using different alkyl chain lengths (a). The red dashed line is the fitting curve used to obtain the Young's modulus. The resulting Young's modulus Figure 19 Algorithm flow chart of constructing the crosslinked structure from the EH mixture configuration. (a) Converting procedure presentation of functional groups to crosslink bond which are within the cut-off distance. Figure 20 TC according to crosslinked ratio p where the box size was 50 Å. The error bars are from the 95% confidence interval range of independent Figure 21 Convergence of HCACF presentation in long time scale (a) and Figure 22 ARDF heatmaps according to pairwise distance and angle of aromatic groups in the crosslinked polymer. (a) Thermal conductivities of the EH pairs in which bars are represented by the same color for the same groups. The error bars are from the standard deviation of independent runs. (b) $7 \ 3$

Figure 23 Representative snapshot of aligned aromatic groups in the crosslinked

List of Tables

Table 1 Alkylation ratio of each functional group dependir	ıg on alkyl chain
length	
Table 2 The list of EH pairs in our study with molecular struct	ure representation

Chapter 1. Introduction

The polymer industry has been expanding rapidly since about a century ago so its products are utilized in all aspects of our lives now. Synthetic fabrics can be found everywhere in daily-wear clothes, packaging plastics are essential for the food industry, and even thermoset polymers are used for automobiles and airplanes due to their superior properties. Followingly, this man-made material has been widely researched in the field of chemistry, physics, and engineering. Even now, chemists are developing new polymers and suggesting different synthetic processes for them. While, the nature of these complicated long molecules has been explained by physicists in various aspects such as dynamics, thermodynamics, and rheology. In addition, engineers have been optimizing the production process for numerous types of polymers, which results in a massive quantity of polymer production.

Meanwhile, as computational devices and numerical methods are developed, simulations about the polymers also have been conducted to aid in understanding their underground physics. Usually, polymers are literally big macromolecules that are made of hundreds or even thousands of monomers, so indirect modeling methods are used to describe the molecules in simulation systems. Two strategies commonly used; one is by self-consistence field theory and the other one is by bead-spring model. In the self-consistence field theory model, the polymers are considered to be in the chemical potential field which is made by other polymers, so the average positional probability distribution, rather than the explicit positions, of a monomer can be obtained from the simulation. Otherwise, the bead-spring model which is conventionally used for Monte Carlo or molecular dynamics simulation represents a polymer as bead-like particles connected by spring-like bonding potentials. Each bead is considered a monomer or a group of monomers and various types of mathematic bonding potentials are used. These kinds of modeling work well to reproduce and predict polymer structure and dynamics which are utilized to study such as the self-assembled structure of block-co-polymers and rheology of the polymer melt.

However, these conventional methods have limits ignoring the chemical details of polymers and simply considering the interaction among the components by affinities. It becomes especially problematic for recently developed advanced polymers with molecular modifications that are quite different from standard polymers produced in the conventional olefin-based industry. Sometimes short oligomers are functionalized which is not appropriate to assume chain-like conformation or they often contain complex chemical structures which is hard to represent by field theory or bead spring model. To solve this problem, it is needed to consider the molecular structure and chemical properties; the all-atom MD (AAMD) can be a suitable solution. Using the AAMD simulation, the polymeric compounds are fully reproduced by atomistic scale, so it is feasible to investigate ones with short oligomers or characteristic molecular structures.

In this dissertation, therefore, AAMD simulation studies on molecular modified polymeric compounds is presented that detailed chemical structures have significant roles. Due to the AAMD, novel and meaningful interpretations and explanations are provided for three different types of polymeric compounds and corresponding phenomena here. First, a new method to accurately measure the glass transition temperature of polymer is suggested by using the molecular rotor designed by introducing oligomeric farnesyl tail, farnesyl-(2-carboxy-2-cyanovinyl)-julolidine (FCVJ). AAMD proves that the bulky and asymmetric characteristics of the FCVJ derived from the farnesyl tail are the origin of the ability to detect the glass transition temperature of polymers. The farnesyl chain is long and bulky enough to be coupled with the segmental motion of the subject polymers, and also it plasticizes the local neighboring polymer matrix so the anomalous kinetic energy distribution between the head and tail of the rotor arises. From the uneven kinetic energy distribution arises, the glass transition temperature can be obtained. Second, the systematic computational study of the structure-property correlation of alkylated graphene oxide(AGO) is presented by combining Grand Canonical Monte Carlo (GCMC) and AAMD simulation. The molecular structure of AGO, which has remained ambiguous, is constructed in a plausible way by hierarchical modeling. Varying the chain length of the alkyl group, the material structure and property of AGO is investigated which shows a multiple oligomer functionalization effect. Lastly, the thermal conductivities of epoxy resins with mesogenic groups are measured and their correlation with characteristic aligning tendency derived from the chemical structure of different mesogens are examined. To construct stable configurations of crosslinked epoxy resin, the iterative MD simulation is conducted to stabilize polymer melt. The effects of chemical functional groups in mesogens such as biphenyl, imine, and ester groups are clarified by analyzing the network structure in detail. The detailed background information about the investigated systems are provided in the following chapter.

This dissertation is composed of five chapters and the contents of each chapter are as follows. Chapter 1 explains the motivation of the research in the context of polymer simulation. Chapter 2 gives a brief introduction of AAMD and explanations about the polymeric compounds investigated in this dissertation as theoretical background to understand this dissertation. In Chapter 3, two studies about the polymeric compounds with short oligomers are provided; one is about measuring the glass transition temperature of polymers by the molecular rotor, and the other one is about the systematical simulation study about hierarchical modeling of AGO. In Chapter 4, the research about measuring the thermal conductivity of mesogenic epoxy resin is presented to show how detailed chemical structure affects the structures and properties of polymers. Finally, concluding remarks are given in Chapter 5.

Chapter 2. Theoretical Background

2. 1. All-atom Molecular Dynamics

The all-atom molecular dynamics (MD) simulation is the computational modeling procedure to reproduce the motions of atoms in the real world. The movement of atoms can be described by classical Newtonian dynamics with several assumptions such as the Born-Oppenheimer approximation. Therefore, the simple Newton's equations of motions become sufficient to simulate the atoms in the system by MD:

$$F_i = -\frac{\partial E}{\partial r_i}, \ \frac{\mathrm{d}^2 r_i}{\mathrm{d}t^2} = \frac{F_i}{m_i}$$
(2.1)

 F_i , r_i , m_i are the force, position, and mass of *i*th atom, *E* is the total energy of the system, and *t* is time. How to calculate the energy of the system varies on the model of molecules or atoms, where many types of them have been developed to represent different kinds of materials accurately. For example, organic compounds are commonly represented as atoms bonded by harmonic potentials. Otherwise for metallic materials, the strategy is used that considering an atom is embedded into a position with the local electronic density made by other atoms in the system. The mathematical formula for calculating energy and the table of parameters for this are called 'force field' altogether. There are also force fields only for polymers such as PCFF but their application is limited to several commonly used polymers. Alternatively, transferable force fields can be used to simulate a wide variety of polymers with complex and novel structures. They are developed to deal with different types of compounds not only for the compounds used as fitting data but

also for a new molecule that a user wants to simulate. The optimized potentials for liquid simulations (OPLS) force field is a representative transferable force field where the total energy of the system is calculated as follow:

$$E = E_{bonds} + E_{angle} + E_{dihedrals} + E_{nonbonded}$$

$$E_{bonds} = \sum_{bonds} K_r (r - r_0)^2$$

$$E_{angles} = \sum_{angles} k_{\theta} (\theta - \theta_0)^2$$

$$E_{dihedrals} = \sum_{dihedrals} (\frac{V_1}{2} [1 + \cos(\phi - \phi_1)] + \frac{V_2}{2} [1 - \cos(2\phi - \phi_2)] + \frac{V_3}{2} [1 + \cos(3\phi - \phi_3)] + \frac{V_4}{2} [1 - \cos(4\phi - \phi_4)])$$

$$E_{nonbonded} = \sum_{i>j} f_{ij} (\frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}} + \frac{q_i q_j e^2}{4\pi\epsilon_0 r_{ij}}) \qquad (2.2)$$

In short, the all-atom MD for polymeric compounds with a transferable force field proceeds as calculating force and updating the positions and velocities of atoms during the simulation time based on equations such as eq (2.2).

Even though the main idea of MD simulation is quite simple, many technical computation methodologies have been developed to embody the real substances into digital data and perform simulations according to the right physics. First of all, the integrator to update the positions and velocities of atoms from a time step to the next is important to do sampling in phase space appropriately. The most commonly used algorithm is the velocity Verlet algorithm:

$$v_{i}\left(t + \frac{1}{2}\Delta t\right) = v_{i}(t) + \frac{\Delta t}{2m}F_{i}(t)$$

$$r_{i}\left(t + \frac{1}{2}\Delta t\right) = r_{i}(t) + \Delta t v_{i}\left(t + \frac{1}{2}\Delta t\right)$$

$$v_{i}(t + \Delta t) = v_{i}\left(t + \frac{1}{2}\Delta t\right) + \frac{\Delta t}{2m}F_{i}(t + \Delta t)$$
(2.3)

It is known to satisfy several criteria for right sampling like the time reversibility and the symplectic properties.

Calculating the Coulombic energy and force needs a large computational cost due to it is not easily converging. Therefore, the slowly-converging interaction function converted to two quickly-converging terms and a constant term by the Ewald summation method:

$$V = V_{dir} + V_{rec} + V_0$$

$$V_{dir} = \frac{f}{2} \sum_{i,j}^{N} \sum_{n_x} \sum_{n_y} \sum_{n_z} \frac{q_i q_j \operatorname{erfc}(\beta r_{i,j,n})}{r_{i,j,n}}$$

$$V_{rec} = \frac{f}{2\pi V} \sum_{i,j}^{N} q_i q_j \sum_{m_x} \sum_{m_y} \sum_{m_z} \frac{\exp\left(-\left(\frac{\pi \mathbf{m}}{\beta}\right)^2 + 2\pi \mathbf{m} \cdot (\mathbf{r}_i - \mathbf{r}_j)\right)}{\mathbf{m}^2} 2\pi i \mathbf{m} \cdot (\mathbf{r}_i - \mathbf{r}_j)$$

$$V_0 = -\frac{f\beta}{\sqrt{\pi}} \sum_{i}^{N} q_i^2$$
(2.4)

In addition, a more developed method, the Particle-mech Ewald method reduces the computation cost by calculating the summation of wave vectors by assigning them to grid points by interpolation.

Even though the AAMD is designed to simulate atomic system realistically, every motions of nanoscale moieties can not be considered practically and also not required.

One of example of such a type of motion is vibration of hydrogens bonded to other heavy atoms which do not affect significantly property of material or phenomena in the system. Therefore, constraint algorithms are developed to perform simulation excluding minor motions in the system. The SHAKE algorithm is utilized widely where a set of unconstrained coordinates \mathbf{r}' are converted to a set of constrained coordinates \mathbf{r}'' :

SHAKE
$$(\mathbf{r}' \rightarrow \mathbf{r}''; \mathbf{r})$$
 (2.5)

There are also other techniques applied to the AAMD for various purposes such as temperature and pressure coupling algorithms and advanced sampling methods to explore non-equilibrium states. Not just advances in software and computing algorithms, but new hardware and processors contribute versatility of the AAMD by accelerating calculation. Especially, the multicore processors such as GPUs and parallel computing algorithms have been boosting the speed of the AAMD significantly. Finally, the AAMD for complex and large systems like polymers becomes available in these days due to all these advances in computer sciences.

2. 2. FCVJ Molecular Rotor

The glass transition in nanoconfined polymers is an important topic in polymer science. Nanoconfinement affects the mechanical properties of a polymer through its influence on the glass transition temperature (T_g) .¹ Some fluorescent probes have been demonstrated to be useful for studying the spatial variation of a polymer's T_g near a nanoconfining interface because their fluorescence intensities vary in response to a change in the free volume of the polymer matrix.² ³ Conventional fluorescent probes commonly used for this purpose (such as pyrene), however, only work for certain types of polymers but not for others,⁴ which limits their utility in T_g measurement. A subclass of fluorescent probes called "molecular rotors" have been demonstrated to be capable of measuring microviscosities for biological membranes5 and also such mechanical properties as Young's modulus and physical aging for polymers.^{5, 6} However, a previous attempt to use fluorescent molecular rotors for polymer T_g measurement was unsuccessful, because the intramolecular rotation of rotor molecules was not strongly coupled to the motions of the polymer segments.

In the respect of the coupling with the polymer segmental motion, it has been reported that the internal rotational motions of julolidine-based rotors are highly sensitive to the local friction produced by the surrounding material regardless of the polarity of the material.^{7, 8} However, 9-(2,2-dicyanovinyl)julolidine (DCVJ) and other rotors were found to be incapable of reliably detecting glass transition in polymers.^{9, 10} Interestingly, a different julolidine derivative, farnesyl-(2-carboxy-2-cyanovinyl)-julolidine (FCVJ), was found to be able to detect the effect of chain

entanglement on the melt viscosity of poly(propylene oxide),¹¹ which suggests that FCVJ is sensitive to changes in the segmental relaxation of the polymer. As shown in **Figure 1**, unlike DCVJ, FCVJ has a long farnesyl segment; a double bond separates the rigid julolidine headgroup from the relatively long farnesyl tail. This double bond is the location of internal rotation under photoexcitation because the pi bond is destabilized in the excited electronic state.^{12, 13} In short, it can be inferred that the FCVJ is able to detect the glass transition temperature of the polymer matrix by tracking the motion of the molecule related to the farnesyl chain group.



Figure 1 Chemical structures of julolidine-based fluorescent molecular rotors, (Left) DCVJ and (Right) FCVJ. Upon electronic excitation, these rotor molecules can relax non-radiatively by internal rotation around the double bond (marked with an asterisk) which separates the julolidine headgroup from the tail moiety.

2. 3. AGO

Graphene is a representative two-dimensional (2D) material with fascinating properties, including high elasticity, mechanical strength, electron-transport properties, and thermal conductivity.¹⁴⁻¹⁷ However, the practical application of graphene is limited due to the high cost of its synthetic processes, such as mechanical exfoliation from graphite or chemical vapor deposition (CVD). To address this issue, graphene oxide (GO) has been widely studied as an alternative material because it can be easily produced by exfoliating chemically oxidized graphite.^{18, 19} Early research was concentrated on reducing GO using a chemical or thermal process that produces reduced GO, which has properties comparable to those of graphene. In addition, methods to utilize its reactivity have been studied by functionalizing it for various purposes, such as dispersion, drug delivery, and modifying its surface properties.²⁰⁻²³ For example, the Nguyen group reported electrically conductive "alkylated" graphene, which was treated in the presence of structure-stabilizing hexylamine before a thermal treatment step.²⁴ This is a simple structural modification, but it provides many possible applications to alkylated GO (AGO). Yeo et al. took further steps to fabricate a bulk material.²⁵ Using a microfluidics process, they produced macroscale closed cellular graphene bubbles, which are low-density and high-strength materials. These previous studies have also suggested that systematic material design is possible by controlling the reaction between the oxide groups on GO and the alkylamine. Since long alkyl groups are interdigitated between the GO sheets, the architecture of the alkylamine affects the properties of the assembled structure, depending on the number or length of alkyl chains. Therefore, one can

adjust the properties of AGOs by elaborately modifying the alkylamine, which results in the utilization of AGO as a controllable building unit for the construction of hierarchical bulk molecular structures.

In this respect, it can be inferred that the atomic structure of the molecular building units plays a significant role in determining its bulk properties, and considerable research has previously been conducted to investigate the chemical composition and molecular structure of GO. ²⁶⁻²⁸ The basic GO model bearing epoxy and hydroxyl groups on the basal plane and carboxylic acid groups on the side was suggested by Lerf et al.²⁹ Subsequently, various studies on the molecular structure of GO have been conducted experimentally as well as computationally. Szabó et al. discovered the existence of other functional groups, such as tertiary alcohols, ketones, and 1,3epoxy groups, and investigated carbon network structures based on the results obtained using elemental analysis, various spectroscopic methods, diffraction methods, and NMR spectroscopy.³⁰ Gómez-Navarro et al. obtained an atomic force microscopy (AFM) image of a GO monolayer to directly observe the oxidized zone.³¹ Regarding the theoretical approach, Boukhvalov conducted an extensive simulation study on modeling GO using density functional theory (DFT) calculations to test the energetic stability of GO with various functional groups.³² Recently, MD simulations have enabled the exploration of various GO structures with different oxidation levels, types of oxide groups, and defects.³³⁻³⁷ Furthermore, phenomena associated with more than one GO molecule, such as the aggregation of GO sheets or transport properties between the GO layers have been investigated using MD simulations.³⁸⁻⁴¹ However, the theoretical model of GO remains incomplete despite these research efforts, and even fewer studies have been conducted on the structures

of its derivatives, such as AGO. Qing et al. analyzed the self-assembled structures of hexafluorotribenzo[a,g,m]coronene with alkyl chains using scanning tunneling microscopy and DFT calculations, although the molecular size was smaller than that of conventional 2D materials.⁴² The self-assembled structures of AGO for detection of Cu(II) ions have been studied by Wen et al.⁴³ Nevertheless, the molecular structure of AGO has not been dealt with by these studies so little is known about it yet.

2. 4. Mesogen Epoxy Resin

Thermosetting epoxy resins with crosslinked structures are widely used as packaging materials for electronic devices, due to their ability to insulate electrical current, easy processability, chemical resistance, etc. ⁴⁴⁻⁴⁶. However, another property has been required recently which is high thermal conductivity (TC) because electronic devices are getting miniaturized. Smaller electric circuits dissipate heat more locally therefore rapid heat conduction has become essential. Conventionally, highly conductive fillers like graphene or carbon nanotube were incorporated into epoxy resins to enhance their thermal or electric conductivity.⁴⁷⁻⁵² As an alternative approach, functional groups which can enhance transport properties such as mesogens directly have been introduced to epoxy monomer. When mesogens are functionalized into epoxy resin, the ordered domain is formed by phase separation which provides another faster route for phonon transfer rather than along covalent bonds. ⁵³⁻⁵⁶ Lin et. al reviewed a variety of epoxy thermoset resins with the mesogenic groups which can increase the TC up to 1.05W/m·K.⁵⁷

The structural characteristic which makes the mesogens form the ordered domain is their planar structures which are easily aligned in one direction. The phase separation is derived by the π - π stacking among the aromatic groups in the mesogenic groups. Therefore, it can be inferred that understanding the stacking structure among the aromatic groups is the key factor to improve the TC of epoxy resins with mesogens. Especially, the molecular structure of mesogens becomes important as various monomers are utilized recently comparing decades ago when biphenyl-based ones were major compounds. However, investigating alignment structure comparing different mesogen epoxy resins is not trivial so its effect on the TC depending on the chemical characteristics remains unexplored yet.

Chapter 3. Dynamics and Structure of Oligomer Functionalized Compounds

3. 1. Glass Transition Temperature Measurement by FCVJ Molecular Rotor

The first part of this chapter is about the simulation study on the FCVJ probe fluorescence measurement in bulk polymers to determine the T_g of the polymer matrix. Unlike in the situation of other fluorescence probes, the tail group (i.e., the farnesyl chain) of FCVJ has a sufficiently large radius of revolution, and thus its rotation is strongly coupled to the segmental relaxation of the polymer matrix. Mimicking the temperature-dependent fluorescence intensities measurement experiment from FCVJ-doped polymers, AAMD was performed to investigate the conformations and dynamics of the FCVJ probe and the matrix polymer chains. Interestingly, it is discovered that the unique bulky, asymmetric structure of the FCVJ probe, which is comprised of a julolidine head and a farnesyl tail, enables the rotor to determine the T_g of a polymer matrix via MD simulation. Specifically, the kinetic energy distribution between the head and tail groups becomes increasingly uneven with decreasing temperature below T_g ; this phenomenon could be used to detect the glass transition of the polymer. This new way of measuring T_g is meaningful as it overcomes the limitation of other T_g methods with MD simulation due to fast quenching rates.

3. 1. 1. Computational Methods

Atomistic MD simulation of a single FCVJ molecule embedded in the matrix of polystyrene whose degree of polymerization is twenty(PS₂₀) was conducted using GROMACS.⁵⁸⁻⁶¹ The initial density of the amorphous FCVJ/PS mixture was arbitrarily set at 1.0 g/cm³. A topology file of the FCVJ molecule was generated using the LigParGen web server within the 1.14*CMA charge model. 62-64 The interactions between FCVJ and PS were modeled using OPLS-AA parameters. The long-range Coulombic interactions were treated using the particle mesh Ewald summation method.^{65, 66} The simulation box was composed of a single FCVJ molecule surrounded by 20 PS₂₀ chains. From a random initial configuration of the system, the energy was minimized to obtain a stable polymer melt structure. The system was then stabilized at a temperature of 460 K and a pressure of 1 bar by NPT simulation using a velocity-rescale thermostat and the Berendsen pressure coupling method for 10 ns.^{67, 68} Afterwards, the system was further equilibrated by NPT simulation using the Nose-Hoover temperature coupling method and the Parrinello-Rahman barostat for 10 ns to obtain the most stable liquid polymer structure.^{69, 70} After this equilibration, the density of the system was 0.94 g/cm³. Using the same thermostat and barostat settings, a stepwise cooling procedure was conducted to study the behavior of FCVJ-loaded PS. First, the temperature was linearly decreased by 20 K in 5 ns. Next, an additional equilibration was performed for 5 ns at that temperature to measure the thermodynamic properties. This procedure was repeated multiple times until the system reached a temperature of 200 K. Twenty independent simulation runs were performed using the same quenching procedure but different initial configurations in order to obtain statistically reliable estimates. The absorption of light by FCVJ was imitated by incorporating excess thermal energy to FCVJ in the amount equal to half the difference between the FCVJ's absorption and emission energies (which can be likened to the process of vibrational relaxation toward the Franck–Condon region);17 the FCVJ molecule was simulated using a separate thermostat set at a temperature 1000 K higher than the temperature of the PS matrix (i.e., the amount of excess thermal energy applied was 86 meV). At each temperature, the computed thermodynamic properties were averaged over 1 ns simulation trajectories across the 20 independent simulation runs.

3. 1. 2. Molecular Conformation of FCVJ in a PS Matrix

Upon photoexcitation, FCVJ can relax by emitting light and/or by undergoing a nonradiative transition via internal rotation/conversion similarly to other julolidinebased rotors.^{11, 71} The axis of internal rotation is the double bond between the planar julolidine headgroup and the long farnesyl ester tail (Figure 2 (a)); photoexcitation turns the *pi* bonding molecular orbital (π) of the double bond into a *pi* antibonding molecular orbital (π^*), and the stabilization in going from the π back to π^* orbital generates internal rotation of the FCVJ molecule.^{12, 13} Note the farnesyl chain is an oligomer containing 3 trans-1,4-isoprene monomer units. An all-atom MD simulation of a single FCVJ molecule placed in a polystyrene matrix (PS_{20} where the subscript denotes the degree of polymerization) confirmed that the root mean square (RMS) radius of gyration of the julolidine headgroup $(R_{g,head})$ is nearly invariant with temperature due to its rigid structure (Figure 2 (b)). Interestingly, both the RMS radius of gyration and end-to-end distance of the farnesyl tail (Rg,tail and Re,tail, respectively) were also found to be independent of temperature (Figure 2(b)). The farnesyl tail is thought to assume an open coil-like structure regardless of temperature, because the Flory–Huggins interaction parameter between the farnesyl segment (equivalent to an oligomeric version of PI) and the matrix polymer (PS) $(\chi_{PS-PI} = 0.15 - 0.06 \text{ over the temperature range of } 200 - 500 \text{ K})^{72}$ is insufficient to induce a coil-globule transition of the farnesyl tail (DP = 3). Note that the pervasive size of the farnesyl tail is about 1.5-times larger than that of the headgroup $(R_{g,tail})$ $R_{\rm g,head}$).



Figure 2 (a) A molecular structure t of an FCVJ embedded in a PS_{20} matrix. The double bond (separating the julolidine headgroup from the farnesyl tail) is the axis of rotation (marked with an arrow). (b) The radii of gyration of the head and tail groups ($R_{g,head}$ and $R_{g,tail}$, respectively) and the end-to-end distance of the tail group ($R_{e,tail}$) calculated as functions of temperature by MD simulation.

3. 1. 3. Coupling between Rotor Motion and Segmental Relaxation

The coupling between the diffusion processes of FCVJ and the PS₂₀ chains was examined from MD simulation results. Specifically, the mean-squared displacements (MSDs) of different subunits (head and tail) of the FCVJ and PS monomers were calculated in the steady state limit; a simulation of the internal rotation of FCVJ was not feasible, because the generation of statistically reliable predictions would require $>10^3$ non-equilibrium runs in our simulation setup.¹³ The center-of-mass MSD PS repeat units ($\langle r^2 \rangle_{mon}$) exhibited a plateau before the Rouse sub-diffusive ($\langle r^2 \rangle \sim t^{0.5}$ at large t) regimes (Figure 3). This cage effect was more pronounced (its range increased) as T was reduced past the T_g (= 326 K), which is consistent with previous literature.^{73, 74} The center-of-mass MSDs of the head and tail moieties ($< r^2 >_{head}$ and $< r^2 >_{tail}$, respectively) of FCVJ molecules embedded in the PS_{20} matrix were calculated under thermal excitation at 1,000 K (= 86 meV, which is roughly half the energy of the Stokes shift between absorption and emission by FCVJ) which would correspond to the vibrational relaxation processes that occur prior to the $S_1 \rightarrow S_0$ electronic transition in an excited FCVJ molecule.¹² As shown in Figure 5, both the FCVJ headgroup and farnesyl tail MSD curves follow the MSD trace of PS monomers, which suggests that the head and tail moieties of FCVJ are trapped within cages of PS monomers and, as a result, their diffusion is coupled to the monomer diffusion.



Figure 3 The center-of-mass mean square displacements (MSDs) of center of mass of the PS20 monomers and of the head and tail moieties of FCVJ calculated by allatom MD simulation. Data represent averages over 20 independent MD simulation runs at each temperature.

3. 1. 4. Determination of T_g via Evaluation of FCVJ Kinetic Energies

The kinetic energies of the head and tail groups of FCVJ embedded in the PS₂₀ matrix were also evaluated as a function of temperature. As shown in **Figure 4**, the kinetic energies of head and tail (E_{head} and E_{tail} , respectively) exhibit a slope change at an identical temperature (328 ± 1 K) during cooling at rate of 2 × 10⁹ K/s. This transition temperature agrees with the T_g determined by DSC (326 K); Thus, this temperature will be referred to as the T_g based on FCVJ kinetic energy analysis ($T_{g,KE}$). As T is decreased past $T_{g,KE}$, the slope of the E_{head} vs. T line decreases, whereas the slope of the E_{tail} vs. T line increases; note that the slope changes are opposite in sign to maintain a constant total kinetic energy for the FCVJ molecule ($E_{head} + E_{tail}$).

Figure 5 displays the ratio of the kinetic energies per atom of the FCVJ's head and tail groups calculated as a function of temperature. In our simulation, the FCVJ continuously dissipates excess kinetic energy (provided by a thermostat) to the surroundings (the polymer chains in its vicinity). An imbalance in kinetic energies between the head and tail groups suggests a difference in the degree of freedom and thus in the rate of kinetic energy dissipation between the two moieties. At T > $T_{g,KE}$, the kinetic energy per atom ratio (E_{head}/E_{tail}) is constant and close to unity, which suggests that the head and tail groups have comparable rates of energy dissipation because they experience similar local viscous environments (**Figure 6**). At $T < T_{g,KE}$, the E_{head}/E_{tail} ratio is greater than unity, and it increases with decreasing T, which suggests that the dissipation rate of the head group becomes slower than that of the tail group with cooling. As described in **Figure 6**, we suspect that the polymer matrix
surrounding the julolidine head group became glassy at $T < T_{g,KE}$, whereas the immediate vicinity of the farnesyl tail was relatively plasticized because of the relatively long and flexible nature of the farnesyl tail.



Figure 4 The total kinetic energies (i.e., the sums of the kinetic energies over all atoms) of the FCVJ molecule and also of the head and tail groups of the FCVJ molecule embedded in the PS₂₀ matrix as function of temperature. The $T_{g,KE}$ was determined by fitting the FCVJ head and tail kinetic energy profiles to a Heaviside step function based on two different linear equations for high- and low-temperature regions.



Figure 5 The ratio of kinetic energies per atom of the head and tail groups of FCVJ. The ratio is constant and nearly equal to unity at $T > T_{g,KE}$ but deviates from unity at $T < T_{g,KE}$.



Figure 6 Schematic illustration of local frictional environments of FCVJ's head and tail groups. The farnesyl tail plasticizes the PS matrix because of its conformational flexibility; in the immediate vicinity of the tail, the polymer may remain liquid-like (viscous) at $T < T_{g,KE}$.

The temperature dependences of the FCVJ's head and tail group volumes were also evaluated (Figure 7). The local volume of the julolidine headgroup showed a slope change at $T_{g,V_{local}} = 331$ K (Figure 7), which is consistent with what was observed for its kinetic energy ($T_{g,KE} = 329$ K) (Figure 4). The local volume of the farnesyl tail appeared to show a similar behavior, although it was not possible to accurately determine the $T_{g,V_{local}}$ because of the noisiness of the data (Figure 7 (b)). The data displayed in Figure 4 and Figure 7 demonstrate that the kinetic energy analysis is a more reliable way of determining T_g than the local volume analysis. We believe that the uneven distribution of the kinetic energies between the FCVJ's head and tail at $T < T_g$ (Figure 5) is a result of two effects: (i) thermal coupling and (ii) difference in friction between the head and tail domains (Figure 6). To test this hypothesis, the kinetic energies of 9-methyljulolidine and farnesyl cyanoacetate individually embedded in PS₂₀ were also estimated as a function of temperature. As shown in Figure 9, no transition in the slope of the E vs. T curves was observed in both cases, which supports that the chemical connectivity between the two asymmetric units is indeed responsible for producing an uneven distribution of kinetic energy between the julolidine and farnesyl moieties at $T < T_g$ and is thus required to detect the glass transition of the matrix polymer.



Figure 7 The local volumes of the FCVJ's (**a**) head and (**b**) tail groups as a function of temperature. The head and tail volumes were estimated using the convex hull method; the boundary of the FCVJ molecule was defined using midpoints between an individual atom of the FCVJ molecule and the ten nearest atoms from the matrix PS chains surrounding that particular atom of the FCVJ molecule.



Figure 8 The specific volume of PS_{20} calculated as a function of temperature by MD simulation.



Figure 9 The kinetic energies per atom of (a) 9-methyljulolidine and (b) farnesyl cyanoacetic ester embedded in PS_{20} . MD simulations were performed using the same procedure as used to obtain data shown in Figure 4 of the main text.

It is well known that the T_g of a polymer measured by atomistic MD simulation is overestimated. Specific volume analysis based on all-atom MD calculations typically gives higher T_g by 30 - 40 K because of the limitations in sampling time (<1 µs) and cooling rate (>1 K/ns),^{73, 74} that is, because the specific volumes are estimated in the non-ergodic states during cooling. As shown in Figure 8, we confirmed that MD calculations of the specific volume of PS₂₀ gives an estimate of T_g (T_{g,V_m} = 369 K) that is over 40 K higher than the experimentally determined value of $T_g = 326$ K. To avoid this non-ergodicity issue, a T_g simulation method based on calculations of short-time relaxation data has been proposed.75 This previous method evaluates the monomer relaxation times (<10 μ s) of a polymer in the liquid state via coarse-grained MD simulation and determines the $T_{\rm g}$ by extrapolation of the relaxation time into the glass transition region using theoretical formulas (such as the Vogel-Fulcher-Tammann theory); the T_g was arbitrarily defined as the temperature at which the relaxation time reaches a value of 100 s.75 However, this method is expected to be prone to error because of the large range of relaxation times (~ 10 μ s – 100 s) over which the extrapolation is extend. The results of the present study suggest a new method of accurately determining the $T_{\rm g}$ of polymers-the use of FDVJ as a dynamic probe of the local environment in atomistic MD simulation. An accurate T_g determination was possible with relatively short sampling times (<10 ns) because of the relatively small size of the probe molecule. The computation could be performed within the ergodic limit of the FCVJ relaxation process even when the $T_{\rm g}$ of the matrix polymer was traversed; there was no need for extrapolation of data to cover the long relaxation times of the polymer.

3.1.5. Summary

All-atom steady-state MD simulation was performed to investigate the atomic-scale dynamics and energetics of FCVJ embedded in the matrix of PS₂₀. Simulated MSD vs. time profiles for the julolidine head and farnesyl tail groups showed that both the head and tail moieties are dynamically trapped in the cages formed by monomers of surrounding PS chains, which rationalizes that the motion of FCVJ is coupled to the segmental relaxation of the matrix polymer and therefore it is able to detect the glass transition of the polymer. Also, the asymmetry in conformational flexibility between the julolidine and farnesyl moieties appeared to cause an anomalous (uneven) distribution of kinetic energy between those two subgroups of the FCVJ molecule at $T < T_{g}$. The T_{g} determined by this kinetic energy analysis ($T_{g,KE}$) well-matched the experimentally determined T_{g} value, whereas the T_{g} estimated from MD calculations of the specific volume of the polymer (T_{g,V_m}) was significantly greater than the experimental value of $T_{\rm g}$ as has been previously documented in the literature. These results demonstrate a new concept for quantitatively determining the $T_{\rm g}$ of polymers—the use of a bulky, chemically asymmetric molecular rotor (such as FCVJ) as a dynamic probe of the local environment in atomistic MD simulation.

3. 2. Structure-property Correlation of Alkylated Graphene Oxide

In this part, the effect of modification on the structure and properties of the material derived from AGO is provided. Specifically, the AAMD simulation was performed to investigate the effect of alkyl chain length on the layered structure of the AGO molecules, which are the simplest AGO assembly structure, based on hierarchical modeling. For this purpose, it has been systematically modeled that the assembly of AGO from pristine graphene to GO, AGO, and its layered structures. At first, the GO molecular configurations were constructed considering the formation energy of different types of oxide groups. Then, the GCMC simulation was conducted to measure the alkylation ratio depending on alkyl chain length considering excluded volume effect. Finally, an MD simulation was performed to derive the layered structure of the AGOs, and the effect of the chain length on the layer structure was measured to provide a representative example used to predict the bulk material properties based on our model.

3. 2. 1. AGO Molecule Configuration Modeling

The overall procedure of our work is illustrated in **Figure 10**. The molecular configuration of GO was initially based on the Lerf–Klinowski model so that the oxide groups were categorized by five types: basal epoxy, basal hydroxy, side epoxy, side carboxylic acid, and side hydroxy groups. A Boltzmann distribution was assumed for the number of oxide groups and the carbon/oxygen ratio, $r_{C/O}$, was set to 2.145. The formation energy of each type of oxide group was reported in a previous *ab initio* simulation study which was used as the energy parameter for the Boltzmann distribution.⁷⁶ Consequently, the number of oxide group of type *i*, N_{oxide}^i , was determined as follow:

$$N_{Oxide}^{i} = \frac{N_C}{r_{C/O} \sum_i N_O^i}$$
(3.1)

where N_C is the number of carbon atoms in the graphene plane, N_o^i is the number of oxygen atoms in the oxide group of type *i*, E_F^i is the formation energy of the oxide group of type *i*, *k* is the Boltzmann constant, and *T* is the temperature. This procedure gives a reasonable configuration of GO molecules where the ratio of different oxide groups depends on their type and position of them.

GCMC simulations were performed through RASPA 2.0 software based on the GO configuration obtained from the above process to construct the AGO molecular configuration, including the adsorption number and positional distribution of the alkyl chains.⁷⁷ Because it is impractical to consider every condition and variable

during the alkylation process, the GO surface reaction with alkylamine was simplified by decoupling it into alkylamine physisorption on the GO and the chemical reaction step. Physisorption was assumed to result in a chemical reaction. This assumption can be justified because the Coulombic interactions between the amine groups in the alkylamines and oxide groups in GO are strong enough to maintain their coordination and lead to a reaction once they encounter one another. In addition, a configurational-bias Monte Carlo (CBMC) scheme was implemented to obtain the appropriate equilibrium adsorption number of alkyl chains to accelerate the simulation because the probability of the insertion of long-chain alkylamines is too low due to the inter- and intramolecular overlap.⁷⁸ The CBMC scheme inserts chain molecules atom by atom toward the energetically stable configuration of long-chain molecules by avoiding molecular overlap. Thus, the significantly reduced overlap of molecules induces the enhanced sampling of the long-chain alkylamine insertion. Consequently, an appropriate alkylation ratio depending on the chain length of the alkylation and the types of oxide groups was obtained.

All atomic MD simulations were conducted to investigate the structural and mechanical properties of layered AGO using the molecular configuration of the AGO, which was constructed according to the alkylation probability including the excluded volume factor. While constructing the AGO configuration, the position of the alkyl chain was selected one by one. Before the selection, the alkylation probabilities were assigned to all epoxide and carboxylic groups which are not alkylated. The alkylation probability was determined differently depending on the number of already selected and adjacent alkylation sites to consider the excluded volume effect. If there is no adjacent alkylated site near an oxide group, the excluded volume effect is not considered so the alkylation ratio defined as Eq (2) was used as the alkylation probability of the oxide group.

$$P_{Alkylation}^{i,N} = \frac{N_{Chain}^{i,N}}{N_{Oxide}^{i}}$$
(3.2)

where $N_{Chain}^{i,N}$ is the number of the adsorbed anchored alkyl chain of chain length N to the *i* type of oxide which is measured from the GCMC simulation. However, if there are *n* alkylated sites near an oxide group, the regulated alkylation probability of the oxide group ($P_{Exclude}$) is adjusted as follow:

$$P_{Exclude}(n) = P_{Alkylation}^{i,N} \left(1 - \frac{V_{Chain}^{N}}{R_{g}^{N^{3}}}\right)^{n}$$
(3.3)

where R_g^N is the radius of gyration of the alkyl chain of chain length *N* and V_{chain}^N is the volume of the same length of chain. If number of the positions of alkylation sites for all types of oxide groups denoted by $N_{Chain}^{i,N}$ were selected, the initial coordinate of the AGO molecular configuration was constructed. All MD simulations were performed using GROMACS software.⁵⁸⁻⁶¹ The OPLS-AA force field was used, in which the atomic types of graphene oxides were assigned according to previous research.⁷⁹ The LigParGen generated topologies of the segmental molecular configurations of GO and AGO were used for the omitted types of interaction parameters and dihedral angle potentials in the GROMACS table.⁶²⁻⁶⁴

Therefore, it is possible to perform simulations of GO and AGO materials with arbitrary structures.



Figure 10 An overall schematic representation of procedure to construct layered AGOs. The structure of AGO was obtained using the hierarchical multiscale simulation method; the representative configurations of each step are illustrated for pristine graphene, GO, AGO, and layered AGO. The computational modeling methods and results are provided below the corresponding configuration.

3. 2. 2. Computational Details

To obtain the equilibrium adsorption number of alkylamine on GO, the GCMC simulation with a single GO sheet was initialized in box size of $10nm \times 10nm \times 3nm$ with an imaginary alkylamine chemical reservoir. The GCMC simulation was conducted until the saturation of the total adsorption number with different alkylamine length until 10^6 MC cycles. Every cycle was defined as max($20, N_{Molecule}$) MC steps, where $N_{Molecule}$ is the number of molecules in the system. The insertion move of the chemical reservoir is accepted with probability as below⁸⁰:

$$p(n \to n+1) = \min\left[1, \frac{V}{\Lambda^3(n+1)} \exp\{\beta[\mu^B - U(n+1) + U(n)]\}\right]$$
(3.4)

and the removal move of the particle is accepted with probability as below:

$$p(n \to n-1) = \min\left[1, \frac{\Lambda^3 n}{V} \exp\{-\beta[\mu^B + U(n-1) - U(n)]\}\right]$$
(3.5)

where μ^{B} was chemical potential, V was system volume, and Λ was the de Broglie wavelength. The chemical potential of the alkylamine reservoir derived from the Peng-Robinson equation of state with experimental parameters from the reference tables following the previous studies.⁸¹⁻⁸⁴ Inter- and intramolecular potential energy U(n) was modeled by the OPLS-UA force field.⁸⁵ Independent 7 simulations were averaged to find equilibrium total adsorption number and each adsorption number on the alkylamine-reactive group (basal epoxy, side epoxy, side carboxyl group) of GO using the nearest neighbor algorithm with cutoff 5Å.

As a first step of the MD simulation, five AGO molecules with the different structures were simulated independently; energy minimization and 5ns NVT simulation at 300K were conducted sequentially. The five AGO molecules were inserted in the simulation box with size of the 8nm x 8nm x 17.5nm using PACKMOL.⁸⁶ The layered structure of the AGOs was derived by the compression in z-direction. 5ns of the NPT simulation was conducted where the temperature was 300K and the pressure was 100 bar in the z-direction, and 1 bar in x- and y-direction. The layered structure, then, was annealed to relax the internal stress by NPT simulations where the temperature profile was as follow; i) 3ns annealing from 300K to 800K, ii) stepwise quenching from 800K to 300K where the cooling by 100K for Ins and another Ins of equilibration at constant temperature was iterated five times, therefore the total simulation was for 10ns. Finally, the NVT simulation was performed for 10ns to analyze the structural property of layered structure where the last 1ns of the simulation was used. The velocity rescaling thermostat was used for the first two simulations; NVT simulation of single layer AGO equilibration and compression simulation to derive the layered structure of AGOs.⁶⁷ The Nose-Hoover temperature coupling method was used for flowing steps.^{69, 70} In the case of the pressure coupling method, the Berendsen barostat was applied during compression and the Parrinello-Rahman pressure coupling method was used for the annealing simulation.^{68, 87, 88}The long-range charge interaction was treated by the particle mesh Ewald method.⁶⁶ All bonds associated with hydrogen atoms were constrained by LINCS algorithm.⁸⁹ The leap-frog algorithm was used to integrate Newton's equation of motion where the time step was 2fs.

The tensile test was conducted to measure Young's modulus by elongating the simulation box in the x- and y-direction. The simulation was performed for 3ns where the deformation rate was 0.05 m/s, resulting in the simulation box being elongated by 0.15nm for each direction. The x and y directional modulus, E_x and E_y , were obtained from the elastic range of the strain-stress curve and the lateral Young's modulus (*E*) could be calculated from them.

$$\sigma_{x} = E_{x}\varepsilon_{x}$$

$$\sigma_{y} = E_{y}\varepsilon_{y}$$

$$E = \frac{E_{x} + E_{y}}{2}$$
(3.6)

The persistence length of the alkyl group was calculated which shows the length of the rigid part of the alkyl chain. Physically it is explained as the distance that polymer chain become decorrelated which is determined from the bond autocorrelation function ($C(N_{bond})$) which is defined as follow:

$$C(N_{bond}) = <\cos\theta_{N_{bond}} >$$
(3.7)

From the equation, $C(N_{bond})$ means how the angle of two bond vectors of the monomers ($\theta_{N_{bond}}$) are correlated when they are separated by N_{bond} bonds. The persistence length is calculated by fitting the $C(N_{bond})$ to exponential decay function,

$$C(N_{bond}) \approx \exp(-\frac{N_{bond}l_b}{l_p})$$
 (3.8)

where l_b is average bond length, and l_p is the persistence length. From the MD simulation trajectory when the chain length equals 18, the $C(N_{bond})$ was obtained which is presented in **Figure 11** (a) and the l_p was calculated as 8 Å



Figure 11 The bond autocorrelation function depending on the separating bond number. The black square is the calculated results. The red dashed line is fitting result to calculated persistence length. (a) The end-to-end distance of the alkyl chains as a function of the chain length. (b)

3. 2. 3. Alkylated Ratio Depending on Chain Lengths

The adsorption number and adsorbed oxide sites of the alkylamines on GO were determined using GCMC simulations. It was probed the adsorption of alkylamine using the number of amine groups coordinated to the GO functional groups within a cut-off distance of 5 Å. The adsorption number for each functional group and the total adsorption number depending on the chain length of the alkylamines are presented in Figure 12. The adsorption number rapidly increases during the initial stage due to the attractive interactions between the alkylamine and GO functional groups. During the later stage, the enthalpic gain of the insertion of alkylamine becomes comparable to the chemical potential of an alkylamine, resulting in the equilibration of the insertion and deletion steps (Figure 12 (a)–(c)). A representative snapshot of the GO framework and adsorbed chains is shown in Figure 13. The equilibrium adsorption numbers were converted into the alkylation ratio $(P_{Alkylation}^{N,i})$, which are tabulated in Table S1 depending on the chain length and type of oxide group. The adsorption number decreases upon increasing the chain length, as shown in Figure 12 (d). This was attributed to the steric hindrance originating from the neighboring chains, which decreases the adsorption number and intensifies the effect of the longer alkyl chains. Consequently, the AGO structure can be constructed by incorporating the excluded volume effect of the long alkyl chains. In addition, it is noteworthy that the total fraction of carbon was nearly constant regardless of the alkyl chain length, as shown in Figure 14. This is due to the trade-off between the chain length and adsorption number; the longer the alkyl chain, the less adsorption occurs. Therefore, this is a consistent result reflecting the excluded volume effect of the alkyl chains.



Figure 12 (a-c) MC cycle evolution of the adsorption number of n-butylamine (black curve) and n-octadecylamine (blue curve) on each functional group: Side epoxy group (a), basal epoxy group (b), and side carboxyl group (c). (d) Total adsorption number of alkylamine on GO as a function of the chain length (*N*).



Figure 13 The representative GCMC snapshot after the adsorption number converged.

Table 1	Alkylation	ratio of each	functional	group	depending of	on alkyl	chain	length
---------	------------	---------------	------------	-------	--------------	----------	-------	--------

Chain length N	4	5	6	7	8	9
Side epoxy	1.0	1.0	1.0	0.92	0.65	0.71
Basal epoxy	0.25	0.21	0.20	0.16	0.16	0.14
Carboxy	0.41	0.47	0.32	0.25	0.24	0.17

Chain length N	10	11	12	14	16	18
Side epoxy	1.0	0.71	0.84	0.43	0.46	0.37
Basal epoxy	0.12	0.10	0.10	0.08	0.07	0.06
Carboxy	0.16	0.12	0.15	0.12	0.13	0.09



Figure 14 The carbon content depending on the chain length.

3. 2. 4. AGO Layer Structure Analysis

The layered structure of AGO was investigated using the positional information obtained from the MD simulation results. The probability distribution of the graphene sheets in Cartesian coordinates and their transformed distribution in reciprocal space using 3D FFT are illustrated in Figure 15 (a) and (b). As the probability distribution in reciprocal space contains information on the characteristic length of the structure, the interlayer distance of the layered AGO can be calculated in the stacking direction by converting the peak location of the density map in reciprocal space. The interlayer distance exhibited decreasing trend as a function of the chain length as shown in Figure 15 (c). This trend can be explained by the configuration entropy of the alkyl chains and chain-graphene interaction. The short chains grafted on graphene plane which have end-to-end distance comparable to the persistence length (Figure 11) have normal direction stretching conformation as shown in **Figure 16** (a). Meanwhile, the configuration entropy induces more parallel conformation of long chains to the graphene plane due to the enhanced degree of freedom in conformation as presented in Figure 16 (b). Therefore, the long chains derive a closer interlayer distance between the graphene plane due to the high chaingraphene interaction energy. In addition, the deformation of the graphene plane was estimated using the modified Gaussian curvature parameter shown in Figure 17, where it is noticed that the curvature slightly increases according to the chain length. This also can be attributed to the stronger chain-graphene interaction by long chains. Meanwhile, to provide a more practical bulk property, the density of AGO was measured which is represented in Figure 15 (d). Here, the density as a function of the chain length shows a consistent trend of the interlayer distance. These results

suggest that modulating the material structure and properties on a larger scale is possible by simply modifying the molecular details.



Figure 15 Structure analysis of the AGO layers using MD simulations. The positional distribution (**a**) and probability distribution in reciprocal space (**b**). The interlayer distance (**c**) and density (**d**) depend on the alkyl chain length.



Figure 16 The snapshot of AGO molecules to present the chain conformations whose chain length is 4 (a) and 18 (b).



Figure 17 The Gaussian curvature parameter depending on the chain length.

3.2.5. Toughness of AGO

The Young's modulus of AGO was measured as a mechanical property of the material, and its correlation with the layer structure was investigated. The resulting strain-stress curves obtained for N = 4, 8, and 12 are presented in Figure 4 (a), where only the elastic deformation range was used for linear fitting. Figure 4 (b) shows that long alkyl chains enhance the Young's modulus of AGO in the lateral direction. This is consistent with the structural analysis, where the interlayer distance is closer when a longer alkyl chain is used. A shorter interlayer distance implies stronger intermolecular interaction, which contributes to greater resistance to deformation. In addition, a noticeable trend is observed for the increasing Young's modulus, decreasing interlayer distance, and increasing curvature when the chain length is relatively short (N < 8). It can be explained the different increasing or decreasing rates of the properties depending on the alkyl chain length by the persistence length estimation results in Figure S3. The persistence length is about 8 Å which corresponds to the end-to-end distance of the n-octylamine (N = 8). As the alkyl chain can be considered rod-like conformation when the length is shorter than the persistence length, the increment of the chain length is relatively large in the short chain length regime. Therefore, the large increment of the chain length induces more intermolecular interaction and the drastic changes in the properties of the layered AGO in a short chain length regime. Combining the structural analysis results, we can provide significant insight into the material design; appropriate materials can be made depending on whether the desired property is the low density or high mechanical strength.



Figure 18 The strain-stress curves obtained from MD simulations using different alkyl chain lengths (a). The red dashed line is the fitting curve used to obtain the Young's modulus. The resulting Young's modulus depending on the alkyl chain length is presented in (b).

3. 2. 6. Summary

In summary, A method was developed for modeling the microscopic structure of AGO according to alkyl chain length and performed MD simulations to understand the effect of the alkyl chain length on the molecular and layered structures and material properties of AGO. Starting from pristine graphene, the molecular structures of GO and AGO were modeled considering the formation energy of the oxide groups and the excluded volume of the alkyl chains for each material. The steric hindrance caused by the bulkiness of the chains was incorporated into the GCMC simulations, and the alkylation ratios for various chain lengths and types of oxide groups were obtained. From the GCMC results, AGO single molecules were constructed, and their equilibrated layered structures were derived using MD simulations. Structural analysis revealed that the distance between the layers decreased when the alkyl chain length increased, which can be attributed to the higher interaction energies of the long alkyl chains among themselves and the graphene plane. In practice, the density and Young's modulus were also measured. Both properties increased according to the alkyl chain length because of the stronger interactions between the AGO molecules and longer alkyl chains. Consequently, this study provides physical insights into the multiscale structure of AGO and suggests how computational methodologies can be utilized in real problems.

Chapter 4. Effects of Chemical Structure of Functional Groups on Bulk Material

4. 1. Thermal Conductivity of Mesogenic Epoxy Resin

In this part the all-atomic MD simulation study on various kinds of cross-linked polymers is provided to reveal the effect of their molecular architectures on the TC. The iterative annealing and crosslinking simulations were performed to generate realistic network structures. Then, the aligned structure of cross-linked polymers was investigated by calculating the angle-dependent radial distribution function (ARDF) among aromatic groups and measured the thermal conductivities using the Green-Kubo relation. As the aligning behavior showed distinct characteristics according to chemical motifs, it can be classified the studied epoxy resins into three different groups. Meanwhile, the TC of resins were higher than conventional polymer materials as expected from the aligned structure noticed in ARDF even though any quantitive correlation was not found between them. Therefore, two additional structural factors were studied by comparing resins within the same group; the first is a flexible alkyl chain that is introduced into monomers as a spacer, and the second is the functional groups in hardeners whose polarity affects interaction with monomers. The results indicated that the aligning behavior of epoxy monomers and the TC of resins were both affected by those geometric factors complicatedly. The detailed atomistic investigation by MD simulation gives a direction to enhance the thermal conductivities by exploiting the relationship between the chemical structure of molecules, the resultant aligned structure, and the thermal conductivity.

4.1.1. Crosslinked Polymer Construction

The crosslinked polymer structure was constructed from the epoxy and hardener molecules where the overall procedure is presented in **Figure 19** (**a**). The initial mixture of epoxy (E) and hardener (H) was constructed by randomly distributing the molecules with the Packmol software package to get an initial coordinate of the amorphous structure.⁸⁶ The molecular representations of studied EH pairs are listed in **Table 2**. The number of each molecule was determined so that the initial density be 1g/mL in a cubic simulation box with the side length of 50Å where the E:H ratio was set to 2:1 to prevent remaining functional groups when all molecules participated in the reaction. The initial configuration of the EH mixture was equilibrated by several steps of procedures as explained in the next section.

To generate epoxy crosslinking from an equilibrated EH mixture, all pairs of epoxy and amine functional groups were scanned, and the pairs closer than a prescribed cut-off distance were converted to crosslink bonds. The cut-off distance for the reaction was initially set to 4Å but if no functional group pair was found the cut-off was increased by 1Å. In addition, to prevent the formation of unphysically long bonds with extreme forces, the cut-off distance was not increased beyond the maximum cut-off of 6Å. The positions and interaction parameters of atoms in the selected functional groups were modified to make crosslinked bond structure mimicking the real ring-opening reaction of epoxy and amine groups as depicted in **Figure 19 (b)**. The equilibrating MD procedures were then conducted again to stabilize the modified configuration. The MD simulation and crosslink formation with adaptive cut-off were iterated until the target crosslink ratio (p_{target}) was
reached, where the crosslink ratio p was defined by the ratio of the number of the reacted epoxy groups, n_{cross} , to the entire initial number of the epoxy groups, n_{epoxy} .

$$p = \frac{n_{cross}}{n_{epoxy}} \tag{4.1}$$

For all EH pairs studied in this work, p_{target} was set as 0.6 to compromise computational cost and also to be above the percolation threshold, $p_c = 0.577$, of the epoxy resins made from diamine and diepoxide assuming the random reaction.⁹⁰ As expected, the TC was affected by the crosslink ratio as represented in **Figure 20** which is noteworthy that the TC went up rapidly after p = 0.7. It also corresponds with the previous study of Vasilev et al. about TC of crosslinked polyisoprene and polybutadiene.⁹¹ However highly cross-linked polymers are considered to have unstable structures from the unphysically connected topology as most reaction sites are exhausted in the later stages of crosslinking iterations. Therefore, it is reasonable to set p_{target} to be just above the p_c to prevent numerical artifacts in calculating TC.



Figure 19 Algorithm flow chart of constructing the crosslinked structure from the EH mixture configuration. (a) Converting procedure presentation of functional groups to crosslink bond which are within the cut-off distance. (b)

	Epoxy (E)	Hardener (H)
EH1	$ \begin{tabular}{ c c c c } \hline & & & & & & & & & & & & & & & & & & $	
EH2		
EH3		
EH4		
EH5		
EH6		
EH7		
EH8	$ \begin{tabular}{cccccccccccccccccccccccccccccccccccc$	11.V

Table 2 The list of EH pairs in our study with molecular structure representation



Figure 20 TC according to crosslinked ratio p where the box size was 50 Å. The error bars are from the 95% confidence interval range of independent runs.

4.1.2. MD Simulation Details

The initial configuration of the E and H mixture was equilibrated before going to the iterative MD simulation step to make the crosslinked structure. At first, the energy minimization was performed to adjust the positions of atoms, bond lengths, angles, and dihedrals. The steepest descent and the conjugate gradient method were conducted consecutively. Then we performed annealing MD simulations in NPT ensemble, with thermostat and barostat set to 500K and 1atm, respectively, for 250ps. The system was further equilibrated at the decreased temperature of 300K for an additional 100ps. The high temperature of 500K was to relax the internal constraints from the unstable location of molecules.

During the crosslinking iterations, similar series of simulations were conducted to equilibrate the mixture containing newly formed crosslinking bonds. After searching for the epoxy-amine pairs and generating the crosslink bonds, the energy minimization was conducted with the steepest descent, conjugate gradient, and fire algorithms, consecutively.⁹² Then five steps of NVT simulations were followed: the system was equilibrated at 300K, 400K, and 500K, where the temperature was linearly ramped between the equilibration runs, where each equilibration and ramping stages were 10ps long. Finally, we conducted two rounds of NPT simulations at 1atm, each 20ps long, with the thermostat temperature set to 500K and 300K.

Starting from the equilibrated network structure, the TC of the crosslinked polymer was calculated using the Green-Kubo equilibrium simulation. The network was initially equilibrated for 200ps in the NPT ensemble, and the production NVE

6 5

simulation was conducted for 1ns. The heat flux was computed and saved every step to calculate the thermal conductivity from its time correlation function. The heat current autocorrelation function (HCACF) was obtained from 10 repeated independent runs with different initial velocities to get proper statistics.

The TC of crosslinked polymer, κ , could be calculated by integrating HCACF over lag time t according to the Green-Kubo relationship where the heat flux J was from the history of energy follow.

$$\kappa = \frac{V}{3k_B T^2} \int_0^\infty \langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle dt$$
(4.2)

where k_B is Boltzmann constant and T, V are temperature and volume of the system, respectively. The term $\langle J(0) \cdot J(t) \rangle$ is called HCACF where heat flux J is defined as,

$$\mathbf{J} = \frac{1}{V} [\sum_{i} e_{i} \mathbf{v}_{i} - \sum_{i} \mathbf{S}_{i} \mathbf{v}_{i} \cdot]$$
(4.3)

where the e_i , \mathbf{v}_i and \mathbf{S}_i are the per-atom energy, the velocity, and atomic stress of the ith atom, respectively. The HCACF of EH1 in **Table 2** according to lag time is in **Figure 21** as an example to show the convergence of the simulation.

All simulations were conducted using LAMMPS software.⁹³ The timestep of integration was set to 1fs in the crosslinking step and 2fs in the TC calculation step. All bonds associated with hydrogen atoms were constrained by the SHAKE algorithm.⁹⁴ The OPLS-AA forcefield with 1.14*CM1A partial atomic charges were used to describe interactions among the atoms as obtained from the LigParGen

server.^{63, 64, 94, 95} The Moltemplate software was used to tabulate interaction parameters from the LigParGen and the initial system topology file.^{94, 96} The interaction parameters for the crosslinked structure were from the topology files of monomer, hardener, dimer (one epoxy monomer + one hardener), and trimer (two epoxy monomers + one hardener) molecules where the original monomer and hardener parameters were replaced when the crosslinked structure. We assumed that the reaction changes only the interaction parameters related to crosslinking bond groups; therefore, only the products from one amine reaction site, which are a dimer with a secondary amine and an alcohol and a trimer with a tertiary amine and two alcohol groups, were considered. The Nose-Hoover thermostat and MTK barostat were used to maintain system temperature and pressure at the desired value.^{69, 70, 94, 97-99}



Figure 21 Convergence of HCACF presentation in long time scale (a) and zoomed short time scale (b).

4. 1. 3. Monomer Effect

Before delving into the analysis of thermal conductivities, we first examined the molecular alignment of the crosslinked polymers in molecular level. We calculated the pairwise distances r and the mutual angles θ between all aromatic group pairs in the system including both monomer and hardener molecules, where r is the Euclidean distance between the centers of mass of the phenyl groups, and θ is defined as the angle between the normal vectors of the 6-carbon planes. In **Figure 22 (a)**, we plot the angle-dependent radial distribution function $g(r, \theta)$,

$$g(r,\theta) = \frac{1}{\langle \rho \rangle} \frac{1}{N} \frac{\langle \sum_{i} \delta(r_{i} - r, \theta_{i} - \theta) \rangle}{2\pi r^{2} \sin \theta}$$
(4.4)

, where *N* is the number of aromatic groups, and ρ is the number density of aromatic groups.

The peaks near $r = 4 \sim 7$ Å and $\theta = 0 \sim 40^{\circ}$ were observed commonly throughout different resins, implying that there exist aligned structures in constructed crosslinked polymer MD configurations where the representative snapshot of the aligned aromatic group is inserted in **Figure 23**. The specific structure of the $r - \theta$ distributions differed among the choices of monomer and hardener, which can be attributed to the chemical environment of the aromatic groups in each molecule. Merging the information of **Figure 22** (a) and chemical features of the monomers and hardeners, the EH pairs in **Table 2** were classified into three groups for explanation based on the connection group between two aromatic groups in monomers: first, monomers with biphenyl groups (EH1, EH2); second, monomers with imine groups (EH3, EH4, EH5); third, monomers of which aromatic groups are separated by ester groups (EH6, EH7, EH8). On the other hand, the hardeners have similar structures connected with two or three bonds which have fewer effects on ARDF results compared to the monomers.

First, EH1 and EH2 resins with biphenyl groups in monomer exhibited a single peak in **Figure 22 (a)** near r = 4Å, whereas all other resins showed a separation of the peak, which featured also broad-angle peak in the narrow distance area. The narrow distance peak distribution is attributed to similar inter-distance of two aromatic groups of biphenyl group and hardener. Whereas the angular distribution can be explained by the structural mismatch of the straightly connected biphenyl groups and the two aromatic rings connected by two bent bonds in hardener, where one pair of aromatic rings in hardener and monomer should be stacked obliquely when the other pair is stacked in parallel.

The EH3, EH4, and EH5 showed two vividly split peaks along the distance axis in $r - \theta$ distribution which is attributed to the imine group among the three aromatic groups in monomer where it is also non-rotatable but the distance between two aromatic groups is farther than the biphenyl group. This difference of inter-distance between aromatic groups also affects angle distribution; if one pair of aromatic groups of a monomer and a hardener are staked, the other aromatic group in hardener should be located in farther distance from another aromatic group of a monomer obliquely. Therefore, the former pair is comparatively stable due to less competition with the latter pair which results in contributing to the first narrow peak in the a θ axis, while the second peak came from the latter pair with broad-angle distribution

due to their mismatch of the connected bond angle between monomer and hardener like EH1 and EH2.

Finally, the aromatic groups in EH6, EH7, and EH8 monomers are separated by ester groups which have similar structures of imine groups resulted in double peaks in the distance axis in the same manner of EH3, EH4, and EH5. A distinct characteristic in this third group was the intense peak near the r = 4Å which is attributed to rotatable bonds in ester groups, unlike biphenyl or imine groups. Without the planar restriction, the aromatic groups could be stacked easily in parallel by changing configurations.

In summary, it was presented from the ARDF results that the aligning behavior of aromatic groups in crosslinked polymers and how it was affected by molecular structure. As a next step, we tried to correlate the microscopic stacked structure of aromatic groups and the TC results in **Figure 22 (b)**. The thermal conductivities of the resins were from 0.62 to 0.85 W/m·K which were higher than commonly used polymer materials which can be expected from the alignment peaks in **Figure 22 (a)**. It is also accord with well-known physics that crystalline likely stacked the aromatic groups contribute to faster phonon transport way than which through the bond of polymers¹⁰⁰. However, any aligning parameter that quantitative correlates the TC and the ARDF was not found and quite large deviations of the TC were noticed even in the same group. This is because different molecular structures other than connecting part of aromatic groups in epoxy monomers also affect crosslinked polymer complicatedly. Therefore, we conducted further comparative analysis for several cases affected only by each factor which resulted in finding two structural factors affecting TC; one is flexible chains included in epoxy monomer as spacers and the

other one is the functional groups of hardeners connecting two aromatic groups. In the following sections, it is described how the molecular motifs affect TC considering their chemical properties from the further analysis.



Figure 22 ARDF heatmaps according to pairwise distance and angle of aromatic groups in the crosslinked polymer. (a) Thermal conductivities of the EH pairs in which bars are represented by the same color for the same groups. The error bars are from the standard deviation of independent runs. (b)



Figure 23 Representative snapshot of aligned aromatic groups in the crosslinked polymer. The aligned aromatic groups are colored red and with the dashed line where only part of near and connected with the groups are depicted.

4.1.4. Flexible Chain Spacer Effect

Among the molecules in Table 2, EH2 and EH7 are modifications of EH1 and EH6 molecules, respectively, introduced to study the effect of alkyl spacers. In our results as presented in Figure 22 (b), the TC of EH2 was 0.64W/m·K, lower than that of EH1 which was 0.72W/m·K where the EH6/EH7 cases showed the same trend for TC where the TC of EH7 was 0.62W/m·K and the TC of EH6 was 0.66 W/m·K. Otherwise, in the respect of alignment it was noticed that the spacer increased stacked structures of aromatic groups as presented in Figure 24; the $g(r, \theta = 0)$ peaks have higher values in Figure 24 (a) and Figure 24 (b) which means there are more stable stacked aromatic group pairs in parallel, also the zoomed ARDF heatmaps in Figure 24 (c) indicate that overall aligning behavior was facilitated by alkyl spacers. Unfortunately, the TC results seemed to contradict the previous reports that the spacers in epoxy monomer with mesogenic groups derive ordered phase which could increase the TC.94, 101-104. The difference could result from the small length scale of the MD simulations which is about a few nanometers long, whereas the size of the ordered domains in experiments was an order of magnitude larger than our MD simulation box. Therefore, it can be said that the flexibility of the spacer gives more chance for a stable alignment of the mesogenic groups, but in the MD scale without large ordered domains, the contributions from the alkyl spacers dominated over the stability of the alignments, resulting in an overall lowering of TC. Furthermore, the connecting group chemistry among epoxies also affected the opposite trends in the molecular alignment of spacers depending on their types. The monomer of EH7 including ester groups that can rotate freely makes it relatively easy to be entangled with the alkyl chain resulted in fewer effects on aligning

behavior but the EH2 biphenyl occupied linear volume straightly which prevents the structure to be disordered. The results give a microscopic understanding of how spacer can be used to enhance the TC of crosslinked polymer. In other respect, it is remarkable that the spacer can also increase the processability of polymer resin by decreasing glass transition temperature which broadens the applicability of our results.¹⁰⁵



Figure 24 Comparative representation to show the effect of the spacer in the epoxy monomer on aligning behavior. Radial distribution functions, $g(r)_{\theta=0}$, of aromatic group pairs when the angle between normal vector is zero are represented for EH1/EH2 (a) and EH6/EH7 (b). The ARDF density maps of Figure 3 for EH1/EH2 and EH6/EH7 cases are zoomed in to show peak level increment in EH2 and EH7 (c).

4.1.5. Hardener Effect

In Figure 22 (b), the TC of EH5 was much lower than EH3 and EH4 about 0.2 $W/m \cdot K$ which was a distinct large deviation considering the similarity of molecular structures of epoxy and hardener in this group. Because the difference among them is mainly from the connecting parts of hardeners it can be inferred that the properties of the connecting motifs affect the structure and TC of the crosslinked polymer. Therefore, in this section, the effect of the hardener structure was investigated in detail. In Figure 25 (a), EH3, EH4, and EH5 were featured by two peaks in $g(r, \theta =$ near the $r \cong 4\text{\AA}$ and $r \cong 7\text{\AA}$ in common, whereas another small peak was 0) observed in EH5 between the two peaks. As explained in the previous section, the common two peaks are from the two pairs of aligned aromatic groups that one is stacked straight up and the other is distanced relatively far; therefore, another peak in the EH5 implies a hardener can be located at the intermediate position which makes aromatic group pairs be distanced farther than the former pair and closer than the latter pair. (Figure 26) This coordination of the hardener to the epoxy in EH5 is attributed to the strong polar interaction between the sulfone group in the hardener and the imine group in the epoxy which is noticed from Figure 25 (b) as sulfur atoms were coordinated near the nitrogen atoms in imine groups. Consequently, the lower TC of EH5 is explained as a result of the polar interaction between polar connecting groups in hardener and epoxy which hinders the aligning tendency by competing with the pi-pi interaction of aromatic groups.

In the same manner, the ester groups of the hardener in the EH3 and the EH8 also were expected to have polar interaction with the imine group and the ester group in epoxy. In the case of the EH3, the $g(r, \theta = 0)$ at $r \approx 5.5$ Å which is the location of the peak in EH5 derived by the polar interaction was even higher than the peak value though there was no distinct peak as presented in Figure 25 (a). Also, in Figure 25 (b), it was observed that carbon atoms in the hardener also coordinated to nitrogen atoms in the epoxy. However, as the TC of the EH3 was not low as much as the EH5, it can be inferred that the polar interaction between the ester and the imine groups is not enough to affect heat transport. Even more, the ester-ester interaction which is included in the EH8 had more subtle effects on the crosslinked polymer; it is noticed that the lower value at the first peak in $g(r, \theta = 0)$ and slightly higher value of the $g(r)_{center}$ between the carbons in ester group as presented in Figure 25 (b) and Figure 25 (d). As the small disadvantage of the polar interaction is offset by the structural similarity between the epoxy and hardener, the TC of the EH8 was a little higher than the EH7. Conclusively, it was noticed that the chemical structure of hardener also has effects on the aligning behavior of mesogenic groups but is less important than other factors except for the EH5 case that there is strong polar interaction. This result suggests that it is important to take into account the characteristics of chemical motifs in monomers and hardeners carefully since they affect the alignment and TC of the crosslinked polymer complicatedly.



Figure 25 $\mathbf{g}(\mathbf{r})_{\theta=0}$ of aromatic group pairs for EH3/EH4/EH5 (a) and EH7/EH8 (c) and radial distribution function between center atoms, $\mathbf{g}(\mathbf{r})_{center}$, in connecting groups between hardener groups that label represent which atom in epoxy and hardener were analyzed in order; EH3:N-C means the $\mathbf{g}(\mathbf{r})_{center}$ calculated from positions of nitrogen atoms in imine group of epoxy and carbon atoms in ester group of hardener. (b, d)



Figure 26 Representative snapshot of the aromatic group pair(red) in EH5 which are distanced by the intermediate distance(5.5 Å) due to coordination of the nitrogen(blue) and sulfur(yellow).

4.1.6. Summary

The TC of various epoxy-based crosslinked polymers with mesogenic motifs was studied to elucidate the relation between the structural alignment of the aromatic groups and the enhancement of thermal conductivity. The stable atomistic configuration of crosslinked polymers was constructed by gradually converting pairs of epoxy and amine functional groups to crosslink bonds, followed by extensive equilibration. The structural analysis provided microscopic evidence that there exists molecular alignment regardless of the EH pairs used, where the aromatic groups were aligned with the most probable pair distance and angle of $r = 4 \sim 7$ Å and $\theta =$ $0 \sim 40^\circ$. Furthermore, the EH pairs were categorized into three groups by analyzing the ARDF peaks which explains how the molecular structure of mesogenic groups affect aligning behavior. Due to contribution of stacking of aromatic groups the TC of resins were higher than conventional polymers but no distinct overall correlation with aligned structure was found. However, by comparing EH pairs within the same groups, two structural factors were found to affect the aligning behavior of crosslinked polymers: a flexible chain spacer in the monomer and chemical motif of connecting part in the hardener. First, the flexible chains improved the stability of the stacked structure while decreasing the TC of the crosslinked polymers in the MD scale. This result seems to originate from the limited length scale of the MD simulation, where the contribution of alkyl chains dominated over the gain of TC from ordering of mesoscopic domains as reported in experiments. Second, the polar group in the hardener lowered the TC of the resin when it has strong interaction with other polar group in the monomer as the interaction compete with the pi-pi interaction. These computational results provide physical understanding of the highTC crosslinked polymers with mesogenic groups, especially in respect of microscopic length scale that is accessible by atomistic MD simulation. It could give insights to an efficient design of thermosetting polymers with superior thermal dissipation performance by modifying the molecular structure.

Chapter 5. Concluding Remarks 5. 1. Conclusion

In this thesis, molecular-modified polymeric compounds were investigated by the AAMD. Such molecular-level alterations can not be dealt with by the conventional simulation methods for polymers so atomistic modeling is required to entail chemical details. Two cases which are suitable for AAMD were dealt with in this dissertation. The first case is about the compounds functionalized by oligomers that are too short to assume long chain-like molecules as other conventional simulation models do. In this case, two compounds were dealt with in chapter 3 that one is about the FCVJ molecular rotor which is simply functionalized by an oligomer. The other system is the AGO which is a more complicated compound that is functionalized by multiple alkyl groups. The second case is the modification by literally various kinds of chemical moieties. In chapter 4, the epoxy resins with various mesogens were compared to understand the chemical structure effect on the aligning tendency of mesogens and TC.

To be specific, the FCVJ molecular rotor, which is selected as the simplest case, has functionalized structure by the farnesyl group, which enables measuring the T_g of a polymer matrix. In chapter 3, the AAMD was performed to reproduce the fluorescent T_g measurement by coupling a high-temperature thermostat to the FCVJ molecule. The conformation and dynamics analysis of the FCVJ hint that the farnesyl group is bulky enough and its motion is coupled with the segmental relaxation of polymer matrices so it can measure T_g by detecting local environmental changes. Indeed, comparable T_g with experimental value was obtained by MD from the point that the uneven kinetic energy distribution arises at the head and tail part of the rotor. As a similar T_g was obtained from the second-order transition point of the local volume near the rotor too, it was explicitly shown that the ability of the rotor to detect glass transition from the local environmental change. In contrast, the T_g could not be measured when the molecule with only the head or tail part was doped in a polymer matrix. After all, it was elucidated that the bulkiness and structural heterogeneity functionalized by the farnesyl group was the origin of the ability of the FCVJ measuring T_g .

In the same chapter, the structure and properties of AGO were also studied where many alkyl groups are functionalized. Even though the molecular structure of AGO is not been discovered, reasonable configurations including the number and position of the alkyl group were obtained by the hierarchical modeling. In a bottom-up way, the AGO molecule was constructed from the pristine graphene to the GO, the GO to the AGO. For each step, the formation energies of oxidation groups and the alkylation ratio depending on the chain lengths were used as parameters, where the former was obtained from the reference *ab initio* study and the latter from the GCMC simulation conducted in this research. Finally, how microscopic alkyl groups affect the bulk-scale material structure and properties of AGO was elucidated depending on the length of alkyl chains by AAMD. To summarize the results, dense and tough layered AGO structure can be made with long alkyl groups, otherwise light and more deformable one can be obtained by short alkyl groups.

In chapter 4, mesogen epoxy resins, literally various chemical groups were introduced, were explored as the other type of molecular modification. The correlation between TC and the aligning tendency of mesogens was studied. The aligning tendency clearly affected by the molecular structure of the mesogens so the epoxy resins could be categorized. Even though the quantitative correlation between the aligning tendency and the TC could not be found, a more subtle effect of the molecular structure on the aligning tendency and TC was explained by considering additional structural factors. It was identified that the alkyl chain spacers in the epoxy monomer derive more aligning structures but decrease TC. While, if there is strong polar group interaction between monomer and hardener by other functional groups, it competes with the stacking interaction and significantly decreases TC. This study shows how small parts of the molecule in polymers such as minor functional groups can affect significantly overall structures and properties of the material.

Conclusively, this thesis convinces the importance of the atomistic details in the polymeric system even though they have been neglected because of the complexity and high computational cost through three representative cases. Furthermore, in this respect, it proves that the AAMD can be utilized as a powerful tool to understand the underlying physics of polymers by molecular-level observation.

5.2. Future Directions

As shown in this dissertation, the AAMD becomes a more applicable computation method in the polymer physics and engineering area, especially for the systems where the molecular-level structure or interaction has an important role to understand them. Still, extended works can be conducted about those compounds e.g. one can try other functionalizing oligomers for GO rather than simple alkyl groups to investigate the effect of their property. However, the cases dealt with in this dissertation are just representative examples that should be considered with atomistic details to show the usefulness of AAMD, therefore any other polymers also can be simulated to observe them in the sub-nano scale. In addition, the performance of the AAMD has been improved compared with several years ago so the computation cost for larger systems is affordable now. Thus, the system with longer and more chains can be simulated currently such as self-assembled structured deblock-copolymers even in lab-scale workstations. Furthermore, new computational algorithms are being developed which can be combined with the AAMD to broaden its ability. Advanced sampling methods such as umbrella sampling or metadynamics are relatively common now and drastically developing neural networks have been successfully utilized to analyze or aid the AAMD. Accompanied by these advances in many areas, one day even it would be possible to simulate long polymer chains with a size comparable to synthetically produced ones. Consequently, it can be suggested to conduct research on various polymeric systems with AAMD and the analyzing methods or explanations in this dissertation would be a reference for them.

Bibliography

(1) Bailey, E. J.; Winey, K. I. Dynamics of polymer segments, polymer chains, and nanoparticles in polymer nanocomposite melts: A review. *Progress in Polymer Science* **2020**, *105*, 101242.

(2) Ellison, C. J.; Torkelson, J. M. The distribution of glass-transition temperatures in nanoscopically confined glass formers. *Nature materials* **2003**, *2* (10), 695-700.

(3) Priestley, R. D.; Ellison, C. J.; Broadbelt, L. J.; Torkelson, J. M. Structural relaxation of polymer glasses at surfaces, interfaces, and in between. *Science* **2005**, *309* (5733), 456-459.

(4) Ellison, C. J.; Torkelson, J. M. Sensing the glass transition in thin and ultrathin polymer films via fluorescence probes and labels. *Journal of Polymer Science Part B: Polymer Physics* **2002**, *40* (24), 2745-2758.

(5) Royal, J. S.; Torkelson, J. M. Physical aging effects on molecular-scale polymer relaxations monitored with mobility-sensitive fluorescent molecules. *Macromolecules* **1993**, 26 (20), 5331-5335.

(6) Jee, A.-Y.; Bae, E.; Lee, M. Internal twisting dynamics of dicyanovinyljulolidine in polymers. *The Journal of Physical Chemistry B* **2009**, *113* (52), 16508-16512.

(7) Jin, H.; Liang, M.; Arzhantsev, S.; Li, X.; Maroncelli, M. Photophysical characterization of benzylidene malononitriles as probes of solvent friction. *The Journal of Physical Chemistry B* **2010**, *114* (22), 7565-7578.

(8) Loutfy, R. O.; Arnold, B. A. Effect of viscosity and temperature on torsional relaxation of molecular rotors. *The Journal of Physical Chemistry* **1982**, *86* (21), 4205-4211.

(9) Hooker, J. C.; Torkelson, J. M. Coupling of probe reorientation dynamics and rotor motions to polymer relaxation as sensed by second harmonic generation and fluorescence. *Macromolecules* **1995**, *28* (23), 7683-7692.

(10) Loutfy, R. O. Effect of polystyrene molecular weight on the fluorescence of molecular rotors. *Macromolecules* **1983**, *16* (4), 678-680.

(11) Zhu, D.; Haidekker, M. A.; Lee, J.-S.; Won, Y.-Y.; Lee, J. C.-M. Application of molecular rotors to the determination of the molecular weight dependence of viscosity in polymer melts. *Macromolecules* **2007**, *40* (21), 7730-7732.

(12) Allen, B. D.; Benniston, A. C.; Harriman, A.; Rostron, S. A.; Yu, C. The photophysical properties of a julolidene-based molecular rotor. *Physical Chemistry Chemical Physics* **2005**, 7 (16), 3035-3040.

(13) Swalina, C.; Maroncelli, M. Nonradiative deactivation in benzylidene malononitriles. *The Journal of Physical Chemistry C* **2010**, *114* (12), 5602-5610.

(14) Balandin, A. A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C. N. Superior thermal conductivity of single-layer graphene. *Nano letters* **2008**, *8* (3), 902-907.

(15) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I.; Dubonos, S.; Firsov; AA. Two-dimensional gas of massless Dirac fermions in graphene. *nature* **2005**, *438* (7065), 197-200.

(16) Novoselov, K. S.; Jiang, Z.; Zhang, Y.; Morozov, S.; Stormer, H. L.; Zeitler, U.; Maan, J.; Boebinger, G.; Kim, P.; Geim, A. K. Room-temperature quantum Hall effect in graphene. *Science* **2007**, *315* (5817), 1379-1379.

(17) Zhang, Y.; Tan, Y.-W.; Stormer, H. L.; Kim, P. Experimental observation of the quantum Hall effect and Berry's phase in graphene. *nature* **2005**, *438* (7065), 201-204.

(18) Hirata, M.; Gotou, T.; Horiuchi, S.; Fujiwara, M.; Ohba, M. Thin-film particles of graphite oxide 1:: High-yield synthesis and flexibility of the particles. *Carbon* **2004**, *42* (14), 2929-2937.

(19) Stankovich, S.; Piner, R. D.; Chen, X.; Wu, N.; Nguyen, S. T.; Ruoff, R. S. Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly (sodium 4-styrenesulfonate). *Journal of Materials Chemistry* **2006**, *16* (2), 155-158.

(20) Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *carbon* **2007**, *45* (7), 1558-1565.

(21) Niyogi, S.; Bekyarova, E.; Itkis, M. E.; McWilliams, J. L.; Hamon, M. A.; Haddon, R. C. Solution Properties of Graphite and Graphene. *Journal of the American Chemical Society* **2006**, *128* (24), 7720-7721.

(22) Yang, X.; Zhang, X.; Liu, Z.; Ma, Y.; Huang, Y.; Chen, Y. High-Efficiency Loading and Controlled Release of Doxorubicin Hydrochloride on Graphene Oxide. *The Journal of Physical Chemistry C* **2008**, *112* (45), 17554-17558.

(23) Kang, S. M.; Park, S.; Kim, D.; Park, S. Y.; Ruoff, R. S.; Lee, H. Simultaneous Reduction and Surface Functionalization of Graphene Oxide by Mussel-Inspired Chemistry. *Advanced Functional Materials* **2011**, *21* (1), 108-112.

(24) Compton, O. C.; Dikin, D. A.; Putz, K. W.; Brinson, L. C.; Nguyen, S. T. Electrically conductive "alkylated" graphene paper via chemical reduction of amine-functionalized graphene oxide paper. *Adv Mater* **2010**, *22* (8), 892-896.

(25) Yeo, S. J.; Oh, M. J.; Jun, H. M.; Lee, M.; Bae, J. G.; Kim, Y.; Park, K. J.; Lee, S.; Lee, D.; Weon, B. M.; et al. A Plesiohedral Cellular Network of Graphene Bubbles for Ultralight, Strong, and Superelastic Materials. *Adv Mater* **2018**, *30* (45), e1802997.

(26) Ruess, G. Über das graphitoxyhydroxyd (graphitoxyd). Monatshefte für Chemie und verwandte Teile anderer Wissenschaften **1947**, 76 (3), 381-417.

(27) Scholz, W.; Boehm, H. Untersuchungen am graphitoxid. VI. Betrachtungen zur struktur des graphitoxids. *Zeitschrift für anorganische und allgemeine Chemie* **1969**, *369* (3-6), 327-340.

(28) Nakajima, T.; Mabuchi, A.; Hagiwara, R. A new structure model of graphite oxide. *Carbon* **1988**, *26* (3), 357-361.

(29) Lerf, A.; He, H.; Forster, M.; Klinowski, J. Structure of Graphite Oxide Revisited. *The Journal of Physical Chemistry B* **1998**, *102* (23), 4477-4482.

(30) Szabó, T.; Berkesi, O.; Forgó, P.; Josepovits, K.; Sanakis, Y.; Petridis, D.; Dékány, I. Evolution of surface functional groups in a series of progressively oxidized graphite oxides. *Chemistry of materials* **2006**, *18* (11), 2740-2749.

(31) Gómez-Navarro, C.; Weitz, R. T.; Bittner, A. M.; Scolari, M.; Mews, A.; Burghard, M.; Kern, K. Electronic transport properties of individual chemically reduced graphene oxide sheets. *Nano letters* **2007**, *7* (11), 3499-3503.

(32) Boukhvalov, D. W.; Katsnelson, M. I. Modeling of graphite oxide. *Journal of the American Chemical Society* **2008**, *130* (32), 10697-10701.

(33) Khoei, A. R.; Khorrami, M. S. Mechanical properties of graphene oxide: A molecular dynamics study. *Fullerenes, Nanotubes and Carbon Nanostructures* **2016**, *24* (9), 594-603.

(34) Mu, X.; Wu, X.; Zhang, T.; Go, D. B.; Luo, T. Thermal transport in graphene oxide-

from ballistic extreme to amorphous limit. Scientific reports 2014, 4 (1), 1-9.

(35) Sinclair, R. C.; Coveney, P. V. Modeling Nanostructure in Graphene Oxide: Inhomogeneity and the Percolation Threshold. *J Chem Inf Model* **2019**, *59* (6), 2741-2745.

(36) Sun, Y.; Chen, L.; Cui, L.; Zhang, Y.; Du, X. Molecular dynamics simulation of the effect of oxygen-containing functional groups on the thermal conductivity of reduced graphene oxide. *Computational Materials Science* **2018**, *148*, 176-183.

(37) Yang, Y.; Cao, J.; Wei, N.; Meng, D.; Wang, L.; Ren, G.; Yan, R.; Zhang, N. Thermal Conductivity of Defective Graphene Oxide: A Molecular Dynamic Study. *Molecules* **2019**, *24* (6).

(38) Devanathan, R.; Chase-Woods, D.; Shin, Y.; Gotthold, D. W. Molecular dynamics simulations reveal that water diffusion between graphene oxide layers is slow. *Scientific reports* **2016**, 6 (1), 1-8.

(39) Fonseca, A. F.; Liang, T.; Zhang, D.; Choudhary, K.; Sinnott, S. B. Probing the accuracy of reactive and non-reactive force fields to describe physical and chemical properties of graphene-oxide. *Computational Materials Science* **2016**, *114*, 236-243.

(40) Hou, D.; Yang, T. A reactive molecular dynamics study of graphene oxide sheets in different saturated states: structure, reactivity and mechanical properties. *Phys Chem Chem Phys* **2018**, *20* (16), 11053-11066.

(41) Tang, H.; Zhao, Y.; Yang, X.; Liu, D.; Shao, P.; Zhu, Z.; Shan, S.; Cui, F.; Xing, B. New Insight into the Aggregation of Graphene Oxide Using Molecular Dynamics Simulations and Extended Derjaguin-Landau-Verwey-Overbeek Theory. *Environ Sci Technol* **2017**, *51* (17), 9674-9682.

(42) Chen, Q.; Chen, T.; Pan, G.-B.; Yan, H.-J.; Song, W.-G.; Wan, L.-J.; Li, Z.-T.; Wang, Z.-H.; Shang, B.; Yuan, L.-F. Structural selection of graphene supramolecular assembly oriented by molecular conformation and alkyl chain. *Proceedings of the National Academy of Sciences* **2008**, *105* (44), 16849-16854.

(43) Zhang, W.; Wei, J.; Zhu, H.; Zhang, K.; Ma, F.; Mei, Q.; Zhang, Z.; Wang, S. Self-assembled multilayer of alkyl graphene oxide for highly selective detection of copper (II) based on anodic stripping voltammetry. *Journal of Materials Chemistry* **2012**, *22* (42), 22631-22636.

(44) Lin, L.-L.; Ho, T.-H.; Wang, C.-S. Synthesis of novel trifunctional epoxy resins and their modification with polydimethylsiloxane for electronic application. *Polymer* **1997**, *38* (8), 1997-2003.

(45) Ho, T.-H.; Wang, C.-S. Modification of epoxy resins with polysiloxane thermoplastic polyurethane for electronic encapsulation: 1. *Polymer* **1996**, *37* (13), 2733-2742.

(46) Jin, F.-L.; Li, X.; Park, S.-J. Synthesis and application of epoxy resins: A review. *Journal of Industrial and Engineering Chemistry* **2015**, *29*, 1-11.

(47) Biercuk, M. J.; Llaguno, M. C.; Radosavljevic, M.; Hyun, J. K.; Johnson, A. T.; Fischer, J. E. Carbon nanotube composites for thermal management. *Applied Physics Letters* **2002**, *80* (15), 2767-2769..

(48) Du, F.; Guthy, C.; Kashiwagi, T.; Fischer, J. E.; Winey, K. I. An infiltration method for preparing single-wall nanotube/epoxy composites with improved thermal conductivity. *Journal of Polymer Science Part B: Polymer Physics* **2006**, *44* (10), 1513-1519.

(49) Hussein, S. I.; Abd-Elnaiem, A. M.; Asafa, T. B.; Jaafar, H. I. Effect of incorporation of conductive fillers on mechanical properties and thermal conductivity of epoxy resin composite. *Applied Physics A* **2018**, *124* (7), 475.

(50) Li, Q.; Guo, Y.; Li, W.; Qiu, S.; Zhu, C.; Wei, X.; Chen, M.; Liu, C.; Liao, S.; Gong, Y.; et al. Ultrahigh Thermal Conductivity of Assembled Aligned Multilayer Graphene/Epoxy Composite. *Chemistry of Materials* **2014**, *26* (15), 4459-4465.

(51) Wang, F.; Drzal, L. T.; Qin, Y.; Huang, Z. Mechanical properties and thermal conductivity of graphene nanoplatelet/epoxy composites. *Journal of Materials Science* **2014**, *50* (3), 1082-1093.

(52) Xiao, C.; Chen, L.; Tang, Y.; Zhang, X.; Zheng, K.; Tian, X. Enhanced thermal conductivity of silicon carbide nanowires (SiCw)/epoxy resin composite with segregated structure. *Composites Part A: Applied Science and Manufacturing* **2019**, *116*, 98-105.

(53) Song, S.-h.; Katagi, H.; Takezawa, Y. Study on high thermal conductivity of mesogenic epoxy resin with spherulite structure. *Polymer* **2012**, *53* (20), 4489-4492.

(54) Islam, A. M.; Lim, H.; You, N.-H.; Ahn, S.; Goh, M.; Hahn, J. R.; Yeo, H.; Jang, S. G. Enhanced Thermal Conductivity of Liquid Crystalline Epoxy Resin using Controlled Linear Polymerization. *ACS Macro Letters* **2018**, *7* (10), 1180-1185.

(55) Harada, M.; Morioka, D.; Ochi, M. Thermal and mechanical properties of tetrafunctional mesogenic type epoxy resin cured with aromatic amine. *Journal of Applied Polymer Science* **2018**, *135* (16).

(56) Yang, X.; Zhong, X.; Zhang, J.; Gu, J. Intrinsic high thermal conductive liquid crystal epoxy film simultaneously combining with excellent intrinsic self-healing performance. *Journal of Materials Science & Technology* **2021**, *68*, 209-215.

(57) Lin, Y.; Huang, X.; Chen, J.; Jiang, P. Epoxy thermoset resins with high pristine thermal conductivity. *High Voltage* **2017**, *2* (3), 139-146.

(58) Berendsen, H. J. C.; van der Spoel, D.; van Drunen, R. GROMACS: A message-passing parallel molecular dynamics implementation. *Computer Physics Communications* **1995**, *91* (1), 43-56.

(59) Lindahl, E.; Hess, B.; van der Spoel, D. GROMACS 3.0: a package for molecular simulation and trajectory analysis. *Molecular modeling annual* **2001**, *7* (8), 306-317.

(60) Van Der Spoel, D.; Lindahl, E.; Hess, B.; Groenhof, G.; Mark, A. E.; Berendsen, H. J. GROMACS: fast, flexible, and free. *Journal of computational chemistry* **2005**, *26* (16), 1701-1718.

(61) Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. GROMACS 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation. *Journal of Chemical Theory and Computation* **2008**, *4* (3), 435-447.

(62) Jorgensen, W. L.; Tirado-Rives, J. Chemical theory and computation special feature: potential energy functions for atomic-level simulations of water and organic and biomolecular systems. In *Proceedings of the National Academy of Science*, 2005; Vol. 102, pp 6665-6670.

(63) Dodda, L. S.; Vilseck, J. Z.; Tirado-Rives, J.; Jorgensen, W. L. 1.14*CM1A-LBCC: Localized Bond-Charge Corrected CM1A Charges for Condensed-Phase Simulations. *The Journal of Physical Chemistry B* **2017**, *121* (15), 3864-3870.

(64) Dodda, L. S.; Cabeza de Vaca, I.; Tirado-Rives, J.; Jorgensen, W. L. LigParGen web server: an automatic OPLS-AA parameter generator for organic ligands. *Nucleic Acids Research* **2017**, *45* (W1), W331-W336.

(65) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *Journal of the American Chemical Society* **1996**, *118* (45), 11225-11236.

(66) Darden, T.; York, D.; Pedersen, L. Particle mesh Ewald: An N \cdot log (N) method for Ewald sums in large systems. *The Journal of chemical physics* **1993**, *98* (12), 10089-10092.

(67) Bussi, G.; Donadio, D.; Parrinello, M. Canonical sampling through velocity rescaling. *The Journal of chemical physics* **2007**, *126* (1), 014101.

(68) Berendsen, H. J.; Postma, J. v.; Van Gunsteren, W. F.; DiNola, A.; Haak, J. R. Molecular dynamics with coupling to an external bath. *The Journal of chemical physics* **1984**, *81* (8), 3684-3690.

(69) Hoover, W. G. Canonical dynamics: Equilibrium phase-space distributions. *Physical Review A* **1985**, *31* (3), 1695-1697.

(70) Nosé, S. A molecular dynamics method for simulations in the canonical ensemble. *Molecular Physics* **1984**, *52* (2), 255-268.

(71) Haidekker, M. A.; Ling, T.; Anglo, M.; Stevens, H. Y.; Frangos, J. A.; Theodorakis, E. A. New fluorescent probes for the measurement of cell membrane viscosity. *Chemistry & biology* **2001**, *8* (2), 123-131.

(72) Lin, C.; Jonnalagadda, S.; Kesani, P.; Dai, H.; Balsara, N. Effect of molecular structure on the thermodynamics of block copolymer melts. *Macromolecules* **1994**, *27* (26), 7769-7780.

(73) Chen, X.; Ye, Y.; Hao, L. Atomistic picture of isothermal volume relaxation behavior of atactic polystyrene glass provided by a molecular dynamics simulation. *The Journal of Chemical Physics* **2012**, *137* (4), 044907.

(74) Xie, S.-J.; Qian, H.-J.; Lu, Z.-Y. The influence of internal rotational barriers and temperature on static and dynamic properties of bulk atactic polystyrene. *The Journal of Chemical Physics* **2012**, *137* (24), 244903.

(75) Hung, J.-H.; Patra, T. K.; Simmons, D. S. Forecasting the experimental glass transition from short time relaxation data. *Journal of Non-Crystalline Solids* **2020**, *544*, 120205.

(76) Chaban, V. V.; Prezhdo, O. V. Structure and energetics of graphene oxide isomers: ab initio thermodynamic analysis. *Nanoscale* **2015**, *7* (40), 17055-17062.

(77) Dubbeldam, D.; Calero, S.; Ellis, D. E.; Snurr, R. Q. RASPA: molecular simulation software for adsorption and diffusion in flexible nanoporous materials. *Molecular Simulation* **2015**, *42* (2), 81-101.

(78) Siepmann, J. I.; Frenkel, D. Configurational bias Monte Carlo: a new sampling scheme for flexible chains. *Molecular Physics* **1992**, *75* (1), 59-70.

(79) Tang, H.; Liu, D.; Zhao, Y.; Yang, X.; Lu, J.; Cui, F. Molecular Dynamics Study of the Aggregation Process of Graphene Oxide in Water. *The Journal of Physical Chemistry C* **2015**, *119* (47), 26712-26718.

(80) Smit, B. Grand canonical Monte Carlo simulations of chain molecules: adsorption isotherms of alkanes in zeolites. *Molecular Physics* **1995**, *85* (1), 153-172.

(81) Zhang, J.; Liu, K.; Clennell, M. B.; Dewhurst, D. N.; Pervukhina, M. Molecular simulation of CO2–CH4 competitive adsorption and induced coal swelling. *Fuel* **2015**, *160*, 309-317.

(82) Song, W.; Yao, J.; Ma, J.; Li, A.; Li, Y.; Sun, H.; Zhang, L. Grand canonical Monte Carlo simulations of pore structure influence on methane adsorption in micro-porous carbons with applications to coal and shale systems. *Fuel* **2018**, *215*, 196-203.

(83) Wang, S.; Feng, Q.; Javadpour, F.; Hu, Q.; Wu, K. Competitive adsorption of methane and ethane in montmorillonite nanopores of shale at supercritical conditions: A grand canonical Monte Carlo simulation study. *Chemical Engineering Journal* **2019**, *355*, 76-90.

(84) Yaws, C. L. *Thermophysical properties of chemicals and hydrocarbons*; William Andrew, 2008.

(85) Jorgensen, W. L.; Tirado-Rives, J. The OPLS [optimized potentials for liquid simulations] potential functions for proteins, energy minimizations for crystals of cyclic peptides and crambin. *Journal of the American Chemical Society* **1988**, *110* (6), 1657-1666.

(86) Martínez, L.; Andrade, R.; Birgin, E. G.; Martínez, J. M. PACKMOL: a package for building initial configurations for molecular dynamics simulations. *J Comput Chem* **2009**, *30* (13), 2157-2164.

(87) Parrinello, M.; Rahman, A. Polymorphic transitions in single crystals: A new molecular dynamics method. *Journal of Applied physics* **1981**, *52* (12), 7182-7190.

(88) Nosé, S.; Klein, M. Constant pressure molecular dynamics for molecular systems. *Molecular Physics* **1983**, *50* (5), 1055-1076.

(89) Hess, B. P-LINCS: A parallel linear constraint solver for molecular simulation. *Journal of chemical theory and computation* **2008**, *4* (1), 116-122.

(90) Dušek, K.; Ilavský, M.; Luňák, S. Curing of epoxy resins. I. Statistics of curing of diepoxides with diamines. In *Journal of polymer science: Polymer Symposia*, 1975; Wiley Online Library: Vol. 53, pp 29-44.

(91) Vasilev, A.; Lorenz, T.; Breitkopf, C. Thermal Conductivities of Crosslinked Polyisoprene and Polybutadiene from Molecular Dynamics Simulations. *Polymers (Basel)* **2021**, *13* (3).

(92) Bitzek, E.; Koskinen, P.; Gähler, F.; Moseler, M.; Gumbsch, P. Structural Relaxation Made Simple. *Physical Review Letters* **2006**, *97* (17), 170201.

(93) Plimpton, S. Fast parallel algorithms for short-range molecular dynamics. *Journal of computational physics* **1995**, *117* (1), 1-19.

(94) Ryckaert, J.-P.; Ciccotti, G.; Berendsen, H. J. C. Numerical integration of the cartesian equations of motion of a system with constraints: molecular dynamics of n-alkanes. *Journal of Computational Physics* **1977**, *23* (3), 327-341.

(95) Jorgensen, W. L.; Tirado-Rives, J. Potential energy functions for atomic-level simulations of water and organic and biomolecular systems. *Proceedings of the National Academy of Sciences of the United States of America* **2005**, *102* (19), 6665.

(96) Jewett, A. I.; Stelter, D.; Lambert, J.; Saladi, S. M.; Roscioni, O. M.; Ricci, M.; Autin, L.; Maritan, M.; Bashusqeh, S. M.; Keyes, T.; et al. Moltemplate: A Tool for Coarse-Grained Modeling of Complex Biological Matter and Soft Condensed Matter Physics. *Journal of Molecular Biology* **2021**, *433* (11), 166841.

(97) Shinoda, W.; Shiga, M.; Mikami, M. Rapid estimation of elastic constants by molecular dynamics simulation under constant stress. *Physical Review B* **2004**, *69* (13).

(98) Martyna, G. J.; Tobias, D. J.; Klein, M. L. Constant pressure molecular dynamics algorithms. *The Journal of Chemical Physics* **1994**, *101* (5), 4177-4189.

(99) Tuckerman, M. E.; Alejandre, J.; López-Rendón, R.; Jochim, A. L.; Martyna, G. J. A Liouville-operator derived measure-preserving integrator for molecular dynamics simulations in the isothermal–isobaric ensemble. *Journal of Physics A: Mathematical and General* **2006**, *39* (19), 5629-5651.

(100) Burger, N.; Laachachi, A.; Ferriol, M.; Lutz, M.; Toniazzo, V.; Ruch, D. Review of thermal conductivity in composites: Mechanisms, parameters and theory. *Progress in Polymer Science* **2016**, *61*, 1-28.

(101) Takezawa, Y.; Akatsuka, M.; Farren, C. High thermal conductive epoxy resins with controlled high order structure. In *Proceedings of the 7th International Conference on Properties and Applications of Dielectric Materials (Cat. No.03CH37417)*, 1-5 June 2003, 2003; Vol. 3, pp 1146-1149 vol.1143.

(102) Akatsuka, M.; Takazawa, Y.; Sugaware, K. Thermosetting resin compounds. US20060276568 2006.

(103) Fukushima, K.; Takahashi, H.; Takezawa, Y.; Hattori, M.; Itoh, M.; Yonekura, M. High thermal conductive epoxy resins with controlled high-order structure [electrical insulation applications]. In *The 17th Annual Meeting of the IEEE Lasers and Electro-Optics Society, 2004. LEOS 2004.*, 20-20 Oct. 2004, 2004; pp 340-343.

(104) Zhang, Q.; Chen, G.; Wu, K.; Shi, J.; Liang, L.; Lu, M. Biphenyl liquid crystal epoxy containing flexible chain: Synthesis and thermal properties. *Journal of Applied Polymer Science* **2020**, *137* (38).

(105) Harada, M.; Okamoto, N.; Ochi, M. Influence of the introduction of flexible alkyl chains on the thermal behavior and mechanical properties of mesogenic epoxy thermosets. *Journal of Applied Polymer Science* **2016**, *133* (47).

요약(국문초록)

본 논문에서는 고분자 화합물을 전원자 분자동역학 전산모사를 활용하여 연구하였다. 기존에 고분자에 대해서는 긴 사슬과 같은 분자 구조를 모사하기 위해 원자 수준의 구조는 무시하는 계산 기법들이 보다 널리 이용되어 왔다. 하지만 분자 수준의 조작을 통해 새로운 구조의 고분자 화합물들이 합성됨에 따라 이러한 원자 수준의 구조가 점점 더 중요해지고 있다. 따라서 원자 수준의 모델링 없이는 전산적으로 구현이 힘든 두 종류의 분자 개질 고분자 화합물에 대한 연구를 본 논문에서 제시하였다. 짧은 올리고머의 기능화를 통해 합성된 분자 개질 화합물을 먼저 다루었으며, 다양한 구조의 기능기를 포함한 고분자를 다음으로 다루었다. 짧은 올리고머에 대한 연구에서 파르네실 기능기가 도입된 분자 회전체와 알킬화 그래핀 산화물을, 다양한 기능기에 대한 연구에서 메소젠 에폭시 수지를 다루어 총 세개의 시스템을 연구하였다.

먼저, FCVJ(farnesyl-(2-carboxy-2-cyanovinyl)-julolidine)는 일종의 형광 분자 회전체로 파르네실 기능기의 도입으로 고분자의 유리전이 온도를 측정할 수 있다. FCVJ 분자에 고온을 커플링 시키는 분자동역학 전산모사를 진행했고 FCVJ를 활용한 형광 실험을 통한 유리전이 온도 측정을 재현하였다. 계산 결과 분자 회전체의 불균등 운동에너지 분배가 나타났고 이로부터 유리전이 온도를 측정할 수 있었으며 실험치와 근사한 값을 얻었다. 또한, 추가적인 분석을 통해 파르네실 기능기의 도입으로 얻어진 벌키하고 구조적 비대칭성이 유리전이 온도 측정을 가능하게 했음을 밝혔다. 다음으로, 알킬화 그래핀 산화물은 가장 간단한 그래핀 산화물의 유도체로 기능화된 알킬 기능기의 구조나 수에 따라 그 특성을 조절할 수 있다. 알킬화 그래핀 산화물의 분자구조는 잘 알려져 있지 않기에, GCMC(grand canonical Monte Calro)와 분자동역학을 활용하여 분자식을 모델링하였다. 알킬 기능기의 길이에 따른 알킬화 그래핀 산화물의 층상 구조와 그 기계적 물성을 측정하여 재료 설계적인

95

관점에서 방향을 제시할 수 있었다. 마지막으로, 메소젠 에폭시 수지는 고열전도성 플라스틱 재료로 많이 연구되고 있다. 메소젠은 고분자 수지 내에서 한 방향으로 정렬하여 미세상을 이루는 것으로 알려져 있으며, 이를 통해 포논 전달을 가속화하고 높은 열전도율을 얻게 한다. 전원자 분자동역학 전산모사를 통한 원자 수준에서의 관찰을 통해 메소젠 기능기의 화학적 구조가 어떻게 이들의 정렬과 이들이 포함된 고분자 수지의 열전도도에 영향을 미치는지 알 수 있었다.

따라서 본 논문은 전원자 분자 동역학을 활용한 자세한 관찰을 통해 대표적인 고분자 시스템에 대한 연구 사례를 보이며, 분자 수준에서의 조작이 어떻게 시스템 전체의 구조와 물성에 영향을 미치는지 보임으로써 고분자 연구에서도 원자 수준의 자세한 관찰이 필요함을 보인다.
감사의 글

진심으로 존경하는 이원보 교수님과 연구를 도와 주신 모든 분들, 그리고 연구실 식구들, 사랑하는 가족들, 가족처럼 사랑하는 모든 분들께 감사하다는 말을 전합니다.