Chapter 3

Molecular Modeling

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1. INTRODUCTION

About 10,000 years ago, humans began to domesticate plants and animals. Now, it is time for us to domesticate molecules. In today's polymer materials science, many scientists have synthesized a large number of synthetic polymers, which have been widely used in people's lives. In a sense, natural polymers, like natural rubber, cellulose, etc., are of less importance than ever before. It is well known that the properties of the materials are closely related to their composition and bulk state at the molecular level. However, regarding the experimental studies, most of the breakthroughs in polymer materials are still based on a try-error-try loop, and it indeed wastes the resources and energies to a great extent. To the best of our knowledge, molecular modeling may be the only method that can reveal the nature of materials directly at the molecular level. It could be much more effective if we combine the traditional experimental study with molecular modeling. For these reasons, molecular modeling has evolved from an academic curiosity to an essential predictive tool for materials design within the past 20 years (Figure 1) [1]. However, in this chapter, we confine our discussion on the basic concept of molecular modeling and its applications to polybenzoxazine.

What is molecular modeling? Molecular modeling is the science of representing molecular structures numerically and simulating their behavior with the equations of quantum and classical physics [2]. Using computer programs, polymer scientists could directly generate and obtain molecular data including geometries (bond lengths, bond angles, torsion angles), energies (heat of formation, activation energy, etc.), electronic properties (charges, electron affinity), spectroscopic properties (vibrational modes and intensities), and bulk properties (volumes, diffusion, viscosity, modulus, etc.) [3]. Today's mainstream simulation methods include the *ab initio* quantum chemistry method, molecular mechanics (MM), molecular dynamics (MD), and Monte Carlo (MC) methods. The *ab initio* method, which has the highest accuracy among the above methods, is based on the Schrödinger equation, and it was often applied to deal with the electronic structure of organic molecules and their conformation and spectra properties. However, in terms of the polymer, it cannot be simulated directly by the *ab initio* method because of its high molecular weight. By contrast, MM and MD simulation, which is based on classical mechanics, can solve this problem well. They have been widely used to simulate the conformation of a single polymer chain and bulk properties of polymers. The MC method is a statistical method, which can be used to predict the preferred conformations of polymers. It can simulate many more atoms in polymer system, but its primary disadvantage is that dynamic information cannot be obtained by the MC method.

In the following parts of chapter, we review some applications of molecular modeling in polybenzoxazine. Section 2 concerns the chemical reactions of benzoxazine. Section 3 focuses on the structure analysis of polybenzoxazine with different level structures. Section 4 addresses the prediction of properties of polybenzoxazine using MD modeling.

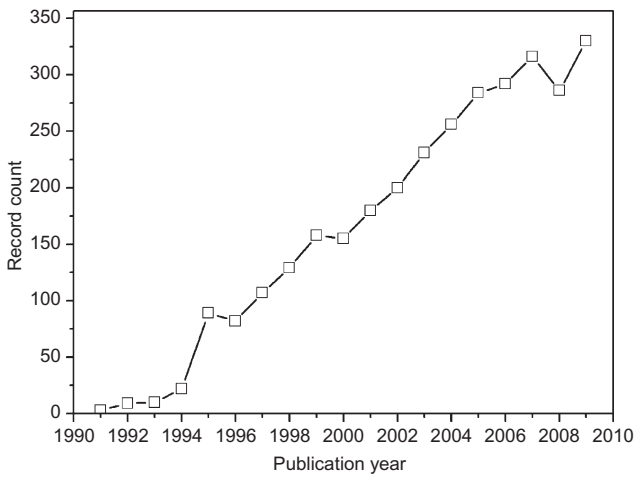


FIGURE 1 The number of papers on polymer modeling indexed by Science Citation Index (SCI) from 1991 to 2009.

2. CHEMICAL REACTION

The ring-opening mechanism of benzoxazine is always regarded as a nightmare for the researchers in this field because of its multiple reactive points in the benzoxazine structure. However, some researchers used molecular modeling to study benzoxazine's electronic structure and its ring-opening point. These studies have provided some direct or indirect evidence at the molecular level for experimental research.

Pei [4] used semiempirical quantum chemistry AM1 method (Gaussian software [5]) to study benzoxazine's structure, and found that the oxazine ring in a benzoxazine molecule showed a distorted semichair structure. The distorted ring strain could stimulate the benzoxazine to undergo ring-opening reactions in some circumstances. Furthermore, based on the results of calculated bond order and bond length, he predicted the ring-opening point of benzoxazine is the O–CH_2 bond when it is catalyzed by the active hydrogen compound or Lewis acid.

Moreover, Liu and Gu [6] made a colorless monoclinic crystal of 2,4-dichloro-benzoxazine and confirmed the spatial molecular structure of benzoxazine by single crystal x-ray diffraction analysis and molecular modeling analysis (Figure 2). The corresponding cell parameters were listed as follows: monoclinic, space group $P2_1/n$, $a = 7.421(10)$, $b = 16.749(2)$, $c = 10.395(10)$ Å, $\beta = 105.860(10)$ degrees. And then they applied MM simulation (Cerius 2 Software [7]) to study the effect of substituting groups (Figure 3) on ring-opening reactions of various benzoxazine model compounds by comparison of their bond lengths, bond angles, torsion angles, and charge distribution. The ring-opening reaction was expected to happen at the C–O bond, for the O atom has more electronegativity than N atoms in oxazine and the C7–O band is longer than the C7–N band. The substituting groups on the benzene ring connecting to the oxazine could have great influence on the ring-opening reactivity of benzoxazine. The ring-opening reaction of benzoxazine linked with electron-withdrawing group was more likely to happen than the ones linked with electron-donating groups, because of the lower charge density of the O atom. By contrast, substituting groups linked to the N atom have negligible effects on the ring-opening reaction of benzoxazine. Recently, Chutayothin and Ishida [8] used a similar method (CS Chem3D Pro software [9]) to calculate the charge distribution of benzoxazines, and agreed well with the results from Liu's study.

For the difunctional benzoxazine monomer, Wang and Gu [10] used the density function theory method (DFT, Dmol 3 module in Materials Studio Software [11]), which is a popular quantum chemistry method, to discuss the electronic effect of spacers of bisphenolic compounds on the ring-closing and ring-opening polymerization of benzoxazines (Figure 4). When the biphenols were linked with electron-donating groups (like BA-a), the charge of C1 would increase significantly and therefore, it was much easier to undergo a ring-closing reaction to form benzoxazine monomer. Furthermore, its bond length of C2–O in the oxazine ring was shorter than the ones linked with electron-withdrawing spacers (like BZ-a). Thereby, the curing temperature of BA-a was much higher than that of BZ-a, for it needed much more energy to initiate the ring-opening reaction.

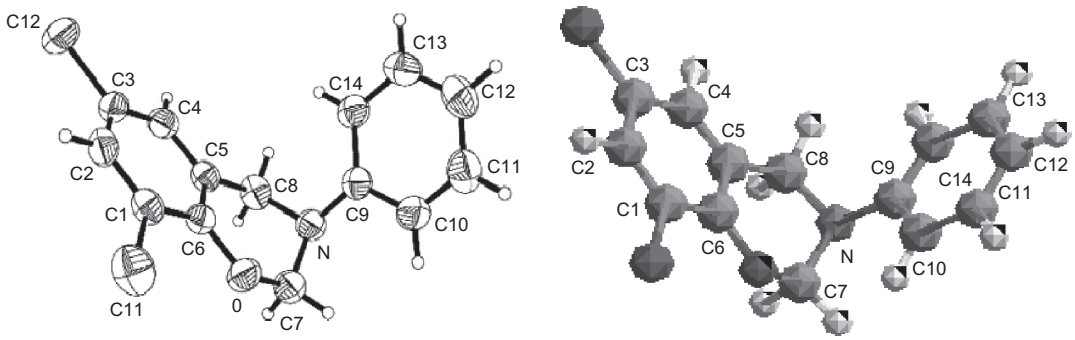
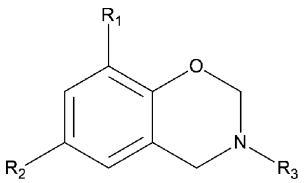


FIGURE 2 The spatial molecular structure of benzoxazine [6].



(1) R_1=R_2=Cl, R_3=C_6H_5.
(2) R_1=H, R_2=Cl, R_3=C_6H_5.
(3) R_1=R_2=CH_3, R_3=C_6H_5.
(4) R_1=H, R_2=CH_3, R_3=C_6H_5.
(5) R_1=R_2=H, R_3=C_6H_5.
(6) R_1=H, R_2=NH_2, R_3=C_6H_5.
(7) R_1=H, R_2=COOH, R_3=C_6H_5.
(8) R_1=R_2=H, R_3=CH_3.
(9) R_1=R_2=H, R_3=C_6H_{11}.
(10) R_1=R_2=H, R_3=$C_6H_4CO_2H$.

FIGURE 3 The chemical structures of benzoxazines with different substituting groups [6].

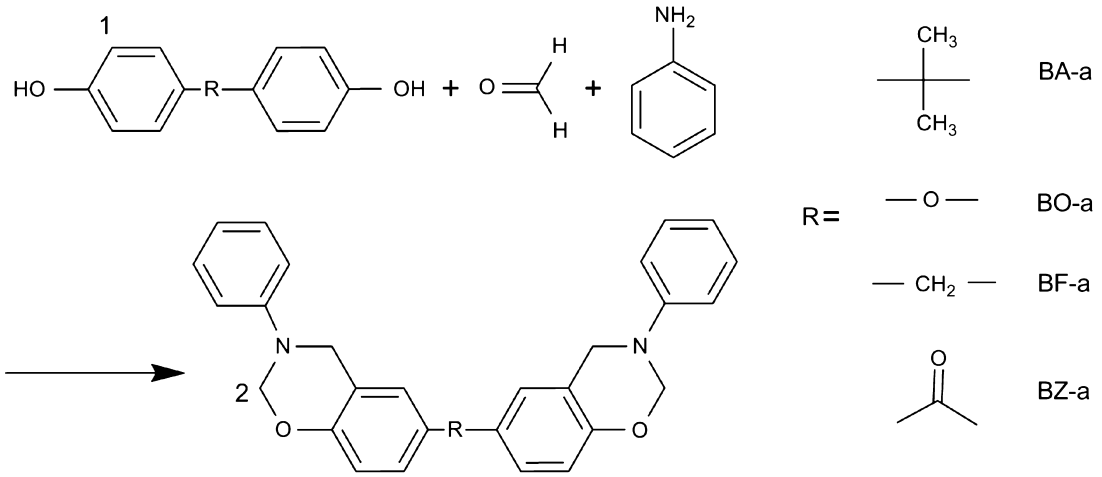
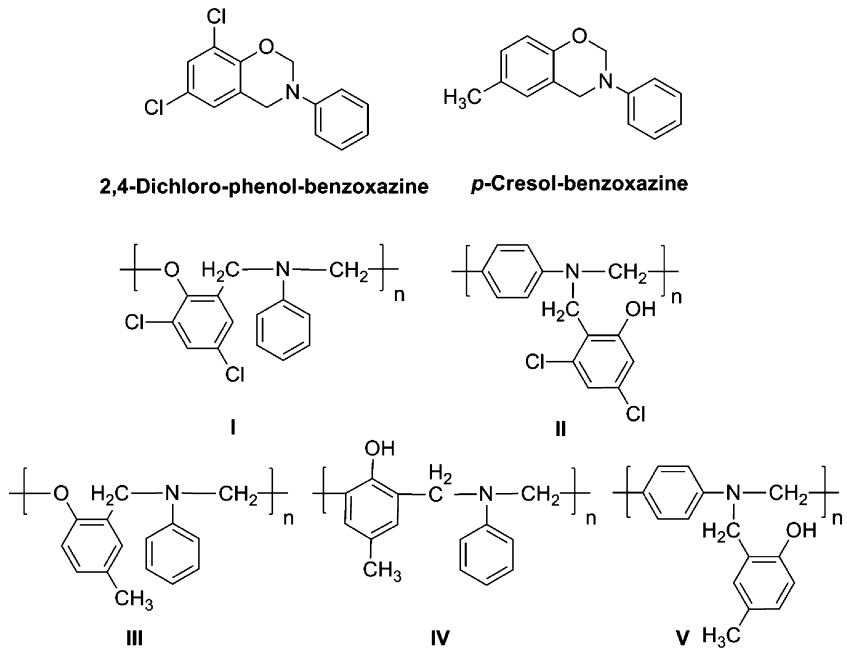


FIGURE 4 The scheme to prepare difunctional benzoxazine monomers [10].

FIGURE 5 The chemical structure of benzoxazine monomers and their possible polymer structures (I-V) [12].



I: 2,4-Dichloro-phenol-polybenzoxazine (containing ether bonds)
II:2,4-Dichloro-phenol-polybenzoxazine (containing *p*-amino bonds)
III: *p*-Cresol-polybenzoxazine (containing ether bonds)
IV: *p*-Cresol-polybenzoxazine (containing *o*-hydroxyl bonds)
V: *p*-Cresol-polybenzoxazine (containing *p*-amino bonds)

3. STRUCTURE ANALYSIS

3.1. Single Chain Spatial Structure

Figure 5 shows three kinds of polybenzoxazine chains containing ether bonds (I and III), *p*-amino groups (II and V) or *o*-hydroxyl groups (IV). Using MM simulation methods (Cerius 2 Software [7]), Liu and Gu [12] provided detailed pictures of these optimized isolated polymer chains with 10 repeat units (Figure 6). From the full views of these chains, the spatial shape and the extending direction of the polybenzoxazine chains can be understood. On the other hand, the end views of these polymer chains give the interesting pictures of the three-dimensional spatial arrangements and the comparative positions of the atoms on the polybenzoxazine chains. From the end views, the shape of the chains I and III looks like a solid glob and a solid

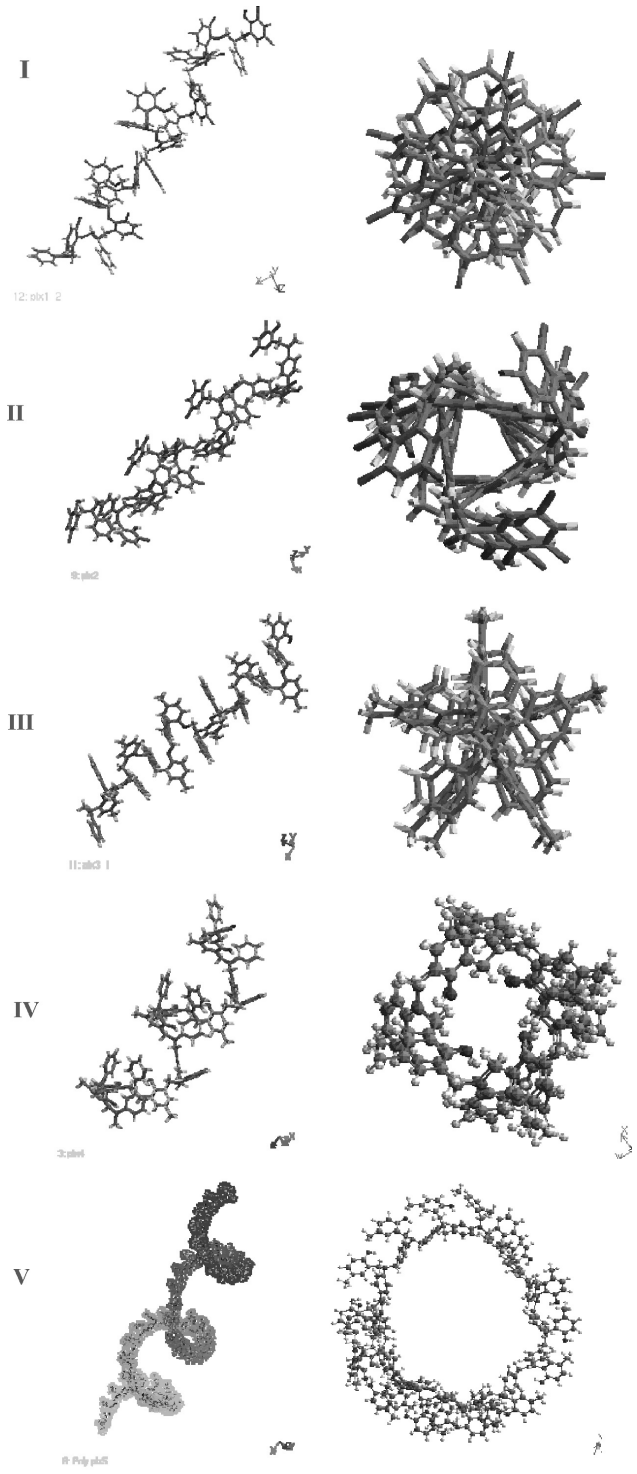


FIGURE 6 Spatial structures of optimized single polybenzoxazine chains (corresponding to I to V in Figure 5): (a) Full view; (b) End view [12].

five-pointed star, respectively, but the chains II, IV, and V all have a large hollow cavity. All the O and N atoms with a large electronegativity are converging to the axial positions in the polymer chain containing ether bonds, but distributing well in the polymer chains containing *p*-amino groups or *o*-hydroxyl groups.

3.2. Supramolecular Structure

A large number of hydrogen bonding exists in the polymer network after the ring-opening polymerization of the benzoxazine monomer. Moreover, it is the hydrogen bonding that leads to the fascinating properties of polybenzoxazines, like high glass transition temperature and high modulus, etc. Unfortunately, we often fail to characterize hydrogen bonding by conventional methods. Therefore, several researchers have attempted to obtain thorough information by combining Fourier transform infrared (FT-IR) spectroscopy with advanced solid state nuclear magnetic resonance (NMR) spectroscopy and molecular modeling.

Dunkers et al. [13] first proved the hydrogen-bonding structures within benzoxazine dimers, using the semiempirical quantum chemistry method (SYBYL 6.0 Molecular Modeling Software [14]). It was shown that the intramolecular hydrogen bonding existed in both benzoxazine dimers (Figure 7). However, only the hydroxyl group of the *N*-methyl dimer could present hydrogen bonding to both the nitrogen and the other oxygen atom. The hydroxyl proton of *N*-tert-butyl dimer preferred to form hydrogen bonding only with the other oxygen, not nitrogen atom. Goward et al. [16] used the DFT method (Car-Parrinello Molecular Dynamics simulation package [17]) to predict the hydrogen-bonding structures in a series of benzoxazine oligomers. The results of ^{1}H-NMR chemical shift obtained by DFT method were in agreement with the experimental results. Thus, it further confirms the existence of these hydrogen-bonding structures.

Besides, using DFT method (Materials Studio Software [11]), Phongtamrug et al. [18] predicted that a cage-like structure could be formed between two benzoxazine dimers through intra- and intermolecular hydrogen bonding. When Cu ions were added in the system, it was shown that the

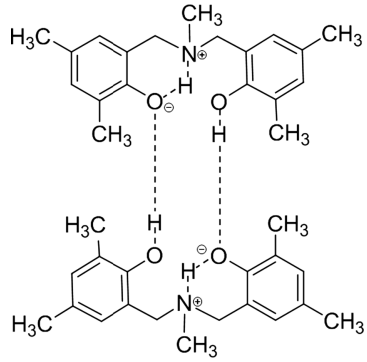


FIGURE 7 A schematic representation of a pair of benzoxazine dimers linked by an extended hydrogen-bonding arrangement [13,15].

coordinated bonds between Cu ions and N or O atoms were formed by charge transfer, while the hydrogen bonding was destroyed then (Figure 8). Nevertheless, by comparing its single crystal structure from experimental study, the crystal can be well maintained before and after complexation.

3.3. Network Structure

For the difunctional polybenzoxazine, Hamerton et al. [19] successfully constructed a polybenzoxazine network by Cerius 2 Software [7] (Figure 9). Using the ring-opening product (b) of the benzoxazine monomer (a), the polybenzoxazine oligomer (c) was constructed and packed into the bulk amorphous state (d). Finally, the supercell of the polybenzoxazine oligomer was obtained and we can regard it as the polybenzoxazine network (e) after linking the reactive atoms in the polybenzoxazine oligomers. Moreover, the simulated glass transition temperature and mechanical strength were obtained from MD simulation, and were comparable to the experimental value. Recently, Hall et al. [20] applied a similar method to compare the results simulated by two mainstream molecular modeling softwares (Materials Studio [11] and Cerius 2 Software [7]), and suggested that the Materials Studio Software could produce a more accurate result.

4. STRUCTURE-PROPERTY RELATIONSHIP

The structure-property relationship is of great importance for the polymeric materials design. Experiments to learn the details of polymer structure, to measure polymer properties, and to try to establish between two can be very time consuming and expensive [3]. However, as mentioned in the introduction, molecular modeling could offer another measurement insight into the nature of materials, contributing greatly to the polymer materials design.

Kim and Mattice [21–24] have done a series of work on mono-functional polybenzoxazine using Cerius 2 Software [7]. The rotational isomeric state (RIS) model was applied

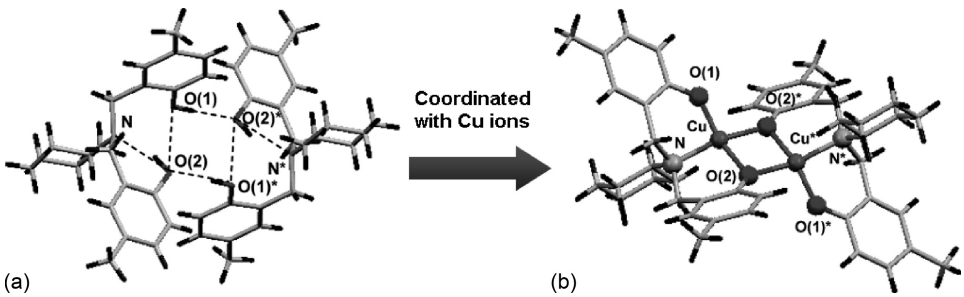


FIGURE 8 The self-assembly frameworks of two benzoxazine dimers' cage structure (a) and coordinated compounds of benzoxazine-Cu (b) [18].

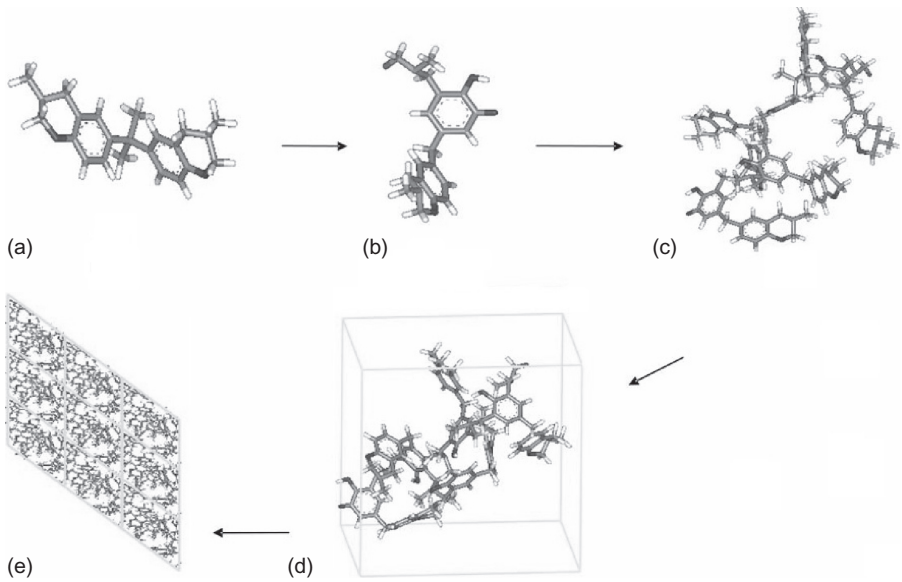


FIGURE 9 The Simulation scheme to prepare a polybenzoxazine network: (a) benzoxazine monomer, (b) ring-opening product of benzoxazine monomer, (c) polybenzoxazine oligomer, (d) polybenzoxazine oligomer in the bulk state, and (e) polybenzoxazine network [19].

to discuss the preferred conformation of a single polybenzoxazine chain, which laid the foundation for the study on polybenzoxazine bulk structure and properties [21]. In the research of bulk state, the solubility parameters, the radius distribution function (RDF), and free volume of *p*-cresol-polybenzoxazine (IV in Figure 5) were obtained. The Hildebrand solubility parameter is 8.3 ± 0.7 $(cal/cm^3)^{1/2}$. Hydrogen bonds are mainly formed as OH–N. About 70% of the hydroxyl groups participate in hydrogen bonds, and about 70% of the acceptors are nitrogen atoms. Most of the hydrogen bonds arise from the intramolecular part of the structure, and there were fewer hydrogen bonds in the polybenzoxazine bulk than in its single chain (Table 1). The fraction of the volume unoccupied is 0.29. About 250 voids were found for each microstructure, but only a few voids were found to be larger than 3 $Å^3$. The phenyl rings in the polybenzoxazine were oriented when they were separated less than 0.5 nm, while the nonpolar element, such as methyl groups and hydrogen atoms bonded to carbon atoms, were enriched around the voids in polymer bulk [22].

Moreover, Kim also studied the thin film of polybenzoxazine, and predicted its surface energy from MD simulation. They found that the density of films dropped rapidly at a distance of 0.7 nm from the surface. The nonpolar components of polybenzoxazine were enriched on the surface of thin film, while the polar atoms were aggregated in the interior of the film [23]. The diffusion behaviors of water and oxygen in the polybenzoxazine bulk was also studied [24]. The results of RDF indicated that the hydrogen bonding existed between polybenzoxazine and water; however, it did not have a significant effect on the diffusion behaviors of water, for the average lifetime of hydrogen bonds between donors and acceptors provided by polybenzoxazine is much longer than the lifetime of hydrogen bonds with water, according to the calculation from the autocorrelation function.

Besides, Liu predicted the stability of preferable structures of polybenzoxazine by comparing the energies of a series of possible polybenzoxazine chains (Figure 5) using MM and MD simulation, which contain energy terms of bond, angle, torsion, inversion (out-of-plane), van der Waals, and electrostatic interactions (Table 2) [12]. From the MM energy minimization calculation, the total energies of polybenzoxazines with ether bonds (I and III) are much higher than those of polybenzoxazine with *p*-amino

TABLE 1 The Number of Hydrogen Bonds in the Polybenzoxazine Isolated Parent Chain and Its Bulk [22]

Cell	Isolated parent chain	Bulk structure
1	35 (31)[a]	26 (20)
2	38 (32)	26 (17)
3	28 (27)	22 (13)
4	37 (32)	17 (12)
5	39 (31)	23 (17)
Average ± std. deviation	35.4 ± 3.9 (30.6 ± 1.9)	22.8 ± 3.3 (15.8 ± 2.9)

[a]*The number of nitrogen atoms serving as acceptors is in parentheses.*

TABLE 2 The Energy (kJ/mol of Chains) for the Decomposition of the Single Polybenzoxazine Chains (Corresponding to I-V in Figure 5) [12]

Component	I	II	III	IV	V
Bond	46.309	53.010	49.681	59.235	49.976
Angles	88.278	99.547	120.101	101.858	71.593
Torsions	75.128	25.889	−6.222	−49.381	16.814
Inversions	0.443	0.121	0.191	0.235	0.467
Van de Waals	75.587	119.649	131.432	120.378	152.348
Electrostatic	82.706	−68.004	−107.726	−139.337	−162.112
Total energy	600.286	407.509	518.646	49.970	197.157

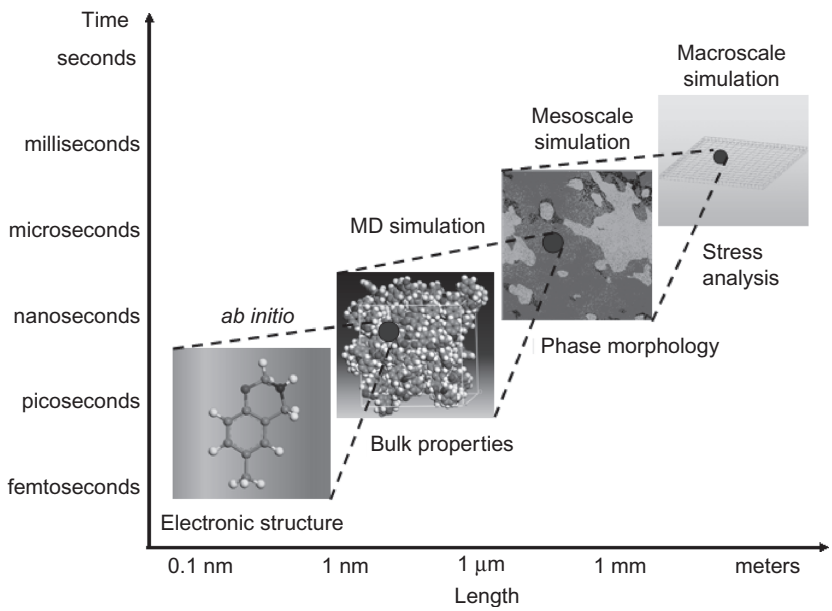


FIGURE 10 Length and time scales involved in modeling electronic, atomistic, mesoscale, and macroscale levels [27]. From left to right: charge density of benzoxazine monomer predicted by *ab initio* method; polybenzoxazine network with MD simulation; phase morphology of benzoxazine/epoxy blends; stress analysis of polybenzoxazine plate after processing.

structure (II and V) or *o*-hydroxyl structure (IV). It means that the chains with ether bonds are unstable. A reasonable explanation, combining the spatial structure of polybenzoxazine chains in Figure 6, is that the exclusion of the electrostatic energies among the O and N atoms concentrated on the chain axis results in an increase in the torsion energies. Such simulation results are in good agreement with those of experimental study. Also, the RDFs, free volume, and mechanical strength were also predicted by MD simulation [25].

5. SUMMARY AND REMARKS

From the above analysis, we can safely conclude that molecular modeling indeed provides another insight into the discussion on the chemical reactions, structures, and properties of polybenzoxazine. However, it should be recognized that there is still much room for us to further our understanding in this field. Therefore, the remarks and outlook were given as follows:

- Chemical reaction: the polymerization mechanism of benzoxazine resin is still not well established [26]. It is rational for us to combine the modern characterization method and molecular modeling to further the understanding on the reaction mechanism of benzoxazine.
- Structure analysis: although the hydrogen-bonding structures in the benzoxazine dimer or oligomer could provide valuable guidance for us to understand the nature of hydrogen bonding in the polybenzoxazine bulk, there has been no systematic study on this topic untill now, especially on molecular modeling. Maybe using MD simulation to predict the hydrogen-bonding structures in polybenzoxazine bulk will be an amazing research direction in the future.
- Structure-properties relationship: there are few studies of molecular modeling on the functional polybenzoxazine and their hybrids with inorganic materials, in spite of the fact that these materials have been widely used in the electronic and aviation industries.
- Multiscale simulation method: it should be noted that the structure and properties of polymers are determined by the various time and length scale (Figure 10). In this way, we should apply a variety of simulation methods to reveal the nature of polymer materials thoroughly.

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