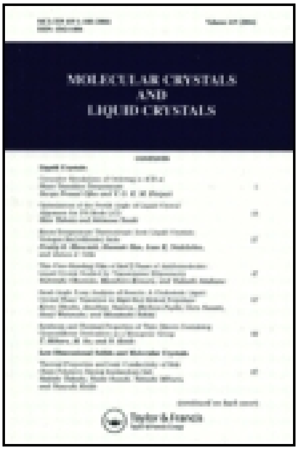

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Molecular Modeling of a Polar Rod-Like Aromatic Polyester Forming Nematic Liquid Crystal. Part 2. Molecular Dynamics Simulation for Polar Association of Molecules

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Molecular Modeling of a Polar Rod-Like Aromatic Polyester Forming Nematic Liquid Crystal. Part 2. Molecular Dynamics Simulation for Polar Association of Molecules

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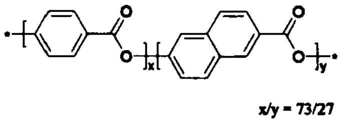
The most stable molecular packing systems of aromatic polyester molecules have been investigated by molecular dynamics (MD) simulations performed for decamer (ten repeating units) of *p*-hydroxybenzoic acid (HBA) in the nematic phase. The MD simulations were started from eight possible packing structures. Among them, we found the polar ordering structure with the intermolecular ester carbonyl groups aligned in the same direction is energetically most favorable. This is consistent with our previous experimental observation for the second-harmonic generation (SHG) intensity measurement.

Keywords: molecular dynamics simulation; polar rod-like aromatic polyester; nematic liquid crystal

Introduction

As described in Part 1, the polar rod-like aromatic polyester shows strong SHG-activity without visible absorption and we have clarified the origin of the SHG-activity by *ab initio* molecular orbital calculations.[1]

We found the polar ordering in the nematic liquid crystal phase of the aromatic copolymer comprising *p*-hydroxy benzoic acid (HBA) and 6-hydroxy-2-naphtoic acid (HNA) in a molar ratio of 73 / 27, the so-called super-engineering plastic, 'Bektra' (see Scheme 1).[2] It was found that the second harmonic generation (SHG) appeared in compounds with a high degree of polymerization.



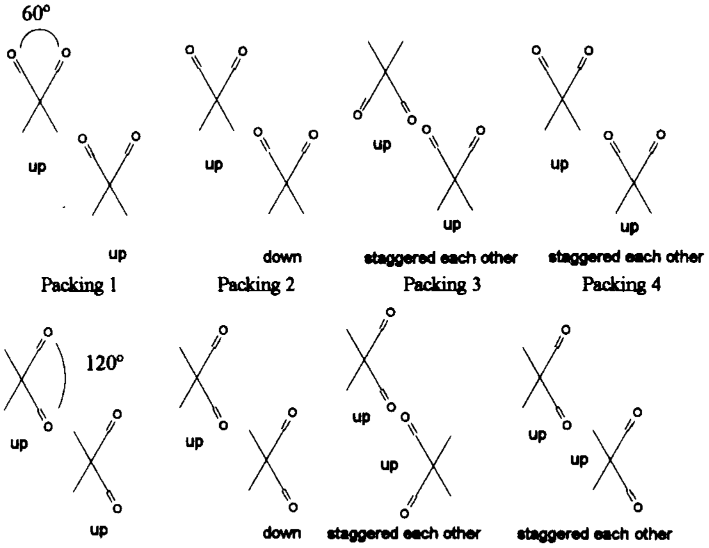
Scheme 1.

From the detailed SHG intensity measurement, we concluded that Bektra is a ferroelectric nematic liquid crystal with biaxial polarity, *i.e.*, there is a regularity in the head-to-tail molecular alignment; in addition, the intermolecular carbonyl groups align in the same direction (see packing 4 in Scheme 2). Because of these facts, we suggested that the strong dipole-dipole interactions between the polar rod-like molecules play an important role for the appearance of the polar ordering.

In this study, we examined the various ways of packing a polar rod-like aromatic polyester by performing MD simulations of the decamers of HBA.

Model

We selected eight initial molecular packing configurations for the MD simulations (see Scheme 2). It is known that neighboring monomer units in an HBA polymer have two equilibrium conformations without energy difference, as described in Part 1.[1] One has a dihedral angle of 60° between the two benzene rings (conformer I in Packing 1-4) and another has that of about 120° (conformer II in Packing 5-8). These two conformations were also taken into account in the initial molecular

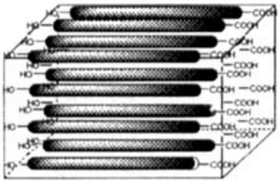


Packing 1 Packing 2 Packing 3 Packing 4

Packing 5 Packing 6 Packing 7 Packing 8

Scheme 2

geometry. Further, molecules have the head-tail character, and hence there are two types of molecular alignments with respect to the polarity, up and down. According to Lieser's previous investigation,[3] we selected a = 7.5 Å, b = 5.7 Å as the basal plane dimensions in orthorhombic unit cell parameter of poly-HBA. 16 molecules of HBA decamer were packed in a box of 68 × 23 × 15 Å. A side view of the initial packing is illustrated in Scheme 3.



Scheme 3

Results and Discussion

At first, the system was equilibrated under a 10 ps NVT simulation (constant particle number N, volume V, and temperature T) at 498 K for each of the initial packing configurations. The CFF91[4] force field was used and all bond lengths, angles and dihedral angles were not fixed throughout the simulations. As an example, Figure 1 shows the total energy change during a 10 ps simulation for packing 4. The total energy levels off at the end of the period. Therefore the system was assumed to have reached equilibrium. Equilibration of the other packings was also confirmed in a similar fashion.

Then, subsequent simulation was carried out under more realistic conditions, *i.e.*, a 15 ps NPT simulation (constant particle number N, pressure P, and temperature T) at 498 K. The temperature was controlled by the Nosé-Hoover thermostat [5,6] and the pressure was kept constant at 1 atm by the Parrinello-Rahman methods.[7] After an equilibration time of 10 ps, an additional simulation run of 5 ps was carried out for data sampling. Figure 2 shows an example of the total energy change during a 15 ps NPT simulation for packing 4. From the figure, we assumed that the system had reached equilibrium.

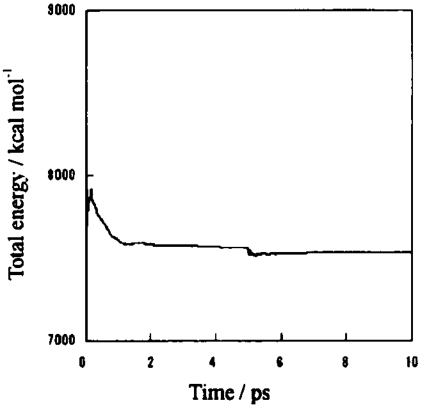


Figure 1. Total energy plotted against time for the packing 4 during NVT simulation at 498 K

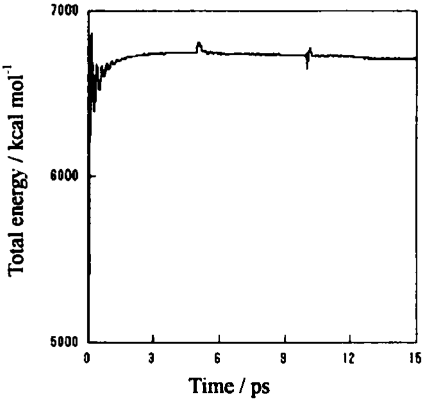


Figure 2. Total energy plotted against time for the packing 4 during NPT simulation at 498 K

Equilibration of other packings was also confirmed in a similar fashion. The initial oscillations and the spikes caused by restart runs in Figure 2 may be due to the timestep (0.25 fs), which may not be small enough.

A snapshot of packing 4 after 15 ps NPT simulation is shown in Figure 3. It is in the nematic liquid crystalline state, because the system shows the ordering for the long axis direction and the disordering for the center of mass.

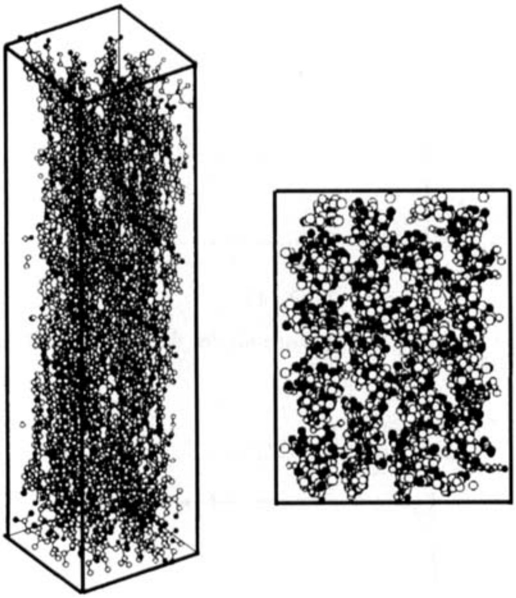


Figure 3. Snapshot of a configuration of packing 4 after 1 15 ps NPT simulation at 498 K. Hydrogen atoms are blanked out for clarity.

Average densities of each packing system after 15 ps of NPT simulation are listed in Table 1. The calculated densities at 498 K are 1.30-1.37 g cm^{-3}. These are close to experimental values of HBA/HNA copolymer (about 1.40 g cm^{-3}).[8,9]

Table 1. Average densities after 15 ps NPT simulations of HBA decamer.

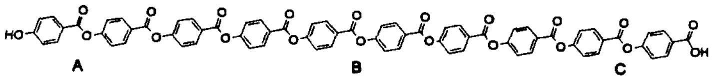
packing	1	2	3	4	5	6	7	8
<density> / g cm^{-3}	1.30	1.35	1.35	1.28	1.34	1.37	1.35	1.32

The liquid crystalline state is characterized by the order parameter, which is a measure of the degree of orientational ordering defined as

$$S = \frac{1}{2}\left\langle 3\cos^2\theta - 1\right\rangle$$

where θ is the angle between the direction of preferred orientation and the long principal axis of the molecule. The calculated order parameter was found to deviate only slightly from unity in the simulations performed. An experimental value of 0.81 has been reported from X-ray diffraction for 58/42 HBA/HNA copolymer.[10] This difference may be due to the limitation of the model and simulations.

In order to examine the local conformational change of an HBA decamer, the variation of the dihedral angle between two neighboring benzene planes was monitored for packing 4. Figure 4 shows the change of the dihedral angle at three local regions in the HBA molecule (region A, B and C labeled in Scheme 4).



Scheme 4

In region C (vicinity of the –COOH terminal group), the average angle is about 104° with variation from about 50° to 130°. The significant variation in region C reflects the property of the dihedral angle between two neighboring benzene planes of an isolated aromatic polyester, *i.e.*, the rotation barrier is small and the benzene plane is allowed to rotate between about 60° and 120°.[11] However, the dihedral angles in region A (vicinity of the –OH terminal group) and B (in the center of an HBA decamer) are constrained by packing.

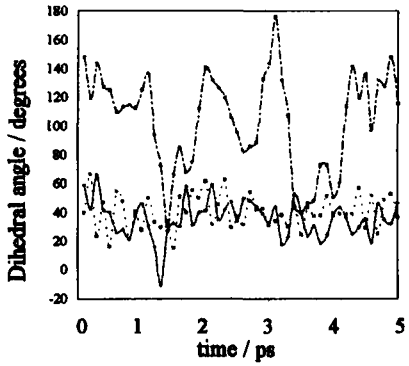


Figure 4. Changes of dihedral angle between two benzene planes of HBA decamer in packing 4: dihedral angles in region A (——), in region B (----) and in region C (—·—·). Data are sampled at each 100 fs through out NPT simulation (498 K).

The average total energy of each packing after 15 ps of NPT simulations are shown in Table 2. In the NPT simulation at 498 K, the most stable system is packing 4, therefore, as expected experimentally,[2] the polar ordering structure with the intermolecular carbonyl groups aligned in the same direction is energetically favored.

Table 2. Total energy after 15 ps NPT simulations of HBA decamer.

packing	<total energy> / kcal mol^{-1} 498 K
1	7490
2	7408
3	7090
4	6764
5	7269
6	7372
7	7288
8	7354

Conclusions

The most stable molecular packing system of the HBA polymer has been investigated by an MD simulation performed for an HBA decamer. The polar-ordering packing (packing 4) is energetically favored at a simulation temperature of 498 K. The results of the MD simulations support the experimental conclusion that Bektra exhibits a ferroelectric nematic liquid crystal with biaxial polarity.

The most stable arrangement of packing should be estimated with the basis of the free energy. It is, however, very difficult task to calculate entropic quantities with any reasonable accuracy within a finite simulation time. The lowest energy state of the system from the present simulation may be still metastable and not the true equilibrium state. Therefore, we still need to carry out further MD simulations. Further theoretical studies to explain the origin of the polar-ordering association of molecules are in progress.

Acknowledgment

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