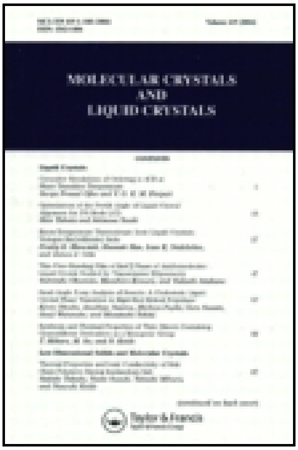

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Parameterization of the Gay-Berne Potential for *n*CB and Molecular Dynamics Simulation of 5CB

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We have determined sets of coarse-grained potentials for *n*CB (4-n-alkyl-4′-cyanobiphenyl) starting from the united atom pair potential of the OPLS force field. As a coarse-grained model, we employed a hybrid Gay-Berne/Lennard-Jones model consisting of a rigid core and a chain of spheres. Using the coarse-grained potentials, we have carried out MD simulations of 5CB to examine the parameter dependency of the structure, the density of the ordered state and the transition temperature. We found that if the length of the rigid core is kept constant, the isotropic phase becomes favored with increasing the aspect ratio of the core. This can be explained as the effect of the thickness of the tail part.

Keywords: Gay-Berne potentual; 5CB; molecular dynamics

INTRODUCTION

Most of mesogens used in real applications possess at least one flexible tail bonded to a rigid non-spherical core and the tail plays an important role in determining their phase behaviors. *n*CB (4-n-alkyl-4'-cyanobiphenyl) is an example of this type of mesogens and has been widely studied experimentally. *n*CB molecules show two liquid crystalline phases depending on their chain length; nematic phase for n between 5 and 9 and smectic A phase for n between 8 and 12[1]. The temperature ranges in which the liquid crystalline phases are stable also change with the length of the tail. The mechanism of this dependence, however, has not been fully understood yet.

Computer simulation is a useful tool for understanding the phase behavior of mesogens. However, systematic studies for *n*CB series have not been carried out, though some pinpoint studies on the nematic phase of 5CB[2] and the smectic phase of 8CB[3] based on molecular dynamics (MD) simulation with the atom-atom pair potential have been reported. The reason is that the simulations with the atomistic potential take huge CPU resources. Alternatively, a hybrid Gay-Berne(GB)/Lennard-Jones(LJ) model was used to save computer time over the atomistic model, but the potential parameters used in the simulations have not been fully optimized for real molecules[4,5]. The purpose of this study is to examine the dependence of the phase behavior on the parameters of the coarse-grained potential, and to analyze the effect of the tail.

PARAMETERIZATION OF THE GAY-BERNE POTENTIAL

We employed a hybrid GB/LJ model as a coarse-grained model. In our model an nCB molecule was divided into a rigid part represented by an ellipsoid (4-methyl-4'-cyanobiphenyl moiety; CB), and a flexible part represented by a chain of spherical united atoms (UA's). In order to approximate the CB part as an ellipsoid, the CB–CB and CB–UA pair potentials, U_{av}, was obtained by averaging the OPLS potential[6,7], U_{LJ}, over the rotation angle α of CB around the principal axis of the ellipsoid,

$$U_{av}(\hat{\boldsymbol{u}}_i, \hat{\boldsymbol{u}}_j, \boldsymbol{r}_{ij}, T_{eff}) = \frac{\int_0^{2\pi}\int_0^{2\pi} U_{LJ}\exp(-U_{LJ}/k_B T_{eff})d\alpha_i d\alpha_j}{\int_0^{2\pi}\int_0^{2\pi}\exp(-U_{LJ}/k_B T_{eff})d\alpha_i d\alpha_j}, \qquad (1)$$

where $\hat{\boldsymbol{u}}_i$ is the unit vector along the principal axis of the i'th CB part and $\boldsymbol{r}_{ij}$ is the vector linking the center of mass of the i'th and j'th CB parts, and T_{eff} is an effective temperature which will be discussed later.

The resulting CB–CB and CB–UA potentials were fitted by the following generalized Gay-Berne potential form[8] which has been proposed as a model potential between two ellipsoids and that between an ellipsoid and a sphere.

$$U(\hat{\boldsymbol{u}}_i, \hat{\boldsymbol{u}}_j, \boldsymbol{r}_{ij}) = 4\epsilon_0\left[1 - \chi^2(\hat{\boldsymbol{u}}_i \cdot \hat{\boldsymbol{u}}_j)^2\right]^{-\nu/2}\epsilon'(\hat{\boldsymbol{u}}_i, \hat{\boldsymbol{u}}_j, \hat{\boldsymbol{r}}_{ij})^{\mu}$$
$$\left[\left(\frac{\sigma_0}{r_{ij} - \sigma(\hat{\boldsymbol{u}}_i, \hat{\boldsymbol{u}}_j, \hat{\boldsymbol{r}}_{ij}) + \sigma_0}\right)^{12} - \left(\frac{\sigma_0}{r_{ij} - \sigma(\hat{\boldsymbol{u}}_i, \hat{\boldsymbol{u}}_j, \hat{\boldsymbol{r}}_{ij}) + \sigma_0}\right)^{6}\right], \qquad (2)$$

$$\sigma(\hat{\boldsymbol{u}}_i, \hat{\boldsymbol{u}}_j, \hat{\boldsymbol{r}}_{ij}) = \sigma_0\left[1 - \frac{\chi}{2}\left\{\frac{(\alpha(\hat{\boldsymbol{r}}_{ij} \cdot \hat{\boldsymbol{u}}_i) + \alpha^{-1}(\hat{\boldsymbol{r}}_{ij} \cdot \hat{\boldsymbol{u}}_j))^2}{1 + \chi(\hat{\boldsymbol{u}}_i \cdot \hat{\boldsymbol{u}}_j)}\right.\right.$$
$$\left.\left.+\frac{(\alpha(\hat{\boldsymbol{r}}_{ij} \cdot \hat{\boldsymbol{u}}_i) - \alpha^{-1}(\hat{\boldsymbol{r}}_{ij} \cdot \hat{\boldsymbol{u}}_j))^2}{1 - \chi(\hat{\boldsymbol{u}}_i \cdot \hat{\boldsymbol{u}}_j)}\right\}\right]^{-1/2}, \qquad (3)$$

$$\epsilon'(\hat{\boldsymbol{u}}_i, \hat{\boldsymbol{u}}_j, \hat{\boldsymbol{r}}_{ij}) = 1 - \frac{\chi'}{2}\left\{\frac{(\alpha'(\hat{\boldsymbol{r}}_{ij}\cdot\hat{\boldsymbol{u}}_i) + \alpha'^{-1}(\hat{\boldsymbol{r}}_{ij}\cdot\hat{\boldsymbol{u}}_j))^2}{1+\chi'(\hat{\boldsymbol{u}}_i\cdot\hat{\boldsymbol{u}}_j)} + \frac{(\alpha'(\hat{\boldsymbol{r}}_{ij}\cdot\hat{\boldsymbol{u}}_i) - \alpha'^{-1}(\hat{\boldsymbol{r}}_{ij}\cdot\hat{\boldsymbol{u}}_j))^2}{1-\chi'(\hat{\boldsymbol{u}}_i\cdot\hat{\boldsymbol{u}}_j)}\right\}, \tag{4}$$

$$\chi = \left(\frac{(l_i^2 - d_i^2)(l_j^2 - d_j^2)}{(l_j^2 + d_i^2)(l_i^2 + d_j^2)}\right)^{1/2}, \tag{5}$$

$$\alpha = \left(\frac{(l_i^2 - d_i^2)(l_j^2 + d_i^2)}{(l_j^2 - d_j^2)(l_i^2 + d_j^2)}\right)^{1/2}, \tag{6}$$

where l and d represent the length and breadth of the ellipsoid, respectively. For the interaction between two ellipsoids, $\chi = [\kappa^2 - 1]/[\kappa^2 + 1]$, $\alpha = 1$, $\chi' = [\kappa'^{1/\mu} - 1]/[\kappa'^{1/\mu} + 1]$ and $\alpha' = 1$, if $\kappa = l/d$ and $\kappa' = \epsilon_s/\epsilon_e$. Here ϵ_s and ϵ_e stand for the potential depths for the side-by-side and end-to-end configurations, respectively. For the ellipsoid–sphere interaction, $\chi\alpha^{-2} = 1 - \kappa^{-2}$ and $\chi'\alpha'^{-2} = 1 - \kappa'^{1/\mu}$, if $\kappa = l/d$ and $\kappa' = \epsilon_s/\epsilon_e$. Here ϵ_s and ϵ_e mean the potential depths for the side and end configurations, respectively. The parameters for the CB–CB and CB–UA pairs were determined by directly comparing the Gay-Berne potential with the averaged potentials at specific configurations such as the side-by-side and end-to-end ones[9]. The UA–UA potential was assumed to be the same as the original OPLS potential.

Figure 1(a) shows the averaged OPLS potentials for the side-by-side configuration of the CB–CB pair obtained with several T_{eff}. The three local minima correspond to the π–π, π–CH and CH–CH stackings. The similar local minima were also recognized for the cross configuration. If the actual simulation temperature T (e.g. 300K) is used for T_{eff}, the dominant configuration is the π–π stacking of the

CB–CB pair. However most CB–CB pairs in the condensed state can not take the most stable configurations, because a CB molecule is surrounded by many other CB molecules. Even in the crystal structure of 1CB, the π–π and π–CH configurations coexist. Thus the temperature T_{eff} can not be taken to be the actual temperature[10]. Moreover, the averaged OPLS potentials have complicated forms and it is not possible to reproduce them completely by the Gay-Berne potential. Due to these difficulties, it is not feasible to determine the best set of GB parameters for CB–CB interaction by the averaging process alone. Therefore we have used four different sets of GB parameters to study the effect of the parameters on the phase behavior. The four sets of parameters for CB-CB interaction are listed in Table 1 (CB–CB-1 through CB–CB-4), and the potential curves for the side-by-side configurations are shown in Figure 1(b). For the CB–CH_2 and CB–CH_3 interactions, only single set of parameters was used.

TABLE 1 : Gay-Berne potential parameters for the CB–CB and CB–UA pairs.

Name	$d=\sigma_0$	l	ϵ_0	ϵ_s	ϵ_e	μ	ν
CB–CB-1	3.607	14.551	2.488	3.347	0.385	0.574	0.389
CB–CB-2	4.455	14.551	2.488	3.347	0.385	0.498	0.511
CB–CB-3	4.811	14.551	2.488	3.347	0.385	0.498	0.573
CB–CB-4	4.283	14.551	2.488	3.068	0.385	0.420	0.342
CB–CH_2	4.510	9.759	0.542	0.542	0.217	0.375	–
CB–CH_3	4.510	9.759	0.660	0.660	0.264	0.373	–

length in Åunit and energy in *kcal/mol* unit.

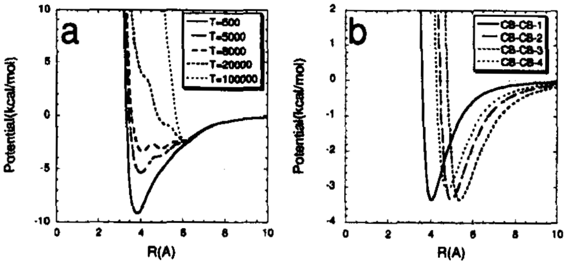

FIGURE 1 : (a) The averaged OPLS potentials for the side-by-side configuration of the CB–CB pair and (b) the Gay-Berne potential used in the simulations (CB–CB-1 through CB–CB-4).

MD SIMULATIONS

We have carried out molecular dynamics simulations for 5CB consisting of 256 molecules in a cubic cell. In the simulations, the NPT ensemble by the loose-coupling algorithm was employed. The potential energy was calculated as a sum of harmonic angle, OPLS torsion, Gay-Berne (for CB–CB and CB–UA pairs) and Lennard-Jones (for UA–UA pair) terms. All bond lengths were fixed by the rattle algorithm. The equations of motion were integrated by using the velocity Verlet algorithm with a time step of 5fs. The simulations were carried out for several tens of nanosecond to get equilibrium state.

For all the four potentials the simulations show sharp transition from the isotropic to an ordered phase. The ordered phase has a layer structure as smectic A phase; no nematic phase has been observed. The density ρ and the second rank order parameter P_2 just below and above the transition temperature are shown in Table 2. The layer spacing d in the ordered phase is also shown in the Table. In the case of three potentials CB–CB-1, 2 and 3, the ellipsoid representing the CB part has the same length but different thickness. Table 2 shows that the molecule with the lowest aspect ratio κ (CB–CB-3) has the highest transition temperature. Thus the isotropic phase is favored by increasing the anisotropy of the CB part. This rather surprising result can be understood as the effect of the tail. If the CB part becomes too thin compared with the breadth of the tail part (including its fluctuation), the ordered phase becomes unfavored. Note that the layer spacing increases as the thickness of the CB part decreases.

TABLE 2 : Physical properties just above (T(I)) and below (T(O)) the transition.

Potential	T(I) K	ρ(I) g/cm^3	P_2(I)	T(O) K	ρ(O) g/cm^3	P_2(O)	d /Å
CB–CB-1	395	0.96	0.10	390	1.15	0.88	20.2
CB–CB-2	400	0.95	0.10	395	0.91	0.83	18.7
CB–CB-3	415	0.74	0.08	410	0.84	0.90	17.3
CB–CB-4	335	0.90	0.08	330	0.99	0.81	18.4

The potential CB–CB-4 is similar to CB–CB-2 but has shallower minimum for the side-by-side configurations. The transition temperature was reduced, but the nematic phase was still not observed. Further reduction of the potential depth would be required to obtain the nematic phase.

CONCLUSION

We have studied the dependence of the phase behavior of 5CB on the Gay-Berne potential parameters. If the length of the ellipsoid is kept constant, the isotropic phase becomes favored with increasing the aspect ratio of the ellipsoid due to the finite thickness of the tail part.

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