Effects of polymer surface structures on liquid crystal alignment studied with molecular dynamics simulations

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Effects of polymer surface structures on liquid crystal alignment studied with molecular dynamics simulations

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Effects of polymer surface structures on surface alignment of liquid crystal molecules were studied by comparison with our previous results of molecular dynamics simulations. An adsorption-related liquid crystal molecule alignment on the packed polyimide surface was found in the simulation study. In this article, we first compared the alignment on a sparse polyimide surface with the previous results of the packed polyimide surface to see effects of polymer surface density. The excluded volume effect with the polyimide domain edges additionally contributed to alignment of the liquid crystal molecules on the sparse surface, and resulted in a similar alignment structure (i.e. alignment direction and tilt angle) to the packed cases. Secondly, we made similar simulations by changing the polymer from a polyimide to a polyamide with similar polymer chain density. Differences between the corresponding packed polyimide case were found mainly in the energetics (the polyamide had about two thirds of the adsorption energy of the liquid crystal molecule as the polyimide did). The alignment structures were not so different.

1. Introduction

Uniaxial alignment of liquid crystal (LC) molecules on substrate surfaces over a several inch diagonal area is indispensable for operation of liquid crystal displays (LCDs). Rubbed polymer layers coated on the substrate surface serve to provide such an alignment for virtually all of today's LCDs. The rubbing surface treatment effectively produces the uniaxial alignment in the rubbing direction with a few degrees tilt of the LC molecules from the surface. Despite the relative simplicity of this aligning technique, its complex mechanisms are not fully understood. It was thought that, micro-grooves which might be generated during the rubbing process, were the main cause of LC molecule alignment [1]. However, recent studies [2, 3] support a hypothesis that the polymer chains near the rubbed surface are re-oriented in the rubbing directions and then these aligned chains serve as an anisotropic template for LC alignment [4]. Actually good LC alignment without rubbing has been reported with Langmuir–Blodgett (LB) films in which polymer chains were well oriented by lifting the substrate in the LB film formation process [5]. However the general mechanisms, especially about producing the tilt out from surface of the LC molecules, are still being

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actively discussed. Except for a topological alignment (i.e. alignment by the grooves), all alignment mechanisms are basically governed by precise intermolecular interactions between the substrate surface and LC molecules. Consequently, a molecular simulation approach to elucidate the alignment mechanisms is considered to be effective since intermolecular interactions are more easily analysed in molecular simulations than actual experiments.

In a previous article [6], we reported results from molecular dynamics simulations of the LC molecule alignment on a polyimide monolayer using an oligomer as a polymer model. By placing an LC monolayer on the polyimide monolayer (whose structure was obtained in prestage simulations), we simulated a three-layer system, i.e. LC monolayer/polyimide monolayer/basal plane of graphite. The interface of the liquid crystal/ polyimide monolayer can be considered as a simplified model for the actual interface in an LCD. In the prestage simulations with only a polyimide monolayer on the graphite surface, we considered the polyimide adsorption structure to be a well-aligned one since polyimide chains are thought to be aligned at the actual LCD aligning layer due to the rubbing [3]. This meant that only the chain re-orientation aspect of the rubbing process was taken into account and the rubbed polymer surface was modelled as a well-aligned one. In this respect, the

interface model more directly corresponded to LC alignment with Langmuir–Blodgett films which were mentioned above. From our simulation results of the packed polyimide surface, the most probable alignment of LC molecules, 4-n-octyl-4'-cyanobiphenyl (8CB), on the polyimide, pyromelltic dianhydride-p-phenylene diamine (PMDA-PPD), monolayer was roughly along the chain direction with almost zero tilt to the monolayer. The results corresponded reasonably to experimental results on the LC alignment by PMDA-PPD Langmuir–Blodgett films [5]. We concluded from a precise analysis of the intermolecular interactions at the interface that the main origin of this alignment was the adsorption of 8CB molecules onto the PMDA-PPD chains with the carbonyl groups of the PMDA-PPD acting as the main adsorption sites.

In this article, we analyse the effect of the polymer surface structure on the alignment of LC molecules using similar interface models as above. First, we change the polymer surface density for the middle polyimide monolayer in the three-layer system. Secondly, we change the polymer chemical structure from a polyimide to a polyamide with similar polymer chain density. Polyamide is rarely used as an alignment polymer in actual LCDs, but has good alignment properties with the rubbing treatment [7]. In both altered systems, the simulated results are compared with the original system in the previous study to see the effects of the alteration of the surface structures.

2. Method

2.1. Simulation model

As in the previous papers [6, 8], polyimide and polyamide oligomers were used as models for the corresponding polymers and only one surface graphite layer was considered to save computational time. The simulated
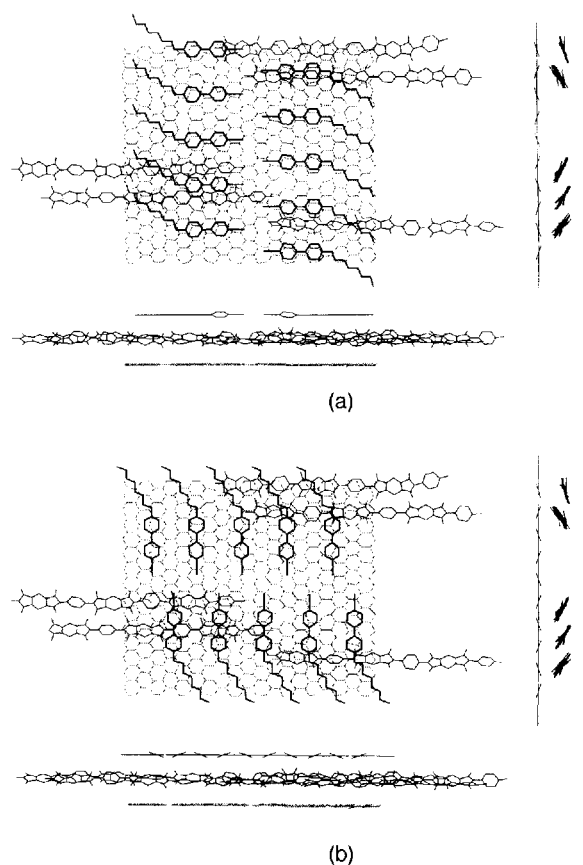

(a)

(b)

Figure 2.　Initial structures for the sparse polyimide surface.

LC molecule, polyimide and polyamide oligomer were 4-n-octyl-4'-cyanobiphenyl (8CB), three repeating units of pyromelltic dianhydride-p-phenylene diamine (PMDA-PPD) and four repeating units of ε-caprolactam, respectively.
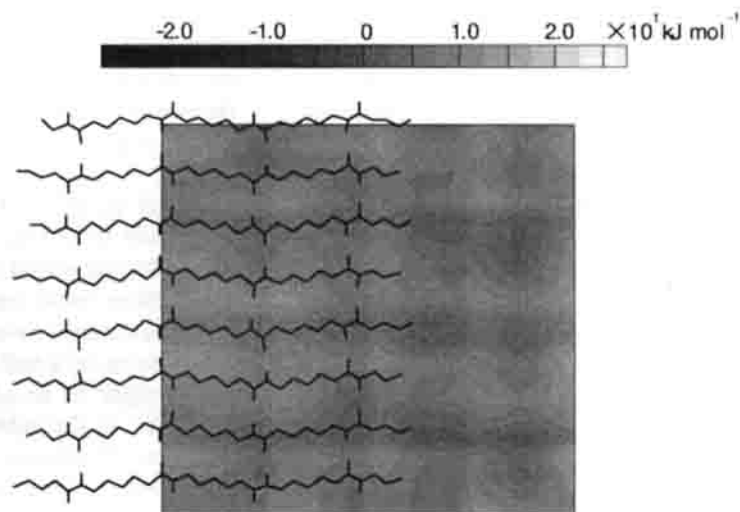

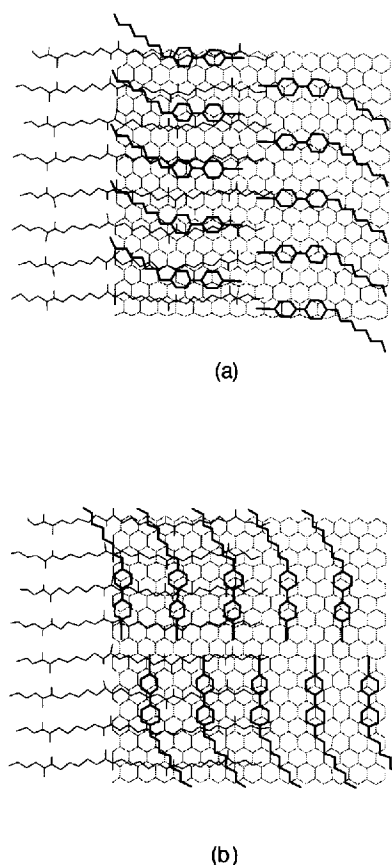Figure 1.　Electrostatic potentials over the polyamide monolayer.

(a)

(b)

Figure 3. Initial structures for the packed polyamide surface.

(a)

(b)

Figure 4. Averaged structures on the sparse polyimide surface.

The following GROMOS force field [9] was used for inter- and intramolecular interaction potentials.

$$
U_{total} = \sum_{atomic\ pairs} \left(\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right)
$$

$$
+ \sum_{bonds} \frac{k_d}{2}(d - d_0)^2 + \sum_{angles} \frac{k_\theta}{2}(\theta - \theta_0)^2
$$

$$
+ \sum_{imp.dih.s} \frac{k_\psi}{2}(\psi - \psi_0)^2 \tag{1}
$$

$$
+ \sum_{dihedrals} k_\phi (1 + \cos(n\phi - \delta)).
$$

The first term represents the non-bonding interaction due to the Lennard–Jones and Coulomb potentials. The remaining terms correspond to bond stretching, bond angle bending, and improper (out of plane) and proper dihedral angle torsioning potentials, respectively. All the molecular models were detailed atomic models, except for the CH_2 and CH_3 groups, which were regarded as united atoms. The ends of the oligomer chains were terminated by united CH_3 atoms. Only hydrogen atoms bonded to nitrogen atoms (which occur in the polyamide oligomer here) were explicitly considered to account for
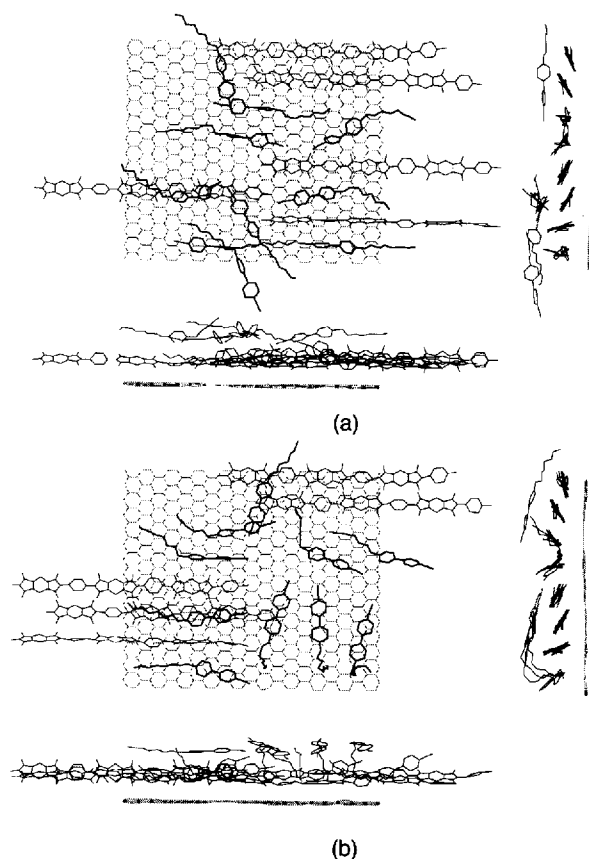
hydrogen bonding. In the GROMOS force field, the hydrogen bonding interaction is treated as a simple Coulomb interaction. Basically, force field parameters were taken from GROMOS force field parameters. The parameters specific to 8CB and the partial atomic charge distribution of the 8CB molecules were taken from those of Picken *et al.* [10]. The parameter values specific to the oligomers and atomic charges were set to the same as in the previous papers and listed in the appendices of the papers. The (spherical) cut-off length of the non-bonding interactions was set to 1·8 nm.

The graphite surface model we used was also the same as in the previous papers, i.e. the flexible graphite model. The basal plane of the graphite was located on the *x*–*y* plane, and we applied a two-dimensional periodic boundary condition (to the whole system) in this plane to avoid unfavourable edge effects. The actual size of the periodically repeated section of the graphite plane was 4·26 × 3·69 nm for the system with polyimide, and 3·94 × 3·83 nm for the system with polyamide.

2.2. Simulation procedures

We set up the three-layered system by adding a LC layer onto the oligomer layers (with about a 0·4 nm layer
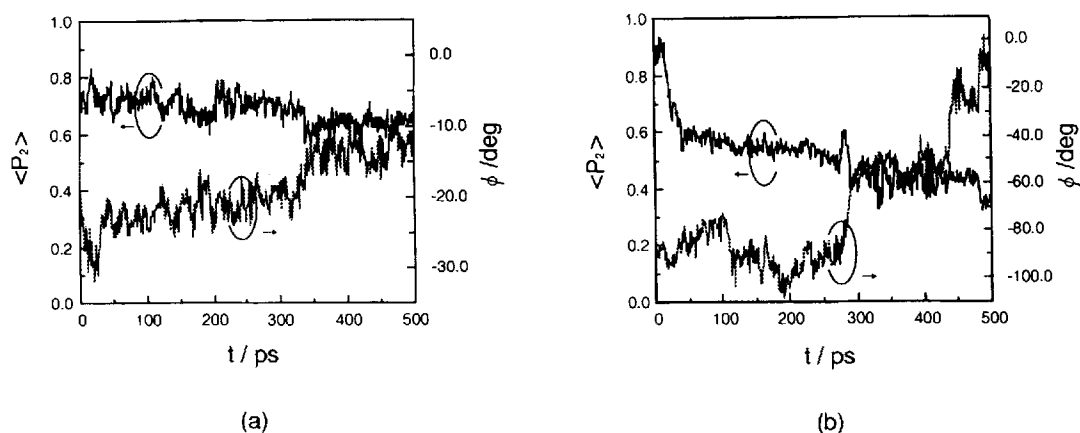
(a)   (b)

Figure 5.   Time evolutions of the order parameter and director direction (sparse case).

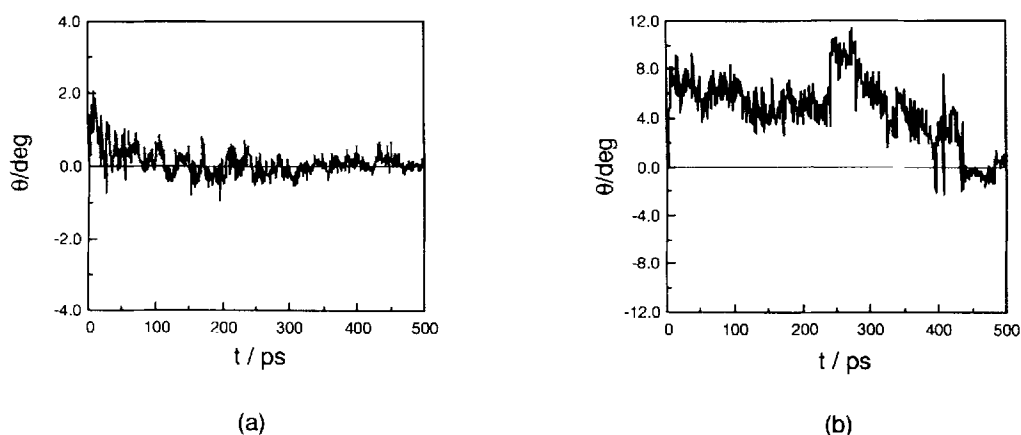(a)   (b)

Figure 6.   Time evolutions of the director tilt angles (sparse case).

spacing) which were obtained in the previous papers [6, 8]. Regarding the polyimide, the sparse (low density) surface structure was used to compare the results for the packed (high density) one in the previous paper [6]. The latter packed structure was characterized by strong dipole coupling between carbonyl groups of the polyimide oligomer. As a result of this coupling, net dipole moments of these carbonyl group would not be pronounced above this polyimide layer. On the other hand, relatively large electrostatic potentials in comparison to the packed surface, were found in the calculated electrostatic potentials over the sparse polyimide monolayer (see figure 16(a) of reference [6]) and they were mainly at the edge of the polyimide oligomer which had no adjacent oligomer to cause dipole coupling. These results suggested the edge regions of the well-aligned oligomer domain play an important role in LC alignment due to their strong electronic potentials.

For the case of polyamide, the surface structure utilized was structure C in the simulation of polyamide

oligomers on graphite [8]. This surface structure corresponds to the packed polyimide surface in chain density. The electrostatic potential over the polyamide monolayer which was calculated in the same manner as in the previous paper [6] is shown in figure 1. The potentials are less than one tenth of that for the corresponding packed polyimide one. This implies a very weak contribution from the Coulomb interactions for the adsorption of 8CB molecules on the polyamide monolayer.

The initial structure of the LC layer on the polyimide layers was the same as that in the simulation of 8CB on graphite by Yoneya and Iwakabe [11]. This LC monolayer consisted of ten 8CB molecules with an adjacent separation of 7·4 nm. We also tried two initial structure settings which differed in the relative orientation of the LC molecule and the polyimide oligomer chain direction, one with the 8CB biphenyl axes oriented in the oligomer chain direction and the other with the axes perpendicular to the chain direction, hereinafter designated as parallel and perpendicular (initial) settings, respectively. Initial
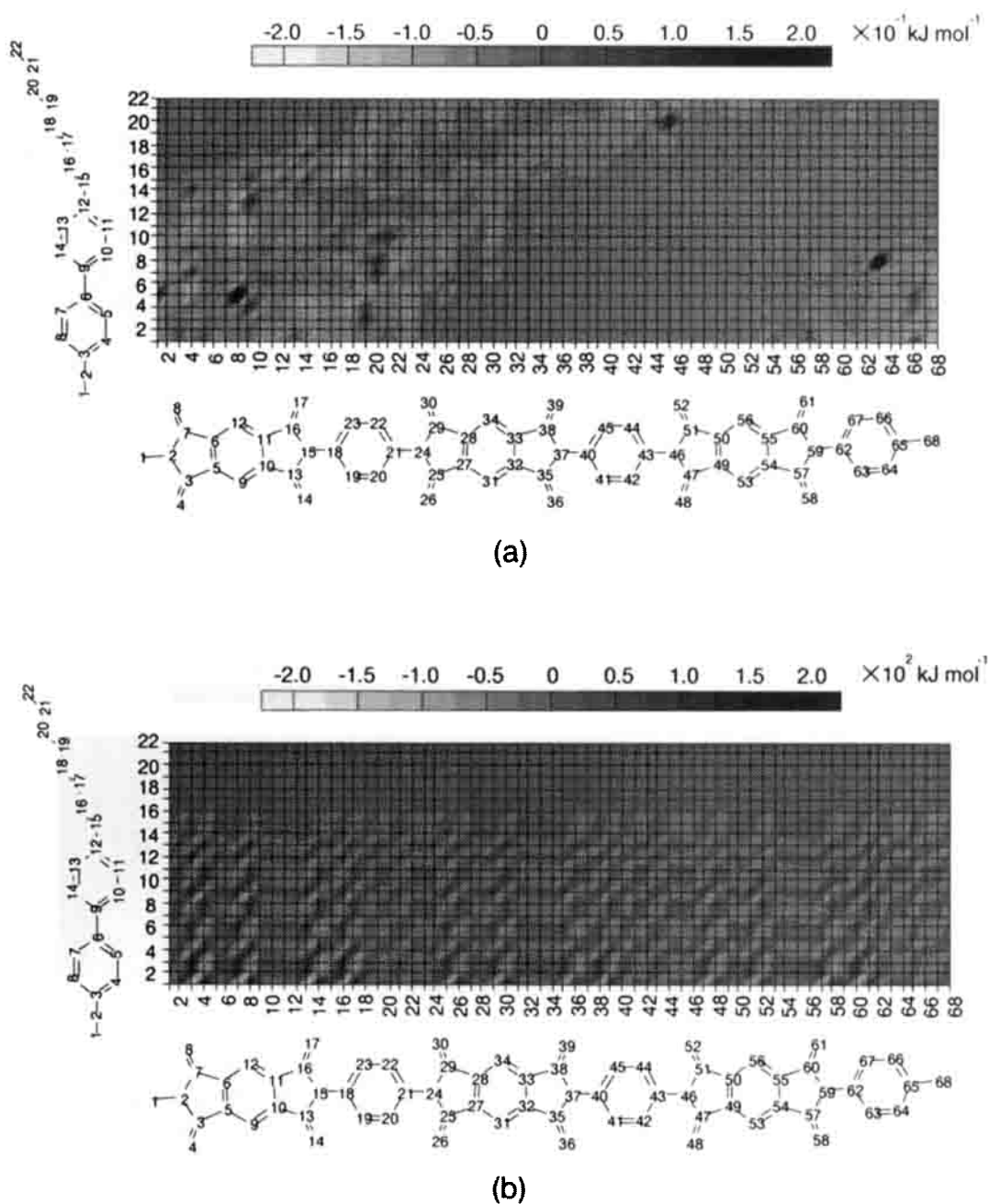
(a)

(b)

Figure 7. Atomwise interactions (parallel setting).

structures for the sparse polyimide and packed poly-amide cases are shown in figures 2 and 3, respectively.

Starting from these structures, and after the same initial minimization and relaxation dynamics as in the previous paper [6], we did production runs up to 500 ps (corresponding to 10^6 simulation steps) with a time-integration step of 0·5 fs. The temperature of the system was maintained around 300 K by using weak coupling to a heat bath [12] as in the previous papers.

3. Results

3.1. *The sparse polyimide surface*

We show the averaged (in the last 10 ps) structures after 500 ps MD runs for the sparse surface, starting from the parallel and perpendicular initial settings, in figures 4 (a) and (b), respectively. The order parameter and corresponding director direction of 8CB molecules were calculated by following the method described by Zannoni [13] as in the previous paper (i.e. calculate the largest
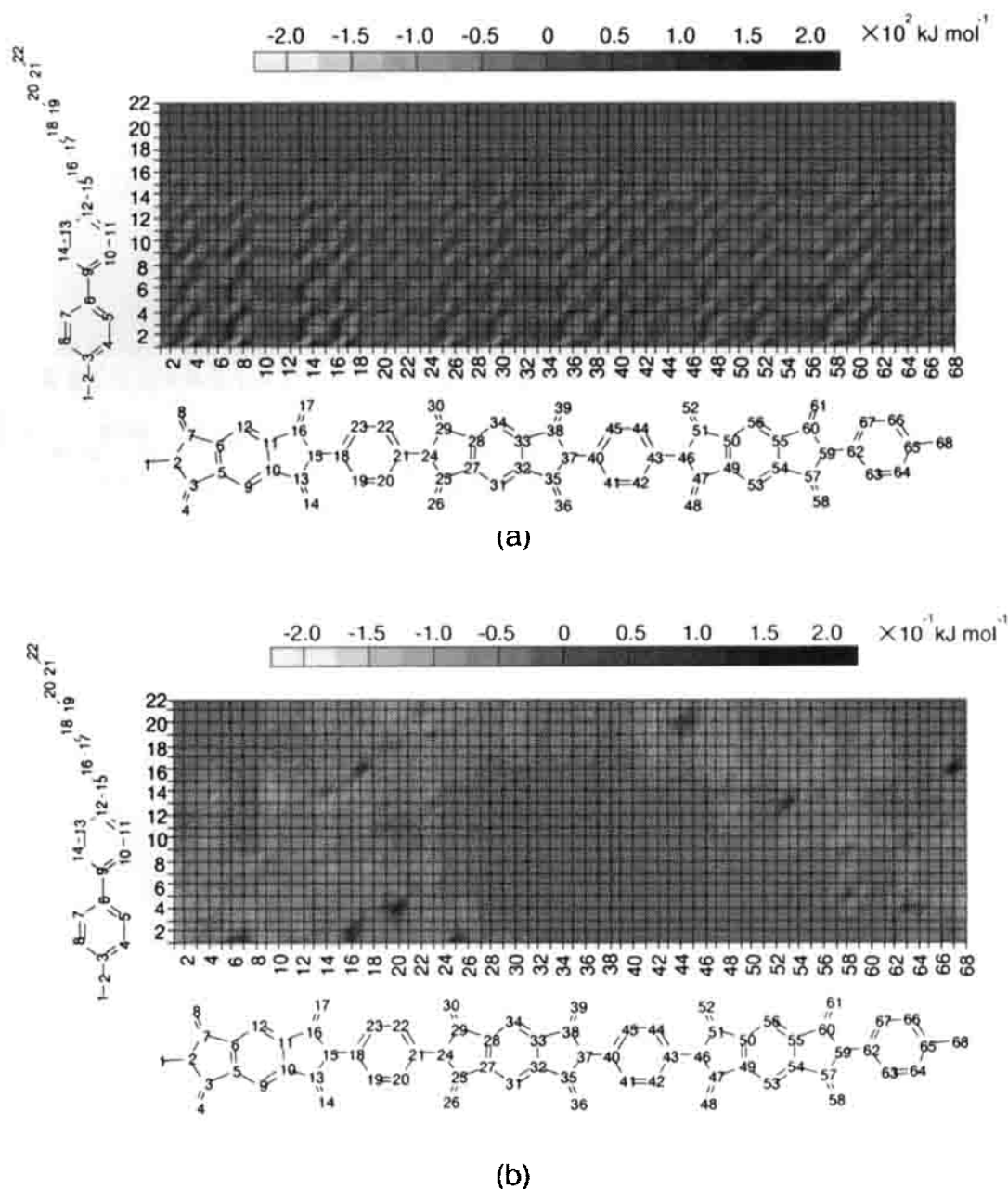
Figure 8.   Atomwise interactions (perpendicular setting).

positive eigenvalue and eigenvector of the order para-meter tensor which is made up of molecular long axis vectors that were determined by the principal axis of inertia of the molecules). The time evolutions of the order parameter $\langle P_2 \rangle$ and director angle ϕ in the x–y plane (measured from the chain direction) are shown in figures 5 (a) and (b) for runs from the parallel and perpendicular initial settings, respectively. Corresponding director tilt angles θ from the x–y plane are shown in figure 6. From these figures, we concluded the 8CB molecules on this sparse polyimide surface were aligned with lower order-parameters (around 0·6 for the parallel initial setting and less than 0·4 for the perpendicular setting) than those on the packed polyimide surface cases (around 0·8 and 0·7, respectively). As for the director tilt angle, it was almost zero in the run from the parallel initial setting, whereas the run from the perpendicular initial setting possibly yielded tilt angles values. The latter run, however, might not be well-equilibrated yet and longer behaviour should be looked at.
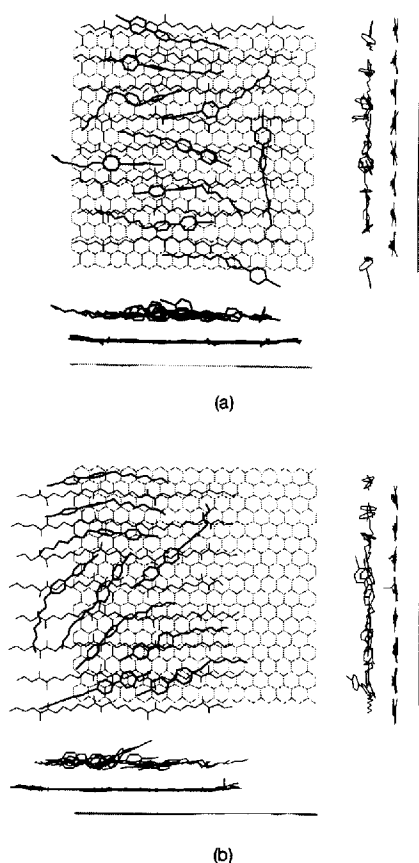
Figure 9. Averaged structures on the packed polyamide surface.

(a)

(b)

Figure 10. Time evolutions of the order parameter and director direction (packed case).

On looking closely at figure 4, we could recognize three different patterns for LC molecule alignments. The first pattern had an alignment roughly along the polyimide chain direction on the polyimide chain domains. The second one was also along the polyimide chain, but in between the chain domains (i.e. the parts where the graphite surface were bare). The last alignment was in a direction almost perpendicular to the polyimide chains. In these alignment patterns, the first one would be similar to the alignment on the packed polyimide surface in the previous paper [6], i.e. the adsorption origin alignment. The second alignment pattern originated in the excluded volume effect (repulsive force) by the domain edges of polyimide chains. One possible origin for the last alignment pattern would be the dipolic interaction between the cyano group of 8CB and the carbonyl group of the polyimide. This was deduced from the clear association of these dipole directions, especially in the three 8CB molecules in the lower right part of figure 4(b), which causes tilting of 8CB molecules. Moreover, most of the cyano groups are placed at the polyimide chain edge regions where the electrostatic potentials are much larger than the other regions.
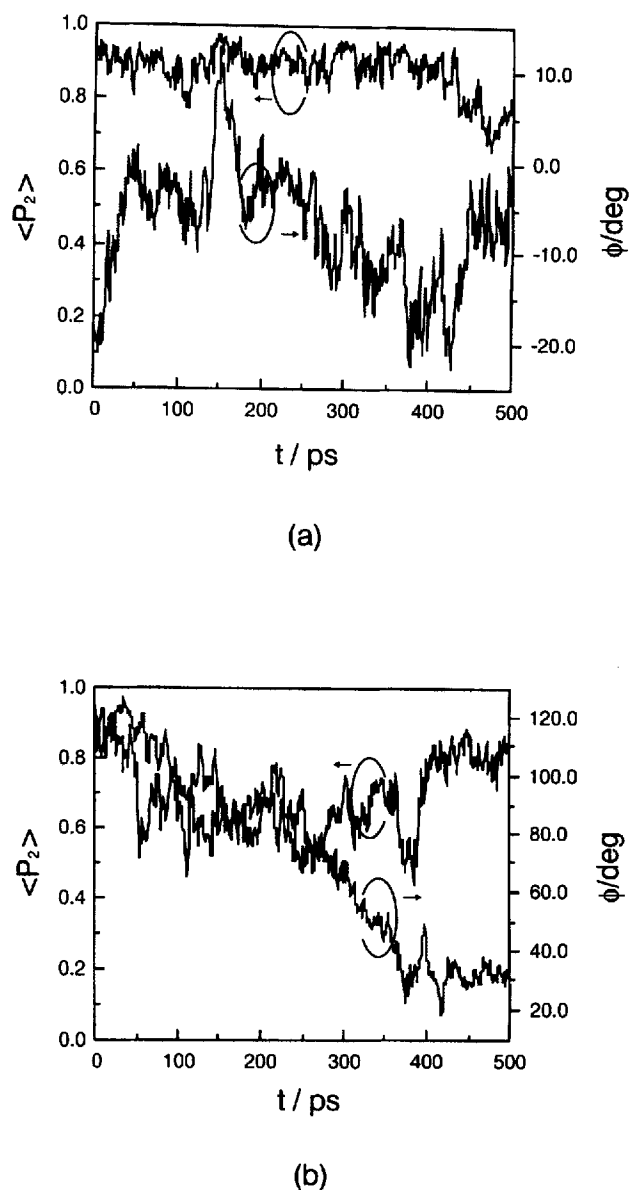
Regarding energetics, we estimated adsorption energies of the 8CB molecule onto the sparse polyimide monolayer were 138 and 128 kJ mol^{-1} for the parallel and perpendicular initial settings, respectively. These were a bit larger than the corresponding values for the packed polyimide results (128 and 126 kJ mol^{-1}, respectively). Averaged atomwise interaction energies between the atoms in 8CB and oligomer are shown in figures 7 and 8, corresponding to the structures in figures 4(a) and (b), respectively. These interaction patterns differed greatly from the ones for the packed case, especially in the Lennard–Jones contributions, i.e. clear adsorption sites at the carbonyl groups in the previous packed
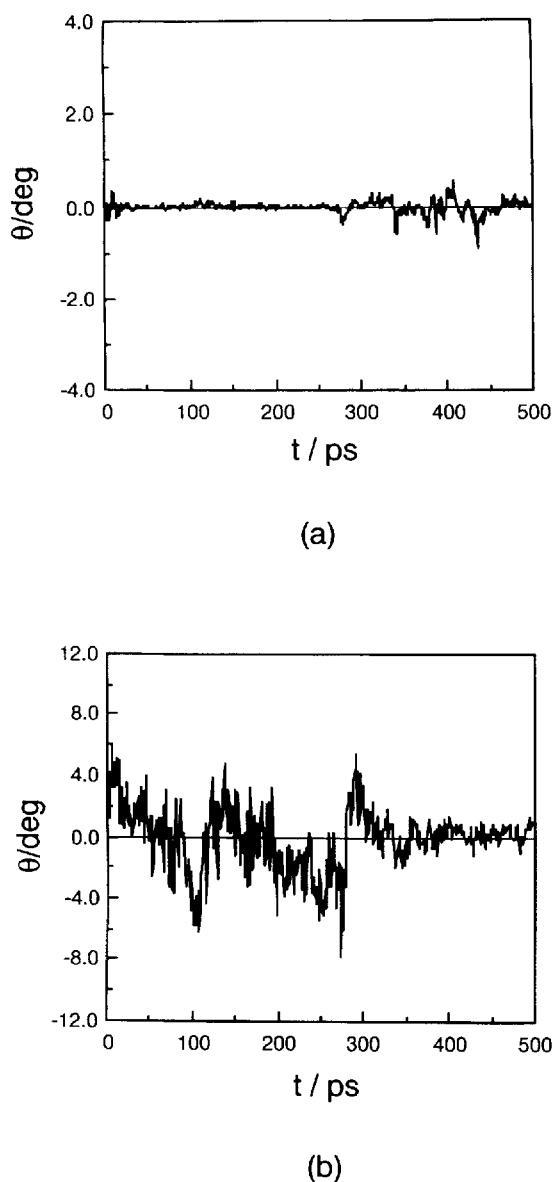
(a)

(b)

Figure 11.   Time evolutions of the director tilt angles (packed case).

polyimide surface cases had almost disappeared and the adsorption sites themselves were weakened or had become strong repulsive sites (dark spots in the figures). These changes would correspond to the second alignment pattern described above, i.e. the repulsive origin contribution by the chain domain edges. The overall contribution of Coulomb interaction to the Lennard–Jones interaction had the ratios of 0·8 and 0·5 for the resultant structures from the parallel and perpendicular initial settings, respectively, and these were larger than for the packed polyimide surface case (0·2 and 0·3). This meant that cancellation of the net dipole moments of

the carbonyl group was incomplete for the sparse polyimide surface cases as compared to the packed ones.

3.2.   The packed polyamide surface

We made similar MD runs for the packed polyamide surface case. In figures 9 (a) and (b), we show the averaged (in the last 10 ps) structures after 500 ps MD runs, starting from the parallel and perpendicular initial settings, respectively. The time evolutions of the order parameter $\langle P_2 \rangle$ and director direction angle ϕ in the x–y plane are shown in figure 10. Their corresponding director tilt angles θ from the x–y plane are shown in figure 11. From these figures, we noted the 8CB molecules kept their alignment roughly along the oligomer chain direction with an order parameter of more than 0·8 (see figure 10(a)) in the simulation from the parallel initial setting. Whereas the 8CB molecules changed their direction from roughly perpendicular to 30° to the chain direction and the order parameter decreased until it was less than 0·5 (see figure 10(b)) and then recovered to around 0·8 in the run from the perpendicular initial setting. Although behaviour over a longer time should be examined, the latter could be considered to show that the 8CB molecules were aligning with the polyamide chains. The director tilt angles (see figures 11 (a) and (b)) in both were about zero on average, but the fluctuation amplitude was very different between the two runs same as in the corresponding packed polyimide simulations [6].

Regarding energetics, estimated adsorption energies of the 8CB molecule onto the packed polyamide monolayer were 77 and 90 kJ mol^{-1} for the parallel and perpendicular initial settings, respectively. These values were about two thirds of the corresponding results for the packed polyamide monolayer. Averaged atomwise interaction energies between the atoms in 8CB and oligomer are shown in figures 12 and 13, corresponding to the structures in figures 9 (a) and (b), respectively. In both cases, the alkyl chain parts of the polyamide were considered to be the main Lennard–Jones adsorption sites for the 8CB molecules. The overall contribution of the Coulomb interaction to the Lennard–Jones interaction between them was considerably smaller (1/20–1/30) than for the packed polyimide surface case with the ratios of 0·01 and 0·009 for the resultant structures from the parallel and perpendicular initial settings, respectively. This directly corresponded to the greater weakness of the electrostatic potentials over the polyamide monolayer than over the polyimide monolayer as in figure 1.

4.   Discussion

In our previous results [6], the most probable alignment of the 8CB molecules on the packed polyimide
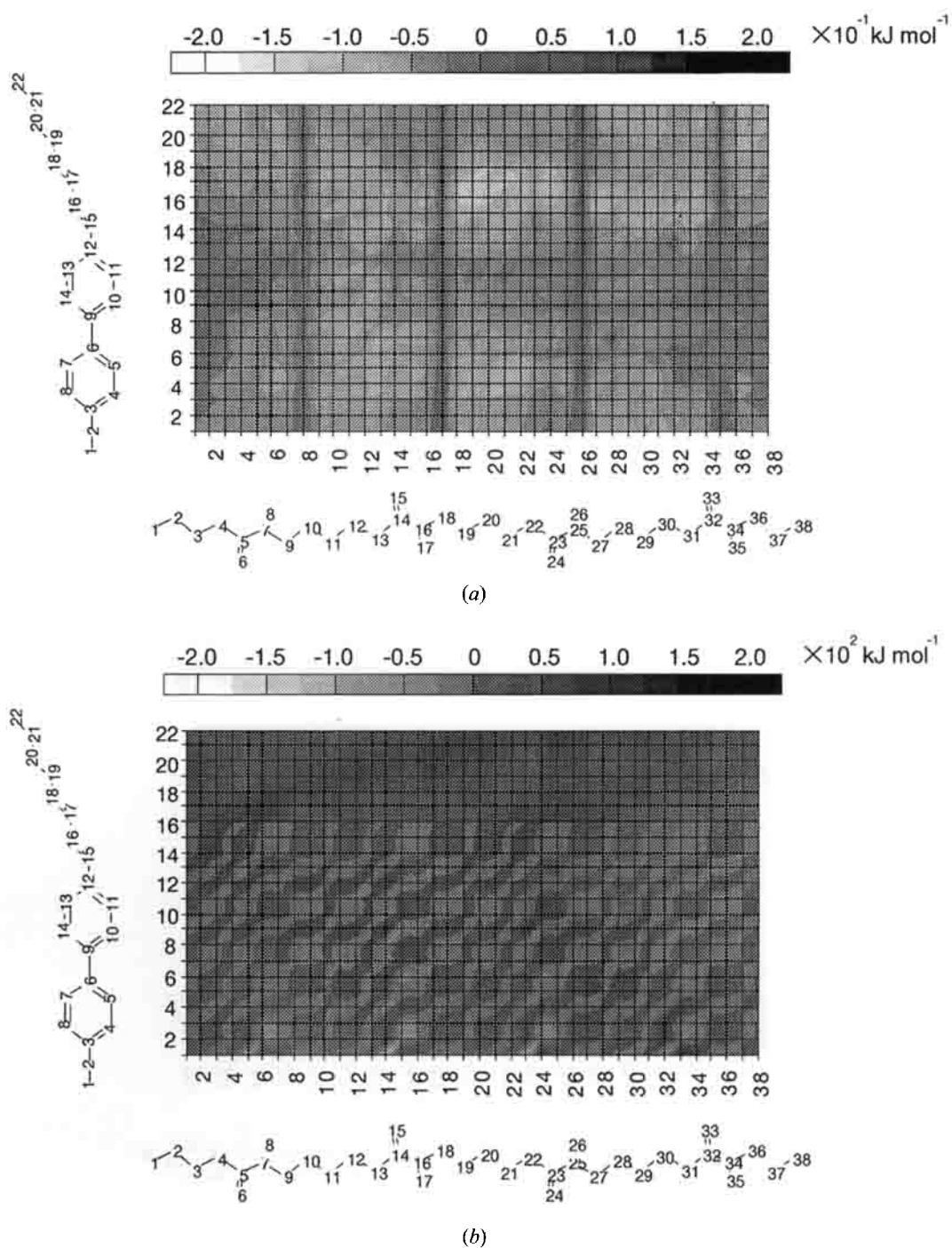
(a)

(b)

Figure 12. Atomwise interactions (parallel setting).

(PMDA–PPD) monolayer was roughly along the PMDA–PPD chain direction with almost zero tilting from the monolayer. We concluded the main origin of this alignment was the adsorption of 8CB molecules onto the PMDA–PPD chains with the carbonyl groups of the PMDA–PPD acting as the main adsorption sites. Whereas from the results above, the excluded volume

effect with the PMDA–PPD domain edges provides an additional contribution to alignment of the 8CB molecules (also with the chain direction) in the case of the sparse polyimide surface cases, and results in a similar alignment structure (i.e. alignment direction and surface tilting) to the packed cases. For any actual polymer surfaces, both alignment mechanisms (i.e. the adsorption
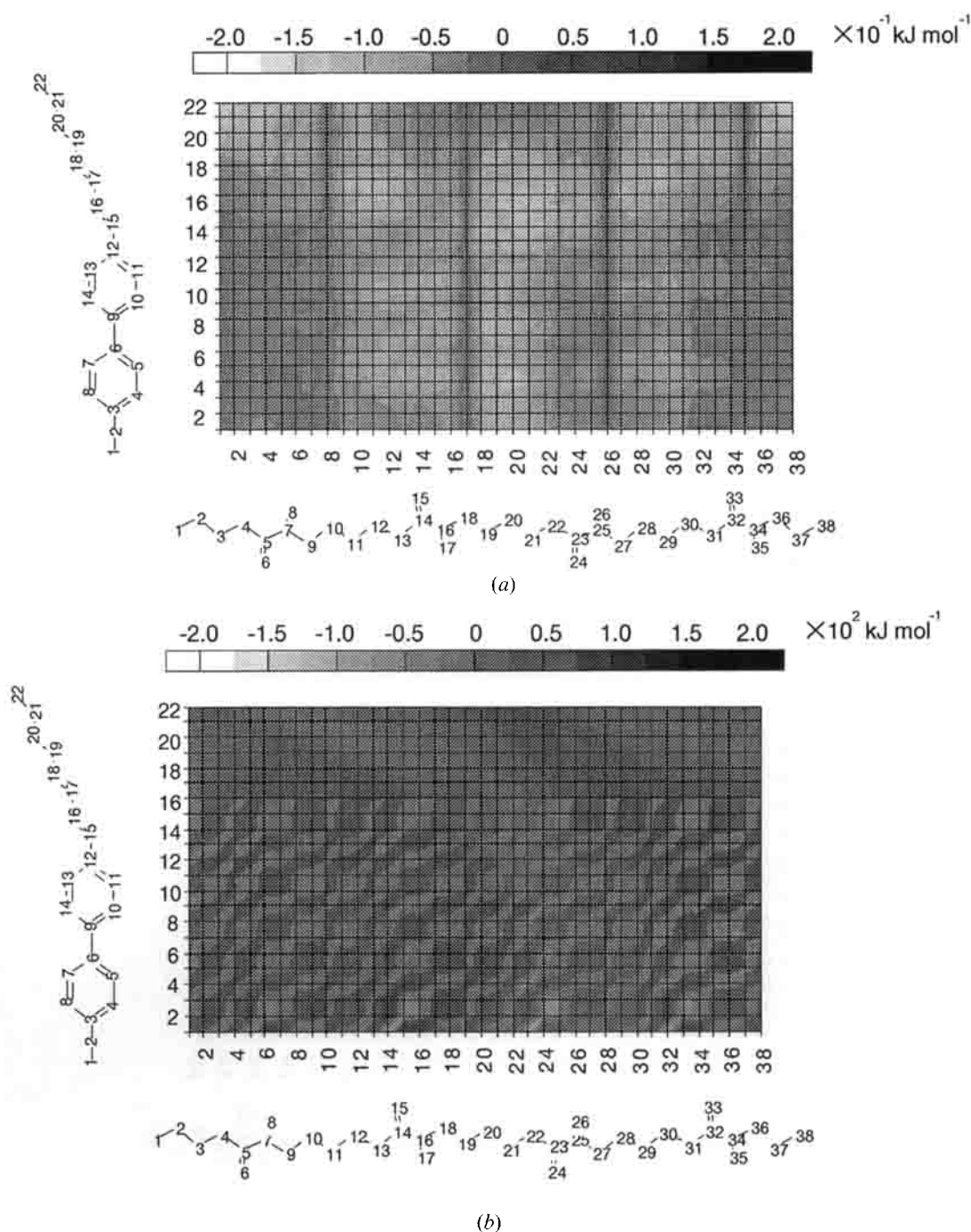
Figure 13. Atomwise interactions (perpendicular setting).

and the excluded volume effect) would be present since it is rare to get surfaces with mono-domain polymer chain packing. For the sparse polyimide surface, the Coulomb interaction with relatively large electrostatic potentials from the polyimide domain edges does not seem to contribute to aligning the 8CB molecules according to the major alignment direction (i.e. the chain direction), but to aligning 8CB molecules perpendicular to the chain directions. This latter alignment is accompanied by a few degrees tilting of the 8CB molecules and it suggests some aspects of a surface tilting mechanism.

Regarding the results on the packed polyamide surface, the differences between the corresponding packed

polyimide case are mainly in the energetics of the 8CB/polyamide interactions and the structural aspects of the 8CB molecule alignment are considered to be similar in both polymers. The clear differences in the adsorption energies and the contribution ratio of Coulomb interaction may possibly result from the monomer-level (local) difference of the polymer chemical structures. However, contributions of non-local differences of polymer characteristics such as chain flexibilities and the degree of surface chain entanglement (which we intensively neglect in our simulation model) to the LC aligning ability of polymer surfaces may also be significant. Clarification of these is a possible future study for the molecular simulation approach.

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