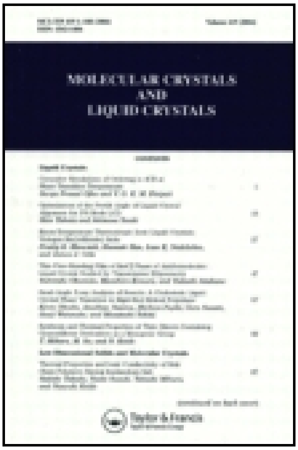

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Investigation of the Alignment Mechanism of Polyimide Langmuir-Blodgett Films by Monte Carlo Simulation

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Version of record first published: 04 Oct 2006.

To cite this article: Yang-Ming Zhu , Zu-Hong Lu & Yu Wei (1994): Investigation of the Alignment Mechanism of Polyimide Langmuir-Blodgett Films by Monte Carlo Simulation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 238:1, 125-128

To link to this article: http://dx.doi.org/10.1080/10587259408046921

Mol. Cryst. Liq. Cryst., 1994, Vol. 238, pp. 125–128
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Printed in the United States of America

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(Received November 19, 1992; in final form March 25, 1993)

Ordered chain orientation of polyimide in Langmuir-Blodgett films is necessary for liquid crystal alignment. In this paper the influence of dipping process on the polyimide chain direction is studied by Monte Carlo method. It is found that the oriented polyimide chain is caused by dipping process and its orientation is almost parallel to the dipping direction. The linearity of the chain depends upon the dipping velocity, which is reinforced by fractal dimension analysis.

Keywords: liquid crystal alignment, polyimide Langmuir-Blodgett films, chain orientation, dipping process, self-avoiding random walk

Traditionally, homogeneous alignment of liquid crystal (LC) molecules can be achieved by rubbed polyimide coats. The rubbing process can produce parallel grooves[1] or reorient the polyimide chains parallel to the rubbing direction through a shearing deformation.[2] Recently, some researchers reported that the polyimide Langmuir-Blodgett (LB) films could induce homogeneous alignment of LCs without rubbing process.[3–5] Considering the alignment mechanisms of LCs on rubbed polyimide coats, it is conjectured that the alignment on polyimide LB films acts through grooves or scratches, or through the orientation of polyimide molecules. Fang *et al.*[6,7] and others such as Fujiwara *et al.*[8] lately proved that the polyimide LB films have uniform structures on a macroscopic scale, i.e., without grooves or scratches by scanning electron microscopy study; while scanning tunneling microscopy (STM) images indicated that the molecular chains of polyimide in LB films are oriented in the dipping direction. The same results were also reported in other systems.[9] The orientation of polyimide chains may be ascribed to the dipping process.[6,7] However, how the dipping process affects the chain orientation remains open.

Usually, it is believed that LB deposition is carried out under the influence of the gravitation force, and the direction of the long chain of polymer molecules tends to align parallel to the direction of the force. Such a concept may be misleading. As a matter of fact, the polymer chain direction in LB films may be governed by several factors, such as the property of the polymer, the interaction between the polymer and the subphase, the interaction between the polymer and the substrate surface, the gravitation force and so on. But, according to our experience, the aligning ability of polymer LB films seems to depend upon the dipping velocity, which implies that the dipping velocity may be the dominant factor affecting the polymer chain direction in LB films prepared by vertical dipping.

To understand the influence of dipping process on the orientation of polyimide chains, in this paper we do a Monte Carlo study. To this purpose, the modified self-avoiding random walk (SARW) model is employed. Although the SARW model has already been used to study the polymer configuration in solvents or on two-dimensional surfaces,[10,11] the influence of dipping process on the polymer, particularly polyimide, configuration has not been considered yet.

In the context of standard SARW model the polyimide is considered to be composed of a certain number of links, which may be monomers, and each link takes one direction randomly at one step on fixed lattices such as plane-square or triangular ones, provided that in this direction the link does not intersect with other links previously settled. In order to take the dipping process into account, one can increment the probability for the link determining its direction near the dipping direction, but it is difficult to adjust the probability. To avoid this problem, here we take another approach, which we describe below.

First we abandon the lattice model. In fact the walker does not need to wander on fixed lattices no matter what kind of lattices they are. Suppose the walker has a constant velocity, but its direction is chosen randomly from three directions, i.e., up, down and forward with respect to the previous direction the walker has taken, provided that in these directions it will not intersect with other links settled before; otherwise it will take one direction from two or even one available ones on chance.

Obviously, if the dipping process is not taken into consideration, this scheme is similar to the standard SARW model with square lattices. Now assuming the dipping velocity is a times the walking velocity, then the walker also has a relative velocity caused by dipping process, whose value is the dipping velocity with opposite direction with respect to the dipping substrate. Thus, the walker has a total relative velocity with respect to the substrate, which is determined by dipping velocity and random walking velocity, and the direction of the total velocity is taken as the instantaneous link direction reasonably. One may find that if a is an integer number, our proposal is a version of SARW in the velocity field rather than in the spatial field.

Using our proposed modified SARW model we carried out Monte Carlo simulation. For simplicity we focused on one polyimide molecule with excluded nearest-neighbor forces, i.e., we emulated the dipping process when the surface pressure of polyimide monolayer at air/water interface in a Langmuir trough is not too high so that the forces between polyimide molecules are weak. The Monte Carlo method is restricted in accuracy by the inevitable statistical fluctuations, but quite long walks (50–1000) can be sampled.[10] Here, 100 walks were simulated.

Taking into dipping process into account, the traces of polyimide chain with 100 links are given in Figure 1, assuming dipping velocity a) $a = 1$, b) $a = 2$ and c) $a = 3$, respectively. The dipping direction is indicated in the figure. It can be seen that the polyimide chain is almost parallel to the dipping direction and the higher

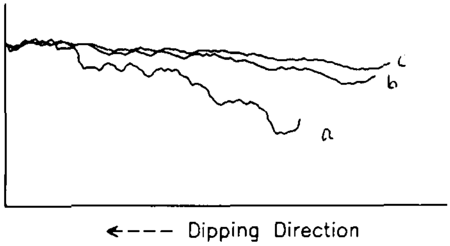

FIGURE 1 Profiles of polyimide chain on substrates with dipping velocity a) 1, b) 2 and c) 3, respectively.

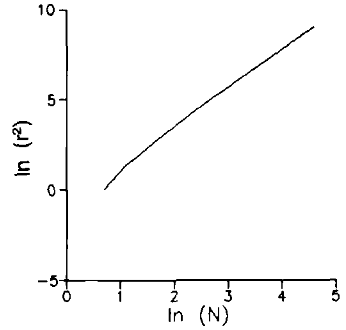

FIGURE 2 A sample plot of number of links versus end-end distance (log-log). The slope of the plot gives the fractal dimension about 1.08.

the dipping velocity is, the more approximate the polyimide chain is a straight line. It is safe to say that the oriented polyimide chain is caused by dipping process.

To quantitatively evaluate the linearity of polyimide chain, we calculated its fractal dimension (Hausdroff dimension). As we know, the smaller the fractal dimension (between 1 and 2) is, the better the linearity of the profile is. First we computed the mean square distance the walker traveled versus the number of links (steps) and found that the relationship between them obeys a power-law, i.e., $\langle r^2 \rangle \propto N^{\nu}$, where scalar r is the end to end distance, N number of walks, angle brackets indicating ensemble average. For one sample, the plot of the distance vs. the number of links (log-log) is shown in Figure 2 ($a = 2$). The Hausdroff dimension of the SARW path is given by $d = 2/\nu$. We calculated the fractal dimension for the above cases (all about 1.05) and found that the fractal dimension of the modified SARW path changes slightly with dipping velocity when dipping velocity a is larger than one. When the dipping velocity is high, the dimension of the chain profile is small and asymptotic to one (an ideal line), which means that the linearity of polyimide chain increases as the dipping velocity tends infinite.

In conclusion, the influence of dipping process on the polyimide chain configuration on substrates is studied by Monte Carlo method. We found that the polyimide chain direction is almost parallel to the dipping direction, which is consistent with the results obtained by STM study. The linearity of the polyimide chain depends upon the dipping velocity, and the chain trace shows a fractal character. The fractal dimension decreases to 1 as the dipping velocity tends to infinite.

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