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M. Nishikawa [a b], N. Bessho [a], T. Natsui [c], Y. Ohta [c], N. Yoshida [d], D.-S. Seo [d], Y. Iimura [d] & S. Kobayashi [d]

[a] Tokyo Research Laboratory, Japan Synthetic Rubber Co. Ltd, 3-5-1 Higashi-yurigaoka, Asao-ku, Kawasaki, 215

[b] M. Nishikawa is also enrolled at the Graduate School of Technology, Tokyo University of Agriculture and Technology

[c] Tsukuba Research Laboratory, Japan Synthetic Rubber Co. Ltd., 25 Miyukigaoka, Tsukuba, Ibaraki, 305

[d] Division of Electronic and Information Engineering, The Graduate School of Technology, Tokyo University of Agriculture and Technology, 2-24-76 Nakamachi, Koganei, Tokyo, 184

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A Model of the Unidirectional Alignment Accompanying the Pretilt Angle of a Nematic Liquid Crystal (NLC), 5CB, Oriented on Rubbed Organic-Solvent-Soluble Polyimide Film

M. NISHIKAWA*, N. BESSHO, T. NATSUI[1], Y. OHTA[1], N. YOSHIDA[2], D.-S. SEO[2], Y. IIMURA[2] and S. KOBAYASHI[2]

Tokyo Research Laboratory, Japan Synthetic Rubber Co. Ltd. 3-5-1 Higashi-yurigaoka, Asao-ku, Kawasaki 215

[1] *Tsukuba Research Laboratory, Japan Synthetic Rubber Co. Ltd. 25 Miyukigaoka, Tsukuba, Ibaraki 305*

[2] *Division of Electronic and Information Engineering, The Graduate School of Technology, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei, Tokyo 184*

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We report a model of the unidirectional alignment accompanying the pretilt angle of a nematic liquid crystal (NLC), 5CB, oriented on rubbed organic-solvent-soluble polyimide (PI) film, which is useful for color active matrix liquid crystal displays. According to our computer calculation, the main chain of the PI molecule, which contains special moieties, forms a helicoidal structure. The model suggested in this paper for the NLC alignment claims that rubbing gives rise to the permanent stretching and deformation of the helicoidal structure that results in the NLC unidirectional alignment and pretilt angle, where the latter is attributed to the formation of asymmetric microscopic triangles.

Keywords: Alignment model, nematic liquid crystal, organic-solvent-soluble polyimide film, pretilt angle, optical retardation

1. INTRODUCTION

Almost all nematic liquid crystal (NLC) samples and devices are fabricated by using NLC molecular orientation techniques to obtain well-oriented and defect-free NLC molecular conformations.[1–3] A good example is the twisted NLC displays (TN-LCDs) which are fabricated using mechanically rubbed polyimide (PI) films as NLC alignment films.

* M. Nishikawa is also enrolled at the Graduate School of Technology, Tokyo University of Agriculture and Technology.

+ The formation of micro-grooves having asymmetric triangles is also effective to generate a pretilt angle of NLC.

It is of considerable practical and theoretical interest to understand the mechanisms of the unidirectional NLC alignment accompanying pretilt angle, where the NLC molecules are aligned on rubbed PI surfaces.

Three models for the unidirectional alignment of NLC molecules oriented on rubbed PI films have been proposed: they are the anisotropic van der Waals force by Okano *et al.*,[4] the groove theory by Berreman,[5] and a steric interaction model for NLC alignment on a smooth surface suggested by Okano.[6]

Regarding the generation of the pretilt angle of NLC, we suggested that the generation of the pretilt angle may be attributed to the alignment of NLC molecules on asymmetric microscopic triangles.[+] These triangles will be formed by performing rubbing on PI having alkyl-branches,[7,8] PI having undulated main chain,[9] and PI having a zigzag main chain with CF_3 moieties.[10] However, these models did not take into account their molecular conformation. To elucidate the generation mechanism of the pretilt angle more in detail, it is important to know the PI conformation composed of moieties. This paper proposes a revised model for the latter case.

The revision has been made by knowing the molecular conformation of the main chain of the organic-solvent-soluble PI. According to our computer calculation, it is suggested that the PI molecules synthesized by our group have a helicoidal structure.

The purpose of this research was to have a model for the unidirectional molecular alignment accompanying the pretilt angle of NLC oriented on the rubbed organic-solvent-soluble PI films which contain special moieties such as CF_3 containing diamines.

In this paper, we report the results of the observation of the textures of the aligned phase of NLC, optical retardation occurring on the surface of alignment film and the pretilt angle as a function of rubbing strength, the calculation of the molecular conformation of the main chain of the organic-solvent-soluble PI, and we report the model of the unidirectional alginment accompanying the pretilt angle of NLC oriented on rubbed organic-solvent-soluble PI films.

2. EXPERIMENTS

2.1. Synthesis of Organic-Solvent-Soluble PI

The novel organic-solvent-soluble PI was synthesized from the chemical imidization of the precursor polyamic acid. This method is basically the same as that reported in a previous paper except for the moieties used.[11] The precursor polyamic acid was prepared from the reaction of 2, 3, 5-tricarboxycyclopentyl acetic dianhydride (TCA·AH) and 2, 2-bis(4-aminophenyl) hexafluropropane (HFDA) in γ-butyrolactone at 60°C as shown in Figure 1. The novel soluble (hereafter for simplicity, we omit the word "organic-solvent") PI was obtained by chemical imidization of the corresponding polyamic acid at 120°C in the presence of pyridine and acetic anhydride.

2.2. Preparation of NLC Cells

NLC cells were fabricated to evaluate the aligned phase of NLC and to measure the pretilt angle of the NLC aligned on the orientation films. The orientation films were

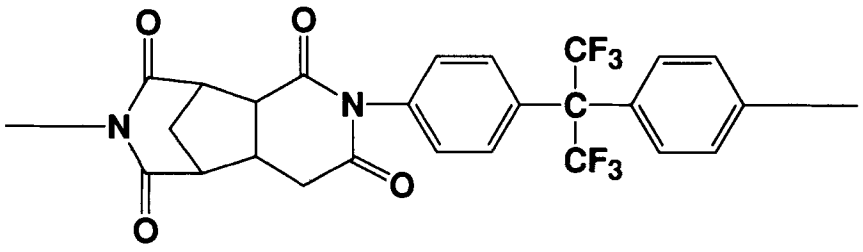

FIGURE 1 Chemical structure of polyimide.

deposited first by spin-coating of diluted solution of PI with γ-butyrolactone and then cured at 180°C for an hour. The thicknesses of polyimide film was kept at 100 nm. The PI films were rubbed by a rubbing machine using nylon cloth. Pairs of substrates were assembled in an antiparallel configuration. The NLC used in the measurements was 5CB (Merck Ltd.).

2.3. Measurement Method of Pretilt Angle and Optical Retardation

For measuring the pretilt angle of aligned NLCs in the cell by changing the rubbing strength,[12] we adopted the crystal rotation method[13] for the rubbed NLC cells and the capacitance method for the non-rubbed NLC cell (rubbing strength = 0 mm). The optical retardations occurring on the surfaces of the PI films by rubbing were measured by changing the rubbing strength with an instrument described in a paper by Seo *et al.*[14]

2.4. Measurement Method of Rubbed Polymer Inclination Angle

For comparing the rubbed polymer inclination angles, we measured the shift angle of the maximum optical retardation of the rubbed PI film from the normal incident light to PI films by the similar way to crystal rotation method.[15] The PI films were coated on quartz glasses and rubbed by changing rubbing strength.

2.5. Calculation Method of PI Conformation

The calculation of the conformation of the PI chain was carried out in the following manner with CONVEX C201 mini-super computer and VAX6310 computer.

The most stable structure of monomer molecules (TCA·AH and HFDA was at first calculated by MOPAC Ver. 6[16] program with AM1 parameters. Next, the oligomer of the PI was constructed by joining the optimized monomer molecules, and then the most stable geometry of the oligomer was calculated in taking only rotation (i.e. torsional angle) along the bonds between monomers into consideration by means of the Molecular Mechanics method.[17]

The conformation of a long PI chain was at last determined on the assumption that the geometry of the oligomer repeated under the periodic condition by means of Chem-X 3D graphics software (Chemical Design Ltd.).

3. RESULTS AND DISCUSSION

3.1. Alignment of NLC on Soluble PI

The pretilt angles of NLC, 5CB, on the rubbed PI surface and the optical retardation of the rubbed PI film for the rubbing strength are shown in Figure 2. The pretilt angle of NLC gradually increases from 0° and, with increasing rubbing strength, reaches saturation at about 1.5° and then decreases to about 1.0°. On the other hand, the optical retardation of PI film increases monotonically with increasing rubbing strength.

3.2. Molecular Inclination of Rubbed PI Film

The shift value of the maximum optical retardation of the rubbed PI film from the normal incident light to PI films is shown in Figure 3. The shift value of the maximum optical retardation increases with increasing rubbing strength, shows the maximum shift value of about 10° and then decreases. This result suggests that the optical axis of PI film is inclined by rubbing treatment.

3.3. What is Known about the Rubbed PI Surface?

Some important information concerning the rubbed PI surface and the obtained NLC alignment is already known and it may be summarized as follows:

A) NLC molecules align along the rubbing direction.[11]

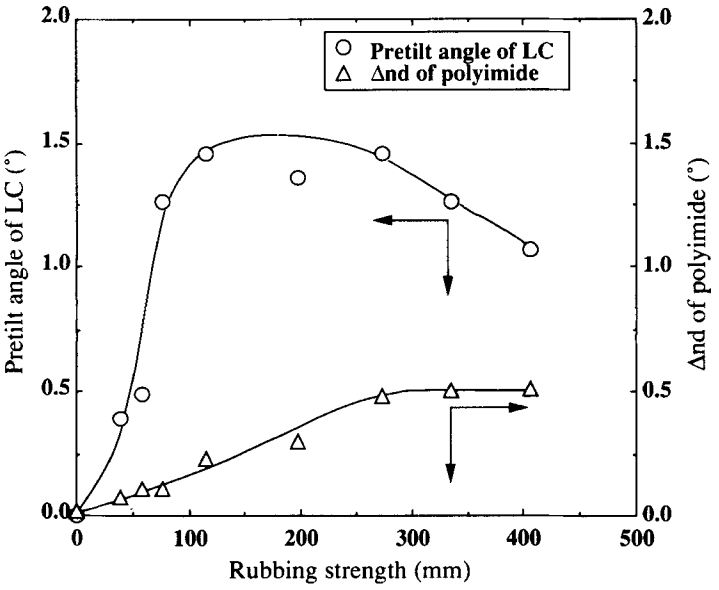

FIGURE 2 Dependence of pretilt angle of NLC and optical retardation of polyimide film on rubbing strength.

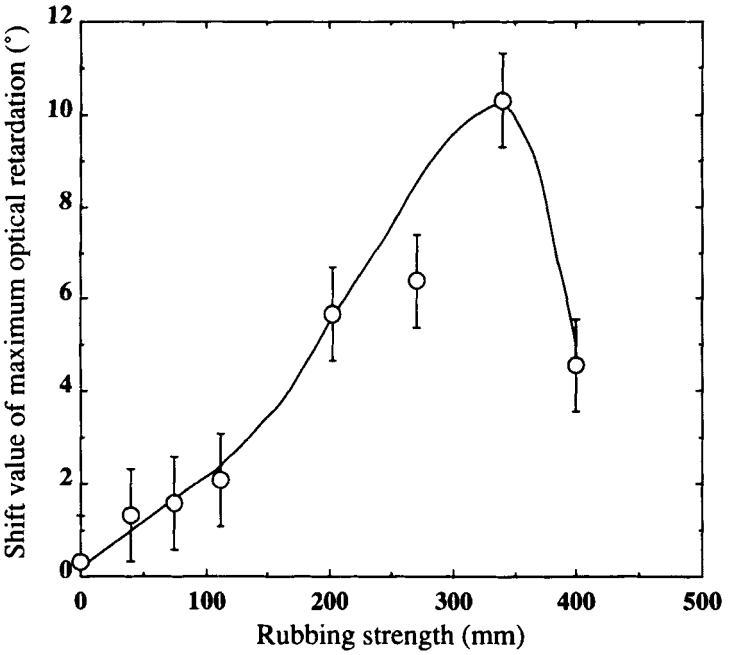

FIGURE 3 Dependence of shift value of maximum optical retardation of rubbed PI film from normal incident light on rubbing strength.

B) PI films are expanded to the rubbing direction by the rubbing.[11]
C) Pretilt angles are generated towards the rubbing direction.[18]
D) Optical retardations of PIs are generated towards the oblique direction for the film thickness.[15,19]
E) Pretilt angles of NLC decrease or increase depending on the nature of PIs while the optical retardations of PI films increase with the increase of rubbing strength and tend to saturate.[10,20]

3.4. Effect of the Rubbing to the PI

In general, rubbing is performed by contacting and moving a rotating cylinder, covered with a rubbing cloth, over a polymer-coated substrate with a constant velocity. A schematic diagram of rubbing process is shown in Figure 4(a). In this rubbing process, three types of force act on the alignment film. The first one is the rubbing cloth pressed force, which is perpendicular to the alignment film, the second one is the rotation force of the rotation cylinder, and the third one is the translating force of the substrate. The second and third forces are parallel to the alignment film. The combination of these forces leads to the force exerting on the alignment film, which is obliquely inclined to the alignment film as shown in Figure 4(b). This model has already been suggested by Geary *et al.*[21]

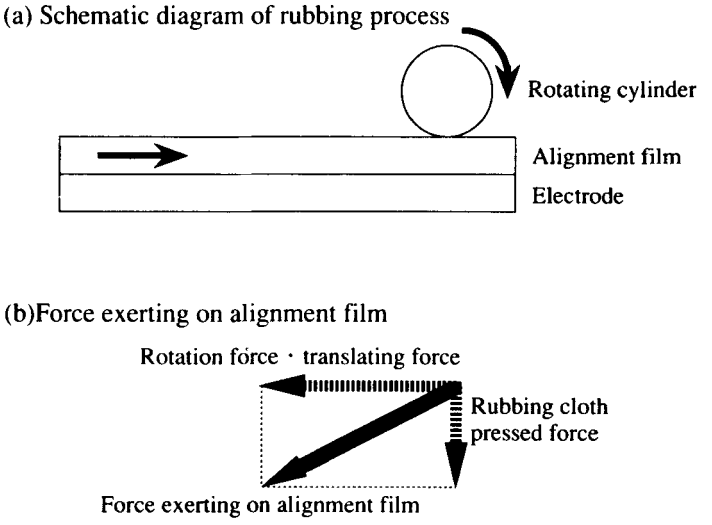

FIGURE 4 Schematic diagram of rubbing process.

3.5. PI Conformation Based on a Computer Simulation

We calculated the molecular conformation of the PI structure as shown in Figure 1. The obtained PI conformation is shown in Figure 5. Figure 5 shows that the PI chain makes a helicoidal conformation. The models of our PI are shown in Figure 6. Figure 6(a) shows the conformation of PI that contains moieties such as TCA·AH and HFDA. Figure 6(a) shows the simplified PI conformation model using the skeleton of a polymer chain. Using these models, we suggest the new NLC alignment model for the unidirectional NLC molecules alignment accompanying the pretilt angle.

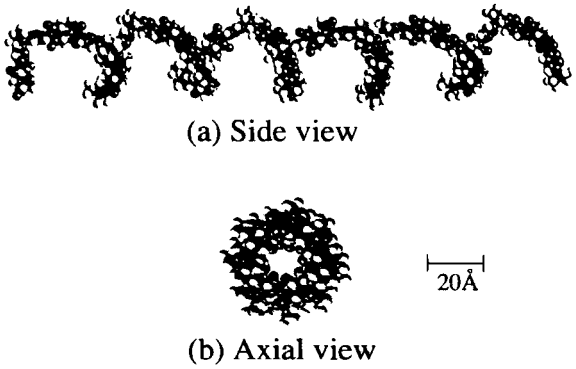

FIGURE 5 Conformations of polyimide chain calculated using MOPAC.

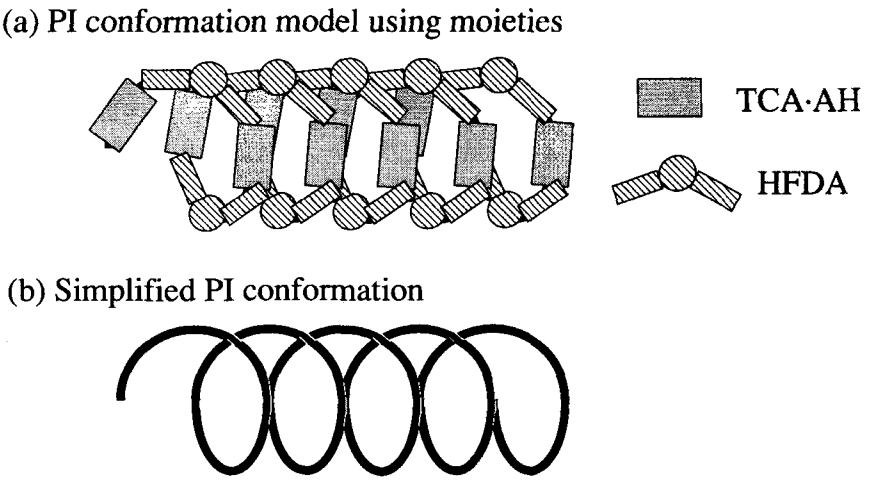

FIGURE 6 Conformation models of polyimide chain.

3.6. PI Conformation Change by Rubbing Treatment

As mentioned above, the rubbing treatment generates the obliquely inclined force to the alignment films. The results are shown in Figure 7. Before the rubbing treatment, PI chains in the side and the overview show a zigzag conformation, and the PI chain in the axial view shows a circle conformation. After the rubbing treatment, the PI chain generates the expansion of the PI chain in the side view and the inclination of the zigzag

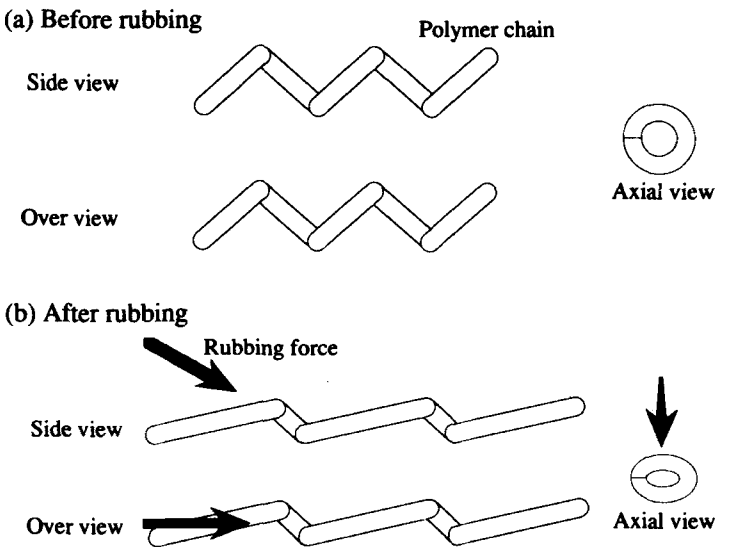

FIGURE 7 Conformation change of polyimide chain before and after rubbing treatment.

PI chain. The PI chain in the overview generates the expansion of PI chains. The PI chain in the axial view becomes an oblate one. It is thought that the inclined PI chain is stably adhering to the surface due to a high glass transition temperature of PI (more than 300°C) and the van der Waals interaction of PI chains. In our NLC alignment model, the optical retardation of the rubbed PI film shows the obliquely inclined axis to the rubbing direction. However, we claim that the generation of microscopic asymmetric triangles may be the origin of the pretilt angle.

3.7. NLC Alignment on Rubbed PI Surface

Typical molecular conformation of LC, 5CB, is shown in Figure 8. The size of long axis of LC is about 20 A. The LC size nearly coincides with the helicoidal pitch of PI conformation as shown in Figure 5. We assume that the NLC alignment on alignment film may be attributed to the anisotropic van der Waals interaction between alignment film and NLC.[4] According to the van der Waals interaction between PI and NLC, NLC molecules align along the PI chain. The microscopic azimuthal LC alignment on the rubbed PI molecules shows the deviation from the rubbing direction, because the expansion of the PI chain in the overview is inclined to the rubbing direction as shown in Figure 7(b). However, the macroscopic azimuthal LC alignment coincides with the rubbing direction, because the rotating direction of the helicoidal PI molecules is random. Furthermore, according to the anisotropic-exclude-volume-effect,[9] NLC molecules align along the inclined zigzag PI chain. From the comparison of the LC size and the helicoidal pitch of the PI conformation, it is thought that the LC alignment according to the anisotropic-exclude-volume-effect between LC and PI is quite reasonable. In this way, NLC molecules are aligned accompanying the pretilt angles in the rubbing direction. In the case that substrates are non-rubbed PI films, this NLC alignment gives rise to the bulk pretilt angle of NLC to 0° due to the random distribution of NLC molecules even though there are local pretilted domains as shown in Figure 9(a). In the case of the NLC alignment on the rubbed PI film, the alignment of NLC molecules shows the unidirectional generation of the pretilt angle along the

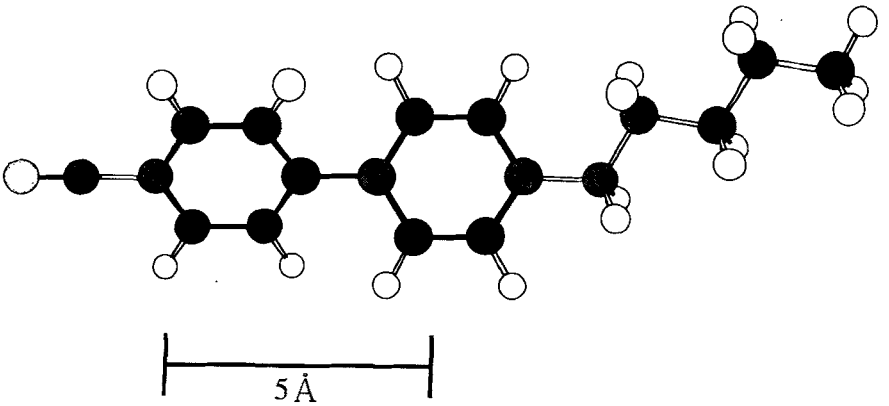

FIGURE 8 Molecular conformation 5CB.

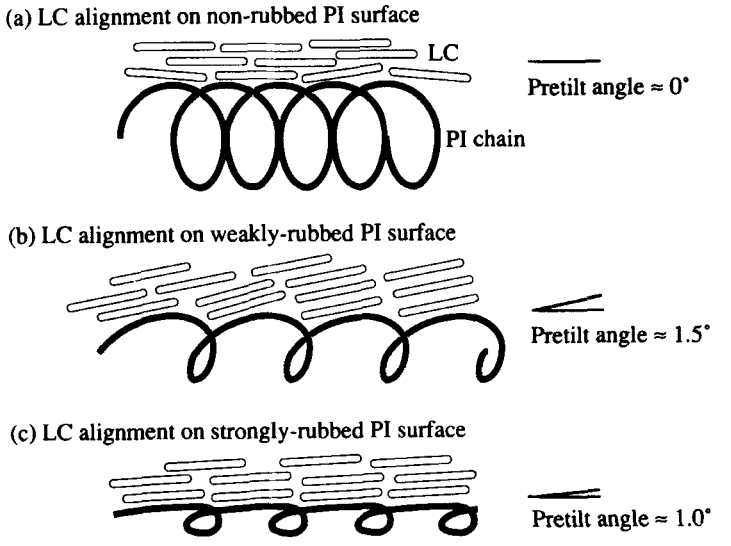

FIGURE 9 Alignment models of NLC on rubbed polyimide surface.

inclination of the zigzag PI chains by a rubbing treatment as shown in Figures 9(b) and (c). NLC alignment on the weakly rubbed PI surface shows the pretilt angle of 1.5° as shown in Figure 9(b). On the other hand, the pretilt angle of NLC on the strongly rubbed PI surface decreases to 1.0° due to the decrease of the inclination of the zigzag PI chain by strong rubbing as shown in Figure 9(c).

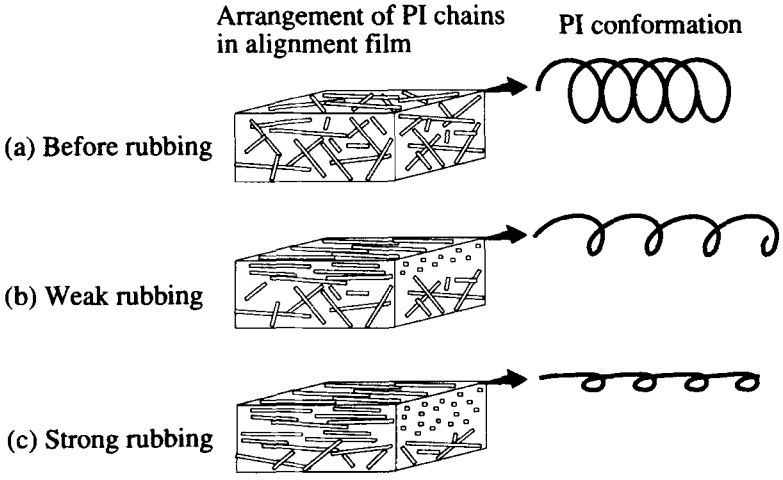

FIGURE 10 Macroscopic arrangement of polyimide chains in alignment film.

3.8. Effect of Rubbing on Alignment Films

A macroscopic schematic figure for the arrangement of PI chains in alignment film by rubbing treatment is shown in Figure 10. Before the rubbing treatment, the arrangement of PI chains in the alignment film are random as shown in Figure 10(a). In this state, PI chains in alignment films have no inclination towards rubbing treatment. At weak rubbing, the PI chains near the surface align to the rubbing direction as shown in Figure 10(b). In this state, PI chains in the aligned film have the inclination of the PI chain by rubbing treatment. At strong rubbing, the PI chains align deeply in the alignment film as shown in Figure 10(c). This model has already been suggested by Aerle *et al.*, whose experiments show that the depth of alignment in PI films is varied by variation of the rubbing strength.[22] In this state, PI chains in the aligned film show a decrease of the inclination of the PI chain by rubbing treatment.

4. CONCLUSION

We report a new NLC alignment model on rubbed PI films, which is based on experimental results and the computer simulation of the PI structure. The well-known results concerning the rubbed PI surface and the obtained NLC alignment, the optical retardation properties of alignment films, the alignment properties and the pretilt angle properties of NLCs, are explained according to our new NLC alignment model. However, the temperature dependence of pretilt angles of NLCs could not be explained in our model.[23] The analytical simulations to elucidate the temperature dependence of pretilt angles in our model are now underway and the results will be published elsewhere.

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