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

A Model of Inclined Orientation of Polyimide Backbone Structures in Rubbed Films

Ryuichi Arafune [a], Kenji Sakamoto [a] & Sukekatsu Ushioda [a]

[a] Research Institute of Electrical Communication Tohoku University, 2-1-1 Katahira, Sendai, 80-8577, Japan

Version of record first published: 24 Sep 2006

To cite this article: Ryuichi Arafune, Kenji Sakamoto & Sukekatsu Ushioda (1999): A Model of Inclined Orientation of Polyimide Backbone Structures in Rubbed Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 329:1, 153-160

To link to this article: http://dx.doi.org/10.1080/10587259908025936

Mol. Cryst. Liq. Cryst., 1999, Vol. 329, pp. 153-160
Reprints available directly from the publisher
Photocopying permitted by license only

A Model of Inclined Orientation of Polyimide Backbone Structures in Rubbed Films

RYUICHI ARAFUNE, KENJI SAKAMOTO and SUKEKATSU USHIODA

Research Institute of Electrical Communication Tohoku University, 2–1–1 Katahira, Sendai 980–8577, Japan

For alignment of liquid crystal molecules in displays, a rubbing process is used to induce anisotropy of molecular orientation in a polyimide alignment film. The polyimide backbone structures in a rubbed film have been found to be on average oriented along the rubbing direction with a certain inclination angle from the film plane. We first derive the tensor order parameters of the film from the infrared dielectric constant. Then by using the tensor order parameters we demonstrate that the molecular structure of this film can be modeled by a series of asymmetric triangular structures proposed by Seo et al. [Jpn. J. Appl. Phys. **34**, L503 (1995)]. We also present a feasible picture of the polyimide backbone structures in a rubbed film.

Keywords: rubbed polyimide film; model of inclined orientation; tensor order parameter

INTRODUCTION

Rubbed polyimide films are widely used as alignment layers in the fabrication of liquid crystal (LC) displays. The average orientation direction of LC (the director) in contact with the alignment layer is tilted up from the substrate plane and lies along the rubbing direction. The angle between the director and the substrate plane is called the "pretilt angle." The mechanism for generation of the pretilt angle is a subject not only of technological importance but also of scientific interest. There have been many investigations on the mechanisms[1-8], but so far no definitive understanding has been reached.

Previously we measured the orientation distribution of polyimide backbone structures in rubbed films by polarized infrared absorption (IR) spectroscopy[9-15]. In rubbed films polyimide backbone structures are oriented

on average along the rubbing direction with a certain vertical inclination angle. To determine the orientation distribution of the polyimide backbone structures, we used the dielectric tensor at the resonant frequency ω_ν of an IR active vibration that is polarized along the polyimide backbone structure. Since the molecular polarizability of the polyimide along the length of the chain has a large imaginary part at ω_ν (IR absorption), the average orientation direction of the polyimide backbone structures coincides with the dielectric principal axis of the film having the largest value of the imaginary part of the dielectric tensor. The average inclination angle is defined by the angle between the average orientation direction and the substrate surface. In our recent study[14, 15] we found that the pretilt angle of LC in contact with the rubbed polyimide film is proportional to the inclination angle of the polyimide backbone structures. This experimental result indicates that the inclination of the polyimide backbone structures has a dominant effect in determining the pretilt angle of LC.

To deepen our understanding of LC alignment mechanisms, it is useful to consider the conformation of the polyimide chains that results in the inclined orientation of the molecules on average. The length of the polyimide chains used in our study is 3000 ~ 4000 Å[16], and the depth of the effect of rubbing reaches approximately 125 Å from the surface[9]. Since the long polyimide chains must be packed in such a thin layer, we must find a conformation model of the polyimide backbone structures that can produce the average inclined orientation under this geometrical restriction.

Seo et al[17]. proposed a model for the conformation change of polyimide chains induced by rubbing. Their model is shown in Fig. 1. In their model, polyimide chains form a series of symmetric triangular structures in an unrubbed film. The original structure is deformed into a series of asymmetric triangular structures by rubbing. The polyimide chains can fit in a very thin layer if they consist of these zigzag structures. If this model can account for the average inclined orientation of the polyimide backbone structures observed by our previous experiment, that will add further credibility to the model for rubbed films. In the present paper we demonstrate that the conformation model that comprises a series of asymmetric triangular structures can account for the inclined orientation of the polyimide backbone structures in rubbed films. At the end we show feasible pictures of the conformation of polyimide backbone structures based on this model.

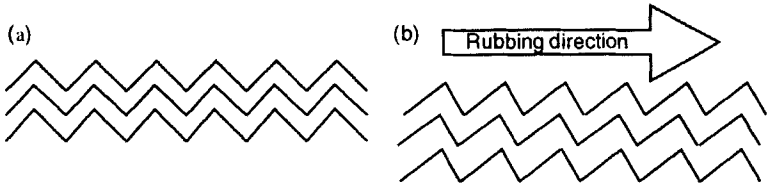

FIGURE 1 Models of rubbing-induced conformation change of the polyimide backbone structures proposed by Seo et al. Figure 1(a) is the model of the conformation of polyimide backbone structures in an unrubbed film. Figure 1(b) is the model of the conformation of polyimide backbone structures in a rubbed film.

THEORY

The main purpose of this study is to show that the conformation model suggested by Seo et al.[17] can reproduce the average inclined orientation of polyimide backbone structures that we found by polarized IR measurements[9-15]. We assume that the repeat unit of polyimide that make up the triangular structures is a rigid rod. The direction of the repeat unit is defined by its long axis. Since the orientation distribution of polyimide backbone structures in a rubbed film is biaxial[9-15], we need to use a set of tensor order parameters[18] to represent the orientation distribution of the repeat units. The element of the tensor order parameter Q_{IJ} with respect to a Cartesian coordinate XYZ is defined by :

$$Q_{IJ} = \frac{1}{2}\left\langle 3\mu_I\mu_J - \delta_{IJ} \right\rangle \qquad (I,J = X,Y,Z) \qquad (1)$$

where μ_I is the I-component of the unit vector $\hat{\mu}$ of the repeat unit direction; δ_{IJ} is the Kronecker delta; and the angular brackets denote an average over molecular orientations.

It is difficult to identify the average orientation direction of the repeat units from the tensor order parameter written with respect to an arbitrary coordinate system. However, one can identify this direction easily from the tensor order

parameter Q_{ii} with respect to the dielectric principal axes x, y, and z of the film. In terms of the dielectric tensor element ε_{ii} with respect to the principal axes of the film, the diagonal elements of the tensor order parameter Q_{ii} can be written[19]:

$$Q_{ii} = \frac{1}{2\mathrm{Tr}\left[\mathrm{Im}\left[\varepsilon_{ii}(\omega_v)\right]\right]}\left(\mathrm{Im}\left[\varepsilon_{ii}(\omega_v)\right] - \frac{1}{3}\mathrm{Tr}\left[\mathrm{Im}\left[\varepsilon_{ii}(\omega_v)\right]\right]\right) \quad (i = x, y, z). \quad (2)$$

where ω_v is the resonant frequency of the molecular vibration polarized parallel to the repeat unit. i.e. the polarization direction is coincident with $\hat{\mu}$. $\varepsilon_{ii}(\omega_v)$ is the dielectric tensor element at the IR absorption frequency ω_v. From Eq. (2) one can see that the axis with the largest Q_{ii} corresponds to the dielectric principal axis with the largest value of the imaginary part of the dielectric tensor. If $\mathrm{Im}[\varepsilon_{ii}(\omega_v)]$ is largest along the i-axis, that means the repeat units (polarization direction of the IR vibration) are oriented on average along the i-axis. Thus the axis with the largest Q_{ii} coincides with the average orientation direction of the repeat units.

Now we derive the tensor order parameters of the repeat units from the model conformation that consists of a series of asymmetric triangles. The asymmetric triangular structure used in this model is shown in Fig. 2 along with the coordinate systems. The X and Z axes are defined by the rubbing direction and the surface normal, respectively. We denote the dielectric principal axes by x, y, and z. L_1 and L_2 are the lengths of the left and right side leg of the triangle, respectively. Θ_1 and Θ_2 are the base angles for the left and right side of the triangle, respectively. We assume that each "series of asymmetric triangles" consists of more than one repeat units of polyimide, and that all of the asymmetric triangles have an identical shape. To focus on the conformation of the polyimide backbone structures in a film section, we initially consider the case where the plane of the triangles is parallel to the XZ plane. Furthermore we assume that the base of the triangles is parallel to the X axis in calculating the tensor order parameters from the shape of the triangles.

The shape of a triangle is uniquely determined by the base angles Θ_1 and Θ_2. The ratio between the number of repeat units in the left side leg and that in the right side leg is equal to the ratio of the length of the legs. The ratio of the lengths of the legs (L_1:L_2) equals $\sin\Theta_2$: $\sin\Theta_1$. Therefore the tensor order parameter with respect to the XYZ coordinates can be written:

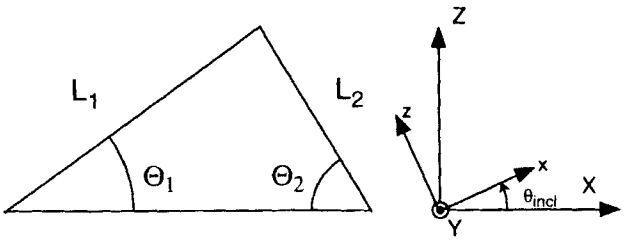

FIGURE 2 Asymmetric triangular structure. X and Z axes are defined by the rubbing direction and the surface normal, respectively. L_1 and L_2 are the lengths of the legs of the triangle. Θ_1 and Θ_2 are the base angles of the triangle.

$$Q_{XX} = \frac{1}{2}\frac{(3\cos^2\Theta_1 - 1)\sin\Theta_2 + (3\cos^2\Theta_2 - 1)\sin\Theta_1}{\sin\Theta_1 + \sin\Theta_2} \tag{3a}$$

$$Q_{YY} = -\frac{1}{2} \tag{3b}$$

$$Q_{ZZ} = \frac{1}{2}\frac{(3\sin^2\Theta_1 - 1)\sin\Theta_2 + (3\sin^2\Theta_2 - 1)\sin\Theta_1}{\sin\Theta_1 + \sin\Theta_2} \tag{3c}$$

$$Q_{XZ}\frac{3}{2}\frac{\sin\Theta_1\cos\Theta_1\sin\Theta_2 - \sin\Theta_2\cos\Theta_2\sin\Theta 1}{\sin\Theta_1 + \sin\Theta_2} \tag{3d}$$

from Eq. (1). Since the XZ plane is a mirror plane, all other components vanish.

Because of the presence of the XZ mirror plane, we can obtain the diagonalized tensor order parameters Q_{ii} by a rotation of angle θ_{incl} around the Y axis. This rotation angle θ_{incl} is given by:

$$\theta_{incl} = \frac{1}{2}\tan^{-1}\left(\frac{2Q_{XZ}}{Q_{XX} - Q_{ZZ}}\right). \tag{4}$$

θ_{incl} is the angle between x and X axes as shown in Fig. 2. If Q_{xx} has the largest value among Q_{ii}, the x axis is the average orientation direction of the repeat units. In this case θ_{incl} is the average inclination angle of the repeat units of polyimide.

TABLE I The base angles of the triangular structure (Θ_1, Θ_2), the rotation angle θ_{incl}, and the tensor order parameter Q_{xx} and Q_{zz} respect to the dielectric principal axes xyz.

Θ_1 and Θ_2	20°	35°	30°	100°	20°	65°	30°	70°
Q_{xx}	0.71		0.77		0.59		0.51	
Q_{zz}	-0.21		-0.27		-0.09		-0.01	
θ_{incl}	2.4°		44°		17°		40°	

RESULTS AND DISCUSSION

We have calculated the value of θ_{incl} for four sample sets of asymmetric triangular structures by using Eq. (3) and (4). The calculated values of θ_{incl} are shown in Table I along with the input values of Θ_1 and Θ_2. Table I also includes the values of Q_{xx} and Q_{zz}. Q_{yy} is constant and equal to -1/2 under our assumptions. In Table I, Q_{xx} is larger than Q_{yy} and Q_{zz}, and θ_{incl} has a positive value for all sets of Θ_1 and Θ_2. This result clearly shows that with appropriate choices of Θ_1 and Θ_2 the model that consists of a series of asymmetric triangles can reproduce the inclined average orientation of the repeat units of the polyimide.

Next we present a feasible picture of the conformation of the polyimide backbone structures based on triangles. The real conformation of the polyimide backbone structures probably does not consist of sharp cornered triangles. Furthermore the orientation distribution of the polyimide backbone structures in unrubbed film is random in the XY plane. Taking these two factors into account, we proposed the following picture of the conformation of polyimide backbone structures in a film before and after rubbing.

The proposed pictures based on the above model are shown in Fig. 3. Figure 3(a) is a picture of the conformation of polyimide backbone structures in an unrubbed film. The polyimide backbone structures consist of a series of symmetric rounded triangles. Although there are various angles between the substrate plane and the plane of the triangles in a real film, we only show the case where the plane of the triangles is normal to the substrate. This is because we wish to focus on the inclined orientation of the polyimide

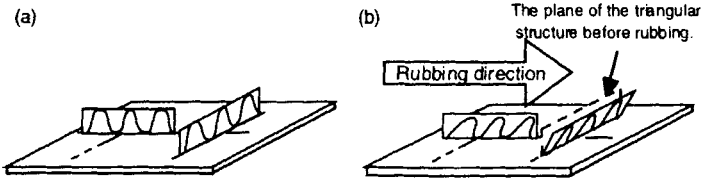

FIGURE 3 Picture of the conformation of polyimide backbone structures in a film before and after rubbing. Figure 3(a) is the picture of the conformation in an unrubbed film. Figure 3(b) is the picture of the conformation in a rubbed film. Rectangles and parallelograms mean the plane of the triangular structures.

backbone structures. The polyimide chains whose plane of triangles is parallel to the substrate surface do not contribute to the inclined molecular orientation.

Figure 3(b) is a picture of the conformation of polyimide backbone structures in a rubbed film. Since the frictional force due to rubbing is parallel to the rubbing direction, the polyimide chains oriented along the rubbing direction are deformed into a series of asymmetric rounded triangles as shown in Fig. 3(b). On the other hand for the polyimide chains oriented perpendicular to the rubbing direction, the frictional force tilts the plane of the symmetric triangles as shown in Fig. 3(b). For the polyimide chains oriented between 0° and 90° in the substrate plane, the conformation change is effected by both of the above mechanisms. It is clear that the changed conformation results in the inclined orientation of the polyimide backbone structures on average. The real conformation of the polyimide chains is likely to be much more complex than the picture we have just presented. We believe that a combination of these conformation types make up the real conformation of the polyimide backbone structure after rubbing.

CONCLUSION

We found that the conformation model of polyimide films comprising a series of asymmetric triangular structures proposed by Seo et al.[17] can account for

the average inclined orientation of the polyimide backbone structures in rubbed films. This structure is one of the convincing models for the conformation of the polyimide backbone structures in rubbed films. We have presented a feasible picture of the polyimide backbone structures in rubbed films based on this model.

References

[1] J.M. Geary, J.W. Goodby, A.R. Kmetz, and J.S. Pastel, *J. Appl. Phys.* **62,** 4100(1987).
[2] D.W. Berreman, *Phys. Rev. Lett.* **28,** 1683 (1972).
[3] E.S. Lee, Y. Saito, and T. Uchida, *Jpn. J. Appl. Phys.* **32,** L1882 (1993).
[4] Y. Ouchi, I. Mori, M. Sei, E. Ito, T. Araki, H. Ishii, K. Seki, and K. Kondo, *Physica B* **208/209,** 407 (1995).
[5] M.F. Toney, T.P. Russell, J.A. Logan, H. Kikuchi, J.M. Sands, and S.K. Kumar, *Nature* **374**, 1995 (1995).
[6] K. Shirota, K. Ishikawa, H. Takazoe, A. Fukuda, and T. Shiibashi, *Jpn. J. Appl. Phys.* **34,** L316, (1995).
[7] M. Barmentlo, R.W.J. Hollering, and N.A.J.M. van Aerle, *Phys. Rev. A* **46** R4490(1992).
[8] X. Zhuang, L. Marrucci, and Y.R. Shen, *Phys. Rev. Lett.* **73**, 1513 (1994).
[9] K. Sakamoto, R. Arafune, N. Ito, S. Ushioda, Y. Suzuki, and S. Morokawa, *Jpn. J. Appl. Phys.* **33**, L1323 (1994).
[10] K. Sakamoto, R. Arafune, N. Ito, S. Ushioda, Y. Suzuki, and S. Morokawa, *J. Appl. Phys.* **80**, 431 (1996).
[11] R. Arafune, K. Sakamoto, D. Yamakawa, and S. Ushioda, *Appl. Surf. Sci.* **368,** 208 (1996).
[12] K. Sakamoto, R. Arafune, and S. Ushioda, *Appl. Spectrosc.* **51,** 541 (1997).
[13] K. Sakamoto, N. Abe, R. Arafune, and S. Ushioda, *Mol. Cryst. Liq. Cryst.* **299,** 169 (1997).
[14] R. Arafune, K. Sakamoto, and S. Ushioda, *Appl. Phys. Lett.* **71,** 2755 (1997).
[15] R. Arafune, K. Sakamoto, S. Ushioda, S. Tanioka, and S. Murata, *Phys. Rev. E.* **58**, 5914 (1998).
[16] S. Murata, Private Communication.
[17] D.-S. Seo, K. Araya, N. Yoshida, M. Nishikawa, Y. Yabe, and S. Kobayashi, *Jpn. J. Appl. Phys.* **34,** L503 (1995).
[18] P.G. de Gennes, and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon, Oxford, 1993).
[19] M.C.J.M. Vissenberg, S. Stallinga, and G. Vertogen, *Phys. Rev. E* **55**, 4367 (1997).