Summary of the thesis: The alignment of liquid crystals and the viscoelastic dynamics of polymers at the interface

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It is important and basic problem to align liquid crystalline (LC) molecules uniformly when applying them to liquid crystal displays (LCDs). LC molecules are usually aligned by solid polymer films coated on the glass substrates of LC cells. An LC cell has a structure, where LC molecules are sandwiched between two substrates. The rubbing to the polymer-coated substrates is widely used to provide the anisotropy at the surface to align LC molecules. One of the characteristic parameters for the alignment is the anchoring energy W_s [1]. However, the aligning mechanism of nematic LC molecules (NLCs) on the rubbed surface is still not clear. It is explained that the anisotropy of polymer films on the substrates induced by the rubbing aligns NLCs homogeneously [2]. The other explanation is that the periodical grooves due to rubbing minimize the elastic energy of NLCs to fit the director along the groove [3].

Let us consider the alignment of NLCs on the surface of the liquid phase of the melting polymer [4]. In this system, the director at the substrate surface can be steered by a very weak magnetic field. As a result, the planar homogeneous alignment of the NLCs is achieved on the liquid surface. Since there is no interaction which anchors the NLC director on the interface n_s between the bulk NLCs and the polymers, this anchoring condition is called "zero anchoring". On the other hand, when electric or magnetic field parallel to the substrates, on which the alignment PMMA film is pre-coated, is applied with different angles to the alignment direction in homogeneously aligned NLCs, the director on the aligning surface is slightly rotated near the liquid-glass transition temperature [5,6]. It is similar to the zero anchoring state for the rotation of n_s, except that the strong field is required to induce the rotation. However, after turning off the field, n_s is going to relax to the intermediate direction between the initial direction and the applied field direction. These phenomena are called "gliding".

In this thesis, I focused on the viscoelasticity of the polymer films near the liquid-glass transition and studied the alignment phenomena of NLCs on the surface of the polymer films. In the first half of the thesis (Chap.2), I fabricated NLCs sandwiched cells made of two substrates coated with a soft polymer film, PMMA, without the rubbing treatment. When PMMA is melted at high temperature, (~85∘C), NLCs were perfectly aligned to arbitrary directions along the low applied magnetic field (10 mT) parallel to the substrates. This behavior is consistent that the anchoring energy becomes zero on the interface between NLCs and the melted polymer. When this cell was cooled down to the temperature of 25∘C, where the PMMA is going into the glass state, the director is spontaneously anchored preserving the same perfect alignment. Thus, the anchoring energy becomes sufficiently strong as well as

that in the rubbed surface, and the orientation hardly changes even in the application of the high field (440 mT). We call this aligning method "self-alignment". I measured the corresponding anchoring energy W_s at room temperature. It was found that the obtained values of W_s are almost the same in the rubbed ((1.4±0.1)x10^{-6} J/m^2) and "self-alignment" PMMA cells ((1.6±0.9)x10^{-6} J/m^2)), suggesting that W_s is a unique parameter produced by the local interaction between NLCs and polymers to be independent of aligning methods. In other words, "alignment" and "anchoring" are essentially different.

In the second half part of the thesis (Chap.3), I investigated the origin of the "gliding" phenomena and relationship to the liquid-glass transition of the alignment polymer films. There are two types of explanation for the gliding phenomena. First type of the explanation is that the rotation of the surface directors is dominated by adsorption and desorption of the NLCs to the substrates [5]. Second type of the explanation is that the polymers adsorbed by NLCs are deformed by applying the external torque. The viscosity of polymers dominates the speed of the surface director [6].

The director on the interface between the NLCs and polymers shows the gliding at temperatures between 84°C and 25°C on the PMMA film. This behavior is similar to the viscoelastic response of the polymer near the liquid-glass transition under the stress. Thus, I used the mechanical model with three elements to explain the gliding. A Voigt element and a dashpot are connected in series. The Voigt element has the temperature dependent relaxation time near liquid-glass transition of PMMA. The relaxation time dominated by the viscosity originated from the friction of polymer chains with surrounding chains and the elasticity originated from the entropic elasticity which prevents the decrease in the conformation numbers of polymer chains. The single dashpot corresponds to the true viscous flow of the center of mass of polymer molecules originated from slipping of the transient cross-linking of polymer chains. When we remove the stress, the Voigt element relaxes to the initial position perfectly, but the deformation of the dashpot remains.

This indicates that the gliding can be explained by the viscoelasticity of polymers. The obtained values of two viscosities and elasticity diverged when cooling toward the liquid-glass transition of PMMA. We fitted two temperature dependences of viscosities by the Arrhenius type equation to obtain the activation energy. The results show that the divergence of the viscosities corresponds to that of the alpha relaxation at the surface of polymers related to the liquid-glass transition.

References: [1] M. Kleman and O. D. Lavrentovich, Soft Matter Physics and Introduction (Springer, 2002). [2] J. M. Geary, J. W. Goodby, A. R. Kmetz and J.S. Patel, J. Appl. Phys. 62, 4100 (1987). [3] D. Berreman, Phys. Rev. Lett. 28, 1683 (1972). [4] J. Yamamoto, H. Yokoyama, N. Tomikawa, and J. Watanabe, Japan Liquid Crystal Society Annual Meeting Proceedings Book (Nagoya, 2004), 1C08, p. 274. [5] P. Vetter, Y. Ohmura, and T. Uchida, Jpn. J. of Appl. Phys. 32, L1239 (1993). [6] I. Janossy and T. Kosa, Physical Review E 70, 052701 (2004).