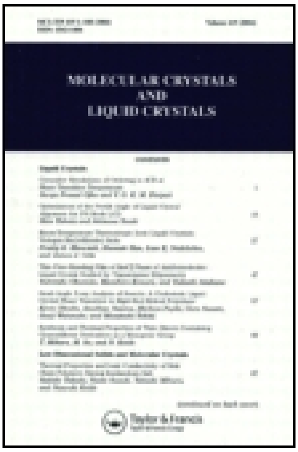

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Anchoring Phase Transition and Bulk Phase Sequence of Liquid Crystals Studied by Scanning Tunneling Microscopy

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ANCHORING PHASE TRANSITION AND BULK PHASE SEQUENCE OF LIQUID CRYSTALS STUDIED BY SCANNING TUNNELING MICROSCOPY

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Abstract On the basis of the highly reproducible scanning tunneling microscopy (STM) images, the anchoring structures of a homologous series of liquid crystals, *n*-alkylcyanobiphenyls (*m*CBs) are clearly divided into two categories; a single-row type and a double-row type. We have proposed that the single-row is the anchoring structure of a nematic phase, while the double-row is the one of a smectic phase. Furthermore, a new phase transition only available at the boundary has been confirmed for the first time in the binary mixtures. The correlation between those anchoring structures and the bulk phase diagrams is discussed from the viewpoint of anchoring phase formation at a molecular level.

INTRODUCTION

The molecular alignment on solid substrates is important both to fundamental issues in physics and chemistry and to practical applications such as optoelectronic devices. It has been well known that the orderings of adsorbed molecules in the anchoring region near the substrate, which we call here "anchoring phases", are strongly affected by the substrate surface structure and the balance of molecule-molecule and molecule-substrate interactions. This is especially evident in the case of liquid crystals, where such an alignment technique with boundary effects at the substrate surface has been widely used to produce director configurations in the monodomain cells such as flat-panel displays and optical shutters. However, the actual mechanism of their orientation at the interface is still unclear, because there have been technical difficulties in the analysis of the anchoring structures at a molecular level.

Recently, scanning tunneling microscopy (STM) has been successfully applied to direct observations of the interfacial structure with molecular resolution, and used to study positional and orientational order in organic monolayers on solid substrates, especially liquid crystal monolayers.[1] The STM images of such monolayers have been reported for smectic,[2-5] nematic,[6,7] and antiferroelectric liquid crystals.[8] Actually, high-resolution STM images now allow us to make the real-space analysis of the molecular alignment at the interface on the individual molecular scale. In this paper, we discuss the "anchoring phases" on the basis of the highly reproducible STM images of a homologous series of *n*-alkylcyanobiphenyls (*m*CBs: $m = 7\sim12$, number of carbon atoms in the alkyl chains) and various bulk compositions of 8CB-12CB binary mixtures. We then consider the correlation between those anchoring structures and the bulk phase diagrams from the viewpoint of anchoring phase formation.

EXPERIMENTAL

In our previous paper,[4] we have introduced a molybdenum disulfide (MoS_2) single crystal as a substrate for STM imaging of organic adsorbates for the first time and proposed that the anchoring structures on MoS_2 reflect well the corresponding bulk phase sequences compared with those on graphite because of the higher degree of freedom allowed for the alignment of rod-like molecules on MoS_2.[7] We will return to this important aspect in the discussion of substrate dependence.

The samples for STM imaging were prepared by placing a drop of the pure and mixed *m*CBs on the surface of a freshly cleaved MoS_2 and highly oriented pyrolytic graphite (HOPG) and heating it to the isotropic phase. After slowly cooling the sample down to room temperature, a sharp Pt/Ir tip was positioned at the interface and scanned over it in air at room temperature. All images were obtained in the constant current mode. Typical operating conditions were 0.09 to 0.4 nA and 0.8 to 2.0 V (tip negative). The STM system used in this study was a commercially available NanoScope II (Digital Instruments, Inc., Santa Barbara, CA, USA). The STM images were digitally filtered to remove only high-frequency noise.

RESULTS AND DISCUSSION

Figure 1 shows typical STM images of *m*CB molecules; (a, left) 8CB, (b, middle) 8CB-12CB binary mixtures, and (c, right) 12CB adsorbed on MoS_2. Individually distinguishable rodlike patterns and regular alignment are observed. As we have claimed previously,[6] each rodlike pattern shows the individual liquid crystal molecules. In numerous such studies on MoS_2, the anchoring structures are clearly divided into two categories; a "single-row" type (7CB, 8CB (Fig. 1(a)), 9CB, and 11CB) in which cyanobiphenyl head groups and alkyl tails alternate in each row and a

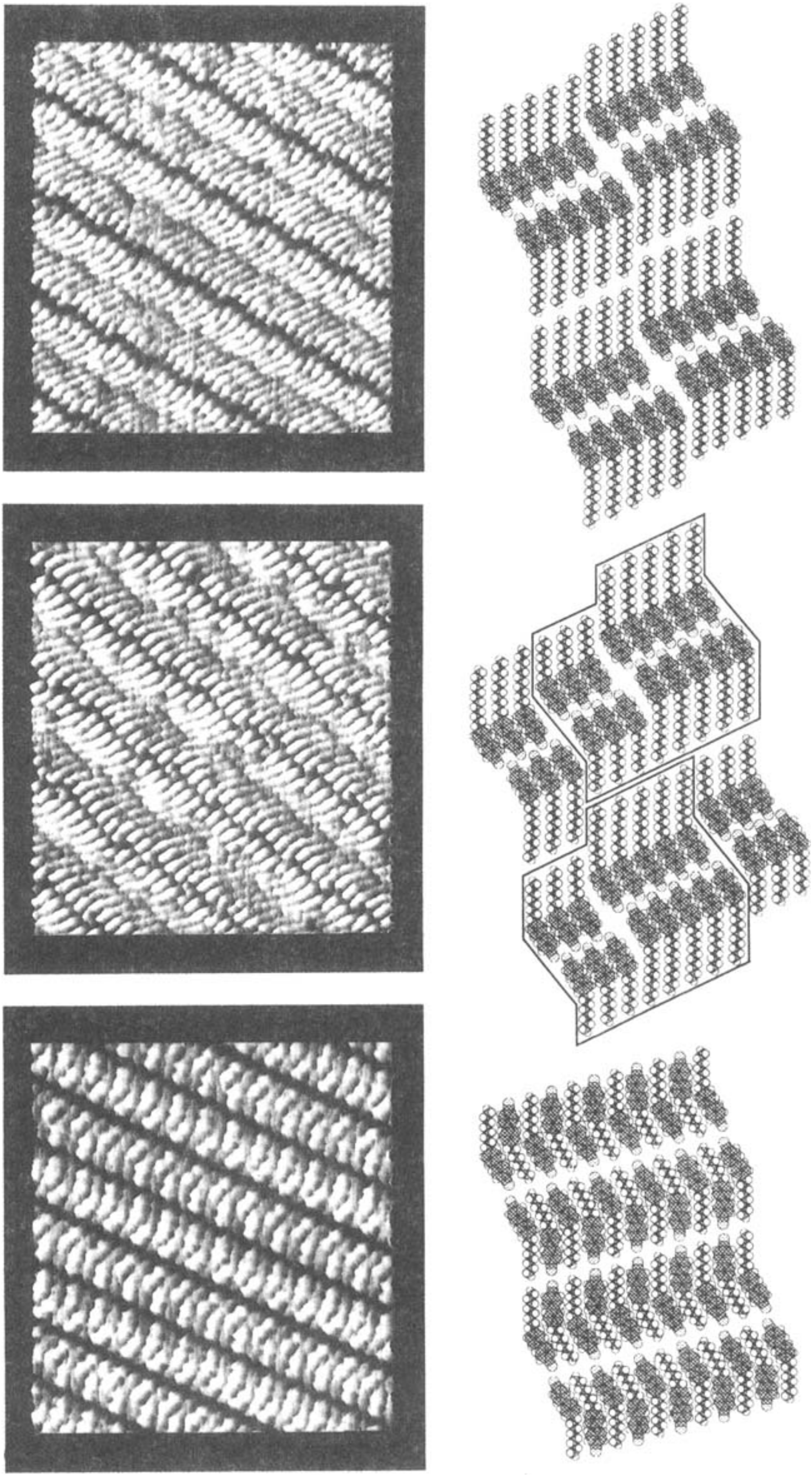

Figure 1 STM images and models showing the anchoring structures of *m*CBs on MoS2. **(a, left)** Homogeneous 8CB "Single-Row" (15 x 15 nm). **(b, middle)** Inhomogeneous (Mixed) "Double-Row" (20 x 20 nm). **(c, right)** Homogeneous 12CB "Double-Row" (20 x 20 nm). [14]

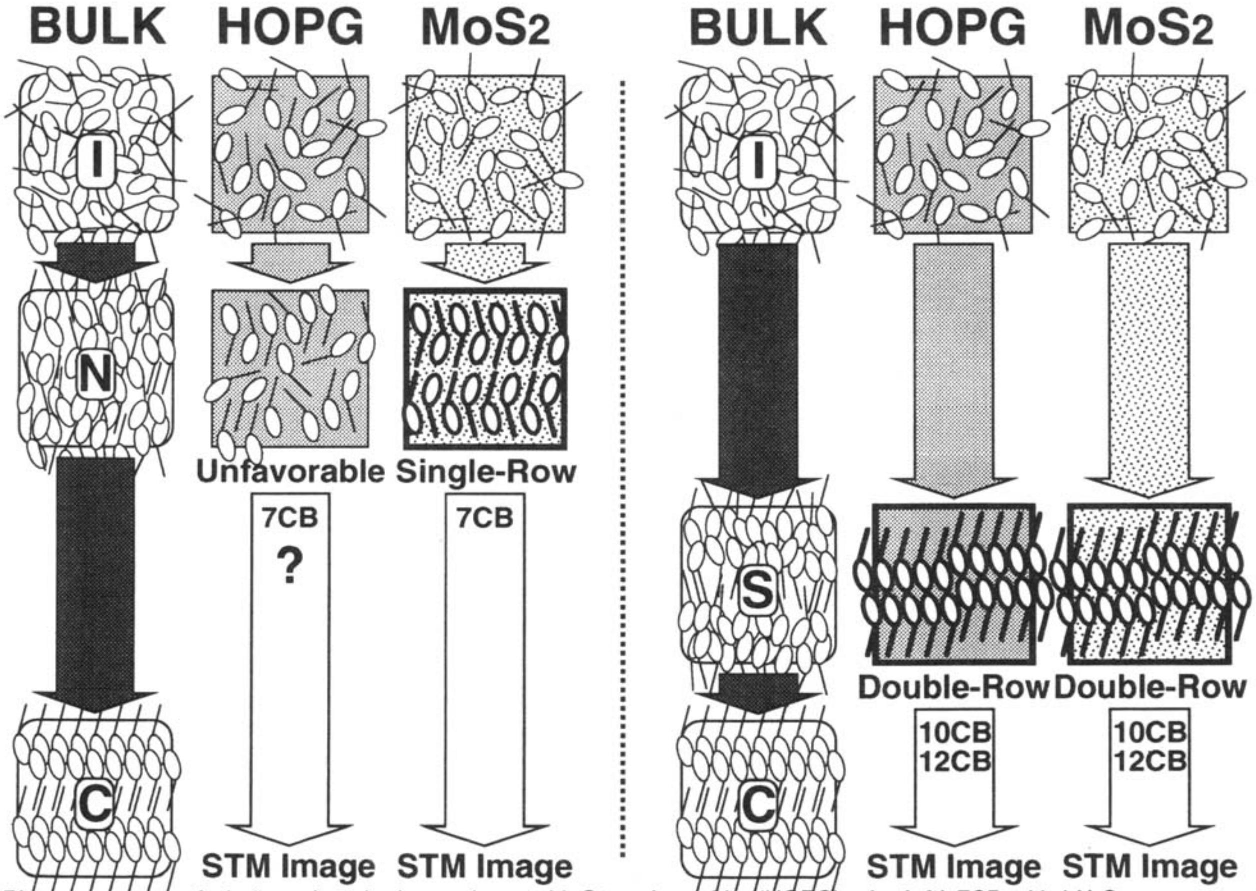

Figure 2 Phase sequences in bulk and anchoring region on MoS2 and graphite (HOPG). **(a, left)** 7CB with I-N-C sequence. Energetically favorable anchoring phase does not form on graphite because of no S phase, while "Single-Row" forms during I-N bulk transition on MoS2. **(b, right)** 10 and 12CBs with I-S-C sequence. Same "Double-Row" forms both on MoS2 and graphite during I-S bulk transition.

"double-row" type (10CB and 12CB (Fig 1(c))) in which cyano groups are facing one another. In the case of the binary mixtures, on the other hand, it has been realized that there exists an inhomogeneous (mixed) double-row type consisting of 8CB and 12CB (Fig. 1(b)).

Origin of "Single-Row" and "Double-Row" Phases

While there might exist various possible models for the formation of the anchoring phases, we have proposed the origin of the two phases from the viewpoint of their phase sequences in the bulk, as schematically shown in Fig. 2. Firstly, while 10CB and 12CB only have a smectic (S) liquid crystal phase between isotropic (I) and solid crystal (C) phases, STM images of both molecules exhibit the same double-row structure equivalent to the bulk S phase ordering. Then it is natural to assume that the double-row is formed at the interface when the phase transition takes place from I to the ordered S phase in the bulk. This double-row then can be attributed to the anchoring phase of the S phase (Fig. 2(b)). Secondly, while 7CB has only a nematic (N) liquid crystal phase, the STM image exhibits a single-row structure on MoS_2. Comparing the results for 7CB (phase sequence I-N-C) with those for 10CB and 12CB (I-S-C), the single-row can be attributed to the anchoring phase of the N phase (Fig. 2(a)). In the same manner, if the liquid crystals have a phase sequence I-N-S-C, the molecules should be ordered in the N phase which actually appears first when the temperature is decreased during the sample preparation. In fact, the STM images of pure 8CB samples, for example, which possess N phase in a higher temperature region than S phase in the bulk (I-N-S-C, Fig. 3), exhibit a single-row phase on MoS_2. From this point of view, we proposed that the single-row and double-row are attributed to the formation of anchoring phases from N and S phases, respectively.

Substrate Dependence: MoS2 and Graphite (HOPG)

Before we introduced MoS_2 as a substrate, the STM imaging of organic molecules had been carried out mainly on graphite (HOPG). Actually, it has been well accepted that 8CB, 10CB and 12CB exhibit the smectic-like double-row on graphite, while those molecules are so-called smectic liquid crystals.[3] From the viewpoint of our interpretation for the anchoring phases, however, this result on graphite suggests that 8CB did not form energetically favorable anchoring phase on graphite in the N phase (single-row), but rather in the S phase (double-row). We attributed this difference to the different surface structures of the substrates.

In the case of graphite, the cleaved surface consists of a condensed ring of six carbon atoms. In addition, it has been well known that the hydrogen orbitals of *n*-

alkanes can fit into the holes of the carbon rings on graphite with nearly commensurate condition, resulting in only three degrees of freedom for the stable anchoring of alkyl chains. The alkyl chains are then the most stable when the angle between chains is 0° or 60°. On the other hand, the cleaved surface of MoS_2 consists of a hexagonal lattice of sulfur atoms and there are at least six degrees of freedom for the anchoring of alkyl chains with multiples of 30°. The angle between alkyl chains in the single-row is 0° for every second molecule and approximately 30° for neighboring molecules. For this reason, since the 30°-required single-row is unstable on graphite, 8CB is not adsorbed stably in N phase, which appears first with decreasing temperature, but rather is adsorbed in the subsequent S phase (Fig. 3). In fact, STM images of 7CB on graphite exhibit neither single-row nor double-row structures (Fig. 2(a)). This result can be explained as 7CB forming only N phase on graphite, resulting in instability of the single-row on graphite.

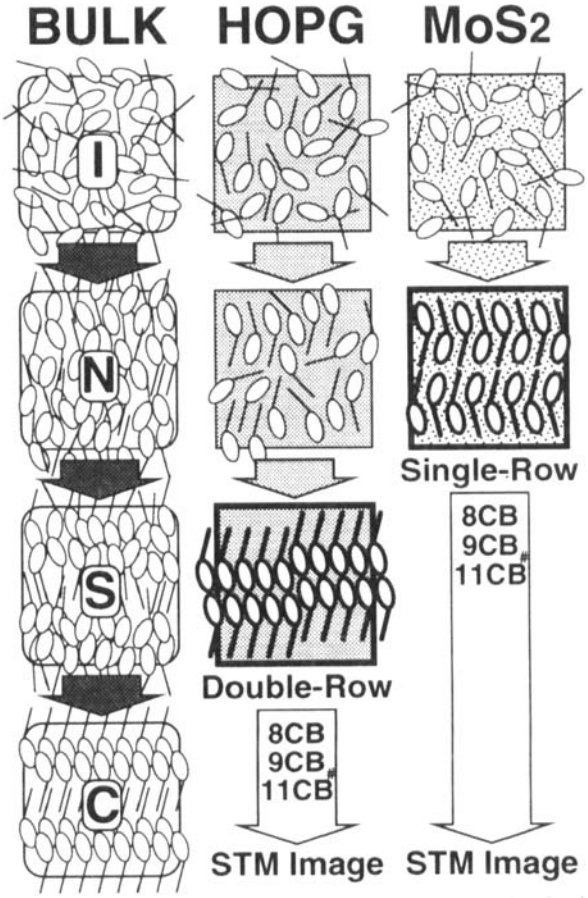

Figure 3 Substrate dependence of anchoring phase sequences. Anchoring phase transition takes place during I-N bulk transition on MoS_2, while it takes place during N-S bulk transition on graphite. # It has turned out that N-S transition of 11CB was caused by impurity. [10]

Anchoring Phase of Binary Mixtures

While there arise some questions and counter examples against our interpretation,[9-12] we have proceeded to the miscibility test using binary mixtures of *m*CBs, which has long been accepted as one of the most useful and simple methods to study the aspects of phase sequences in the liquid crystal field. Actually in the case of mixtures, bulk phase sequences can be changed continuously in various compositions. In 8CB-12CB binary mixtures, for example, there are N and S phases (I-N-S-C) below 40 mol% 12CB, but above it, there exists only S phase between I and C phases (I-S-C).

A complete set of STM images in various compositions of the 8CB-12CB binary mixtures has revealed that the anchoring phases are drastically changed from the single-row to the double-row at 40 mol% 12CB, while there are two types of double-rows, inhomogeneous (mixed) and homogeneous double-rows, as shown in Figs. 1 and 4.[13,14] This fact strongly supports our interpretation for the origin of the anchoring phases based on the phase sequences in the bulk. Namely, the single-row and double-row are determined by the I-N and I-S phase transitions in the bulk, respectively.

As schematically shown in Fig. 4, another important finding is that the ratio of 8CB and 12CB adsorbed on MoS_2 in all mixtures is different from that in the bulk; a homogeneous 8CB single-row consisting of only 8CB (100% 8CB) below 40 mol% 12CB (I-N-S-C), an inhomogeneous (mixed) double-row consisting of three pairs of 8CB and five pairs of 12CB (8CB:12CB = 3:5) from 40 to 70 mol% 12CB (I-S-C), and a homogeneous 12CB double-row consisting of only 12CB (100% 12CB) above 80 mol% 12CB (I-S-C). In addition, it has been confirmed that there exists additional phase transition at the boundary from inhomogenous (mixed) to homogenous double-row phases, while the bulk phase sequences remain the same as I-S-C.

Since these mixtures have shown a continuous miscibility without a significant phase separation, it has been considered that 12CB (8CB) should be mixed with the 8CB shingle-row (12CB double-row) ordering continuously. It is surprising, however, that 12CB (8CB) molecules are absent in the anchoring phase, in spite of the presence of 12CB (8CB) in the bulk below 40 mol% (above 80 mol%) 12CB. We assume that this is because such a homogeneous single-row (double-row) consisting of only 8CB (12CB) is energetically favorable in the anchoring phase in this mole percent region showing the phase sequence of I-N-S-C (I-S-C). If 12CB (8CB) molecules migrate into the 8CB single-row (12CB double-row), the substrate area covered with the molecules would decrease and the structure would lead to energetically unfavorable vacancies. For the inhomogeneous (mixed) double-row,

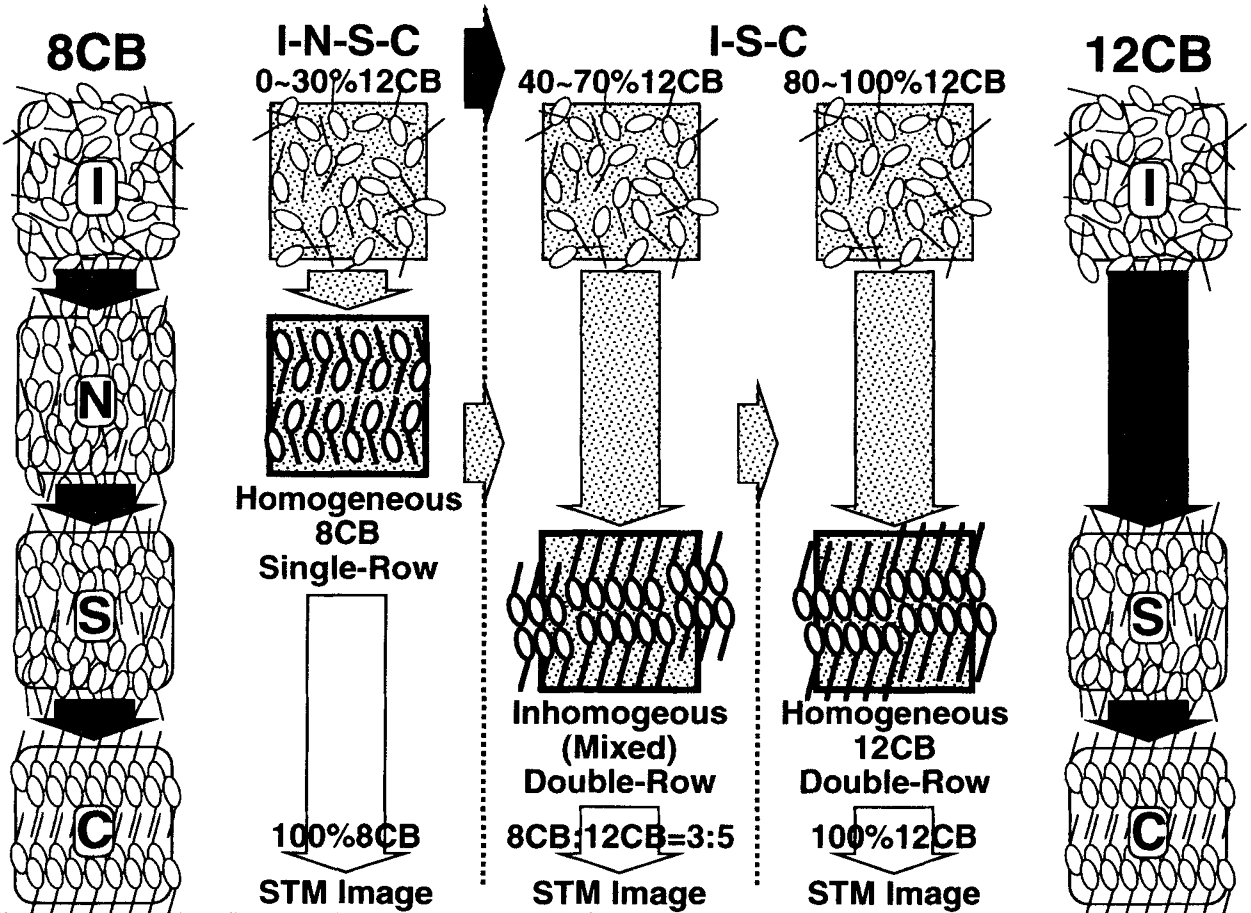

Figure 4 Phase sequences in bulk and anchoring region of 8CB-12CB binary mixtures on MoS2. Below 40 mol% of 12CB, I-Homogeneous 8CB "Single-Row", while the bulk phase sequence is I-N-S-C. From 40 to 70 mol%, I-Inhomogeneous (Mixed) "Double-Row", and above 80 mol%, I-Homogeneous 12CB "Double-Row", while the bulk one is I-S-C. In this I-S-C region, the anchoring phase transition takes place at the boundary. [14]

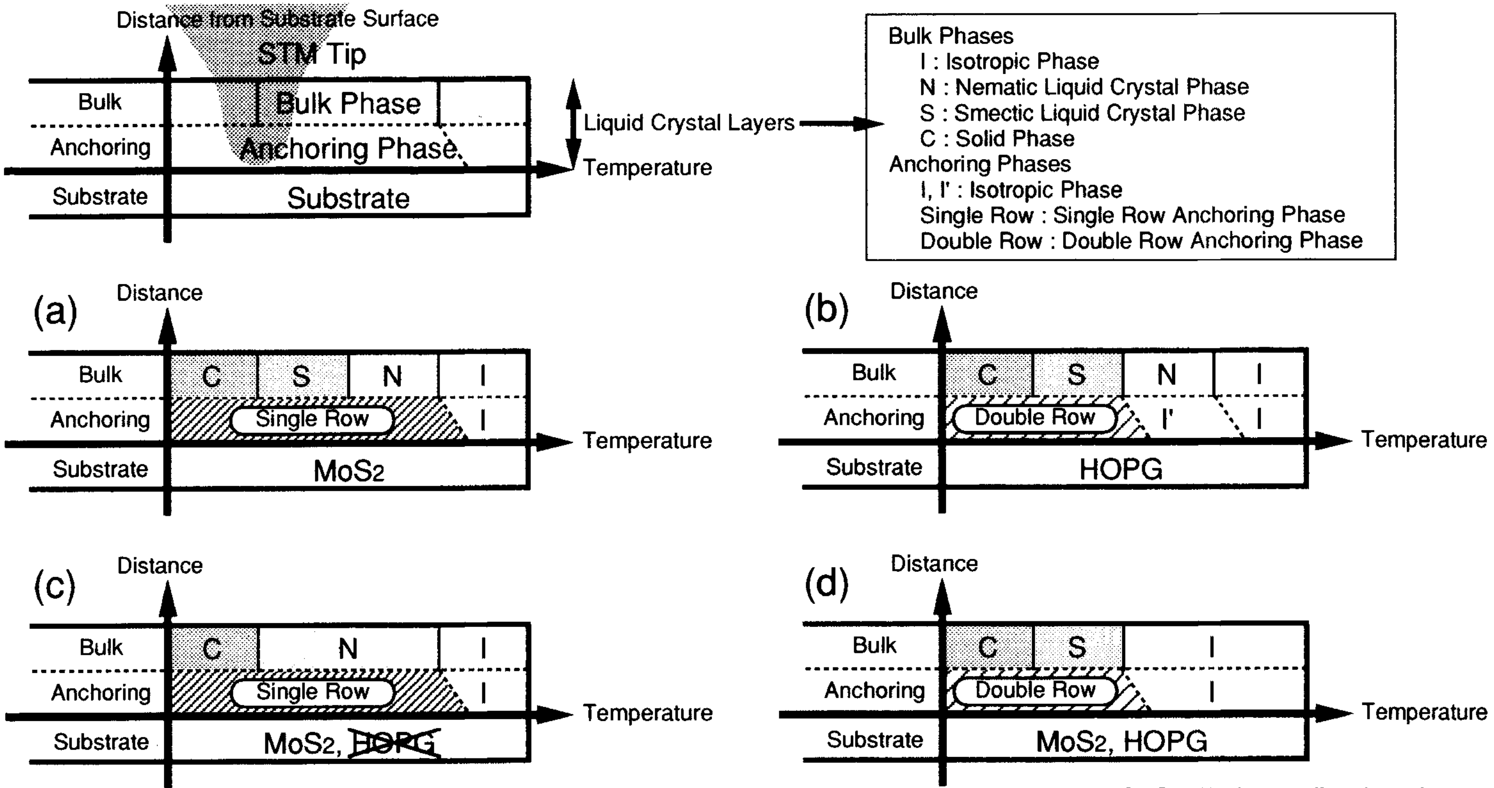

Figure 5 Schematic diagram of the phase sequences in bulk and anchoring region on MoS2 and graphite (HOPG). During cooling the substrate down to room temperature, phase transitions take place from isotropic (I) phase to solid (C) phase through liquid crystal phases, nematic (N) and/or smectic (S), in bulk. In the anchoring region, on the other hand, the anchoring phase forms during the bulk phase transition from the I phase to the ordered liquid crystal phase, N or S. **(a)** 8, 9 and 11CBs with bulk phase sequence, I-N-S-C. Anchoring phase transition takes place during I-N bulk transition on MoS2. **(b)** Anchoring phase transition takes place during N-S bulk transition on graphite. **(c)** 7CB with I-N-C sequence. Energetically favorable anchoring phase does not form on graphite because of no S phase, while it forms during I-N bulk transition on MoS2. **(d)** 10 and 12CBs with I-S-C sequence. Same anchoring phase forms both on MoS2 and graphite during I-S bulk transition.

we can attribute the behavior in the same manner to an anchoring phase consisting of the 8CB-12CB unit cell (three pairs of 8CB and five pairs of 12CB) being energetically favorable at the boundary. Then the energetically favorable mixed double-row repeating units (Fig. 1(b)) determine the ratio of 8CB and 12CB at the boundary, resulting in the inconsistency with that of 8CB and 12CB in the bulk.

CONCLUSIONS

The anchoring structures of a homologous series of *m*CBs and various bulk compositions from 0 to 100 mol% 8CB-12CB binary mixtures are directly observed on MoS_2 by STM in order to investigate the boundary condition of adsorbed molecules in the anchoring region. Although there is no necessity to have the anchoring phase transitions at the same temperature where the bulk I-N or I-S phase transition occurs, it is evident that such anchoring phase transitions are dominantly induced by the I-N or I-S phase transition and there is a strong correlation between the anchoring phase formation and the bulk phase diagram (Fig. 5). In addition, those STM images suggest that the energetically favorable repeating units at the boundary and phase separations also play an important role in the anchoring phase formation of organic molecular systems.

REFERENCES

1. J. E. Frommer, Angew. Chem., Int. Ed. Engl., 31, 1265 (1992).
2. J. S. Foster and J. E. Frommer, Nature, 333, 542 (1988).
3. D. P. E. Smith, H. Hörber, Ch. Gerber and G. Binnig, Science, 245, 43 (1989).
4. M. Hara, Y. Iwakabe, K. Tochigi, H. Sasabe, A. F. Garito and A. Yamada, Nature, 344, 228 (1990).
5. D. P. E. Smith, J. K. H. Hörber, G. Binnig and H. Nejoh, Nature, 344, 641 (1990).
6. Y. Iwakabe, M. Hara, K. Kondo, K. Tochigi, A. Mukoh, A. F. Garito, H. Sasabe and A. Yamada, Jpn. J. Appl. Phys., 29, L2243 (1990).
7. Y. Iwakabe, M. Hara, K. Kondo, K. Tochigi, A. Mukoh, A. Yamada, A. F. Garito and H. Sasabe, Jpn. J. Appl. Phys., 30, 2542 (1991).
8. M. Hara, T. Umemoto, H. Takezoe, A. F. Garito and H. Sasabe, Jpn. J. Appl. Phys., 30, L2052 (1991).
9. D. P. E. Smith, personal communication.
10. Data Sheet distributed by BDH Ltd. (Poole, UK).
11. J. S. Foster, J. E. Frommer and J. K. Spong, Proc. SPIE, Liquid Crystal Chemistry, Physics and Applications, 1080, 200 (1989).
12. W. M. Heckl, Thin Solid Films, 210/211, 640 (1992).
13. Y. Iwakabe, M. Hara, K. Kondo, S. Oh-hara, A. Mukoh and H. Sasabe, Jpn. J. Appl. Phys., 31, L1771 (1992).
14. Y. Iwakabe, K. Kondo, S. Oh-hara, A. Mukoh, M. Hara and H. Sasabe, Langmuir, 10, 3201 (1994).