

Review

DNA as functional material with one-dimensionally oriented molecular chains

Nahoko Morii† and Hisayuki Morii*

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8566, Japan

Received January 19, 2009; Accepted February 18, 2009

Materials with the structures in nanometer scale have emerging importance in the technology. In the present article, the development in molecular chain alignment of DNA was reviewed, including our recent new technologies to fabricate molecular chain-oriented DNA films. It was found that two different mechanisms play essential roles in the orientation of DNA molecular chains. One is the alignment along the boundary of a solution of DNA, which occurs as liquid crystal formation accompanying the concentrating process caused by the evaporation and the transportation in a droplet. The other is a magnetic effect, which regulates aromatic groups such as nucleic acid bases to be in parallel to a magnetic field. The best result was obtained by the combination of these for a thin-layer solution of diluted DNA. The method for DNA materials with one-dimensionally oriented molecular chains could be applied to the fabrication of the various composite materials bearing anisotropic properties. Furthermore, this is, in turn, found to be useful and convenient for determining the DNA-binding manners of pharmaceutical compounds such as anticancer reagents.

Keywords: DNA molecular chain, orientation, interfacial effect, magnetic field, anisotropic material

Introduction

Engineered membrane with one-dimensionally oriented organic molecules is one of the frontiers of developing functional materials [1-4]. The technology to regulate molecular orientation is expected to enhance the potential of materials. As for the orientation of DNA, for example, a meniscus-driven method along with the translation of an interface, the Langmuir-Blodgett method, a method using dielectric polarization, and a mechanical stretching method have been developed [5-8]. As extrinsic factors, both electric field and magnetic one are generally known for the handling of molecules including the orientation. The former is widespread and applied to apparatuses such as electrophoresis. In contrast, the latter is less popular for the purpose of molecular handling. Though these two extrinsic fields resemble each other, the actions are quite different. For example, electric field can

cause transport of molecules, however magnetic field is almost limited to bringing about the change in molecular orientation [9,10].

The representative action of magnetic field is expressed as “Aromatic ring is suited for being in parallel as for a magnetic field”. This originates in relatively large diamagnetic effect of an aromatic molecule in the orientation perpendicular to outer magnetic field (Fig. 1). In a DNA molecule, aromatic groups with anisotropic response for a magnetic field are nucleic acid bases, which form stacking structure regularly along the axis of double-stranded DNA molecule. Therefore, molecular chain of DNA should orientate in perpendicular to magnetic field. However, this does not mean one-dimensional orientation, because the perpendicular direction is not unique but distributed by 360 degrees circumferentially like vanes of a windmill in the wind. In other words, one-dimensional orientation cannot be realized if only by a magnetic field. Additionally, magnetically-induced mechanical energy is extremely smaller than the energy of thermal motion causing random orientation. The former is evaluated to be 10^{-25} – 10^{-23}

*Corresponding author: tel., +81-29-861-9466;
e-mail, morii.hi@aist.go.jp

† present address; National Institute for Materials
Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan

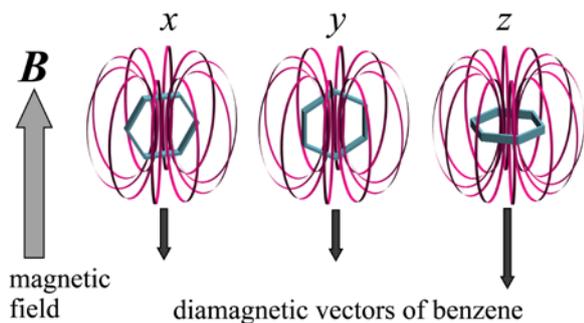


Fig. 1. Anisotropy of magnetic susceptibility of benzene as a representative aromatic compound. The benzene molecule was located in 3 orientations so as to make its 3 orthogonal directions, x, y, and z, lie along a magnetic field, respectively. The lines of induced magnetic force are shown around the molecules. Overall diamagnetic vectors are indicated with black arrows.

J for a general molecule in 10-tesla magnetic field and the latter is 2×10^{-21} J per a degree of freedom estimated with Boltzmann constant [11]. As explained below, such disadvantageous situation was overcome by intrinsic feature of DNA molecules as forming liquid-crystal structure [12]. DNA membrane with one-dimensional orientation came true due to liquid-crystal formation based on two cooperative regulations, that is, magnetic effect and interface-dependent orientation [12]. In the present paper, we describe the methods and the mechanism for one-dimensionally oriented DNA molecules, which is the world's first, referring to interesting phenomena discovered in the course of research.

The DNA membrane with one-dimensional orientation is expected to be applied to various fields. The DNA membranes including DNA-binding dyes such as intercalators will be useful as optically-anisotropic films. One promising application on the basis of the same principle is our originally developed method to determine the DNA-binding manner, which can conveniently clarify whether a newly synthesized pharmaceutical molecule, e.g., anticancer agent, is intercalator type or minor-groove binding one for DNA [13]. For fundamental science, the chain-oriented DNA membrane may contribute to revealing the electric conductivity of DNA, which would be a candidate of electronic device in future [14-16]. DNA itself as a molecule has been investigated since more than half a century ago [17]. When Wilkins and Franklin analyzed X-ray diffraction of DNA in 1930's, it was necessary to

align the direction of DNA molecular chains [18,19]. The atomic-resolution structure was differently revealed by X-ray crystallography for oligo DNA in 1980 at last [20]. Meanwhile, various efforts have been made to realize the orientation of DNA molecules, resulting in the developments of a drawing-brush method, a stretch process, and induced polarization in a solution under the electric field [5,6,7,21]. These methods have respective merits, however our method applying the magnetic field gave the best orientation of DNA in a solid film [12].

Methods for preparation of DNA solid film with molecular chain orientation

Recently, mass production of DNA as a material becomes possible by using a large amount of salmon sperm as by-product of food industry. In our study, such commercially available DNA was used only after sonication to provide several classes of averaged molecular weight. In order to realize molecular orientation we examined two different methods, namely 'method A' and 'method B', for the fabrication of DNA films as described below (Fig. 2). The 'method A' involves the process to dry a droplet

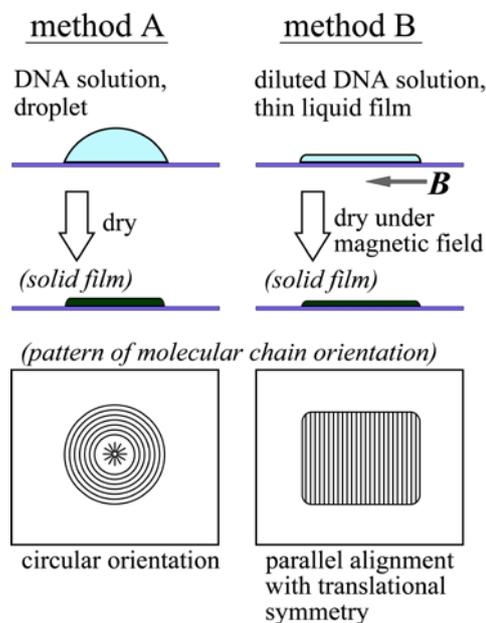


Fig. 2. Two types of method for preparation of DNA solid films. In the method A and B, the drying process starts from a thick-layer solution and a thin-layer one on glass plates, respectively. As for the method B, the DNA solution is relatively diluted and a horizontal magnetic field is given all through the drying process. In the bottom of the Figure, the patterns of molecular orientation are exhibited with thin lines and curves.

of DNA solution in the ordinary atmosphere, providing DNA solid films bearing a strange pattern of molecular orientation made up of both annular and radial ones as shown in Fig. 2 [22]. On the other hand, ‘method B’ involves the drying process for thin-layered DNA solution under a magnetic field [12]. For this method, it is crucial that the initial concentration of DNA solution is rather low enough not to form liquid crystal structure. The DNA film with good molecular orientation was obtained at the initial concentration of 50 mM DNA, and 10 tesla magnetic field brought about a favorable result.

Evaluation and analysis on molecular orientation of DNA

The X-ray diffraction of hydrated DNA fibers is well known to show X-shaped pattern characteristic of helical structures. Also, there appears the intensive axial diffraction of 0.34 nm corresponding to the interval of stacking base-pairs [19]. Our DNA film obtained by method B using a magnetic field was found to have a similar X-ray diffraction pattern as above. By using X-ray radiation from three different directions, the orientation of DNA in the film was analyzed. The dependence of diffraction intensity at 0.34 nm on the azimuthal angles is shown in Fig. 3. Characteristically, the radiation along the normal of the film (Fig. 3a) and that tilted to the direction of a magnetic field used for the preparation (Fig. 3c) gave homologous diffraction patterns (Figs. 3b and 3d, respectively). On the other hand, the diffraction pattern for the film tilted in a perpendicular manner as for the case of Fig. 3e showed rather broad peaks (Fig. 3f), which had biased intensities. These results suggest that the DNA molecular chains are oriented in parallel each other and in perpendicular to the magnetic field (Figs. 3g and 3h). In conclusion, the unique orientation of DNA molecular chains in parallel for the film can be realized by the method B [22].

The orientation of DNA molecular chains could be also confirmed by polarization microscopy. The polarization property was analyzed by using the equipment of a sensitive tint plate at 530 nm (Fig. 4a). Based on the color changes caused by the rotation of the sample by 45 degrees, the DNA film prepared by a drawing-brush method was found to have almost one-dimensional orientation of DNA

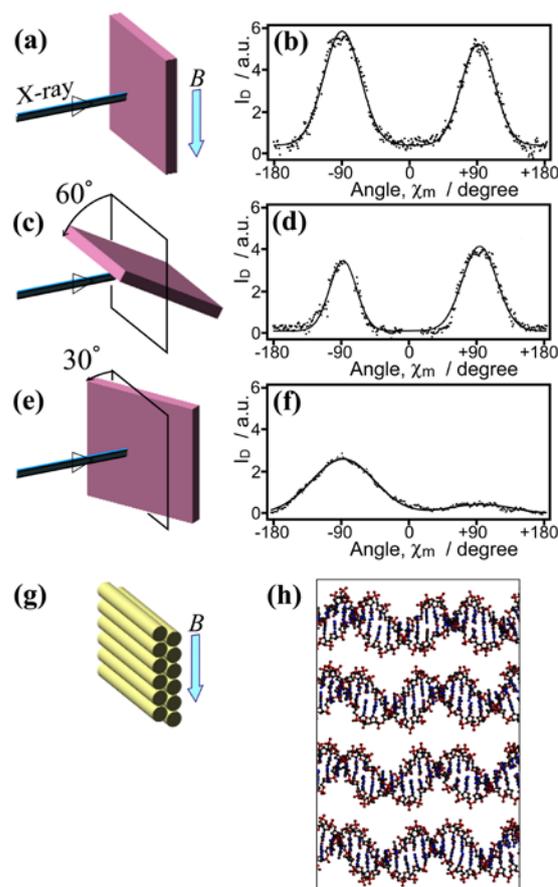


Fig. 3. Evaluation on the extent of molecular chain orientation. The X-ray was radiated to DNA films mounted at vertical or tilted positions (a, c, and e). The diffraction intensities, I_D , corresponding to the spacing periodicity of base-pair stacking were plotted against azimuthal angles, χ_m (b for a, d for c, and f for e). The estimated molecular chain orientation in the film is exhibited with a cylinder model (g) and a ball-and-stick model (h) in the same location. The magnetic field for the fabrication is indicated with an arrow B . The structural model in Fig. 3h was adopted from the data 1IO4 in Protein Data Bank.

molecules (Fig. 4b). Similarly, the DNA film by method B had well-aligned one-dimensional orientation (Fig. 4c). The homogeneous appearance of colors for the latter film means a uniform thickness of the film.

Additionally, by UV spectroscopy with linearly polarized light it was revealed that these DNA films have linear dichroism reflecting the anisotropy of electronic transition dipole moments. The absorbance of the films was the largest at the arrangement where the polarization vector accords with the plane of nucleic acid bases. This is consistent with the result by X-ray diffraction, so that the polarization UV

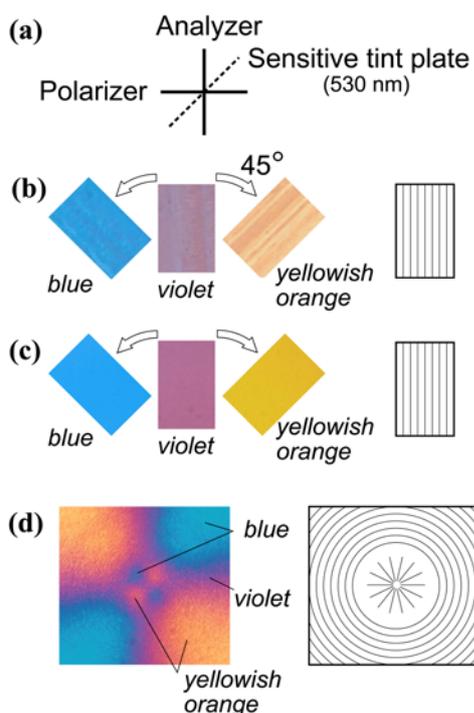


Fig. 4. Analysis on molecular chain-oriented DNA films by polarization microscopy with sensitive tint plate. The observation was carried out using the sensitive tint plate inclined by 45 degrees (a). The DNA films prepared by drawing-brush method and by the method B changed in apparent colors depending on the rotational angles (b and c, respectively). The film prepared by the method A showed two different manners of orientation (d). Estimated molecular chain orientations are exhibited with thin lines and curves at the right of the corresponding photographs (b, c, and d). (See original Figures in the references for the actual colors under observation [12,22].)

measurement seems convenient to identify the direction of DNA molecular orientation.

In the course of experiment for molecular orientation, we observed a peculiar pattern of orientation in a DNA film prepared by method A without a magnetic field (Fig. 4d). Since the difference in colors, i.e., blue or yellowish, corresponds to the orientation of molecules, we can easily identify the directions of DNA molecular chains at respective positions by the method using a sensitive tint plate. The orientation of DNA in this film was rotationally symmetric as for the center of the droplet of initial DNA solution. At the central part of the droplet-derived film, the DNA chains oriented in radial directions. In contrast, at its outer region the orientation was found completely annular. In the region around the boundary of these two, DNA molecular chains were less-ordered. These

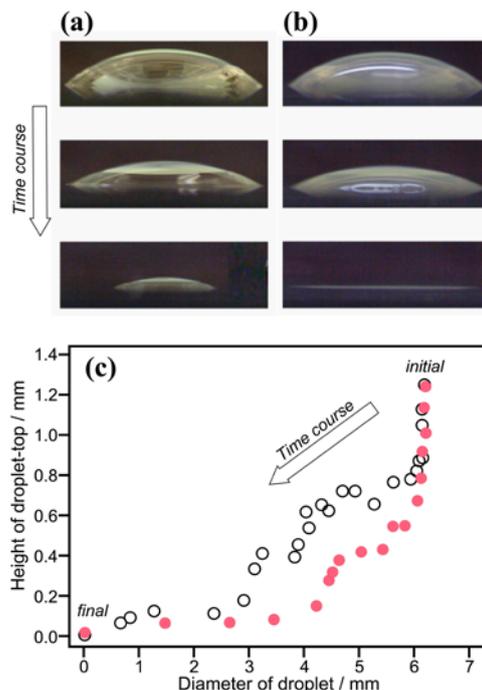


Fig. 5. Time course of the drying process. The changes in the side views of droplets are shown from the top to the bottom (a for pure water, b for DNA solution). The correlation between the diameter and the height of a droplet was plotted (c; open circle, water; closed circle, DNA solution).

orientation patterns seems to be brought about in a manner of ‘interface-induced orientation’ as explained below.

Mechanism for the orientation of DNA by interfacial effect

The DNA film involving annular orientation of molecular chains can be obtained by drying a droplet of DNA solution [22]. To reveal the mechanism underlying this phenomenon, we tracked the time course of drying for a droplet solution on a glass plate in the atmosphere (Fig. 5). After an initial quick decrease in the thickness, a droplet of pure water underwent a further drying course, keeping the contact angle constant at the edge (Figs. 5a and 5c). In other words, the droplet became small in a similar form during this process. In contrast with pure water, a droplet of DNA solution underwent a transition of lowering the thickness of the droplet without changing its diameter largely (see Fig. 5b and the region from 6 to 4.5 nm in diameter shown in Fig. 5c). Following this process, only the diameter decreased from 4.5 to 2 nm, and at the final stage the droplet became dried up rapidly.

The rate of decrease in the thickness was evaluated as 0.08 mm/min in this experiment. On the other hand, the diffusion rate of DNA molecules is estimated on the basis of Einstein-Stokes equation to be only one tenth of the above (Fig. 6a) [23]. Therefore, it is suggested that longer DNA molecules are prone to remain near air-liquid interface due to

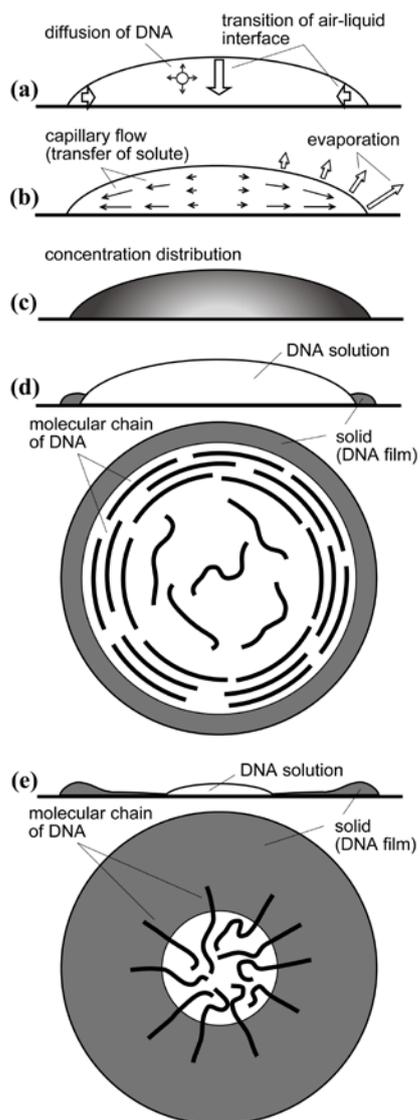


Fig. 6. Proposed model for the phenomena occurring in the drying process. **a**, Diffusion of DNA and transition of air-liquid interface, indicating the former is slower than the latter. **b**, Uneven evaporation from the surface of a droplet and capillary flow in a solution induced by the evaporation. **c**, Estimation for the distribution of DNA concentration. **d**, The early stage of the local formation of a solid DNA film at the boundary edge of a droplet. The top plan view exhibits the formation of molecular chain alignment along the shape of the edge. **e**, The closing stage of film formation. The rapid transition of the boundary towards the center causes the trailing of molecular chains.

such slow movement (Fig. 6c). In fact, the concentration of DNA near the surface of a solution was found to be higher than that at its bottom by analyzing local solutions sampled directly. As well as the vertical concentrating as described above, the horizontal accumulation of the mass is likely to occur in a drying course, because the DNA film thus prepared was found to have unequal thickness along radial direction (Fig. 6e). Especially, the region close to the initial edge was remarkably thick. Thus, the first stage of a drying course can be elucidated by both the accumulation at the air-liquid interface and the transportation to the edge of the droplet, which seem to be induced by the evaporation of water (Figs. 6a and 6b). The thick edge region of the film should be brought about by the radial flow called 'capillary flow' toward the boundary of the droplet, which occurs due to relatively high rate of evaporation in the edge region [24].

Though the initial concentration is quite low in comparison with that for the formation of DNA liquid crystal, the local concentration near the surface and also at the edge of a droplet should come up to be high enough to form the liquid crystal owing to the evaporation. The process of accumulation also seems to cause molecular packing of DNA along the surface of the solution, which would lead to the liquid crystal. Since the molecular orientation of DNA is aligned in parallel to the outer edge of the droplet as revealed by polarization microscopy (Figs. 4d and 6d), the formation of liquid crystal should be conducted by the boundary of the droplet.

This hypothetical model for the annular orientation of DNA molecules could be supported by other related experiments (Table 1). In the case using DNA samples with short molecular chains and/or single-stranded ones, the obtained films were found to have no molecular orientation. This is probably due to their small hydrodynamic radii. In addition, the preparation of DNA film under low temperature resulted in poor orientation. In these unfavorable conditions, it is suggested that the movement of DNA molecules seems to be faster than the transition speed of air-liquid interface due to rapid diffusion or slow decrease in the thickness of a solution. These experiments clearly showed that relatively low motility of the molecules in comparison with the accumulation and the transportation is an important

Table 1. Comparison of various conditions for the preparation of DNA solid films. The case 1 is a standard and the others, the case 2, 3, and 4, are different from the case 1 in the points denoted by underlined bold characters. (* theoretically calculated values, ** experimentally obtained values)

DNA sample and condition	case 1	case 2	case 3	case 4
Strand type	double	double	double	<u>single</u>
Molecular weight [kbp]**	29	<u>1</u>	29	29
Chain length [nm]	1000	30	1000	1000
Statistical chain element [nm]*	100	100	100	1
Radius of coil structure [nm]*	500	50	500	50
Temperature [°C]**	23	23	<u>0</u>	23
Averaged rate of diffusion [mm/min]*	8	20	8	20<
Descending rate of liquid surface [mm/min]**	80	80	4	80
Extent of molecular chain alignment	high	low	very low	very low

factor for molecular orientation of DNA. In summary, it is proposed that annular orientation of DNA molecular chains is based on the mechanism illustrated in Figs. 6a–6d.

The molecular chain orientation in a central region of the droplet was different from that in a edge region as mentioned above, showing radial orientation (Fig. 6e). This orientation occurred at the final stage of a drying course. Since the boundary of a droplet displaces rapidly to the center, the accumulation of DNA molecules seems to be difficult. Instead, each molecular chain should exist in both solid and liquid phases at once in a form spanning the liquid-solid interface. Accompanying the displacement of the interface, a part of DNA molecule in liquid phase seems to be transported but the other part remains fixed in solid phase. Consequently, it is suggested that the rapid displacement of the interface make DNA molecular chain trailed along the direction to the center (Fig. 6e). Thus, two different manners of molecular chain orientation occur depending on the speed of liquid-solid interface.

Mechanism for magnetically-induced orientation of DNA

Organic compounds are generally diamagnetic [11]. Especially, aromatic compounds such as benzene also have remarkable anisotropy in magnetization property, which derives from spatially anisotropic π -electron system [25]. Aromatic groups have larger diamagnetic susceptibility in the direction along its normal than in the other directions, so that the parallel orientation of the normal with respect to a magnetic field is relatively unstable (Fig. 7). Similarly, DNA molecules are expected to have

the anisotropy because of the structure with nucleic acid bases stacked in parallel. The magnetic susceptibilities were experimentally evaluated for 4 kinds of nucleic acid bases in 1960's [26]. Then, it was reported that DNA molecules actually respond to a magnetic field in a solution [27,28]. Since the normal of each nucleic acid base is in line with the axis of molecular chain of double-stranded DNA, the molecular chains of DNA should favor the orientations perpendicular to a magnetic field (Fig. 8a). This is at least consistent with the experimental results shown in Fig. 2. However, DNA molecular chains under a magnetic field cannot have a unique orientation in a solution but exist in the forms along various directions with two-dimensional freedom as shown in Fig. 8b. Therefore, another effect in addition to a magnetic one should be taken into

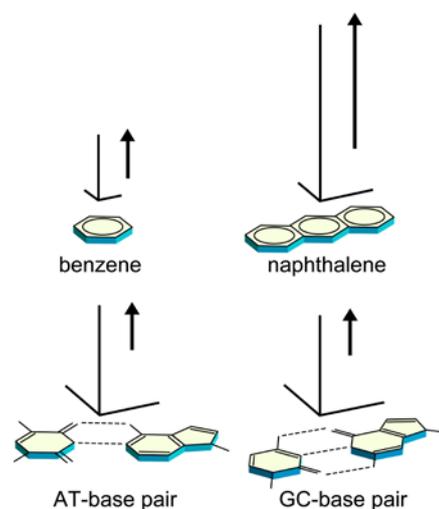


Fig. 7. Diamagnetic susceptibility of the aromatic compounds and the base pairs of DNA. Three orthogonal line segments above the molecules indicate the components of the susceptibility along x, y, and z coordinates of the molecules. The vectors exhibit the direction and the intensity of overall anisotropy.

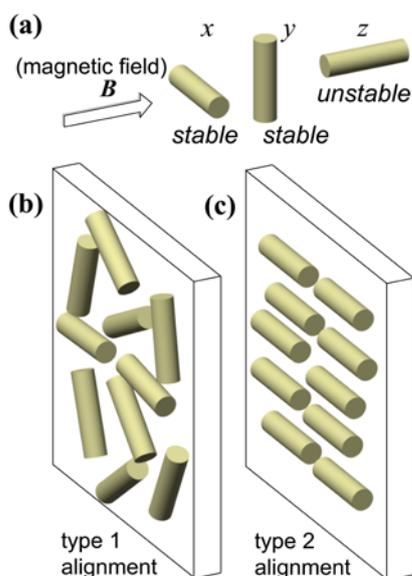


Fig. 8. Model illustration for the orientation of DNA molecular chains. **a**, Comparison of the stabilities for 3 orthogonal orientations under a magnetic field B . DNA molecular chains are represented with cylinders. **b**, Probable orientations of DNA chains in a solution under a horizontal magnetic field. The directions of the molecular chains distribute 2-dimensionally. **c**, Molecular chain alignment by the interfacial effect in addition to the orientation shown in Fig. 8b.

consideration to elucidate the formation of DNA films with completely aligned molecular chains as Fig. 8c.

By the simple method as drying in a magnetic field, we have succeeded in preparing highly-ordered DNA films [12]. The extent of molecular chain orientation seems superior to that by the method without a magnetic field, such as method A in Fig. 2 or a drawing-brush method. As for the preparation of molecular chain-oriented DNA films under a magnetic field, we have proposed the mechanism as follows. In a early stage of drying from thin-layer solution according to the method B shown in Fig. 2, DNA molecules are oriented to various directions but lie in a plane directed by a horizontal magnetic field (Fig. 8b). Subsequently, following the evaporation from the surface of the solution, DNA molecules are concentrated in parallel to fit the air-liquid interface. When the concentration near the surface rises above a critical concentration for liquid-crystal formation, the parallel orientation of DNA chains are fixed from top to bottom to be a solid DNA film finally. Thus, for the molecular chain orientation by the method B, it is concluded that both the magnetic field and the

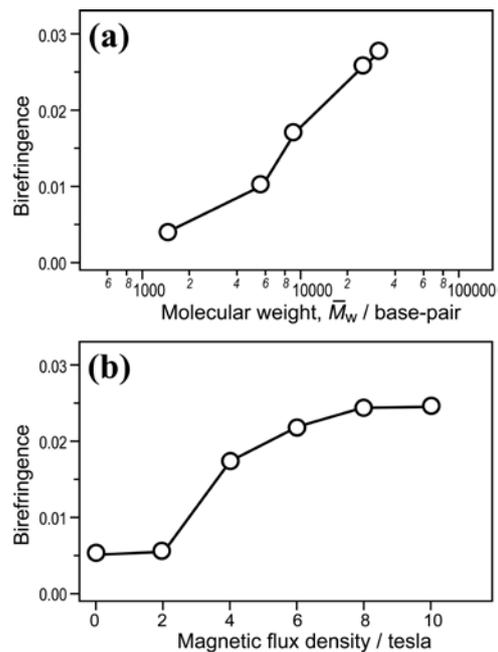


Fig. 9. Dependence of the extent of DNA molecular orientation on the molecular weights (**a**) and magnetic intensities (**b**). The extent of orientations was evaluated with the values of birefringence. The orientation at 0 tesla occurred only by the interfacial effect.

interfacial effect are crucially important [12].

In addition, unlike with thin-layer solution system, drying thick-layer solution of DNA in a magnetic field resulted in very characteristic zonal patterns of molecular orientation depending on the magnetic intensity (Figure not shown). In this case, major interfacial effect appeared at the parts of the boundary edge of a droplet locating in perpendicular to a magnetic field. For not only the method of drying from thin-layer solution but also that from thick-layer one, the significant molecular orientation is perpendicular to a magnetic field and the extent of regularity was found remarkably high. It is important for good results that the initial concentration of DNA is low enough to assure molecular motion for orientation without causing a tangle in the course of concentrating.

Effect of molecular weight and magnetic intensity on molecular orientation

In order to explore the possibility for the improvement of molecular orientation, its dependence on the molecular weight was examined. DNA molecular chains are known to be cut

mechanically by the action of sonication without losing intact double-stranded structure. By selecting the time period of treatment with ultrasonic wave, various DNA samples with different averaged molecular weights can be prepared. DNA solid films were fabricated from the solutions of these DNA samples by the method B in the same conditions under a magnetic field. The extent of molecular chain orientation was evaluated as birefringence by using polarization microscopy (Fig. 9a). As increasing the averaged molecular weight, the birefringence of the DNA films increased. This suggests that the molecular orientation depends on the balance between the motility and the liquid crystal formation. Probably, DNA molecules with larger molecular weight would have an advantage in respects of slow diffusion, slow rotation, and large stabilization energy by a magnetic field, which are favorable for the molecular alignment through the process from its concentrating to the formation of liquid crystal.

By means of similar experiments under a magnetic field with various intensities, the extent of molecular alignment was evaluated. The birefringence of the obtained DNA films were plotted against magnetic intensities (Fig. 9b). The orientation of molecular chain was significantly enhanced above 4 tesla of a magnetic field. And, it reached a saturation level at 8 tesla, so that the regulation of the orientation by a magnetic field should sufficiently overcome the randomization due to thermal motion at this magnetic intensity.

General aspects on magnetic effect for polymer chains

The availability of a magnetic field for molecular orientation is not limited to the process from isotropic solution to anisotropic solid films as the case of DNA described above. For example, synthetic polymers such as polyamide are fabricated by the method of melt spinning in some cases to have anisotropic properties involving mechanical toughness and excellent thermal resistance. The application of a magnetic field may be effective in regulating the molecular chain alignment of such polymers at the stage after the achievement of basic orientation by a mechanical method. Polyamides contain at least amide groups and, in a case, aromatic groups in a main chain. The normals of these

π -electron systems are generally perpendicular to the axis of the polymers in contrast with the case of DNA. Therefore, these two representative types of polymers are illustrated in Fig. 10, where DNA and polyamide are indicated with cylinders and slender plates, respectively, at the stage that some preliminary orientations of polymer chains are performed.

Considering the anisotropic magnetic susceptibility, the application of a magnetic field in the direction perpendicular to polymer axes seems effective for the orientation of DNA as shown with a short black arrow (Fig. 10a). On the other hand, some of polyamide chains are likely to be disconcerted at first as shown with a white arrow (Fig. 10b). However, this change is expected to be settled in the form parallel to a magnetic field, so that this process may be effective for the secondary regulation of polyamide chains. In contrast, the application of a magnetic field parallel to polymer axes seems to cause the dislocation of aligned polymer chains of DNA (Fig. 10c). Though, the parallel magnetic field will be advantageous to the regulation of polyamide chains as shown with short

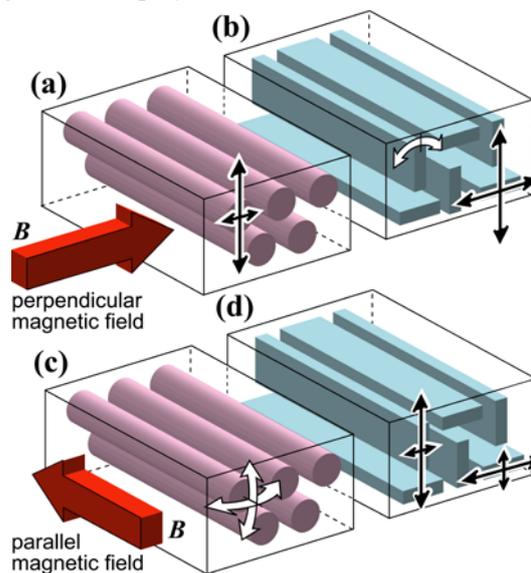


Fig. 10. Regulation of molecular orientation by a magnetic field for the different types of polymers in semi-oriented states. A magnetic field was given from the direction perpendicular (a and b) and parallel (c and d) to the axes of the polymers. DNA was represented with cylinders (a and c) and polyamide chains were with slim thin plate (b and d). Black arrows indicate possible extents of wobbling motions under a magnetic field. White arrows express the forces towards stable orientations originated from the anisotropic susceptibility.

black arrows (Fig. 10d). Thus, depending on the initial states of polymer chain orientation, the method with a magnetic field would be available for further regulation of the orientation. It should be noted that the magnetic effect has permeability even for the deep inside of materials. This is a great merit for the regulation of molecular orientation and further development in the applications is expected.

Composite materials of molecular chain-oriented DNA with other compounds

In the previous sections, DNA solid films with well-aligned molecular chains were described. For the DNA films by the method B, it was revealed that the orientation of DNA molecular chains are regulated by both the magnetic field and the interfacial effect including the formation of liquid crystal. The simplicity of the procedure is one of the advantages in its applications. As for the extent of molecular orientation, the X-ray diffraction analysis gave relatively broad patterns (Fig. 3), which can be attributed to that the normals of nucleic acid bases intrinsically incline by a little degrees from the axis of a molecular chain. The actual regularity in the orientation is estimated to be rather fairly high enough to be used in various applications.

Based on the methods for the fabrication of molecular chain-oriented DNA films, the composite DNA films with organic dyes were developed [13]. The dye-DNA films were prepared by drying the mixed solutions of DNA and the dyes such as acridine orange, ethidium bromide, and Hoechst 33258 under a magnetic field. The obtained composite films were found to have excellent optical anisotropy, exhibiting not only dichroism in optical absorption but also secondary dichroism in fluorescence emission. The optical anisotropy of these dye-DNA films seem to be comparable to organic liquid crystals. The advantage may be expressed in the easy selection of specific wavelengths bearing dichroism only by the choice of organic dyes. It is obvious that the anisotropy of dye-DNA films is closely relevant to the well-aligned orientation of DNA chains and specific binding manners of the dyes, i.e., the minor-groove binding or the intercalation.

In addition, this method was applied for the composite films of DNA and porphyrins [29].

Though it is predicted that the porphyrin derivatives are too large to undergo specific binding manners for DNA unlike the dyes such as acridine orange, several types of porphyrins were found to have characteristic orientation in porphyrin-DNA films. Tetra(4-sulfonatophenyl)-porphyrin formed H-aggregation bearing the orientation, in which the normal of porphyrin plane was parallel to the axis of DNA. In contrast, tetra(*N*-methylpyridinium-4-yl)-porphyrin exhibited the patch-like binding for the surface of DNA. These finding may pioneer a new technology for molecular orientation in addition to that the chain-aligned DNA can provide linear void space for guest molecules.

In summary, composite films based on molecular chain-oriented DNA are expected to be promising anisotropic materials. The convenient procedure for their preparation would enhance the availability of this technique. Furthermore, this method is useful not only for the development of anisotropic composite materials but also for analysis of the binding manners of organic compounds to DNA. It should be noted that the latter application may enable the high throughput analysis for DNA-binding manners of pharmaceutical products.

Acknowledgments

The authors are grateful to Prof. Dr. Giyuu Kido (National Institute for Material Science) and Prof. Dr. Takeo Konakahara (Tokyo University of Science), and also to the members of the related laboratories in AIST and NIMS for various supports in the works described here.

References

1. Takenaka, S., Yamashita, K., Takagi, M., Uto, Y., Kondo, H. *Anal. Chem.* **2000**, *72*, 1334-1341.
2. Gu, J., Cai, L., Tanaka, S., Otuka, Y., Tabata, H., Kawai, T. *J. Appl. Phys.* **2002**, *92*, 2816-2820.
3. Uemura, S., Shimakawa, T., Kusabuka, K., Nakahira, T., Kobayashi, N. *J. Mater. Chem.* **2001**, *11*, 267-268.
4. Liang, X., Asanuma, H., Komiyama, M. *J. Am. Chem. Soc.* **2002**, *124*, 1877-1883.
5. Bensimon, A., Simon, A., Chiffaudel, V., Heslot, F., Bensimon, D. *Science* **1994**, *265*, 2096-2098.
6. Okahata, Y., Kobayashi, T., Tanaka, K., Shimomura, M. *J. Am. Chem. Soc.* **1998**, *120*, 6165-6166.

7. Kabata, H., Krosawa, O., Arai, I., Washizu, M., Margaron, S. A., Glass, R. E., Shimamoto, N. *Science* **1993**, 262, 1561-1563.
8. Ijio, K., Shimomura, M., Tanaka, M., Nakamura, H., Hasebe, K. *Thin Solid Films* **1996**, 284, 780-783.
9. Worcester, D. L. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, 75, 5475-5477.
10. Kimura, T., Ago, H., Tobita, M., Ohshima, S., Kyotani, M., Yumura, M. *Adv. Mater.* **2002**, 14, 1380-1383.
11. Kitazawa, K., Ed. *Magnetic Science*, IPC Press, Tokyo, **2002**.
12. Morii, N., Kido, G., Suzuki, H., Nimori, S., Morii, H. *Biomacromolecules* **2004**, 5, 2297-2307.
13. Morii, N., Kido, G., Konakahara, T., Morii, H. *J. Phys. Chem.* **2005**, B 109, 15636-15644.
14. Magan, J. D., Blau, W., Croke, D. T., McConnell, D. J., Kelly, J. M. *Chem. Phys. Lett.* **1987**, 141, 489-491.
15. Yang, C. Y., Yang, W. J., Moses, D., Morse, D., Heeger, A. J. *Synth. Met.* **2003**, 137, 1459-1460.
16. Maeda, Y., Kawai, T. *Jpn. J. Appl. Phys.* **1998**, 38, L1211-1212.
17. Watson, J. D., Crick, F. H. C. *Nature* **1953**, 171, 737-738.
18. Wilkins, M. H. F., Stokes, A. R., Wilson, H. R. *Nature* **1953**, 171, 738-740.
19. Franklin, R. E., Gosling, R. G. *Nature* **1953**, 171, 740-741.
20. Wing, R., Drew, H., Takano, T., Broka, C., Tanaka, S., Ikura, K., Dickerson, R. E. *Nature* **1980**, 287, 755-758.
21. Brandes, R., Kearns, D. R. *Biochemistry* **1986**, 25, 5890-5895.
22. Morii, N., Kido, G., Suzuki, H., Morii, H. *Biopolymers* **2005**, 77, 163-172.
23. Kuhn, H., Försterling, H.-D. *Principles of Physical Chemistry*; John Wiley & Sons Ltd., New York, **1999**; Japanese tr. ed., Maruzen-co-Wiley, **2002**.
24. Deegan, R. D., Bakajin, O., Dupont, T. F., Huber, G., Nagel, S. R., Witten, T. A. *Nature* **1997**, 389, 827-829.
25. Pauling, P. J. *Chem. Phys.* **1936**, 4, 673-677.
26. Marmur, J., Doty, P. *J. Mol. Biol.* **1962**, 5, 109-118.
27. Veillard, A., Pullman, B., Berthier, G. *C. R. Acad. Sci.* **1961**, 252, 2321-2322.
28. Maret, G., Schickfus, M. V., Mayer, A., Dransfeld, K. *Phys. Rev. Lett.* **1975**, 35, 397-400.
29. Morii, N., Kido, G., Konakahara, T., Morii, H. *Biomacromolecules* **2005**, 6, 3259-3266.

Communicated by Masayuki Oda