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1.Highlights in 2007

The bent-shaped molecule with a central naphthalene core, N(2,7)-12-PIMB, forms the low birefringent B2 (LB-B2) phase with the TGB-like helical structure and, then the low birefringent B4 (LB-B4) phase on cooling from the isotropic melt. By applying the electric field, the LB-B2 phase is altered to the highly birefringent B2 (HB-B2) phase because of unwinding of TGB-like helix. The HB-B2 phase is transformed to the HB-B4 phase without a loss of birefringence. These four phases show the characteristic circular dichroism spectra. The source of the chirality in achiral banana molecular system and the correlation in the chirality between these phases are discussed.

Thermoelastic response of a cross-linked main-chain polyester was examined in the nematic temperature region from 80°C to 150°C. The monodomain nematic elastomer decreased its length in the orientation direction by 45% on heating from 80°C to 150°C and recovered it on cooling to 80°C without change in the degree of orientational ordering. This reversible distortion of the nematic elastomer is well explained by the configurational change of the polymer chain including hairpin folding, the probability of which is proportional to the Boltzmann factor of hairpin energy.

Rigidity and chirality are topical characteristics of α-helical polypeptides and explain the tendency for polypeptide molecules to form a cholesteric liquid crystal (LC) in concentrated solutions. The transition behavior from isotropic to LC solution and the resulting superhelicoidal cholesteric structure form the basis of research for clarifying the self-organization of biological macromolecules in living material systems. Another feature of polypeptide helices, the polarity, is also important. Since the helical conformation of polypeptides is built up by intramolecular hydrogen bonds between the proton donor N-H group and the proton accepter C=O group, residue dipole components accumulate along the polymer chain, producing an extremely large dipole moment along the molecular axis; for example, μ = 3000D for a single α-helical chain with a degree of polymerization of 1000. This extremely large dipole moment is of interest because of the possibility of forming a polar or ferroelectric liquid crystal, which is predicted by theoretical calculations and computer simulations. However, few experimental researchers have been concerned with studies related to this area. Here, we report the certain second-harmonic generation (SHG) response from lyotropic LC solutions of racemic mixtures of poly(γ-benzyl glutamate) dissolved in benzyl alcohol, showing the spontaneous formation of polar nematic phase in lyotropic LC solutions and polar-to-nonpolar transition upon increasing the temperature or decreasing the concentration. The result strongly suggests the importance of polar structure in supermolecular associated materials of living systems composed of fibrous proteins, polysaccharides and DNA.

The shear flow orientation in the diblock copolymers composed of polystyrene (PS) and side-chain liquid crystal polymer (LCP) was investigated by the wide and small angle X-ray diffraction methods. Two diblock copolymers prepared by atom transfer radical polymerization have the weight fractions of the PS segment of 0.13 and 0.21, and form the well defined microsegregation structure with PS cylinders hexagonally packed in a matrix of LCP which forms smectic A, nematic and isotropic phases in an order of increasing temperature. Two types of shear flow orientation have been observed depending on the type of the phase in the LCP matrix. The shear flow at nematic temperatures orients well the PS microcylinders as well as the LC mesogens in the velocity direction. This parallel-*b* orientation is expectable from the general orientation of the microcylinders and LC mesogens in shear flow. When the LCP matrix transforms to the smectic LC, the mesogens are aligned parallel to the velocity gradient direction entailing significant disturbance for the microcylinders. By annealing this sample at nematic temperature, the well-defined perpendicular-*c* orientation can be attained with both the microcylinders and mesogens lying parallel to the velocity gradient direction. These two characteristic orientations could be explained to arise as a compromise between orientations of microcylinder and LC mesogen.

2. Articles (original article, comment/book)

１．Sonna Banana no chirality、Junji Watanabe、mirai-zairyo、7, 5-7 (2007)

2. Magnetic Orientation of Microcylinders in Liquid Crystalline Diblock Copolymer and Clarification of its Orientation Mechanism
Mitsu-aki Adachi, Fumihiro Takazawa, Naoki Tomikawa, Masatoshi Tokita, and Junji Watanabe
Polym. J., 39, 155-162 (2007)

3. TEM observation due to surface replica method for layer undulation in solid X_1 phase of banana molecule
Sungmin Kang, Jun Koki, Masatoshi Tokita and Junji Watanabe
JJAP, 46, 3518-3520 (2007)

4. Unusual nematic liquid crystal with polar Cs symmetry formed from aromatic polyesters with head-tail character
Masao Koike, Chu-Chun Yen, Liu Yuqing, Hitoshi Tsuchiya, Masatoshi Tokita, Susumu Kawauchi, Hideo Takezoe and Junji Watanabe
Macromolecules, 40, 2524-2531(2007)

5. Thermally reversible distortion along the director observed for monodomain nematic elastomer of cross-linked main-chain polyester
M. Tokita, H. Tagawa, R. Ishige, K. Osada, and J. Watanabe
Mol. Cryst. Liq. Cryst., 465, 193-202(2007)

6. Chirality Transfer between weakly birefringent and electric-field-induced highly bireferingent B2 phases in a bent-core mesogen
S.K.Lee, L.Shi, M. Tokita, H. Takezoe, and J. Watanabe
J. Phys. Chem. Lett. 111, 8698-8701(2007)

7. Chirality induced by circularly polarized light in liquid crystalline twin dimmers with azo linkages,
Y. Hoshino, S.-W.Choi, T. Izumi, Y. Takanishi, K. Ishikawa, J. Watanabe and H. Takezoe
Mol. Cryst. Liq. Cryst., 465, 193-202(2007)

8. Collective Fluctuation in Chiral Smectic Phases of Main-Chain Liquid Crystalline Polymers
K. Hiraoka, T. Nose, Y. Uematsu, M. Tokita and J. Watanabe
Liquid Crystals, 34, 305-310 (2007)

9. Why Achiral Rodlike Compound with Ester Group Amplifies Chiral Power in Chiral Mesophase
Susumu Kawauchi, Suk-Won Choi, N. Fukuda, Junji Watanabe, and Hideo Takezoe
Chem. Lett., 36, 750-751 (2007)

10. Temperature-induced reversible distortion along the director observed for monodomain nematic elastomer of cross-linked main-chain polyester
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11. Successful preparation of monodomain polymer cholesteric films with beautiful colors like beetle

Junji Watanabe, Proceeding for the sendai symposium on insect mimetics and nano materials (invited), Sendai, Japan, June 20-21, 2007.

12. Synthesis and self-assembling of wholly aromatic co-oligomers: oligo(ether sulfone)-b-oligo(ether ketone) with sulfonic acid terminal groups
R. Goseki, T. Hayakawa, M. Kakimoto, M. Tokita and J. Watanabe
J. Photopolym. Sci. Tech. 20, 189-192(2007)

13. Relationship between Chemical Structure and Helical Twisting Power in Optically Active Imine Dopants Derived from R-(+)-1-(1-Naphthyl)ethylamine
Kaoru FUKUDA, Hideyuki SUZUKI, Jin NI, Masatoshi TOKITA and Junji WATANABE
JJAP, 5280-521, 46(2007)

14 Vibrational Circular Dichroism Spectroscopic Study on Circularly Polarized Light-Induced Chiral Domains in the B4 Phase of a Bent Mesogen
Suk-Won Choi, Susumu Kawauchi, Shingo Tanaka, Junji Watanabe and Hideo Takezoe
Chemistry Letters, 36, 1018-1019(2007)

15. Mesomorphic behaviour in bent-shaped molecules with side wings at different positions of central naphthalene core
Seng Kue Lee, Yu Naito, Lu Shi, Masatoshi Tokita and Junji Watanabe
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16. Characteristic Shear-Flow Orientation in LC Block Copolymer Resulting from Compromise between Orientations of Microcylinder and LC Mesogen
Masatoshi Tokita, Mitsu-aki Adachi, Satoshi Masuyama, Fumihiro Takazawa, and Junji Watanabe
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S.-W.Choi, S. Kang, Y. Takanishi, K. Ishikawa, J. Watanabe and H. Takezoe
Chirality, 19, 250-254 (2007)

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N. Fukuda, H. Suzuki, M. Tokita, J. Watanabe and S. Kawauchi

J. Mol. Struct. Theochem., 821, 95-100(2007).

20. Magentic Potassium Clusters in a Nanographite Host System

K. Takai, S. Eto, M. Inaguchi, T. Enoki, H. Ogata, M. Tokita and J. Watanabe

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Yasutaka Nagai, Daisuke Miyagishi, Tomoko Akagawa, Fujio Ohishi, Hitoshi Ueno, Koji Kobayashi, Katsuhisa Yamashita and Junji Watanabe

Polymer Degradable and Stability, 93, 134-138 (2008).

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Masatoshi Tokita, Mitsu-aki Adachi, Fumihiro Takazawa, and Junji Watanabe

JJAP, in press.

26. Sequential palladium-catalyzed coupling reactions on solid-phase

T. Doi, H. Inoue, M. Tokita, J. Watanabe, T. Takahashi

J. Comb. Chem., in press

27. Phase diagram for solutions of α–helical poly(L-glutamate)s in *m*-cresol including isotropic, cholesteric and columnar phases
Chu-Chun Yen, Susumu Edo, Hideki Oka, Masatoshi Tokita and Junji Watanabe
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28. Chiral correlation between low birefringent phases with TGB-like helix and highly birefringent phases with layer chirality as elucidated from CD observations
Seng Kue Lee, Lu Shi, Masatoshi Tokita, and Junji Watanabe
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Ryohei Ishige, Masatoshi Tokita*, Yu Naito, Chun Ying Zhang, Junji Watanabe
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Tsuyoshi Michinobu, Nozomu Fujii, Masatoshi Tokita, Junji Watanabe, Kiyotaka Shigehara

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