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1. Main Research Results

1) Formation of nano-ordered structure due to the spontaneous organization of polymers (9,16,17,18)

The fracture surface morphology of solid chiral S_C^* polymer was studied by SEM and AFM observations. Very clear undulation with a regular repeating can be detected by both methods. The peak to peak distance corresponds to the helical pitch of chiral S_C^* phase (150nm ~600nm depending on the chiral content in the polymers) and the depth from top to bottom is around 20-70 nm. Such an undulation mode in the fracture surface is due to the helical arrangement of polymers to form the helical S_C^* structure; the easily cleaved direction is along the polymer chain forming a helical conformation. The undulation morphology is also observed on the film surface of homogeneously aligned sample, however the depth, relatively smaller than that observed on the fracture surface, is around 2-5 nm. The source for the undulation in both cases may be the same, but in the latter, the interfacial tension is considered to act to produce a more gentle undulation.

We synthesized the helical poly[*n*-decyl-2-methylpropylsilane] with a wide variety of molecular weights of 13,700 to 151,000 and the narrow molecular weight distributions of 1.07 to 1.39. Together with a clarification of their thermotropic phase behavior with columnar-SmA-nematic-isotropic phase sequence, the layer structure of the SmA phase was analyzed by small-angle X-ray and AFM methods. AFM images show that the SmA layer structure is regularly formed from all the polymers. The layers are regularly piled up throughout the area of $10 \times 10 \mu\text{m}^2$ without significant defects and the long correlation length along the layer is beyond $10 \mu\text{m}$ even for the high molecular weight polymers irrespective of a very small number density of polymer ends. The layer thickness varying from 10 to 110 nm nearly corresponds to the molecular length. Such a consistent formation of the smectic layer structures with various layer spacings gives the opportunity to produce large-area nanostructures for optical devices at easy processing.

2) Polar nematic liquid crystals in hard-rod polar polymers (6,19,20,21)

Steady shear flow viscosity was measured for nematic liquid crystalline (LC) in aromatic copolyesters composed of 4-hydroxy benzoic acid (HBA), 6-hydroxy-2-naphthoic acid (HNA), terephthalic acid and biphenol whose molar contents are 0.73-*x*, 0.27-*x*, *x* and *x*, respectively. Second harmonic generation (SHG) measurements showed that a polar nematic LC formed by poly(HBA/HNA) with *x* = 0 was altered to a conventional non-polar nematic LC with an increase in *x* up to 0.07. The shear-rate dependence of melt viscosity measured for nematic LCs of these copolymers showed four characteristic regions; a Newtonian plateau in lowest shear-rate region 0 in addition to the well-known three regions, low-shear-rate shear-thinning region I, the intermediate Newtonian plateau region II and high-shear-rate shear-thinning region III. The SHG-active structure in nematic LCs reflected on the Newtonian plateau region 0, in which the viscosity of the SHG-active nematic LC was 10 times higher than that of the non-SHG-active nematic LC. The higher viscosity of the SHG-active nematic LC was clearly connected

to the smaller domain size (or larger number of disclinations) estimated by small-angle light scattering. In the non-polar nematic LC, many disclinations initially formed are easily annihilated because of the coalescence of two disclinations with opposite signs, whereas in the polar nematic, such an annihilation occurs hardly because of the polar packing symmetry.

The ferroelectric ordering in nematic liquid crystals of polar molecules is of fundamental and practical interest. However, there are only a few experimental reports on this. In this paper, we examine the SHG measurement for lyotropic nematic liquid crystals of racemic mixtures of poly(α -benzyl glutamate) dissolved in benzyl alcohol. We recognize the formation of polar nematic liquid crystal, by observing the clear transition from polar phase to non-polar phase with the increase of temperature. The polar to non-polar transition temperature increases with the increase of the concentration, which corresponds to a theoretical expect.

3) Liquid crystals in main-chain polymers (2,12,13,22,24)

Twin dimers with 3-methyl pentane spacer behave as the U-typed molecule if m is longer than 12 and form the S_A phase. This behavior is in contrast to that in the homologous dimers with linear pentane spacer which assume the extended conformation and form the antiferroelectric S_{CA}^b phase. Twin dimers in the smectic field, hence, can select another way to accommodate the alkyl tail groups fairly longer than the alkyl spacer ones, suggesting new potentiality in spontaneous molecular organization.

The main-chain type of liquid crystal (LC) polymer was prepared with a combination of bibenzoate mesogen and 2-phenyl propane spacer. It forms the fluid smectic LC. However, the smectic phase has a two-dimensional frustrated structure with a (parallel to the layer) = 12.9 Å, c (along the polymer chain) = 20.6 Å and $\beta = 70.0^\circ$. The occurrence of such a characteristic frustration is due to the bulky phenyl group sticking out of the propane spacer that is incompatible with a conventional smectic structure. The polymer assumes the regular chain folding conformation excluding the obstructive phenyl groups within a limited column-like space, and the resulting columns embedded in a smectic matrix are aligned with a two-dimensional positional order.

The main-chain BB/PDA-5(3-Me) polyester containing photo-crosslinkable p -phenylenediacrylate (PDA) moiety was synthesized and its transparent monodomain S_{CA} was crosslinked by UV irradiation. The monodomain S_{CA} elastomer contracted about 40% of original length along n -director on heating to the isotropic phase and recovered only 5 % at the liquid crystallization on cooling. Irrespective of such a small recovery, the liquid crystal is well formed with a high orientation, but the smectic structure formed is of a S_A type with the layer spacing two times larger than that of the original S_{CA} phase. By elongation of this contracted elastomer, the S_A structure is altered to the S_{CA} one, showing quasi-plateau in the stress-strain curve. The connection between the structural transformation and the stress-strain behavior lets us propose the folding lamellar S_A structure in which the chain folding arises in each of two units. Such a characteristic folding structure may be formed because of the limited mobility of mesogens in networks

4) Liquid crystals in side-chain polymers (4,11,14)

Side chain LC poly(fumarate)s carrying cyanobiphenyl mesogens display thermoreversible contraction and extension movements of the layer spacing over a wide smectic A phase temperature range. A significantly large contraction ratio, e.g., 15.2%, was revealed to originate from a lowering of the orientational order parameter based on an X-ray diffraction analysis of the magnetically oriented samples.

5) Banana liquid crystals (3,7,8,10,15,23)

We prepared a homologous bent-shaped molecule with the same central naphthalene core and long side wings in which one phenyl ring is attached to the classic one via an ester linkage. As a result of the expanded mesophase temperature region, an anti-ferroelectric banana phase similar to the typical B2 phase was formed here in addition to the solid B4 phase. The ferro- and anti-ferro-electric switching of polar smectic phases can be applied for the in-plane switching display using a homeotropically aligned cell.^{15,16} From this perspective, the high spontaneous polarization (800 nC/cm²) and high birefringence due to the small bent angle endow this molecule with advantages over the conventional banana molecule with a high bend angle. Thus, the present result opens up prospects for new, considerably extended molecular designs for bent-shaped molecules in both fundamental and application fields.

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.

6) Others (1,5,25)

2. List of publication (original article, comment/book)

1) Original Papers

- (1) Photodegradation mechanisms in poly(2,6-butylene naphthalate-co-tetramethylene glycol) (PBN-PTMG). III: Photodegradation induced by the carbonyl group in an n, π^* excited state. 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).
- (2) Unusual Formation of Smectic A Structure in Crosslinked Monodomain Elastomer of Main-Chain LC Polyester with 3-Methyl Pentane Spacer Ryohei Ishige, Masatoshi Tokita, Yu Naito, Chun Ying Zhang, Junji Watanabe *Macromolecules*, 41, 2671-2676(2008)
- (3) Sequential palladium-catalyzed coupling reactions on solid-phase; T. Doi, H. Inoue, M. Tokita, J. Watanabe, T. Takahashi: *J. Comb. Chem.*, 10, 135-141(2008)

- (4) Unexpected phase behaviors of poly(fumarate)s carrying tolane-based mesogenic side chains; Tsuyoshi Michinobu, Hiroshi Noguchi, Nozomu Fujii, Masatoshi Tokita, Junji Watanabe, Kiyotaka Shigehara: Chem. Lett., 37, 356-357 (2008)
- (5) Phase diagram for solutions of \square -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: Macromolecules, 41, 3727-3733 (2008)
- (6) Polar nematic phase in lyotropic solutions of poly(\square -benzyl glutamate) and its temperature instability; Chu-Chun Yen, Yoshiaki Taguchi, Masatoshi Tokita and Junji Watanabe: Macromolecules, 41, 2755-2758 (2008).
- (7) 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: J. Phys. Chem. B 112, 6762-6766(2008)
- (8) Effect of molecular structure on smectic phase structures in two homologues series of bent-shaped molecules with asymmetric central naphthalene core; Seng Kue Lee, Masatoshi Tokita, Hideo Takezoe and Junji Watanabe: Ferroelectrics, 365, 1-11 (2008)
- (9) Regular undulation morphology observed in fracture surface of glassy chiral SC* solid; Chun Ying Zhang, Susumu Edo, Ryouhei Ishige, Masatoshi Tokita and Junji Watanabe: Macromolecules, 41, 5361-5364 (2008)
- (10) Mesomorphic behavior of bent-shaped molecules with non-aromatic central core based on bis(*p*-hydroxyphenyl)methane; Seng Kue Lee, Lu Shi, Masatoshi Tokita, and Junji Watanabe: Chem Lett. 37, 1134 (2008)
- (11) 11. Side Chain Liquid Crystal Poly(fumarate)s Bearing Tolane-based Mesogens; Nozomu Fujii, Masatoshi Tokita, Junji Watanabe, Kiyotaka Shigehara: Journal of Polymer Science Part A: Polymer Chemistry, 46, 5101-5114 (2008)
- (12) Smectic A formation by twin dimers assuming U-shaped conformation; Yu Naito, Ryohei Ishige, Manabu Itoh, Masatoshi Tokita and Junji Watanabe: Chem. Lett., 37, 880-881 (2008) .
- (13) Elongation behavior of a main-chain smectic liquid crystalline elastomer; Ryohei Ishige, Kensuke Osada, Hirotaka Tagawa, Masatoshi Tokita and Junji Watanabe: Macromolecules, 41, 7566-7570 (2008).
- (14) Thermoreversible Contraction and Extension of Layer Spacing in Smectic phase of Side Chain Liquid Crystal Poly(fumarate)s; Tsuyoshi Michinobu, Nozomu Fujii, Masatoshi Tokita, Junji Watanabe, Kiyotaka Shigehara: Macromolecular Rapid Communications, 29, 1593-1597(2008)
- (15) Antiferroelectric Banana Phase in Bent-shaped Molecule with Small Bent-Angle of 60°; Seng Kue Lee, Lu Shi, Ryohei Ishige, Sungmin Kang, Masatoshi Tokita, and Junji Watanabe: Chem Lett., 37, 1230-1231 (2008).
- (16) High chiral induction in aromatic polymers with chiral naphthyl ethylamine groups at their ends; K. Fukuda, H. Suzuki, M. Muto, S. Edo, M. Tokita and J. Watanabe: Jpn. J. Appl. Phys., 47, 8479(2008).
- (17) Structural Characteristics of thermotropic SmA layer phase formed from rigid-rod polysilanes;

- Hideki Oka, Goro Suzuki, Susumu Edo, Suzuki Akiko, Masatoshi Tokita and Junji Watanabe: *Macromolecules*, 4, 7783-7786 (2008).
- (18) Twofold helical inversion in the chiral SmC phase of optically active materials derived from (R)-(+)-1-(1-phenyl)ethylamine; Masakane Muto, Hideyuki Suzuki, Kaoru Fukuda, Seng Kue Lee, Sungmin Kang, Masatoshi Tokita, and Junji Watanabe: *J. Phys. Chem. B*, 112, 1521 (2008).
- (19) Synthesis and Chemical Properties of Dielectric Polyphenylenes with Nitro Group.; Masahiro Abe, Masatoshi Tokita, Junji Watanabe, Yoshimasa Sakai, Takakazu Yamamoto: *J. Appl. Polym. Sci.*, 111, 2426-2435 (2009).
- (20) Spontaneous formation of Polar Liquid Crystal in lyotropic solution of helical polypeptide molecules; Chu-Chun Yen*, Yoshiaki Taguchi, Masatoshi Tokita, and Junji Watanabe: *Mol. Cryst. Liq. Cryst.*, in press.
- (21) Difference in steady shear flow viscosity between polar and non-polar nematic liquid crystals in aromatic polyesters derived from Vectra; Yoshiaki Taguchi, Chu-Chun Yen, Sunming Kang, Masatoshi Tokita, and Junji Watanabe: *Macromolecules*, in print
- (22) Spontaneous deformation of main-chain liquid-crystalline elastomers composed of smectic polyesters; Kazuyuki Hiraoka, Tohru Tashiro: *Liquid Crystals*, in print.
- (23) AFM Observation of Nano-Ordered Undulation Structure formed by Bent-shaped Molecules; Susumu Edo, Sungmin Kang, Masatoshi Tokita and Junji Watanabe: *Jpn. J. Appl. Phys.*, in print.
- (24) Regular formation of chain folding in main-chain BB-3(2-Ph) polymer in smectic phase followed by columnar association of phenyl side group in propane spacer; Ryohei Ishige, Yu Naito, Sungmin Kang, Masatoshi Tokita and Junji Watanabe: *Macromolecules*, in print.
- (25) Cyanobacterial Megamolecules Show Liquid Crystalline Phase in Very Dilute Solutions.; Maiko K. Okajima, Daisaku Kaneko, Tetsu Mitsumata, Tatsuo Kaneko, Junji Watanabe: *Macromolecules*, in press.

3. Invited/Plenary Talks in Conference

1) International Conference or Workshop

- (1) Unusual nematic liquid crystal with polar Cs symmetry formed from aromatic polyesters with head-tail character; Junji Watanabe (as plenary lecturer): Polycondensation, September 8-11, Tokyo Institute of Technology, Tokyo (2008)
- (2) Structural Characteristics of thermotropic SmA layer phase formed from rigid-rod polysilanes; Junji Watanabe (invited lecturer); Annual meeting of Polymer society of Korea, October 9, Souel (2008)
- (3) Regular undulation morphology observed in fracture surface of glassy chiral SC* solid; Chun Ying Zhang, Susumu Edo, Ryouhei Ishige, Masatoshi Tokita and Junji Watanabe: "The 3rd korean-Hungarian International Joint Workshop: Frontier Topology and Design Concept for Neo-Mesomorphism", 4-7 July 2008, Gumi (Korea) (Invited lecture)
- (4) Polar nematic phase in lyotropic solutions of poly(\square -benzyl glutamate) and its temperature instability as detected by SHG measurement; Chu-Chun Yen*, Yoshiaki Taguchi, Masatoshi Tokita,

& Junji Watanabe: “The 4th Japanese-Italian Workshop on Liquid Crystals JILC’08”, July 7-9, 2008, Nara, Japan.

4. Award

- 1) The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology; “Research on Banana-shaped Liquid Crystals”: April 15, 2008
- 2) Japan Liquid Crystal Award; “Introduction to Liquid Crystal and Polymer” (Shokabo, 2004): Sep. 4, 2009